

Decoupling the Mechanistic Effects of CeO2-x-Based Catalytic Heterojunctions: Chemisorbed MoO3 vs Physisorbed RuO2

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Publication Date: 2021

DOI: https://doi.org/10.26190/unsworks/2289

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Decoupling the Mechanistic Effects of CeO_{2-x}-Based Catalytic Heterojunctions: Chemisorbed MoO₃ vs Physisorbed RuO₂

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A thesis in fulfilment of the requirements for the degree of Master by Research

School of Material Science and Engineering

Faculty of Science

February 2021

Thesis Title

Decoupling the Mechanistic Effects of CeO2-x-Based Catalytic Heterojunctions: Chemisorbed MoO3 vs Physisorbed RuO2

Thesis Abstract

The present work explores the role of defects in materials properties by considering the critical role of defect equilibria in terms of the effects of solid solubility and charge compensation mechanisms on the resultant physicochemical properties and catalytic performance of bulk CeO_{2x} as well as $MOQ_{2}-CeO_{2x}$ and $RuO_{2}-CeO_{2x}$ heterojunctions. Electrodeposition was used to synthesise holey nanosheets and heterojunctions were created using wet chemistry. Analyses consisted of XRD, Raman, SEM, HRTEM, EDS, SAED, AFM, XPS, EPR, PL, KPFM, and UV-Vis. DFT was used to calculate the optical indirect band gap (E_0) values for the different solubility mechanisms for the dopant valences. The catalytic performance was assessed by HER and ozonation testing. The combination of XPS data, their detailed and extensive analyses, and consideration of all possible defect equilibria is a powerful tool to interpret the physicochemical properties and catalytic performance of bulk materials and heterojunction nanostructures based on them. With this information, it is possible to decouple multifarious data for disparate materials such as bulk materials, chemisorbed heterojunction nanostructures, and physisorbed heterojunction nanostructures.

A key outcome of the present work is that the primary factor in both the properties and performance unambiguously is Ce³⁺ ions, not oxygen vacancies. This is manifested through the solubility mechanisms of the dopants, which are interstitial, and the charge compensation mechanisms, which are ionic for Mo doping and ionic + redox for Ru doping. The hydrogen evolution reaction (HER) performance was dominated by the heterojunctions, where the strong bonding from chemisorption, intervalence charge transfer (IVCT), and homogeneous and high distribution density of small heterojunction particles with Mo doping resulted in significant performance enhancement. The HER with Ru doping was poor owing to the weak bonding from the inhomogeneous and low distribution density of large physisorbed heterojunction particles. The ozonation performances generally were outstanding but adversely affected by cerium vacancies. While this performance for Mo doping was improved by reduction owing to IVCT, that for Ru was uniformly poor owing to the high cerium vacancy concentration. The performance for bulk CeO_{2xx} was poor owing to structural destabilisation during reduction, thus suggesting stabilising effects from the heterojunction particles.

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Acknowledgements

I would like to thank my supervisor, Dr. Pramod Koshy, who provided extraordinarily extensive technical and practical assistance throughout the tenure of the thesis. I am a much better scientist for his help. I also would like to thank my joint supervisor Prof. Charles C Sorrell. His professionalism, enthusiasm, and meticulous attention to detail toward research have been an inspiration. The combination of Dr. Koshy's approachability and receptiveness as counterpoints to Prof. Sorrell's exacting and challenging demands was never anything less than embracing. I also am highly indebted to my co-supervisor, Dr. Sajjad Seifi Mofarah, whose introduction to experimental approaches and scientific imagination continuously has opened my eyes.

Finally, I wish to express my very great appreciation to my parents, whose support and encouragement have been essential throughout my life.

Abstract

CeO_{2-x} and CeO_{2-x}-based catalysts are emerging as important functional materials in many energy- and environment-related applications. However, there remain uncertainties and misconceptions in the interpretation of the fundamental function of defects in determining the characteristics of materials. The present work explores this relationship in detail by considering the critical role of defect equilibria in terms of the effects of solid solubility and charge compensation mechanisms on the resultant physicochemical properties and catalytic performance of bulk CeO2-x as well as MoO3-CeO2-x and RuO2-CeO_{2-x} heterojunctions. Electrodeposition was used to synthesise holey nanosheets and heterojunctions were created using wet chemistry. Analyses consisted of XRD, Raman, SEM, HRTEM, EDS, SAED, AFM, XPS, EPR, PL, KPFM, and UV-Vis. DFT was used to calculate the optical indirect band gap (Eg) values for the different solubility mechanisms for the dopant valences. The catalytic performance was assessed by HER and ozonation testing. The combination of XPS data, their detailed and extensive analyses, and consideration of all possible defect equilibria represents a powerful tool to interpret the physicochemical properties and catalytic performance of bulk materials and heterojunction nanostructures based on them. With this information, it is possible to decouple multifarious data for disparate materials such as bulk materials, chemisorbed heterojunction nanostructures, and physisorbed heterojunction nanostructures. A key outcome of the present work is that the primary factor in both the properties and performance unambiguously is Ce³⁺ ions, not oxygen vacancies. This is manifested through the solubility mechanisms of the dopants, which are interstitial, and the charge compensation mechanisms, which are ionic for Mo doping and ionic + redox for Ru doping. The latter mechanisms may be altered by three F centres (viz., colour centres), which derive from oxygen vacancies, and intervalence charge transfer (IVCT) in the case of Mo doping. The F centres and metal interstitials also are key factors in raising the Fermi level (E_f) of the doped materials, effectively reducing the E_g, particularly for Mo doping. The hydrogen evolution reaction (HER) performance was dominated by the heterojunctions, where the strong bonding from chemisorption, IVCT, and homogeneous and high distribution density of small heterojunction particles with Mo doping resulted in enhancement such that this performance is the best yet reported for CeO_{2-x}-based materials. In contrast, the HER with Ru doping was relatively poor owing to the weak bonding from the inhomogeneous and low distribution density of large physisorbed heterojunction particles. The ozonation performance was outstanding but adversely affected by cerium vacancies. While this performance for Mo doping was improved by reduction owing to IVCT, that for Ru was uniformly poor owing to the high cerium vacancy concentration. The performance for bulk CeO_{2-x} was poor owing to structural destabilisation during reduction, thus suggesting stabilising effects from the heterojunction particles.

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1 Introduction

Heterojunction nanostructures have become increasingly important owing to their advantageous properties in many technological areas, including thermocatalysis (1), electrocatalysis (2), photocatalysis (3), and photovoltaics (4). Heterojunction nanostructures generally refer to two physically and/or chemically bonded semiconductors of different band gaps for the purpose of band alignment (5), although multijunction structures of more than two phases also are known (6). In catalytic applications, heterojunction nanostructures leverage defect engineering as well as surface, structural, and morphological characteristics in order to enhance the performance owing to the synergism between the materials. The morphological characteristics of such materials are characteristic in that they reflect the alteration of a range of physicochemical features, including crystal structure, exposed crystallographic planes, surface charges and polarities, defect types and densities, and associated anisotropies. The importance of the morphology has been highlighted by the recent emergence of the outstanding catalytic performance of nanosheets of various systems owing to the high densities of active sites deriving from their high surface areas (7). While there is a large body of work on heterojunction parent structures based on nanosheet-structured graphene (8) and transition metal dichalcogenides (TMDs) (9), these materials have the shortcomings that they are subject to oxidation and are relatively expensive to synthesise. In contrast, heterojunctions based on nanosheet-structured oxides can overcome these shortcomings but there are fewer reports of these since most such structures are not inherently morphologically two-dimensional (2D). Consequently, an alternative strategy to generate such structures is the conversion of coordination polymers (CPs), including metal-organic frameworks (MOFs), to 2D oxide nanostructures (10). However, these often have the shortcomings of incomplete conversion and the presence of residual organic material following oxidation (11).

In addition to morphological engineering, a second key strategy to modify the catalytic properties of heterojunction materials is defect engineering. These strategies can exploit 0D point defects, the interfaces associated with 1D and 2D defects, and the surface areas deriving from 3D defects (*12*). Manipulation of defect type, concentration, and distribution can be used to enhance the material properties, including electronic, optical, chemical, physical, and catalytic. In effect, defect engineering at all levels can be

employed with semiconducting transition and rare earth metal oxides through doping (0D defects), heterojunction formation (1D and 2D defects), and the introduction of multiple vacancies in the form of divacancies and clusters and mesoporosity (3D defects). These strategies target the enhancement of the semiconducting properties through defect generation, band alignment through heterojunction establishment, and increase in active site distribution density through the introduction of new interfacial areas. Point defects are particularly important because they can reduce the band gap, introduce midgap states to facilitate charge carrier transitions, enhance charge separation and reduce recombination by providing trapping sites, and introduce active sites (*e.g.*, oxygen vacancies, $V_0^{\bullet,\bullet}$) (13). Also, midgap states as well as charge compensation by redox effects, facilitated by the variable valences of transition and rare earth metals, further enhance the capacity to engineer the types and amounts of point defects (14).

Pure CeO_{2-x} contains intrinsic $V_0^{\bullet\bullet}$ as 0D point defects owing to the easy reversibility of the Ce³⁺-Ce⁴⁺ oxidation states, which can be attributed to the low standard redox potential of 1.72 eV (*15*). However, this value depends on the nature and concentration of the electrolyte as well as the pH of the solution. In acidic media, the potential is in around 1.76 V (*16*) and, in basic media, the voltage is around -0.7 V (*17*).

Further, such intrinsic properties of CeO_{2-x} are likely to be altered by doping with acceptors or donors, which introduces defects in the forms of vacancies, interstitials, and altered valence states. The capacity to dope CeO_{2-x} with cations through solid solubility is high owing to the large central interstice of ionic radius 0.110 nm, which is larger than most cations, and the large interstice (0.160 nm) in the repulsive Ce sublattice, through which the dopant cation must pass (*18*). However, size is not the only consideration, as suggested by Hume-Rothery's rules for substitutional and interstitial solid solubility is favoured by similar sizes, valences, and electronegativities of dopant (solute) and matrix (solvent) ions. However, Hume-Rothery's rules are for close-packed non-directionally-bonded metals while CeO_{2-x} is a directionally-bonded ionic-covalent. That is, for ceramics, Hume-Rothery's considerations for substitutional solid solubility generally apply but there are many differences for interstitial solid solubility.

Another potential outcome of doping is reaction to form secondary phases. In the case of Mo doping of CeO₂, the reported MoO₃-CeO₂ phase diagram (20) shows that both Ce₂(MoO₄)₃ and Ce₂(MoO₃)(MoO₄)₃ can form. No solid solubilities were indicated but these did not appear to have been investigated. These equilibria products indicate that, for both phases, MoO₃ \rightarrow MoO₄²⁻ oxidation is balanced by 2Ce⁴⁺ \rightarrow 2Ce³⁺ reduction. In the case of Ru doping of CeO₂, the calculated RuO₂-CeO₂ phase diagram is dominated by high-temperature spinodal decomposition. However, there are several studies that confirm that substantial Ru solid solubility at temperatures in the range 450°C (21, 22) to 600°C (23, 24) occurs.

CeO_{2-x} nanosheets recently have been applied for a range of catalytic applications, including thermocatalysis (carbon monoxide oxidation) (25), electrocatalysis (hydrogen evolution reaction) (26), and photocatalysis (air purification) (27). Improvement in the catalytic performance of CeO_{2-x} has been achieved through the use of doping (28) and heterojunction formation (29), which aim to alter the semiconducting properties by electronic band modification of CeO_{2-x} in order to address the two principal shortcomings of such semiconductors, which are wide band gaps and short recombination times (30). However, there are pitfalls to the doping strategies reported to address these two issues and these often are embodied in assumptions, which may be incorrect, about (1) the types and extents of solid solubility of the dopant(s) in the matrix, (2) the mechanism(s) of charge compensation, and (3) the mechanisms of charge transfer. Further, there are pitfalls to the potential to form heterojunctions and these generally involve studies of precipitation and possibly heat treatment (31), where assumptions of charge transfer are contingent upon the establishment of (1) chemisorption, where transfer takes place, rather than (2) physisorption, where transfer is more difficult if not impossible. These doping and heterojunction strategies are contingent upon the application of experimental approaches to utilise what generally are unreported solid solubilities. That is, under equilibrium conditions, the ability to dope a material requires the use of appropriate temperatures and/or adequate times in order to achieve partial or complete solid solubility. In contrast, the ability to form a heterojunction ideally requires the establishment of a chemical bond. In the absence of solubility, epitaxial alignment facilities such bonding. When there is solid solubility, it is essential to avoid complete solubility and to ensure that the system involves the partial solubility that facilitates interphase bonding.

The present work reports outstanding catalytic performance data for CeO_{2-x} holey nanosheets, which were fabricated by electrodeposition using Ce(NO₃)₃·6H₂O to for a novel Ce-based coordination polymer (CeCP; Ce(TCA)₂(OH)₂·2H₂O, where TCA is trichloroacetate (32)), exfoliation in triethanolamine (TEA), wet-chemical coating by MoCl₃ or RuCl₃, and oxidation to doped CeO_{2-x} by heat treatment at 450°C for 3 h. The nanosheets were characterised by X-ray diffraction (XRD), laser Raman microspectroscopy (Raman), field emission scanning electron microscopy (FESEM), high-resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED), energy dispersive spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), electron paramagnetic resonance (EPR) spectroscopy, photoluminescence (PL), atomic force microscopy (AFM), Kelvin probe force microscopy (KPFM), and UV-Vis spectrophotometry (UV-Vis). The optical indirect band gaps (Eg) for the dopants in both substitutional and interstitial solid solubility as well as those of the heterojunctions themselves were calculated by density functional theory (DFT). The performance of the nanosheets was characterised by the hydrogen evolution reaction (HER) in an acidic environment and ozonation. However, the work focusses on the development of mechanistic interpretations of the data in terms of the solid solubility, defect formation, charge compensation, charge transfer (within lattice and between heterojunction and catalyst), electronic band modification, sorption (HER), and active site formation (ozonation).

2 Literature Review

2.1 Cerium Oxide (CeO₂)

2.1.1 Properties

Cerium oxide has attracted such attention due to its thermal stability, biocompatibility, and redox properties. Cerium is the most abundant rare-earth element in the lanthanides series (33). It is distinct from other lanthanide series elements owing to it possessing two different stable valence states (3+/4+) (34). The electronic configuration of Ce is [Xe]4f1 5d1 6s2, which means it can lose three electrons from its 5d and 6s orbitals to form Ce³⁺, and also form a stable empty 4f orbital by losing another electron from it, leading to the more stable valence (Ce⁴⁺)(35). These two valences can easily undergo redox switching leading to the formation and annihilation of intrinsic oxygen vacancies ($V_0^{\bullet\bullet}$) owing to charge compensation mechanisms (36).

Stoichiometric CeO₂ shows a cubic-fluorite structure where the cerium cations occupy the face-centred positions with eightfold (VIII) coordination and these are surrounded by fourfold (IV) coordinated O anions (37). The crystal structure based on the corresponding crystal radii calculated by Shannon and with the calculated crystallographic parameters of CeO₂ is shown as **Figure 2.1** (18). The central interstice (ionic radius) is 0.110 nm and this distance is greater than that seen for the radii of most cations. Further, the much larger interstice in the repulsive Ce sublattice (0.160 nm) can allow most dopant cations to be located there and this gives CeO₂ the ability to form solid solutions with many cations (18).



Figure 2.1. (a) Cubic fluorite crystal structure of CeO_2 (Ce = purple spheres, O = red spheres); Ball-and-stick models of various low-index planes in CeO₂ determined by first principles DFT simulations: (b) {111}; (c) {110}; (d) {100}

The cubic fluorite structure in CeO₂ mainly shows three low index surfaces, namely the $\{111\}$ (38, 39), $\{110\}$ (40) and $\{100\}$ (41) (Figure 2.2) (42). The $\{111\}$ surface of ceria comprises alternating layers of O²⁻-Ce⁴⁺-O²⁻ trilayers belonging to type II polar terminations and this arrangement does not create a dipole moment (43). The $\{110\}$ surface has zero charge due to a stoichiometric balance of anions and cations in each plane; this surface has alternately charged planes with a repeat unit of only two planes (44). The stability of these three planes follows the order: $\{111\} > \{110\} > \{100\}$, whereas their activities follow the reverse order (45). High-resolution transmission electron microscopy (HRTEM) imaging of ceria nanocubes showed the presence of three different surface lattices and these are shown in Figure 2.2 (46). The analysis revealed that the {111} surface is terminated by oxygen atoms, {110} surface has flat CeO_{2-x} terminations with oxygen vacancies, while a complex mixture of structures of Ce, O, reduced Ce-O terminations are present on the exposed $\{100\}$ surface (46). These results confirmed more defects (oxygen vacancies) on $\{110\}$ and $\{100\}$ planes than $\{111\}$ due to the formation energy of oxygen vacancies being higher for the {111} facet compared to the $\{110\}$ and $\{100\}$ facets (47).



Figure 2.2. Schematic of low-index surface planes: (a) $\{111\}$, (b) $\{110\}$ and (c) $\{100\}$ in stoichiometric CeO₂ crystal; (green sphere: O ion, pink sphere: Ce ion) (d) atomic HRTEM images of exposed $\{111\}$, $\{110\}$ and $\{100\}$ facets in CeO₂ nano cubes (46)

2.1.2 Defect Properties

The thermal and dynamic processes involved in the synthesis of cerium oxides can introduce imperfections in crystal structures owing to lattice distortion leading to displacement of atoms from their positions. In ceria, due to its cation redox switching and pH-dependent ability, it is possible to form intrinsic defects easily and the relevant equations for the formation of these intrinsic defects are given in **Table 2.1** (*18*). The different types of defects that can form in the ceria lattice are as follows:

Formation	Process	Defect Equilibria	
O Vacancy	Ionic Charge Compensation	$2Ce_{Ce}^{x} + 4O_{0}^{x} \xrightarrow{CeO_{2}} 2Ce_{Ce}' + 3O_{0}^{x} + V_{0}^{\bullet\bullet} + \frac{1}{2}O_{2} (g)$	(2.1)
	Electronic Charge Compensation	$\operatorname{Ce}_{\operatorname{Ce}}^{\operatorname{x}} + 20_{\operatorname{O}}^{\operatorname{x}} \xrightarrow{\operatorname{CeO}_2} \operatorname{Ce}_{\operatorname{Ce}}' + 20_{\operatorname{O}}^{\operatorname{x}} + \operatorname{h}^{\bullet}$	(2.2)
Ce Vacancy	Ionic Charge Compensation	$[4Ce'_{Ce}] + \{60^{x}_{O} + 2V^{\bullet\bullet}_{O} + 0_{2} (g)\} \xrightarrow{CeO_{2}} \{4Ce^{x}_{Ce} + V^{\prime\prime\prime\prime}_{Ce} + Ce^{x}_{S}\} + \{60^{x}_{O} + 2V^{\bullet\bullet}_{O} + 0_{2} (g)\}$	(2.3)
	Electronic Charge Compensation	$[4Ce'_{Ce}] + \{60^{x}_{O} + 2V^{\bullet\bullet}_{O} + O_{2}(g)\} \xrightarrow{CeO_{2}} \{4Ce^{x}_{Ce} + V^{\prime\prime\prime\prime}_{Ce} + Ce^{x}_{S}\} + \{80^{x}_{O} + 4h^{\bullet}\}$	(2.4)
	Ionic Charge Compensation	$Ce_{Ce}^{x} + 2O_{0}^{x} \xrightarrow{CeO_{2}} V_{Ce}^{\prime\prime\prime\prime\prime} + Ce_{S}^{x} + 2V_{0}^{\bullet\bullet} + O_{2} (g)$	(2.5)
Schottky Pair	Electronic Charge Compensation	$Ce_{Ce}^{x} + 20_{O}^{x} \xrightarrow{CeO_{2}} V_{Ce}^{\prime\prime\prime\prime\prime} + Ce_{S}^{x} + V_{O}^{\bullet\bullet} + 2h^{\bullet} + 20_{O}^{x}$	(2.6)
Frenkel Defect	Ce Interstitial	$Ce_{Ce}^{x} + 20_{0}^{x} \xrightarrow{CeO_{2}} Ce_{i}^{\dots} + V_{Ce}^{\prime\prime\prime\prime} + 20_{0}^{x}$	(2.7)
	O Interstitial	$Ce_{Ce}^{x} + 2O_{0}^{x} \xrightarrow{CeO_{2}} Ce_{Ce}^{x} + 2O_{i}^{\prime\prime} + 2V_{0}^{\bullet\bullet}$	(2.8)

Table 2.1. Potential defect equilibria for different defect formation mechanisms in CeO_{2-x} (18)

Electrochemical	Acidic Conditions	$2Ce_{Ce}^{x} + 40_{0}^{x} + 2H^{\bullet}(aq) + 2e'(ext) \xrightarrow{CeO_{2}} 2Ce_{Ce}' + 30_{0}^{x} + V_{0}^{\bullet\bullet} + H_{2}O(aq)$	(2.9)
	Basic Conditions	$2Ce_{Ce}^{x} + 40_{0}^{x} + H_{2}O(aq) + 2e'(ext) \xrightarrow{CeO_{2}} 4Ce_{Ce}' + 60_{0}^{x} + 2V_{0}^{\bullet\bullet} + 2OH'(aq) + \frac{1}{2}O_{2}(g)$	(2.10)
	F ⁰ -Centre	$\operatorname{Ce}_{\operatorname{Ce}}^{\operatorname{x}} + 20_{0}^{\operatorname{x}} \xrightarrow{\operatorname{CeO}_{2}} V_{\operatorname{Ce}}^{\prime\prime\prime\prime\prime} + \operatorname{Ce}_{\operatorname{S}}^{\operatorname{x}} + 2V_{0}^{\bullet\bullet} + O_{2} (g)$	(2.11)
Colour Centre	F ⁺ -Centre	$Ce_{Ce}^{x} + 2O_{O}^{x} \xrightarrow{CeO_{2}} V_{Ce}^{\prime\prime\prime\prime\prime} + Ce_{S}^{x} + 2V_{O}^{\bullet\bullet} + O_{2} (g) \xrightarrow{CeO_{2}} V_{Ce}^{\prime\prime\prime\prime} + Ce_{S}^{x} + V_{O}^{\bullet} + V_{O}^{\bullet\bullet} + O_{2} (g)$	(2.12)
	F ⁺⁺ -Centre	$2Ce_{Ce}^{x} + 40_{O}^{x} \xrightarrow{CeO_{2}} 2V_{Ce}^{\prime\prime\prime\prime\prime} + 2Ce_{S}^{x} + 4V_{O}^{\bullet\bullet} + 2O_{2} (g) \xrightarrow{CeO_{2}} 2V_{Ce}^{\prime\prime\prime} + 2Ce_{S}^{x} + 2V_{O}^{x} + 3V_{O}^{\bullet\bullet} + 2O_{2} (g) \xrightarrow{CeO_{2}} 2V_{Ce}^{\prime\prime\prime\prime} + 2Ce_{S}^{x} + 2V_{O}^{x} + 3V_{O}^{\bullet\bullet} + 2O_{2} (g) \xrightarrow{CeO_{2}} 2V_{Ce}^{\prime\prime\prime\prime} + 2Ce_{S}^{x} + 2V_{O}^{x} + 3V_{O}^{\bullet\bullet} + 2O_{2} (g) \xrightarrow{CeO_{2}} 2V_{Ce}^{\prime\prime\prime\prime} + 2Ce_{S}^{x} + 2V_{O}^{\bullet\bullet} + 2O_{2} (g) \xrightarrow{CeO_{2}} 2V_{Ce}^{\prime\prime\prime\prime} + 2Ce_{S}^{x} + 2V_{O}^{\bullet\bullet} + 2O_{2} (g) \xrightarrow{CeO_{2}} 2V_{Ce}^{\prime\prime\prime\prime} + 2Ce_{S}^{x} + 2V_{O}^{\bullet\bullet} + 2O_{2} (g) \xrightarrow{CeO_{2}} 2V_{Ce}^{\prime\prime\prime\prime} + 2Ce_{S}^{x} + 2V_{O}^{\bullet\bullet} + 2O_{2} (g) \xrightarrow{CeO_{2}} 2V_{Ce}^{\prime\prime\prime\prime} + 2Ce_{S}^{x} + 2V_{O}^{\bullet\bullet} + 2O_{2} (g) \xrightarrow{CeO_{2}} 2V_{Ce}^{\prime\prime\prime\prime} + 2Ce_{S}^{x} + 2V_{O}^{\bullet\bullet} + 2O_{2} (g) \xrightarrow{CeO_{2}} 2V_{Ce}^{\prime\prime\prime\prime} + 2Ce_{S}^{x} + 2V_{O}^{\bullet\bullet} + 2O_{2} (g) \xrightarrow{CeO_{2}} 2V_{Ce}^{\prime\prime\prime\prime\prime} + 2Ce_{S}^{x} + 2V_{O}^{\bullet\bullet} + 2O_{2} (g) \xrightarrow{CeO_{2}} 2V_{Ce}^{\prime\prime\prime\prime\prime} + 2Ce_{S}^{x} + 2V_{O}^{\bullet\bullet} + 2O_{2} (g) \xrightarrow{CeO_{2}} 2V_{Ce}^{\prime\prime\prime\prime\prime} + 2Ce_{S}^{x} + 2V_{O}^{\bullet\bullet} + 2O_{2} (g) \xrightarrow{CeO_{2}} 2V_{Ce}^{\prime\prime\prime\prime\prime} + 2Ce_{S}^{x} + 2V_{O}^{\bullet\bullet} + 2O_{2} (g) \xrightarrow{CeO_{2}} 2V_{Ce}^{\prime\prime\prime\prime\prime} + 2Ce_{S}^{x} + 2V_{O}^{\bullet\bullet} + 2O_{2} (g) \xrightarrow{CeO_{2}} 2V_{Ce}^{\prime\prime\prime\prime} + 2Ce_{S}^{x} + 2V_{O}^{\bullet\bullet} + 2O_{2} (g) \xrightarrow{CeO_{2}} 2V_{Ce}^{\prime\prime\prime\prime} + 2Ce_{S}^{*} + 2V_{O}^{*} + 2Ce_{S}^{*} + 2V_{O}^{\bullet\bullet} + 2O_{2} (g) \xrightarrow{CeO_{2}} 2V_{Ce}^{\prime\prime\prime\prime} + 2Ce_{S}^{*} + 2V_{O}^{\bullet\bullet} + 2O_{2} (g) \xrightarrow{CeO_{2}} 2V_{Ce}^{\prime\prime\prime\prime} + 2Ce_{S}^{*} + 2V_{O}^{\bullet\bullet} + 2O_{2} (g) \xrightarrow{CeO_{2}} 2V_{Ce}^{\prime\prime\prime} + 2Ce_{S}^{*} + 2V_{O}^{*} + 2O_{2} (g) \xrightarrow{CeO_{2}} 2V_{Ce}^{\prime\prime\prime} + 2Ce_{S}^{*} + 2V_{O}^{*} + 2Ce_{S}^{*} + 2Ce_{S$) (2.13)

• Oxygen vacancy (V₀^{••}): These are mainly formed from the intrinsic ionic charge compensation (Ce⁴⁺ → Ce³⁺) in the CeO₂ (**Table 2.1**) and have a low formation energy (2.10 eV) (48) The formation of oxygen vacancy within the crystal structure is shown in **Figure 2.3**. This intrinsic property can enable the CeO₂ to release significant levels of oxygen at low oxygen partial pressures, showing fundamental oxygen storage capacity (OSC) (33). The oxygen vacancy has a positive charge and has reductive ability which can attract and subsequently adsorb reactive oxygen species (ROS); these play an active role in the pathogenesis of different human diseases and in different catalytic applications (49). Further, the generation of V₀^{••} due to the Ce³⁺/Ce⁴⁺ redox reaction can result in active sites in the oxide for catalytic applications such as CO oxidation (50), water–gas shift (WGS) reaction (51), selective catalytic reduction of NO_x (52), oxidation of volatile organic compounds (VOCs) (53), and soot combustion (54).



Figure 2.3. Schematic of oxygen vacancy formation in CeO_2 (55)

In pure CeO_{2-x}, the formation of V₀^{••} (associated with Ce⁴⁺ \rightarrow Ce³⁺ charge compensation) is affected by both structural and morphological properties. Using Ce³⁺ and Ce⁴⁺ mapping, combined STEM and EELS analyses reveal that the {001} plane exhibits higher surface reduction and V₀^{••} concentration, than the {111} plane (56). The same approach also has revealed that CeO_{2-x} exhibits a radial increasing gradient in the Ce³⁺ and V₀^{••} concentrations in going from the bulk to the surface (57). These data are supported by DFT calculations that indicated that surface truncation corners, kinks, and steps at the surface are highly reactive sites, where Ce³⁺ ions are concentrated (58, 59).

Additionally, the $V_0^{\bullet\bullet}$ can enhance visible light adsorption by generating energy levels below the conduction band and these can also act as recombination centres since they can attract electrons. The $V_0^{\bullet\bullet}$ can act as a shallow donor and this can improve the donor density and electrical conductivity while also narrowing the bandgap and thereby enhancing the photocatalytic capability (*60*). The modulation of electronic structure through the presence of $V_0^{\bullet\bullet}$ and the high mobility of electrons as small polarons inside the CeO₂ can accelerate the charge transfer for electrocatalytic reaction (*61*). The lattice distortion and deformation from the formation of $V_0^{\bullet\bullet}$ can result in the increased exposure of active sites and improve the ionic conductivity (*61*). The defect-rich characteristics can be applied in various engineering applications (*62*). The direct and/or indirect presence and/or amount of $V_0^{\bullet\bullet}$ have been analysed by Raman (*63*), XPS (*64*), HRTEM (*65*), STEM (*66*), PL (*67*), EPR (*68*), EELS (*66*), and cathodoluminescence (CL) spectroscopy (*69*).

• Cerium vacancy $(V_{Ce}^{'''})$: Compared to oxygen vacancies, the formation of $V_{Ce}^{'''}$ is relatively difficult to achieve owing to its larger formation energy (23). However, it is possible to create the $V_{Ce}^{'''}$ by introduction of donor dopants owing to the resultant ionic charge compensation. The formation of cerium vacancy in the ceria lattice is shown in **Figure 2.4.** Cation vacancies play a crucial role in energy and environmental applications, since these can increase the electronic conductivity, promote charge transfer, modify redox reaction kinetics, lower the energy barrier for ion intercalation/deintercalation, and provide extra sites for charge storage; this leads to enhanced energy capacity and charge transfer property as it facilitates ionic diffusion process in energy storage (70). The cation vacancies also can lower the activation energy for proton transport through the lattice, and thus it can enhance the reactivity of the materials and improve the photocatalytic ability.

In electrochemical energy storage, this defect allows for the increased electrochemical intercalation of electrolyte cations near the cation vacancies, which leads to enhanced rate capability for electrochemical intercalation/deintercalation (71). These defects also can serve as host sites for insertion of protons or alkali cations for facilitating ionic diffusion in supercapacitors. In electrocatalysis, the reaction barrier can be reduced owing to the cation vacancy effect in modifying the

electronic properties and shifting the reaction rate-limiting step (72, 73) $V_{Ce}^{\prime\prime\prime\prime}$ can be indirectly or directly detected through EDS (HAADF) (73), STEM (74), X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) (75), X-ray PDF analysis (76), ICP-AES (77), and positron annihilation spectrometry (PAS) (78).



Figure 2.4. Schematic of cerium vacancy in $CeO_2(55)$

- Ce³⁺ ions: The Ce³⁺ ion has excellent and unique characteristics such as ferromagnetism owing to the presence of one unpaired electron in the 4*f* orbital (79). Its low band gap (2.4 eV) (80) is able to shift CeO₂ electron excitation region from ultraviolet light to visible light, improving photocatalytic ability (81). The unstable electron on 4*f* orbital in Ce³⁺ can be as catalytic active site facilitating H₂ production, when water vapour is used as an oxidant (82). Further, this unstable electron characteristic in Ce₂O₃ can address the poor electrical conductivity issue in CeO₂. In catalytic application, due to lower-oxidation-state cations having the lower electronegativity, Ce³⁺ ions show faster adsorption and desorption capability compared to Ce⁴⁺ ions (83).
- Schottky pair: The highly coordinated cubic fluorite structure can allow the formation of a Schottky pair; however, the difference in ionic radius between Ce and O can have a negative impact on Schottky pair generation (84). According to the defect equilibria,

 $V_{Ce}^{\prime\prime\prime\prime}/2V_{O}^{\bullet\bullet}$ pairs are formed which may create isolated $V_{Ce}^{\prime\prime\prime\prime}$ and $V_{O}^{\bullet\bullet}$ clusters (Figure 2.5).



Figure 2.5. Schematic of Schottky pair formation in CeO₂ (38)

• $V_0^{\bullet\bullet}$ cluster: Since the $V_0^{\bullet\bullet}$ are strongly localized in the crystal lattice, it easy to form the oxygen vacancy clusters. The annealing time can promote oxygen vacancy cluster formation as seen from atomic scanning tunnelling microscopy (STM) images shown in **Figure 2.6** (*85*). The $V_0^{\bullet\bullet}$ cluster exists because of a synergistic effect between $V_0^{\bullet\bullet}$ which can promote simultaneous adsorption and activation of oxidizing species and serve as efficient active sites for catalytic reactions (*86*). Further, the $V_0^{\bullet\bullet}$ clusters can easily lose electrons from the trap sites and thus show better catalytic activity compared to single $V_0^{\bullet\bullet}$ (*87*).



Figure 2.6: Atomic STM images of vacancies in the CeO₂ lattice (85)

Frenkel defect: These have high formation enthalpy which need external energy such as electronic excitation (88), thermo-kinetic energy (89), and element irradiation (89). In this case, the cation Frenkel defect (Figure 2.7a) in CeO₂ shows extremely high formation energy (6.38 eV) and this limits its existence (generation of V_{Ce}^{'''}/Ce_i^{'''} pairs) (90). However, anion Frenkel defects (Figure 2.7b) are formed relatively easily owing to its low formation energy (2.04 eV) compared to the Schottky pair and cation Frenkel pair in CeO₂.(55) The O_i^{''}/V₀^{••} pair implies the possible dynamics of oxygen-assisted defects (vacancy formation, migration, etc.) which would enhance the oxygen storage and reversible catalytic behaviour (91). This unique mobile oxygen species and high ionic conductivity will account for applications in solid oxide fuel cell (SOFC) and thermo catalysis for CO oxidation and soot oxidation reaction.(63, 88, 91, 92)



Figure 2.7. Schematic of Frenkel defects in ceria: (a) cation Frenkel defect (b) anion Frenkel defect in the CeO₂ (Ce atom: white circles; O atom: red circles; electron: blue circles).(55)

• Fabre-Centre (colour centre): The appearance of F-centres has been ignored mostly when considering the formation of intrinsic defects in CeO₂. The F-centre plays a vital role in determining the solid colour owing to it arising from the negatively charged ions acting as a trap to attract electrons; electrons on different trapping sites can be excited by different wavelengths of light, giving rise to different colours (93) The schematic of F centre formation in the lattice is shown in Figure 2.8. The pale yellow-white colour of CeO₂ is likely from the existence of F-centres. The oxygen vacancy is a main constituent unit of F-centre and can trap different numbers of electrons and these are represented as V₀^x, V₀^o, and V₀^{oo} (18).



Figure 2.8. Schematic of colour centre on CeO_2 (black sphere: cation; white sphere: anion) (94)

These F-centres can be generated through high-energy irradiation, thermo-kinetic mechanisms, and by magnetic ion doping causing F-centre exchange (FCE) coupling (95). The stability diagram (**Figure 2.9**) shows that based on theoretical calculations, at temperatures above 1000°C, singly ionized vacancies (V_0^{\bullet}) are abundant in CeO_{2-x}.(45) The different types, namely V_0^{\bullet} , V_0^{\bullet} , and $V_0^{\bullet\bullet}$ will modify the electronic structure by causing changes in the mid gap position and the existence of V_0^{\bullet} and V_0^{\bullet} can resolve the issue of fast recombination of photogenerated electron-hole pairs in CeO₂ caused by $V_0^{\bullet\bullet}$ being present as a mid-gap state (96). The V_0^{\bullet} in CeO₂, defined as only one electron trapped in positive vacancy position, has F-centre exchange mechanism, which can manifest in terms of ferromagnetic properties (97-99).



Figure 2.9. Electrical conductivity as a function of pO_2 in a series of isotherms based on oxygen vacancy model [solid line (curves are theoretical fit line), dashed lines (boundaries at which the defect mechanisms change)] (45)

2.1.3 Electronic Band Properties

CeO₂ is a n-type semiconductor with band gap of 3.1 eV which requires high excitation energy (100). The stoichiometric CeO₂ band gap energy is about 6 eV and was determined from the O 2p orbital as valence band (VB) to Ce 5d orbital as conduction band (CB) (101). However, DFT calculations show the empty Ce 4f states lie above the Fermi level and within the band gap, and thus, the band gap in CeO₂ can be measured as 3 eV, which is the distance from O 2p orbital (VB) to the bottom of the empty Ce 4f orbital (CB) and this is shown schematically in **Figure 2.10** (59, 102). The intrinsic defects in the CeO₂, can act as mid-gap state to modify the electric band structure (103). The V₀^{••} is the most common defect and has two positive holes since the two electrons left behind are trapped at two cerium sites. At such cerium sites, the electron prefers to occupy an empty Ce 4f state that splits the Ce4f band into two sub-bands: an occupied Ce4f full band and an empty Ce 4f empty band as shown in **Figure 2.10**. Practically, the reduction limit of non-stoichiometric ceria is Ce₂O₃, where all cerium ions are Ce³⁺. The electronic band structure of Ce_2O_3 bears resemblance to that of partially reduced ceria, in which Ce 4*f* empty and Ce5*d* bands have been merged together in the conduction band as shown in **Figure 2.10** (*102*).



Figure 2.10. Schematic electronic structures of (a) stoichiometric CeO₂, (b) partially reduced CeO_{2-x} and (c) Ce₂O₃. Blue bands represent O 2*p* orbitals as valence band (VB), whereas green and red bands represent Ce electronic band identified as conduction band (CB) (*102*)

The position of the CB edge and VB edge can be calculated at the point of zero charge, according to the following equations 2.14 and 2.15 (*104*):

$$E_{CB}^{0}(CeO_{2}) = \chi(CeO_{2}) - E_{c} - \frac{1}{2}E_{g}(CeO_{2})$$
(2.14)

$$E_{VB}^{0}(CeO_{2}) = E_{g}(CeO_{2}) - E_{CB}^{0}(CeO_{2})$$
(2.15)

* where $E_{CB}^{0}(CeO_{2})$ and $E_{VB}^{0}(CeO_{2})$ as conduction and valence band potentials, respectively; χ is the absolute electronegativity of the semiconductor, which is the geometric mean of the electronegativity of the constituent atoms (5.56 eV for CeO₂); $E_{g}(CeO_{2})$ is the band gap energy; and E_{c} is the energy of free electrons on the hydrogen scale (~4.5 eV).

According to the calculation, band gap energy is $\sim 3 \text{ eV}$ and the corresponding $E_{CB}^{0}(CeO_2)$ and $E_{VB}^{0}(CeO_2)$ are -0.44 and 2.56 eV, respectively.

2.2 Energy and Environmental Applications of Ceria

2.2.1 Supercapacitors

Pseudocapacitance is a variation of the supercapacitor behaviour based on faradaic charge storage mechanism (105). The supercapacitor functions through the occurrence of rapid and highly reversible redox reactions on the surface and/or near-surface of the electrodes to achieve charging and discharging, which involves charge transfer between the electrode and the electrolyte (**Figure 2.11**) (106).



Figure 2.11. Schematic of the operation of a pseudocapacitor (107)

CeO₂ is considered to be a highly promising supercapacitor electrode material owing to its excellent redox properties and high theoretical capacitance (560 $\text{F} \cdot \text{g}^{-1}$) (108). The switching capability between Ce³⁺ and Ce⁴⁺ ensures that CeO₂ can be used in this application. In the CeO₂-based supercapacitor, there are mainly two ways to achieve charging and discharging, as shown in the following equations (2.16-2.20) (109-111):

(1) Intercalation/deintercalation:

Charging:

Anode:
$$E_{S1} + A^- \xrightarrow{charging} E_{S1}^+ \parallel A^- + e^-$$
 (2.16)

Cathode:
$$E_{S2} + C^+ + e^- \xrightarrow{charging} E_{S2}^- \parallel C^+$$
 (2.17)

Discharging:

Anode:
$$E_{S2}^- \parallel C^+ \xrightarrow{discharging} E_{S2} + C^+ + e^-$$
 (2.18)

Cathode:
$$E_{S1}^+ \parallel A^- + e^- \xrightarrow{discharging} E_{S1} + A^-$$
 (2.19)

* E_{S1} and E_{S2} represent two electrode surfaces; A^- represents an anion in the electrolyte; C^+ represent a cation in the electrolyte is C+; \parallel represent the electrode/electrolyte interface.

(2) Redox reaction:

$$CeO_x(OM)_y + \delta M^+ + \delta e^- \leftrightarrow Ce_{x-\delta}(OM)_{y+\delta}$$
 (2.20)

* M⁺ indicates cations such as K⁺ as well as protons (H⁺) in electrolyte; $CeO_x(OM)_y$ and $CeO_{x-\delta}(OM)_{y+\delta}$ represents CeO₂·nH₂O in high and low oxidation states.

However, CeO₂ still has some drawbacks as an electrode material:

- 1. Low electrical conductivity: Semiconductor metal oxides with wide bandgaps typically exhibit poor electrical conductivity, which is detrimental for obtaining good electrode performance (112).
- 2. Metal oxides generally suffer from poor ion diffusion kinetics, especially in the form of bulk materials with small surface area and nonporous structures (113). Other than through the preparation of materials with large surface area and porous structures, the generation of cationic vacancies in electrode materials is considered as an effective strategy to improve their electrochemical energy storage performance, since it effectively reduces the diffusion energy barriers, thus promoting the ion intercalation during electrochemical cycling. Moreover, the cation vacancies, or vacancy clusters can also serve as extra host sites for ion storage, thus providing higher charge storage capacity (114). Koketsu *et al.* presented a broad range of experimental result (Figure 2.12) and this shows that the formation of cation vacancies can result in a much greater capacity compared to pure TiO₂, owing to the insertion of multivalent ions into titanium vacancies (115).


Figure 2.12. (a-e) High-resolution TEM image of a $TiO_{1.12}F_{0.40}(OH)_{0.48}$ nanoparticle. (f-g), Galvanostatic discharge–charge curves for TiO_2 and vacancy-containing anatase versus Mg, Al. Cells were cycled under 20 mA g⁻¹ in the potential range 0.05–2.3 V versus Mg²⁺/Mg and Al³⁺/Al (*115*)

2.2.2 Photocatalysis

A photocatalytic reaction on a semiconductor includes at least five main steps as shown in **Figure 2.13**) light absorption by the semiconductor, ii) formation of photogenerated electron–hole pairs, iii) migration and recombination of the photogenerated electron–hole pairs, iv) adsorption of reactants and desorption of products, and v) occurrence of redox reactions on the semiconductor surface (*3*).



Figure 2.13. Schematic of the reaction mechanisms that occur in photocatalysis (116)

Owing to its special conduction band position, the capacity to form nonstoichiometric oxygen-deficient CeO_{2-x}, high oxygen mobility, and reversible transformation between Ce⁴⁺/Ce³⁺ has gained attention for use in photocatalytic applications (*117*). The oxygen vacancy can be regarded as photocatalytic active sites for oxidizing organic pollutant based on Mars and van Krevelen (MvK) mechanism (*118*). Further, oxygen vacancies can be used as adsorption site to attract reactants (*e.g.*, molecules of pollutants and water) to accelerate the catalysis reaction. (*119, 120*).

Cerium oxide exhibits strong absorption in the UV region, and high transparency in the VIS region and near IR region (121). The photogenerated $e^{-/h+}$ pairs have much longer lifetimes than those generated in TiO₂ (104). Figure 2.14 shows the positions of CB and VB in CeO₂ including the potentials of the production of reactive oxide species (ROS) and hydroxyl radical and superoxide anion radical formation; these reactive oxide species can be formed at the semiconductor surface and can participate in the degradation of pollutants. Furthermore, the potential of CB in CeO₂ is in the proximity of the potential of hydrogen evolution and the VB potential includes the potential of oxygen evolution as seen in Figure 2.14(122). This the CeO₂ can be a effective catalyst for photocatalytic hydrogen generation. However, H₂ and O₂ formed during the water splitting process can undergo the recombination reaction, which is hard to prevent (123).



Figure 2.14. Schematic of band gap structure of CeO₂ relative to different reactions (104)

There still are several inherent flaws of CeO₂ that hinder its photocatalytic performance:

1. The high band-gap energies limit their use in visible light range and thus irradiation excitation with UV light at wavelengths < 360 nm (3% of the solar spectrum) is required (124)

2. High rate of charge carrier recombination (125)

3. The catalytic activity of CeO₂ strongly depends not only on the particle size, but also on the morphology and exposed planes and the photocatalytic activity of common exposed plane in CeO₂ follows the order: $\{100\} > \{110\} > \{111\}$ (117).

2.2.3 Electrocatalysis

Electrocatalysis can be applied for different reactions and these include oxygen evolution reaction (OER), oxygen reduction reaction (ORR), hydrogen evolution reaction (HER), hydrogen oxidation reaction (HOR), methanol electrooxidation reaction (MOR), ethanol electrooxidation reaction (EOR), and electrocatalytic nitrogen reduction reaction (NRR) (*126*). Electrocatalytic HER is essentially an electrochemical process where redox reactions take place at the electrode/electrolyte interface. The schematic of the process of HER by electrocatalysis is shown in **Figure 2.15**. Based on the pH value of the electrolyte, H₂ is generated *via* the reduction of either protons (H⁺) or H₂O, both of which involve a series of elementary steps (*127*). At the beginning of HER, a H⁺ adsorbs on the

catalyst surface to form an adsorbed hydrogen atom (H^*) and this process is called the Volmer step or the discharge step (128).



Figure 2.15. Schematic of acidic and basic HER occurring by electrocatalysis (123)

Then a H* combines with a H⁺ and an electron (e^{\bullet}) to form a H₂ molecule, and this step is the Heyrovsky step or the electrochemical desorption step (*129*). Meanwhile, H₂ could be formed *via* the Tafel step by two adsorbed hydrogen atoms combining and this is the chemical desorption step. In the alkaline environment, due to the lack of H⁺, the HER in alkaline media starts from the dissociation of H₂O molecules to provide protons and this process is less energetically feasible. The following reactions are known to take place as shown in equations (2.21-2.25) (*130*):

Volmer step (discharge step):

Acid:
$$H^+ + e^{\bullet} \rightarrow H^*$$
 (2.21)

Alkaline:
$$H_2 O + e^{\bullet} \rightarrow H^* + OH^{\bullet}$$
 (2.22)

Heyrovsky step (chemical desorption step):

Acid:
$$H^+ + H^* + e^{\bullet} \rightarrow H_2$$
 (2.23)

Alkaline:
$$H^* + H_2 O + e^{\bullet} \rightarrow H_2 + OH^{\bullet}$$
 (2.24)

Tafel step (chemical desorption step):

Acid, Alkaline:
$$H^* \to H_2$$
 (2.25)

There is very limited research on CeO_2 materials as an electrocatalyst for HER. CeO_2 has excellent ionic conductivity, high oxygen storage capacity, reversible oxidation state of Ce^{3+}/Ce^{4+} and acts as a water dissociation promoter to produce hydrogen intermediates;

thus, CeO_2 has emerged as predominant candidates for HER electrocatalysis (131-133). However, the disadvantages of CeO_2 in HER catalytic reaction cannot be ignored:

- 1. The limited CeO_2 electronic conductivity hinders the electron transfer from the materials bulk to surface for electrocatalysis reaction.(*134, 135*)
- 2. In the reaction step of H* conversion into H₂, a thermo-neutral ΔG_{H^*} value of 0 eV is desired, which corresponds to the balance between the rate of proton reduction and the ease of removal of adsorbed hydrogen from the surface. The Gibbs free energy of water dissociation step (ΔG_{H2O}) on CeO₂ (111) plane is -1.75 eV, which is too high and thus H* desorption and H₂ production would be hindered (*136*).

The heterojunction of a metal with CeO₂ thus becomes an effective strategy owing to the alignment effect between positive Gibbs free energy (ΔG_{H^*}) material with CeO₂ leading to the reduction in the strong hydrogen absorption ability of CeO₂. Wang *et al.* explored a hydrothermal method using metal Ti as template to synthesise Co₃O₄-CeO₂ and a novel CeO₂–CoP nanoarrayed electrocatalyst obtained from Co₃O₄-CeO₂ by calcining at 300°C, which provided an overpotential of only 43 mV (*137*) at current density of 10 mA cm⁻² in electrochemical water splitting. Density functional theory calculations showed that the CeO₂–CoP interfacial structure was conducive to water dissociation to provide extra H⁺ ions, with more desirable ΔG_{H^*} (–0.18 eV) closer to zero (Pt[ΔG_{H^*}]) in the CeO₂–CoP heterojunction structure, which balances the rate of proton reduction and that of adsorbed hydrogen removal from the surface (**Figure 2.16**) (*138*).



Figure 2.16. (a) Schematic illustration of the selective phosphidation in the CoP–CeO₂ catalyst synthesis and the catalytic process; (b) DFT calculated reaction energy diagram of water dissociation and Δ GH* for CoP(211) and CoP(211)/CeO₂(111) plane.(*138*)

3. A high surface area is required since the whole reaction process is occurring mainly on the surface and involves adsorption and desorption.

2.2.4 Ozonation Catalysis

Ozone (O₃) is widely used in water treatment processes to efficiently oxidize organic pollutants containing aromatic rings, amino groups, or conjugated double bonds (*139*, *140*). The O₃ has high oxidation potential [2.07 V] and can act as a catalyst to increase formation of ROS species such as hydroxyl radicals (•OH) [2.8 eV] in water to decompose and even mineralize pollutants (*141*).

However, during ozonation process, it suffers from low efficiency owing to ozone's low solubility and high stability in water (142). Catalytic ozonation is designed to overcome these problems because it can promote O_3 decomposition and promote active free radical (ROS) generation. CeO₂ is considered as a novel ozonation catalyst in waste water

treatment owing to its varying types of defects (such as intrinsic oxygen vacancy), the proper CB position (close to ROS formation energy level), and acid/basic switching ability from Ce³⁺/Ce⁴⁺ species (*143*), but there is limited research on such applications. Wu *et al.* reported a facile impregnation–calcination method to synthesise mesoporous γ -Al₂O₃-supported manganese–cerium mixed oxides. This heterojunction structure as ozonation catalyst shows relatively high Total Organic Carbon (TOC) removal rate of 51.6% compared with 31.5% for γ -Al₂O₃ and 9.6% in sole ozonation after 120 min (**Figure 2.17b**) (*144*). The effect of inter valence charge transfer (IVCT) for ozonation catalysis was observed in this case. In MnO_x and CeO₂ heterojunction, the Mn³⁺/Mn⁴⁺ and Ce⁴⁺/Ce³⁺ species show IVCT, which promotes electron transfer. These species also can act as active sites for ozone decomposition of ROS species (**Figure 2.17a**).



Figure 2.17. (a) Influence of tert-butyl alcohol (TBA) on the degradation efficiency of phenol with different catalysts (CeO₂-T: nano size [7 nm]; CeO₂-W: nano size [15 nm]) Effect of TBA on phenol adsorption (*144*)

Thus there is a urgent need to use different approaches to modify the CeO₂ properties to overcome limitations such as non-active surface area (145) and low exposed active site (146). There are three common approaches that are used, namely heterojunction formation, doping, and morphological modification.

2.3 Heterojunction Formation

Heterostructures are widely used as a basic building block in advanced semiconductor devices owing to their essential and attractive structural, interfacial, and electronic properties. In general, heterostructures have a comparatively better electrical and optical performance with respect to the layers of individual materials owing to the charge transfer (3). The charge transport mechanism in the heterostructures depend on various parameters such as materials, their band alignments, surface behaviour, interfacial characteristics, and the mobility of charge carriers (147). Heterojunctions physically or chemically juxtapose two different semiconductor materials, which also usually have different dopants. In the physical absorption heterostructures, the interaction between these materials is weak; therefore, there is limited work in this regard. The formation of physical absorption heterostructures is likely because of the incompatibility between these two materials or the limited saturability of host material. In the metal–semiconductor heterojunction, the physical absorption heterojunction can form Schottky barriers (148).

Combining transition metal oxides with conducting materials or other metal oxides forming chemical heterojunctions is a common way to enhance the electrical conductivity and electrochemical reactivity (5). According to charge separation mechanisms, the heterojunctions can be classified as shown in **Figure 2.18** (*149*):

(1) Type I heterojunction: The mechanism of type I band alignment is based on Anderson's rule. Semiconductor 1 (SC1) has lower VB and higher CB positions than Semiconductor 2 (SC2), which indicate that the SC1 band gap is larger than that of SC2. When a heterojunction between SC1 and SC2 is formed, the VB holes and CB electrons in SC1 tend to migrate to SC2 owing to the having lower band gap of the latter.

- (2)Type II heterojunction: The mechanism of type II band alignment also is based on Anderson's rule. SC1 has higher VB and CB positions than those of SC2. In this case, the SC1 and SC2 band gaps are dissimilar and, upon heterojunction formation, the holes transfer to the lower-energy VB and the electrons transfer to the higher-energy CB.
- (3) P–N type heterojunction: The working mechanism is similar to that of type II heterojunction. The SC1 and SC2 usually have the same band gap and p-type SC1 have greater electron affinity than n-type SC2.
- (4) Schottky junction: The mechanism of type II band alignment also is based on Taroff's rule. Electrons in SC1conduction band will tune into metal like SC2 to generate builtin electric field and drives the charge flow, causing Schottky effect.
- (5) Z-type heterojunction: This system is constructed of two semiconductors with suitable intermediate redox ion couples and/or conductor (*e.g.* metal); electrons on the lower value CB of SC2 directly combine with VB of SC1.
- (6) S-type heterojunction: The working mechanism is similar to Z-type heterojunction. This S-scheme heterojunction does not need intermediate species to achieve the charge transfer. Instead of that, extra energy through an electric field or ultraviolet light irradiation is required.

The heterojunction structure can effectively avoid the recombination of photo generated electrons and holes. The use of heterojunction structure can be applied in different applications such as photocatalysis (150), electrocatalysis (151), energy storage (152), and ozonation catalysis (153).



Figure 2.18. Band structure of various types of heterojunctions in a photocatalytic hybrid nanocomposite: (a) type I heterojunction, (b) type II heterojunction, (c) p–n junction, (d) Schottky junction, (e) Z-scheme heterojunction, and (f) S-scheme heterojunction. A, D and E_f represent electron acceptor, electron donor and Fermi level, respectively (*154*)

The heterojunction structure results in an interfacial effect that can promote the separation of photogenerated holes and electrons and thus prolong the lifetime of the charge carriers and thus enhance the photocatalytic effect (*155*). Further, Mofarah *et al.* reported the fabrication of ultra-thin CeO₂ nanosheets that showed a synergistic effect with different types of transition metals which were added to engineer their band alignments; the formation of heterojunction nanostructures were proven by DFT analysis shown in **Figure 2.19** (*32*). The band gap, valence band position, and work function of the sample were analysed by Uv-vis, XPS and KPFM, respectively. The new band position of heterojunction Fe₂O₃-CeO₂ became shallow and was closer to the level of the formation of reactive oxygen species compared to pure CeO₂. This band alignment by heterojunction formation can provide a solution to the issues related to the wide band gap of CeO₂.



Figure 2.19. Band structure characterization of CeO_{2-x} and 0D/2D heterostructures. (a) Topography of CeO_{2-x} holey nanosheet. (b) Contact potential difference measured by KPFM of (c) XPS valence band plot. (d) Tauc plot from UV–vis (e) Electronic energy level diagram for CeO_{2-x} holey nanosheet and 0D/2D heterostructures. (f) First-principle DFT computations of electronic densities of states and bandgaps of CeO_2 nanosheets and bulk CeO_2 . (g–i) DFT computations of electronic densities of states and bandgaps of states and bandgaps of 0D/2D heterostructures (*32*)

In electrocatalysis, by constructing a highly coupled interface in the heterojunction structure, the electronic state, chemical properties, and electrical conductivity can be significantly improved (*156*). The chemical heterojunction can also improve the performance of electrocatalysts due to fast electronic diffusion and effect of intimate electronic coupling. The CoO-CeO₂ heterostructure was made by refluxing with zeolitic imidazolate frameworks and then thermal annealing at 320°C (**Figure 2.20a**). It showed impressive OER performance requiring only 287 mV to reach the current density of 10 mA/cm while also having long-term stability (**Figure 2.20b**) owing to the heterojunction effect causing a rearrangement of the electronic configuration of CeO₂ to improve the electron conductivity; (this was proven through the EIS analysis curve) and large active sites on electrochemical surface area (*157*).



Figure 2.20. (a) Schematic illustration of the formation of CoO-CeO₂ heterostructures.(b) Electrochemical performance of CoO-CeO₂ heterostructures (*157*)

CeO₂-based heterojunctions such as TiO₂-CeO₂ (158), ZnO-CeO₂ (159), Fe₂O₃-CeO₂ (160), and Cu₂O-CeO₂ (161) all show enhanced performance in photocatalysis, CO oxidation, ozonation catalysis, and photo-electronic behaviour, respectively. The synthesis methods of heterojunction are similar to doping engineering methods such as wet chemistry (162) and coprecipitation (163). This is because the formation of heterojunctions result from the dopant addition level exceeding the solid solubility limit (164). The heterojunction also can be formed through physical synthesis methods such as *ex situ* assembly method (165) and *in situ* growth methods (166) where Van der Waals' forces assist in forming the bond.

2.4 Doping

The large void sizes of the CeO₂ central interstice (radius: 0.110 nm), Ce sublattice (radius: 0.160 nm), and O sublattice (radius: 0.067 nm) allow for dopant ions to be incorporated in the lattice (18). These data illustrate the considerable capacity for interstitial solid solubility as two of the three voids are larger than the ionic radii of the nearly all cations. Dopants can be either acceptors (valence less than host), donors (valence greater than host), or natural dopant (same valence as the host). The acceptor doping can introduce numrous $V_0^{\bullet \bullet}$ by ionic charge compensation. Rangaswamy *et al.* used coprecipitation to synthesise two different types of solid solutions CeO2-Sm2O3 and CeO2-La2O3 which represent acceptor doping and as a result there was an increase in $V_0^{\bullet \bullet}$ concentration as seen from the increase in the ratio of Ce^{3+}/Ce^{4+} ([Ce^{3+}]) in XPS analysis. $CeO_2-Sm_2O_3$ showed the highest $V_0^{\bullet\bullet}$ concentration value and the best performance in soot oxidation reaction compared with CeO₂-La₂O₃ and CeO₂ (Figure 2.21) (167). From the smaller crystallite size of CeO₂-Sm₂O₃, it can be assumed that there is higher solid solubility of Sm ions because of higher amounts are incorporated into the host lattice such that it hinders the growth of CeO₂ crystals (168). The Sm crystal radius (0.1098 nm) is smaller than La (0.1178 nm), which also allows easier diffusion into CeO₂ when considering Hume-Rothery rules for solid solubility (169). Acceptor doping can thus be as an effective strategy to stabilize intrinsic oxygen vacancies and create more extrinsic oxygen vacancies (170). The common acceptor dopants for CeO₂ are Cu⁺ (171), Mn³⁺ (172), and Fe^{3+} (173).



Figure 2.21. (a) Schematic illustration of the formation of CoO-CeO₂ heterostructures.(b) electrochemical performance of CoO-CeO₂ heterostructures (*167*)

Although the donor and natural dopant will cause the oxygen vacancy annihilation owing to the electronic and redox charge compensation, these will easily produce more stable $V_{Ce}^{\prime\prime\prime\prime}$ by ionic charge compensation (*18*). The cation vacancies will create more mobile electrons to modify the conductivity (*75*). Ru is a natural dopant with valence of 4+. RuO₂ has metallic character showing excellent electronic conductivity (*14*) and can form a solid solution of Ru-CeO_{2-x} (*21, 24*). **Table 2.2** summarises the outcomes of Ru doping of CeO₂ for use in different applications.

No	Sample	Fabrication	Morphology	BET(m ² /g)	Application	Ref.
1	Ru-CeO ₂ (3 wt%)	Hydrothermal; Precipitation deposition	N/A	$S_{BET} = 34.2$	Catalyst toward CO ₂ Methanation	(174)
2	Ru/CeO ₂ (0.4 wt%)	Hydrothermal; Wet impregnation	Nanorods (t) Nanocubes (c) Nanooctahedra (o)	$S_{BET(Ru-CeO2-r)} = 58$ $S_{BET(Ru-CeO2-c)} = 21$ $S_{BET(Ru-CeO2-o)} = 18$	Catalytic combustion of chlorobenzene	(175)
3	Ru/CeO ₂ (5 wt%)	Wet impregnation	N/A	S _{BET} = 125	Catalyst wet air oxidation of aqueous solutions of maleic acid	(176)
4	Pt-Ru/CeO ₂ /c arbon nanotube (10 wt% of Pt-Ru)	Rapid sonication- facilitated deposition method	Nanoparticles	N/A	Direct methanol fuel cells	(177)

Table 2.2. Summary of studies on Ru doped CeO₂ and the major outcomes in terms of properties and performance of the nanostructures

No	Sample	Fabrication	Morphology	BET(m ² /g)	Application	Ref.
5	Ru-CeO ₂ /C & Ru/C; (1.5 wt% Ru)	Consecutive impregnation	N/A	$S_{BET} = 160$	Catalytic wet air oxidation of phenol and acrylic acid	(178)
6	Ru/CeO ₂ (2.5 wt%)	Hydrothermal; impregnation	Nanoparticles	$S_{BET} = 76.7$	Catalysts for ammonia synthesis	(179)
7	(2 wt%) Ru/ (30%) CeO ₂ / Al ₂ O ₃	Impregnation	Al ₂ O ₃ : nanorods; CeO ₂ : Porous nanoparticles	$S_{BET(CeO2)} = 115$	Promotion of CO ₂ methanation activity	(180)
8	Ru/CeO ₂	Precipitation Impregnation	Nanoparticles; Nanorods; Nanocubes	N/A	Linear-regioselective hydro- methoxy-carbonylation of styrene	(181)
9	Ti-Ru (3 wt%)/CeO ₂	Hydrothermal; sol gel; incipient wetness	Nanorods; Nanocubes	$S_{BET-s} = 62$ $S_{BET-E} = 30$	Ammonia synthesis	(182)

No	Sample	Fabrication	Morphology	BET(m ² /g)	Application	Ref.
10	Ru/CeO ₂ (5 wt%)	Hydrothermal; precipitation; impregnation	Nanorods: Nanocube; Nano-octahedra	$S_{BET} = 108.4$	Low temperature CO oxidation	(183)
11	Ru/Ni/Rh- CeO ₂ ; SiO ₂ ; TiO ₂	Precipitation; Co-impregnation	Nanoparticles	$S_{BET-CeO2} = 87$	CO ₂ methanation & sulphur tolerance	(184)
12	Ru/CeO ₂ (1, 1.5, 1.65, 1.85, 2, 3, 5 wt%)	Wet impregnation	N/A	$S_{BET(Ru1.67)} = 89$	Catalytic oxidation organic compounds	(185)
13	Ru/CeO ₂ (2 wt%)	Impregnation acid exchange	Nanoparticles	$S_{BET} = 42.1$	Catalytic ozonation	(93)
14	Ru/CeO ₂ (10 wt%)	Hydrothermal; impregnation	Nanorods; Nanocube	$S_{BET(CeO2-r)} = 76$ $S_{BET(CeO2-c)} = 23$ $S_{BET(Ru-CeO2-r)} = 68$ $S_{BET(Ru-CeO2-r)} = 19$	Catalysts for ammonia synthesis	(186)

No	Sample	Fabrication	Morphology	BET(m ² /g)	Application	Ref.
15	Ru/CeO ₂	Sol gel hydrothermal loading method	Mesoporous nanoparticles; mesoporous flowerlike microspheres	N/A	Solid oxide fuel cells	(187)

Mo is another potential dopant being a transition metal with different valence states (6+, 5+, 4+). This gives rise to the possibility of electron exchange between dopant and matrix ions through inter valent charge transfer (IVCT) (*18*). In the case of Mo doping of CeO₂, the reported MoO₃-CeO₂ phase diagram (**Figure 2.22**) shows that both Ce₂(MoO₄)₃ and Ce₂(MoO₃)(MoO₄)₃ can be formed at 1073K (*188*).



Figure 2.22. Phase diagram of MoO₃- CeO₂ system at 1073 K (188)

No solid solubilities were indicated but these did not appear to have been investigated. These equilibria products indicate that, for both phases, $MoO_3 \rightarrow MoO_4^{2-}$ oxidation is balanced by $2Ce^{4+} \rightarrow 2Ce^{3+}$ reduction; the newest research is summarized in **Table 2.3**. **Tables 2.3-2.4** show that there is limited discussion of the effects of donor and natural doping on forming cation vacancies. There is an increased number of theoretical oxygen vacancies based on XPS analysis in these studies and this is owing to the redox charge compensation and IVCT between the host and dopant leading to the creation of additional Ce^{3+} ions. Therefore, the different dopants can be selectively applied to modify the properties of ceria for different applications, not only owing to the effect of dopant addition but also owing to the formation of different defects.

	Material	Fabrication Route	Morphology	BET (m ² /g)	Applications	Ref.
1	$Pt/Ce_{1-x}Mo_xO_{2-\delta}$	Solvothermal	Nanoparticle	S = 168	Electrocatalysis in direct methanol fuel cells	(189)
2	Mo/CeO ₂ (Al ₂ O ₃)	Impregnation; Co-precipitation	N/A	S = 16.2	CO adsorption/ thermal stability	(190)
3	$Ce_{1-x}Mo_xO_{2+d}$	Solid-state reaction	Nanoparticle	N/A	High electrical conductivity	(191)
4	CeO ₂ /TiO ₂ -MoO ₃	Hydrothermal impregnation	N/A	S = 121	Thermocatalysis performance	(192)
5	MoO ₃ /CeO ₂ (8 wt%)	Impregnation co-precipitation	N/A	S = 96	CO oxidation activity	(193)
6	MoO ₃ -CeO ₂	Wet impregnation	N/A	N/A	Raman	(194)

Table 2.3. Summary of studies on Mo doped CeO₂ and the major outcomes in terms of properties and performance of the nanostructures

	Material	Fabrication Route	Morphology	BET (m ² /g)	Applications	Ref.
7	MoO ₃ /CeO ₂ (5 wt%)	Calcination precipitation impregnation	Nanoparticle	S = 96	Sulfur-resistant methanation	(195)
8	Mo/CeO ₂ (5 wt%; 7%; 10%)	Fuel combustion	Nanoparticle	S = 15.1	Carbon-air solid oxide fuel cell	(196)
9	MoO ₃ -doped CeO ₂ -ZrO ₂ (5 wt%)	Hydrothermal	N/A	N/A	Catalytic reduction of NO _x	(197)
10	MoO ₃ -CeO ₂ -SiO ₂	Sol-gel method	N/A	N/A	Oxidative desulfurization Catalysts	(198)
11	CeO ₂ /Bi ₂ MoO ₆	Hydrothermal	Heterostructure microspheres	N/A	Enhancement of photogenerated charge separation	(199)
12	MoO ₃ /CeO ₂ & CuO/MoO ₃ /CeO ₂	Impregnation	N/A	N/A	NO + NH ₃ + O ₂ " reaction and surface acid properties	(200)

	Material	Fabrication Route	Morphology	BET (m ² /g)	Applications	Ref.
13	Mo-Ni/CeO ₂	Impregnation	Nanoparticle	N/A	Hydro-deoxygenation of Octanoic Acid	(201)
14	MoO ₃ -promoted CeO ₂ /TiO ₂	Impregnation	N/A	N/A	Selective catalytic reduction of NO _x	(202)
15	MoO ₃ /CeO ₂ / Al ₂ O ₃ (20 wt%)	Coprecipitation; Impregnation	Needle; Nanoparticle	S = 119	Sulfur-resistant methanation	(203)
16	MoO ₃ -CeO ₂	Sol-gel electrospinning	Nanofibers	N/A	Photocatalysis	(204)
17	MoO ₃ /CeO ₂	Calcination	N/A	N/A	Raman	(205)
18	MoO ₃ doped CeO ₂ /TiO ₂	Impregnation calcination	N/A	S = 56.3	Selective catalytic reduction of NO _x	(206)
19	M _x O _y /MoO ₃ /CeO ₂ (Fe,Cu,Ni)	Calcination impregnating	N/A	N/A	Surface structure analysis	(207)
20	Y ₂ O ₃ -Al ₂ O ₃ /MoO ₃ / CeO ₂ ;;MoO ₃ -CeO ₂	Impregnation co-impregnation	N/A	S = 213	Thermocatalytic cracking	(208)

	Material	Fabrication Route	Morphology	BET (m ² /g)	Applications	Ref.
21	Mo/CeO ₂ (3, 6, 9, 12, 15 and 18 wt%)	Hydrothermal	Nanoparticle	S = 98	Sensitive colorimetric detection	(209)
22	MoO ₃ -CeO ₂	Hydrothermal; Impregnation	Sheet	S = 245.03	Removal of elemental mercury	(210)
23	MoFeBeta@CeO ₂	Hydrothermal	Core-shell structure	402.0	Selective catalytic reduction of NO	(39)

2.5 Morphological Engineering

2.5.1 CeO₂ Nanostructure Fabrication

Morphological engineering is the general way to improve the catalytic ability by increasing the exposure of the active crystal planes and increasing the ratio of reactive surface area in the volume. The morphology of CeO₂ can be easily changed by alteration of the synthesis parameters (temperature, time, synthesis method). Crystal growth behaviour plays an important role in its final morphology. Through control of kinetics and reaction time, the isotropic crystal symmetry can be broken to prepare ceria nanostructures of different shape and sizes with different exposed planes, providing the possibility to undertake defect engineering (*211*). Gao *et al.* synthesised three common single crystals of CeO₂ (nanorod, nanocube, nanooctahedra) by hydrothermal method by varying the times and temperatures (**Figure 2.23**). The result shows that, with the same Pt loading, the catalytic performance follows the order nanorod-CeO₂ > naocube-CeO₂ > nano octahedra-CeO₂ in CO oxidation, and this is related to the higher extent of exposed planes in nanorods which have high catalytic activity (*42*).



Figure 2.23. (a) TEM images of ceria , nanorods, and nanocubes, and nanooctahedra,(b) corresponding catalytic performance of Pt/CeO₂ catalysts in CO oxidation (212)

In most materials, owing to their polycrystalline nature, the exposed planes are not important. In these cases, the large surface area and porous/hollow structures can facilitate the catalytic performance (213). Miceli *et al.* reported that two different ceria catalysts were prepared with different methods having different specific surface area (SSA) of 29 m²/g and 124 m²/g and the samples with higher SSA showed a better activity towards soot oxidation (**Figure 2.24**) (41).



Figure 2.24. (a-b) SEM images of CeO_2 prepared by self-assembled (high SSA) and solution combustion synthesis (low SSA), (c) Soot conversion catalyst performance of these two samples with cycling experiment (41)

In terms of morphology, two-dimensional nanostructures provide large specific surface area and large active sites (155). Most work on two-dimensional material-based nanostructures have centred on graphene and transition metal dichalcogenides (TMDs) owing to their natural planar crystal structure (214). Although the mobility, flexibility, and stability of graphene-based heterojunction nanostructures cannot be ignored, the susceptibility of graphene to oxidative environments is still a major unresolved issue (215).

Another fresh strategy is the combine metal ions with the precursor template coordination polymers (CP) to synthesis metal–organic frameworks (MOF) owing to their improved

functionalities, but these are still limited by its fragile, unstable, nature as well as difficulties in processing and recovery of materials (216). Therefore, there is growing interest to explore the fabrication of nanosheets based on metal oxides.

2.5.2 Nanosheet Synthesis Method

Metal oxide 2D nanosheets exhibit high performance in catalysis and capacitance owing to their high reaction surface areas and increased exposed surface-active sites (217). Rare earth-based heterojunctions are been trialled owing to their low cost, varying oxidation states and good catalytic ability. The synthesis method of materials can effectively control the morphology and performance of materials and this has an effect on the potential for commercialization. **Table 2.4** lists common synthesis methods and the characteristics of the resultant nanosheets.

Synthesis Methods	Thickness	BET (m²/g)	Applications	Ref.
Incipient wetness impregnation	20–50 nm	75	Catalytic oxidation of dichloromethane	(218)
Low tempature precipitation	20–50 nm	68	Catalytic oxidation of CO	(219)
Hydrothemal method	~50 nm		Electrocatalysis alkaline hydrogen evolution	(220)
Electrochemical deposition method	50 nm		Magnetic property measurement system	(221)
Electrodeposition	50 nm	28	Formaldehyde thermal oxidation and photocatalytic oxidation	(222)
Hydrothermal method	22.3 nm		Catalytic soot combustion.	(223)
Post-treatment transformations from coordination polymers (CP)	1 nm	270	Photocatalysis	(32)
Framework composition method	Single- atomic Layer		Catalytic CO oxidation	(224)

Table 2.4. Different CeO₂ nanosheet synthesis methods and resultant characteristics

Therefore, compared with the different synthesis methods, the post-treatment transformations involving metal oxide nanosheet exfoliation from metal coordination polymers (CP) show the highest surface area along with ultrathin thickness. This type of metal oxide structure can avoid the issue of MOFs such as generation of harmful by-

products, amorphization and/or phase transformation. Mofarah *et al.* used electrodeposition to synthesise unstable metal-based coordination polymer (metal-CP) which can be achieved through a rapid disassembly/reassembly process by controlling the thermodynamics and kinetics of the process. This novel metal-CP nanomaterial can easily be transformed to metal oxides with different morphologies by changing the parameter such as temperature and reactant concentration (*225*). This provides the possibility to modify the morphology of this unstably metal-CP by controlling supersaturation factor (reactant concentration) and kinetics of recrystallisation (temperature) as shown in **Figure 2.25**.



Figure 2.25. Formation mechanism for the Ce-CP nanostructures (225)

2.6 Summary

This review mainly introduces the properties of CeO₂ and how these can be manipulated to enhance its applicability for different devices. CeO₂ has numerous intrinsic $V_0^{\bullet\bullet}$ which is due to the switching ability of Ce³⁺ and Ce⁴⁺ valence states. However, there are other types of defects that have been ignored such as F centres and cation vacancies. The introduction of cation vacancies can improve electronic conductivity and reduce the energy barrier in ion diffusion for electrochemistry. However, there is limited research into these aspects.

The review also introduces mechanisms related to different applications and the advantages and limitations of CeO_2 when used in each area. CeO_2 has several drawbacks that cannot be ignored, namely the wide band gap, poor electronic conductivity, and bulk

like nanostructure. Therefore, three engineering strategies are recommended to modify the CeO_2 and these are doping (intrinsic), heterojunction formation (extrinsic), and morphology modification (extrinsic). Doping engineering involves controlling the type of dopants to tune the defects; acceptor doping is favourable to increase the number of oxygen vacancies, but donor dopant is favourable for introducing cerium vacancies. However, there is still limited understanding of the effect of these factors on the properties and performance.

Heterojunction engineering can be widely used for catalytic applications particularly for band alignment. The heterojunctions involving chemisorption have excellent electron conductivity which can improve the electrocatalytic properties. The physisorption based heterojunction has not been investigated a lot probably due to the limited charge transfer.

Finally, the morphological engineering is achieved by changing the numbers of exposed active planes and by changing the morphology and using effective synthesis methods to increase the reaction surface area. In this regard nanosheets are impressive owing to their outstanding high surface area and large amount of exposed active sites; metal oxide nanosheets are hard to form owing to increased chances for agglomeration. Compared to different synthesis methods, the new strategy based on CeCp establishes new pathways to engineer nanostructures and advance their functionalities for catalysis. Molybdenum and ruthenium are common donor and natural dopants for CeO₂ but there is limited discussion of doping mechanism and defect formation in the host material. These critical aspects will be the focus of the present thesis.

3 Experimental

3.1 Chemical and Materials

The following chemicals and materials were used in the present work:

- Cerium (III) nitrate hexahydrate [Ce(NO₃)₆·6H₂O (99.00 wt%), Sigma Aldrich (Sydney, Australia)];
- Molybdenum(III) chloride [MoCl₃ (99.95 wt%), Sigma Aldrich (Sydney, Australia)];
- Ruthenium(III) chloride [RuCl₃ (99.95 wt%), Sigma Aldrich (Sydney, Australia)];
- Triethanolamine [TEA; (≥98.00 wt%), Sigma Aldrich (Sydney, Australia)];
- Sodium hydroxide [NaOH (98.00 wt%), Chem-Supply Pty Ltd. (Sydney, Australia)];
- Trichloroacetic acid [TCA; Cl₃CCOOH; (≥99.00%), Chem–Supply Pty Ltd. (Sydney, Australia)];
- Fluorine–doped tin oxide on glass [FTO] working electrode (uhan Ge ao Scientific Education Instrument, Wuhan, China; film resistivity ~21 Ω cm⁻¹)
- Pt plate ($A = 4 \text{ cm}^2$) counter electrode (Basic Inc., Evansville, IN, USA)
- Ag/AgCl reference electrode (Basic Inc., Evansville, IN, USA)

3.2 Synthesis

3.2.1 Synthesis of CeCP Precursors

The following process was adopted:

- 1. FTO substrates were cleaned progressively by ultrasonication in acetone, ethanol, and DI water (5 min for each). This was followed by immersion in 40% nitric acid for 2 min to activate the surface, after which the same cleaning process was used, followed by drying with compressed air.
- 43.42 g of Ce(NO₃)₃.6H₂O, 16.34 g of TCA, and 4.00 g of NaOH were dissolved separately in 100 mL of deionized water to make 1 M solutions of each chemical in 150 mL Pyrex beakers.
- 3. The initial mixture of electrolytes was prepared by adding 0.05 M TCA and 0.05 M Ce(NO₃)₃·6H₂O in deionized (DI) water to make 150 mL of aqueous solution. The initial pH was 4.2, which subsequently was adjusted to 6.2 using concentrated 1 M NaOH solution.

- 4. The electrochemical cell was set up with an electrochemical working station system which is connected to a three-electrode system, *including* the counter (Platinum), reference (silver/silver chloride), and working electrode (FTO substrate).
- 5. The synthesis was done using a chronoamperometry technique conducted for 2 h incorporating an electrochemical station (*Ezstat Pro, Crown Point, IN, USA; resolution 300 \muV and 3 nA in the \pm 100 \muA range) and the abovenamed electrodes. The applied constant current was 30 mA for an FTO surface area of 15 cm² as this yielded high-quality films at rapid deposition rates.*

3.2.2 Synthesis of CeCP and Derived CeO_{2-x} Morphologies

The following process was adopted:

- 1. 300 mg of CeCP precursor was dispersed in 50 mL of 1 M NaOH aqueous solution and soaked for 30 min.
- The suspension was transferred to a plastic test tube, sealed, and centrifuged at 5000 rpm for 10 min. The same process was used five more times but with DI water for the removing any remnant impurities.
- 3. The resultant depolymerized CeCP was dried at 80°C in oven for 24 h.
- The 2D–3D CeO_{2-x} nanostructure was fabricated by dispersing the depolymerized CeCP in 4 ml TEA solution for 5 min using a magnetic stirrer at 300 rpm
- The suspension then was transferred to an alumina crucible and calcined at 450°C for 4 h (heating rate 5°C/min).
- 6. The resultant CeO_{2-x} nanosheet powders were stored in sealed containers prior to characterization and testing.

3.2.2 Synthesis of TMO Hybrid Nanostructures

The following process was adopted:

- 1. 6.57 g of MoCl₃ and 6.74 g of RuCl₃ were dissolved separately in 50 mL of deionized water to make 0.65 M solutions, respectively, in 100 mL Pyrex beakers.
- 2. The Mo-based hybrid nanostructures (4 mol%, metal basis) were synthesized using an identical procedure to that for 300 mg depolymerized CeO_{2-x} powders by addition of 10 mM MoCl₃ which was dispersed in 4 mL TEA solution for 5 min using a magnetic stirrer at 300 rpm.

- The mixture was then heated to 450°C with heating rate of 5°C/min and dwelling time of 3 h. The resultant powder was then cooled and collected.
- 4. The Ru–based hybrid nanostructures (4 mol%, metal basis) were synthesized using the preceding steps 2 and 3 but with RuCl₃ as dopant.

3.3 Characterization

3.3.1 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) patterns for the nanostructures were obtained using a Philips X'Pert Multipurpose X-ray diffractometer (Almelo, Netherlands) with CuK α radiation, 40 kV, 20 mA, scan range 20°–70° 2 θ , scan speed 0.2 2 θ /min). The peaks were analysed using X'Pert High Score Plus software (Malvern, Gloucestershire, UK).

3.3.2 Laser Raman Microspectroscopy (Raman)

Laser Raman microspectra were obtained using a Renishaw in Via confocal Raman microscope (Renishaw, Derbyshire, UK; helium–neon green laser, diffraction grating 1800 grooves/mm). All Raman data were recorded over the range 200–1500 cm⁻¹ (resolution 1 cm⁻¹; laser power 35 mW; spot size ~2 μ m diameter). The data analyses were performed using Renishaw WiRE 4.4 software and the spectra were calibrated against the silicon peak at ~520 cm⁻¹.

3.3.3 Transmission Electron Microscopy (TEM)

Electron microscopy was done using dry CeO_{2-x} nanosheet powders that were suspended in water and drop–cast onto a carbon–coated Cu grid, followed by drying at room temperature. High–resolution transmission TEM (HRTEM) images and selected area electron diffraction (SAED) patterns of the nanostructures were done using a Philips CM 200 TEM (Eindhoven, the Netherlands).

3.3.4 Scanning Electron Microscopy (SEM)

Images were obtained using an FEI Nova Nano SEM (Hillsboro, OR, USA) in primary and secondary emission modes with accelerating voltage in the range 10–15 kV.

3.3.5 Energy Dispersive X–Ray Spectroscopy (EDS)

EDS analyses of the nanostructures were obtained using SEM FEI Nova NanoSEM; secondary electron emission; accelerating voltage 5 kV, Hillsboro, OR, USA)

3.3.6 X–Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was done using a Thermo Fisher Scientific ESCALAB 250Xi spectrometer (Loughborough, Leicestershire, UK) equipped with a monochromatic AlK α source (1486.6 eV) hemispherical analyser. The chamber pressure during the analysis was held constant at < 0.8–1.0 kPa. The binding energies were referenced to the C1s signal corrected to 285 eV and the spectra were fitted using a convolution of Lorentzian and Gaussian profiles. The data were normalised to eliminate the contributions from adventitious C (C 1s, 285 and 286 eV) and adsorbed H₂O or OH– (O 1s, 531 eV).

3.3.7 Photoluminescence (PL) Spectroscopy

Photoluminescence (PL) spectroscopy was done using a Shimadzu Spectro Fluorophotometer RF–5301PC (Kyoto, Japan) with the range being 350-800 nm.

3.3.8 Electron Paramagnetic Resonance (EPR)

EPR analysis was conducted using a Bruker EMX X–Band ESR Spectrometer (Billerica, MA, USA), with constant frequency at 9.8 GHz. The EPR data were recorded over the centre Field at 3200 mT, modulation amplitude at 4 G, and microwave power at 0.6325 mW. The processing on EPR spectra were carried out using Bruker Xenon software.

3.3.9 Atomic Force Microscopy (AFM)

The thicknesses of the nanosheets were measured using a Bruker Dimension Icon SPM atomic force microscope (AFM; peak force tapping mode). The samples were deposited on glass substrates by extraction from the surface of a homogenous nanosheet/DI water suspension, deposition on a glass substrate, and drying in air. The AFM probe was a Bruker Nano Inc. ScanAsyst–Air Probe. The pixel resolution was 512 samples/line.

The scan size was set to 2 μ m × 2 μ m, with a scan rate of 0.7 Hz. The peak force set point and the feedback gain settings were optimized accordingly. The AFM images were processed using Nano scope Analysis 1.7 and the thicknesses of the holey 2D nanosheets were determined using the height profile from the processed images.

3.3.10 Amplitude modulated Kelvin probe force microscopy (AM–KPFM)

Amplitude modulated Kelvin probe force microscopy (AM–KPFM) was performed using a Bruker Dimension ICON SPM with a Nano Scope V controller. A Bruker SCM–PIT–V2 platinum–iridium coated AFM tip was used to determine the work function changes.

3.3.11 BET Specific Surface Areas (SSA)

Specific surface areas (SSA) and pore size distributions were obtained using the N₂ physisorption technique at –196°C on a Micrometrics Tristar 3030 (Altanta, GA, USA). These data were determined using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. Prior to analysis, the samples were degassed under vacuum at 150°C for 3 h using a Micromeritics Smart VacPrep unit (Atlanta, GA, USA).

3.3.12 Ultraviolet-Visible (UV-Vis) Spectrophotometry

The UV–Vis data were collected using a PerkinElmer Lambda 1050 double–beam UV/Vis/NIR spectrophotometer (Waltham, MA, USA), with a triple detector for maximal sensitivity; the wavelength range was 200–1500 nm.

3.3.13 Scanning Transmission Electron Microscopy (STEM)

STEM was obtained using a Philips F200 TEM with the spectrum imaging mode with sub-pixel scanning. This procedure ensured that at all the times during the acquisition, the beam was moving and the local fluence was minimised.

3.4 Application Tests

3.4.1 Electrocatalysis Test
To prepare the electrodes, 5 mg of catalyst were suspended in 0.5 mL deionized water and ethanol mixture (1:1, v/v), followed by the addition of 25 μ L of Nafion solution (Sigma Aldrich, 99.99%). The mixture was sonicated thoroughly to form a homogeneous ink. The working electrodes then were prepared by drop–casting the catalyst ink onto Teflon–lined carbon–fibre paper in order to achieve a total catalyst loading of 0.5 mg cm⁻². The working electrode, graphite rod counter electrode, and saturated calomel reference electrode (SCE) were placed in a cell containing 60 mL of 1 M H₂SO₄ (pH = 0). All electrochemical measurements were done using a (*CH Instruments, Inc. CHI 760E electrochemical workstation, Bee Cave, TX, USA*). All potentials (E) measured were converted to the reversible hydrogen electrode (RHE) reference for the purpose of comparison, using the equation (3.1):

$$E_{RHE} (V) = E_{SCE} (V) + 0.245 + 0.059 \times pH$$
(3.1)

3.4.2 Electrochemical Measurements

Impedance electron spectroscopy (EIS) and cyclic voltammetry (CV) were carried out in $0.5 \text{ M} \text{ Na}_2\text{SO}_4$ solution at pH 6.8. EIS was measured under -0.4 V vs RHE with frequencies from 100 kHz to 0.1 Hz. Different scan rates were used in the cyclic voltametric measurement at the potential window of 0.6-0.65 V vs. RHE in order to obtain the electrochemical capacitance current for evaluation of the relative electrochemically active surface area (ECSA).

3.4.3 Hydrogen Thermal Treatment

Hydrogen thermal treatment is a simple and effective technique for generating defects like oxygen vacancy on the surface of the catalysts. Hence, as-prepared samples were reduced with hydrogen using a cylindrical electric furnace. In this procedure, samples were initially heated to 150°C under 30 mL min⁻¹ pure nitrogen for 30 min to remove the surface moisture and impurities. Then, samples were cooled down to the ambient temperature and reheated to 500°C nder N₂ atmosphere. After heating to 500°C, the gas was changed to 10% H₂ and 90% N₂ (*99.99% Coregas, Australia*) and the temperature was maintained at 500°C for 180 min.

3.4.4 Catalytic Ozonation

The catalytic ozonation reaction with salicylic acid (SA) as model contaminant was carried out in a semi batch reactor in which the aqueous phases including organic contaminant was in batch state and ozone gas was continuously bubbled into the solution from the bottom of the reactor. Experiments were performed under ambient conditions using simulated wastewater containing SA with the initial concentration of 200 mg/L. In each trial, 10 mg/L of catalyst was added to the reactor and magnetically stirred for 60 min at 750 rpm to reach the adsorption-desorption equilibrium. Ozone was introduced to the reactor with a flowrate of 750 ml min⁻¹ using a BMT 802 N ozone generator (*Messtechnik, Germany*).

Samples were withdrawn from the reactor at selected times (0, 5, 10, 15, 30, 45 and 60 min) using a dispenser and filtered through a 0.45 μ m. Then, 0.025 mol of ozone was added to these samples to quench the residual aqueous ozone and then analysed. All experiments were repeated to determine the reproducibility of the results.

The aqueous ozone concentration was measured using the indigo colorimetric technique. The difference in light absorption between a blank (*MiliQ water*) and taken sample at wavelength of 600 nm is the basis of this technique. A Shimadzu 3000 UV-vis spectrophotometer was utilised to measure the light absorption. In addition, the total organic carbon (TOC) as an index of catalyst performance by Shimadzu TOC-VCH analyser.

3.5 First-Principles Calculations

Spin-polarised density functional theory (DFT) calculations were performed to theoretically characterise the electronic properties of MoO₃/RuO₂-CeO₂ heterojunctions and Mo/Ru-CeO₂ interstitial solid solutions. The PBEsol functional was used as implemented in the VASP software. A "Hubbard-*U*" scheme with U=3 eV was employed for a better treatment of the localized Ce 4*f* and Mo/Ru 4*d* electronic orbitals. The "projector augmented wave" method was used to represent the ionic cores by considering the following electrons as valence: Ce 4*f*, 5*d*, 6*s*, and 4*d*; Mo 4*d* and 5*s*; Ru 4*d* and 5*s*;

and O 2*s* and 2*p*. Wave functions were represented in a plane-wave basis truncated at 650 eV.

For integrations within the first Brillouin zone, the Monkhorst-Pack k-point grids were employed with a density equivalent to that of 16x16x16 for the fluorite CeO₂ unit cell. Periodic boundary conditions were applied along the three lattice vectors defining the simulation supercell; geometry relaxations were performed with a conjugate-gradient algorithm that optimized the ionic positions and the volume and shape of the simulation cell. The relaxations were halted when the forces in the atoms were all below $0.01 \text{ eV} \cdot \text{Å}^{-1}$. By using these technical parameters, the obtained energies were converged to within 0.5 meV per formula unit. The range-separated hybrid HSE06 exchange-correlation functional was used to accurately estimate the electronic energy levels of the equilibrium geometries generated with the PBEsol+*U* functional. The value of the theoretical valence and conduction energy band edges referred to the Fermi energy level were determined through analysis of the projected densities of electronic states obtained in the spin polarised DFT calculations.

For the MoO₃/RuO₂-CeO₂ heterojunction calculations, ceria nanosheets were simulated as two-unit cells thick CeO₂ slabs oriented along the {111} direction (with chemical formula Ce₁₆O₃₂). A vacuum region of 25 Å was considered in all the slab simulations. Subsequently, a number of Mo and Ru ions compatible with compositions MoO₃/RuO₂-CeO₂ and the crystal symmetries of bulk MoO₃ (space group *Pnma*) and RuO₂ (space group *Fm-3m*) were absorbed on both sides of the CeO₂ slabs. To describe the Mo/Ru-CeO_{2-x} interstitial solid solutions, a conventional CeO₂ fluorite unit cell containing 12 ions (with chemical formula Ce₄O₈) was used.

The interstitial concentration in our DFT simulations calculations was fixed to 20% and the position of the interstitial ions were identified with the high-symmetry octahedral fluorite sites $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ [in pseudo-Cartesian notation]. The reduced species Mo⁵⁺ and Mo⁴⁺ were generated by introducing one and two oxygen vacancies, respectively, near the introduced transition metal ions.

4. Decoupling the Mechanistic Effects of CeO_{2-x}-Based Catalytic Heterojunctions: Chemisorbed MoO₃ vs Physisorbed RuO₂

4.1 Overview

The fabrication strategy of heterojunction nanostructures has been established previously and is based on the dispersion of a flexible, stratified, cerium–based coordination polymer (CeCP), which can be transformed readily into CeO_{2-x} 2D/3D nanosheets with high oxygen vacancy concentrations ($[V_0^{\bullet\bullet}]$).(32) Cation doping of the CeO_{2-x} bulk or the surface can be effected by immersion in transition metal salt (TMS) solutions, followed by low-temperature heating that results in the controllable formation of solid solutions or transition metal oxide (TMO) heterojunction nanostructures.

According to Hume–Rothery's rules, which are for close-packed metals, the prognosis and type and amount of solid solubility (and the associated defect formation and charge compensation) are enhanced by similarities in a number of factors, which include crystal structure, ionic radii, valences, electronegativities, and solubility ranges.(*19*) For ceramics, the size and valence and, to a lesser extent, the electronegativity often are important considerations. In the present work, the relevant considerations are that (1) the rare earth Ce⁴⁺ have a crystal radii that 30-50% larger than the transition metals Mo⁴⁺, Mo⁵⁺, Mo⁶⁺, and Ru⁴⁺, (2) the electronegativity of Ce is approximately half that of Mo and Ru, and (3) the cubic CeO₂ crystal structure is different from those of the dopant oxides (**Table 4.1**). From the perspective of size and structure, interstitial solubility would be expected. From the perspective of valence, Mo⁴⁺ and Ru⁴⁺ would favour interstitial solubility but Mo⁵⁺ and Mo⁶⁺ would favour substitutional. There would be no differentiation in terms of the electronegativities.

Samplas	Flomont	Crystal Radius	Electronegativity	Ovida	Crystal
Samples	Liement	(nm)	(Pauling Units)	Oxide	Structure
CeO _{2-x}	Ce(IV)	0.111	1.12	CeO ₂	Cubic
Mo-CeO _{2-x}	Mo(IV)	0.079		MoO ₂	Tetragonal
	Mo(V)	0.060	2.16	M04O11	Orthorhombic
	Mo(VI)	0.055		MoO ₃	Orthorhombic
Ru-CeO _{2-x}	Ru(IV)	0.076	2.20	RuO ₂	Tetragonal

Table 4.1. Crystal parameters of CeO_{2-x}, Mo-CeO_{2-x}, and Ru-CeO_{2-x} (226-228)

Since the synthesis stages of the present work were done at the relatively modest conditions of 4 h at 450°C, then the role of kinetics in the potential to achieve equilibrium is relevant. That is, although a high solid solubility may be possible, low or nil solubility may result. Further, the absence of solubility data raises the potential for the formation of undersaturated, saturated, and/or oversaturated solid solutions (*164*). These issues impact on the range of adsorption mechanisms that may be exhibited by solids and heterojunction nanostructures. **Figure 4.1** illustrates the range of such possibilities as well as some common defects that may be observed in mesoporous CeO_{2-x} nanosheets doped with cations that undergo interstitial solid solubility; this image reflects the experimental outcomes of the present work.



Figure 4.1. Defect formation in mesoporous CeO_{2-x} nanosheets from adsorption, interstitial solid solubility, intrinsic $V_0^{\bullet\bullet}$, and charge-compensation (ionic and redox): 0D point defects, 0-2D physiosorbed heterojunction interfaces, 2D chemisorbed heterojunction interfaces, 3D vacancy clusters, and 3D mesopores.

Examination of the potential defect equilibria (**Tables 4.2-4.4**) combined with the valence data provided by X-ray photoelectron spectroscopy (XPS) often can allow an unambiguous inference about the nature of the solid solubility mechanism. Of particular importance are (1) donor (Mo⁶⁺ and Mo⁵⁺) and neutral (Mo⁴⁺ and Ru⁴⁺) dopants cannot generate $V_0^{\bullet\bullet}$, (2) intervalence charge transfer (IVCT) can result in mutual valence changes between matrix and dopant cations, (3) redox charge compensation causes Ce⁴⁺ \leftrightarrow Ce³⁺ equilibria, (4) electronic charge compensation cannot generate $V_0^{\bullet\bullet}$ or alter the Ce⁴⁺ \leftrightarrow Ce³⁺ equilibria, and (5) defect equilibria at the surface and bulk may differ significantly. Thus, the changes in $[V_0^{\bullet\bullet}]$, [Ce⁴⁺], [Ce³⁺], and dopant valences provide key information about the solid solubility as well as the charge compensation required for doping.

Mo-Doping						
Region/Interface	Process	Substitutional Solid Solubility				
	Ionic Charge Compensation	$5\text{Mo}_{\text{Mo}}^{\text{x}} + 150_{0}^{\text{x}} \xrightarrow{\text{CeO}_{2}} 3\text{Mo}_{\text{Ce}}^{\bullet} + 2\text{Mo}_{\text{Ce}}^{\bullet} + 2\text{V}_{\text{Ce}}^{\prime\prime\prime\prime\prime} + 2\text{Ce}_{\text{S}}^{\text{x}} + 150_{0}^{\text{x}} (4.1)$				
Heterojunction	Electronic Charge Compensation	$2\mathrm{Mo}_{\mathrm{Mo}}^{\mathrm{x}} + 6\mathrm{O}_{\mathrm{O}}^{\mathrm{x}} \xrightarrow{\mathrm{CeO}_{2}} \mathrm{Mo}_{\mathrm{Ce}}^{\bullet} + \mathrm{Mo}_{\mathrm{Ce}}^{\bullet} + 4\mathrm{O}_{\mathrm{O}}^{\mathrm{x}} + \mathrm{O}_{2}(\mathrm{g}) + 3e' \qquad (4.2)$				
	Redox Charge Compensation	$2\mathrm{Mo}_{\mathrm{Mo}}^{\mathrm{x}} + 6\mathrm{O}_{\mathrm{O}}^{\mathrm{x}} \xrightarrow{\mathrm{CeO}_{2}} \mathrm{Mo}_{\mathrm{Ce}}^{\bullet} + \mathrm{Mo}_{\mathrm{Ce}}^{\bullet} + 4\mathrm{O}_{\mathrm{O}}^{\mathrm{x}} + \mathrm{O}_{2}(\mathrm{g}) + 3\mathcal{C}e_{\mathcal{C}e}^{\prime} (4.3)$				
Region/Interface	Process	Interstitial Solid Solubility				
	Ionic Charge Compensation	$3\text{Mo}_{\text{Mo}}^{x} + 90_{0}^{x} \xrightarrow{\text{CeO}_{2}} \text{Mo}_{i}^{\text{cem}} + 2\text{Mo}_{i}^{\text{cem}} + 4\text{V}_{\text{Ce}}^{\prime\prime\prime\prime\prime} + 4\text{Ce}_{\text{S}}^{x} + 90_{0}^{x} (4.4)$				
Heterojunction	Electronic Charge Compensation	$2\operatorname{Mo}_{\operatorname{Mo}}^{x} + 60_{0}^{x} \xrightarrow{\operatorname{CeO}_{2}} \operatorname{Mo}_{i}^{\operatorname{max}} + \operatorname{Mo}_{i}^{\operatorname{max}} + 40_{0}^{x} + 0_{2} (g) + 11e' (4.5)$				
	Redox Charge Compensation	$2\operatorname{Mo}_{\operatorname{Mo}}^{x} + 6\operatorname{O}_{O}^{x} \xrightarrow{\operatorname{CeO}_{2}} \operatorname{Mo}_{i}^{\dots} + \operatorname{Mo}_{i}^{\dots} + 4\operatorname{O}_{O}^{x} + \operatorname{O}_{2}(g) + 11Ce_{Ce}'(4.6)$				
	Ru	ı-Doping				
Region/Interface	Process	Substitutional Solid Solubility				
	Ionic Charge Compensation	$Ru_{Ru}^{x} + 20_{0}^{x} \xrightarrow{CeO_{2}} Ru_{Ce}^{x} + 20_{0}^{x} $ (4.7)				
Heterojunction	Electronic Charge Compensation	$\operatorname{Ru}_{\operatorname{Ru}}^{x} + 2\operatorname{O}_{O}^{x} \xrightarrow{\operatorname{CeO}_{2}} \operatorname{Ru}_{\operatorname{Ce}}^{x} + 2\operatorname{O}_{O}^{x} $ (4.8)				
	Redox Charge Compensation	$Ru_{Ru}^{x} + 2O_{0}^{x} \xrightarrow{CeO_{2}} Ru_{Ce}^{x} + 2O_{0}^{x} $ (4.9)				
Region/Interface	Process	Interstitial Solid Solubility				

Table 4.2. Heterojunction formation defect equilibria for Mo and Ru doping of CeO_{2-x}

	Ionic Charge Compensation	$\operatorname{Ru}_{\operatorname{Ru}}^{\operatorname{x}} + 2O_{O}^{\operatorname{x}} \xrightarrow{\operatorname{CeO}_{2}} \operatorname{Ru}_{i}^{\operatorname{m}} + V_{\operatorname{Ce}}^{\prime\prime\prime\prime\prime} + \operatorname{Ce}_{\operatorname{S}}^{\operatorname{x}} + 2O_{O}^{\operatorname{x}}$	(4.10)
Heterojunction	Electronic Charge Compensation	$\operatorname{Ru}_{\operatorname{Ru}}^{\operatorname{x}} + 2O_{O}^{\operatorname{x}} \xrightarrow{\operatorname{CeO}_{2}} \operatorname{Ru}_{\operatorname{i}}^{\operatorname{\bullet}\operatorname{\bullet}\operatorname{\bullet}} + 2O_{O}^{\operatorname{x}} + 4e'$	(4.11)
	Redox Charge Compensation	$\operatorname{Ru}_{\operatorname{Ru}}^{\operatorname{x}} + 20_{\operatorname{O}}^{\operatorname{x}} \xrightarrow{\operatorname{CeO}_2} \operatorname{Ru}_{\operatorname{i}}^{\operatorname{\operatorname{cov}}} + 20_{\operatorname{O}}^{\operatorname{x}} + 4Ce_{Ce}'$	(4.12)

Mo-Doping – Interstitial Solid Solubility					
Region/Interface	Process	Defect Equilibria			
Heterojunction-to-Surface	IVCT	$Mo^{6+} + Ce^{3+} \rightarrow Mo^{5+} + Ce^{4+}$	(4.13)		
	Ionic Charge Compensation	$4\text{Mo}_{\text{Mo}}^{\text{x}} + 100_{0}^{\text{x}} \xrightarrow{\text{CeO}_{2}} 4\text{Mo}_{i}^{\text{\bullet\bullet\bullet\bullet\bullet}} + 5V_{\text{Ce}}^{\prime\prime\prime\prime\prime} + 5\text{Ce}_{\text{S}}^{\text{x}} + 100_{0}^{\text{x}}$	(4.14)		
Surface	Electronic Charge Compensation	$2\mathrm{Mo}_{\mathrm{Mo}}^{\mathrm{x}} + 50_{\mathrm{O}}^{\mathrm{x}} \xrightarrow{\mathrm{CeO}_{2}} 2\mathrm{Mo}_{\mathrm{i}}^{\mathrm{e}\mathrm{e}\mathrm{e}\mathrm{i}} + 40_{\mathrm{O}}^{\mathrm{x}} + \frac{1}{2}\mathrm{O}_{2}(\mathrm{g}) + 10e'$	(4.15)		
	Redox Charge Compensation	$2\text{Mo}_{\text{Mo}}^{\text{x}} + 50_0^{\text{x}} \xrightarrow{\text{CeO}_2} 2\text{Mo}_i^{\text{com}} + 40_0^{\text{x}} + \frac{1}{2}0_2 \text{ (g)} + 10Ce_{Ce}^{\prime}$	(4.16)		
Surface-to-Subsurface	IVCT	$Mo^{5+} + Ce^{3+} \rightarrow Mo^{4+} + Ce^{4+}$	(4.17)		
	Ionic Charge Compensation	$Mo_{Mo}^{x} + 2O_{O}^{x} \xrightarrow{CeO_{2}} Mo_{i}^{\dots} + V_{Ce}^{\prime\prime\prime\prime} + Ce_{S}^{x} + 2O_{O}^{x}$	(4.18)		
Subsurface	Electronic Charge Compensation	$Mo_{Mo}^{x} + 20_{O}^{x} \xrightarrow{CeO_{2}} Mo_{i}^{\bullet\bullet\bullet\bullet} + 20_{O}^{x} + 4e'$	(4.19)		
	Redox Charge Compensation	$Mo_{Mo}^{x} + 2O_{0}^{x} \xrightarrow{CeO_{2}} Mo_{i}^{\bullet \bullet \bullet \bullet} + 2O_{0}^{x} + 4Ce_{Ce}^{\prime}$	(4.20)		
	Ru-Doping – Interstiti	al Solid Solubility			
Region/Interface	Process	Defect Equilibria			
	Ionic Charge Compensation	$\operatorname{Ru}_{\operatorname{Ru}}^{\operatorname{x}} + 20_{\operatorname{O}}^{\operatorname{x}} \xrightarrow{\operatorname{CeO}_2} \operatorname{Ru}_{\operatorname{i}}^{\operatorname{\operatorname{cev}}} + V_{\operatorname{Ce}}^{\prime\prime\prime\prime\prime} + \operatorname{Ce}_{\operatorname{S}}^{\operatorname{x}} + 20_{\operatorname{O}}^{\operatorname{x}}$	(4.21)		
Surface/Subsurface/Bulk	Electronic Charge Compensation	$\operatorname{Ru}_{\operatorname{Ru}}^{\operatorname{x}} + 2O_{O}^{\operatorname{x}} \xrightarrow{\operatorname{CeO}_{2}} \operatorname{Ru}_{i}^{\operatorname{\bullet\bullet\bullet\bullet}} + 2O_{O}^{\operatorname{x}} + 4e'$	(4.22)		
	Redox Charge Compensation	$\operatorname{Ru}_{\operatorname{Ru}}^{x} + 2O_{0}^{x} \xrightarrow{\operatorname{CeO}_{2}} \operatorname{Ru}_{i}^{\bullet \bullet \bullet \bullet} + 2O_{0}^{x} + 4Ce_{Ce}^{\prime}$	(4.23)		

Table 4.3. Interstitial solid solubility defect equilibria for Mo and Ru doping

Mo-Doping – Substitutional Solid Solubility					
Region/Interface	Process	Defect Equilibria			
Heterojunction-to-Surface	IVCT	$Mo^{6+} + Ce^{3+} \rightarrow Mo^{5+} + Ce^{4+}$	(4.24)		
	Ionic Charge Compensation	$4\mathrm{Mo}_{\mathrm{Mo}}^{\mathrm{x}} + 100_{\mathrm{O}}^{\mathrm{x}} \xrightarrow{\mathrm{CeO}_{2}} 4\mathrm{Mo}_{\mathrm{Ce}}^{\bullet} + V_{\mathrm{Ce}}^{\prime\prime\prime\prime\prime} + \mathrm{Ce}_{\mathrm{S}}^{\mathrm{x}} + 100_{\mathrm{O}}^{\mathrm{x}}$	(4.25)		
Surface	Electronic Charge Compensation	$2\mathrm{Mo}_{\mathrm{Mo}}^{\mathrm{x}} + 50_{\mathrm{O}}^{\mathrm{x}} \xrightarrow{\mathrm{CeO}_{2}} 2\mathrm{Mo}_{\mathrm{Ce}}^{\bullet} + 40_{\mathrm{O}}^{\mathrm{x}} + \frac{1}{2}\mathrm{O}_{2}(\mathrm{g}) + 2e'$	(4.26)		
	Redox Charge Compensation	$2\text{Mo}_{\text{Mo}}^{\text{x}} + 50_{0}^{\text{x}} \xrightarrow{\text{CeO}_{2}} 2\text{Mo}_{\text{Ce}}^{\bullet} + 40_{0}^{\text{x}} + \frac{1}{2}0_{2} \text{ (g)} + 2\text{Ce}_{\text{Ce}}^{\prime}$	(4.27)		
Surface-to-Subsurface	IVCT	$Mo^{5+} + Ce^{3+} \rightarrow Mo^{4+} + Ce^{4+}$	(4.28)		
	Ionic Charge Compensation	$Mo_{Mo}^{x} + 2O_{O}^{x} \xrightarrow{CeO_{2}} Mo_{Ce}^{x} + 2O_{O}^{x}$	(4.29)		
Subsurface	Electronic Charge Compensation	$Mo_{Mo}^{x} + 20_{O}^{x} \xrightarrow{CeO_{2}} Mo_{Ce}^{x} + 20_{O}^{x}$	(4.30)		
	Redox Charge Compensation	$Mo_{Mo}^{x} + 2O_{O}^{x} \xrightarrow{CeO_{2}} Mo_{Ce}^{x} + 2O_{O}^{x}$	(4.31)		
	Ru-Doping – Substitut	ional Solid Solubility			
Region/Interface	Process	Defect Equilibria			
	Ionic Charge Compensation	$\operatorname{Ru}_{\operatorname{Ru}}^{\operatorname{x}} + 2\operatorname{O}_{\operatorname{O}}^{\operatorname{x}} \xrightarrow{\operatorname{CeO}_2} \operatorname{Ru}_{\operatorname{Ce}}^{\operatorname{x}} + 2\operatorname{O}_{\operatorname{O}}^{\operatorname{x}}$	(4.32)		
Surface/Subsurface/Bulk	Electronic Charge Compensation	$\operatorname{Ru}_{\operatorname{Ru}}^{\operatorname{x}} + 2O_{O}^{\operatorname{x}} \xrightarrow{\operatorname{CeO}_{2}} \operatorname{Ru}_{\operatorname{Ce}}^{\operatorname{x}} + 2O_{O}^{\operatorname{x}}$	(4.33)		
	Redox Charge Compensation	$\operatorname{Ru}_{\operatorname{Ru}}^{x} + 20_{O}^{x} \xrightarrow{\operatorname{CeO}_{2}} \operatorname{Ru}_{\operatorname{Ce}}^{x} + 20_{O}^{x}$	(4.34)		

Table 4.4.	Substitutional	solid	solubility	y defect e	quilibria	for Mo and	l Ru do	ping of	CeO _{2-x}
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4.2. Mineralogical Characteristics

4.2.1 XRD Analysis

The crystal structures obtained through wet–chemistry synthesis of CeCP and transition metal solution were studied using X–ray diffraction (XRD) and laser Raman spectroscopy, as shown in **Figure 4.2** and **Figure 4.3**. The XRD pattern for the pristine nanostructure derived directly from CeCP transformation matched with Fm–3m space group of cubic fluorites–type CeO₂ structure (JCPDS 81–0792). Addition of Mo–salt in the CeCP resulted in the formation of a heterojunction structure comprised of α –MoO₃ and CeO₂. The structure of α –MoO₃ is confirmed (JCPDS 05–0508). Similar to the case of Mo–based nanostructure, addition of Ru–salt yielded a heterojunction structure of RuO₂ and CeO₂. The presence of RuO₂ is confirmed by matching the XRD pattern to the orthorhombic structure of RuO₂ with space group of Pnnm (JCPDS 88–0323). The presence of these secondary phases indicates probable heterojunction formation.



Figure 4.2. XRD patterns (identically scaled intensities) of CeO_{2-x} , Mo– CeO_{2-x} , and Ru– CeO_{2-x}

The crystallite size of CeO₂ is calculated by Scherrer equation (Equation 4.35):

$$\tau = \frac{K \cdot \lambda}{\beta \cdot \cos\vartheta} \tag{4.35}$$

*where τ is equal to size of the ordered (crystalline) domains; K is shape factor, usually as 0.9; λ is X-ray wavelength; β is the line broadening at half the maximum intensity (FWHM); ϑ is the Bragg angle.

Compared with CeO_{2-x}, the Mo-CeO_{2-x} and Ru-CeO_{2-x}, shows \sim 30-35% reduction in CeO_{2-x} crystallite size (**Table 4.5**). It also suggests solid solubility of both dopant ions. The introduction of impurities leads to hindering the growth of CeO₂ crystals and the Ru–CeO_{2-x} samples shows the smallest crystallite size probably due to relatively high solubility of Ru ions

Samples	{hkl}	20 (°)	FWHM (d0)	Crystallite Size (nm)	Average (nm)
	{111}	28.45701	0.97668	8.39139	
CoOr	{200}	32.98885	0.92237	8.98256	0 12/20
CeO _{2-x}	{220)	47.43510	1.06891	8.11777	8.13438
	{311}	56.31622	1.13832	7.91580	
	{111}	28.80664	1.59368	5.14663	_
Mo-	{200}	33.59743	1.50628	5.50921	5 60770
CeO _{2-x}	{220)	48.01269	1.54590	5.62554	5.00770
	{311}	56.45820	1.46627	6.14941	
_	{111}	28.70051	1.68100	4.87813	
Ru-	{200}	33.23056	1.65840	4.99906	5 06322
CeO _{2-x}	{220)	47.64309	1.72466	5.03525	5.00522
	{311}	56.62231	1.68968	5.34045	

 Table 4.5. Comparison of CeO2 XRD parameters in CeO2-x, Mo-CeO2-x, and

 Ru-CeO2-x

4.2.2 Raman Analysis

Figures 4.3 illustrates the Raman microspectra for the Mo–CeO_{2-x} and Ru–CeO_{2-x} nanostructures and these peaks were fit using Gaussian functions. The pure–CeO₂ exhibits strong Raman active peaks at 464 cm⁻¹ (229), which is associated with triply degenerate F_{2g} vibrational mode, that originates from symmetrical stretching vibration of Ce(IV) ions and eight surrounding oxygens. The Mo–CeO_{2-x} also exhibits the strong F_{2g} peak of ceria, while a red shift to lower energy of 460 cm⁻¹ is observed. These changes occur due to the formation of higher numbers of defects in the structure.(*36*) Further, the presence of the D peak (600 cm⁻¹) is indicative of the presence of defects that may been defined as (1) $V_{Ce}^{\prime\prime\prime} - 2V_0^{\circ\bullet}$ Frenkel pair (ionic charge compensation) (*63, 230, 231*); (2) $2Ce'_{Ce} - V_0^{\circ\bullet}$ pair (Ce⁴⁺ \rightarrow Ce³⁺ intrinsic redox charge compensation) (*234-237*); or (4) *e.g.*, $M_{Ce}^{5+} - Ce_{Ce}^{4+} \rightarrow M_{e}^{6+} + Ce^{3+}$ (IVCT), where M is a metal dopant.



Figure 4.3 Laser Raman spectra of CeO_{2-x}, Mo–CeO_{2-x}, and Ru–CeO_{2-x}

The Mo–CeO_{2-x} spectra also show several peaks that can be assigned to MoO_x structure (*194, 205, 238-240*), the peak at 790 cm⁻¹ is identified as O–Mo⁵⁺–O band vibrations in Mo₄O₁₁. The 907 cm⁻¹ represents stretching vibration of terminal Mo⁵⁺–O vibrations in Mo₄O₁₁. The peaks at 805 cm⁻¹ is assigned to Mo⁶⁺–O–X [X = Mo⁵⁺ or Ce] band vibration. Two bands at 995 and 823 cm⁻¹ which are identified as A_g vibration modes for MoO₃ assigned to the asymmetric and symmetric stretching of terminal oxygen atoms in Mo=O band, respectively. The peak at 950 cm⁻¹ is Mo⁶⁺=O band vibrations ,which is assumed as Mo species in an octahedral environment.

Additionally, the Raman spectra for the heterojunction structure of RuO_2 and CeO_2 is shown in **Figure 4.3**. These also exhibit the peaks corresponding to CeO_2 and an increase in the full width at half maximum (FWHM) of the main peak is an indication of small crystallite size. The peaks positioned at 644 cm⁻¹ and 716 cm⁻¹ represent A_{1g} and B_{2g} vibrational modes in RuO₂, respectively (*241, 242*). The asymmetrical broad peak at 975 cm⁻¹ is characteristic of Ru–O–Ce band.

4.3 Nano structural Characteristics

4.3.1 SEM Analysis

Figures 4.4 show SEM images that illustrate the 2D/3D flower-like nanosheets of CeO_{2-x} . With the introduction of Mo ions, the compact flower-like nanosheets become slightly exfoliated, which supports the conclusion of deposition of surface heterojunction particles and/or alteration of the surface charge through solid solubility. With the introduction of Ru ions, there is considerably more exfoliation, suggesting amplification of the effect from Mo doping.



Figure 4.4. SEM images of (a) CeO_{2-x}, (b) Mo–CeO_{2-x}, and (c) Ru–CeO_{2-x}

4.3.2 TEM Analysis

All three nanostructures reveal mesoporosity. The calculated pore sizes (**Table 4.6**) form the BET analysis are in the range ~6.0-7.6 nm, which can be proven by the TEM images (**Figure 4.5**). The calculated crystallite sizes (**Table 4.5**) suggest that the crystallite size of CeO_{2-x} (~8.1 nm) is large that that of Mo–CeO_{2-x} (~5.6 nm) and Ru–CeO_{2-x} (~5.1 nm), and this is confirmed from the TEM images. The HRTEM images clearly shows heterojunction structure of Mo–CeO_{2-x}, and Ru–CeO_{2-x} in **Figure 4.5 d and g**.

Samples	BET Surface Area (m ² g ⁻¹)	Pore Volume (cm ³ g ⁻¹)	Median Pore Size (nm)
CeO _{2-x}	146.02	0.38	7.11
Mo-CeO _{2-x}	147.73	0.33	6.04
Ru-CeO _{2-x}	270.54	0.76	7.60

Table 4.6. Nanostructural characteristics of CeO2-x, Mo-CeO2-x, and Ru-CeO2-x



Figure 4.5. TEM images of (a-c) CeO_{2-x}, (d-f) Mo-CeO_{2-x}, and (c-e) Ru-CeO_{2-x}

The SAED images of CeO_{2-x} , Mo– CeO_{2-x} and Ru– CeO_{2-x} are shown in Figure 4.6. These are comprised of rings with discrete dots suggesting a randomly oriented polycrystalline structure for the heterojunctions.(*243, 244*) Further, the SAED patterns were indexed to the fluorite cubic structure of CeO₂, while the rings are compared relative to those obtained for pristine–CeO₂ in **Figure 4.6a**. The diffracted facets for MoO₃ were indexed as illustrated in **Figure 4.6b**. Similarly, the coexistence of RuO₂ and CeO₂ were confirmed by indexing the diffraction patterns highlighted in **Figure 4.6c**. The existence of spots demonstrated the presence of small amounts of dopants and the intensity of the diffraction patterns reveal that the nanostructures are slightly disordered, with the crystallinity increasing in the order CeO_{2-x} < Mo–CeO_{2-x} < Ru–CeO_{2-x}. These data are consistent with the XRD and Raman data in that they reflect increasing levels of solid solubility.



Figure 4.6. SAED images for: (a) CeO_{2-x} (b) Mo– CeO_{2-x} , (c) Ru– CeO_{2-x}

The EDS mapping shows in **Figure 4.7** for CeO_{2-x} Mo– CeO_{2-x} , and Ru– CeO_{2-x} . The matched Ce, O, and dopant distributions show that both doped materials exhibit homogeneously distributed dopant solid solutions.



Figure 4.7. EDS images for: (a) CeO_{2-x} (b) Mo– CeO_{2-x} , (c) Ru– CeO_{2-x}

4.3.2 AFM Analysis

AFM images and corresponding height profiles are shown as **Figure 4.8**. CeO_{2-x} forms stacked nanosheets, the examined particle of which was \sim 35.0 nm thick. However, the thicknesses of the individual doped nanosheets again reveal the roles of heterojunction formation and solid solubility on the recrystallisation.



Figure 4.8. AFM images and corresponding height profile for: (**a**, **b**) CeO_{2-x} (**c**, **d**) Mo–CeO_{2-x}, (**e**, **f**) Ru–CeO_{2-x}

The Mo-CeO_{2-x} holey nanosheets show the lowest thickness (ultrathin) compared to other studies on nanosheets reported in literature (**Table 4.7**); moreover, these samples show the high surface area and pore volume.

Samples	Morphology	Thickness (nm)	Surface Area (m ² g ⁻¹)	Pore Volume (cm ³ g ⁻¹)	Median Pore Size (nm)	Ref.
Mo-CeO _{2-x}	Holey nanosheet	1-3	147.73	0.33	6.04	Present work
CeO _{2-x}	Holey nanosheet	35	146.02	0.38	7.11	Present work
Ru-CeO _{2-x}	Holey nanosheet	5	270.54	0.76	7.60	Present work
C03O4	Holey nanosheet	2	115	N/A	5.8	(245)
C03O4	Nanosheet	2.1-5.8	N/A	N/A	N/A	(246)
In ₂ O ₃ /ZnIn ₂ S e ₄	Nanosheet	2.8	N/A	N/A	N/A	(247)
MnO _{2-x}	Nanosheet	3	94	0.32	13.86	(248)
Co ₃ O ₄ /CeO ₂	Nanosheet	3	N/A	N/A	N/A	(249)
PdO/CeO2- C03O4	Nanosheet	3.3	133.23	0.15	4.5	(250)
CdS-loaded 2D MOF	Nanosheet	7.1	44.7	0.24	21.7	(251)
ZnMn ₂ O ₄	Holey nanosheet	~20	78.64	N/A	N/A	(252)
CeO ₂	Nanosheet	20-50	68	N/A	N/A	(219)
FeSe ₂ /g-C ₃ N ₄	Nanosheet	21.1	34	0.17	3.34	(253)

 Table 4.7. Comparison of physicochemical properties of functional nanosheets from

 literature

In summary, the growth and stacking of Mo–CeO_{2-x} sheets, which are ~1.00 nm thick, are constrained by the homogeneously distributed, fine, chemisorbed MoO_3 heterojunction precipitates. In contrast, the growth and stacking of Ru–CeO_{2-x} were less constrained by inhomogeneously distributed, coarse, physisorbed RuO₂ heterojunction

precipitates. Further, the dopant ion distribution densities revealed by SEM EDS mapping (**Figure 4.9**) indicate that Ru exhibited bulk solubility (lower distribution density) while Mo exhibited surface solubility (higher distribution density). The greater solid solubility and corresponding distribution of nucleation sites (*viz.*, Ru ions) resulted in a greater ease of ready recrystallisation and consequent thicker nanosheets.



Figure 4.9 SEM images and corresponding EDS images for: (a) Mo–CeO_{2–x}, (b) Ru–CeO_{2–x}

The mechanisms behind the variant dopant dispositions are shown in the representative phase diagram of **Figure 4.10**. That is, MoO_3 exhibits what is effectively surface chemisorption owing to the limited solid solubility of Mo in CeO_{2-x} , resulting in a limited but strong interfacial bonding between the precipitate and CeO_{2-x} . In contrast, the high solid solubility of Ru in CeO_{2-x} results in the achievement of saturation solubility of Ru in CeO_{2-x} , after which only large RuO₂ particles precipitate from solution and are weakly bonded by physisorption. These phase relations also suggest the applicability of kinetics through change in temperature in order to alter solid solubilities. Hence, it may be possible to obtain chemisorbed RuO₂ precipitates if the solubility is lowered by reducing the temperature to below that of the solidus.



Figure 4.10. (a) Representative phase diagram for doped CeO_{2-x}, (b) Dopant solid solubilities and valences of Mo and Ru based on present work

The Raman data in **Figure 4.3** suggest that the dopant valences across the Mo–CeO_{2-x} interface are graded (Mo⁶⁺, Mo⁵⁺, Mo⁴⁺), and the EDS data (**Figure 4.9**) suggest that the solubility is limited to the surface. The mechanism by which this is achieved is likely to be intervalence charge transfer (IVCT) (*254, 255*) according to the sequence (**Table 4.3**):

$$Mo^{6+} + Ce^{3+} \rightarrow Mo^{5+} + Ce^{4+}$$
 (4.36)

$$Mo^{5+} + Ce^{3+} \rightarrow Mo^{4+} + Ce^{4+}$$
 (4.37)

Further, it is likely that this process is assisted by the ready transformations between the Magnéli-like Mo–O shear structures (**Figure 4.11**) (*256, 257*). It is considered likely that the final Mo valence is 4+ owing to its much greater stability, as suggested by its melting point of 2300°C, than Mo^{5+} and Mo^{6+} , which exhibit peritectic decomposition in the temperature range 800°-818°C.



Figure 4.11. Mo-O phase diagram adapted from (258)

In contrast, the Raman data in **Figure 4.3** indicate only a single Ru valence and the EDS data (**Figure 4.9**) suggests extensive solid solubility. Both mechanisms of solid solubility appear to be interstitial because the XPS data, presented subsequently, show that the [Ce] decreased by ~10 at% from Mo doping but the [Ce] decreased by ~30 at% from Ru doping (**Table 4.8**), both of which indicate charge compensation from Ce vacancy formation. Further, interstitial solid solubility is very likely for essentially all cations owing to the very large sizes of the central interstice (0.110 nm radius) and the Ce sublattice gap (0.160 nm) through which the cations must pass. These sizes may be compared to the ionic radii (sixfold coordination only are available) of Mo⁶⁺ (0.073 nm), Mo⁵⁺ (0.075 nm), Mo⁴⁺ (0.079 nm), and Ru⁴⁺ (0.076 nm).(*227*)

4.4 Chemical Characteristics

4.4.1 XPS Analysis

The chemical and defect analyses of the heterojunction nanostructures undertaken by surface X ray photoelectron spectroscopy (XPS) are shown in **Figures 4.12**. The relative

atomic concentrations of the two oxidation states Ce3+ and Ce4+ were obtained by deconvolution of the 3d orbital spectra into discrete peaks using Gaussian fitting. As shown in Figure 4.12a, the Ce 3d_{5/2} spectrum of pure CeO_{2-x} exhibits peaks at binding energies ~880 and ~885 eV, which are characteristic of Ce^{3+} (magenta), and peaks at ~882, ~889, and ~898 eV, which are characteristic of Ce⁴⁺ (blue).(259, 260) In principle, for pure CeO_{2-x} and *ionic charge compensation*, the concentration of oxygen vacancies ($[V_0^{\bullet\bullet}]$) is twice the concentration of Ce^{3+} ([Ce^{3+}]), the latter of which is determined from the normalized integrated areas for the Ce³⁺ peaks. However, in the case of CeO_{2-x} doped with cations of variable valence (stoichiometric or fractional), redox charge compensation through intervalence charge transfer (IVCT) can contribute to the formation or annihilation of $V_0^{\bullet\bullet}$.(18) Further, *electronic charge compensation* does not affect the $[V_0^{\bullet\bullet}]$. Figures 4.12e and f highlight the Ce³⁺ peak areas, which were calculated to be 29.5 at%, 28.7 at%, and 29.6 at% for CeO2-x, Mo-CeO2-x, and Ru-CeO2-x, respectively, giving respective $[V_0^{\bullet\bullet}]$ of 14.8%, 14.4%, and 14.8%. Figure 4.12g reveals two discrete peaks at 235.9 and 232.7 eV, which are assigned to the Mo $3d_{3/2}$ and Mo $3d_{5/2}$ orbitals of Mo⁶⁺, (261) respectively. The Ru 3d peaks are problematic owing to overlap with the C 1s peaks from adventitious carbon (262, 263). Consequently, the Ru $3p_{3/2}$ and Ru $3p_{5/2}$ peaks are used for quantitative analysis. Figure 4.12h shows peaks at 464.3 and 485.9 eV, which are characteristic of the Ru $3p_{3/2}$ and Ru $3p_{5/2}$ peaks of Ru⁴⁺, respectively.(264)

The dopant solid solubility and defects can be accurately detected by combination between XPS data and defect equilibria. The formation of solid solution between doping and host material always was determined as dopant sited at substitutional position. However, the large voids in CeO₂ lattice is suitable for two of three cation to achieve interstitial solid solubility. When the dopant is located in the interstitial site, due to the ionic charge comparison, it will rise the appearance of $V_{Ce}^{\prime\prime\prime\prime}$ as shown in **Table 4.2-4.4**. The introduction of donor dopant also will cause $V_{Ce}^{\prime\prime\prime\prime\prime}$ formation owing to the charge balance. The nature of the solid solubility mechanism can be elucidated by consideration of the XPS data in conjunction with the defect equilibria:



Figure 4.12. XPS spectra for CeO_{2-x} , Mo– CeO_{2-x} , Ru– CeO_{2-x} : (a) Ce 3 d for CeO₂, (b) O 1 s for CeO₂, (c) O 1 s for Mo– CeO_{2-x} , (d) O 1 s for Ru– CeO_{2-x} ; (e) Ce 3 d for Mo– CeO_{2-x} , (f) O 1 s for Ru– CeO_{2-x} (g) Mo 3 d orbital of the Mo– CeO_{2-x} and (h) Ru 3 p orbital of Ru– CeO_{2-x} ;

Cerium vacancies form are demonstrated unambiguously.[32]. In the thesis, the defect equilibria are unambiguous: With interstitial cation doping, the only two ionic charge compensation mechanisms are metal vacancy formation and lattice anion stuffing to balance (essentially impossible). However, it can be noted that both electronic charge compensation and redox charge compensation are possibilities, and this do not involve metal vacancy formation. the calculation of the $[V_{Ce}^{\prime\prime\prime\prime}]$ is theoretical, as demonstrated by the use of this work as a subscript.

The complete XPS data for CeO_{2-x}, Mo–CeO_{2-x}, and Ru–CeO_{2-x} are given in **Table 4.8** and these data are interpreted in **Table 4.9**:

Row	Parameter (at%)	Location	CeO _{2-x}	Mo-CeO _{2-x}	Ru-CeO _{2-x}
1	Ce Concentration (at%)	Total Volume	27.7	24.6	19.5
2	[V ^{''''}]Theoretical (at%)	Total Volume	0	3.1	8.2
3	O Concentration (at%)	Total Volume	67.3	67.5	67.8
4	Ce/O Ratio	Total Volume	0.41	0.36	0.28
5	O/Ce Ratio	Total Volume	2.43	2.74	3.48
6	O/(Ce + X) Ratio*	Total Volume	2.43	2.50	2.58
7	Ce/(Ce + O) Concentration	Total Volume	29.2	26.7	22.3
8	Ce ³⁺ /(Ce ³⁺ + Ce ⁴⁺) Concentration	Surface	29.5	28.7	29.6
9	O-Ce ³⁺ /O-Ce ⁴⁺ Concentration	Subsurface	20.3	19.7	38.4
10	O-Ce ³⁺ /(O-Ce ³⁺ + O-Ce ⁴⁺) Concentration	Subsurface	16.9	16.5	27.7
11	Hypothetical V ₀ ^{••} Concentration (at%)	Surface	14.8	14.4	14.8
12	Hypothetical V ₀ ^{••} Concentration (at%)	Subsurface	8.5	8.3	13.8
13	Added Dopant Concentration (at%)*		0.0	4.1	6.8

Table 4.8. Comparison of XPS data for CeO_{2-x}, Mo-CeO_{2-x}, Ru-CeO_{2-x}

Row	Parameter (at%)	Interpretation
1	[Ce]	Small decrease for Mo–CeO _{2-x} and larger decrease for Ru–CeO _{2-x} consistenting with minor surface Mo solubility and major bulk Ru solubility, with ionic charge compensation by $V_{Ce}^{\prime\prime\prime\prime}$
2	$[\mathbf{V_{Ce}^{\prime\prime\prime\prime\prime}}]$ Theoretical	As in Row 1
3	[O]	Similar values for all three are consistent with effective absence of $V_0^{\bullet\bullet}$ formation and hence absence of associated acceptor Mo ³⁺ or Ru ³⁺ ; simultaneous decrease in [Ce] is consistent with formation of $V_{Ce}^{''''}$
4	[Ce]/[O] Ratio	As in Rows 1-3
5	[O]/[Ce] Ratio	As in Rows 1-3
6	[O]/([Ce] + [X]) Ratio	As in Rows 1-3
7	[Ce]/([Ce] + [O])	As in Rows 1-3
8	[Ce ³⁺]/([Ce ³⁺] + [Ce ⁴⁺])	Similar values for all three consistent with unchanged $[Ce^{3+}]$ as well as effectively unchanged surface $[Ce^{4+}]$ owing to exsolution from near-surface and deposition on surface; also consistent with absence of $V_0^{\bullet\bullet}$ formation, IVCT involving Ce, and redox charge compensation involving Ce
9	[O-Ce ³⁺]/[O-Ce ⁴⁺]	Similar CeO _{2-x} and Mo–CeO _{2-x} relative to large increase in Ru–CeO _{2-x} consistent with large bulk Ru solubility, redox charge compensation by Ce'_{Ce} , ionic charge compensation by V''_{Ce} , and loss of associated O–Ce ⁴⁺
10	$[O-Ce^{3+}]/([O-Ce^{3+}] + [O-Ce^{4+}])$) As in Row 9
11	[V ^{••}]Hypothetical	As in Rows 1-3
12	[V ₀ ^{••}]Hypothetical	As in Row 9
13	[Dopant]	As in Rows 1-3

 Table 4.9.
 Interpretation of XPS data summarized in Table 4.8.

- Mo⁴⁺ Solid Solubility: The data in Table 4.8 show that the changes in the concentrations do not allow differentiation between substitutional and interstitial solid solubilities.
- Mo⁵⁺ and Mo⁶⁺ Solid Solubility: These donor dopants could exhibit maximal Mo solubility of 4.1 at% (Table 4.8). Substitutional solid solubility and ionic charge compensation (Tables4.2 and 4.4) involve Mo/V_{Ce}^{'''} ratios of 4.00 and 2.50, respectively, which would result in maximal [V_{Ce}^{''''}] of 1.03 at% and 0.63 at%, respectively. In contrast, interstitial solid solubility and ionic charge compensation (Tables 4.2 and 4.3) involve Mo/V_{Ce}^{''''} ratios of 0.80 and 0.75, respectively, which would result in maximal [V_{Ce}^{''''}] of 5.13 at% and 5.47 at%, respectively. Table 4.8 shows that the [V_{Ce}^{''''}] calculated from the change in [Ce] upon Mo doping is 3.1 at%. Since the maximal solubility is unlikely to have been achieved, then substitutional solubility is not possible and the resultant interstitial solubility, accompanied by ionic charge compensation, of Mo is ~2.4 at% (3.1 at% × [0.80+0.75/2]) However, this is likely to be affected by the probable concentration of the dopant at this low concentration on the surface and subsurface of the particle.
- Ru⁴⁺ Solid Solubility: This neutral dopant shows completely different behavior from that of Mo. Table 4.8 shows that the total [Ce] decreased and the [Ce³⁺] in the bulk increased significantly. If Ru dissolves substitutionally, the [Ce] would decrease but there would be no impact on the [Ce³⁺]. However, the defect equilibria in Table 4.3 show that interstitial solid solubility would result in the formation of $V_{Ce}^{'''}$, thus involving ionic charge compensation, but that redox charge compensation would increase the [Ce³⁺]. Consequently, it is clear that Ru exhibits interstitial solid solubility. Further, the maximal Ru solubility is 6.8 at% (Table 4.8) and interstitial solid solubility (Table 4.3) involves the Mo/V_{Ce}^{''''} ratio of 1.00, which would result in maximal [V_{Ce}^{'''''}] of 6.80 at%. The [V_{Ce}^{'''''} calculated from the change in [Ce] upon Ru doping is 8.2 at% (Table 4.8), this indicates that the dopant is concentrated at the surface, exhibiting the expected diffusion gradient into the bulk. This is an unavoidable result of the probing depth limitation of XPS for CeO₂ of 1-3 nm(*18*) (*265*) and the particle size of ~5 nm (Tables 4.5 and 4.7). However, these data suggest that

all of the dopant has dissolved, so the saturation solid solubility would be ≥ 6.8 at%. In contrast with Mo doping, the higher overall concentration of the dopant is consistent with volumetric solid solubility.

Concerning the data in **Tables 4.8** and **4.9**, values of O/Ce > 2.0 for CeO_{2-x} have been observed before(66, 265, 266), reaching as high as 2.8 in the bulk(265) and 3.15 at the surface (266), although it is uncommon for researchers to report these data. The reason for the oxygen hyperstoichiometry is the greater probing depth of the beam for oxygen detection compared to that for cerium detection(267). A critical point is the approximately constant oxygen concentrations in Table 4.8, which clarify why it is not possible for interdependent substitutional solid solubility, ionic charge compensation, and $V_0^{\bullet\bullet}$ formation to be applicable. The reason for this is that the oxygen concentrations ([O]) are approximately constant (although they actually increase from 67.3 to 67.5 to 67.8 at% upon doping) while the cerium concentrations ([Ce]) decrease significantly (from 27.7 at% to 19.5 at%). In fact, calculations of the other ionic ratios are consistent in demonstrating increasing [O], which is consistent with V₀^{••} annihilation, which results from the charge compensation for donor doping. These phenomena are explained unambiguously by interdependent interstitial solid solubility, ionic (Mo) or ionic plus redox (Ru) charge compensation, and $V_{Ce}^{\prime\prime\prime\prime}$ formation. Thus, the formation of $V_0^{\bullet\bullet}$ plays no role in the equilibria.

The XPS identification of Mo^{6+} , Raman (and subsequent EPR) identification of Mo^{5+} , relative stabilities ($Mo^{6+} > Mo^{4+} > Mo^{5+}$ (268)), solid solubility considerations (*viz.*, Hume-Rothery's rules), the Magnéli-like Mo-O structures, and IVCT considerations all suggest that the Mo/CeO_{2-x} interface is likely to be graded. The XPS data demonstrate interstitial solid solubility and ionic charge compensation, the corresponding defect equilibria across the heterojunction interface, surface, and subsurface of which are:

Interface:
$$3Mo_{Mo}^{x} + 90_{0}^{x} \xrightarrow{CeO_{2}} Mo_{i}^{\dots} + 2Mo_{i}^{\dots} + 4V_{Ce}^{\prime\prime\prime\prime\prime} + 4Ce_{S}^{x} + 90_{0}^{x}$$
 (4.38)

Surface:
$$4\text{Mo}_{\text{Mo}}^{\text{x}} + 100_{0}^{\text{x}} \xrightarrow{\text{CeO}_{2}} 4\text{Mo}_{i}^{\text{cov}} + 5\text{V}_{\text{Ce}}^{\prime\prime\prime\prime} + 5\text{Ce}_{\text{S}}^{\text{x}} + 100_{0}^{\text{x}} \qquad (4.39)$$

Subsurface:
$$\operatorname{Mo}_{Mo}^{x} + 20_{0}^{x} \xrightarrow{\operatorname{cco}_{2}} \operatorname{Mo}_{i}^{\bullet\bullet\bullet\bullet} + \operatorname{V}_{Ce}^{\prime\prime\prime\prime\prime} + \operatorname{Ce}_{S}^{x} + 20_{0}^{x}$$
(4.40)

Since the $[Ce^{3+}]$ is unchanged at the surface but it is present in the bulk, then the greater proximity of the ions in the subsurface and bulk relative to that at the surface indicates:

Graded Bonding				I	IVCT		
Mo ⁶⁺	\rightarrow	$Mo^{6+} + Mo^{5+}$	\rightarrow	$Mo^{5+} + Ce^{3+}$	\leftrightarrow	$Mo^{4+} + Ce^{4+}$	
Adsorbate		Interface		Surface		Subsurface	

As mentioned, the XPS data for $Ru-CeO_{2-x}$ indicate that, although Ru dissolves interstitially, the [Ce] decreases, and the [Ce³⁺] increases. This is explained by the simultaneous presence of both ionic and redox charge compensation mechanisms, which are represented by the defect equilibria:

All Levels:
$$2\operatorname{Ru}_{\operatorname{Ru}}^{x} + 4\operatorname{O}_{O}^{x} \xrightarrow{\operatorname{CeO}_{2}} 2\operatorname{Ru}_{i}^{\cdots} + \operatorname{V}_{\operatorname{Ce}}^{\prime\prime\prime\prime} + \operatorname{Ce}_{S}^{x} + 4\operatorname{O}_{O}^{x} + 4\operatorname{Ce}_{\operatorname{Ce}}^{\prime}$$
(4.41)

These solid solubility and charge compensation mechanisms, which are derive largely from the XPS data, are illustrated in **Figure 4.13**



Figure 4.13. Heterojunction formation, solid solubility, and charge compensation mechanisms based on data in Tables 4.2 (heterojunction defect equilibria), Table 4.3 (graded defect equilibria), Table 4.8 (XPS data summary), and Table 4.9 (XPS data interpretation)

4.5 Defects Characteristics

4.5.1 EPR Analysis

The confirmation of solid solubility through consideration of the nature of the defects was examined by electron paramagnetic resonance (EPR) spectroscopy at room temperature, as shown in the full spectra in **Figure 4.14a** and the enlargements of **Figure 4.14b**.



Figure 4.14. (a) EPR spectra (equal sample masses) for CeO_{2-x}, Mo-CeO_{2-x}, Ru⁻CeO_{2-x};
(b) Expanded plot of (a)

The g factors calculated from these spectra based on equation (4.42) are given in **Table 4.10**, which differentiates between literature assignments and assignments based on the present work.

$$g = \frac{hv}{\beta B} \tag{4.42}$$

*where g is g-factors; h is Planck's constant as 6.62×10^{-34} J·s; β is Bohr magneton as $9.2740154 \times 10^{-24}$ J/T; B is Magnetic field; v is the frequency.

Sample	Magnetic Field (G)	g Factor	Description		
			Present Work	Literature	Reference
	3752	1.880	- Ce ⁴⁺ –Ce ³⁺ redox (subsurface)	Ce ³⁺	(269)
	3656	1.930			
	3589	1.967	Ce ⁴⁺ –Ce ³⁺ redox (bulk)	Ce ⁴⁺ –Ce ³⁺	(270-273)
	3522	2.006	•O ₂ ⁻ –Ce ⁴⁺ (oxygen vacancy cluster)	•O ₂ ⁻ -Ce ⁴⁺ (oxygen vacancy cluster)	(274-277)
	3499	2.011	•O ₂ Ce ⁴⁺ (isolated oxygen vacancy)	•O ₂ ⁻ –Ce ⁴⁺ (isolated oxygen vacancy)	(274-278)
CeO _{2-x}	3473	2.029			
	3457	2.036			
	3438	2.048	• •O ₂ ⁻ -Ce ⁴⁺ (oxygen vacancy cluster)	•O ₂ ⁻ -Ce ⁴⁺ (oxygen vacancy cluster)	(274-278)
	3427	2.050			
	3379	2.080	O ₂ –Ce ³⁺ (adsorbed)	Ce ³⁺	(99, 269)
	3291	2.140			
	3679	1.914	Mo ⁵⁺ (subsurface)	Mo ⁵⁺	(271)
1 v10-CEO2-x	3630	1.940	$Mo^{4+}-Ce^{3+}$ (bulk*)	X–Ce ³⁺	(271, 273, 279)

Table 4.10. Description of observed EPR data for CeO_{2-x}, Mo-CeO_{2-x}, Ru-CeO_{2-x}

	3589	1.967	$Mo^{4+}-Ce^{3+}$ (bulk)	X–Ce ³⁺ ,	(271, 273, 279)
	3471	2.029	•O ₂ ⁻ –Ce ⁴⁺ (isolated oxygen vacancy)	•O ₂ ⁻ -Ce ⁴⁺ (isolated oxygen vacancy)	(274-278)
	3440	2.045	•O ₂ ⁻ -Ce ⁴⁺ (oxygen vacancy cluster)	•O ₂ ⁻ –Ce ⁴⁺ (oxygen vacancy cluster)	(274-278, 280, 281)
Ru-CeO2-x	3630	1.940	$Ru^{4+}-Ce^{3+}$ (bulk)	X–Ce ³⁺ ,	(271, 273, 279)
	3589	1.967	Ru^{4+} – Ce^{3+} (bulk)	X–Ce ³⁺	(271, 273, 279)
	3460	2.037	•O ₂ ⁻ –Ce ⁴⁺ (isolated oxygen vacancy)	•O ₂ ⁻ -Ce ⁴⁺ (isolated oxygen vacancy)	(274-278, 280, 281)
	3439	2.048	•O ₂ ⁻ –Ce ⁴⁺ (oxygen vacancy cluster)	•O ₂ ⁻ -Ce ⁴⁺ (oxygen vacancy cluster)	(274-278, 280, 281)

* In the present work, the failure of Raman, a bulk analytical technique, to detect Mo⁴⁺ indicates that this valence is limited to the subsurface although the EPR signal is assigned to a bulk effect; that is, subsurface and bulk can be considered to be equivalent in EPR. However, it is possible that the Mo⁴⁺ diffusion extends somewhat into the bulk but at a concentration below the level of detection by Raman.

When the g factor is <2.0023, the electrons have low mobilities and so these defects are localized (282, 283). The signal at g = 1.967 (3589 G) represents Ce^{4+}/Ce^{3+} redox species at the surface, which result from the trapping of electrons in the oxygen vacancies. Figure 4.14a reveals that, upon the introduction of either dopant, this signal is strengthened, which is attributed to the Ce^{4+}/Ce^{3+} redox resulting from the interstitial solid solubility of the dopant, $V_{Ce}^{\prime\prime\prime\prime}$ formation, and ionic and redox charge compensation. It can be seen that the intensities increased in the order $CeO_{2-x} < Mo-CeO_{2-x} < Ru-CeO_{2-x}$, which is consistent with the relative amounts of dopants (nil < surface < bulk). More importantly, the observation that both dopants enhance the same peak indicates that the mechanism to create unpaired electrons is the same. Since neutral Ru⁴⁺ clearly dissolves interstitially in the bulk, then this shows that neutral Mo⁴⁺ also dissolves interstitially in the subsurface (which is equivalent to the bulk; see footnote to Table 4.10). This is significant because it confirms the presence of Mo⁴⁺ as the terminating layer in the graded surface. Since surfaces have higher energies than the bulk (284), then the g factors have been differentiated between surface and bulk phenomena. Consequently, although g factors for Mo⁵⁺ has been identified, this can be assigned to the surface since it is not present in the bulk, as shown in **Figure 4.13**. Similarly, there is no g factor for Mo^{6+} because this valence does not bond with CeO_{2-x}. Finally, there are g factors for both surface and bulk Ru⁴⁺ because it is present in both regions.

In contrast, when the g factor is >2.0023, as given in **Table 4.10**, this indicates a signal from O_2^- , which results from the reaction initiated by EPR:

$$Ce^{3+} + O_2 \rightarrow Ce^{4+} - O_2^{-}$$
 (4.43)

The thus indicated oxygen vacancies are oxygen adsorption centres that can be classified as individual or clustered. Importantly, the oxygen is adsorbed into an oxygen vacancy, so the EPR signal represents an indirect measure of $[V_0^{\bullet\bullet}]$. In effect, Equation 4.44 can be revitalized as:

$$\{2Ce^{3+} + V_0^{\bullet\bullet}\} + \{Ce^{3+} + O_2\} \rightarrow \{2Ce^{4+}\} + \{Ce^{4+} - O_2^{-}\}$$
(4.44)

Hence, a single $V_0^{\bullet\bullet}$ is converted to a single O_2^{-} . However, **Table 4.10** shows that two g-factors previously were assigned for Ce³⁺ (99, 269). In the present work, these have been harmonized with Equation 4.44 by assigning these to the other member component, which is Ce³⁺ + O₂. Consequently, these g factors have been assigned by adsorbed oxygen in proximity to Ce³⁺.

Figure 4.14a also shows that the EPR signal intensities for g factors >2.0023 were in the order Mo–CeO_{2-x} < Ru–CeO_{2-x} < CeO_{2-x}. This trend is interpreted in terms of Equation 4.44, which suggests the relative $[V_0^{\bullet\bullet}]$ for the three samples. That is, in contrast to the proposed defect equilibria, which are based on dopant interstitial (*i.e.*, donor dopant) solid solubility and combined ionic and redox charge compensations, an alternative charge compensation mechanism associated with the presence of intrinsic Ce³⁺ and $V_0^{\bullet\bullet}$ in CeO_{2-x} may occur. Using Ru–CeO_{2-x} as the example, the elaborated defect equilibria for dopant and matrix would be:

Ionic Charge Compensation

$$[\operatorname{Ru}_{\operatorname{Ru}}^{x}] + [4\operatorname{Ce}_{\operatorname{Ce}}' + 80_{0}^{x} + 2V_{0}^{\bullet\bullet} + 0_{2} (g)] \xrightarrow{\operatorname{CeO}_{2-x}} [\operatorname{Ru}_{i}^{\bullet\bullet\bullet\bullet}] + [4\operatorname{Ce}_{\operatorname{Ce}}' + 80_{0}^{x}] (4.45)$$

C - 0

Electronic Charge Compensation

$$[\operatorname{Ru}_{\operatorname{Ru}}^{\mathrm{x}}] + [4\operatorname{Ce}_{\operatorname{Ce}}' + 80_{0}^{\mathrm{x}} + 2V_{0}^{\bullet\bullet} + 0_{2} (g)] \xrightarrow{\operatorname{CeO}_{2-\mathrm{x}}} [\operatorname{Ru}_{i}^{\bullet\bullet\bullet\bullet}] + [4\operatorname{Ce}_{\operatorname{Ce}}^{\mathrm{x}} + 80_{0}^{\mathrm{x}} + 4e'] (4.46)$$

Consequently, Mo–CeO_{2-x} exhibits the lowest effect since the solubility is limited to the surface, Ru–CeO_{2-x} exhibits a greater effect owing to its bulk solubility, and CeO_{2-x} has the greatest effect because the $[V_0^{\bullet\bullet}]$ was highest since oxygen vacancy annihilation does not occur. Finally, since **Table 4.8** shows that that $[Ce^{3+}]$ was constant for all three samples, then Equation 4.45 governs, not Equation 4.46 since the latter involves $Ce^{3+} \rightarrow Ce^{4+}$ oxidation.

4.6 F Centres

4.6.1 PL Analysis

Photoluminescence (PL) spectra arise from the presence of point defects that generate energy transitions between ground and excited states associated with luminescent centres, which often are colour or F centres (285-287), where the peak intensities are inversely proportional to the rates of electron-hole recombination. This effect generally is controlled by the diffusion distance (*i.e.*, particle size), the presence of trap states (*i.e.*, defects), and the presence of heterojunctions (*i.e.*, interfaces) (288-290). Figure 4.15 shows the PL data for the samples and the attributed transitions, most of which are associated with the colour centres $F^0(V_0^{\bullet \bullet})$, $F^+(V_0^{\bullet})$, and $F^{++}(V_0^x)$ are summarised in **Table** 4.11. Aškrabić et al. (93) have proposed the most thorough assessment of the PL data for CeO_{2-x} at an excitation wavelength of 325 nm from 15 K to room temperature. These data are interpreted principally in terms of the excitation energies associated with all three types of F Centres. Table 4.12 reveals a reasonable correlation between the peak positions for the samples, which were fabricated by precipitation and self-propagating synthesis and those for the samples of the present work, which were fabricated by electrodeposition to produce a coordination polymer, followed by oxidation (32). However, an aspect of PL that does not appear to have been considered is the potential for the formation and transition between colour centres, the energies of which are associated with the formation of midgap states(291). Consequently, speculative alternative assignments for the major PL peaks are proposed in Table 4.12.



Figure 4.15. PL spectra of the CeO_{2-x} , Mo– CeO_{2-x} , and Ru– CeO_{2-x} 92
Wavelength (nm)	Energy (eV)	Assigned Transition			
310	4.00	F^{++} to O 2 p (VB)			
376	3.3	Ce 4 <i>f</i> 1 to CB			
384	3.23	Ce 4 <i>f</i> 0 to Ce 4 <i>f</i> 1 (Ce4+ to Ce3+)			
404	3.07	F ⁺⁺ to CB			
428-413	2.9-3.0	Ce $4fl$ to F^{++}			
517-496	2.4-2.5	F^+ to CB F^+ to Ce 4f0			
620-590	2.0-2.1	F^0 to CB			
729	1.7	VB to F ⁺			

 Table 4.11. Summary of photoluminescence data for F centre transitions in CeO_{2-x} (93, 121)

 Table 4.12.
 Comparison between photoluminescence data of Aškrabić et al. (93) and present work

Aškrabić <i>et al.</i> (93)			Present Work			
Wavelength (nm)	Energy (eV)	Assigned Transition	Wavelength (nm)	Energy (eV)	Alternative Interpretation	
376	3.3	Ce 4f1 to CB	405	3.1	$V_0^{\bullet}(F^+) \rightarrow V_0^x(F^{++})$	
428-413	2.9-3.0	Ce 4f1 to F ⁺⁺	455	2.7	$V_0^{\bullet\bullet}(F^0) \to V_0^{\bullet}(F^+)$	
517-496	2.4-2.5	F^+ to F^{+*}	540	2.3	$\begin{array}{c} \mathrm{Ce}^{4+} \to \mathrm{Ce}^{3+} \to \mathrm{V}_{\mathrm{O}}^{\bullet} \\ (\mathrm{F}^{+}) \end{array}$	
620-590	2.0-2.1	F^{0} to F^{0*}	590	2.1	$2Ce^{4+} \rightarrow 2Ce^{3+} \rightarrow V_0^{\bullet\bullet}$ (F ⁰)	
729	1.7	VB to F ⁺			$Ce^{4+} \rightarrow Ce^{3+}$	

These alternative assignments suggest that the PL data reflect the effect of increasing energy on the formation sequence of defects (Equation 4.47) and the transitions between the defect states (Equations 4.48 and 4.49):

$$2Ce^{4+} \to Ce^{3+} + (Ce^{3+} + V_0^{\bullet\bullet}) \to Ce^{3+} + (Ce^{4+} + V_0^{\bullet}) \to Ce^{4+} + (Ce^{4+} + V_0^{x})$$
(4.47)

$$Ce^{3+} + V_0^{\bullet\bullet} \to Ce^{4+} + V_0^{\bullet}$$
(4.48)

$$Ce^{3+} + V_0^{\bullet} \to Ce^{4+} + V_0^{x}$$
 (4.49)

Figure 4.15 shows that the PL intensities exhibit a general trend of hole/electron recombination in CeO_{2-x} < Ru-CeO_{2-x} < Mo-CeO_{2-x}. Table 4.7 reveals a direct correlation with the nanosheet thickness (1-3 < 5 < 35 nm) but Table 4.5 shows that the crystallite size do not (5.1 > 5.6 < 8.1). These results are consistent with effects from the heterojunctions and the defects. That is, for the two low-energy PL peaks, the chemisorbed heterojunction of Mo-CeO_{2-x} is more effective than the physisorbed heterojunction of Ru-CeO_{2-x} in facilitating the directional diffusion of the electrons (where these interstitial dopants are donors and hence cause *n*-type conductivity). These heterojunctions would allow some of the charge carriers to circumvent the potential deep trapping states arising from the dopant defects and F centres. While the easy Ce⁴⁺/Ce³⁺ redox switching suggests a low driving force for electron trapping, the F centres in CeO2x represent defects with very strong driving forces to trap electrons, especially V_0^x . Consequently, the significant decreases in the PL intensities for the two high-energy transitions are attributed to transitions to the $F^+(V_0^{\bullet})$ and $F^{++}(V_0^{X})$ centres, which represent effective trapping sites. Although this appears to be counter-intuitive, this effect derives not from trapping *per se* but from the effect of the F centres on the band alignment, where it is known that the E_f can be raised significantly by F centres, even to an energy above that of the conduction band minimum (CBM) (292). Consequently, when electrons are trapped near or above the CBM, most of the electrons are conducting and hence have high mobilities.

4.7 Energy Band Structure

4.7.1 Band Gap Analysis

The heterojunction nanostructures and the corresponding electronic band structures were constructed for CeO₂, Mo–CeO_{2–x}, and Ru–CeO_{2–x}, respectively. The energy band

diagrams of CeO₂, Mo–CeO_{2-x}, and Ru–CeO_{2-x} drawn using the work function (ϕ), band gap (E_g), and valence band (E_{vb}) offsets with respect to the Fermi level (E_f). The valence band offsets were obtained from valence band X–ray photoelectron spectroscopy (XPS). The work function values were obtained by Kelvin probe force microscopy (KPFM) studies. The band gaps were determined from Kubelka-Munk function plots.

The resultant work function (ϕ) of pure-CeO_{2-x} nanosheets is 4.69 eV (293) and the valence band offsets (E_{vb} = 2.52eV) are obtained from the XPS plot shown in **Figure 4.16**. Due to the existence of defects in the 2D CeO_{2-x} nanosheets, a newly occupied state appears within the E_f and valence band edge energy levels.



Figure 4.16. Band energy data for CeO_{2-x} holey nanosheets: (a) XPS valence band plot,(b) Kubelka-Munk plot from UV-Vis spectrophotometry for optical indirect band gap

The Kubelka-Munk plot in Figure 4.16b based on the UV–Vis data reveals that the indirect bandgap of CeO_{2-x} nanosheet is 2.75 eV, which is calculated based on the equation (Equations 4.50 and 4.51.):

$$F(R_{\infty}) = K/S \tag{4.50}$$

$$(\mathbf{F} (\mathbf{R}_{\infty}) \cdot \mathbf{h} v)^{\frac{1}{2}} = \mathbf{B} \cdot (\mathbf{h} v - \mathbf{E}_{g})$$
(4.51)

*where F (R_{∞}) is Kubelka–Munk factor; K is absorption coefficient; S is back-scattering coefficient; B is constant band tailing parameter; h is the Planck's constant; v is the frequency of incident photons.

The AFM images are illustrated in **Figure 4.17a** and the KPFM results for Mo–CeO_{2-x} are shown in **Figure 4.17b**. The value of contact potential difference (CPD) of Mo–CeO_{2-x} nanosheet (lower potential) is -10 mV (-0.01 eV) as a seen from **Figure 4.17b**.



Figure 4.17. Band structure characteristics of heterostructures $Mo-CeO_{2-x}$ holey nanosheet (a) Topography of $Mo-CeO_{2-x}$ holey nanosheet by KPFM imaging; (b) Contact potential difference measured by KPFM; (c) XPS valence band plot; (d) Kubelka-Munk plot from UV–Vis spectrophotometry data.

From this value, the work function (ϕ) can be calculated as 4.49 eV for Mo–CeO_{2-x} because real work function values were calculated from recorded CPD maps after calibration against a material of known work function, highly oriented pyrolytic graphite (HOPG), following the Equation (4.52):

$$\phi_{Mo-CeO_{2-x}} = V_{CPD(Mo-CeO_{2-x})} - V_{CPD(HOPG)} + \phi_{HOPG}$$
(4.52)
*where ϕ is work function; V_{CPD} is contact potential difference.

The work function of ϕ_{HOPG} is 4.60 eV as reported previously and the $V_{CPD(HOPG)}$ was obtained as 0.105 eV, and the HOPG surface was scanned employing the same experimental parameters as before. The valence band offsets ($E_{vb} = 2.60 \text{eV}$) are obtained from the XPS plot shown in **Figure 4.17c**. Due to the existence of defects in the 2D Mo– CeO_{2-x} nanosheets, a newly occupied state appears within the E_f and valence band edge energy levels. The Kubelka-Munk plot shows the existence of an indirect bandgap of 2.62 eV.

The Ru–CeO_{2-x} shows calculated work function, ϕ , of 4.56 eV ,from Figures 4.18a and 18b), the distance from the valence band (VB) to the E_f as E_{vb} (2.50 eV) (Figure 4.18c), and the optical indirect band gap E_g = 1.76 eV (Figure 4.18d).



Figure 4.18. Band energy data for Ru-CeO_{2-x} holey nanosheets: (a) KPFM image of sample topography, (b) KPFM image of contact potential difference, (c) XPS valence band plot, (d) Kubelka-Munk plot from UV-Vis spectrophotometry for optical indirect band gap

The resultant energy band diagrams for CeO₂, Mo–CeO_{2-x}, and Ru–CeO_{2-x} are shown **Figure 4.19**. Based on analogy with Ce-doped TiO₂ (*291*), these calculations show the following:

- The Eg values of the heterojunction systems are significantly less than that of CeO_{2-x}.
- The E_f for Mo–CeO_{2-x} is raised near the CBM.
- The E_f for Ru–CeO_{2-x} is above the CBM.
- The E_f values are, as mentioned previously, consistent with the effect of the F centres.
- As the E_f values for the F centres increase in energy in the order $V_0^{\bullet\bullet} < V_0^{\bullet} < V_0^{x}$, then it is likely that the major effect derives from the F^{++} centre.
- Similarly, the role of oxygen vacancies would be unlikely to be important as this is the most likely to be a deep trapping site.
- The lowering of the CBM values also is consistent with the greater populations of the energy levels immediately below and above the CBM values owing to the shifts in the E_f values. The role of metal interstitials also may be relevant as these would exhibit energy levels near the CBM. However, the PL data show that this effect is unlikely since Mo–CeO_{2–x}, with limited solubility, showed the greatest effect.
- Conversely, the role of interstitials may be altered by IVCT since decreasing the valence results in an increase in the energy level toward the CB.
- The slight lowering of the VBM for Mo–CeO_{2–x} is consistent with the raising of the E_f.
- However, the slight raising the VBM for Ru–CeO_{2-x} is not consistent with the raising the E_f, which suggests the population of a low-energy midgap state. This effect is most likely to be from V^{''''}_{Ce}, the values of which would tend to be close to the VBM.

For Mo–CeO_{2-x}, the proximity of the CBM (0.02 eV) to the redox potential H/H_2 (0.00 eV) (32) and the lowered E_g relative to pure CeO_{2-x} indicate that this heterojunction would be suitable for photocatalytic water splitting.



Figure 4.19. Energy band diagrams (pH = 0) of CeO₂, Mo–CeO_{2-x}, and Ru–CeO_{2-x}

4.7.2 DFT Analysis

First-principles calculations based on density functional theory were performed in order to characterize further the differences in electronic band structures between CeO₂ and Mo and Ru ions in interstitial sites. Schematics of the electronic densities of states are shown in **Figure 4.20** and **4.21** and the optical indirect band gaps obtained from these data are given **Table 4.13**.

Condition -		Optical Indirect Band Gap (eV)					
		CeO ₂	Mo–CeO2		Ru–CeO2		
	Experimental	2.73		2.61		1.76	
DFT 	Interstitial Solid Solubility	3.20	Mo ⁶⁺	2.50	Ru ⁴⁺	1.75	
			Mo ⁵⁺	1.75			
			Mo ⁴⁺	1.00			
	Substitutional Solid Solubility		Mo ⁶⁺	2.20	Ru ⁴⁺	2.50	
			Mo ⁵⁺	1.75			
			Mo ⁴⁺	1.50			
	Heterojunction with CeO ₂		MoO ₃	3.30	RuO ₂	3.10	

Table 4.13. Experimental band gaps from UV-Vis data and calculated by DFT

The correlation between the experimental and calculated E_g values for substitutional (**Figure 4.20**) *vs* interstitial (**Figure 4.21**) solid solubility for Ru–CeO_{2-x} support the conclusion that the solid solubility mechanism is interstitial; the data for in Mo–CeO_{2-x} are less conclusive. However, the close correlation for interstitial Mo⁶⁺ suggests that there may be some solid solubility of this ion in the surface, which is not indicated in **Figure 4.21**.



Figure 4.20. First-principles DFT simulations of electronic densities of states and band gaps (substitutional solid solubility) for: (a) CeO_{2-x} , (b) $Mo^{6+}-CeO_{2-x}$, (c) $Mo^{5+}-CeO_{2-x}$, (d) $Mo^{4+}-CeO_{2-x}$, (e) $Ru^{4+}-CeO_{2-x}$

Based on the DFT simulations, a schematic of the electronic band energy modifications for the Mo-CeO_{2-x} and Ru-CeO_{2-x} systems are shown in **Figure 4.21g**. In the chemisorbed MoO₃–CeO₂ heterojunction structure (**Figure 4.21a**), the CB electrons tend to migrate from CeO₂ to MoO₃ since MoO₃ has a smaller band gap (2.0 eV) (294) and the VB position did not show any charge transfer between them, which probably is due to the common anion rule. The Mo⁶⁺ ions, which exhibit limited interstitial solid solubility at the interfacial surface, are shallow electron traps (**Figure 4.21d**), being close to the VB position. This can result in VB offset, which increases the likelihood of hole transfer from MoO₃ to CeO₂ to promote electron/hole separation; it also effectively reduces the E_g . Hence, these phenomena are consistent with a Type II heterojunction. The greater interstitial solid solubilities of Mo⁵⁺ (surface) and Mo⁴⁺ (subsurface) give rise to a number of deep defect states in the band gap (**Figures 4.21e** and **f**). As these act as electron traps and CeO₂ is an *n*-type semiconductor, they would not be beneficial to the catalytic performance. However, the graded Mo⁵⁺ and Mo⁴⁺ provide a chemically bonded anchor for the MoO₃, which is facilitated by IVCT.

The RuO₂ has a very narrow E_g (0.47 eV) (295). In the physisorbed RuO₂–CeO₂ heterojunction structure (**Figure 4.21b**), the CB electrons would be driven to migrate from CeO₂ to RuO₂ since RuO₂ has a very small band gap. However, the weak physisorbed bond would be likely to preclude a significant proportion of this conductivity. The Ru⁴⁺ ions, which exhibit extensive interstitial solid solubility into the bulk, are relatively shallow electron traps (**Figure 4.21c**). Hence, these phenomena are consistent with a Type I heterojunction. As these midgap states are present in proximity to both the CB (donor) and VB (acceptor), they potentially could aid in charge separation. Further, the midgap Ru 4d band partially overlaps with Ce 4f band, which causes band tail state formation (296), which effectively lowers the E_g.



Figure 4.21. First-principles DFT simulations of electronic densities of states and optical indirect band gaps of: (a) MoO_3 -CeO₂ heterojunction nanostructure; (b) RuO_2 -CeO₂ heterojunction nanostructure; (c) Ru^{4+} -CeO₂ interstitial solid solution; (d) Mo^{6+} -CeO₂; interstitial solid solution; (e) Mo^{5+} -CeO₂; interstitial solid solution; (f) Mo^{4+} -CeO₂; interstitial solid solution; (g) Schematic of electronic band energy modification of CeO_{2-x} from Mo or Ru doping and MoO₃-CeO₂ and RuO₂-CeO₂ heterojunction formation

The experimental E_g of 2.73 eV is considerably less than the typical literature value of 3.00 eV (*103*) and less than the value of 3.2 eV calculated by DFT (**Figure 4.21**). According to Xu *et al.* (*18*), the E_g can be calculated on the basis of the $[V_0^{\bullet\bullet}]$ according to a linear relationship. However, the present work demonstrates that the $[V_0^{\bullet\bullet}]$, which is calculated from the $[Ce^{3+}]$, does not correlate with the $[Ce^{3+}]$ owing to redox charge compensation. Consequently, the reported equation has been converted to utilise the bulk $[Ce^{3+}]$:

$$E_{g} = 3.0 - \frac{1}{2} (0.032 \text{ x} [0 - Ce^{3+}])$$
(4.53)

Using this equation and the $[O-Ce^{3+}]$ of 16.9 at% (**Table 4.8**), the calculated E_g is 2.73 eV, which is an exact match. This outcome suggests that, for pure CeO_{2-x} , determination of the bulk $[Ce^{3+}]$ (*i.e.*, $[O-Ce^{3+}]$) by XPS and use of Equation 4.53 can provide an accurate determination of the E_g . Clearly, the narrowing of the E_g does not derive from the widely perceived effect of the $[V_0^{\bullet\bullet}]$ but from the more reliable effect of $[Ce^{3+}]$, where the unreliability of the former derives from the potential for charge compensation mechanisms other than purely ionic (*viz.*, redox, IVCT, and electronic).

4.8 Electrocatalytic Performance

The electrochemical catalytic performance was assessed by determination of the hydrogen evolution reaction (HER). The polarization curves in **Figure 4.22a** reveal that the incorporation of Mo and Ru into CeO₂ significantly increases the current density (*j*) in acidic environments in the order Mo–CeO_{2-x} > Ru–CeO_{2-x} > CeO_{2-x}. Mo–CeO_{2-x} attains a *j* of 10 mA cm⁻² at 315 mV of overpotential whereas Ru–CeO_{2-x} and CeO_{2-x} require respective additional 60 mV and 275 mV overpotential in order to reach the same *j* (inset, **Figure 4.22a**). The HER kinetics for the catalysts also were determined and are shown in the Tafel plot of **Figure 4.22b**. A similar trend is observed, where Mo–CeO_{2-x} exhibits the lowest Tafel slope (138 mV dec⁻¹).



Figure 4.22. (a) Linear sweep voltammetry curves for Carbon fiber, CeO_{2-x} , $Mo-CeO_{2-x}$, and $Ru-CeO_{2-x}$ electrodes in 1 M H₂SO₄ (pH = 0) at a scan rate of 5 mV s⁻¹ (inset represents the overpotential required to reach 10 mA cm⁻¹); (b) Tafel plots for CeO_{2-x}, Mo-CeO_{2-x}, and Ru-CeO_{2-x} for hydrogen evolution reaction (HER); (c) Electrochemical impedance spectroscopy (EIS) results for CeO_{2-x}, Mo-CeO_{2-x}, and Ru-CeO_{2-x}

Although the Tafel slopes exhibited by the heterojunction catalysts are below those of benchmark Pt-based catalysts of 30 mV dec⁻¹ (297), the Mo–CeO_{2-x} outperforms other CeO_{2-x}-based catalysts (**Table 4.14**). The performance potentially can be improved by altering the dopant levels by increasing the solid solubility by increasing the calcining temperature, decreasing the solid solubility by decreasing calcining temperature, or altering the calcination atmosphere to manipulate the defect equilibria and charge compensation mechanisms. The comparatively poor HER performance by pure CeO_{2-x} results from its inherent nature deriving from its strong adsorption capacity toward hydrogen.

Sample	Solution	Overpotentia l (mV)	Tafel Slope (mV dec ⁻¹)	Reference
Mo (4 wt%)-CeO $_{2-x}$	Acidic	315	138	Present work
Ru (4 wt%)-CeO _{2-x}	Acidic	375	241	Present work
CeO _{2-x}	Acidic	590	357	Present work
Ni alloy matrix doping CeO ₂	Basic	~1050	141	(133)
Ni–S alloy matrix doping CeO ₂	Basic	N/A	157	(298)
NiO/CeO ₂	Basic	400	159	(299)
Ni–S alloy matrix doping CeO ₂	Basic	400	165	(300)

Table 4.14. Comparison of overpotentials and corresponding Tafel slopes ofCeO2-x-based samples

It is common for the catalytic performance to be assessed in terms of the $[V_0^{\bullet*}]$ (29), which are considered to be active sites. However, the minority opinion also considers that $V_{Ce}^{'''}$ are active sites (113). In the present work, **Tables 4.8** and **4.14** reveal that the Tafel slopes do not correlate with the surface $[V_0^{\bullet*}]$, bulk $[V_0^{\bullet*}]$, or $[V_{Ce}^{''''}]$. The Tafel slopes also do not correlate with the surface $[Ce^{3+}]$ or bulk $[Ce^{3+}]$. Further, the Tafel slopes do not correlate with the BET surface areas (**Table 4.7**). Consequently, it is apparent that the nature of the heterojunctions is responsible for the observed HER behaviour. As mentioned previously, the valence-graded Mo–CeO_{2-x} interface in the form of a chemisorbed heterojunction would enhance the directional diffusion of charge carriers, such that it exhibits the best HER performance. Further, the stabilizing effects of IVCT are likely to enhance the performance even more. In contrast, the Ru–CeO_{2-x} interface, which forms a weakly bonded physiosorbed heterojunction, would be much less effective as a chargetransfer medium. CeO_{2-x}, without a heterojunction interface, would be expected to perform the worst.

These phenomena can be interpreted similarly by the electrochemical impedance spectroscopy (EIS) results shown in Figure 22c. The Nyquist radii indicate that the electrical conductivities (*i.e.* inverse impedances) are in the order $CeO_{2-x} < Mo-CeO_{2-x}$ < Ru–CeO_{2-x}. The strong demand of these *n*-type materials for electrons suggests that metal interstitials and F centres would act as electron traps. Also, the tendency for metal vacancies to exhibit midgap states near the VB suggests these defects also would not assist electron transfer. However, the EPR data of Figure 4.14 are significant in that the signal for the g factor of 1.967 (3589 G) for Ru-CeO_{2-x} significantly larger than that for Mo-CeO_{2-x}, which indicates a major presence of unpaired electrons. Table 4.8 shows that the $[O-Ce^{3+}]$ for Ru–CeO_{2-x} is ~40% greater than that for Mo–CeO_{2-x}. Therefore, it is clear that the unpaired electron associated with the Ce^{4+}/Ce^{3+} in the doped bulk of Ru– CeO_{2-x} is a probable cause of the greater electrical conductivity. However, Table 4.7 also shows that the BET surface area of Ru-CeO_{2-x} is ~45% greater than that of Mo- CeO_{2-x} . Consequently, it is probable that the high electrical conductivity of Ru–CeO_{2-x} derives from combined surface and bulk electrical conductivities. The electrical conductivity of Mo-CeO_{2-x} is likely to be dominated by the surface while that of pure CeO_{2-x} is dominated by the bulk.

The similar slopes of the electrochemical surface area (ECSA) measurements in **Figures 4.23a** and **d** reveal that the concentrations of active sites for all three samples are similar. The data for the $V_{Ce}^{\prime\prime\prime\prime}$ active sites in **Table 4.8** suggest that the slopes should be in the order CeO_{2-x} < Mo–CeO_{2-x} < Ru–CeO_{2-x}. However, there is very little difference between the slope, albeit they are in the order Mo–CeO_{2-x} < Ru–CeO_{2-x} < CeO_{2-x}. These results support the previous conclusion that active sites do not play a dominant role and that the heterojunctions are primary. The ECSA of the catalyst is calculated from the double-layer capacitance according to the reported literature.[301] The ECSA of CeO_{2-x}, Mo–CeO_{2-x}, Ru–CeO_{2-x}, are 0.0294 cm², 0.0183 cm², 0.0298 cm², respectively. The intrinsic activity of the catalysts was studied by excluding the contribution of enlarged active surface area, through normalizing the HER current against ECSA (j_{ECSA}) in place of geometric surface area as shown in **Figure 4.23e**. The relatively improved HER performance confirmed that CeO_{2-x} nanosheets intrinsic catalytic activity.



Figure 4.23. Electrochemical surface area (ECSA) measurements for CeO_{2-x} , Mo– CeO_{2-x} , Ru– CeO_{2-x} from cyclic voltammetry (CV) profiles for: **(a)** CeO_{2-x} , **(b)** Mo– CeO_{2-x} , **(c)** Ru– CeO_{2-x} in 1 M Na₂SO₄, **(d)** Dependence of capacitive current on scan rates at applied potential of 0.625 V *vs* RHE **(e)** comparison of the current density from **Figure 4.22a**, normalized to the ECSA

Finally, it is noted that all three types of materials exhibit mesoporosity, which is of benefit to the mass transport required for hydrogen during electrochemical HER. However, the data in **Table 4.8** reveal that the heterojunctions offer the further advantage of $V_{Ce}^{\prime\prime\prime\prime}$, which can act as sites for mass transport; they also feasibly can be used as sites for hydrogen storage (*302*). In these cases, Ru–CeO_{2-x} would be more effective than Mo–CeO_{2-x} because the former has ~60% greater [$V_{Ce}^{\prime\prime\prime\prime}$].

4.9. Ozonation Catalytic Performance

These materials also were examined for their performances in aqueous-phase catalytic ozonation of salicylic acid, which revealed value as high as 98% removal of total organic carbon (TOC) after only 60 min. **Figures 4.24a** and 24**b** show the TOC removal profiles of as-prepared (*i.e.*, oxidized and reduced samples. The atmospheres were altered in order to determine if Ce and/or Mo redox effects would occur. Since ozonation is facilitated in basic solutions (*139*) and the presence of Ce³⁺ also is enhanced in basic solutions (*303*), then the [Ce³⁺], which would be favoured by reducing conditions, is likely to be an indicator of ozonation performance. However, **Table 4.8** shows that the surface [Ce³⁺] was the same for all three samples and the bulk [Ce³⁺] was greatest for Ru–CeO_{2-x}, which exhibits the worst performance, as shown in **Figure 4.24a** (60 min). Further, while the heterojunctions confirmed superior ozonation after reduction, where the performance of Mo–CeO_{2-x} was outstanding, the reverse was the case for CeO_{2-x}.



Figure 4.24. (a) Removal efficiency of bisphenol A (BPA) in catalytic ozonation using samples before and after reduction: Reaction conditions: [Salicylic Acid]₀ = 200 mg/L; catalyst loading = 10 mg/L; oxygen flow rate = 750 mL/min; ozone concentration = 7 mg/L (TOC = total organic carbon); (b) Expanded plot of (a)

Although it is well known that the presence of oxygen vacancies(214) enhances the formation of reactive oxygen species (ROS) and radicals(304), the present work shows

that these defects have little effect on the equilibria. However, the presence of cation vacancies, which have charge opposite to that of oxygen vacancies, can be expected to annihilate ROS and radicals. **Table 4.8** shows that the $[V_{Ce}^{\prime\prime\prime\prime}]$ was in the order $CeO_{2-x} < Mo-CeO_{2-x} < Ru-CeO_{2-x}$, which correlates inversely with the ozonation performance for oxidized samples. While the presence of positively charged solutes would be expected to act similarly to oxygen vacancies, the unknown nature of their precise surface distributions precludes conclusion.

There appear to be two effects that result from reduction under 90% N₂ + 10% H₂ at 500°C for 3 h. First, **Figures 4.24a** and **b** show that the effect of reduction annealing on the TOC removal efficiency was minor (beneficial) for the Ru-CeO_{2-x} and Mo-CeO_{2-x} heterojunctions, but it was more significant (detrimental) for CeO_{2-x}. Since the Mo was limited to the surface and subsurface in Mo-CeO_{2-x}, the valence of Ru is very stable in Ru-CeO_{2-x}, and the easy Ce⁴⁺/Ce³⁺ redox is well known, a larger effect for pure CeO_{2-x} is not surprising. However, since reduction annealing would be expected to increase the [Ce³⁺] in all three cases, then the catalytic performance would be expected to show the same trends, which was not the case. The apparent contradiction is interpreted as follows:

- Reduction annealing of CeO_{2-x} increases the $[Ce^{3+}]$ and the associated $[V_0^{\bullet\bullet}]$ to the point of structural destabilisation.
- Reduction annealing of Mo–CeO_{2-x} and Ru–CeO_{2-x} increased the extents of solid solubility by dissolution of heterojunction particles through the additional annealing time.
- In the case of Mo–CeO_{2-x}, the possible extent of solubility is very low, so this effect would be expected to be minor, so simple reduction and increased [Ce³⁺] explain the enhanced performance.
- In the case of Ru–CeO_{2-x}, the solid solubility was much greater, so this effect would be expected to be significant and facilitated through the dissolution of some of surface heterojunctions.
- While the diminution of the heterojunctions would be expected to reduce the catalytic performance, it increased because the effect of increased solubility must have dominated that of decreased heterojunction effect.

Therefore, the results show increasing solubility of the dopant in the lattice can improve the ozonation catalysis performance and this effect is owing to further modification of the band gaps by increasing numbers of mid gap states to assist electron and hole separation (Mo-CeO_{2-x}; major effect)and forming band tail states which reduces the band gap (Ru-CeO_{2-x}; minor effect) as proven by **Figure 4.21g**.

Second, the ozonation performance altered from that after(134) oxidation, where the rankings after reduction were reversed for CeO_{2-x} and Mo–CeO_{2-x} (Ru–CeO_{2-x} remained the worst). The result is attributed to the role of IVCT on the Mo valences on the surface of Mo–CeO_{2-x}, although this effect decreased the residual TOC only from to 4% to 2%. **Figures 4.25a-b** shows Raman spectra for the samples before and after reduction. The intensity changes in the Mo6+ and Mo5+ peaks in Figure 4.25b are attributed to IVCT and/or direct reduction, although these effects cannot be decoupled (which duplicates Equation 4.54):

$$Mo^{6+} + Ce^{3+} \leftrightarrow Mo^{5+} + Ce^{4+}$$
 (4.54)



Figure 4.25. Raman spectra for CeO_{2-x}, Mo-CeO_{2-x}, and Ru-CeO_{2-x}, (**a**,**b**) comparison between before and after reduction

5 Summary and Conclusions

The catalytic performance was assessed by HER and ozonation testing. The key conclusions from the present work are as follows:

CeO_{2-x}

- (1) The widespread practice of calculating the oxygen vacancy concentration from the cerium III concentration relies on the unproved assumption of ionic charge compensation. The demonstration of redox charge compensation confirms the risk of this approach.
- (2) Calculation of the band gap on the basis of the bulk cerium III concentration gave an exact match with the experimentally measured band gap, suggesting the applicability of the use of these data for this determination for pure CeO_{2-x}.
- (3) The electrocatalytic performance was the poorest of the three types of samples owing to the absence of a heterojunction nanostructure.
- (4) The ozonation performance after oxidation was high owing to the effective absence of cerium vacancies. The ozonation performance after reduction was poor owing to structural destabilisation and associated partial amorphisation from the aggressive reducing conditions.

Mo Doping

- (5) Mo exhibits a low solid solubility (~2.4 at%) in CeO_{2-x} and the solute distribution is limited to the surface and subsurface of the CeO_{2-x} nanosheet.
- (6) The solid solubility mechanism is interstitial, which is supported by both experimental and density functional theory simulations.
- (7) Intervalence charge transfer assists the grading of the solubility region, resulting in an inward gradient of $Mo^{6+} \rightarrow Mo^{5+} \rightarrow Mo^{4+}$.
- (8) The heterojunction MoO₃ particles, which are homogeneously distributed, are bonded strongly to the nanosheets by chemisorption.
- (9) The charge compensation mechanism is ionic through the formation of cerium vacancies. The formation of oxygen vacancies thraough ionic charge compensation is irrelevant.

- (10) The complete charge compensation mechanism also should include the formation and transitions between the three F centres, which are forms of oxygen vacancies and which are significant.
- (11) Band energy calculations reveal that the conduction band lowered significantly, the valence band lowered slightly, the Fermi level raised to near the conduction band, and the band gap decreased slightly from 2.75 to 2.62 eV relative to CeO_{2-x}.
- (12) The slightly decreased band gap is attributed to the raising of the Fermi level to the proximity of the conduction band. This was caused by the effect of the F centres and Mo interstitials.
- (13) The hydrogen evolution reaction performance is superior to that of other CeO_{2-x}based catalysts owing to the facilitation of charge transfer through the homogeneous and high distribution density of small heterojunction particles strongly bonded by chemisorption and the valence-graded interface.
- (14) Active sites on the CeO_{2-x} surface do not appear to play a significant role in electrocatalysis, as shown by the electrochemical impedance spectroscopy and electrochemical surface area measurements owing to the primary role of the heterojunction.
- (15) The ozonation performance for oxidised Mo–CeO_{2-x} was intermediate, which correlated inversely with the cerium vacancy concentration, although any role of oxygen vacancy concentration was uncertain.
- (16) The ozonation performance for reduced Mo–CeO_{2-x} was outstanding, the improvement of which was attributed to the effects of intervalence charge transfer.

Ru Doping

- (17) Ru exhibits extensive solid solubility (≥6.8 at%) in CeO_{2-x} and the solute distribution is through the nanosheet bulk.
- (18) The solid solubility mechanism is interstitial, which is supported by both experimental and density functional theory simulations.
- (19) The heterojunction RuO₂ particles, which are inhomogeneously distributed, are bonded weakly to the nanosheets by physisorption.
- (20) The charge compensation mechanism for Ru doping of CeO_{2-x} is ionic through the formation of cerium vacancies plus Ce⁴⁺/Ce³⁺ redox. Again, the formation of oxygen vacancies through ionic charge compensation is irrelevant.

- (21) The complete charge compensation mechanism also should include the formation and transitions between the three F centres, which are forms of oxygen vacancies and which are less significant than for Mo doping.
- (22) Band energy calculations reveal that the conduction band was lowered significantly, the valence band was raised slightly, the Fermi level was raised above the conduction band, and the band gap decreased significantly from 2.75 to 1.75 eV relative to CeO_{2-x}.
- (23) The significantly decreased band gap is attribued to the raising of the Fermi level to above the conduction band. This was caused by the effect of the F centres and Ru interstitials.
- (24) The HER performance is inferior to that of other CeO_{2-x}-based catalysts owing to the poor charge transfer through the inhomogeneous and lower distribution density of large heterojunction particles weakly bonded by physisorption.
- (25) Active sites on the CeO_{2-x} surface do not appear to play a significant role in the electrocatalysis, as shown by the electrochemical impedance spectroscopy and electrochemical surface area measurements owing to the primary role of the heterojunction.
- (26) The ozonation performance for both oxidised and reduced Ru–CeO_{2-x} was poor, which was attributed to high cerium vacancy concentration.

6 References

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