Size-controlled preparation of Cu₂O nanoparticles from waste printed circuit boards by supercritical water combined with electrokinetic process

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HIGHLIGHTS

- We report a size-controlled process for preparing nano-Cu₂O from waste PCBs.
- Highly uniform and spherical nano-Cu₂O was prepared directly from waste PCBs.
- Up to 90 wt% of the Cu in waste PCBs was recovered as nano-Cu₂O in this study.
- Effect of reaction condition on prepared nano-Cu₂O was studied.

GRAPHICAL ABSTRACT

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ABSTRACT

In this work, an effective and size-controlled process for preparing Cu₂O nanomaterials from waste PCBs by supercritical water (SCW) combined with electrokinetic (EK) technique was developed. SCW was used for the pretreatment of waste PCBs, and highly uniform and monodisperse Cu₂O nanoparticles with different sizes were prepared successfully from waste PCBs in EK process. Cu₂O nanoparticles with average sizes of 5, 11, 25 and 40 nm could be prepared in the presence of nanoparticles stabilizer (PVP) with the concentrations of 40, 30, 20 and 10 g/L, respectively. The average size of Cu₂O nanoparticles decreased from 49.5 to 18.2 nm when current density increased from 10 to 20 mA/cm², and the size uniformity of nanoparticles was improved distinctly at a higher current density. The size of Cu₂O nanoparticles increased with the increase of EK time, and agglomeration of particles was observed after 8 h EK reaction. Up to 90 wt% of the Cu in waste PCBs could be recovered as Cu₂O nanoparticles under optimized condition. It is believed that the process developed in this study is simple and practical for size-controlled preparation of nanomaterials from waste PCBs or other Cu-rich solid wastes.

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1. Introduction

Waste electric and electronic equipment (WEEE) has been taken into consideration not only by the government but also by the public due to its valuable materials and hazardous matters [1]. The U.S. Environmental Protection Agency (USEPA) has found that WEEE

components already constitute 1% of the municipal solid waste (MSW) streams [2]. As the primary elements in most WEEE, printed circuit boards (PCBs) are widely used. Waste PCBs contain many hazardous matters such as brominated flame retardant (BFR) and heavy metals [3]. On the other hand, the content of copper (around 20% in PCBs) turns the wastes into an interesting raw material from the economic point of view [4,5]. Therefore, the development of copper recycling processes from waste PCBs is an important subject for the effective utilization of copper resource. However, it is difficult to separate and purify copper from waste PCBs, because PCBs are a heterogeneous mixture of glass fiber, resin and multiple kinds of metal.

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Many recycling techniques of copper from waste PCBs have been developed such as pyrometallurgy [6], hydrometallurgy [7–9], bioleaching [10,11] and mechanical process [4]. Recently, to obtain high purity products of copper from waste PCBs, many new processes were proposed such as leaching-electrowinning [12,13], mechanical separation-electrometallurgy [14], and vacuum metallurgy [15]. In addition, a process combined supercritical water (SCW) and electrokinetic (EK) technique also was developed for the recovery of high purity copper and other heavy metals from waste PCBs [16,17].

However, all of the above-mentioned processes can only recover metallic copper [4–17]. In our previous study [18], $\text{Cu}_2\text{O}/\text{TiO}_2$ nanomaterials were prepared from waste PCBs by EK process. Cu in waste PCBs could be leached and reduced separately in cathode compartment of EK system, and Cu_2O with average size around 50 nm could be formed on the surface of TiO_2 contained in catholyte. However, it was difficult to obtain size-controlled nanoparticles due to the size of Cu_2O on the surface of $\text{Cu}_2\text{O}/\text{TiO}_2$ depended on the properties of TiO_2 .

In this study, we proposed a size-controlled process for the preparation of Cu_2O nanoparticles from SCW-treated PCBs. The highly uniform and monodisperse Cu_2O nanoparticles with different sizes could be obtained in the cathode compartment in the presence of nanoparticles stabilizer (polyvinyl pyrrolidone, PVP) by controlling EK reaction conditions. The most important advantage of using PVP as a substitute for TiO_2 is that it is a size-controlled process for the preparation of Cu_2O nanoparticles. It is well known that Cu_2O is an important p-type metal oxide semiconductor with direct band gap of 2.2 eV. Cu_2O nanoparticle possesses unique optical and magnetic properties, which makes it a promising material with potential applications in catalysis [19], solar energy conversion [20], gas sensors [21] and negative electrode material of lithium ion batteries [22].

The aim of the present work is to develop an efficient process for size-controlled preparation of high value-added Cu_2O nanoparticles from waste PCBs by SCW combined with EK process, and provide a novel and green route for the reutilization of Cu in WEEE. This study provides theoretical foundation for size-controlled preparation of metal nanomaterials from waste PCBs or other Cu-rich solid wastes.

2. Principle of nano- Cu_2O preparation in EK process

Among various techniques developed for the preparation of metal nanoparticles, electrochemical technique is a promising process [23–27]. But the application is only at the beginning in the treatment of waste.

The schematic drawing of the nano- Cu_2O preparation from SCW-treated PCBs is shown in Fig. 1. In EK system with an assisting agent HCl, copper oxide formed during SCW process could be leached, then the formed Cu^{2+} migrated toward cathodic compartment under the electric field [16–18]. PVP introduced into the cathodic bath could coordinate with Cu^{2+} to form multinuclear complexes on its chain, since each PVP monomer has a lactim group. The structural properties of PVP make it an ideal stabilizer for stabilizing metal particles [28,29] and inhibiting the deposition of metal on cathode [25,26]. Therefore, the PVP-stabilized Cu^{2+} could be reduced near the cathode and quickly leave the surface of cathode under vigorous stirring, and then the PVP-stabilized Cu or Cu_2O nanoparticles were formed. The possible reactions of Cu were as follows:

Fig. 1. Schematic drawing of the EK setup and reaction.

3. Experimental

3.1. Materials

Waste PCBs used in this work were supplied by HUAXING Environmental Protection Company of Beijing. The waste PCBs were mainly disassembled from discarded telephones, PCs, and other electrical equipments. A semi-automated dismantling cell was used for the removal of components (relays, capacitors, etc.). It includes the following subsystems or units: sequential heating units; a part-removal unit; a transport system; a solder removal unit; a component-collection unit [3]. After the components were disassembled, the PCBs were sent to comminute in a cutting mill until the particle size <1 mm. All chemicals used in this study were purchased from Chemical Reagent Company of Beijing in analytical grade and all of them were used as received.

3.2. SCW pretreatment

The SCW pretreatment was conducted in a 200-mL high-pressure reactor made of 316 alloy, and hydrogen peroxide (H_2O_2 , 30 wt%) was used as oxygen source [16–18]. H_2O_2 is decomposed and the released oxygen can be dissolved in supercritical water ($\text{H}_2\text{O}_2 = \text{H}_2\text{O} + 1/2\text{O}_2$). In a typical experiment, 5 g of the sample, 50 mL distilled water, and 40 mL H_2O_2 were employed. The solid-to-liquid ratio (S/L) used was 1:18 (g/mL). In SCW treatment, 713 K, 25 MPa and 1 h were performed since most of the BFR in the waste PCBs could be decomposed and Cu could be oxidized completely in such conditions according to previous reports [16,17].

3.3. Preparation of Cu_2O nanoparticles

Fig. 1 shows the schematic drawing of the EK reaction device. The device was made of glass, compartment II was 10 cm long and the distance between anode and cathode was 14 cm. Compartment I and compartment III were separated by two porous glass frits with 1 mm thickness. Platinum coated electrodes from LEICI Company (Shanghai, China) were used as working electrodes. The electrodes were plates with an active area of 1 cm^2 .

The preparation of nano- Cu_2O was carried out as follows: after each SCW treatment, filtration was conducted using a vacuum filter, and then 2 g of dried residue and 30 mL of 1 M HCl were

Fig. 2. (a) TEM image and (b) particle size distribution for Cu_2O nanoparticles prepared in EK process (PVP: 30 g/L; current density: 20 mA/cm²; EK reaction time: 6 h).

introduced into compartment II of the EK cell. The solid-to-liquid ratio (S/L) used was 1:15 (g/mL). The SCW-treated PCBs were kept in suspension by constant stirring with magnetic stirrer (SH-3 from JBD, Beijing, China). Both anolyte (compartment I) and catholyte (compartment III) initially consisted of 1 M HCl. PVP with different concentrations (10, 20, 30 and 40 g/L) was introduced into the compartment III of EK cell at the beginning of the reaction. The cathodic bath was kept stirring (2000 rpm) during EK process with magnetic stirrer. The constant current density was controlled at 10, 20 and 30 mA/cm², respectively. The EK reaction time was controlled at 2, 4, 6, 8, 10 and 12 h, respectively. After each EK reaction, the cathodic electrolyte was taken out and centrifuged at 10,000 rpm. Then the deposition was washed immediately for three times with a 30% (v/v) water/ethanol mixture to remove water soluble impurities. At last, the obtained particles were dried under vacuum at room temperature.

The concentration of copper ion in the cathodic bath was measured by ICP-OES (OPTIMA 2000, PerkinElmer). Copper content in the SCW-treated PCBs was also measured by ICP-OES after digestion [13]. Copper content in the SCW-treated PCBs was 29.03%.

3.4. Characterization of prepared Cu_2O nanoparticles

The crystalline phases of the prepared particles were characterized by X-ray diffraction spectroscopy (XRD, Philips PW1700) using Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) with 30 kV voltage and 30 mA current. Particles prepared were redispersed in ethanol, and ultraviolet-visible spectroscopic analysis (UV-vis) was conducted on a Shimadzu UV2450 spectrometer. Transmission electron microscopy (TEM) was carried out on a Hitachi H-7500 operating at 100 kV.

4. Results and discussion

4.1. Preparation of Cu_2O nanoparticles

Fig. 2a shows a typical TEM image of nano- Cu_2O prepared in EK process from SCW-treated PCBs. The Cu_2O nanoparticles were nearly spherical particles and were dispersed very well. Fig. 2b shows the size distribution of prepared particles. The size distribution was determined by counting 500 particles and the average size of the particles was 7.7 nm.

In the cathode bath, the presence of PVP was favorable for the formation of nanoparticle. Copper ions could be anchored to the hydrophilic groups of PVP molecule. Once the first copper ions got electrons from cathode and formed the initial copper clusters, the clusters near the cathode surface could act as part of the cathode and obtain the electrode potential by tunneling effect, which was

similar to the preparation of silver nanoparticles in electrochemical system [24–26,30]. Other copper ions could get electrons from the charged copper clusters more easily than from the Pt cathode surface, leading to formation of more copper clusters. At the same time, PVP could prevent the previously formed copper nanoparticles from aggregating due to the twining function of the hydrophobic polyvinyl groups. In addition, vigorous stirring in cathode bath could accelerate transfer of copper particles from cathode surface to bulk cathode bath and reduce aggregation between copper particles.

4.2. Characterization of Cu_2O nanoparticles

To understand the composition of the prepared particles, X-ray powder diffraction examination was performed. The analytical results are shown in Fig. 3. When PVP concentration and EK reaction time were 20 g/L and 6 h, respectively, all the characteristic peaks of the prepared particles in XRD pattern were labeled and could be readily assigned to the crystalline phase of Cu_2O in a cubic structure (standard JCPDS no. 05-0667). No characteristic peaks of CuO and Cu were observed in the XRD pattern, indicating that pure cuprous oxide could be readily prepared in the cathodic compartment. To understand the effect of PVP concentration on the composition of the prepared particles, different PVP concentrations such as 10, 30 and 40 g/L were also used in experiments. However, the XRD patterns of prepared particles were similar to the one prepared with PVP concentration of 20 g/L. Hence, the composition of the prepared particles could not be affected by the PVP concentration.

Fig. 3. XRD pattern of Cu_2O nanoparticles (PVP: 20 g/L; current density: 20 mA/cm²; EK reaction time: 6 h).

In the EK system, Cu^{2+} could be reduced to Cu^0 or Cu^+ near the cathode. The standard potential (E^0) of $\text{Cu}^{2+}/\text{Cu}^0$ and $\text{Cu}^{2+}/\text{Cu}^+$ is 0.337 V and 0.153 V, respectively. There are two possible routes for the formation of Cu_2O nanoparticles. One is the direct forming of Cu_2O from Cu^{2+} near the cathode (see reaction (3)). The other one is that Cu^{2+} is primarily reduced to Cu^0 (see reaction (4)), then the formed Cu^0 -PVP near the cathode quickly transfers to the cathodic solution under vigorous stirring and is oxidized to Cu_2O -PVP by the O_2 dissolved in the system or the high valence metal ions such as Fe^{3+} , Pb^{4+} and Mn^{3+} (Fe, Pb and Mn in PCBs can be oxidized to their high valence state in SCW pretreatment [16]) in the cathodic bath. The E^0 of $\text{Fe}^{3+}/\text{Fe}^{2+}$ (0.77 V), $\text{Pb}^{4+}/\text{Pb}^{2+}$ (1.46 V) and $\text{Mn}^{3+}/\text{Mn}^{2+}$ (1.51 V) is larger than that of Cu^+/Cu^0 (0.52 V). The possible reactions were as follows:

If fresh Cu^0 could not be oxidized to Cu_2O during the EK process, it is still possible to be oxidized in the air after EK reaction. Both the fresh particles and the particles exposed to air for 5 h after EK reaction were redispersed in ethanol followed by analysis of UV–vis absorption spectroscopy. Monitoring the UV–vis absorption spectra of the Cu particles in the course of reaction provides a convenient way to follow the whole reaction of Cu particles [31].

Fig. 4 shows the UV–vis absorption spectra of the fresh particles and the particles exposed to air for 5 h after EK reaction. No change about the spectral feature could be observed. The absorption bands at 360 nm and 460 nm are attributed to the charge transfer transitions in the nano- Cu_2O according to previous report [32]. Cu_2O nanoparticles prepared by different methods have been reported to display absorption bands in the range of 340–360 nm and 440–460 nm [31,32]. Accordingly Cu_2O nanoparticles were supposed to be formed during the EK process (reactions (3)–(8)).

Fig. 4. UV–vis electronic absorption spectra of (a) fresh nanoparticles and (b) nanoparticles exposed to air for 5 h after EK process (PVP: 20 g/L; current density: 20 mA/cm²; EK reaction time: 6 h).

In addition, no absorption band of Cu and CuO could be found in Fig. 4. The surface plasmon resonance band of Cu nanoparticles is in the range of 570–600 nm and the charge transfer transition of CuO is centered at >650 nm [33]. Hence, pure Cu_2O nanoparticles were formed in the cathodic compartment during the EK process. The results were consistent with the XRD analysis of prepared nanoparticles.

4.3. Effect of PVP concentration on Cu_2O nanoparticles

In the EK process, the concentration of PVP had a significant effect on the size of Cu_2O nanoparticles. Fig. 5 shows a set of typical TEM images of Cu_2O nanoparticles prepared at 20 mA/cm² current density in the presence of different PVP concentrations. When the concentration of PVP was 40 g/L, the

Fig. 5. TEM images of Cu_2O nanoparticles prepared in the presence of different PVP concentrations: (a) 40 g/L, (b) 30 g/L, (c) 20 g/L and (d) 10 g/L (current density: 20 mA/cm²; EK reaction time: 8 h).

Fig. 6. TEM images and particle size distribution of Cu₂O nanoparticles prepared at 20 mA/cm² (a and c) and 10 mA/cm² (b and d).

average size was about 5 nm and spherical Cu₂O nanoparticles were highly uniform in size (Fig. 5a). The average size of Cu₂O nanoparticles increased with the decrease of PVP concentration. Cu₂O nanoparticles with average size of 11, 25 and 40 nm

were obtained in the presence of PVP with concentration of 30, 20 and 10 g/L, respectively (Fig. 5b–d). In addition, the size uniformity decreased when PVP concentration decreased to 10 g/L (Fig. 5d).

Fig. 7. TEM images of Cu₂O nanoparticles prepared at (a) 4 h, (b) 8 h, (c) 10 h and (d) 12 h EK reaction (PVP concentration: 20 g/L; current density: 20 mA/cm²).

The effect of PVP concentration on size of Cu_2O can be explained by the adsorption of polymer molecule on the surface of Cu_2O [34,35]. It is believed that PVP kinetically control the growth rate of Cu_2O through adsorption and coordination interaction between PVP and Cu_2O . PVP molecules can interact with Cu_2O through Cu–O and Cu–N coordination bonds. The average size of Cu_2O nanoparticles increased with the decrease of PVP concentration, which could be attributed to that the twining function of PVP decreased under low PVP concentration. When the concentration of PVP was low (10 g/L), the growth rate of Cu_2O whose surface were covered by more PVP molecules could be reduced greatly, and those Cu_2O whose surface were uncovered or covered by less PVP molecules could maintain normal growth rate, leading to a different growth rate for different Cu_2O nanoparticles and the decrease in size uniformity (see Fig. 5d). However, the growth rate of most Cu_2O nanoparticles was inclined to the same and the size decreased significantly when PVP concentration increased to 40 g/L, because nearly every particle was covered by abundant PVP molecules.

4.4. Effect of current density on Cu_2O nanoparticles

Fig. 6a and b shows the TEM images of Cu_2O nanoparticles prepared at 20 and 10 mA/cm², respectively. The higher current density applied, the Cu_2O nanoparticles with smaller size could be obtained. The average size of Cu_2O nanoparticles increased from 18.2 nm to 49.5 nm when the current density decreased from 20 to 10 (mA/cm²). The possible reason is that the increase of current density results in a higher cathodic overpotential, which makes it possible for Cu_2O to nucleate more rapidly compared to its growth rate. The critical radius r_{crit} of adatom cluster at the cathode interface is given by the equation [23]:

$$r_{\text{crit}} = \frac{2M\gamma}{nF\eta\rho} \quad (9)$$

where M is the molecular weight, γ is the surface tension, F is the Faraday constant, η is the overpotential, ρ is the density of the cluster, and n is the valency. Accordingly, r_{crit} is inversely dependent on the overpotential η , which is directly related to the current density. The increase of current density results in a higher overpotential η , and then a smaller r_{crit} is obtained. Hence, Cu_2O nanoparticles with smaller size could be obtained in higher current density.

On the other hand, the size uniformity of nanoparticles decreased at lower current density. The size of prepared nanoparticles varied from 10 to 100 nm (Fig. 6b and d) when the current density decreased to 10 mA/cm².

However, further increasing the current density was not recommended due to that the increase of potential gradient could result in more side reactions and lower current efficiency. Table 1 shows the effect of current density on current efficiency and recovery yield of Cu_2O nanoparticles. The definition of Cu_2O nanoparticles recovery yield in the EK process is expressed as:

$$\text{Cu}_2\text{O nanoparticles recovery yield (\%)} = \frac{M_1 \times 100}{M_2} \quad (10)$$

Table 1
Effect of current density on the recovery yield of Cu_2O nanoparticles in EK process.

CD (mA/cm ²)	PG ⁱ (V/cm)	PG ^f (V/cm)	Cu_2O nanoparticles recovery (%)	CE (%)
10	0.28	0.45	64.1	82
20	0.42	0.66	86.5	75
30	0.58	1.15	92.8	53

EK reaction time: 12 h; PVP: 20 g/L; CD: current density; CE: current efficiency; PGⁱ: initial potential gradient; PG^f: final potential gradient.

Fig. 8. Effect of EK reaction time on the concentration of Cu ions in the cathode bath (PVP concentration: 20 g/L; current density: 20 mA/cm²).

where M_1 is the Cu content calculated from the weight of Cu_2O nanoparticles prepared, M_2 the initial content of Cu in SCW-treated PCBs. The current efficiency was determined and calculated according to literature [16]. The recovery yield of Cu_2O nanoparticles increased with the increase of current density. The highest recovery yield of Cu_2O nanoparticles was obtained when the 30 mA/cm² current density was applied, but the energy consumption was high due to the low current efficiency (53%).

4.5. Effect of EK reaction time on Cu_2O nanoparticles

TEM images of Cu_2O nanoparticles prepared at 4, 8, 10 and 12 h are shown in Fig. 7a–d, respectively. The size of Cu_2O nanoparticles increased with the increase of reaction time before 8 h and the particles were well dispersed with a narrow size distribution (Fig. 7a and b). However, the agglomeration of Cu_2O nanoparticles was observed after 8 h reaction. Some agglomerates (>100 nm) appeared and many new particles were produced at the same time (Fig. 7c and d). The possible reason is the change of copper ion concentration in cathodic bath during EK process. The effect of EK reaction time on the concentration of copper ion in cathodic bath is shown in Fig. 8. The concentration of copper ion in cathodic bath increased with the increase of reaction time during the first 8 h and decreased thereafter. In such a three-compartment EK system, a higher concentration of metal ion in cathode compartment could allow a higher reaction rate [36], which may result in the increase of agglomeration of Cu_2O nanoparticles.

In addition, Fig. 9 shows the effect of EK reaction time on the recovery yield of Cu_2O nanoparticles in cathode bath. The recovery

Fig. 9. Effect of EK reaction time on the recovery yield of Cu_2O nanoparticles in the cathode bath (PVP concentration: 20 g/L; current density: 20 mA/cm²).

yield of Cu₂O nanoparticles increased with the increase of reaction time, especially after 4 h EK. The recovery yield of Cu₂O nanoparticles at 8 h EK was about four times as high as that at 4 h, which could be attributed to the highest concentration of copper ion in compartment III (see Fig. 8) at 8 h EK reaction and a higher reaction rate of copper ion.

5. Conclusions

The results of this work showed that SCW + EK technology was an efficient and promising method to directly prepare high value-added Cu₂O nanoparticles with different size from waste PCBs.

Cu₂O nanoparticles prepared were nearly spherical particles and were dispersed very well. Cu₂O nanoparticles were formed in cathodic compartment during the EK process according to UV–vis spectroscopy and XRD analysis. The size of Cu₂O nanoparticles decreased significantly with increasing PVP concentration due to kinetic control of PVP on the growth rate of Cu₂O through adsorption and coordination interaction, and the size uniformity of Cu₂O was improved in the presence of higher PVP concentration. The increase of current density in EK process resulted in a higher overpotential, a smaller size of Cu₂O nanoparticles, and a higher recovery yield. In addition, the further increase of current density could lead to a lower current efficiency due to the increase of side reactions in the system. The size of Cu₂O nanoparticles increased with increasing reaction time before 8 h and the agglomeration of Cu₂O nanoparticles was observed thereafter. The significant increase of copper ion concentration in cathodic bath during EK process led to a higher reaction rate of copper ion, and the highest concentration of copper ion at 8 h EK reaction resulted in the agglomeration of Cu₂O particles.

The further studies of this work are in progress. For example: (1) the photocatalytic activity of Cu₂O nanoparticles prepared in this work and its application in the detoxification of organic matters in waste water and (2) the application of EK technology in size-controlled preparation of nanomaterials from other metal-rich wastes such as electric arc furnace dust or spent batteries.

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