

Nanostructured Cuprous Oxide Nanoparticles: Synthesis, Growth, and Applications

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**Nanostructured Cuprous Oxide Nanoparticles: Synthesis,
Growth, and Applications**

Master by Research

By

Yi Li

School of Material Science and Engineering

University of New South Wales

February 2017

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The 8th Annual Conference of the ARC Centre of Excellence for Functional Nanomaterials. 15-16 November 2012 Sydney, Australia

Abstract

Cuprous oxide nanoparticles have shown potential capabilities in the field of clean energy, biochemistry, and photocatalysts. The research for the physical and chemical properties of cuprous oxide nanoparticles is vital for understanding the fabrication and growth mechanisms, and surface behaviours control for functional properties and potential applications.

In this thesis, various cuprous oxides have been investigated, including spherical, octahedra and wire-like morphologies. A room-temperature and template-free method was used in the synthesis of cuprous oxides. These cuprous oxides have shown different optical properties due to their nanostructures with different domain crystalline planes. They show different performances in our photocatalytic tests.

To further enhance the functional properties and performance, the nanocomposites composed of the core of cuprous oxide particles and titanium oxide coatings were also investigated in this study. The direct room-temperature solution coating method was studied, which could produce stable nanoparticles for photocatalysts and sensors. In addition, cuprous oxide is easily to dissolve in ammonia solution, so it can be used as a promising material for a sacrificed template. In this thesis an ammonia etching method was used at room temperature to produce cuprous oxide nanocages, which allows further investigation for the applications of the hollow structures.

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Chapter 1 Introduction

1.1 Introduction

There has been a rapid growth in the investigation of nanoparticles and nanocomposites because the properties of nano-scaled particles have attracted the attention of scientists. The term “nanoparticle” is often used to describe particles which show the size of 1-100nm in at least one of its sizes (width, thickness, length). Particles at this dimension contain only tens to millions of atoms; therefore the high surface area to volume ratio creates highly active surfaces compared to those bulk materials. Additionally, the energies can be illustrated as being quantized, in which the material behaves in discrete rather than continuous form[1].

Synthesis of nano metal oxide has attracted extensive research interest because of because their potential applications in optics[2], electrics[3], photo catalysis[4], gas sensors[5], information storage[6], and so forth. It is demonstrated that their properties are decided by the composition.

Among these metal oxides, cuprous oxide (Cu_2O) nanoparticles are particularly interesting not only for the development of synthetic methods, but also for the examinations of their sensing[7], photo catalytic[8], and surface properties[9]. Cuprous oxide nanostructures have been demonstrated to have properties superior for applications in gas sensing [10], carbon monoxide oxidation[11], photo catalysis[12], soft template[13], and organic synthesis[14].

Nevertheless, the treatment at high temperature for binder removal and calcination is required in most synthesis methods. Moreover physical methods require sophisticated

instruments such as vacuum systems and high voltage systems[15, 16]. As a property of cuprous oxide, it is easy to be oxidized. So there are still challenges regarding the fabrication, structure and fundamental understanding of the cuprous oxide[17]. To meet some of the challenges of cuprous oxide, the research aims of this project can be demonstrated as: to study the room-temperature method in order to produce morphology-controlled nanoparticles, and to investigate the interactions of coatings in order to protect cuprous oxide from oxidation and enhance the photocatalysis property at the same time.

1.2 Aim of the research

This thesis will focus on strategies for synthesizing, characterizing and applications of cuprous oxide nanoparticles with morphology and size control. There are six main chapters in this thesis. A brief introduction has been given in chapter 1. In chapter 2, literature review related to cuprous oxide is demonstrated, in which the synthesis approaches, growth mechanisms, and applications are introduced. Chapter 3-5 are going to emphasize on the research work and results on cuprous oxide nanoparticles, including synthesizing cuprous oxide nano spheres, nano octahedron, and nano wires via room temperature method and their growth mechanisms, coating different morphologies with titanium oxide nanoparticles and their applications. Finally, the conclusion and future work are summarized in the last chapter (Chapter 6).

Chapter 2 Literature Review

2.1 Cuprous Oxide Nanoparticles

Cuprous oxide (Cu_2O) is an important semiconductor with potential applications across a lot of technological fields. Being a p-type oxide semiconductor with a direct band gap of 2.17eV[18], Cu_2O has been found in applications of solar energy, gas sensing, photon-activated water splitting, low-temperature CO oxidation, photo degradation of organic dyes, and magnetic storage devices[19], etc. Its unique properties make itself noble and offered important attention for the last several years. Cuprous oxide is also used in red ceramic porcelain glazes[20], red glasses[3] and as a kind of antifouling agent[15] for marine paints. The structure of cuprous oxide has been shown in figure 1. Cuprous oxide, in its multiple phases, may lead the way in the direction of clean, efficient and low-cost new resources of energy. Multiple uses of the material demand more recent synthesis process for appropriate applications. Because of its research importance, morphology and dimension controlled synthesis of Cu_2O micro- and nanostructures has received significant attention in recent years [4].

In the past years, several research reports have been mentioned with regards to the morphology-controlled synthesis of Cu_2O nanoparticles. Cu_2O crystals with different morphologies have been successfully synthesized[13], such as nanowires[21], nanocubes[22], nanorods[23], nanospheres[24], nanocages[25], nanoplates[26], as well as flower-like and hollow structures[27]. However, to get the unconventional morphology is still a challenge because surfaces with high reactivity generally reduce rapidly during the process of crystal growth follow the minimization of surface energy. It is known that the physical and chemical activity usually rely on its structural parameters, such as geometry and shape[27]. In recent years, the method of using

organic templates[28] and/or additives such as polyethylene glycol (PEG) or sodium dodecyl sulphate (SDS) has been widely used to control the morphologies of cuprous oxide through the effects on reaction and growth of inorganic particles. However, the extra templates or surfactants usually result in the impurity of resulting materials, and the controllability of morphologies is not as outstanding as expected[29].

2.2 Synthesis Method

Currently, various synthesis strategies in preparation of cuprous oxide nanoparticles have been reported. In the following section, some important methods, including physical and chemical techniques, which can control parameters of Cu_2O nanoparticles, are introduced. Methods based on chemical process are much more popular approach to synthesize cuprous oxide nanoparticles[30]. Compared to physical methods, chemical strategies provide some unique advantages, such as simple and convenient reaction conditions, controllability in morphology and size, and also high output.

2.2.1 Physical Techniques

2.2.1.1 Sputtering Method

Chandra et al. and Pierson et al. have reported the thin film deposition parameters important for the successful obtaining of single phase, nano crystalline Cu_2O film by using magnetron sputtering method[31]. They have shown that for many materials, sputter-deposition at very high pressures (20–200mTorr) and low substrate temperatures (100–300 K) leads to the forming of nano crystalline thin films. Sputtering was finished in a chamber using an axial, planar magnetron sputtering gun (Atom Tech 320-O). The chamber was initially emptied to about 10^{-6} Torr by a turbo molecular pump. Then a high purified inert gas (He, Ne, Ar, Kr, and Xe) at a pressure of 200mTorr was flowed into the chamber, and sputtering was finished in flowing gas[32]. During each sputtering experiment, the gas pressure was carefully tested since the sputtering current is very sensitive to the pressure of the gas[33]. Sputtering was done at a stable power of

50 W and the substrates (Si wafers or glass plates) were kept at room temperature[34]. The substrates were settled 45 mm away from the 50 mm diameter copper target[35]. The substrates were washed in acetone and ethanol.

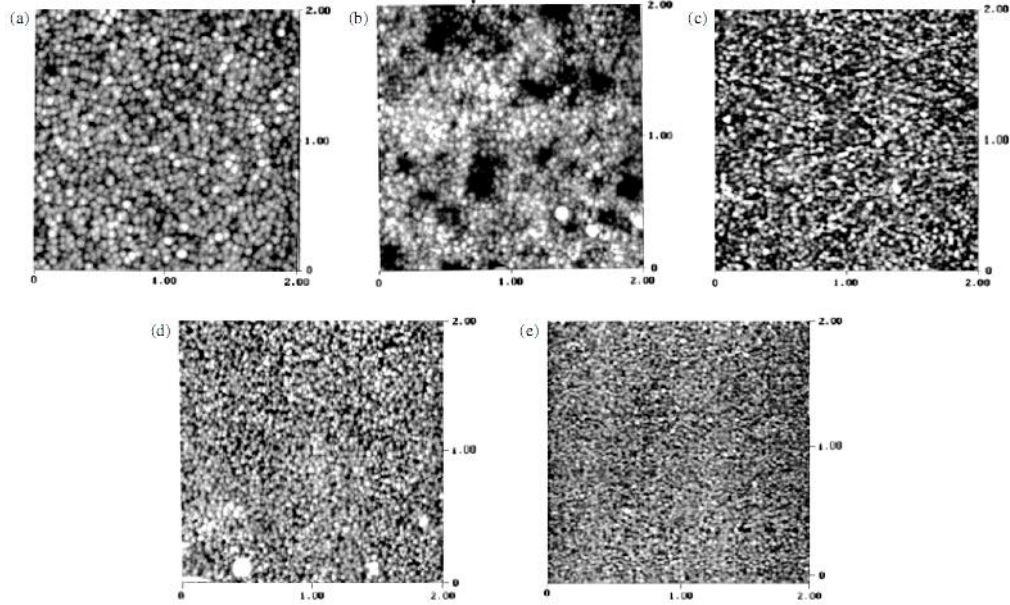


Figure 1 Atomic force micrographs showing $2\mu\text{m} \times 2\mu\text{m}$ surface scans of nano crystalline Cu_2O thin films sputter-deposited in (a) He, (b) Ne, (c) Ar, (d) Kr, and (e) (Xe)[36].

2.2.1.2 Radical Oxidation

Single Cu_2O films can be obtained by radical oxidation of Cu films with N_2 plasma surface treatment and different RF power of oxygen (O_2) at the temperature of 500°C [37]. Synthesis of Cu_2O films can be prepared by radical oxidation of high purity Cu films by a thermal evaporation under high vacuum of 10^{-3} Pa. Annealing the Cu films to 500°C in the hydrogen (H_2) atmosphere, and modify the flow rate and RF power of H_2 to 20sccm and 60 W. The following is oxidation process: Cu films contact with plasma for 90 min at 500°C in the plasma-enhanced metal organic chemical vapour deposition system, in which the O_2 plasma power increase from 0 to 30 W and the flow rate is kept at 50sccm. The Final step is N_2 plasma treatment: the surface of films has

been exposed in N₂ atmosphere for different periods of time. Finally, the N₂ gas flow stays at the rate of 150sccm in the chamber and the substrate temperature slowly decreased to the room temperature[38].

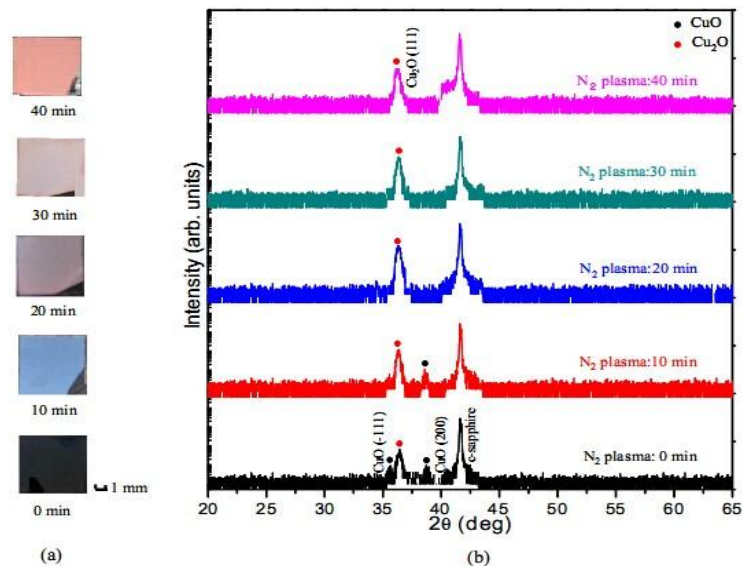


Figure 2 (a) The transmission spectrum of Cu₂O thin films and (b) the calculated band gap of Cu₂O thin films with changing N₂ plasma treatment time[39].

Due to the black CuO easily appears during the oxidation process using the radical oxidation method; researchers have introduced the N₂ plasma treatment to remove this CuO thin cover. Compared with oxygen gas, radical oxidation is expected to have higher energy. So in the experiment of radical oxidation, excited atomic oxygen easily react with the surface of Cu films[34, 40].

2.2.1.3 Galvanic Deposition

Galvanic deposition, as an easy electrochemical method due to the principle of galvanic cell, shows new possibility for the synthesis of functional nanomaterial. Up to now, different kinds of materials such as Cu and Pd nanowires[41], Pt clusters[24], CdS[42], CdTe, have been produced by the galvanic deposition method.

The galvanic deposition system is composed of H60 brass alloy (consists of 40% Zn and 60% Cu) and FTO substrate[43]. The brass sheet, FTO (fluorine-doped tin oxide) substrate and a saturated calomel electrode (SCE) respectively serve as working electrodes. The solution for the deposition of Cu_2O nanoparticles contain $\text{Cu}(\text{NO}_3)_2$ and 12mM supporting electrolyte. NaCl, NaNO_3 , Na_2SO_4 and NaF are supporting electrolytes. The pH value is about 6–7 and the temperature of the electrolyte is kept at 80 °C. Deposition is carried out in an open system by dipping the two electrodes into each bath. After several hours' deposition, the samples would be removed from the electrochemical cell and cleaned with ethanol and distilled water [44].

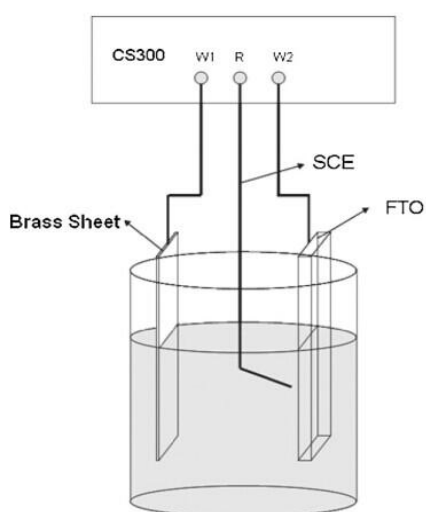


Figure 3 Schematic diagram of galvanic deposition.

2.2.1.4 Thermal Evaporation Deposition

In order to obtain pure Cu_2O , A. Libido's group has tried to identify the temperatures of the phase transitions of the diverse copper oxide family. In-situ DC conductivity measurements are carried out for different annealing temperatures of Cu films prepared by the vacuum thermal evaporation method for the growth of thick Cu films and DC reactive magnetron sputtering for thin Cu films deposition. The copper (Cu) films are deposited onto microscope glass substrates. The vacuum thermal evaporation deposition system has been carried out with a load lock chamber for quick and convenient substrate

modifications[14]. The pressure in the chamber is reduced to 10^{-5} mbar, and the distance between the Cu target and the substrates should be kept at 60 mm. In the process of the deposition, the substrate temperature is kept at 200 °C. The deposition duration is 10 minutes.

Additionally, the annealing process must be performed under air at 250 °C in order to avoid the Cu_4O_3 phase appear, and the disappearance of the Cu_2O phase would happen at 300 °C. The annealing procedure could be stopped when a fall in the conductivity is observed and the establishment of a new stable level. This experiment estimates that a complete oxidation of all metallic Cu according to reaction. The copper thin films have been proved to be fully oxidized, becoming the pure Cu_2O phase. This method must be carried at a high temperature, which is not energy saving.

2.2.2 Chemical Techniques

2.2.2.1 Hydrothermal Method

Five main morphologies of Cu_2O nanocrystals have been synthesized by hydrothermal method[45]. The preparation of cubic, octahedral, and truncated octahedral Cu_2O nanocrystals has been reported by Zhang et al.[46]. In a typical procedure, NaOH solution should be added into CuCl_2 aqueous solution containing various amounts of polyvinylpyrrolidone (PVP, MW= 30 000) (cube: 0 g; octahedral: 4.44g; truncated octahedral: 1.67 g) at 55 °C. After stirring for a while, ascorbic acid aqueous solution would be added into the solution. The obtained solution is also stirred for different times (cubic: 5 h; octahedral: 3 h; truncated octahedral: 3 h)[47].

The following step is etching of Cu_2O nano crystals in ammonia solution. Cu_2O nanocrystals are dispersed into aqueous ammonia solution (pH = 10.5 or 11.4). The solution is stirred for several minutes. The precipitate in the solution is collected by

centrifugation, then cleaned by distilled water and ethanol, and finally is stored in ethanol.

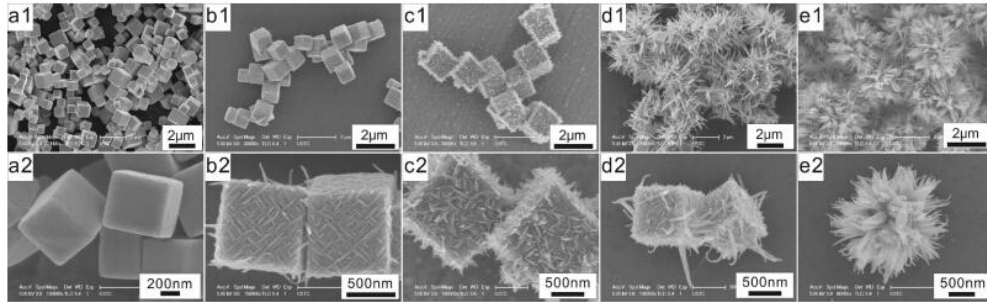


Figure 4 SEM images of as-synthesized Cu_2O cubes (a1 and a2), as-synthesized Cu_2O nanocubes etched in aqueous ammonia solution with $\text{pH} = 10.5$ for 10 min (b1 and b2) and 150 min (c1 and c2), and in aqueous ammonia solution with $\text{pH} = 11.4$ for 3 min (d1 and d2) and 40 min (e1 and e2).

Because homojunctions have no interface strain, they perform better than heterojunction in relevant applications. Si semiconductor p–n homojunctions are well-known and widely used in solar cells. Other semiconductors such as ZnO [48], SnS [49], CdTe [50], and GaN [41], are still under investigation for their potential applications in photo detectors, solar cells and diodes. The synthesis of p–n semiconductor has been tried to use doping method. For instance, phosphorous doping has been carried out to obtain a p-type ZnO layer on an n-type ZnO wafer. However, the direct fabrication of ACT semiconductor layers without post doping has received a few results, even though it is a more simple and low-cost method to achieve p–n homo junctions[51].

Yuchi Cui and co-workers have reported a facile hydrothermal method to synthesis novel Cu_2O core-shell nanospheres. In a typical procedure, $\text{Cu}(\text{Ac})_2$ was dissolved in de-ionized water and mixed with o-anisidine solution to become a reaction mixture. The olive green mixture was transferred to an autoclave. Then, the sealed autoclave was heated at $200\text{ }^\circ\text{C}$ for 8 h and subsequently air cooled to room temperature[52].

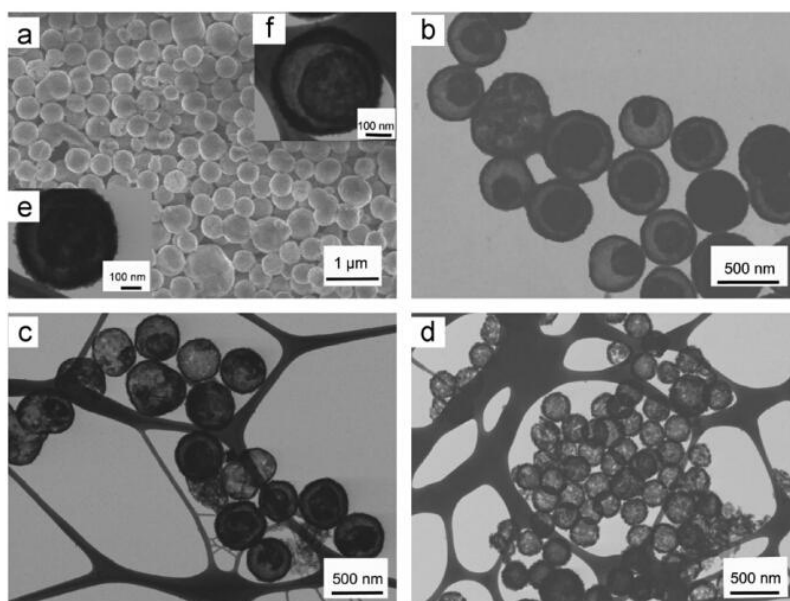


Figure 5 (a) SEM image of the Cu_2O nanospheres fabricated at 30mM o-anisidine after 8 h; STEM images the Cu_2O nanospheres fabricated at (b) 30mM o-anisidine after 5 h, (c) 30mM o-anisidine after 8 h, (d) 50mM o-anisidine after 8 h[53].

Cuprous oxide thin films usually present p-type semiconductor character based on Cu vacancies. Preparation strategies for n-type Cu_2O thin films have received little sound effect. There have been just a few reports on these approaches so far. Based on published reports, Cu_2O thin films with n-type photo-responsive property can be fabricated on different substrates in weak acidic solutions. Cu_2O thin films synthesized by thermal oxidation, chemical bath deposition, electrical deposition, and in alkaline electrolytes display p-type semiconductor property. Some reports have proposed that p-type and n-type Cu_2O thin films may be controlled by modifying the pH of the reaction system. At the same time, although n-type Cu_2O thin films deposition has been obtained, the reason why pH has effect on vacancy type, and thereby the conduction type of Cu_2O , is still under investigation[54].

A clean copper sheet is dipped in copper (II) acetate aqueous solution filled in an autoclave. The pH value of the solution can be modified with acetic acid and ammonium hydroxide. The same hydrothermal reaction conditions will be used for a second reaction, except that the copper (II) acetate aqueous solution changes to absolute ethanol. Additionally, no acetic acid or ammonium hydroxide needs to be added for pH modification. Photo electrochemical experiments are carried out on a electrochemical station in Na_2SO_4 solution with a three-electrode system (Cu₂O/Cu sheet electrodes as working electrodes, platinum wire as counter electrode, and saturated calomel electrode (SCE) as reference electrode, respectively). For Cu₂O p–n homojunctions formation, the n-type layer has been achieved by the hydrothermal method.

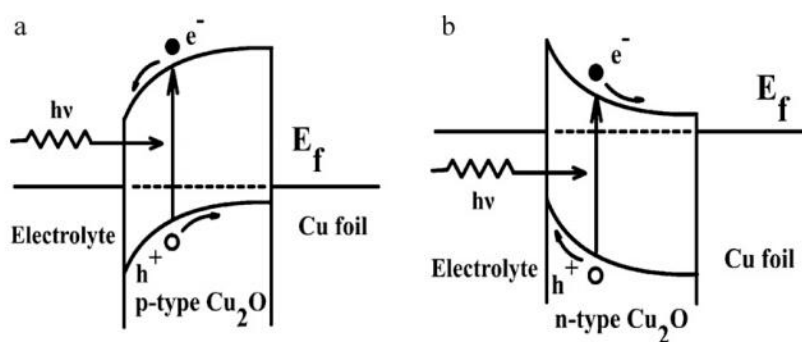
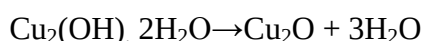
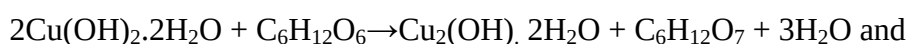
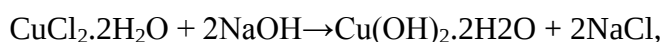


Figure 6 Scheme of photo-excited carrier transfer in p-type (a) and n-type (b) Cu₂O films/electrolyte system[55].

The Cu₂O thin films fabricated in acid and alkaline solutions are n-type and p-type semiconductors, respectively[56]. Honey has been used in the synthesis of noble metals, such as gold, silver and platinum particles. It has been proved that glucose in honey has effect on morphology, size and crystalline of the particles. Cuprous oxide (Cu₂O) particles can be synthesized by using a simple honey aided solution synthesis method. Firstly, three solutions are prepared by properly dissolving honey, copper chloride dehydrates (CuCl₂) and sodium hydroxide (NaOH) powders in distilled water, respectively. The three solutions are then mixed and stirred for 30 min under room

temperature. The pH of this solution should be kept at 12. The mixture is then heated at 60 °C for 1 h. The above procedure is repeated with methanol and ethanol as solvents for CuCl₂. Ethanol is used to increase the availability of hydroxyl ions during the reaction which in turn may enhance the preparation of oxides through hydroxides. The possible chemical reactions (1–3) leading to the formation of Cu₂O particles are as follows:



For these reactions to be correct, the glucose in honey must assume a great importance due to its ability to effectively reduce copper ions in the presence of NaOH solution.

2.2.2.2 Chemical Bath Deposition Method

Chemical bath deposition (CBD), which has been well known as a famous low-temperature aqueous technique for directly depositing large-area films has been widely used because it allows thin films to be deposited on substrates that might not be chemically or mechanically stable at high temperatures. Moreover, it needs no sophisticated instruments, and the starting chemicals are commonly available and not expensive. Also, the preparation parameters are easy to be controlled. Yu et al. has studied Cu₂O nanorods films grown on different substrates by CBD method of immersion cycles with the presence of cetyltrimethylammonium bromide (CTAB), and they illustrate that CTAB plays a significant role in the preparation of nanorods morphology; moreover, the effect of different substrates on structural and optical properties have also been discussed.

In a typical procedure, glucose was added into the mixture of copper sulphate and TSC with the cleaned substrate suspended horizontally in a beaker. Then, the pH value of precursor should be controlled by NaOH solution. The beakers with the precursor solution inside were kept at 80 °C for 4 h in order to achieve the proposed thin films. After deposition, the slide with films was taken out from the solution and washed with distilled water, and dried at 80 °C[57].

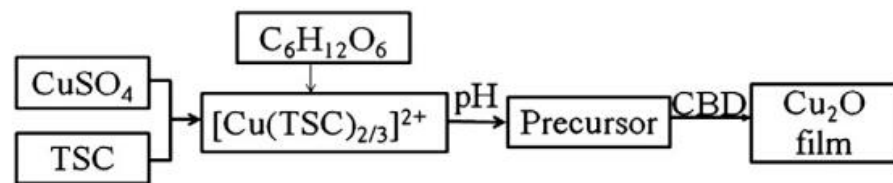


Figure 7 Flow chart of Cu₂O films preparation.

2.2.2.3 Electrochemical Method

Electrical deposition offers a fascinating method to obtain the inorganic photovoltaic materials, because it's a low-cost, convenience, and environmental friendliness method[58]. Through the electrochemical deposition method, well-defined Cu₂O nanostructures such as nanospheres, nanowires, nanocubes, and nano octahedra[59, 60] have been achieved. Recently, researchers have demonstrated for the first time the preparation of 3D hierarchical Cu₂O stars on FTO substrates through a fast and facile electrical deposition approach from aqueous solutions at room temperature[61].

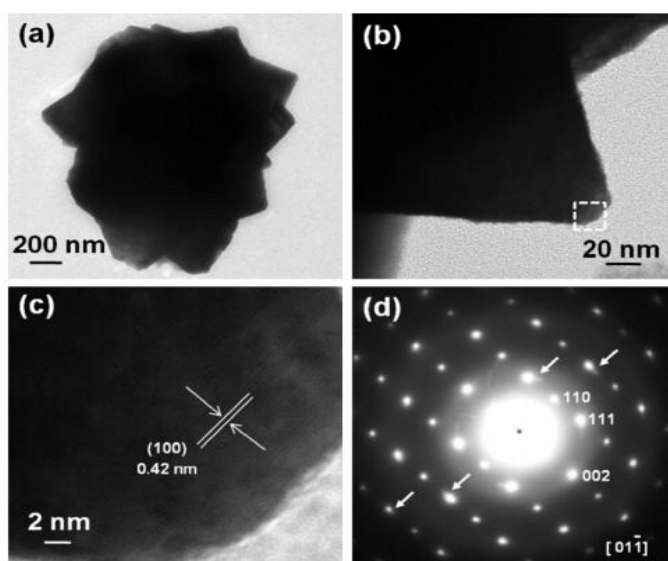


Figure 8 TEM images (a) and (b). (c) HRTEM image recorded from the top area of the nano particle in (b). (d) SAED pattern of the Cu₂O star [62].

The Cu₂O stars have been synthesized via electrical deposition in a solution of 0.01 M Cu(NO₃)²⁺ 0.1 M NH₄NO₃ with a current density of 0.5mA cm⁻² for 60min at 313K. In the study of synthesis, S.Y. Ng[63] has used a direct, low-voltage electrical deposition method to obtain octahedral nano crystals at room temperature with a simple set up[64]. No additives and alkaline medium are needed. Various crystal morphologies of Cu₂O achieved by this electrical deposition technique have been reported.

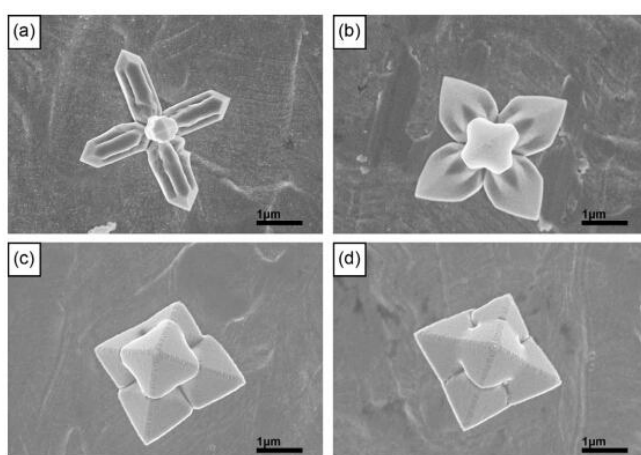


Figure 9 SEM images demonstrating various transient structures of Cu₂O particles deposited on stainless steel at 0.08 V for 60 s [65].

Ruey's group has reported a facile method to fabricate nano dendrites. The electrical deposition of Cu nano dendrites in this work was carried out in a common two electrode plating cell. Cu foils and Si wafers worked as anodic sources and cathode substrates, respectively, for the electrical deposition. Cu dendrites were deposited under a current density of $8.9 \times 10^{-3} \text{ A cm}^{-2}$ and a potential of 60 V was used between the two electrodes. NH_4OH aqueous solution was prepared as an electrolyte. The pH of the electrolyte should be modified to about 6 by using HNO_3 as a controlled group[65]. The fabrication of Cu– Cu_2O core–shell and Cu_2O hollow nano dendrites was carried out by heating the as-synthesized Cu nano dendrites to 200 °C at a pressure of 1 and 760 Torr, respectively, for 4 h and then slowly decreased to room temperature.

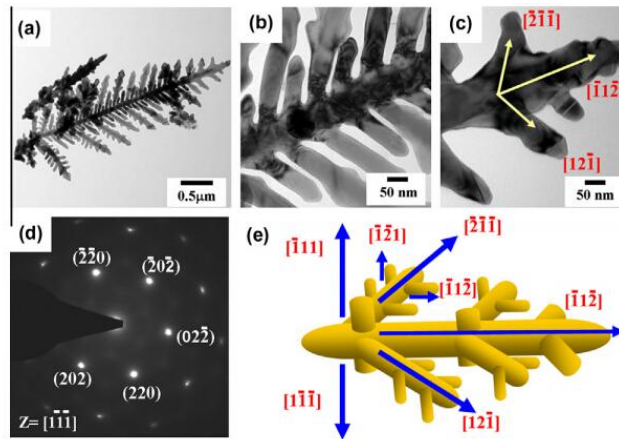


Figure 10 (a–c) TEM bright field images of synthesized Cu nano dendrites; (d) electron diffraction pattern of the whole nano dendrites shown in (b); (e) schematic diagram of the crystal directions of the stem and branches of a dendrite[66].

2.2.2.4 Photoreduction Method

Cuprous oxide nanoparticles are able to be fabricated from nano-restricted copper acetate ($\text{Cu}(\text{OAc})_2$) in micro pores of single-wall carbon nano tubes (SWNTs) by visible-light photoreduction[22]. The particular structure of prepared $\text{Cu}(\text{OAc})_2$ in the

micro pore is necessary for the reduction procedure to Cu_2O by irradiation, because, generally, aqueous solution of $\text{Cu}(\text{OAc})_2$ can be reduced under UV-light irradiated conditions. Micro pores originally are used to produce high-pressure molecular or ionic states even an adsorbent and an adsorbate are in the atmospheric condition[63]. It has been reported that irregular structure of hydration structure surrounded metal ions such as rubidium, zinc, and cobalt ions, in addition, coordination structure surrounded a Cu ion of $\text{Cu}(\text{OAc})_2$ restrict in the carbon micro pores. In this case, $\text{Cu}(\text{OAc})_2$ is a simple coordination compound which forms a complex structure with acetate bridging[67]. The previous study on $\text{Cu}(\text{OAc})_2$ has been focused on the micro pore of activated carbons (ACs). Takahiro Ohkubo's group described the new synthetic method to Cu_2O from $\text{Cu}(\text{OAc})_2$ by applying single-wall carbon nano tube (SWNT) as a nano reactor in the appropriate light-irradiated environment without any additional reducing agents[68].

2.2.2.5 Sonochemical Method

Porous Cu_2O nanospheres with controllable morphology and size have been successfully fabricated by using ascorbic acid as reducing agent and β -cyclodextrin (β -CD) as the capping agent through a sonochemical approach, which is known to be a green and simple method for the controlled synthesis of porous-structure Cu_2O nanospheres[69]. The crystal phase of the product is decided by the concentration of ascorbic acid, but its final product is controlled by the ultrasonic irradiation time and the concentration of β -CD. In addition, porous Cu_2O nanospheres show more enhanced photocatalytic than solid ones[70].

In a typical procedure, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ was dissolved in de-ionized water. Afterwards, β -CD and ascorbic acid were added to the $\text{Cu}(\text{CH}_3\text{COO})_2$ solution with stirring. Subsequently, the reaction system, using ascorbic acid to reduce $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, was exposed to high-intensity ultrasound irradiation under

atmosphere for 15 min. Ultrasound irradiation was carried out with a high-intensity ultrasonic probe diameter and immersed in the reaction system [6].

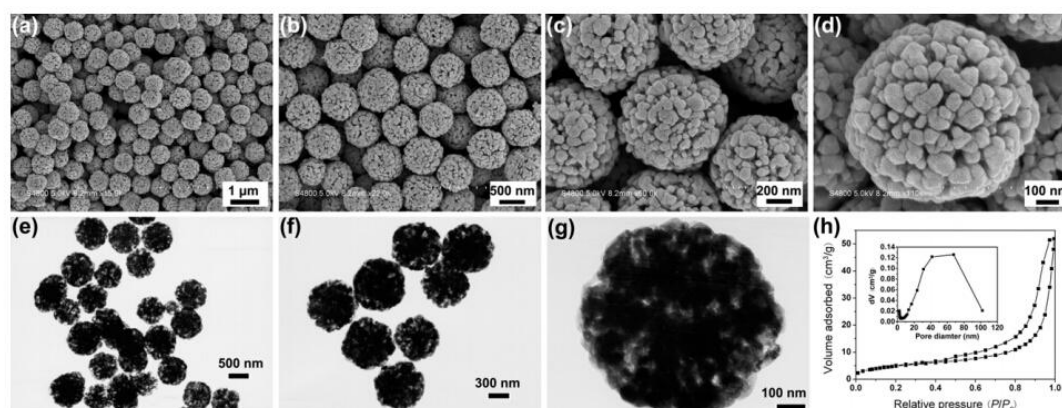


Figure 11(a)–(d) SEM images with different magnifications, (e)–(g) TEM images with different magnifications, and (h) the N₂ adsorption and desorption isotherms and the pore size distribution curve (inset) of the porous Cu₂O nanospheres[69].

2.3 Growth Mechanisms

2.3.1 Growth mechanisms of Cu/Cu₂O/CuO

In the reaction system, the formation of resulting product and different morphologies should be attributed to the influence of lactic acid since no surfactants are added. It has been found that H⁺ or OH⁻ plays a significant role in the decomposition products of lactic acid, for instance, acetaldehyde[41], acrylic acid, carbon monoxide, and carbon dioxide during the whole hydrothermal procedure[22]. Figure 12 illustrates the morphology evolution from Cu, Cu₂O to CuO nanoparticles as the reaction and pH values. Under alkali environment, Cu²⁺ appears firstly as Cu(OH)₂ then to a distort [Cu(OH)₄]²⁻ in the solution through edge sharing complexes with excess OH⁻. It has been reported that the decomposition of lactic acid happens according to (2) and (3) in Figure 12 at the same time, while acetaldehyde was proved to be an effective reducing agent under alkali condition, which become Cu₂O as shown in (7). After more

NaOH add into the solution which illustrates the pH of the solution is adjusted to 14, surplus OH^- are generated by the ionization of NaOH under the solution thermal conditions. It has been accepted that the $[\text{OH}^-]$ condition is less suitable for the decarboxylation of lactic acid seen as (2). In regard of the solution conditions with a small amount of acetaldehyde, many researchers have reported that $[\text{Cu}(\text{OH})_4]^{2-}$ transforms into monoclinic CuO microstructures as a result of dehydration reaction just like the (8)[71].

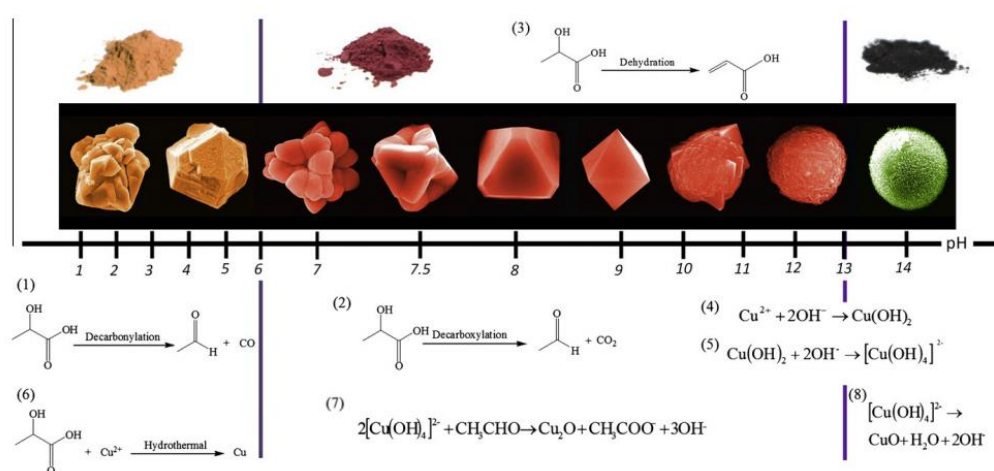


Figure 12 Schematic illustration of the morphology evolution from Cu, Cu_2O to CuO microstructures[4].

With the presence of strong acid, Gunter has reported that lactic acid decarbonizes to acetaldehyde and CO almost at the temperature of 300°C . In order to analyses the reducibility of acetaldehyde under the acid environment; researchers have replaced the lactic acid with acetaldehyde under the same pH value, time, and temperature with various experiments. While no Cu particles appear, which shows that acetaldehyde is not able to reduce Cu^{2+} to Cu [62]. In a typical hydrothermal system at 120°C , a probable mechanism for the appearance of Cu is due to an intermediate carbon-based product like CO as a fascinating reducing agent, which controls the synthesis of pure metallic copper just seen as the (6). From the above discussion, it shows that the

transformation of resulting production depends on the reactions involved with lactic acid under different pH values[72]. In the past decades, systematic control of Cu₂O including shape, crystallinity, and structure has been reported through external agent. Sun and his co-workers have been reported that selective adsorption of ethanol molecules on different planes of Cu₂O octahedral particles result in a designated etching on {111} facet to fabricate etching-limited branching structures[73]. It indicates that the selective adsorption of capping agent in solution to different crystal planes determine the fabrications of various morphologies. In the system under the pH changes from 7 to 13, the capping agent here is the acrylic acid, which is also produced under the alkali conditions[74]. The introduced acrylic acid molecules prefer to adsorb onto the higher energy planes during the particle growth process[75]. The adsorption stabilizes the facets and thus stops the growth rate perpendicular to it, which can modify the growth rates of different crystal directions; it also promotes the surface energy rearrangement of each facet of the Cu₂O. This helps the exposure of the large {111} surfaces and the fabrication of the final Cu₂O microcrystals. Therefore, these new morphologies of Cu₂O nanoparticles form under a kinetic growth regime, however, it still reminds a great challenge to exploit a facile approach to understand the growth habit of {111} facets and achieve the well-defined morphology of Cu₂O growth on {111} planes. The strong alkali added in the precipitation reaction plays an important role during the synthesis based on the experimental results. The high concentration of [Cu(OH)₄]²⁻ in the whole reaction procedure due to the strong alkaline media promotes the dehydration of [Cu(OH)₄]²⁻, which results in the large quantity of CuO nuclei. The formation process of CuO urchin-like nanoparticles could be expressed as follows:[Cu(OH)₄]²⁻ is hydrolysed to CuO nuclei through hydrothermal treatment and the small CuO nuclei are assembled into microparticles under acrylic acid condition at the high energy planes. The fabrication of urchin-like CuO nanostructures is controlled by the kinetics under the high concentration of NaOH solution[76].

2.3.2 Growth mechanism of Cu₂O nanospheres

As well known, template synthesis is a general approach to obtain hollow spheres, and the template serves as a frame which other materials are assembled with the morphology similar to that of the template. However, Cu₂O hollow spheres could be fabricated in ethanol–water solution without any template; therefore, the Ostwald ripening mechanism is raised for the synthesis of Cu₂O hollow spheres[77]. The above mechanism is likely to be highly sensitive to relative speeds of dissolution of the amorphous solid particles and nucleation of the crystalline phase. When the former is very slow then the amorphous particles would transform in situ to solid crystalline spheres, on the other hand, when the latter is relatively slow the amorphous phase would completely resolve to crystallization, which then will happen in the solution. Only when the rates are almost the same as the phase transformation process happens on the surface of the amorphous particles and remains localized as the particle core disappears[78].

In recent years, PVP has been applied as an important surfactant for the fabrication of nano materials, and various nanostructures have been successfully fabricated with the presence of it. In a typically procedure, PVP is of primary significant not only in promoting the dispersion of Cu₂O spheres, but also in the partial stabilization of crystalline phase occurs at a rate accompany with localized Ostwald ripening and self-transformation for producing Cu₂O hollow spheres[79]. It seems rational to assume that the high carbonyl-group density along the PVP structure would supply high surface binding and stabilization of primary clusters of amorphous cuprous oxide initially nucleates from the supersaturated solution[80]. In addition, reduction in the surface charge of these primary clusters by PVP adsorption would promote secondary aggregation. In various surfactant-assisted syntheses of shape-controlled materials, TEA (triethanolamine) , would act as surface modifier, plays a role of “structure-directing agent” that directs the aggregation of the building blocks[81]. In general, the hydroxyl

groups of the TEA rims absorb on Cu_2O nanoparticles and interact with each other, which lead to a linkage or bounding of the neighbouring Cu_2O nanoparticles[82]. And then, the Cu_2O nanoparticles clusters would aggregate together to form spherical aggregation. The increase of TEA concentration results in more TEA molecules coat on the surface of Cu_2O nanoparticles and more hydroxyl groups interact to strengthen the connection between the Cu_2O nanoparticles. Additionally, TEA could attached with Cu^{2+} to form a very stable complex, to avoid the formation of $\text{Cu}(\text{OH})_2$ after sodium alkaline are added into the solution[83].

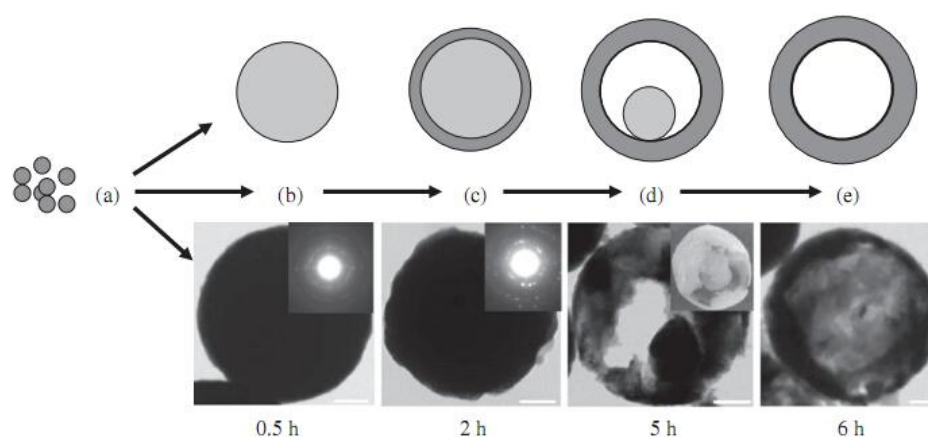


Figure 13 Schematic diagram the formation process of Cu_2O hollow spheres, together with the corresponding FESEM, TEM, and SAED images: (a) formation of Cu_2O nanoparticles in solution. (b) Synthesis of solid spheres. (c) Formation of solid spheres with rough surface. (d) Formation of spheres with core-shell structure. (e) Formation of Cu_2O hollow spheres[84].

The synthesis mechanism of Cu_2O hollow spheres could be explained by a self-transformation procedure of the aggregated particles accompanied by the localized Ostwald ripening[85]. Recently, similar mechanisms have been used to prepare Fe_3O_4 , Co, CdIn_2S_4 , $\alpha\text{-MnO}_2$, rare earth phosphate, and magnetic hybrid copolymer-cobalt hollow spheres. The possible formation mechanism of hollow sphere has been illustrated by the schematic diagram in Figure 13. First of all (Step a), Cu^{2+} in

ethanol–water solution reacts with TEA to form relatively stable complex[86]. In the synthesis process, the formation of copper complex reduces the concentration of free Cu^{2+} ions in the solution; promotes the Cu_2O particles growing slowly. A slow formation rate leads to the separation of nucleation and growth procedure, which is important for high-quality crystal synthesis. Then, at an extremely high temperature and auto generated vapour pressure, the complex reacts with OH^- in solution to form Cu_2O nuclei. In the following step, the small as prepared Cu_2O particles aggregates together to form nanospheres, which demonstrates broad diffraction rings in the electron diffraction analysis (Step b, inset) due to the presence of amorphous or poor crystallized phase[87]. The formed Cu_2O particles would remain out of balance with the surrounding solution due to their higher solubility, and so the interior are resolved gradually and the new Cu_2O nuclei are formed on the surface of the Cu_2O spheres by a dissolution–crystallization mechanism with the presence of PVP[88]. The corresponding TEM image (Step c) shows that the surface of Cu_2O nano sphere becomes rough and the narrow diffraction rings of the samples (Step c, inset) illustrates the enhancement of crystallization. At this situation, crystallites locate on the edge of surface served as the beginning (or nucleation seeds) for the subsequent recrystallization procedure. The outer crystallites become larger crystallites on absorbing the smaller crystallites. The big crystallites on the outermost surface due to a continued surface growth (at a slow rate under low supersaturation) format to be the majority of primary crystallites (at a fast rate under initial high supersaturation). As a result of this procedure, the core size has been reduced slowly while the vacant volume inside the sphere has been enlarged. This self-transformation process is related to localized Ostwald ripening mechanism, and results in the formation of core–shell Cu_2O structure (Step d). The smaller spheres as the core of the sphere with higher curvature compare to the outer particles for a whole sphere. Due to the higher surface energy, the core can be easily dissolved and attached to particles on the outer surface with enough ripening time, leading to the formation of a hollow structure (Step e)[89].

2.3.3 Growth mechanism of Cu₂O nanowires

2.3.3.1 Wet-chemical method

Copper hydroxide nanowires are most widely used for transformation to cuprous oxide nanowires. To form Cu(OH)₂ nanowires, CuCl₂·2H₂O could be used. Dissolve it in distilled water, and then add NaOH. The shaping agent could be either a polymer (PEG) or anodic surfactant (SDS)[90]. The former is used with hydrazine hydrate (N₂H₄·H₂O) for the reduction to copper oxide. The product will be 8 nm thick and 10–20 μm long polycrystalline Cu₂O nanowires. SDS has been used as surfactant by Hei et al[91]. However, for reduction of the as produced copper hydroxide nanowires -irradiation has been used to obtain OH ions instead of N₂H₄·H₂O. The surfactants are useful in the growth of cuprous oxide/hydroxide nanowires by dispersion of ions surfactant: Cu⁺ or Cu(OH)₂, and anionic surfactant: Cu(OH)₂. OH⁻ ions and guide them into a one-dimensional morphology[92]. The polar top of the surfactant chain attaches itself to the ion and relocates it in the light of the surfactant–water interaction. If micelles are fabricated, the ions attached are nucleation spots for nanowire growth in a radial direction from the centres of the micelles. Surfactant can cover a water drop and with it copper ions would transfer to a nanoparticle. The particle is reduced to Cu(OH)₂ by OH⁻ ions that enters the surfactant shell. When the density of surfactant is large enough it would form a larger shell, the volume of surrounded water increases and the morphology of the structure lengthens. In this way a nanowire can be formed instead of a nanoparticle [93, 94].

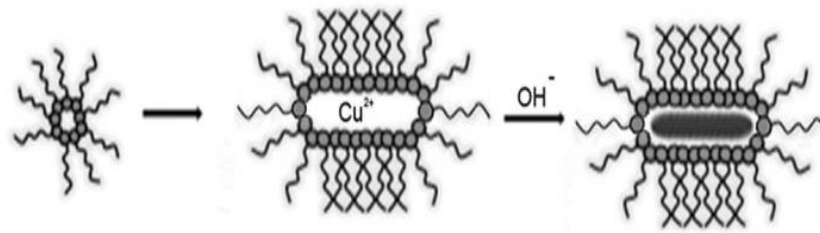


Figure 14 Growth of a $\text{Cu}(\text{OH})_2$ nanowire with the help of a surfactant: surfactant surrounds a water drop with copper ions, forms an elongated rod-like structure and formed a template for the $\text{Cu}(\text{OH})_2$ nanowire[93, 94].

Compared to surfactants, forming polymers (e.g. PEG) do not fabricate typical structures in a water solution. The hydrophilic groups in the polymer chain attach themselves to $\text{Cu}(\text{OH})_2$ nanoparticles and, therefore, stop their quick aggregation and led them into one-dimensional growth and decreased their surface energy at the same time.

2.3.3.2 Electrochemical method

The electrical chemical methods typically apply a porous template to utilize one-dimensional crystal growth[95]. The dimensions of the nanowires and their density are decided by the template pore size and density in the template. For the sake of reducing the diameters of the NWs, a shaping agent, i.e. polymer[96], is used. From the reports on the growth, it leads to a conclusion that the solution pH determines which copper phase will crystallize: pure copper, cuprous or cupric oxide. The use of electric potential can change the pH value around the template, which leads to a different copper phase than the one that is expected from the thermodynamic conditions in the rest of the solution[97].

2.3.3.3 Thermal oxidation method

A diffusion mechanism seems to be a reasonable description for nanowire growth. The metal oxidation procedure involves metal ion diffusion from the bulk copper to the surface through the cuprous oxide layer. On the other hand, oxygen ions diffuse in the opposite direction. The theories for particle diffusion are a grain boundary, a defect region (e.g. twinning defect in bi-crystals) or the lattice itself[98]. When the temperature is below 500 °C, grain boundary diffusion is the prevailing route for the diffusion. However, between 600 °C and 900 °C both lattice diffusion and grain boundary diffusion are valid, and if the temperature is above 800 °C lattice diffusion is the main transformation mechanism for the formation of particles. In the beginning, the surface metal oxide phase grows in all directions. However, the only crystallographic direction which follows the energetically favourable conditions, leads to the greatest diffusion rate and advantageous[99]. The diffusion is even stress driven—stresses to form between the copper surface and the Cu₂O layer due to mismatch in crystal cells. Finally, dislocations in the Cu₂O layer appear and short-circuit diffusion under the parabolic surface also occur[18].

The nanowires are generally grown directly on the bulk copper substrate, but it is also possible to grow them on any temperature-resistant substrate on which a thin film of copper has already been deposited. The thickness of the copper layer provides researchers additional freedom to pre-set the diameters of the nanowires independently of the temperature[100]. The copper nanowires are grown on the copper substrate also in the situation when the copper surface is coated with a thin film of foreign material. The nanowires produced by thermal oxidation are single-, bi- and polycrystalline CuO. The nanowires are homogeneous in radii and lengths, and grow vertically from the copper substrate. On the other hand, no Cu₂O nanowires can be grown directly in a single step. However, the CuO nanowires can be reduced to Cu₂O, as demonstrated above[101]. The reduced nanowires are polycrystalline, even if the prepared CuO nanowires are single-crystalline. In addition, based on research no single-crystalline

Cu₂O nanowires have yet been produced by thermal oxidation approaches and/or reduction of CuO nanowires.

2.3.3.4 Plasma oxidation method

There are two widely used mechanisms that describe metal oxide nanowire growth in plasma. The first one is a solid–liquid–solid model (SLS)[102]. Metals with low melting points are firstly melted and formed liquid droplets. The oxygen from the plasma pumps into the metal melt and oxidizes it. The metal oxide solidifies because it normally has a higher melting point than the pure metal. The solid oxide is deposited on the surface of the metal owing to surface tension, and forms a nucleation site for the nanowires. Nanowires have been grown from the top-down or bottom-up methods. In the top-down approach, the droplet is raised to the top of the nanowire, and the growth carries on until there is still some material left in the droplet[103]. The opposite is the bottom-up approach, where a nanowire is vertical from the liquefied droplet. The second model is solid–solid (SS) and is more reasonable when the temperature of the pretreated sample is lower than the melting temperature. The model illustrates that oxygen atoms diffuse directly in the solid metal. When the concentration of oxygen is high enough, the phase transformation from copper to copper oxide occurs. It is well-known that the oxide films form on copper are Cu₂O, so the diffusion of oxygen and copper atoms through the oxide layer is supposed to be the growth determining factor. Since the diffusion is enhanced with an electric field as shown by Li et al, changes the plasma gas result in the change of the floating potential and activate or prevent the nanowires growth.

2.3.4 Growth mechanism of Cu₂O with systematic shape

Matthew J. Siegfried has introduced a simple and direct method for systematically studying additives' effects on the stability and growth of various crystallographic planes of growing crystals. In the process, crystals with well-defined shapes (e.g., cubic, octahedral) have been obtained and their crystallization has been studied[104]. This

method makes it possible to observe additives' interactions with specific planes (e.g., {100} of a cube and {111} of an octahedron) that already exist. By studying how the original shapes change by time, the role and strength of habit modifiers have been studied in a more methodical manner. Through this examination, a scheme to design new crystal morphologies that cannot be formed via selective adsorption alone is also created.

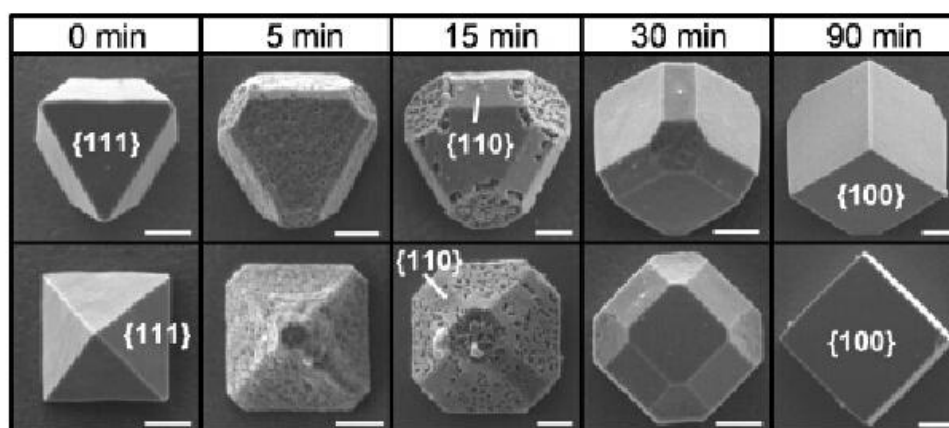


Figure 15 Transformation of pre-grown octahedral Cu_2O crystals over time in a 0.02 M copper nitrate solution containing 0.17 M SDS and 0.004 M NaCl[105].

The time-dependent transformation of octahedral crystals in Figure 15 demonstrates that crystals initially develop both {110} and {100} planes, but only {100} planes remain in their final products, leading to cubic morphology. From the final morphology, the effect of Cl^- ions could be clearly determined; they stabilize {100} planes much more strongly than NO_3^- ions[106]. The temporary appearance of {110} planes supplies data regarding the relative stability of {100}, {111}, and {110} planes in this medium, which is in the order of {111} {110} {100}[107]. When the crystallization process is continuing in the same solution without pre-grown cuprous oxide octahedral crystals, data regarding {110} planes couldn't be obtained because crystals adopt cubic morphologies from the early stages of habit formation[108]. This information, along with the information achieved

with NH_4^+ ions, illustrates that pre forming certain crystal shapes and forcing them to grow in a medium where the initial shape becomes the most unstable morphology can be used as a general scheme to form planes with stabilities between those of the original planes and those of the final planes[109].

The fabrication procedure of these Cu_2O nanoparticles with systematic shape development has been investigated by observing the intermediate structures formed. Nanoparticles with non-smooth surfaces but overall cubic and octahedral morphologies presented, illustrates a rapid crystal growth. These intermediate structures form through the aggregation of smaller particles with the size of 50-100 nm. Meanwhile, small Cu_2O crystals 10-20 nm in diameter attaching on the surfaces of these intermediate structures and irregular nanoparticle aggregate next to octahedral nanoparticles have been observed. These tiny nanoparticles may be in the middle of growing over an existing intermediate structure or becoming a new intermediate structure. From the results of this examination, a growth mechanism of these Cu_2O nanoparticles has been proposed and shown in Figure 2-15[110].

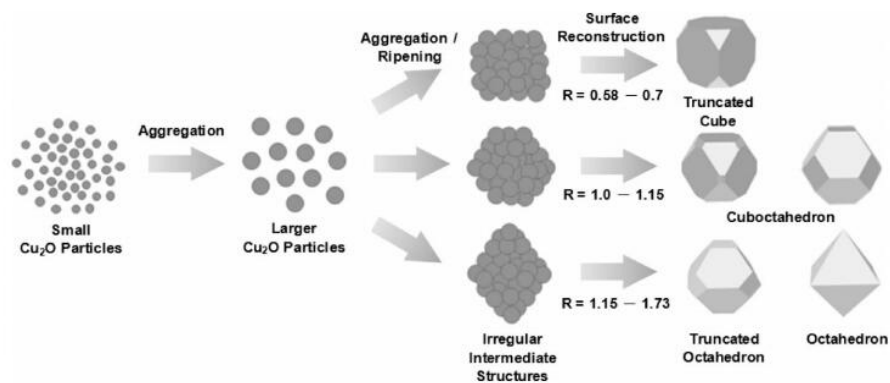


Figure 16 Schematic Illustration of the Cu_2O Nanoparticles Formation Process(R is the ratio of the growth rate along the [100] direction relative to that of the [111] direction)[111].

Immediately after adding $\text{NH}_2\text{OH}\cdot\text{HCl}$ and NaOH in the reaction solution, tiny Cu_2O seed particles form, as evidenced by an instant change of the solution colour. These seed particles quickly aggregate into larger particles with the diameter of tens of nanometres. The aggregation process continues to fabricate the observed intermediate structures in 5 min with sizes near the final product dimensions. For some particle aggregations, intermediate structures resembling the final nano crystals haven't been synthesized. Seed particles continuously attach onto these intermediate structures to encourage a further growth through a ripening process [112, 113]. The capping surfactant SDS and the amount of $\text{NH}_2\text{OH}\cdot\text{HCl}$ added in the solution play important roles in directing the overall morphology of these middle structures. The amount of $\text{NH}_2\text{OH}\cdot\text{HCl}$ could affect the growth rate along the [100] direction relative to that of the [111] direction, or the value of R , and lead to the attendance of the middle structures with roughly cubic, and octahedral structures. For instance, when R is 1.15 and 1.73, truncated octahedral and perfect octahedral particles can be obtained. The middle structures then develop into structurally well-designed products through a surface reconstruction process in 2 h. It is necessary to know how small differences in the amount of the reducing agent $\text{NH}_2\text{OH}\cdot\text{HCl}$ in the solutions could exert such a big effect on the nanoparticles shapes. The appearance of NaOH makes all the solutions alkaline. More $\text{NH}_2\text{OH}\cdot\text{HCl}$ add in the solution exactly makes it slightly less basic, because HCl from $\text{NH}_2\text{OH}\cdot\text{HCl}$ can react with NaOH . Whereas, octahedral nanoparticles could also be synthesized at a pH used to grow truncated cubic particles[114]. This analysis indicates that the amount of NH_2OH added to the solution, but not small changes in the solution pH, is mainly responsible for the morphology control of Cu_2O nanoparticles synthesized in this chemical reaction. The role of SDS in promoting the cubic and octahedral nanoparticles fabrication is modified by replacing SDS with the same mole number of cetyltrimethylammonium bromide (CTAB) as surfactant. The choice of capping surfactant is also very significant for the effective shape-controlled synthesis of these

Cu₂O nanoparticles. The sizes of these cuprous oxide nanoparticles can be modified to some degree by simply changing the amount of NaOH added to the solutions.

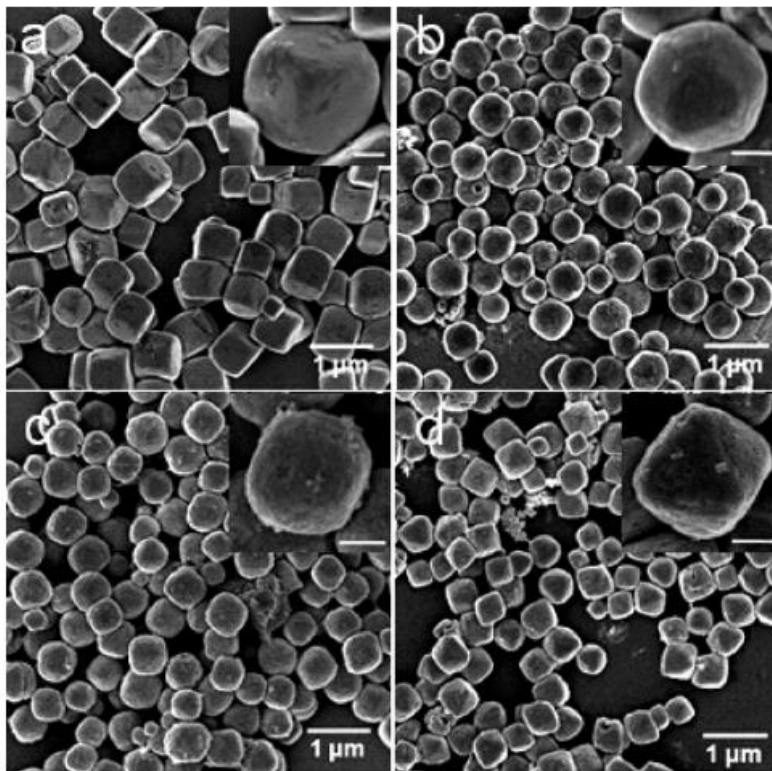


Figure 17 SEM images of the Cu₂O nanocrystals formed in sample bottles by increasing the volume of NaOH added to the reaction mixture to 0.75mL.

Figure 17 provides the SEM images of the Cu₂O nanoparticles formed in samples by increasing the amount of NaOH added to the reaction mixture. The particle shape remains the same as before, but their size increases a lot. The largest diameter increase has been recorded for the octahedral nanoparticles from an average size of 162 nm to an average size of 429 nm. Particle diameter distributions for all the conditions are also narrow with standard deviations of 15% or less. Besides, the pH values of the solutions in samples changes only slightly with different volumes of NaOH (less than a pH value change of 1).

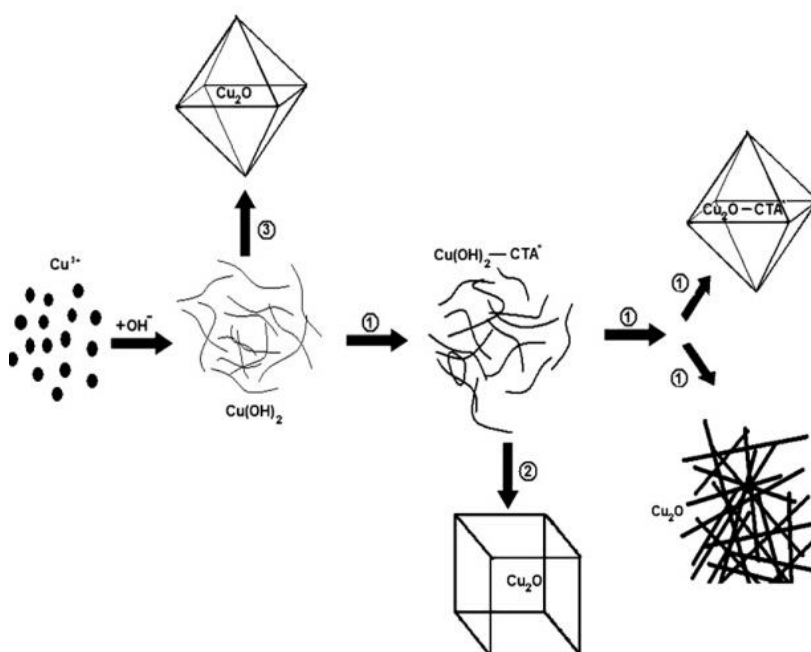


Figure 18 Scheme of Cu_2O nanostructures under different synthetic conditions[115].

The possible mechanisms involved during the morphological growth of nanoparticles under various fabrication conditions are shown in Figure 18. The mechanisms have been explained on the basis of Ostwald ripening and oriented absorption as step 1, 2 and 3. In the first step, the Cu^{2+} species bond with OH^- ions in the reaction solution, provided by the dissociation of NaOH and leads to the blue colloidal suspension of $\text{Cu}(\text{OH})_2$ having small wires-like structure. With the addition of CTAB, the wires aggregate together by electrostatic interaction to form flat ribbon shaped morphology. At first, Cu^{2+} seeds are dispersed as small nucleates within the suspension which has high affinity for network like growth on attaching with other seeds appeared in the reaction solution[116].

The possible mechanism for the synthesis of nanocubes has been shown in Figure 18 as the second step. This follows the similar mechanism based on the formation of $[\text{Cu}(\text{OH})_4]^{2-}$ -CTAB complex as this layer shaped complex is extremely unstable and

takes a role as template for the growth of various morphologies of final product. With the addition of reducing agent, D-glucose, at room temperature no reaction happens which fail to make changes in the morphology as well in the product formation. While by increasing the reaction temperature, the electrostatic interactions happen between surfactant and inorganic precursor which leads to the polymorphic crystallization for the formation of well-defined structure with solidified cubical shape. The octahedrons morphology of the product has been described in step 3, based on the Ostwald ripening, i.e. the fabrication of smaller crystallites is kinetically driven during the initial aggregation and larger crystallites are thermodynamically driven and oriented attachment. This step is similar with the process in step 1 and 2, as $[\text{Cu}(\text{OH})_4]^{2-}$ ions act as basic middle template for the morphology-orientated growth of the nanoparticles without adding CTAB. The positive Cu^{2+} ions attach loosely with the OH^- ions firstly attend in the aqueous media. During the reduction of Cu^{2+} ions by hydrazine nucleate the tiny Cu^+ nanoparticles provide a direct position for the growth of hollow and porous structures through planer growth mechanism.

2.3.5 Growth mechanism of polyhedral Cu_2O crystals

Facile highly symmetric multi-faceted polyhedral Cu_2O crystals surrounded by controllable high-index facets and different low-index facets can be synthesized via a template-free complex-precursor solution approach. The formation and evolution of these polyhedral shapes could be resulted from the aggregation and ripening mechanism with face-selective adsorption. The attendance of these novel polyhedral architectures further promotes the current morphologies of Cu_2O crystals, and might become useful for the fundamental investigation of crystals design[117].

The synthesis of Cu_2O polyhedral architectures with controllable high-index planes have been effectively obtained by a template-free complex-precursor solution method, which has been utilized successfully in the preparation of Cu_2O polyhedral structures.

This approach is based on the reduction of the $\text{Cu}(\text{CH}_3\text{COO})_2/\text{NaOH}/\text{H}_2\text{O}$ system with D-(+)-glucose. NaOH acts as a coordination agent to form the complex-precursor, and the properties of the precursor could decide the aggregation manner of the Cu_2O seeds during the beginning growing stage, and then affect the final product morphologies. D-(+)-glucose acts as a weak reducing agent which ensures the purity of products, which is in a similar way to the reduction mechanism of reported D-(+)-glucose based synthesis of Cu_2O nanoparticles, and it plays a vital role in the particle-based aggregation procedure of seed particles and the subsequent ripening procedure. The complex mechanisms for the formation of these facile highly symmetric multi-faceted polyhedral Cu_2O crystals surrounded by controllable high-index facets and different low-index facets could be proposed based on experimental results. When sufficient amounts of D-(+)-glucose, NaOH and $\text{Cu}(\text{CH}_3\text{COO})_2$ should be added at relatively high reaction temperature, cuprous oxide crystals can be obtained. At first, when OH^- ions add into the copper salts solution, $\text{Cu}(\text{OH})_2$ precipitate from the solution and then become black Cu_2O at 70 °C. When the concentration of OH^- ions is high enough, $[\text{Cu}(\text{OH})_4]^{2-}$ complexes would be obtained. With the addition of D-(+)-glucose, cupric oxide can be reduced to cuprous oxide by the $[\text{Cu}(\text{OH})_4]^{2-}$ species.

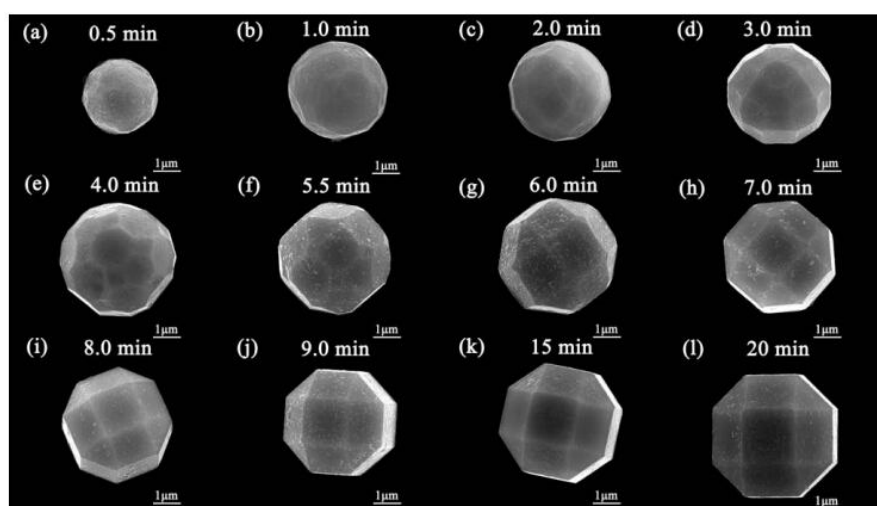


Figure 19 Typical FE-SEM images of the polyhedral Cu_2O crystal achieved at different reaction times. (a) 0.5 min; (b) 1.0 min; (c) 2.0 min; (d) 3.0 min; (e) 4.0 min;

(f) 5.5 min; (g) 6.0 min; (h) 7.0 min; (i) 8.0 min; (j) 9.0 min; (k) 15 min; (l) 20 min[118].

In order to explain the fabrication and evolution mechanism of these facile 50-facet polyhedral Cu_2O crystals, their growth process has been examined by observing the products obtained at different reaction times. Figure 19 shows the FE-SEM images of the samples achieved at different reaction times. It is obviously that the crystal shape-evolution is decided by the reaction time[119]. The FE-SEM results shows that the product has a spherical morphology (Figure 19a) with a diameter of about 2.5 μm in the beginning stage (0.5 min), and various of crystallographic planes could be seen clearly as the aging time increase to 1.0 min (Figure 19b), and the diameter of this product is about 3.5 μm . When the reaction time reaches to 2.0 min, the polyhedral structure with clear multi-facets could be fabricated (Figure 19c). The 50-facet polyhedral Cu_2O crystals with high-index $\{522\}$ planes can completely be obtained as the aging time increase from 3.0 min to 5.0 min. However, the $\{522\}$ planes are gradually reduced from squares (Figure 19f–h) to points (Figure 19i) as the reaction time increase to 8.0 min, therefore a 26-facet polyhedral structure with low-index planes ($\{111\}$, $\{100\}$ and $\{110\}$) is produced. From the results of this experiment, a growth mechanism of these Cu_2O nanoparticles has been put forward. After add D-(+)-glucose into the reaction solution, small Cu_2O seeds are immediately fabricated, as observed by a fast color change from dark to yellow red. In order to decrease the overall energy of the reaction system, seed particles aggregate together, and then the aggregates will develop into well-defined polyhedral architectures through a ripening mechanism. In the reaction system, the seed particles quickly aggregate into larger particles to the observed quasi-spherical middle structures in 0.5 min[120]. It illustrates that these nanoparticles are oriented, which demonstrates the attendance of oriented aggregation. As the reaction continues, seed particles keep attaching on these intermediate structures to promote further growth to form the morphologies as shown in Figure 19b (1.0 min) through the

ripening mechanism, as observed by an increase in the diameter of the nanoparticles. Based on Steno's law, the angles between two corresponding facets on the crystals are constant. Therefore, further growth of $\{110\}$, $\{100\}$ and $\{111\}$ planes on small Cu_2O sphere-like micro particles might be responsible for the fabrication of the as-synthesized polyhedral micro particles with high-index planes. With further ripening, the intermediate morphologies change into structurally well-defined 50-facet polyhedral Cu_2O crystals with $\{522\}$ facets.

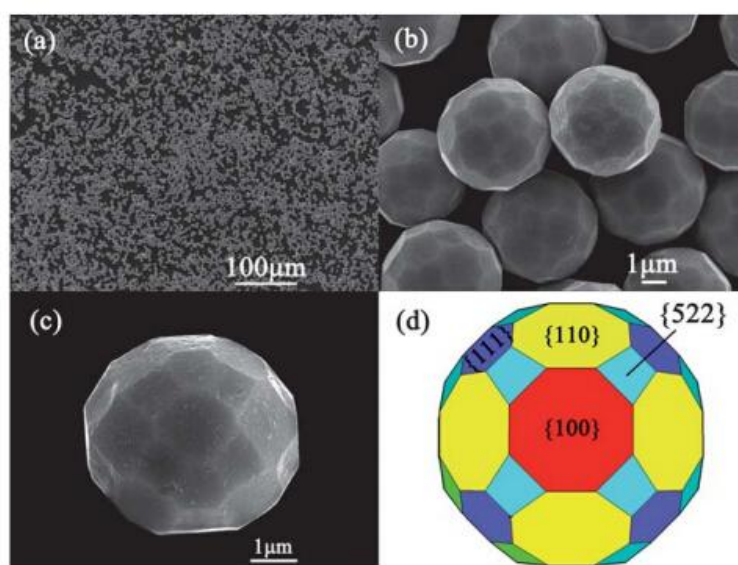


Figure 20 FE-SEM images of the as-prepared 50-facet polyhedral Cu_2O crystals, (a) low- and (b) high-magnification; (c) individual particle; (d) simulated structure.

Because the growth rate on high-index planes is usually much larger than that on low-index ones, so some of them could be easily taken place by low-index ones through a surface reconstruction procedure in certain process. As reported, the shapes of Cu_2O crystals have been decided by the ratio (R) between the growth rates along the $\langle 100 \rangle$ and $\langle 111 \rangle$ directions. It has been found that high-index planes could be formed by suitably changing the R values. Two general synthesis strategies are employed for chemical syntheses of crystals with high-index planes: (i) the use of extraneous energy (such as square-wave potential method), which continually limits the morphologies of

nanoparticles to evolve into high-index planes; and (ii) the use of capping agents (molecules or ions) during nanoparticle growth, Which modifies the R values to control the formation of high-index planes. During a solution reaction system, the reaction conditions (including capping agent, concentration of reagents, anions of investigated metal salts, etc) could have an effect on the R values, and might determine the presence of high-index planes in the final particles. The R values would be tailored due to face-selective adsorption of anions or additions on the middle structures, leading to the fabrication of high-index planes. In this experiment, the morphology of 50-facet polyhedral Cu_2O structures has been found to be related to the anions of the investigated copper salts. A series of experiments were carried by using other different copper salts, including $\text{Cu}(\text{NO}_3)_2$, CuSO_4 and CuCl_2 under the same reaction conditions. It clearly shows that the 50-facet polyhedral Cu_2O structures with high-index $\{522\}$ planes couldn't be formed effectively, indicating that $(\text{CH}_3\text{COO})_2^-$ anions played an important role in the fabrication of 50-facet Cu_2O crystals with high-index $\{522\}$ planes, and the selective adsorption of acid radical anions could have a strong effect on the attendance of high-index planes. In addition, it has been observed that the amount of D-(+)-glucose powder add in the solution plays a vital role in the protection of high-index planes. When the amount of D-(+)-glucose powder increase to 0.9 g, the $\{522\}$ high-index facets could be protected even the reaction time increased to 20 min. The consequence illustrates that the priority of face-selective adsorption of D-(+)-glucose can strongly affect the aggregation and ripening process of tiny Cu_2O particles, determining the appearance of high-index planes in the final crystals. Based on the synthesis method, the precursor $[\text{Cu}(\text{OH})_4]^{2-}$ is reduced by D-(+)-glucose to form Cu_2O , which then would aggregate to form nuclei via an orient- attachment procedure. Once these nuclei grow over a critical size, they would become seeds with varied morphologies under different conditions. The seeds would grow into various middle structures by a ripening process, then these middle structures would become different polyhedral architectures after surface reconstruction and preferential adsorption under different reaction conditions,

which could modify the ratio (R) between the growth rates along the $\langle 100 \rangle$ and $\langle 111 \rangle$ directions, at last, it may lead to the shape-controlled synthesis of polyhedral architectures with controllable-index planes. Thus, the fabrication and evolution of different polyhedral morphologies could be resulted from the collaboration effect of an aggregation and ripening mechanism with face-selective adsorption.

2.4 Applications

2.4.1 Biomedical

A large number of researches have been carried out to observe the potential impact of nanostructured metals and metal oxides on controlling the disease related pathogens like bacteria, fungi. So far, the antibacterial properties of copper@copper oxide nanocomposites have rarely been explored. These nano oxides are of particular interest for having extremely high surface energy and amusing crystal structure.

It has been observed that the rod shaped *E. coli*. gets decreased and the cell wall is damaged upon nanoparticle exposure. Irregular shaped bacteria are fabricated with cavities upon nanoparticle treatment[121]. The potential physical mechanism behind bactericidal effect of copper@copper Oxide nanoparticles is rather complex. Size induced larger surface area enables the nanoparticles to move and enter the bacterial cells. Their ability to attach to the bacterial cell wall stimulates biochemical reactions and results in toxicity to the bacterial cells. The copper nanoparticles act as strong reducing agents is damaged by reacting with deoxyribonucleic acid (DNA) and oxidizes the cell nucleus by extracting electrons and damaging the cell wall. Further the performance of copper oxides may encourage redox reactions and result in hydrogen peroxide which thereby breaks the cytoplasmic membrane of *E. coli*[122].

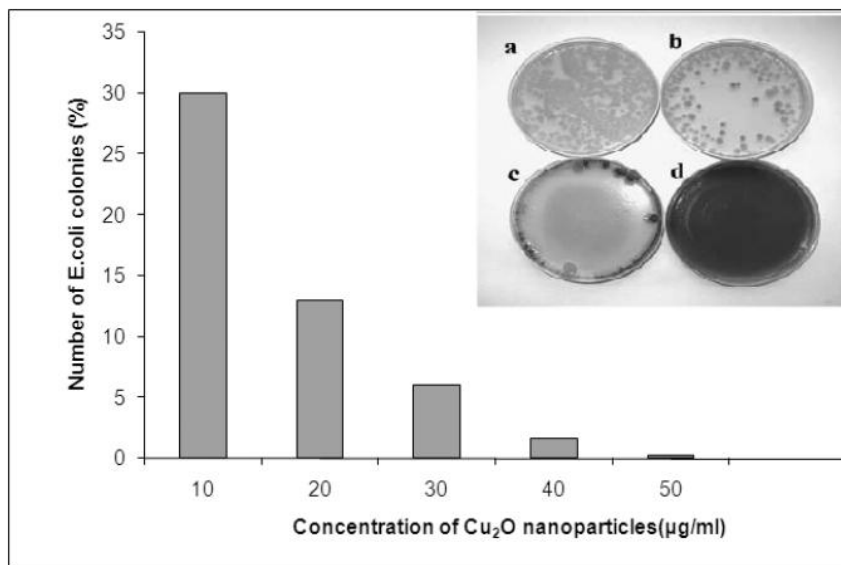


Figure 21 Number of E.Coli colonies as a function of concentration of Cu₂O nanoparticles in LB agar plates expressed as percentage of the number of colonies grown on Cu₂O – free control plates. The photograph inserted in the upper right corner shows LB agar plates containing different concentration of Cu₂O nanoparticles: a) 0, b) 30, c) 40, d) 50 μgcm⁻³.

2.4.2 Sensor

To investigate cuprous oxide morphology-dependent electrochemical properties, electrodes coated with cubic, truncated octahedral, octahedral, and hexapod Cu₂O particles have been synthesized[123]. The electrode current responses can be tested via a three-electrode system in 0.1 M PBS containing electron mediator. Glucose added to the reaction solution is oxidized to glucolactone by the electron mediator. The amperometric current, fabricated in this reaction, is the evidence of the presence of glucose.

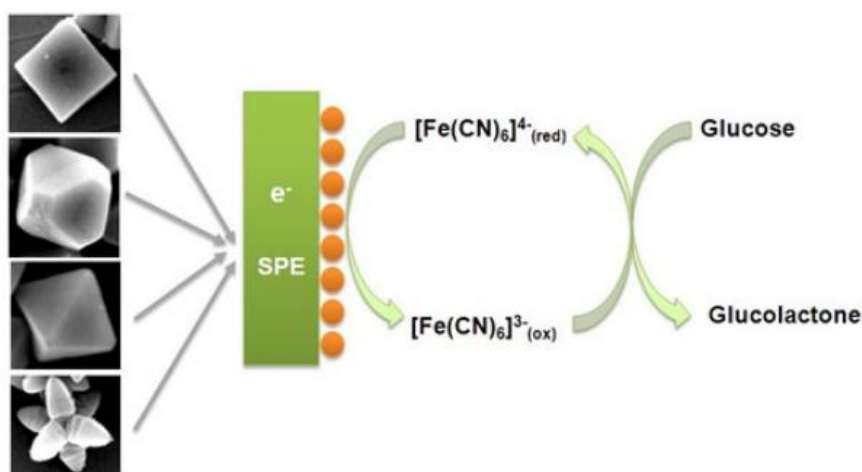


Figure 22 Schematic of Cu₂O-based electrochemical enzyme-free glucose sensors.

The octahedral and hexapod Cu₂O nanoparticles with {111} planes show better electrical catalytical properties than the cubic Cu₂O with {100} orientations. This illustrates that the {111} orientations are more electrical conductive than the {100} facets in Cu₂O particles. However, the electrodes fabricated with octahedral and hexapod Cu₂O particles shows detection limits of physiological relevance concentrations. Meanwhile, the detection limit slightly affects particle orientation, but a larger effect on the sensitivity[124, 125]. Heterogeneous systems with Au NPs deposited on the surface of Cu₂O particles have also been tested. The Au/Cu₂O systems are tested. These materials show that the hexapod shape of Au/Cu₂O greatly combined the effect of the electrocatalytic ability with glucose oxidation of Au NPs. While the physical and chemical properties of the materials themselves play the key role in their electrocatalytic test, and have the opportunity to control the morphologies and surface orientation of various particles[126].

2.4.3 Catalysts

A catalyst operates in a similar way to a sensor in which it attracts atoms and molecules, but a catalyst also converts them into a different species through chemical reactions[127].

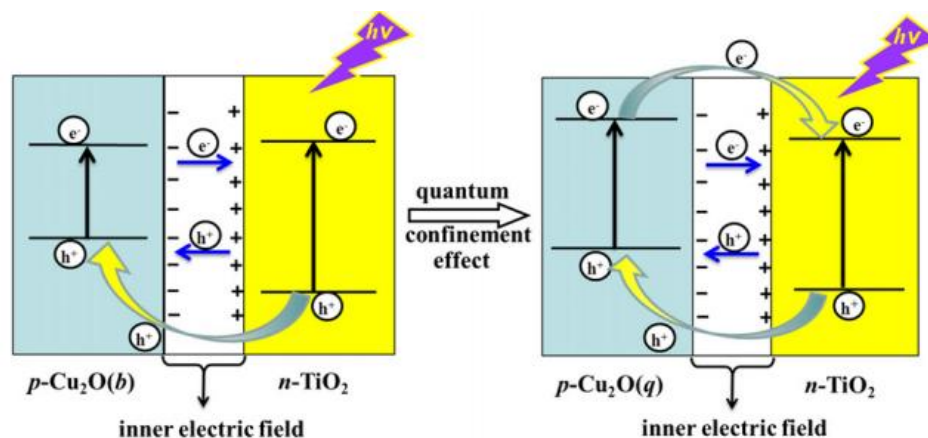


Figure 23 Schematic diagrams of the charge transfer in the as-prepared $\text{Cu}_2\text{O}/\text{TiO}_2$ composites.

The composite 0.9 mol% $\text{Cu}_2\text{O}/\text{TiO}_2$ exhibits a most significant quenching of PL, indicating the efficient charge transfer. This is related with the fact that the 0.9 mol% $\text{Cu}_2\text{O}/\text{TiO}_2$ shows the highest photocatalytic efficient for H_2 evolution[25]. With increasing the Cu concentration, the PL intensity slowly increases, demonstrating the growing recombination of photo generated charge carriers[128]. It has been indicated that the p-n junction in the as-prepared $\text{Cu}_2\text{O}/\text{TiO}_2$ composite system also promote the separation of photo generated charge carriers. This further shows that the excellent photocatalytic efficient for H_2 evolution over the as-prepared $\text{Cu}_2\text{O}/\text{TiO}_2$ composite is from both the quantum confinement effect of Cu_2O nanocrystals and p-n heterojunction system[129].

2.4.4 Template

Enlarging the active surface area of sensor materials is an effective method for enhancing the sensor response performance. In recent years, hollow inorganic

micro/nanospheres are very interesting due to their promising application on gas sensors[130]. Hollow spheres are typical three-dimensional curved structures showing fascinating properties of low density, high specific surface area and good permeation. However, in the area of gas sensors[131], gas-sensitive materials can be also prepared with the structure of hollow spheres. The enhancement in gas sensing properties results from their unique structure, large surface areas, and more surface active planes.

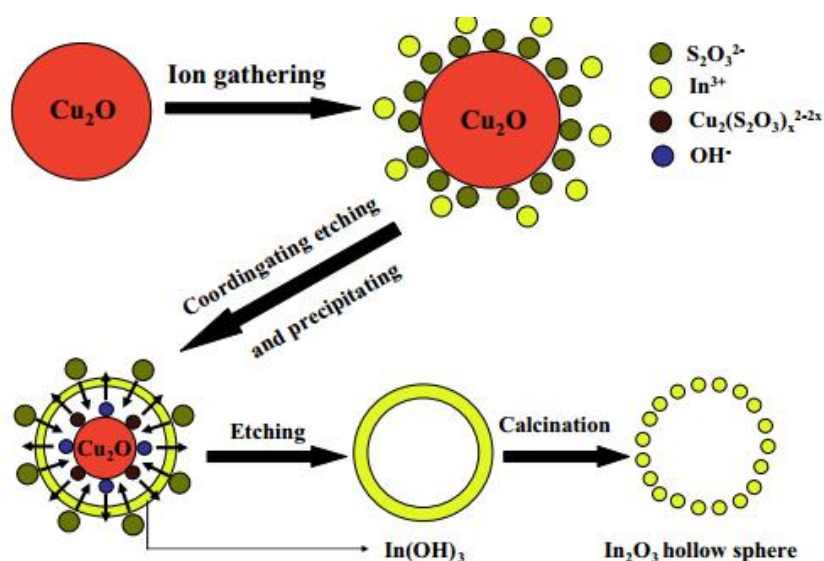


Figure 24 schematic demonstration of the formation of porous In_2O_3 hollow spheres.

The diluted NH_4OH solution can be used for selective etching of the Cu_2O core. As the etching of the core goes on, the colour of the solution changes from yellow (~ 3 h) to sky blue (~ 72 h) in the spheres, from orange to bright green in the cubes, and from red to yellow in the octahedrons[53, 132].

2.5 Summary

The progress of cuprous oxide and its composites has been extensive in the past decade. A number of dimension and morphology control approaches have been explored and the growth mechanisms into various morphologies are well demonstrated. Moreover, many

breakthrough experiments have been successful to synthesize and control the coating with various materials.

The successful surface engineering has led to nanoparticles have better functional properties. For instance, it is possible to perform photocatalysts, bio sensing, and solar cells; they have been surface modified with TiO_2 nanoparticles that are useful for antibacterial area, and coating with polymers and carbon that are highly conductive to be used as lithium batteries and electrical devices[30].

The challenge that researchers still have to deal with is whether the fabricated materials are efficient and /or practical on a large production level. The problem of cuprous oxide is often their stability in atmosphere. Moreover, different functions of different cuprous oxide phases are still under investigation. Our knowledge had improved the efficiency of these materials to provide improved commercial products. Thus, further investigation of cuprous oxide and its nanocomposites are still important for our understanding and design of materials.

Chapter 3 – Cuprous Oxide Nanospheres: Synthesis, Growth and Applications

3.1 Abstract

This study demonstrates simple and effective one-step strategies for the synthesis of shape-controlled cuprous oxide (Cu_2O) nanospheres. The proposed method offer several advantages, including the room-temperature preparation, high yield and potential for large-scale preparation. Various experimental parameters have been investigated, such as concentration of Cu^{2+} , surfactant, and reducing agent, and then we found the best conditions for fabricating cuprous oxide nanospheres. By changing different kinds of surfactant, wire-like morphology appeared which introduced a new topic. To further enhance the functional properties and performance, the nanocomposites composed of core Cu_2O nanospheres and TiO_2 coatings have also been observed. The photocatalytic properties of the Cu_2O and nanostructures have been tested by using methylene blue as the sample dye.

3.2 Introduction

In recent years, the fabrication of metal oxide nanostructures with highly exposed reactive facets has attracted increasing attention. A large number of studies have been reported on the preparation of *n*-type metal oxide nanostructures with exposed reactive crystal planes, including ZnO , SnO_2 , TiO_2 and WO_3 . In contrast, reports on the fabrication of *p*-type metal oxide nanostructures with specifically exposed crystal planes are rarely reported.

Cuprous oxide (Cu_2O), a *p*-type semiconductor with a band-gap (E_g) of 2.1 eV, has gained considerable interest in the field of solar energy conversion, lithium-ion batteries, gas sensors, and catalysis. Up to now, various morphologies of Cu_2O nanostructures

have been prepared, including cubes, nanoplates, nanocages, nanospheres, octahedron, and dodecahedron.

Of the achieved approaches thus far, wet-chemical precipitation method has been extensively used to synthesize cuprous oxide nanospheres. For example, Yuchi Cui and co-workers have reported a facile method to synthesis novel Cu_2O core-shell nanospheres in autoclaves heated to 200 °C. Michael H. Huang has reported a room-temperature method to synthesize Cu_2O nanospheres in organic solution. However, the methods used to produce such nanostructures are often carried out at mild to high temperatures (60-180 °C) in water baths or autoclaves, and/or requires the use of acids or organic capping agents such as oleic acid and hexadecylamine, which can be difficult to remove.

In this study we report the synthesis of Cu_2O nanospheres by one-step processes with the assistance of the surfactants, at room temperature. The effect of experimental parameters on the size and morphology of nanospheres is then studied, such as concentrations, surfactants, and reducing agents. The core-shell structure and its photocatalytic properties are also presented in this chapter, which is important for the enhancement of the functional properties.

3.3 Experimental Section

3.3.1 Chemicals

Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, 99%), sodium hydroxide (NaOH, Reagent grade), ascorbic acid, sodium borohydride (NaBH_4 , 99%), and various surfactants such as polyvinylpyrrolidone (PVP, $\text{MW}=55,000$), sodium dodecyl sulfate (SDS, AR Grade), cetyltrimethylammonium bromide (CTAB, AR Grade) are purchased from Sigma- Aldrich, and used as received without further treatment.

3.3.2 Synthesis of Cu₂O nanospheres

In a typical procedure, 0.125g of CuSO₄·5H₂O powder was first dissolved into 100mL of distilled water to a 0.005M light blue aqueous CuSO₄ solution. Then, surfactant (the mole ratio of surfactant to Cu²⁺ is 1:1) was added into the above solution under strong magnetic stirring. After 15 minutes of stirring, 0.42 mL of 6mol/L NaOH solution was titrated slowly into the mixture solution. After another 15 minutes of stirring, reducing agent solution was wisely dropped into this mixture solution at room temperature and red precipitate began to form. After about 1h, the experiment was stopped and the final products (0.358g/L) were obtained by centrifugation and thoroughly washed several times with ethanol and distilled water.

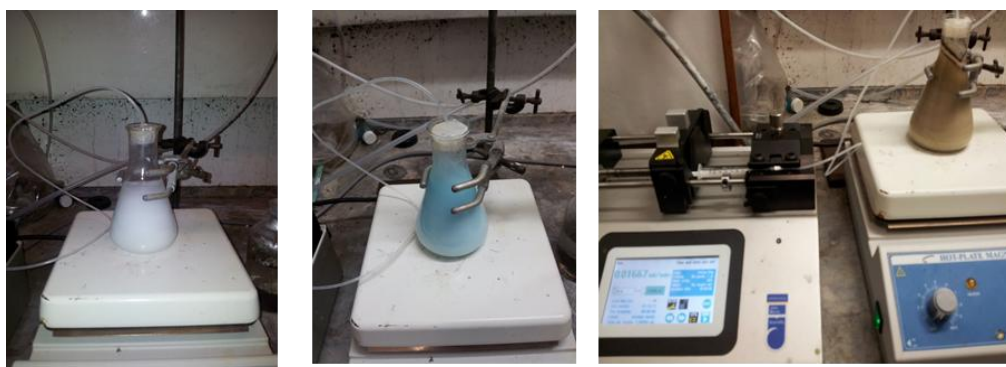


Figure 25 Images showing the steps to synthesize Cu₂O.

Figure 25 show that we use an electrical pump to titrate chemical slowly into the mixture solution to control the speed of the chemical reaction.

3.3.3 Characterizations

The phase composition and purity of the as-prepared Cu₂O nanostructures were examined using Phillips X'pert Multipurpose X-Ray Diffraction System (MPD) with Cu-K α radiation ($\lambda = 1.54 \text{ \AA}$) operated at 40 kV and 40 mA, in the 2θ range of 20-70 °. Scanning electron microscopy (SEM) analysis was conducted using a FEI Nova Nano SEM 230 field emission scanning electron microscope. The transmission electron

microscopy (TEM) images were obtained using a Tecnai G² 20 transmission electron microscope operated at an accelerating voltage of 200 kV. High resolution transmission electron microscopy (HRTEM) images were recorded on a Phillips CM200 field emission gun transmission electron microscope with an accelerating voltage of 200 kV. UV-vis absorption spectrum was obtained on a CARY 5G UV - visible Spectrophotometer (Varian) with a 1cm quartz cell.

3.4 Results and Discussion

3.4.1 Synthesis of spherical nanoparticles

The synthesis of Cu₂O spheres can be explained by two steps. In the first step, Cu²⁺ react with the sufficient OH⁻ species in the reaction solution to give rise to the fabrication of intermediate [Cu(OH)₄]²⁻ ion. Surfactants result in the phase separation with the attendance of inorganic salt and supplied the control over the shape of the nanoparticles during growth process. In the second step, the intermediate [Cu(OH)₄]²⁻ ions are reduced by reducing agent. With this fabricating process, Cu₂O nanoparticles were obtained[133].

3.4.2 Effect of experimental parameters

Using the reducing reaction, we can prepare Cu₂O nanoparticles. It is possible to control sizes and morphologies by changing the conditions of reaction, such as concentration of Cu²⁺, reducing agent, and surfactant.

3.4.2.1 Effect of concentration of Cu²⁺

The property of nanoparticles is mainly determined by shape and size; we could easily change the experimental conditions to vary the dimensions of the Cu₂O nanoparticles via this method.

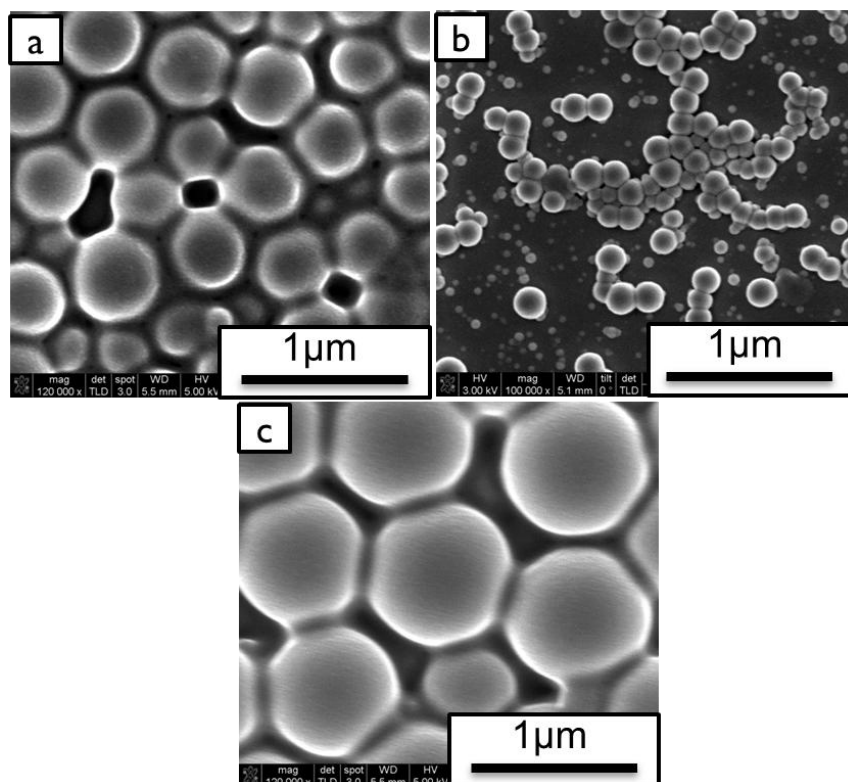


Figure 26 SEM images of Cu_2O synthesized by different Cu^{2+} concentrations: (a) 0.0005mol/L, (b) 0.005mol/L, (c) 0.05mol/L.

The concentration of reactants could affect not only the particle nucleation and growth but also the size of the obtained particles. Figure 26 shows the SEM images that Cu_2O nanoparticles were formed under the conditions of different Cu^{2+} concentrations without any surfactant, and the mole ratio of reducing agent ($\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$) to Cu^{2+} was 1:1. At a lower concentration (0.0005mol/L of Cu^{2+}), nearly spherical nanoparticles were fabricated and the diameter was $\sim 500\text{nm}$ (Figure 26a). When the concentration increased to 0.005mol/L, more cuprous oxide nanoparticles were fabricated and the average diameter decreased to 200nm as showed in Figure 26b. With the higher concentration (0.05mol/L of Cu^{2+}), cuprous oxide nanoparticles are easy to aggregate together to form irregular but big particles as shown in Figure 26c. That is, the concentration of copper ion plays an important role in the formation of Cu_2O particles, and surfactant is necessary for preventing the nanoparticles from aggregation.

3.4.2.2 Effect of reducing agent

In this case, different kinds of reducing agent were used to prepare Cu_2O nanoparticles with the addition of surfactant (SDS). In comparison, it demonstrated that Cu_2O nanospheres were fabricated, as shown in Figure 3-3.

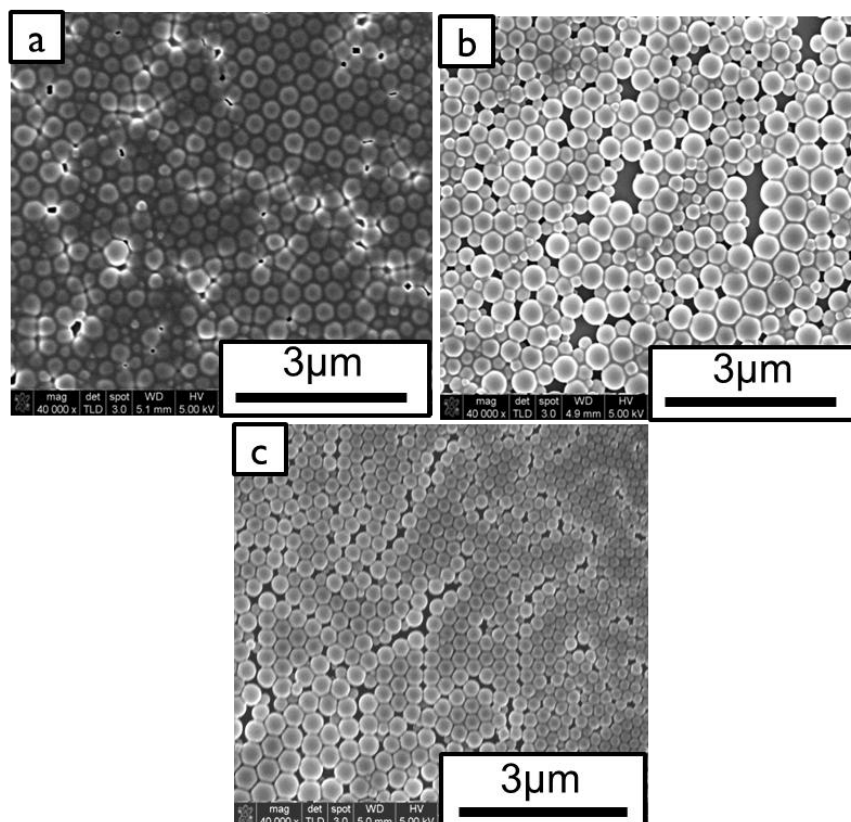


Figure 27 SEM images of Cu_2O reduced by different reducing agents: (a) ascorbic acid, (b) sodium borohydride, (c) hydrazine hydrate.

Figure 27 shows spherical Cu_2O nanoparticles were obtained. However, the particle size and uniformity are significantly different. When ascorbic acid acts as reducing agent, the nanoparticles are easy to aggregate (Figure 27a). In addition, when reducing agent changes to sodium borohydride, the nanoparticles are not very uniform (Figure 27b). Using hydrazine hydrate as reducing agent gives rise to a promising result that the nanoparticles are monodisperse and uniform, as shown in Figure 27c.

3.4.2.3 Effect of surfactant

At present, the influence of surfactant have been reported, however different surfactants used on the p-type Cu_2O nanoparticles are rarely reported. In this part, different kinds of surfactant were added in the reaction solution, and then hydrazine hydrate was added in as reducing agent. Result is shown in Figure 28.

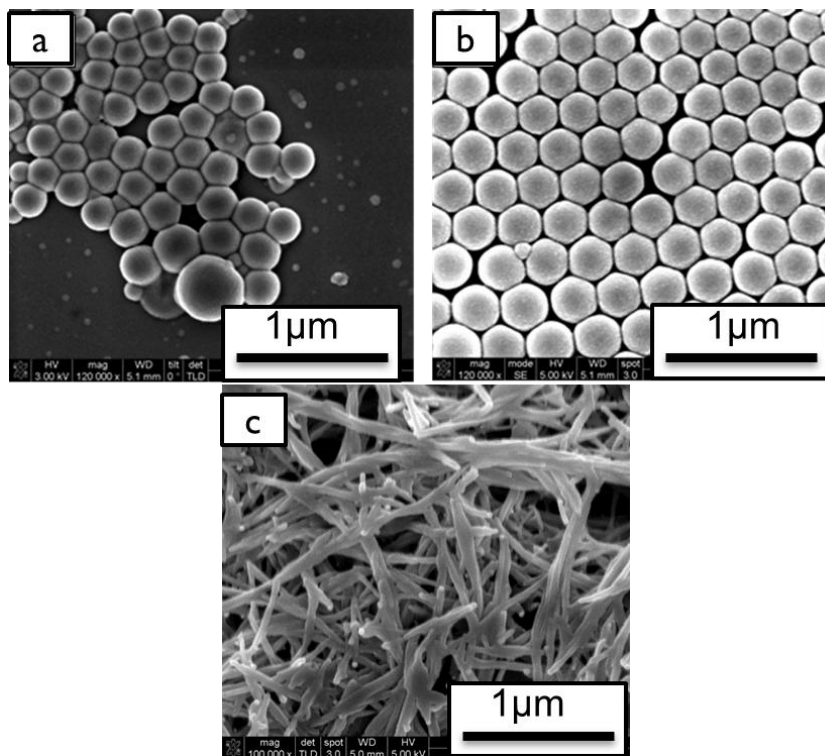


Figure 28 SEM images of Cu_2O fabricated with different surfactants: (a) PVP, (b) SDS, (c) CTAB.

PVP is a kind of widely used surface modifier, however PVP has no significance in this reaction system and the particles can only rely on its isotropic growth. So as shown in Figure 28a the obtained Cu_2O nanoparticles are irregular. With the assistance of CTAB, the nanoparticles become nanowires (Figure 28c). That is CTAB molecules are favorable for the growth of anisotropic morphology (such as nano wires), which will be explained in next chapter. Nanoparticles fabrication is modified by replacing PVP with the same mole ratio of SDS as surfactant, as shown in Figure 28b. The structures of different surfactants have been shown in Figure 29.

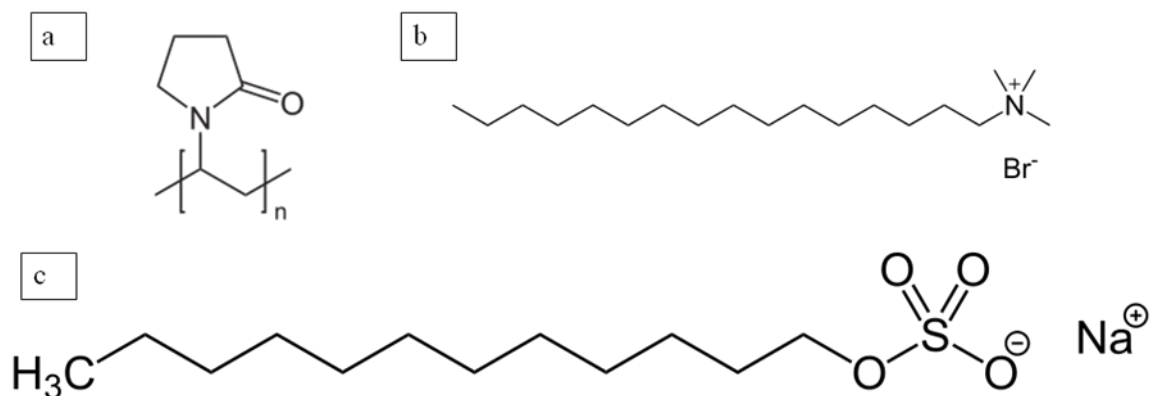


Figure 29 (a) molecular structure of PVP, (b) molecular structure of CTAB, (c) molecular structure of SDS.

3.4.2.4 Best conditions for preparation of Cu_2O nanospheres

Based on the experimental results we can get the best conditions for fabricating Cu_2O nanospheres. That is, the concentration of CuSO_4 is 0.005mol/L; surfactant is SDS and the mole ratio of CuSO_4 to reducing agent ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) is 1:1.

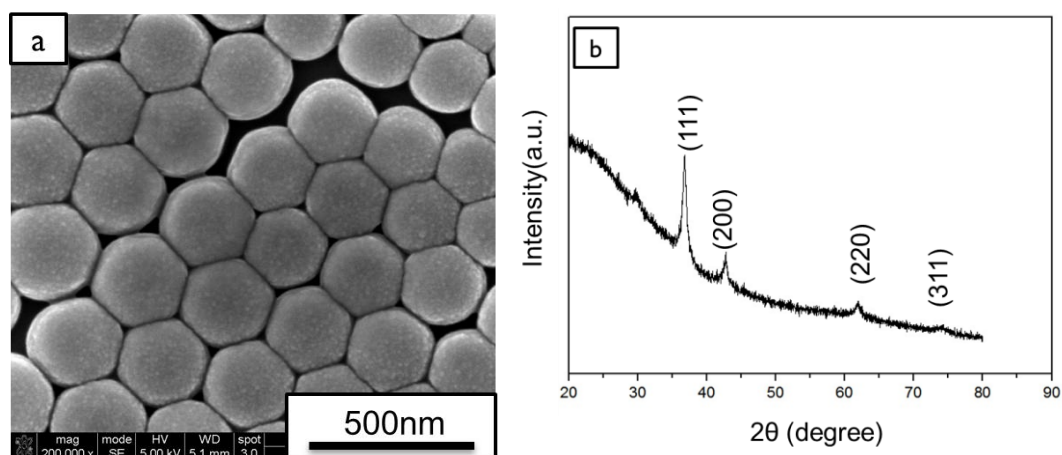


Figure 30(a) SEM image of Cu_2O nanospheres, (b) XRD pattern of Cu_2O nanospheres.

Figure 30a demonstrates uniform Cu_2O nanospheres with a diameter of $\sim 200\text{nm}$ have been successfully fabricated. Figure 30b shows the XRD patterns of the as-prepared Cu_2O nanospheres. Clearly, all of the diffraction peaks of the products can be well-indexed to the cubic FCC phase of Cu_2O (JCPDS No. 78-2706). No impurities,

such as CuO or Cu(OH)₂, are detected in the XRD patterns of these Cu₂O nanostructures.

Firstly, CuSO₄ 5H₂O powder is completely dissolved in the de-ionized water and formed a light blue solution. Under strongly stirring, the hydrazine hydrate aqueous solution is added slowly into the CuSO₄ aqueous solution at room temperature. After about 5min, the light red precipitation begins to form, at the same time a great number of bubbles emerging from the solution. Immediately after adding N₂H₄.H₂O and NaOH in the reaction solution, tiny Cu₂O seed particles form, as evidenced by an instant change of the solution color. These seed particles quickly aggregate into larger particles with the diameter of tens of nanometers. The aggregation process continues to fabricate the observed intermediate structures in 5 min with sizes near the final product dimensions. For some particle aggregations, intermediate structures resembling the final nano crystals haven't been synthesized. Seed particles continuously attach onto these intermediate structures to encourage a further growth through a ripening process. The capping surfactant SDS added in the solution plays an important role in directing the overall morphology of these middle structures. SDS attach uniformly on the surface of middle structures result in the spherical morphology.

3.4.3 Synthesis of spherical Cu₂O coated with TiO₂

It has been illustrated that the excellent corrosion resistance of titanium is a result of its nature. When titanium is exposed to atmosphere environments or solutions, a thin titanium oxide layer will be rapidly formed on the metal, acting as a shell to corrosion reactions. However, this does not exactly mean that titanium oxide is not active. Actually, it is demonstrated that the properties of the titanium oxide layer are necessary for a good contact to the surrounding tissue. Thus, the property control and design of titanium oxide coatings are important for promoting their convenient use on optical devices. In the past decade, research revealed that the titanium oxide can be chemically and physically activated.

Recently, core-shell structure has been a very attractive topic due to their potential applications in different areas, such as optical devices, biochemistry, and photocatalysts. Among the metal oxides, TiO_2 is a promising for various applications including solar energy conversion and photo electronic catalysis. The band gap energies of n-type TiO_2 and p-type Cu_2O are about 3.2 and 2.1 eV, respectively; these band gaps enable photo-absorption transfer from ultraviolet to the visible region. Furthermore, from a thermodynamic view, the conduction band minimum and valence band maximum of TiO_2 lie below that of Cu_2O , which satisfy an important requirement for efficient transfer of both electron and electrical minority carriers.

3.4.3.1 Preparation of $\text{Cu}_2\text{O}@\text{TiO}_2$ core-shell structure

For the preparation of $\text{Cu}_2\text{O}@\text{TiO}_2$ core-shell structure colloids, firstly, 0.05mL titanium (IV) butoxide 97% (TBT) was added to 10mL ethylene glycol (EG). The mixture was magnetically stirred for 8 hours at room temperature as solution A. Secondly, 3mL 0.01M prepared Cu_2O spherical colloids was added into 10mL acetone under stirring for 5 minutes as solution B, leaving it for 1 hour. The yellow brown precipitates were obtained by centrifugation and these precipitates were heated in 100°C water for 2 hours. To get $\text{Cu}_2\text{O}@\text{TiO}_2$ core-shell powder, the colloids were centrifuged at rate of 3000 r/s for 10 minutes and washed with ethanol, at last dried in vacuum at 80°C for 24 hours.

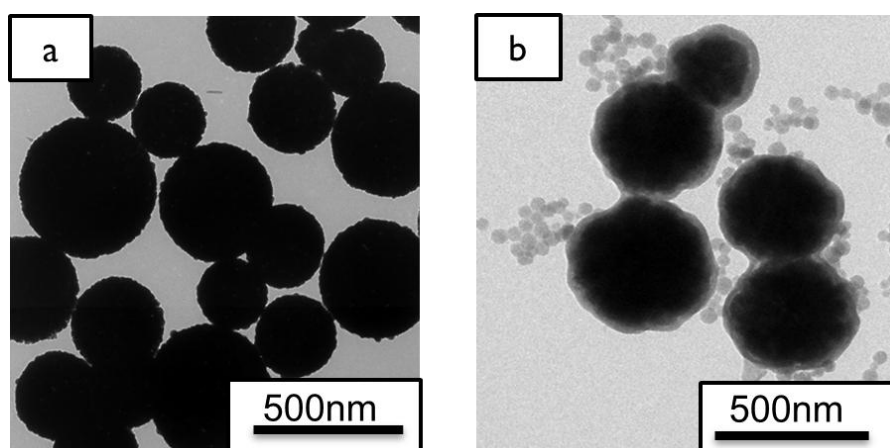
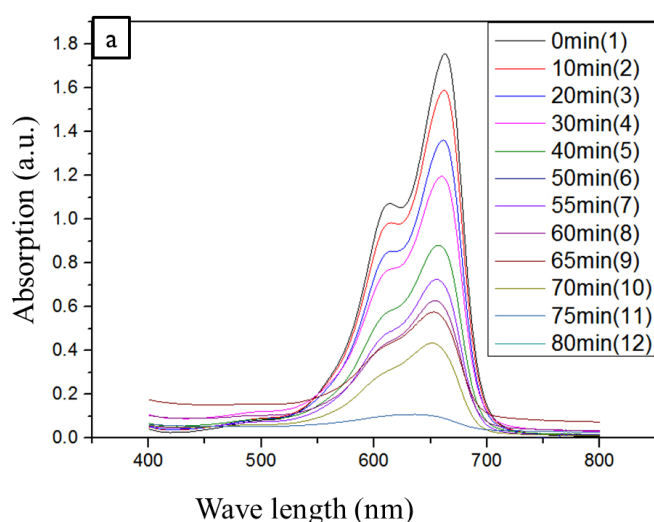


Figure 31(a) TEM image of Cu_2O nanospheres, (b) TEM image of $\text{Cu}_2\text{O}@\text{TiO}_2$ nanospheres.

Figure 31 (a)-(b) illustrate the prepared Cu_2O nanospheres have been coated with TiO_2 colloids. Due to the shell of TiO_2 particles on Cu_2O nanospheres, the surface of $\text{Cu}_2\text{O}@\text{TiO}_2$ is much rougher than that of neat Cu_2O . Additionally, the large interface area between Cu_2O and TiO_2 can be clearly seen, indicating the two components are well contacted with each other to fabricate heterojunction which is beneficial to photocatalysts.

3.4.3.2 Photo catalyst performance of the prepared nanoparticles

For the photocatalytic activity measurements, 20mg synthesized Cu_2O and $\text{Cu}_2\text{O}@\text{TiO}_2$ nanocrystals were used, respectively. The entire centrifuged nanocrystals were dispersed in 90mL of 20mg/L aqueous methylene blue (MB) solution. Before illumination, the cell was constantly stirred for 30 minutes in the dark for the molecules to adsorb onto the particle surfaces. After that the cell was irradiated with light from a 500 W xenon lamp placed 28 cm away. The light intensity reaching the cell was measured to be $500\text{mW}/\text{cm}^2$. UV-vis absorption spectra of the samples were taken before and after every 5-10 minutes of irradiation for up to 80 minutes by removing the cap to withdraw the solution.



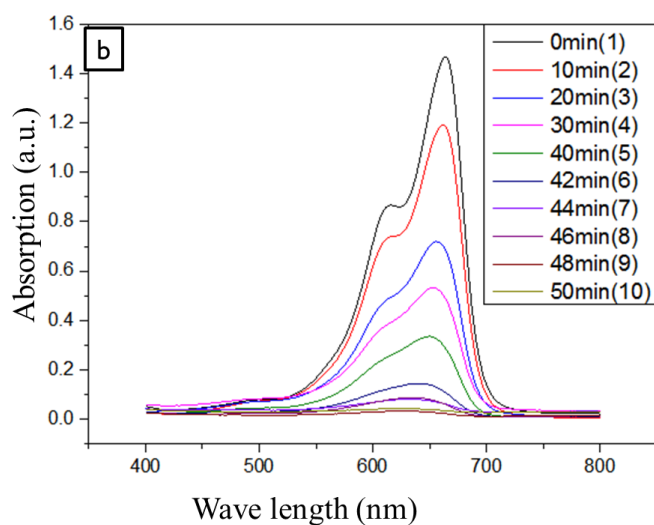


Figure 32(a) Photocatalyst test of Cu_2O nanospheres, (b) Photocatalyst test of $\text{Cu}_2\text{O}@\text{TiO}_2$ nanospheres.

The results of photocatalytic tests have been shown in Figure 32. The composite $\text{Cu}_2\text{O}@\text{TiO}_2$ has shorter degradation time than that of the pure Cu_2O . The degradation time for pure Cu_2O nanospheres and the $\text{Cu}_2\text{O}@\text{TiO}_2$ nanospheres are $\sim 80\text{min}$ and $\sim 50\text{min}$, respectively. The energy transfer from Cu_2O to the TiO_2 through a dipole-dipole interactions and the electron transfer from the Cu_2O core to the TiO_2 shell, are the two possible mechanisms that can describe the degradation process.

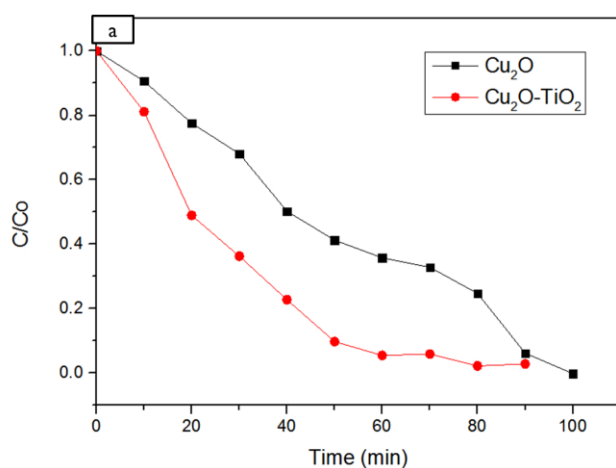


Figure 33(a) the photodegradation of MB in the presence of pure Cu_2O nanospheres and $\text{Cu}_2\text{O}-\text{TiO}_2$ nanospheres.

Langmuir-Hinshelwood model, the degradation of dyes could be described as a pseudo-first-order reaction when C_0 is very small: $\ln (C_0/C) = kt$, where k is the apparent first-order-reaction rate constant. The degradation data were analyzed to facilitate the mathematical interpretation of the degradation rate constant. However, the real degradation process is very complicated. The logarithmic plots of C/C_0 in case of degradation of dyes could not generate the line with only one slope, which results from pseudo-first-order rate constant. Instead, there are two possible k for each photocatalysis process can be used to demonstrate the whole degradation reaction, as described in our testing systems. In the case of degradation of MB, k_1 value for Cu_2O , $\text{Cu}_2\text{O}@\text{TiO}_2$, in the first stage of the reaction was estimated at 7.2, and 8.3 min^{-1} , respectively. While with degradation going, another k_2 value appeared to show the kinetics process increases to 9.2, and 9.4 min^{-1} . The non-linear relationship in kinetics process illustrates the degradation reaction of dyes by photocatalysis is complicated, but only a few reports have been found in the literature. Thus, much more work needs to be done to further research the detailed kinetics of photocatalytic reaction in the future.

Of the reported approaches to achieve $\text{Cu}_2\text{O}@\text{TiO}_2$ nanoparticles, an etching method is widely used. For example, David Low[134] reported a method that uses polycrystalline TiO_2 layer to deposit around the scaffold of Cu_2O polyhedral by the synergy of accelerated hydrolysis of TiF_4 and simultaneous slight etching of Cu_2O by HF released from the hydrolysis of TiF_4 . Our method just coats TiO_2 precursors around Cu_2O and then just heats it in water at low temperature for 2 hours; we do not use strong acid such as HF to form the core-shell structure. We introduce a safe and fast approach to fabricate nanocomposites.

3.5 Conclusions

A SDS-directed synthesis approach was illustrated for uniform nanospheres at room temperature. The findings can be summarized below:

(1) We discuss different parameters to achieve the best conditions to synthesize cuprous oxide nanospheres. The result shows SDS is very important for the formation and

uniformity of nanospheres, which cannot be fabricated with longer aging time or with the use of PVP. By using CTAB as surfactant in the reaction system, wire-like morphology appears which raises a new topic for cuprous oxide synthesis.

(2) We introduce a facile method to fabricate $\text{Cu}_2\text{O}@\text{TiO}_2$ core-shell structures, which is safe and fast. $\text{Cu}_2\text{O}@\text{TiO}_2$ core-shell spheres showed better photodegradation performance than pure Cu_2O nanospheres.

The findings could be useful for generating shape-controlled nanostructures and its core-shell composites, which would improve the functions of nanoparticles.

Chapter 4 – Cuprous Oxide Nanowires: Synthesis, Growth and Applications

4.1 Abstract

This chapter demonstrates a room temperature method to prepare Cu₂O nanowires based on the synthesis of Cu₂O nanospheres in last chapter. The obtained nanowires have a diameter of ~20nm and length up to several micrometers. From last chapter, it is observed that surfactant, cetyltrimethylammonium bromide (CTAB), plays an important role in the growth of nanowires. The result demonstrates that CTAB can strongly benefit the growth of nanowires along [111] direction. By modifying ratios of reducing agent to Cu²⁺, a new morphology (octahedral) was obtained.

Cu₂O nanowires coated with TiO₂ were also investigated. The structure of the nanocomposites is confirmed by TEM, HRTEM and EDS mapping. And also the optical property of the product was tested in the photo catalyst examination.

4.2 Introduction

Copper-based nanowires are of great interest because of their application as interconnects for microelectronics [50]. Copper nanowires and related structures have been obtained by physical and chemical techniques[135]. Our interest is focus on application of copper oxide nanostructures to get high-performance photo catalyst. We synthesized pure Cu₂O nanowires by using a room-temperature chemical method in which the surfactant CTAB was used as a soft template.

Recently, several reports were published on synthesis of one-dimensional (1D) Cu₂O

nanostructures, such as wires, tubes, and belts, due to their unique properties. Most approaches for the synthesis of 1D Cu₂O request tedious processes, templates, high temperatures, and special conditions[136]. For example, P. Grez's group has reported a method, which commercial polycarbonate membranes are used as template to synthesize Cu₂O nanowires[90]. Guanzhong Wang's group has reported an electrodeposition method to achieve cuprous oxide nanowires with a diameter of sub-10nm with the help of PVP[137].

In this communication, we report on a facile fabrication approach, which requires neither sophisticated techniques nor heating equipment, to selectively prepare cuprous oxide nanowires. The final production is with an average wire diameter of approximately 20 nm. The synthesis method for Cu₂O nano-wire synthesis starts with a sequence of reactions to first fabricate precursor Cu(OH)₂ nanowires. The precursor polycrystalline nanowires are used both as reactants for the growth of Cu₂O nanowires and as templates controlling the size and shape of the final products.

4.3 Experimental Section

4.3.1 Chemicals

Copper sulfate (CuSO₄·5H₂O), sodium hydroxide (NaOH, Reagent grade), hydrazine hydrate (N₂H₄·H₂O, 99%), cetyltrimethylammonium bromide (CTAB, AR Grade) are purchased from Sigma- Aldrich, and used as received without further treatment.

4.3.2 Synthesis of Cu₂O Nanowires

In a typical process, 0.125g of CuSO₄·5H₂O powder was first dissolved into 100mL of distilled water to a 0.005M light blue aqueous CuSO₄ solution. Then, CTAB (the ratio of surfactant to Cu²⁺ is 1:1) was added into the above solution under strong magnetic stirring. After 15 minutes of stirring, 0.42mL of 6mol/L NaOH solution was titrated slowly into the mixture solution. After another 15 minutes of stirring, reducing agent

solution ($\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$) was wisely dropped into this mixture solution at room temperature and the mol ration of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ to Cu^{2+} is 1:1. Then red precipitate began to form. After about 1h, the experiment was stopped and the final products were obtained by centrifugation and thoroughly washed several times with ethanol and distilled water.

4.3.3 Characterization

The phase composition and purity of the as-prepared Cu_2O nanostructures were examined using Phillips X'pert Multipurpose X-Ray Diffraction System (MPD) with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) operated at 40 kV and 40 mA, in the 2θ range of 20-70°. Scanning electron microscopy (SEM) analysis was conducted using a FEI Nova Nano SEM 230 field emission scanning electron microscope. The transmission electron microscopy (TEM) images were obtained using a Tecnai G² 20 transmission electron microscope operated at an accelerating voltage of 200 kV. High resolution transmission electron microscopy (HRTEM) images were recorded on a Phillips CM200 field emission gun transmission electron microscope with an accelerating voltage of 200 kV. UV-vis absorption spectrum was obtained on a CARY 5G UV - visible Spectrophotometer (Varian) with a 1cm quartz cell.

4.4 Results and Discussion

4.4.1 Synthesis of wire-like nanoparticles

The synthesis of Cu_2O wires can be explained by two steps. In the first step, Cu^{2+} react with the sufficient OH^- species in the reaction solution to give rise to the fabrication of intermediate $[\text{Cu}(\text{OH})_4]^{2-}$ ion. CTAB result in the phase separation with the attendance of inorganic salt and supplied the control over the shape of the nanoparticles during growth process. In the second step, the intermediate $[\text{Cu}(\text{OH})_4]^{2-}$ ions are reduced by reducing agent. With this fabricating process, Cu_2O nanowires were obtained.

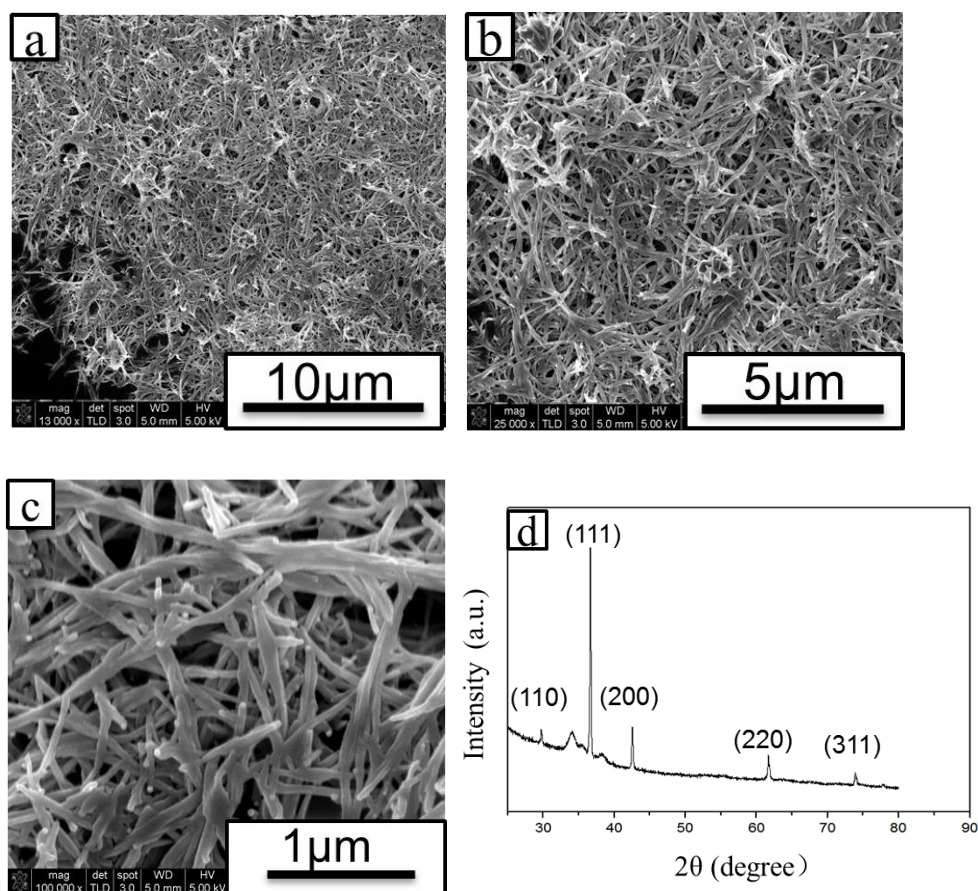
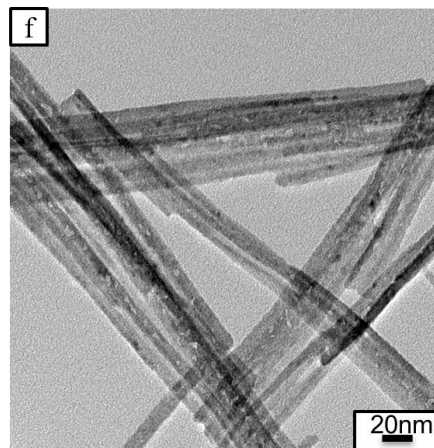
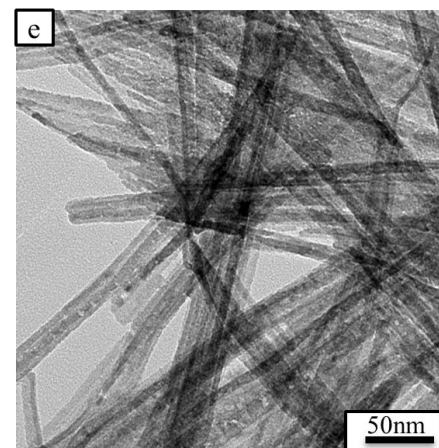
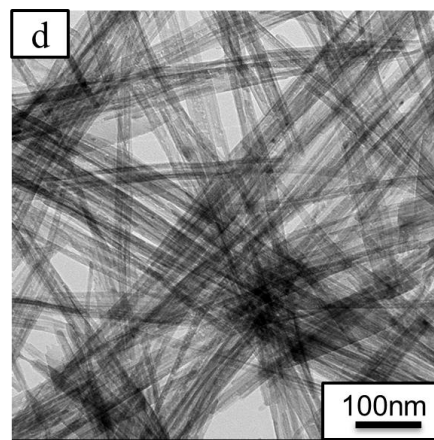
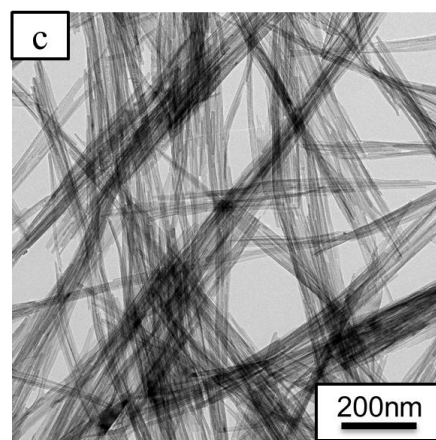
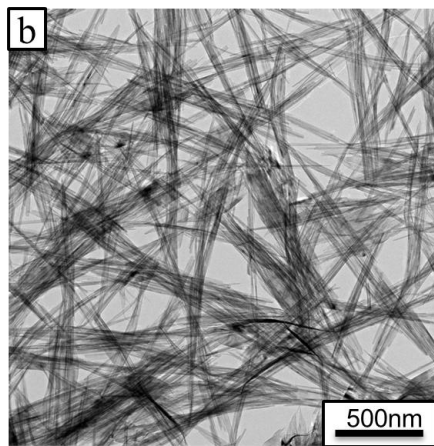
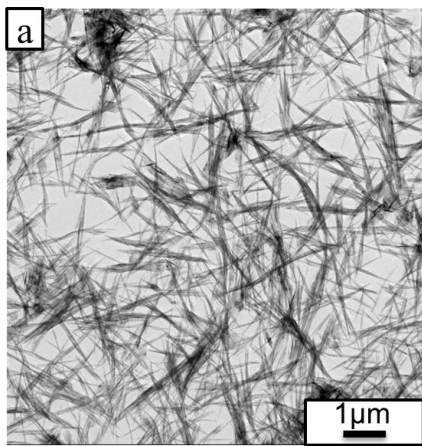


Figure 34(a)-(c) SEM images of the prepared nanowires. (d) XRD pattern of Cu₂O nanowires.

Figure 34 (a)-(c) SEM images shows the morphology and size of Cu₂O nanowires length up to a few micrometers; and the XRD pattern, which is shown in figure 34(d), demonstrates the Cu₂O nanowires are crystallized well. The XRD patterns of the as-prepared Cu₂O nanowires clearly illustrates that all of the diffraction peaks of the products can be well-indexed to the cubic phase of Cu₂O (JCPDS No. 78-2706). No impurities are detected in the XRD patterns of these Cu₂O nanostructures.



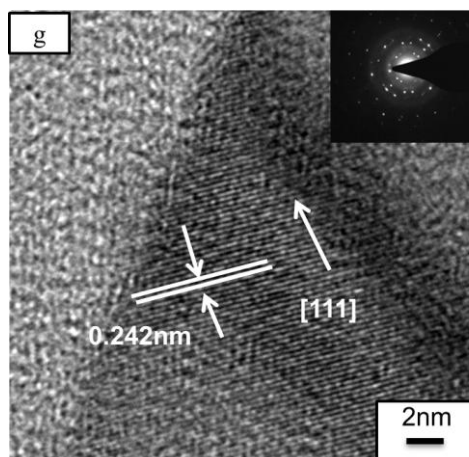


Figure 35(a)-(f) TEM images of the nanowires under different magnifications. (g) HRTEM image of the prepared nanowires and diffraction pattern of the nanowires.

Figure 35 (a)-(f) show a wire-like nanoparticle with a porous surface, and these nanowires are straight with uniform diameters in the range of 5 to 20 nm, with clear lengths of up to several tens of micrometers. For Cu_2O nanowires, the interplanar distance of fringes parallel to the wire axis is 0.242 nm, as shown in the HRTEM image of Cu_2O nanowires, corresponding to the (111) planes of cubic Cu_2O . The diffraction rings of the SAED pattern, inset in figure 35(g), can be indexed on a cubic cell of, showing that the obtained nanowires in this sample consist of only cubic Cu_2O but in form of polycrystalline.

The formation of cuprous oxide nanowires in the solution can follow two paths: (i) precipitant $\text{Cu}(\text{OH})_2$ nanowires are grown and later will be reduced to cuprous oxide nanowires, or, (ii) $\text{Cu}(\text{OH})_2$ particles are formed at the beginning of the reaction and then will be transformed to cuprous oxide nanowires. CTAB is applied to form a copper compound in the shape of nanowires, and the products of chemical reaction are guided into one dimension[138]. Once the nanowires have been achieved, the transformation to cuprous oxide finishes, retaining the original one-dimensional morphology of the precipitate nanowires.

The sufficient OH^- species in the reaction solution give rise to the fabrication of intermediate $[\text{Cu}(\text{OH})_4]^{2-}$ ion. The Cu^{2+} nuclei's further crystallization process via Ostwald ripening which causes weir like morphology. Surfactant CTAB results in the phase separation with the attendance of inorganic salt and forms micelles in the reaction solution. The morphology and structure of micelles in the reaction solution supplied the control over the shape of the nanoparticles during growth process. CTAB micelles exist in layer structure at room temperature which allows the middle structure to take onto weir like morphology along crystal growth direction. The interface between micelles and their respective opposite ions on special crystallographic facets greatly affect the morphology of nanoparticles. These cationic micelles react with $[\text{Cu}(\text{OH})_4]^{2-}$ anions and lead to the formation of unstable middle structure $[\text{Cu}(\text{OH})_4]^{2-}$ -CTAB complex. The $[\text{Cu}(\text{OH})_4]^{2-}$ ions attach preferentially on the surface of cationic micelles to form layer morphology. This weir shape morphology of $[\text{Cu}(\text{OH})_4]^{2-}$ -CTAB complex starts decreasing as the reducing agent is added and octahedral morphology observed by the process of orientated attachment[139]. By increasing the amount of reducing agent, the octahedral morphology is modified to whisker shaped structures. The morphology of nanoparticles is mainly based on the attendance of different kinds of chemical species in the reaction system and the thermodynamic stability of the nanoparticles in the crystalline domain. That is, the CTAB molecules are favorable for the growth of anisotropic morphology.

4.4.2 Synthesis of Cu_2O wires coated with TiO_2

For the preparation of $\text{Cu}_2\text{O}/\text{TiO}_2$ wire-like structure colloids, firstly, 0.05mL titanium (IV) butoxide 97% (TBT) was added to 10mL ethylene glycol (EG). The mixture was magnetically stirred for 8 hours at room temperature as solution A. Secondly, 3mL 0.01M prepared Cu_2O nanowires was added into 10mL acetone under stirring for 5 minutes as solution B, leaving it for 1 hour. The yellow brown precipitates were obtained by centrifugation and these precipitates were heated in 100°C water for 2 hours.

To get $\text{Cu}_2\text{O}/\text{TiO}_2$ nanowires, the colloids were centrifuged at rate of 3000 r/s for 10 minutes and washed with ethanol, at last dried in vacuum at 80°C for 24 hours.

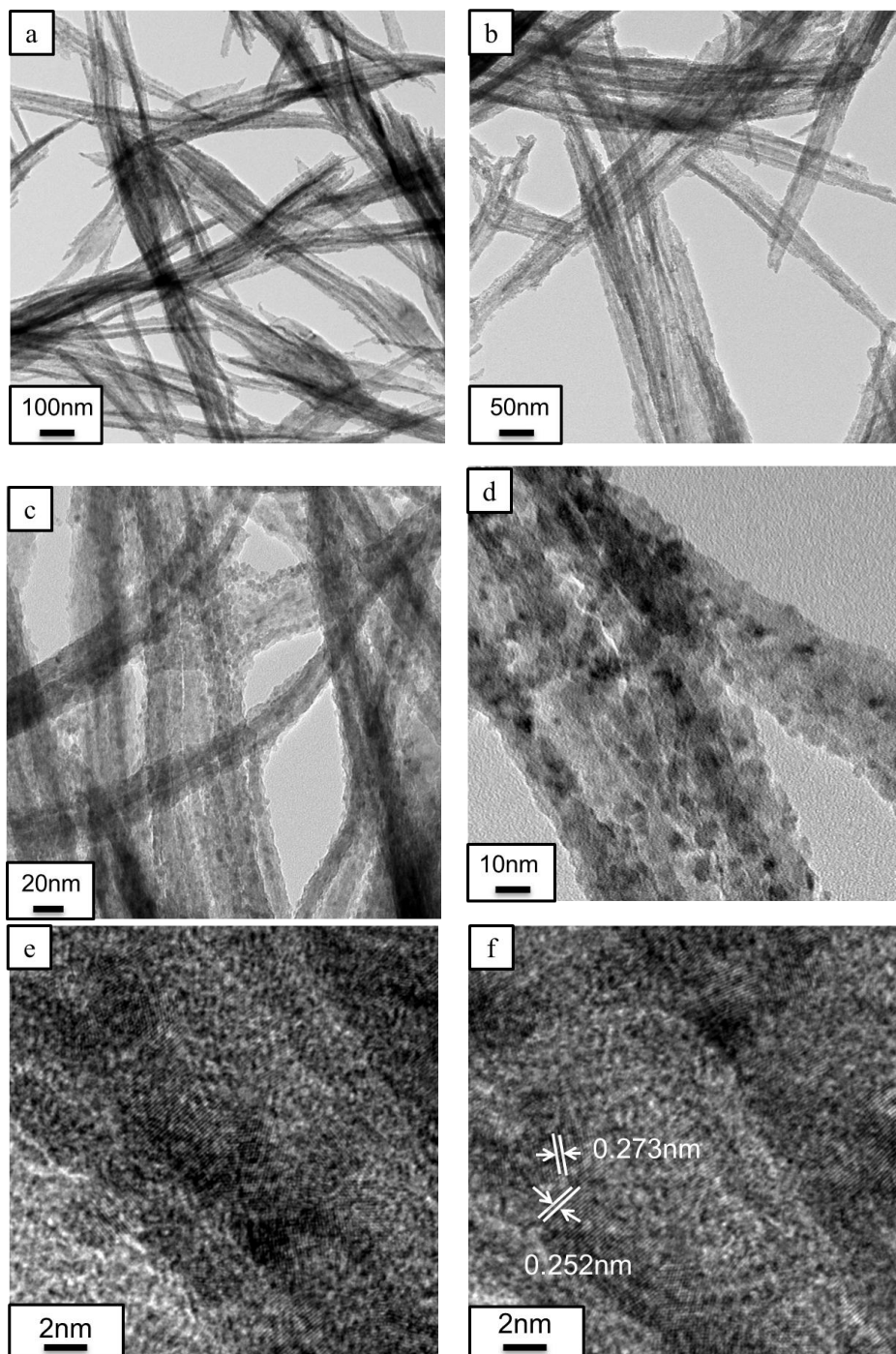


Figure 36(a)-(d) TEM images of the $\text{Cu}_2\text{O}/\text{TiO}_2$ nanowires under different magnifications; (e)-(f) HRTEM image of the $\text{Cu}_2\text{O}/\text{TiO}_2$ nanowires.

The higher magnification TEM images show that a layer of TiO₂ nanoparticles has been successfully coated on the surface of Cu₂O nanowires, which has been confirmed by EDS mapping image in figure 37. The HRTEM images (Figure 36f) shows the lattice fringes of 0.252nm and 0.273nm, respectively.

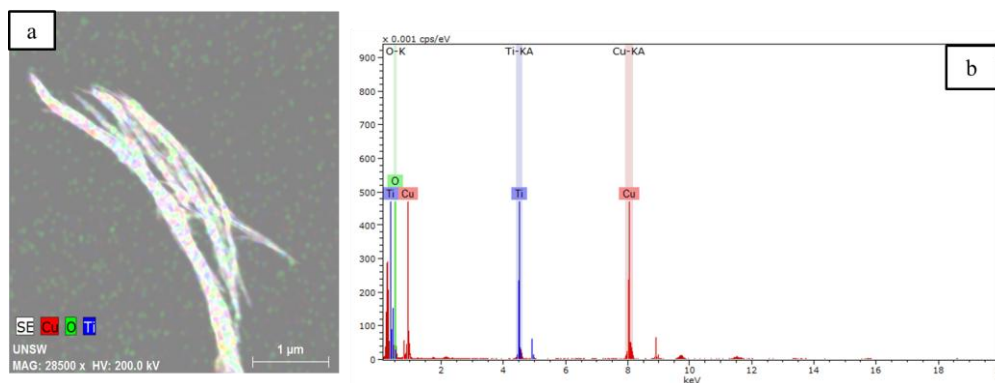


Figure 37 EDS image of the Cu₂O/TiO₂ nanowires; (a) EDS mapping of the prepared Cu₂O/TiO₂ nanowires; (b) Graphic of the prepared Cu₂O/TiO₂ nanowires.

The compositions of the prepared Cu₂O/TiO₂ nanowires were tested by EDS mapping, the graphic of the mapping shows the elements constitution of the nanowires are copper, titanium, and oxygen.

4.4.3 Photocatalyst performance of the prepared nanoparticles

For the photocatalytic activity measurements, 20mg of synthesized Cu₂O and Cu₂O/TiO₂ wire-like nanoparticles were used. The entire centrifuged nanocrystals were dispersed in 90 mL of 20 mg/L aqueous methylene blue solution. Before illumination, the cell was constantly stirred for 30 min in the dark for the molecules to adsorb onto the particle surfaces. After that the cell was irradiated with light from a 500 W xenon lamp placed 28 cm away. The light intensity reaching the cell was measured to be 500mW/cm². UV-vis absorption spectra of the samples were taken before and after every 5-10 min of irradiation for up to 80 minutes by removing the cap to withdraw the solution.

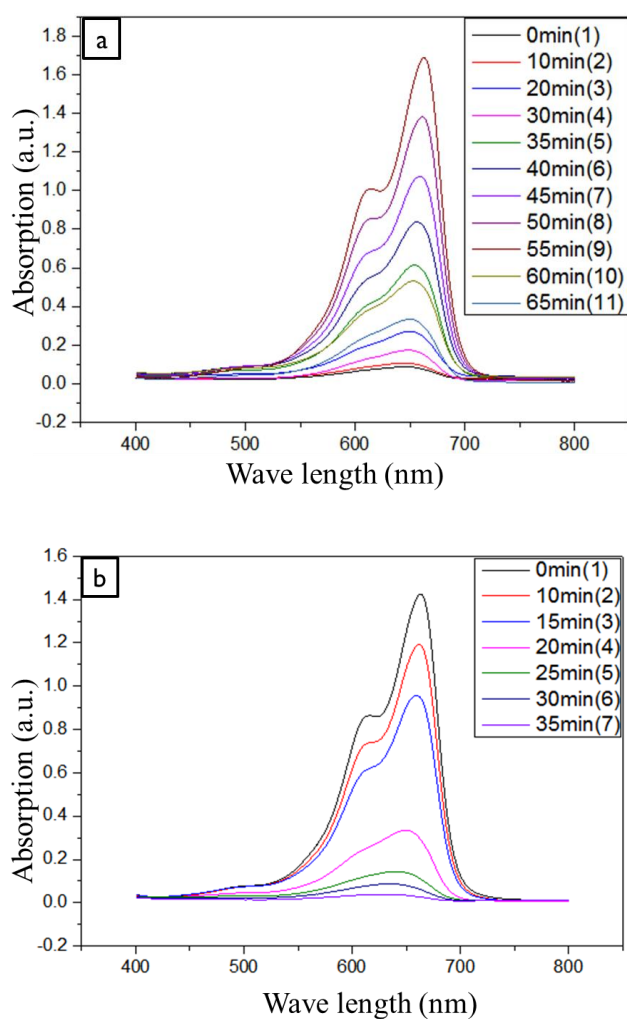


Figure 38(a) Photocatalyst test of Cu_2O nanowires, (b) Photocatalyst test of $\text{Cu}_2\text{O}/\text{TiO}_2$ nanowires.

The results of photocatalysts tests have been shown in Figure 38. The composite $\text{Cu}_2\text{O}/\text{TiO}_2$ nanowires show shorter degradation time than that of the pure Cu_2O nanowires. The degradation time for pure Cu_2O nanowires and the $\text{Cu}_2\text{O}/\text{TiO}_2$ nanowires are ~65min and ~35min, respectively.

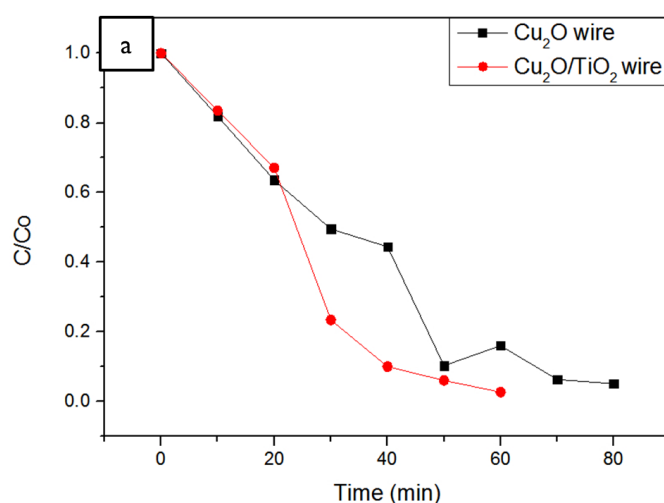


Figure 39(a) the photodegradation of MB in the presence of pure Cu₂O nanowires and Cu₂O/TiO₂ nanowires.

As explained before, Langmuir-Hinshelwood model, the degradation of dyes could be described as a pseudo-first-order reaction when C_0 is very small: $\ln(C_0/C) = kt$, where k is the apparent first-order-reaction rate constant[140]. The degradation data were analyzed to facilitate the mathematical interpretation of the degradation rate constant. The logarithmic plots of C/C_0 in case of degradation of dyes could not generate the line with only one slope, which results from pseudo-first-order rate constant. Instead, there are two possible k for each photocatalysis process can be used to demonstrate the whole degradation reaction, as described in our testing systems. In the case of degradation of MB, k_1 value for Cu₂O nanowires, Cu₂O/TiO₂ nanowires, in the first stage of the reaction was estimated as 8.3, and 8.7 min⁻¹, respectively. While with degradation going, another k_2 value appeared to show the kinetics process increases to 9.3, and 9.5 min⁻¹.

There has been extensive study directed towards modifying the bandgap of titanium and thus extending its photoresponse into the visible region by mixing it with various transition metal oxide dopants with limited success. The presence of metal oxide ions has been found to prevent the photocatalytic efficient of TiO₂; generally, as the visible-spectrum response can be improved by mixing the photo generated electron-hole pair with small-bandgap material, thus keeping all efficiencies at similar levels. The second difficulty to overcome in obtaining an effective material for

photocatalytic applications or water-photolysis is the design of an optimal architecture that uses all the photons having wavelengths within the photosensitive region of the material. This topic is less material-specific in that an optimal material architecture would be inherently desirable for any semiconductor photoelectrode. Promising properties are architectures with minimal reflectance that facilitates charge carrier separation, transport and collection for maximizing the quantum yield. This is a critical topic and one commonly ignored, since in the fabrication of 'practical' photo conversion efficiencies any energy losses during and after absorption can only be compensated by the absorption of additional photons.

Compared with nanospheres, nanowires show a better photocatalysis performance because the larger surface area and porous structure.

4.5 Conclusions

We have demonstrated a facile but efficient approach to synthesis Cu_2O nanowires, and investigated their properties for potential applications. The findings are summarized below:

- (1) The synthesis of Cu_2O nanowires can be readily achieved by choosing suitable surfactant in the solution system. This method has the significant feature in which the nanoparticle is pure and easily to grow at room temperature. The addition of a strong reducing agent allows surface defects or porous sites to be created for stable nanowires. The positively functional groups of the CTAB molecules have been found to highly interact with the side wall surface of the nanowire because of the relatively larger negative energies. CTAB could lead to form 1-D nanostructure.
- (2) The as-prepared nanocomposites ($\text{Cu}_2\text{O}/\text{TiO}_2$) show a better photocatalysis performance than pure Cu_2O nanowires, which illustrates that p-n composites have better functions.
- (3) The mapping result indicates that TiO_2 nanoparticles are easier to load on the pores of the as-prepared Cu_2O nanowires, which illustrates that porous structure has larger surface energy.

The findings would be useful for shape-controlled synthesis of nanowires and nanocomposites of wire-like morphology, which is meaningful for potential applications.

Chapter 5 – Cuprous Oxide Nano octahedrons: Synthesis, Growth, and Applications

5.1 Abstract

This study presents the synthesis process and the growth mechanism of nano octahedral. The approach is from the last chapter, it raise a new topic. That is, both CTAB and hydrazine hydrate are important for the octahedral morphology fabrication.

Based on the coating approach, $\text{Cu}_2\text{O}/\text{TiO}_2$ octahedral core-shell structure was synthesized, and its photo catalyst performance was also tested. Because Cu_2O is easy to dissolve in ammonia solution, it is a promising template for the other materials. In this chapter octahedral nanocages were fabricated based on this ammonia etching method.

5.2 Introduction

As is well known, morphology, dimension and microstructures are the main factors that decide the chemical and physical properties of metal oxides. Thus, it is still of great interest to fabricate single-crystalline octahedral nanoparticles and to control the particle dimension in a narrow size distribution over a wide adjustable range with simple approach at room temperature[141].

Currently, hydrothermal method, template method, and solution-phase synthesis method are the main wet-chemical methods carried out for the fabrication of Cu_2O nanoparticles. In these methods, additives, including organic polymers and inorganic ions, are usually added to modify the morphology and size of the products. However, the additives are usually expensive or toxic, which can be difficult to remove and bad for the

environment. This study reports the synthesis of Cu₂O nano octahedral, which is based on the method raised up in the previous chapters. Only a little modification of the synthesis procedure results in the revolutions of the morphology. The morphology and composition of the products will be characterized by various techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The photocatalytic properties of these Cu₂O nano octahedral will be evaluated using methylene blue (MB) as the test dye. The findings may be useful for future design of metal oxide nanostructures with specifically exposed crystal surfaces with enhanced photocatalytic performance.

Cu₂O@TiO₂ core-shell structure is fabricated in a typical coating procedure, and also be compared with the other morphologies. In this study, a method for etching cuprous oxide is also investigated. Cu₂O as a kind of sacrificed template shows a dissolvable property in ammonia solution, which allows the fabrication of the nanocages. We report a method to get rid of the core Cu₂O without breaking the shell TiO₂, which is important for the investigation for hollow structures.

5.3 Experimental Section

Many methods have been reported for synthesis of Cu₂O octahedrons. However, few of them are room temperature methods. Based on the synthesis method of nanowires, nano octahedrons have been fabricated, and we have found a relationship between morphology, surfactant, and reducing agent.

5.3.1 Chemicals

Copper sulfate (CuSO₄.5H₂O), hydrazine hydrate(N₂H₄.H₂O, 99%), sodium hydroxide (NaOH, Reagent grade), cetyltrimethylammonium bromide (CTAB, AR Grade) are purchased from Sigma- Aldrich, and used as received without further treatment.

5.3.2 Characterization

The phase composition and purity of the as-prepared Cu₂O microstructures were examined using Phillips X'pert Multipurpose X-Ray Diffraction System (MPD) with Cu-K α radiation ($\lambda = 1.54 \text{ \AA}$) operated at 40 kV and 40 mA, in the 2θ range of 20-70 °. Scanning electron microscopy (SEM) analysis was conducted using a FEI Nova Nano SEM 230 field emission scanning electron microscope. The transmission electron microscopy (TEM) images were obtained using a Tecnai G² 20 transmission electron microscope operated at an accelerating voltage of 200 kV. High resolution transmission electron microscopy (HRTEM) images were recorded on a Phillips CM200 field emission gun transmission electron microscope with an accelerating voltage of 200 kV. UV-vis absorption spectrum was obtained on a CARY 5G UV - visible Spectrophotometer (Varian) with a 1cm quartz cell.

5.3.3 Synthesis of Cu₂O octahedrons

In a typical process, 0.125g of CuSO₄.5H₂O powder was first dissolved into 100mL of distilled water to a 0.005M light blue aqueous CuSO₄ solution. Then, surfactant CTAB (the mole ratio of surfactant to Cu²⁺ is 1:1) was added into the above solution under strong magnetic stirring. After 15 minutes of stirring, 0.42 mL of 6mol/L NaOH solution was titrated slowly into the mixture solution. After another 15 minutes of stirring, different amounts of reducing agent solutions were wisely dropped into mixture solution at room temperature as comparisons, and red precipitate began to form. After about 1h, the experiment was stopped and the final products were obtained by centrifugation and thoroughly washed several times with ethanol and distilled water.

5.3.3.1 Effect of reducing agent and surfactant

By adjusting the mol ratio of reducing agent (N₂H₄.H₂O) to Cu²⁺, the forming process of octahedron has been observed.

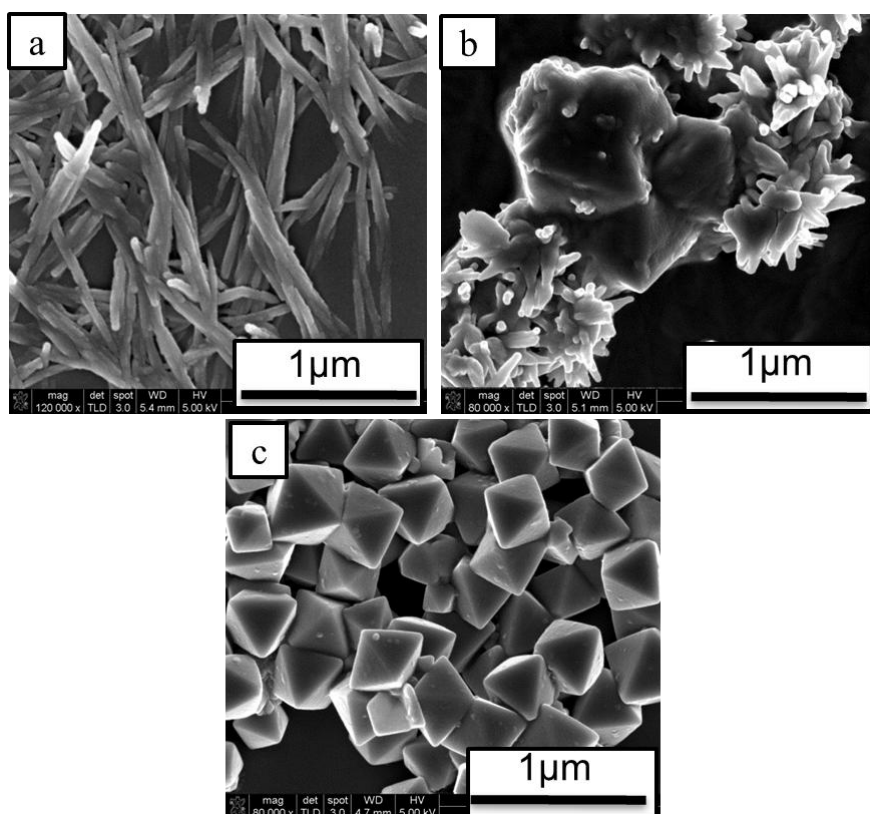


Figure 40 SEM images of Cu_2O synthesized with different mole ratio of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ to Cu^{2+} (a) 1:1, (b) 5:1, (c) 10:1.

Figure 40 shows a morphology revolution from wire to octahedron, which is due to the changing of the amount of reducing agent. When the mole ratio of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ to Cu^{2+} is 1:1, the product is nanowire as reported in the last chapter. However, when the ratio increases to 5:1, figure 40 (b) illustrates a mixture of wire-like and octahedron-like nanoparticles, and the wires start to aggregate. Moreover, the phenomenon has been confirmed by EDS mapping in figure 40 (a). Finally, the ratio reaches 10:1, the morphology is almost pure octahedron, as shown in figure 40 (c).

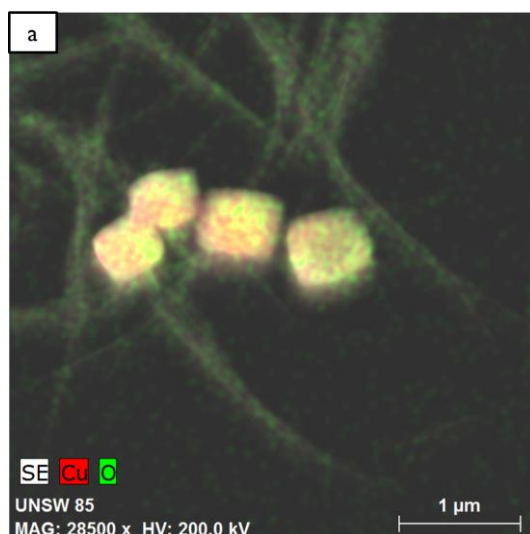


Figure 41 EDS mapping of Cu₂O synthesized with mole ratio of N₂H₄.H₂O to Cu²⁺ is 5:1.

A transformation of Cu₂O octahedrons with the attendance of NH⁴⁺ ions provides more information regarding the effect of NH⁴⁺ ions on the relative stability of the {100}, {111}, and {110} planes, which is opposite to the growth rate along the <100>, <111>, and <110> directions. It has been illustrated that, while the {100} surfaces constantly decreased in area, the {110} surfaces increased area and then decreased[142]. At the same time, the {111} planes continually increased in area, eventually leading to an octahedral morphology. This result indicates that the most stable planes in the medium containing NH⁴⁺ ions are the {111} planes. The temporary appearance of {110} planes is due to the relative stability of planes in this system being in the order of {100} {110} {111}. In this situation, both the {110} and {111} planes are more stable than {100} planes and initially gained in area, but eventually the crystal surface is composed of only the most stable {111} planes[22].

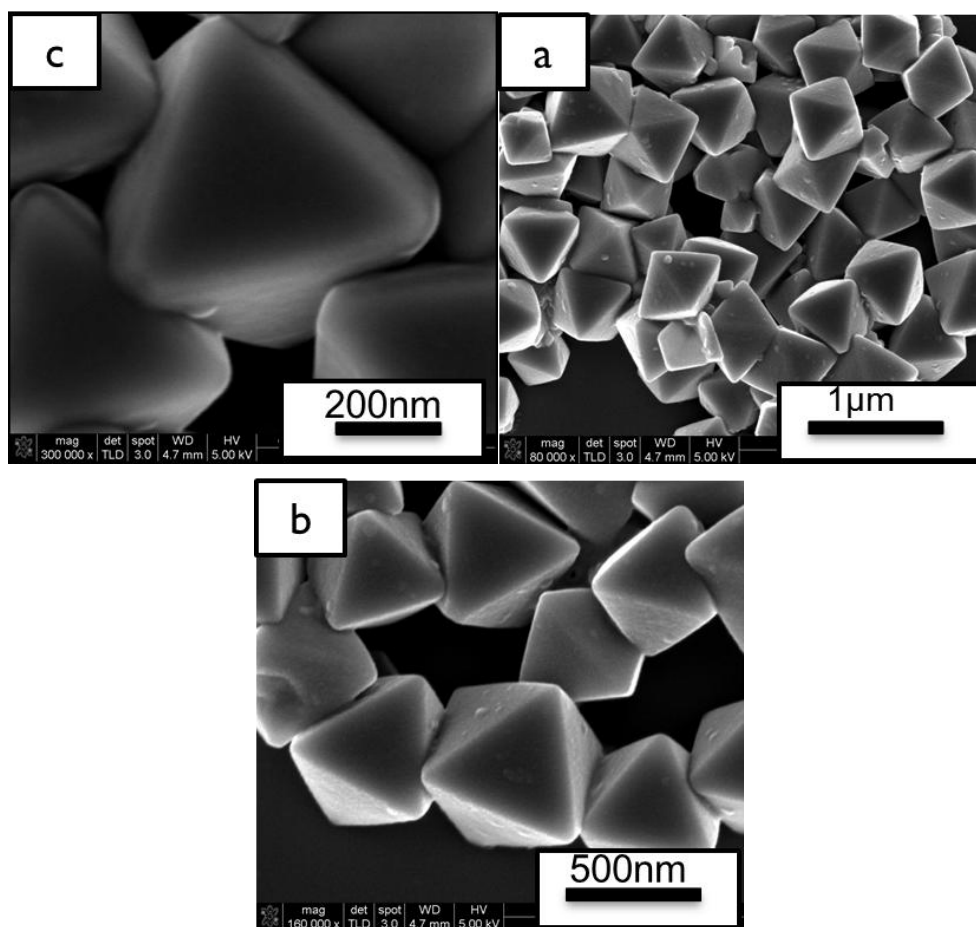


Figure 42 SEM images of Cu₂O octahedrons under different magnifications.

Figure 42 shows as prepared Cu₂O octahedrons under different magnifications. It demonstrates that nearly uniform Cu₂O octahedrons with a diameter of ~500nm have been successfully fabricated.

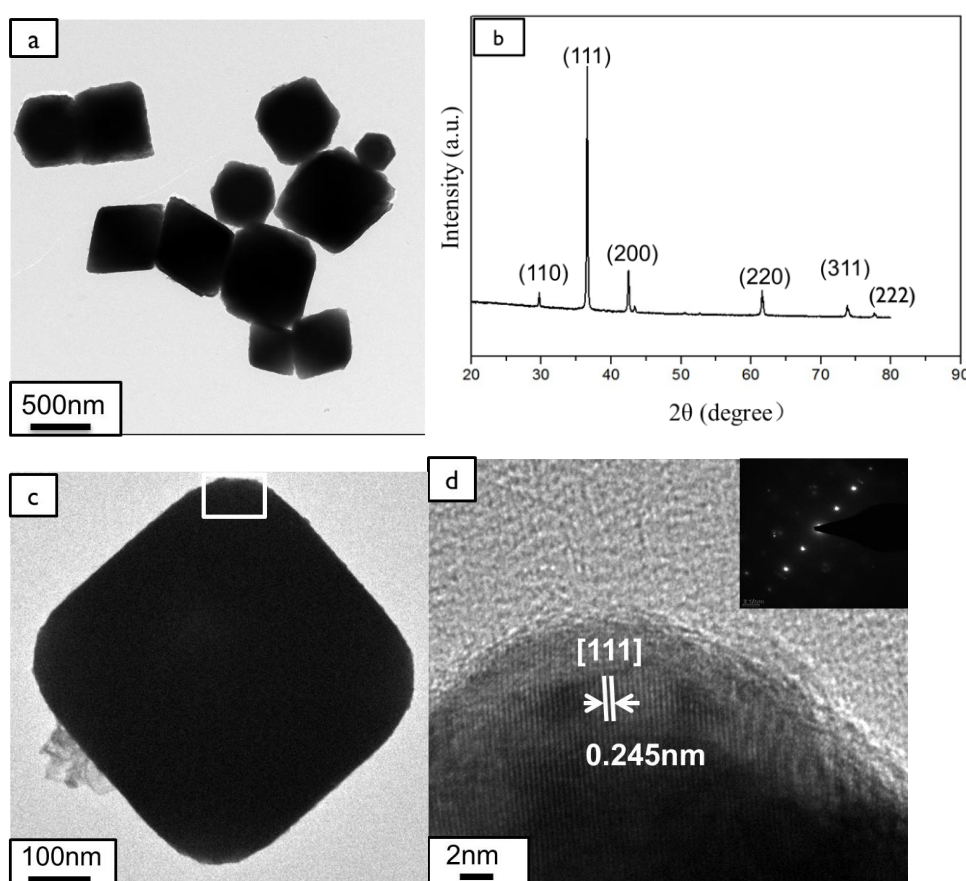


Figure 43 (a) TEM image of Cu_2O octahedrons; (b) XRD pattern of Cu_2O octahedrons; (c) HRTEM image of a Cu_2O octahedron; (d) the lattice structure of one octahedron.

Figure 43(a) demonstrates nearly uniform Cu_2O nano octahedrons with a diameter of $\sim 500\text{nm}$ have been successfully synthesized. Figure 43(b) shows the XRD patterns of the as-prepared Cu_2O octahedrons. Clearly, all of the diffraction peaks of the products can be well-indexed to the cubic FCC phase of Cu_2O (JCPDS No. 78-2706). No impurities, such as CuO or $\text{Cu}(\text{OH})_2$, are detected in the XRD patterns of these Cu_2O nanostructures. Thus, pure Cu_2O nano octahedrons can be fabricated by this method.

For Cu_2O octahedrons, the interplanar distance of fringes parallel to the octahedron axis is 0.245 nm , as shown in the HRTEM image of Cu_2O octahedrons, corresponding to the (111) planes of cubic Cu_2O . The diffraction rings of the SAED pattern, inset in Figure 43(d), can be indexed on a cubic cell of, showing that the obtained nanowires in this

sample consist of only cubic Cu_2O . These results are consistent with the SEM and TEM characterization.

5.3.4 Synthesis of Cu_2O octahedrons coated with TiO_2

For the preparation of $\text{Cu}_2\text{O}@\text{TiO}_2$ octahedrons structure colloids, firstly, 0.05mL titanium (IV) butoxide 97% (TBT) was added to 10mL ethylene glycol (EG). The mixture was magnetically stirred for 8 hours at room temperature as solution A. Secondly, 3mL 0.01M prepared Cu_2O nanowires was added into 10mL acetone under stirring for 5 minutes as solution B, leaving it for 1 hour. The yellow brown precipitates were obtained by centrifugation and these precipitates were heated in 100°C water for 2 hours. To get $\text{Cu}_2\text{O}@\text{TiO}_2$ nano octahedrons, the colloids were centrifuged at rate of 3000 r/s for 10 minutes and washed with ethanol, at last dried in vacuum at 80°C for 24 hours.

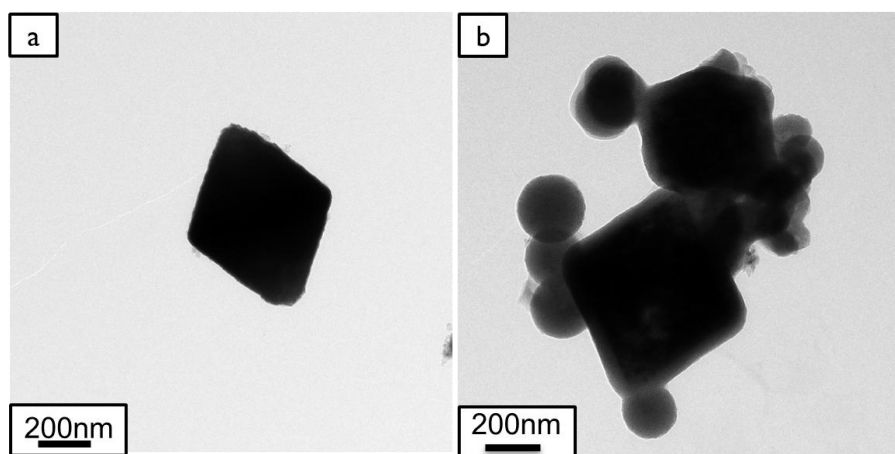


Figure 44 (a) TEM image of Cu_2O octahedron; (b) $\text{Cu}_2\text{O}@\text{TiO}_2$ octahedrons.

Figure 44 (a)-(b) illustrate the prepared Cu_2O octahedrons have been coated with TiO_2 colloids. Additionally, the large interface area between Cu_2O and TiO_2 can be clearly seen, indicating the two components are well contacted with each other to fabricate p-n heterojunction which is beneficial to photocatalysts.

5.3.5 Photo catalyst performance of the prepared nanoparticles

For the photocatalytic activity measurements, 20mg synthesized Cu_2O and $\text{Cu}_2\text{O}@\text{TiO}_2$

octahedrons were used, respectively. The entire centrifuged nanocrystals were dispersed in 90mL of 20mg/L aqueous methylene blue (MB) solution. Before illumination, the cell was constantly stirred for 30 minutes in the dark for the molecules to adsorb onto the particle surfaces. After that the cell was irradiated with light from a 500 W xenon lamp placed 28 cm away. The light intensity reaching the cell was measured to be 500mW/cm². UV-vis absorption spectra of the samples were taken before and after every 5-10 minutes of irradiation for up to 80 minutes by removing the cap to withdraw the solution.

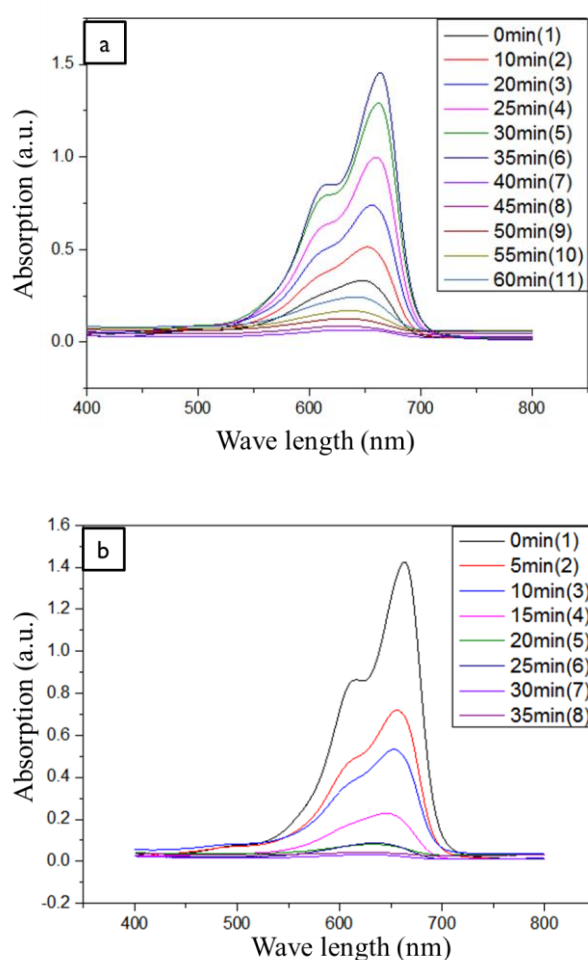


Figure 45(a) Photocatalyst test of Cu_2O octahedrons, (b) Photocatalyst test of $\text{Cu}_2\text{O}@\text{TiO}_2$ octahedrons.

The results of photocatalysts tests have been shown in Figure 45. The composite

$\text{Cu}_2\text{O}@\text{TiO}_2$ has shorter degradation time than that of the pure Cu_2O . The degradation time for pure Cu_2O octahedrons and the $\text{Cu}_2\text{O}@\text{TiO}_2$ octahedrons are $\sim 60\text{min}$ and $\sim 30\text{min}$, respectively. The energy transfer from Cu_2O to the TiO_2 through a dipole-dipole interactions and the electron transfer from the Cu_2O core to the TiO_2 shell, are the two possible mechanisms that can describe the degradation process.

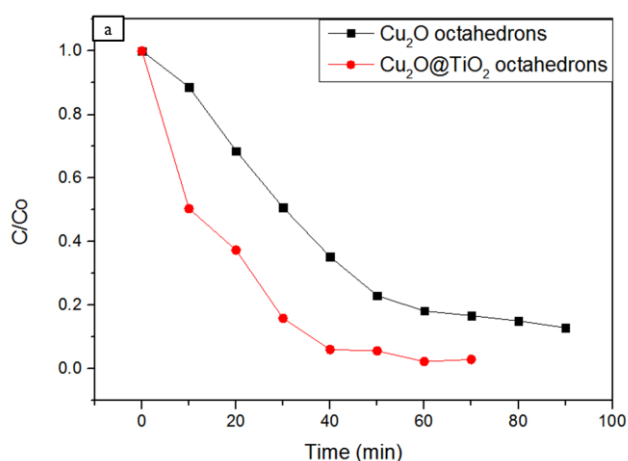


Figure 46(a) the photodegradation of MB in the presence of pure Cu_2O octahedrons and $\text{Cu}_2\text{O}-\text{TiO}_2$ octahedrons.

As reported in last chapter, Langmuir-Hinshelwood model, the degradation of dyes could be described as a pseudo-first-order reaction when C_0 is very small: $\ln(C_0/C) = kt$, where k is the apparent first-order-reaction rate constant. The degradation data were analyzed to facilitate the mathematical interpretation of the degradation rate constant. . In the case of degradation of MB, k_1 value for Cu_2O octahedrons, $\text{Cu}_2\text{O}@\text{TiO}_2$ octahedrons, in the first stage of the reaction was estimated as 8.5, and 8.9 min^{-1} , respectively. While with degradation going, another k_2 value appeared to show the kinetics process increases to 10.1, and 11.3 min^{-1} .

5.3.6 Etching of Cu_2O octahedrons coated with TiO_2

In recent years, hollow micro/nanostructures are very attractive because of their promising application on many areas [143, 144]. Hollow octahedrons are typical three-dimensional structures exhibiting special properties of low density, high specific surface area and active phases. Therefore, in the field of photocatalysis, photo-sensitive

materials can be prepared with the structure of hollow spheres. It has been reported that Zhangetal. has prepared In_2O_3 hollow spheres by using carbon spheres as template[145]. Based on the reports, In_2O_3 hollow spheres showed higher response compared with that of bulk particles. The enhancement in gas sensing properties has been resulted from their unique structure, large surface areas, and more surface active sites, which can be also promising for photocatalysis performance[146].

In this experiment, we report a facile synthesis of porous hollow octahedrons by a template-assisted approach using Cu_2O as the sacrificed template, which is based on the ammonia etching method. The method has the advantages of controllable synthesis, straight-forward equipment, and short reaction time. Furthermore, this approach can be applied for synthesizing other metal oxide hollow octahedrons. The products were characterized by TEM.

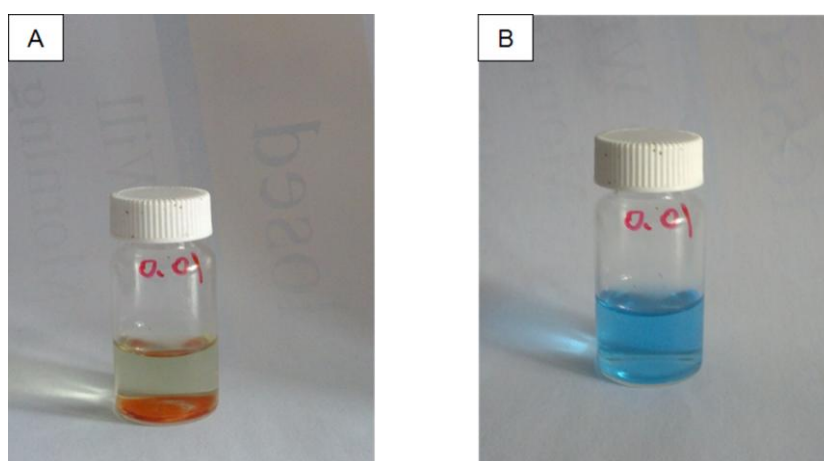


Figure 47(a) the pure Cu_2O octahedrons; (b) Cu_2O octahedrons in 35% ammonia solution for 15 min.

Figure 47 shows an ammonia solution treatment for Cu_2O nanoparticles, which proves the solubility of Cu_2O nanoparticles in ammonia. This could be a method to treat the $\text{Cu}_2\text{O}@\text{TiO}_2$ core-shell structure. That is, ammonia solution can get rid of the Cu_2O core but not damage the TiO_2 shell, then hollow structure can be fabricated[147]. We dissolved as prepared $\text{Cu}_2\text{O}@\text{TiO}_2$ nano octahedrons in the 35% ammonia solution for several hours to confirm that the entire cores Cu_2O have been dissolved.

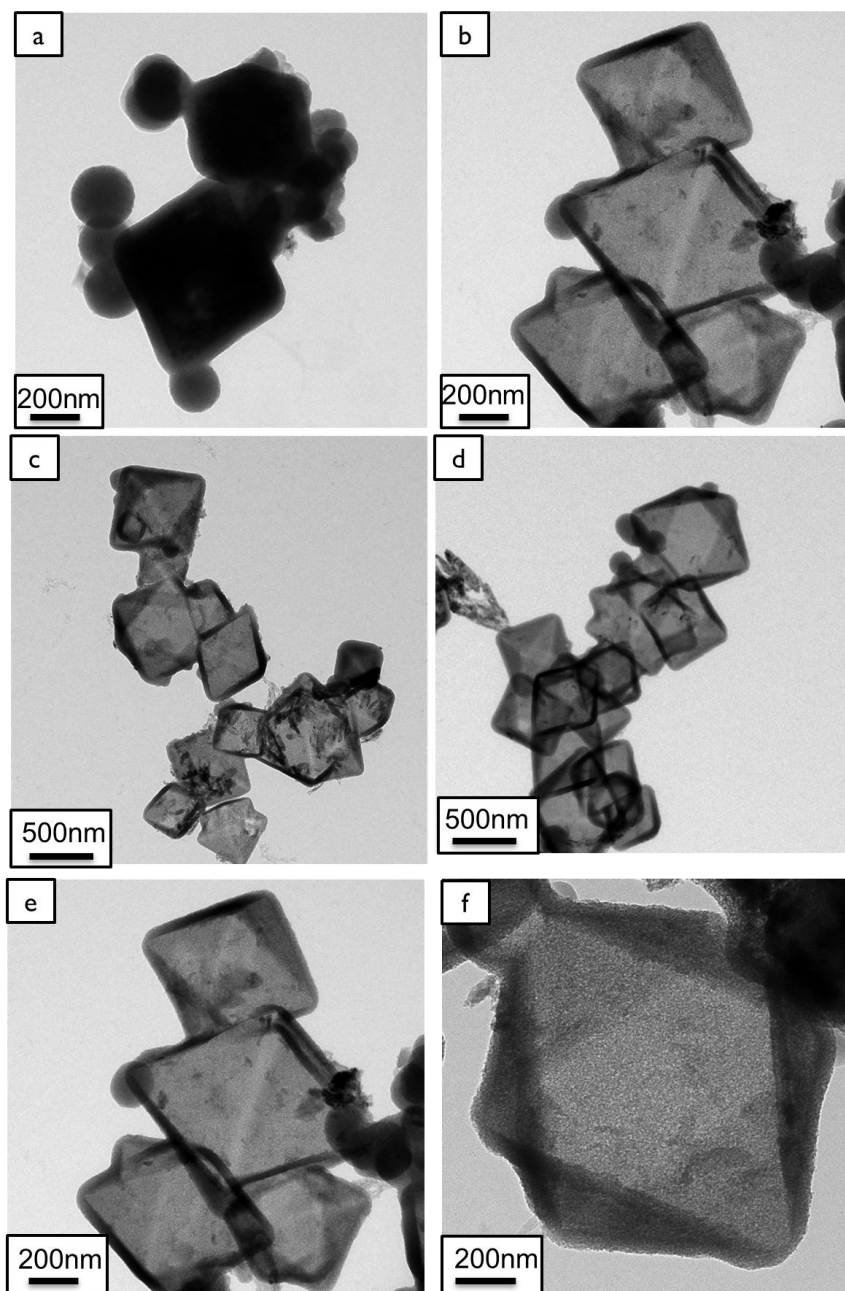


Figure 48(a) the $\text{Cu}_2\text{O}@\text{TiO}_2$ octahedrons; (b)-(f) Cu_2O octahedrons nanocages.

Figure 48 shows that TiO_2 hollow octahedrons have been synthesized at room temperature with the help of ammonia solution. The as prepared Cu_2O octahedrons with the diameter of $\sim 500\text{nm}$ are used as sacrificed template. The hollow octahedrons with low density and high surface area prepared using ammonia etching method could be used as sensors, catalysts, and material encapsulators or carriers[148]. This method is

very simple and safe, which can be also used for other metal oxide nanoparticles with a hollow interior.

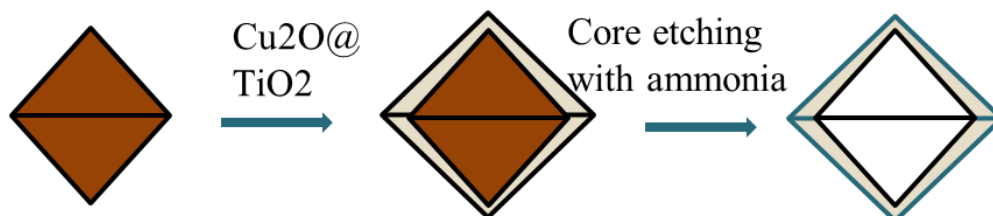


Figure 49(a) Scheme illustrating the etching procedure.

Figure 49 illustrates the simple etching procedure, which is important for the application of cuprous used as sacrificed template.

5.4 Comparisons of the three morphologies-sphere, wire, octahedron

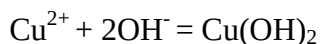
5.4.1 Comparison of synthesis method

	Concentration of CuSO_4 (mol/L)	Surfactant	Mole ratio of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ to CuSO_4
Sphere	0.005	SDS	1:1
Wire	0.005	CTAB	1:1
Octahedron	0.005	CTAB	10:1

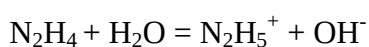
Table 1 Synthesis conditions of the three morphologies

Table 1 illustrates the tiny difference of the synthesis conditions. It indicates that SDS is benefit for the sphere-like structure; however, CTAB is the key to formation of nanowires. With the help of CTAB and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ octahedrons can be fabricated, which illustrates that extra $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ plays an important role in forming octahedrons.

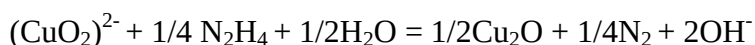
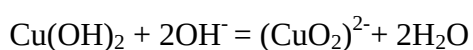
The Cu₂O nanowires are produced by the following reactions. Firstly, the CuSO₄ dissolves in water to generate Cu²⁺ ions in the solution according to Eq. 1:



Similarly, the reducing agent hydrazine hydrate dissolves in water to generate N₂H₅⁺ and OH⁻ ions in the solution, as represented by Eq. 2:



The generated



5.4.2 Comparison of UV-visible Absorption

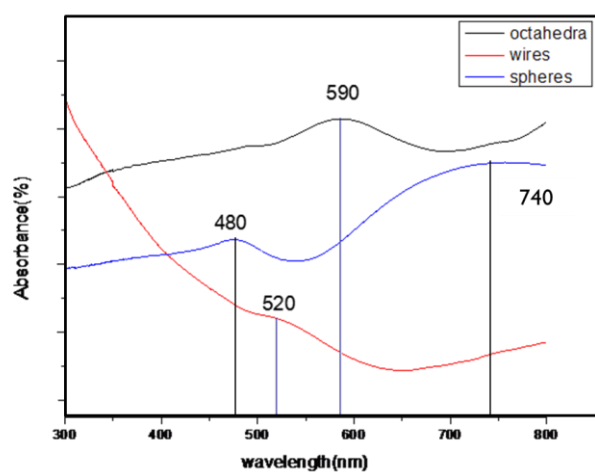


Figure 50 UV-visible absorptions of the three morphologies, nanospheres, nanowires, and nano octahedrons.

The optical properties of the as-prepared Cu₂O nanostructures were analyzed using UV-vis absorption spectroscopy and the absorption spectra of these samples are given in Figure 50. The Cu₂O nanospheres exhibit two strong UV-visible absorption peaks at around 740 and 480 nm, whereas the Cu₂O nanowires display a weak absorption peak at ~520 nm. In contrast, the Cu₂O nano-octahedron show a strong absorption band centered at ~590 nm. An interesting observation made during nanocrystal growth is a series of changes in the solution color. Immediately after addition of NaOH to the aqueous mixture of CuSO₄ and SDS, the solution was light blue from the formation of Cu(OH)₂ and possibly Cu(OH)₄²⁻ species. In the synthesis of Cu₂O nanocubes, the solution color turned from light blue to green within seconds after the introduction of N₂H₄.H₂O to start nanocrystal growth.

5.4.3 Comparison of XRD pattern

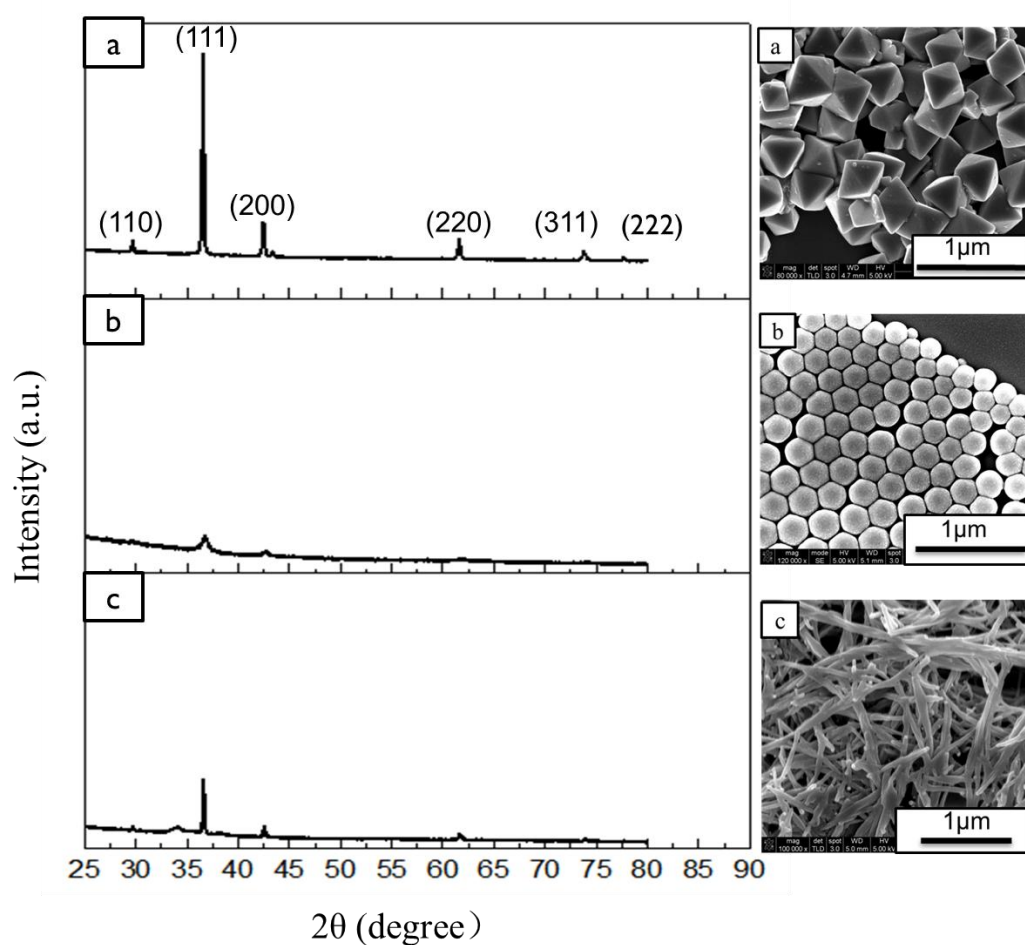


Figure 51 XRD patterns of the three different morphologies.

From Figure 51, it is clear that these Cu_2O nanostructures exhibit different intensity ratios of the (111) and (200) diffraction peaks ($I_{(111)/(200)}$). It is calculated that the $I_{(111)/(200)}$ for the Cu_2O nanospheres, nanowires and nanooctahedra are, respectively, indicating that the as-prepared Cu_2O nanooctahedra exhibit largely exposed (111) crystal planes.

5.4.4 Comparison of photocatalytic test

Cu₂O	Sphere	Wire	Octahedron
Time of degradation(min)	80	65	60
Cu₂O@TiO₂	Sphere	Wire	Octahedron
Time of degradation (min)	50	35	30

Table 2 Comparisons of photocatalytic test.

The {111} surface of Cu₂O nanoparticles has been demonstrated to be the active surface for the photodegradation of dye molecules and splitting of water by comparing the photocatalytic effects of nanospheres, nanowires and nano octahedrons[149].

Octahedrons with entirely {111} surfaces have shown a better performance in the photocatalytic degradation of dye molecules than those of other morphologies. These nanocrystals may exhibit more applications in photocatalysis and organic synthesis.

5.5 Conclusions

This study has demonstrated the role of N₂H₄.H₂O during the synthesis of Cu₂O nano octahedrons and a facile method to etch Cu₂O@TiO₂ nanoparticles. The findings can be summarized below:

(1) The extra N₂H₄.H₂O plays an important role in fabricating nano octahedrons, the result indicates that the most stable planes in the medium containing NH⁴⁺ ions are the {111} planes. In this research, both the {110} and {111} planes are more stable than {100} planes and initially gained in area, but eventually the crystal surface is composed of only the most stable {111} planes.

(2) Ammonia solution is a kind of useful and safe etching solution for $\text{Cu}_2\text{O}@\text{TiO}_2$ core-shell structures. That is ammonia can get rid of the core and leave the shell.

(3) The {111} surface of Cu_2O nanoparticles has been demonstrated to be the active surface for the photodegradation of dye molecules.

These results will be useful for understanding the mechanism of synthesizing octahedrons, especially for the determination of suitable chemicals to produce stable core/shell nanostructures and hollow structures for potential applications.

Chapter 6 Summary and Future Work

6.1 Nanospheres

We demonstrate a simple and effective one-step strategy for the synthesis of shape-controlled cuprous oxide (Cu_2O) nanospheres. The proposed method offer several advantages, including the room-temperature preparation, high yield and potential for large-scale preparation. In addition, SDS helped synthesizing nanospheres. We introduce a facile method to fabricate $\text{Cu}_2\text{O}@\text{TiO}_2$ core-shell structures, which is safe and fast. $\text{Cu}_2\text{O}@\text{TiO}_2$ core-shell spheres showed better photodegradation performance than pure Cu_2O nanospheres.

6.2 Nanowires

A room temperature method to prepare Cu_2O nanowires based on the synthesis of Cu_2O nanospheres has been investigated. The obtained nanowires have a diameter of $\sim 20\text{nm}$ and length up to several micrometers. The result demonstrates that CTAB can strongly benefit the growth of nanowires along $[111]$ direction. The addition of a strong reducing agent allows surface defects or porous sites to be created for stable nanowires. The result indicates that TiO_2 nanoparticles are easier to load on the pores of the as-prepared Cu_2O nanowires, which illustrates that porous structure has larger surface energy.

6.3 Nano Octahedrons

The synthesis investigation shows that both CTAB and hydrazine hydrate are important for the octahedral morphology fabrication. By increasing the mole ratio of reducing agent and CuSO_4 to 10:1, octahedrons can be obtained. The extra $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ plays an important role in fabricating nano octahedrons, the result indicates that the most stable

planes in the medium containing NH_4^+ ions are the {111} planes. In this research, both the {110} and {111} planes are more stable than {100} planes and initially gained in area, but eventually the crystal surface is composed of only the most stable {111} planes.

The {111} surface of Cu_2O nanoparticles has been demonstrated to be the active surface for the photodegradation of dye molecules and splitting of water by comparing the photocatalytic effects of nanospheres, nanowires and nano octahedrons.

Ammonia solution is a kind of useful and safe etching solution for $\text{Cu}_2\text{O}@\text{TiO}_2$ core-shell structures. That is ammonia can get rid of the core and leave the shell. Due to the dissoluble property of Cu_2O in ammonia solution, Cu_2O can be a sacrificed template for the other metal oxides to form hollow structures.

These studies have provided new insights for the formation mechanism of different morphologies and nanocomposites. It is possible to design a kind of nanoparticles that have more promising applications

6.4 Future Work

From the present work on cuprous oxide nanoparticles, nanocomposites, and their applications, there are still many areas that need to explore and may be of interest, including:

- (1) The growth mechanisms of Cu_2O of different morphologies under different surface modifications need to further studied.
- (2) More kinds of nanocomposites should be investigated, because Cu_2O is a p-type semiconductor. Moreover, p-n heterojunction shows better functional properties than the pure ones.
- (3) The investigations of hollow structures need to be carried out, due to the property of

Cu₂O as a template. Cu₂O can be easily removed by ammonia solution, so Cu₂O@metal oxide core-shell structures can be easily etched by ammonia solution. Hollow structures have larger surface energy so they may show more potential applications.

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