Preparation of Cuprous Oxide Particles of Different Crystallinity

Yajie Dong, Yadong Li, Cheng Wang, Aili Cui, and Zhaoxiang Deng
Department of Chemistry, Tsinghua University, Beijing, 100084, People’s Republic of China

Received October 4, 2000; accepted July 21, 2001; published online September 24, 2001

Both the cubic single crystals and the spherical polycrystals of cuprous oxides (Cu$_2$O) were prepared by the reduction of aqueous CuSO$_4$, with hydrazine as a reductant in the presence of different organic molecule additives, such as hexadecyltrimethyl ammonium bromide (CTAB), glucose (C$_6$H$_{12}$O$_6$), ethylene glycol (C$_2$H$_6$O$_2$), and glycerol (C$_3$H$_8$O$_3$), at room temperature. It was found that the organic additives added had an important influence on the formation mechanism of the Cu$_2$O particles and could lead to different microstructures of the resultant Cu$_2$O crystallites. The addition of CTAB to the reaction solution could induce the formation of cubic Cu$_2$O single crystals, while glucose resulted in the formation of spherical polycrystals. All the samples were characterized by X-ray powder diffraction and transmission electron microscope (TEM). TEM observations indicated that the nanosized primary particles formed immediately after the reactants were mixed, followed by the competition between diffusion of the reactive constituents and aggregation of the nanosized primary particles. In the presence of CTAB, the diffusion of the reactants was a major factor contributing to the single crystal morphology of the Cu$_2$O products, while the aggregation of the primary nano-particles into polycrystallites prevailed when glucose existed in the reaction system.

Key Words: cuprous oxide; competition of diffusion and aggregation; surfactant CTAB; glucose.

INTRODUCTION

Cuprous oxide (Cu$_2$O) and related materials have been the subject of much current research interest. Cu$_2$O has a direct band gap of 2.2 eV, which makes it a promising material in solar energy conversion applications. Recently, the water-splitting activity of cuprous oxide has been the focus of many debates (1–4), as its exact role in this process still remains unknown. Cuprous oxide can be produced by electrolysis (5, 6), thermal oxidation (7), hydrothermal production (8), reduction of cupric salts (9, 10) or copper oxide (11) in solution, and by the $\gamma$-irradiation method (12). Control of the crystallinity of Cu$_2$O in order to obtain either single crystals or polycrystals through a simple solution chemical route at room temperature is still, however, not in sight in the literature. Photostability of Cu$_2$O, which plays an important role in its application, is strongly correlated with its crystallinity (3).

In this work, hydrazine, a rather strong reducing agent, was used for the reduction of aqueous CuSO$_4$. Two kinds of organic molecules, surfactant CTAB and glucose, were used as molecular additives to control the reduction and growth process to prepare phase-pure cuprous oxide particles of various crystallinity, single crystals, or polycrystals, at room temperature.

As stated by Stupp and co-workers (13), the use of organic molecules, even in very small amounts, could help control the microstructures of inorganic solid products. The present study attempts to shed some light on the roles that CTAB and glucose play in influencing the microstructures of the cuprous oxide particles.

EXPERIMENTAL

Materials

Copper sulphate (CuSO$_4 \cdot 5$H$_2$O), sodium hydroxide (NaOH), hydrazine hydrate, hexadecyltrimethyl ammonium bromide (CTAB), glucose (C$_6$H$_{12}$O$_6$), ethylene glycol (C$_2$H$_6$O$_2$), and glycerol (C$_3$H$_8$O$_3$) were purchased from Beijing Chemical Reagent Company and used as received.

Synthesis of Cu$_2$O in the Absence of Organic Additives

A colloid was formed by adding 50 ml of 0.1M CuSO$_4 \cdot 5$H$_2$O into 100 ml 1M NaOH at room temperature under vigorous stirring. Different amounts of 1M N$_2$H$_4$ solution (0.3 ml, 0.75 ml, 1.5 ml, 3 ml) were then added rapidly to the colloid accompanied by strong stirring. The resulting mixture was then aged in air at room temperature. The precipitates so produced were filtered, rinsed with deionized water, and then dried in vacuum at 60°C for 2 h. The optimal quantity of the N$_2$H$_4$ solution used was found to be 3 ml.

Preparation of Cu$_2$O Particles in the Presence of Organic Additives

Other synthetic conditions and procedures for the synthesis of Cu$_2$O were the same as above. However, before 3 ml 1M N$_2$H$_4$ solution was added, tiny (10 ml 0.001M) and large (1 g) amounts of CTAB were used as modifiers to prepare single crystals. Various amounts of 1M glucose (4.5 ml, 9.0 ml, 54.0 ml, 150.0 ml)
were used to produce Cu$_2$O polycrystals. In order to elucidate
the role of glucose, which is a hydroxyl compound, in the forma-
tion of polycrystalline Cu$_2$O, separate control experiments were
also carried out with ethylene glycol or glycerol as additives
under similar synthetic conditions. To study the growth process
of the Cu$_2$O particles, the products were collected at different
aging periods and examined by TEM.

**Characterization of the Cu$_2$O Particles**

Powder X-ray diffraction (XRD) patterns of all samples were
measured on a Bruker D8-advance X-ray powder diffractometer
with CuK$_\alpha$ radiation ($\lambda = 1.5418$ Å). The operation voltage and
current were 40 kV and 40 mA, respectively. XRD data were
recorded with a resolution of 0.02° and a scan rate of 0.5 s
per point. Transmission electron microscopy (TEM) images
were taken with a Hitachi Model-800 transmission electron mi-
croscope using an accelerating voltage of 200 kV. The crystal-
lite size was calculated from Scherrer’s equation, based on the
Cu$_2$O(111) diffraction peak.

**RESULTS AND DISCUSSION**

The overall reaction of the system we used is usually thought
to be as follows:

$$\text{N}_2\text{H}_4 + 4\text{Cu(OH)}_2 \rightarrow 2\text{Cu}_2\text{O} + \text{N}_2 + 6\text{H}_2\text{O} + 8\text{OH}^-.$$ 

However, in this system, the Cu$^{2+}$ ions are reduced first to Cu$^+$
by N$_2$H$_4$ (14), followed by three possible reactions in competi-
tion for the Cu$^+$ ions:

$$\text{Cu}^+ \rightarrow \text{Cu}^0 \quad [1]$$
$$2\text{Cu}^+ \rightarrow \text{Cu}^0 + \text{Cu}^{2+} \quad [2]$$
$$2\text{Cu}^+ + 2\text{OH}^- \rightarrow 2\text{CuOH} \rightarrow \text{Cu}_2\text{O}. \quad [3]$$

Only the reaction [3] leads to the formation of cuprous oxide.

XRD results in Fig. 1 show that in the absence of the additives,
before Cu(OH)$_2$ transforms completely to Cu$_2$O, the reflectances
of Cu appeared with the increase of the N$_2$H$_4$ concentration. It
is very difficult to produce phase-pure Cu$_2$O in the absence of
appropriate organic additives. It could be concluded that when
no modifier is present, the reaction corresponding to Eq. [1] will
occur as a result of the high local concentration of N$_2$H$_4$, which
is a strong reducing agent.

XRD patterns of the samples prepared in the presence of
CTAB or glucose were given in Fig. 2; all the reflectance peaks
could be indexed to a cubic Cu$_2$O phase. No diffractions raised
from impurities appear in the XRD patterns corresponding to the
products synthesized in the existence of CTAB or glucose. The
XRD results also indicate the improved crystallinity of Cu$_2$O
particles (depicted by #) with increased quantity of CTAB. How-
ever, in the case of glucose as an additive, the crystallinity of
resulting Cu$_2$O becomes worse with more glucose in the reac-
tion solution. The TEM micrographs of the as-prepared Cu$_2$O
particles in the presence of CTAB are provided in Fig. 3a,
which illustrates a hexagonal shape of the sample particles. The

**FIG. 1.** XRD patterns of the products obtained with (a) 0.3 ml, (b) 0.75 ml,
(c) 1.5 ml, and (d) 3.0 ml of 1 M N$_2$H$_4$, in the absence of organic additives. o, Cu(OH)$_2$; #, Cu$_2$O; *, Cu.

**FIG. 2.** XRD patterns of the Cu$_2$O prepared in the presence of different modifiers: (c) in the absence of any modifiers; (f) and (g) in the presence of increasing amounts of CTAB; (d), (c), (b) and (a) in the presence of increasing amounts of glucose from 4.5 to 150 ml. #, Cu$_2$O; *, Cu.

**FIG. 3.** (a) Transmission electron micrographs of Cu$_2$O in the presence of
CTAB; (b) SAED graph of the sample in (a).
selected area electron diffraction (SAED) pattern of the particle shown in Fig. 1a unambiguously reveals that it is a perfect cubic Cu$_2$O single crystal. Figure 4 shows the TEM and SAED micrographs of the particles obtained in presence of large amounts of glucose. The TEM image clearly indicates the spherical morphology of thus synthesized Cu$_2$O samples. However, different from the single crystallinity of the products prepared with CTAB as the organic additive, these spherical particles are all polycrystals, as evidenced by the ring-like SAED pattern taken on these spherical particles. Therefore, both single crystal particles and polycrystalline powders can be prepared selectively in similar procedures by simply changing the additives.

As we know, two completely different mechanisms are usually used to explain the formation of single crystals and polycrystals. A diffusion mechanism originally suggested by LaMer (15, 16) was generally accepted to explain the formation of monodispersed single crystals. According to this scheme, the precipitation process begins with a short burst of nuclei once a critical supersaturation of the particle-forming species is reached. The nucleation stage is then followed by diffusions of the constituent complexes to these primary particles until the supply is exhausted. On the other hand, an aggregation mechanism (17–21) was also employed to explain the formation of monodispersed polycrystals. This mechanism assumes that the nucleation stage is followed by the aggregation of uniform single crystalline sub-units into the final larger polycrystalline assemblies.

Generally, the differences between these two mechanisms are often emphasized in the literature. However, the results of the present work imply that these two mechanisms could have action on the morphologies of the resultant Cu$_2$O particles in a competitive way, i.e., the nucleation is followed not only by diffusion, but also by aggregation. In the presence of one modifier, the diffusion may be a dominating factor, and the single crystalline particles may be obtained, while with another modifier under almost the same conditions, aggregation prevails, and thus polycrystals might be obtained.

The TEM and SAED images in Figs. 3 and 4 clearly demonstrate the mechanism we mentioned above. With CTAB as the modifier, the nucleation is followed by diffusion, and single crystals are obtained, while with enough amounts of glucose under almost the same conditions, nucleation is followed by aggregation, and polycrystals are obtained.

The transmission electron micrographs of the particles obtained with increasing usage of glucose are given in Fig. 5. With the increase in the amount of glucose added, the Cu$_2$O particles evolve from cubic single crystals to spherical polycrystals gradually, indicating that the aggregation action is prevailing with the increased quantity of glucose.

In order to elucidate the mechanism of particle formation, the samples were collected at different periods during the aging process. The TEM micrographs in Fig. 6 exhibit the morphologies of the resulting solids formed under the conditions of sample E as listed in Table 1. Nanosized particles (Fig. 6a) were obtained without further aging treatment. However, these nano-particles started to aggregate upon aging (Fig. 6b), and Fig. 6c shows the particles already aggregated into a sphere. The
TABLE 1
Comparative Results with Three Kinds of Compounds as Modifiers

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Modifiers</th>
<th>Amounts/ml</th>
<th>Product</th>
<th>TEM nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>glucose</td>
<td>4.5</td>
<td>Cu₂O</td>
<td>cubic 30</td>
</tr>
<tr>
<td>B</td>
<td>glucose</td>
<td>9</td>
<td>Cu₂O</td>
<td>cubic 21</td>
</tr>
<tr>
<td>C</td>
<td>glucose</td>
<td>18</td>
<td>Cu₂O</td>
<td>cubic and spherical 19</td>
</tr>
<tr>
<td>D</td>
<td>glucose</td>
<td>54</td>
<td>Cu₂O</td>
<td>spherical 15</td>
</tr>
<tr>
<td>E</td>
<td>glucose</td>
<td>150</td>
<td>Cu₂O</td>
<td>spherical 9</td>
</tr>
<tr>
<td>F</td>
<td>glycol</td>
<td>3</td>
<td>Cu₂O + CuO</td>
<td>cubic 34</td>
</tr>
<tr>
<td>G</td>
<td>glycol</td>
<td>20</td>
<td>Cu₂O + Cu</td>
<td>cubic 18</td>
</tr>
<tr>
<td>H</td>
<td>glycol</td>
<td>30</td>
<td>Cu₂O</td>
<td>12</td>
</tr>
<tr>
<td>I</td>
<td>glycerol</td>
<td>3</td>
<td>Cu₂O + Cu</td>
<td>cubic 23</td>
</tr>
<tr>
<td>J</td>
<td>glycerol</td>
<td>10</td>
<td>Cu₂O + Cu</td>
<td>15</td>
</tr>
</tbody>
</table>

Notes. The concentration of the glucose solution is 1M. Glycol and glycerol are used without further dilution and purification. The amounts and concentrations of other reagents are described in the experimental part. The particle sizes were calculated from Scherrer’s equation, based on the Cu₂O (111) diffraction peak.

Roles of CTAB

CTAB could play two different roles in the formation of Cu₂O particles. The tiny nuclei of Cu₂O absorb OH⁻ in the solution and thus become negatively charged. The positively charged CTAB cations are then attracted by the Cu₂O nuclei and finally form a covering layer. On one hand, this layer might limit the diffusion of N₂H₄ to the nuclei and thus inhibit the reduction of Cu⁺ into Cu. On the other hand, the covering layer could isolate the nuclei and prevent them from aggregating.

Roles of Glucose

The influences of other organic additives, such as two kinds of polyols, ethylene glycol, and glycerol, were also investigated. Comparative results in the presence of these substances and glucose are listed in Table 1. The results clearly show that although all of them can help to form smaller particles than in the absence of them, only glucose can lead to the formation of pure Cu₂O particles. The protective role of glucose might not be due only to polyol, as special steric structure might be involved. We believe that glucose’s protective role arises from its much larger steric effect as compared to the other two compounds. As depicted in Fig. 7, the hydroxyl ligand of glucose forms a cage that shuts...
Cu²⁺ ions in. Small OH⁻ ions can permeate into the cage freely, while it is relatively difficult for the much larger N₂H₄ molecule to do this. Consequently, once the Cu⁺ ion is produced through the reduction of Cu²⁺ by N₂H₄, it will combine quickly with OH⁻, which is more competitive than N₂H₄ in the cage because of the better permeability, to form CuOH. Then the reaction corresponding to Eq. [3] might occur to form pure Cu₂O.

CONCLUSIONS

Phase-pure cuprous oxides particles of either single crystals or polycrystals could be prepared selectively at room temperature by using CTAB or glucose as the modifiers. The competition between the diffusion of the reactive species and the aggregation of the primary particles is employed to explain the formation of the Cu₂O particles with monodispersed single or polycrystalline structures. The roles that CTAB and glucose play are discussed in detail, which might be instructive in the search of other organic molecules for the control of the microstructures of other particles and their aggregations.

ACKNOWLEDGMENT

This project was supported by National Nature Science Foundation of China and State Key Project of Fundamental Research.

REFERENCES
