

在酸性条件下合成氧化亚铜纳米立方体

朱红飞 陈乾旺* 牛和林 彭振猛 孙 钱

(中国科技大学结构分析重点实验室和化学与材料学院,合肥 230026)

在微酸性(pH:4~6)的水热体系中 130 °C 反应 18 h 合成了氧化亚铜纳米粒子,粒径约为 100 nm,呈立方体外形。乙二胺和十六烷基胺在反应体系中充当缓冲试剂,调节反应液的 pH 值并控制体系中游离 Cu^{2+} 的浓度,使得 Cu^{2+} 不会被迅速还原成单质铜。所合成的纳米立方体的能带宽度约为 2.51 eV,比氧化亚铜体材料和氧化亚铜纳米线蓝移了 0.51 eV 和 0.17 eV,它有利于把太阳光谱中能量高的可见光转化成其他形式的能量。

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Growth of Cuprite Nanocubes under Acidic Conditions

ZHU Hong-Fei CHEN Qian-Wang* NIU He-Lin PENG Zhen-Meng SUN Qian

(Structure Research Laboratory and Department of Materials Science & Engineering,
University of Science & Technology of China, Hefei 230026)

A novel hydrothermal approach was developed to prepare cuprite at 130 °C for 18 h under slightly acidic conditions (pH: 4~6). The yielded particles are, about 100 nm in size, cubic in shape. It was found that diaminoethane and hexadecylamine acting as the buffering reagents for controlling the pH value and concentration of free Cu^{2+} in the solution play a critical role to avoid Cu^{2+} being reduced to Cu. The band gap of the nanocubes is about 2.51 eV, which is blue shifted 0.51 eV compared to that of the corresponding bulk material and 0.17 eV compared to that of the nanowires of cuprite. The material could be a promising candidate in solar energy conversion since the sample can make use of higher energy visible lights of solar spectrum. PACS: 71.35.Cc.

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0 Introduction

Cuprite (Cu_2O) and its related materials such as CuAlO_2 have obtained much attention^[1]. Cu_2O is simple cubic lattice with 4 Cu and 2 O atoms in its cell. The oxygen atoms form a tetrahedral diamond-like coordination structure and a Cu^+ ion occupies between two neighboring O^{2-} ions to form common linear $[\text{O}-\text{Cu}-\text{O}]^{3-}$ dumb-bell unit, while the Cu^+ ions form a face-centered cubic lattice, every unit contains eight

Cu_4 tetrahedra and four octahedral holes between them^[1,2]. The octahedral hole is a position of high potential energy, because it is surrounded by six O^{2-} ions at distances of 0.21 and 0.30 nm, where the tails of the oxygen single zeta model functions overlay significantly. The natural structure of cuprite makes it a promising material for the conversion solar energy into other forms of energy such as electrical energy, chemical energy and other kind of light^[3]. Recently Cu_2O

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* 通讯联系人。E-mail: cqw@ustc.edu.cn, Fax: +86-551-3631760, Tel: +86-551-3607292

第一作者:朱红飞,男,27岁,硕士研究生;研究方向:材料合成。

particles with different morphologies and applications have been synthesized with various methods^[4]. For instance, Cu_2O submicrospheres can be used as negative electrode materials for lithium nanobatteries^[5], Cu_2O microcubes of high uniformity could be applied in the field of solar energy conversion^[6], Cu_2O nanowires might have advantages in nanowire light emitting device with extreme low power consumption^[7].

Cu_2O is a weakly alkaline covalent compound, which can only exist in the alkaline or neutral atmosphere. At present, common methods to prepare Cu_2O by reducing Cu^{2+} to Cu^+ are under alkaline conditions (pH=10~12), and the reduction agents mainly concerned with N_2H_4 ^[8], sodium ascorbate^[6], and so on. As a rule, Cu_2O is disproportionated into Cu and Cu^{2+} ions in acidic atmosphere even a weak one immediately, making it hardly exists in the acidic atmosphere. Therefore, it is difficult to synthesize Cu_2O under acidic atmosphere directly. It could also be the main reason that there is no report on preparing it under acidic atmosphere. In this paper, a novel strategy was developed to prepare Cu_2O in a solution with pH varying from 4 to 6. The size of Cu_2O nanocubes can be decreased to 100 nm.

1 Experiment

All the chemical reagents used in this work were analytical grade. Cu_2O nanocubes were synthesized by the following procedure: 0.12 g of $\text{Cu}(\text{Ac})_2$ was dissolved in 40 mL distilled water, stirred for 5 min, when $\text{Cu}(\text{Ac})_2$ dissolved completely, 0.07 mL of anhydrous diaminoethane and 0.096 g of hexadecylamine were added to the solution, stirred violently, 10 minute later, the solution became turbid, 0.062 7 mL of 88% HCOOH was added to the solution, continued to stir for 5 minutes, the solution became clear. The ultimate pH value before the reaction was around 5. The solution was transferred into a Teflon cell, and kept at 130 °C for 18 h. The pH value after reaction was about 7. Then yellow or brick red product was separated from the clear solution. The products were washed with distilled water for 3 times, and centrifuged at 4 000 rpm for 30 minutes to remove hexadecylamine from the samples. XRD patterns were carried out on an 18 kW advance X-ray diffractome-

ter with $\text{CuK}\alpha$ radiation ($\lambda=0.154\ 056\ \text{nm}$). Transmission electron microscope (TEM) analysis was taken on a Hitachi H-800 microscope with a tungsten filament, using an accelerating voltage of 200 kV. The ultraviolet and visible light (UV-Vis) spectrum was obtained via a JGNA Specord 200 PC UV-vis spectrophotometer at room temperature.

2 Results and Discussion

From Fig.1, it is found that the formation of Cu_2O occurs in the temperature range from 120 °C to 150 °C, and 130 °C is the optimal temperature for the preparation of pure Cu_2O . With the increase of the temperature, Cu^{2+} tends to be reduced to copper. For example, as the temperature increases from 130 °C to 140 °C, copper appears (Fig.1C); and as the temperature rises from 140 °C to 150 °C, the content of the copper increases (Fig.1D), while the content of Cu_2O decreases. When the temperature is lower than 120 °C, reactions will be reluctant to take place, however, when the temperature is higher than 150 °C, the reduction agent HCOOH will decompose.

As shown in Fig.2, the relative intensity between the peaks of (220) and (200) changes significantly as

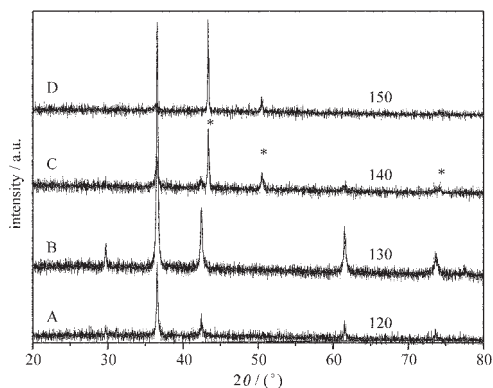


Fig.1 (A), (B), (C) and (D) are the XRD patterns of the products obtained at different temperatures. These samples were prepared with fixed concentration of $\text{Cu}(\text{Ac})_2$: $0.015\ \text{mol}\cdot\text{L}^{-1}$, HCOOH : 0.062 7 mL, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$: $0.001\ 75\ \text{mol}\cdot\text{L}^{-1}$, hexadecylamine: $0.015\ \text{mol}\cdot\text{L}^{-1}$. Solid circle in (A) represents the peak can not be identified, the stars in (C) represent the peaks of elemental copper, the solid square in (D) indicates a peak of cuprite.

the amount of $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ increases from 0.05 to 0.08 mL (pH value changes from 4 to 6), this intensity variation is due to oriented growth of the particles under high concentration of $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$.

Fig.3 shows the amount of $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ is out of the range from 0.05 to 0.08 mL, impurity will surely appear. Fig.2 and Fig.3 reveal the amount of $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ in the reaction system plays an important role on the formation of Cu_2O . When the pH value is in the range from 4 to 6 (the amount of $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ changes from 0.05 to 0.08 mL), pure Cu_2O can be obtained at 130 °C; as the pH value is lower than 4 (the amount of $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ is less than 0.05 mL), the reaction tends to generate copper; while higher than 6 (the amount of $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ is more than 0.08 mL), the products contain complex impurity phase. Further increase the pH value to 7 or higher, the reducing agent HCOOH will not take effect, and no product can be obtained.

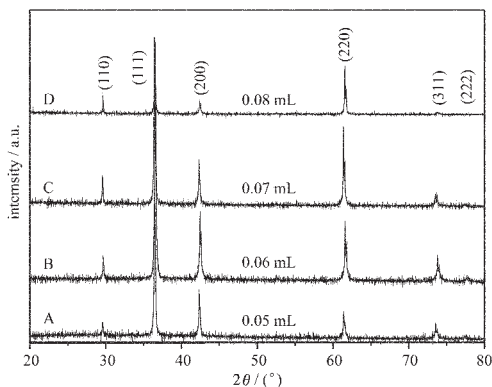


Fig.2 (A), (B), (C) and (D) are the XRD patterns of products obtained with fixed concentrations of $\text{Cu}(\text{Ac})_2$: $0.015 \text{ mol} \cdot \text{L}^{-1}$, HCOOH : 0.0627 mL , hexadecylamine: $0.015 \text{ mol} \cdot \text{L}^{-1}$ at 130 °C and with different amounts of $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ added

At the first stage of the reaction, HCOOH will react according to Scheme 1, and the products are formate [reaction (1), (2)]. The possibility for the formation of amides could be less due to the mild condition. It is well known that hexadecylamine is insoluble in aqueous solution due to its long alkyl. When HCOOH was added to the aqueous solution, reaction (2) takes place, so $\text{H}_2\text{NC}_{16}\text{H}_{31}$ could dissolve rapidly in the water with the presence of formate, even with the coexistence of diaminoethane.

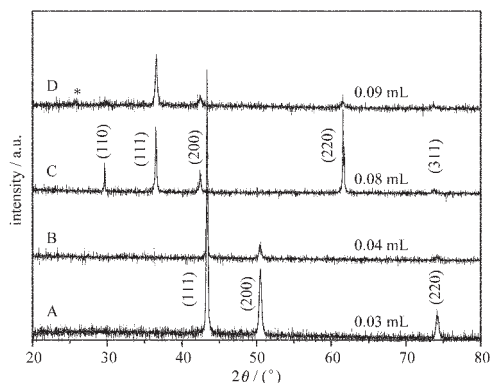
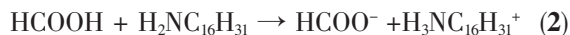
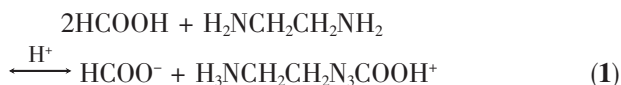


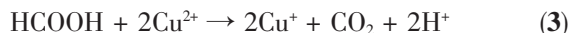
Fig.3 (A), (B), (C) and (D) are the XRD patterns of the products obtained at 130 °C with different amount of $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$

Solid square in (B) and star in (D) represent the peaks can't be identified. In (A) and (B) the pH value is lower than 4 and in (D) the pH value is higher than 6.



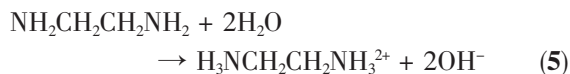
Scheme 1 Reactions of HCOOH in the system

Scheme 1 shows the reaction of HCOOH with diaminoethane and hexadecylamine, which is essential for controlling the concentration of HCOOH . Meanwhile HCOOH also takes the role as reducing agent for the formation of Cu^+ [reaction (3)], and forms a mediate through reaction (4)^[9].



Scheme 2 Reduction of Cu^{2+} to Cu^+ by HCOOH

In the system, the well-known reaction (5) would also take place.



Scheme 3 Hydrolyzation of $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$

Scheme 4 shows two possible approaches for the formation of Cu_2O . As we know that Cu_2O cannot exist in the acidic atmosphere. Based on above discussion, the following formation mechanism was suggested: With reaction (3) and (4) going on, more and more HCOOH was consumed to generate $\text{Cu}(\text{HCOOH})$ as a mediate. Meanwhile, the pH value also increases, at the end of the reaction it can reach 7. Hence, Cu_2O could be formed via reaction (6) under hydrothermal conditions. Cu_2O might not be produced through reac-

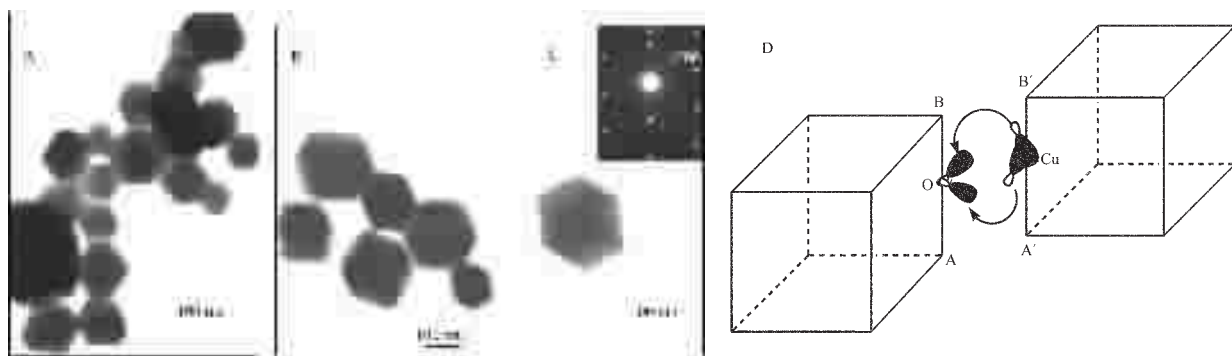
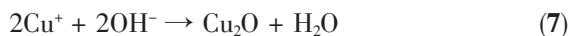


Fig.4 (A) TEM images of Cu₂O obtained at 130 °C for 18h with the addition of 0.001 75 mol·L⁻¹ diaminoethane and the concentration of hexadecylamine is 0.015 mol·L⁻¹

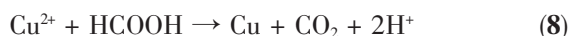
The self-arranged nanocubes are connected by edges to form a chain structure as marked by line a. (B) Side view of the edge-connected nanocubes. (C) One of typical nanocube with the width about 100 nm and its Electron diffraction pattern (Inset). (D) The sketch map of the edge-to-edge connection of two cubes. The black solid circle represents the copper atom and the empty circle represents the oxygen atom, respectively. (AB and A'B' are the edges of two cubes).

tion (7) due to low concentration of Cu⁺ in the solution.



Scheme 4 Two routes for generating Cu₂O

While, it is well known that HCOOH is a relative strong reducing reagent compared to Cu²⁺, excessive amount of HCOOH can lead to the formation of elemental copper, and the reaction is as follows:



Scheme 5 Subsidiary reaction of the system

However, as discussed above, when the pH value is higher than 4, equation (8) might not take place. The reaction of HCOOH with diaminoethane and hexadecylamine would also decrease the concentration of HCOOH and pH value. Furthermore, Cu²⁺ could coordinate with the N atom in the C₁₆H₃₁NH₂ and H₂NCH₂CH₂NH₂ molecules, therefore, the possibility of reaction (8) may decrease significantly. As a result Cu²⁺ can be reduced mildly to Cu⁺ through reaction (3). From these discussions, it can be seen there are two functions for diaminoethane: Controlling the pH value of the solution and acting as the buffering reagents for Cu²⁺. Fig. 4A shows highly aligned nanocubes (indicated with arrow a), the nanocubes tend to connect each other by edges rather than by faces (Fig.4(A,B)). Fig.4C shows a single nanocube with diameter about 100 nm. The inset is the electronic diffraction pattern of the

nanocube, which was indexed by (111) and (200) of Cu₂O. The weak covalent bonds between cubes might cause the connection of two nanocubes at the edges, and the long alkyl chain of hexadecylamine could act as the template for the nanocubes to assemble along a line. As shown in Fig.4D, the extended dangling bonds at the corner may adsorb each other to form [O-Cu-O]³⁻ dumb-bell unit, as they act in the microcosmic structure of cuprite lattice^[1], and then the two cubes self-assembled together.

Fig.5 shows nanocuboids with a width around 100 nm, formed as the concentration of hexadecylamine increased to 0.02 mol·L⁻¹. From the comparison between Fig.5 and Fig.4(A,B), it is suggested that hexadecylamine may also play the role on the oriented growth of the particles; its long alkyl chain may act as the template for the nanocubes to grow into nanocuboids. Diaminoethane could also take two kinds of roles in this system. The first one is as the buffering reagent, it holds the HCOOH at first not to let HCOOH react with Cu²⁺ completely, and reaction (8) will not take place at certain concentrations of hexadecylamine and diaminoethane. The second one is as the template for the oriented growth of the nanoparticles.

These nanocubes are much smaller than the hexagonal nanoparticles (700 nm) produced by Yajie Dong.^[8] In this work, the smaller size, higher unifor-

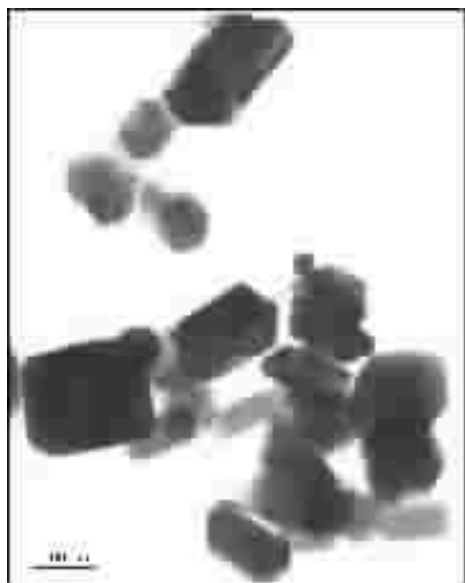


Fig.5 Cu_2O nanocuboids prepared at 130 °C for 18 h with the addition of $0.001\ 75\ \text{mol}\cdot\text{L}^{-1}$ diaminoethane and $0.02\ \text{mol}\cdot\text{L}^{-1}$ hexadecylamine

mity nanocubes of cuprite make it a more promising candidate in conversion of solar energy than larger particles, since it can make use high-energy visible rays of solar spectrum.

Fig 6 shows Energy- α^2 curve of the as-prepared sample, it is easy to obtain the absorption coefficient α , about $0.67\ \text{cm}^{-1}$; and it is also easy to know from point A that the sharpest optical absorption peak corresponds to the band gap transition at 2.51 eV. Compared with the band gap (2.0 eV) of bulk Cu_2O and other morphologies of Cu_2O (2.1~2.34 eV)^[10,11], the band gap of the nanocubes shows a significant blue shift.

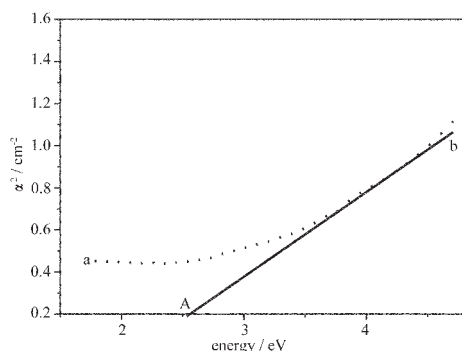


Fig.6 Energy- α^2 curve obtained from the data get from a set of UV-Vis spectrum (a)

Line b is the tangent of curve a. Line b intersects with Energy axis at point A. The data at point A represents the band gap of the Cu_2O nanoparticle.

This kind of significant blue shift makes it possible for Cu_2O to absorb the high-energy solar rays in the range of visible spectrum.

3 Conclusions

Cu_2O nanocubes were successfully prepared under acidic conditions. The optimal condition for synthesizing pure Cu_2O is as follows: the pH value of the solution is in the range of 4~6, temperature at 130 °C. The nanocubes were 100 nm in average size, and connected one by one through the edges of the cubes. It was found the diaminoethane and hexadecylamine serving as buffering agent for Cu^{2+} is critical for the formation of Cu_2O rather than elemental Cu. The band gap of the Cu_2O nanocubes blue shifts to 2.51 eV, making it possible for this material to utilize higher energy rays of solar visible spectrum in the field of converting solar energy.

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