Preparation of nano-Cu₂O/TiO₂ photocatalyst from waste printed circuit boards by electrokinetic process

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ABSTRACT

It is difficult for separation and reutilization of Cu in waste printed circuit boards (PCBs) due to the heterogeneous mix of polymer materials, multiple kinds of metals and glass fiber. In this study, waste PCBs were pretreated by supercritical water oxidation (SCWO), then introduced into an electrokinetic (EK) system with nano-TiO₂ suspension as catholyte. In the EK process, Cu could be leached and reduced separately from the complicated multi-metal system in cathode compartment, and Cu₂O could be formed in nano-size on TiO₂ surface. The properties of the composite catalysts Cu₂O/TiO₂ were examined and their photocatalytic efficiencies were determined for methylene blue (MB) degradation. The results indicated that the catalytic effect increased with increasing EK preparation time but decreased afterwards. The most effective catalyst (4.53 wt.% Cu₂O/TiO₂), whose degradation ability was found to be much higher in comparison with commercial P25, was prepared by 6 h EK treatment. It was found that the loading of Cu₂O on TiO₂ surface could greatly enhance the photocatalytic effect of the catalyst. It is believed that the EK technology is effective and green for direct preparation of high value-added Cu nanocomposite materials from waste PCBs or other Cu-rich wastes.

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1. Introduction

As the primary elements in most electronic products, printed circuit boards (PCBs) are widely used. Each year huge amounts of electronic wastes generate great volume of waste PCBs, among which few are processed by any techniques [1]. Waste PCBs contains many hazardous matters such as brominated flame retardant (BFR) and heavy metals and also valuable metals such as copper and precious metals. Especially PCBs contains around 20 wt.% of copper as metallic constituents [2]. Hence, it is very important to reutilize these copper resources. However, it is difficult for separation and reutilization of Cu in waste PCBs due to the heterogeneous mix of polymer materials, multiple kinds of metals and glass fiber.

Many separation and recycling techniques for Cu in waste PCBs have been developed such as pyrometallurgical [3], hydrometallurgical [4], bioleaching technology [5] and mechanical process [2]. In recent years, to obtain high purity Cu products from waste PCBs, many researchers [6–8] proposed some new process such as leaching-electrowinning [6], mechanical-electrometallurgy [7] and vacuum metallurgy technology [8]. Recently, Chien et al. [9] reported that supercritical water oxidation (SCWO) method can be used for simultaneously effectively removing BFR and oxidize metals in waste PCBs. On the other hand, electrokinetic processes

(EK) have been widely used for metals recovery from soil and solid wastes [10,11]. The EK method uses direct current as the “cleaning agent”, combining the electrokinetic movement of ions in the matrix. Metals could be leached and migrate to cathode or anode compartment, then recovered by reducing to form a deposit on the cathode or by other methods. In our previous study [12,13], a process combined SCWO and EK techniques was developed for the treatment of waste PCBs. Cu was recovered as a deposit on the cathode [12] and other heavy metals were recovered as concentrated solutions in anode or cathode compartment of EK system [13].

However, all of the processes above-mentioned can only recover the metallic material of copper [6–8,12]. There will have good prospects for direct preparing high value-added functional materials from waste PCBs. In this study, we found that Cu₂O/TiO₂ nanocomposites could be prepared with nano-TiO₂ suspension as catholyte in the EK process. Transition metal deposition is believed could increase photocatalytic activity of TiO₂ by avoiding electron-hole recombination [14–16]. As a transition metal deposited catalyst, Cu species/TiO₂ has been studied widely because it has been indicated that Cu species modification could improve the photocatalytic activity of TiO₂ effectively [17–20].

The mechanism of the Cu₂O/TiO₂ synthesis through EK process was discussed, and the photocatalytic activity of the catalysts prepared was evaluated through methylene blue (MB) degradation. This study provides theoretical foundation for direct preparation of high value-added Cu nanocomposite materials from waste PCBs or other Cu-rich wastes.

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Fig. 1. Schematic drawing of the EK setup.

2. Materials and methods

2.1. Materials

Waste PCBs used in this work were supplied by HUAXING Environmental Protection Company (Beijing). After the components (relays, capacitors, etc.) were disassembled, the PCBs were sent to comminute in a cutting mill until the fractions reached particle size smaller than 0.1 mm. All chemicals were purchased from Chemical Reagent Company of Beijing in analytical grade.

2.2. SCWO pretreatment experiments

The SCWO treatment experiments were conducted according to a previous literature [9]. In a typical experiment, 1 g of the sample and 20 ml of distilled water were introduced into a 200-ml high-pressure reactor made of 316 alloy, while 10 ml of hydrogen peroxide (H_2O_2 , 30 wt.%) was used as oxygen source. 1 g of NaOH was used as catch agent of Br species for removing the BFR [9]. Experimental conditions were 713 K, 25 MPa and 1 h, respectively. Most of the BFR in the waste PCBs could be removed and Cu could be oxidized completely at such conditions according to previous reports [9,12].

2.3. Preparation of $\text{Cu}_2\text{O}/\text{TiO}_2$ catalysts in the EK process

A series of $\text{Cu}_2\text{O}/\text{TiO}_2$ were prepared from SCWO-treated PCBs in the EK process, in which Cu-deposited amounts were in the range of 0.67–9.06 wt.%. The deposited amount was calculated base on the Cu. Fig. 1 shows a schematic drawing of the EK setup. The setup was made of glass. The compartment I and compartment III were separated by two porous glass frits with 1 mm thickness. Platinum-coated rod-like electrodes with the diameter 2 mm from LEICI Company (Shanghai, China) were used as working electrodes.

The preparation of catalyst was carried out as follows: after each SCWO treatment, the solution obtained was filtrated using a vacuum filter, and then the dried residue and 1 M HCl were introduced into compartment II of the EK cell. The SCWO-treated PCBs was kept in the suspension by constant stirring with magnetic stirrer (SH-3 from JBD, Beijing, China). 1 g titanium dioxide (P25, Degussa (80% anatase)) was added into 1 M HCl to form a suspension after 30 min ultrasonic dispersion, and then the suspension was introduced into compartment III of EK cell at the beginning of the reaction. The titanium dioxide suspension was kept constant vigorous stirring (2000 rpm) during EK process with magnetic stirrer. The anolyte (compartment I) also initially consisted of 1 M HCl. The constant current density and initial potential gradient was $20 \text{ mA}/\text{cm}^2$ and $0.4 \text{ V}/\text{cm}$, respectively. The EK time was controlled at 1, 2, 3, 4, 5, 6, 7 and 8 h, respectively. After each EK reaction, the cathodic

electrolyte was taken out and centrifugated. Then the deposition was washed immediately by distilled water three times. At last, the obtained composites were dried in a vacuum oven at 105°C overnight, then kept in a vacuum dryer.

The amount of deposited metal on the surface of TiO_2 was controlled by EK reaction time. The amount of Cu and other heavy metals was determined as follows: the sample was first digested with aqua regia and metal concentration in the filtrate was analyzed by inductively coupled plasma optical emission spectrometer (ICP-OES, OPTIMA2000, PerkinElmer, USA).

2.4. Characterization of $\text{Cu}_2\text{O}/\text{TiO}_2$ catalysts

The surface areas of $\text{Cu}_2\text{O}/\text{TiO}_2$ catalysts prepared were determined by N_2 adsorption at the temperature of liquid N_2 employing the BET method using a Micromeritics ASAP2000. The crystalline phases of the catalysts prepared were characterized by X-ray diffraction spectroscopy (XRD, Philips PW1700) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Transmission electron microscopy (TEM) was carried out on a Hitachi H-7500 operating at 100 kV.

2.5. Photocatalytic activity

MB was used as a model contaminant to investigate the photocatalytic degradation efficiency of the catalysts prepared. In each photocatalytic experiment, 0.1 g photocatalyst was added into 500 ml 10 ppm MB aqueous solution with strong stirring to form a suspension. Irradiation was performed with the 250-W high-pressure mercury lamp. The suspension was sampled in every 10 min interval and centrifugated to separate the catalyst particles. The filtrate was analyzed by UV–vis spectra with a spectrophotometer (Shimadzu UV2450) by measuring its absorbance at 664 nm, which is the maximum absorbance of MB. The degradation efficiency of MB was calculated as follows:

$$\text{MB degradation (\%)} = \frac{(C_0 - C_t) \times 100}{C_0} \quad (1)$$

where C_0 is the initial concentration of MB and C_t the MB concentration after illumination time t .

3. Results and discussion

3.1. Mechanism about EK preparation of $\text{Cu}_2\text{O}/\text{TiO}_2$ catalysts

Fig. 2 shows a typical TEM image of $\text{Cu}_2\text{O}/\text{TiO}_2$ nanocomposites prepared in the presence of TiO_2 by EK process from SCWO-treated PCBs. The cubic crystals are Cu_2O particles and the round particles are TiO_2 . It can be seen that the Cu_2O nanoparticles are closely adjoined to TiO_2 . The average size of Cu_2O formed was about 40 nm. The Cu_2O deposits were uniformly spread over the whole surface of TiO_2 particle and disperse well.

There have been several reports about the synthesis of metal nanoparticles by direct electroreduction of bulk metal ions in aqueous electrolytes [21–23]. The main difficulty is that electroreduction of metal ions involves a competition of two completely opposite cathode surface processes: the formation of metal nanoparticles and the metal electrodeposition on cathode [24]. Hence the use of stabilizer is very important. A good stabilizer not only greatly accelerates the rate of metal particle formation and markedly reduces the rate of metal deposition, but also protects the metal nanoparticles from agglomeration [22]. Stabilizer contains ligands with a polyfunctional group such as poly (N-vinylpyrrolidone), PVP, has been used to electrochemical synthesize the Au and Ag nanoparticles [22]. Other researchers [18] found that nano- TiO_2 has also the function as a stabilizer to promote the forming of nano-size particles in aqueous system. In addition,

Fig. 2. TEM image of $\text{Cu}_2\text{O}/\text{TiO}_2$ nanocomposites prepared by EK process (current density: $20 \text{ mA}/\text{cm}^2$, EK time: 8 h).

to obtain nanometer metal particle materials in reductive system, keeping low metal ion concentration is also essential. Many authors used complexing agent to regulate the concentration of metal ion [25]. In EK reaction system, it is easy to control the lower concentration of metal ion in cathodic bath due to the gradual leaching and migration process of metal ions under the electric field, without using the complexing agent.

Fig. 1 shows a schematic drawing of the preparation mechanism of composites. In the EK system of SCWO-treated PCBs with an assisting agent HCl, Cu and other metals could be leached and migrate toward either anodic or cathodic bath. Three measures were taken to acquire Cu species/ TiO_2 nanocomposites: (1) nano- TiO_2 (P25) was introduced into the cathodic bath as a stabilizer in order to enhance the metal particle formation rate and to reduce the metal deposition rate, and then to form Cu species/ TiO_2 nanocomposites; (2) vigorous stirring in cathodic bath was used to accelerate the transfer of the formed composites (Cu species/ TiO_2) from the cathode vicinity to the cathodic bulk solution; (3) a platinum electrode was employed as the cathode in order to reduce the deposition tendency of Cu ions, because the great difference in radius and lattice parameters for Pt and Cu favors particle formation. Therefore, the TiO_2 -stabilized Cu ions could be reduced near the cathode and then leave the surface of cathode quickly under the vigorous agitation so as to form TiO_2 -stabilized Cu_2O nanoparticles

Table 1

BET and crystallite size of $\text{Cu}_2\text{O}/\text{TiO}_2$ composites.

Sample	Cu (wt.%)	Crystallite size (nm)	BET surface area (m^2/g)
P25	0	30–50	50
CuP067	0.67	30–50	51
CuP192	1.92	30–50	51
CuP324	3.24	30–50	50
CuP453	4.53	30–50	52
CuP678	6.78	30–50	51
CuP906	9.06	30–50	52

and dispersed well. The EK reaction process of Cu was as follows:

3.2. Characterization of $\text{Cu}_2\text{O}/\text{TiO}_2$ catalysts

Measurements of specific surface area and size of all Cu_2O modified TiO_2 samples prepared from waste PCBs are listed in Table 1. It can be found that the loaded Cu_2O onto the surface of TiO_2 by the EK preparation did not significantly change the size and surface area of TiO_2 . Hence, the role of Cu_2O in the photocatalytic activity was not based on the difference of surface area between TiO_2 and $\text{Cu}_2\text{O}/\text{TiO}_2$.

TEM images of the catalysts prepared at EK time of 0, 3 and 6 h are presented in Fig. 3a–c, respectively. The deposited amount of Cu_2O on the surface of TiO_2 increased with the increase of EK time, but the Cu_2O nanoparticles still disperse very well. Therefore, it is reasonable to believe that the existence of nano- TiO_2 in the cathodic bath can make the reductive Cu_2O in nano-size due to the stabilization of P25 colloid.

To further understand the composition of the prepared catalysts, XRD examination was conducted and the analytical results of the modified catalysts prepared at various EK time were shown in Fig. 4. Comparing with the unloaded one (P25), all samples showed quite similar XRD diffractograms. The dominant peaks at 2θ of about 25.28° , 27.42° represent anatase and rutile, respectively. No characteristic peaks of deposited Cu species were detected when the EK time was less than 5 h and the Cu species deposited amount on TiO_2 was less than 3.24 wt.%, and this may be attributed to the fact that the Cu_2O amount was too small and dispersed very well. Characteristic peaks of Cu_2O was observed at copper loading of 3.24, 4.53, 6.78 and 9.06 wt.% (5, 6, 7 and 8 h EK time, respectively), all the diffraction characteristic peaks of the Cu species in XRD can be

Fig. 3. TEM images of modified TiO_2 photocatalysts prepared by (a) 0 h, (b) 3 h and (c) 6 h EK process (current density: $20 \text{ mA}/\text{cm}^2$).

Fig. 4. XRD patterns of modified TiO₂ photocatalysts prepared at various EK time.

readily assigned to the crystalline phase Cu₂O in a cubic structure (standard JCPDS no.05-0667). No characteristic peaks of CuO and Cu are observed in the XRD patterns, indicating that phase-pure Cu₂O can be formed on the surface of TiO₂ in the EK system. However, the peak intensity of Cu₂O was fairly weak.

It is well known that Cu²⁺ could be reduced to Cu⁰ more easily than other heavy metals in waste PCBs such as Pb, Cd, Cr, Zn, Ni and As due to the more positive potential of Cu²⁺/Cu⁰ ($E^0 = 0.34$ V) couple than that of other metal couples. There are two possible routes for the formation of Cu₂O. One is the direct formatting of Cu₂O from Cu²⁺ near the cathode (see reaction (4)). The other one was as follows: the Cu⁰ was obtained initially by the reduction of Cu²⁺, then the formed Cu⁰-TiO₂ could transfer quickly from the cathode vicinity to the cathodic bulk solution under the vigorous stirring, avoiding the occurrence of flocculates in the vicinity of the cathode. The freshly formed Cu⁰ on the surface of TiO₂ could be readily oxidized and converted into Cu₂O by O₂ or some high valence metal ions such as Fe³⁺, because Fe in PCBs could be oxidized to their high valence state in SCWO pretreatment which was an oxidizing atmosphere. The standard reduction potential (E^0) of Fe³⁺/Fe²⁺, 0.77 V is larger than that of Cu⁺/Cu⁰, 0.52 V. The reaction process of Cu was as follows:

3.3. Effect of EK time on Cu-deposited amount on TiO₂

The effect of EK time on Cu₂O deposited amount on TiO₂ can be seen in Table 2. In our preparation system only copper could be deposited on the surface of TiO₂ during the EK process and the amount of Cu₂O deposited on the TiO₂ surface increased with the increase of EK treatment time. The deposits of other metals such as Ni, Zn, Pb, Cd, Cr and As on the surface of TiO₂ cannot be

Table 2
Effect of EK time on Cu deposition amount on TiO₂.

	EK time (h)							
	1	2	3	4	5	6	7	8
Cu (wt.%TiO ₂)	n.d.	n.d.	0.67	1.92	3.24	4.53	6.78	9.06

n.d.: non-detectable.

Fig. 5. Effect of EK time on Cu ion concentration in cathode compartment.

determined according to the ICP analysis result, which could be attributed to their kinetically slow process of reduction in electrochemical system and their lower content compared to Cu in the cathodic bath during the EK process. The standard redox potential of Ni, Zn, Pb, Cd, Cr and As was too negative compared to Cu. In addition, many heavy metals such as Pb, Cd and Zn can form complexes with Cl⁻ and the complexes can be positive, negative or uncharged (MeCl⁺, MeCl₂(aq), MeCl₃⁻ and MeCl₄²⁻), especially Pb and Cd form stable complexes with Cl⁻. So the formed charged complexes could migrate to either anode or cathode bath under electric field. According to the Nernst equation, the decrease of metal ions in cathodic bath could decrease their redox potentials, which make their reduction near cathode more difficult.

It can also be found in Table 2 that the deposition rate of Cu species on the surface of TiO₂ was accelerated during the later stage of EK process. One possible reason is that the initially deposited Cu species could act as crystallized nucleus which could help the deposition of Cu on TiO₂ surface more easily. The other reason is that Cu concentration in cathodic bath increased rapidly after 4 h EK treatment due to the increase of the leaching efficiency at that stage. The effect of EK time on the Cu ion concentration in cathode compartment was shown in Fig. 5. It can be seen that Cu ion concentration in cathode compartment increased with the increase of EK time before 8 h and decreased thereafter.

3.4. Photocatalytic degradation of MB

It can be seen from Fig. 6 that the composite catalysts, with Cu₂O deposited on TiO₂, are quite effective for MB degradation under UV irradiation. The catalytic efficiency increased with the increase of Cu depositing amount on TiO₂ in a certain range (0.67–4.53 wt.%), but decreased at higher Cu loading (6.78 wt.% and 9.06 wt.%). The photocatalytic activity of Cu₂O/TiO₂ with Cu-deposited content in the range of 1.92–4.53 wt.% was higher than that of P25. The highest degradation ability could be obtained by using the 4.53 wt.% loading one.

Fig. 7 shows a linear correlation between $\ln(C_0/C)$ and t for MB photocatalytic degradation over 4.53 wt.% Cu₂O/TiO₂, the result suggested the first-order kinetics. The rate constant was found to be 0.08401 min⁻¹.

It has been proved that the accumulation of electron on TiO₂ particles will increase the rate of electron-hole recombination. Many researchers [19,26] suggested that electron transfer to oxygen might be the rate-limiting step in photocatalytic reaction, and Cu₂O can accelerate this step. According to many studies [18,27], light irradiated Cu₂O could absorb large numbers of oxygen in bulk and possess very strong ability to reduce O₂. Thus it is reasonable to believe that Cu₂O deposited on the TiO₂ surface have an

Fig. 6. Effect of copper deposition amount on photocatalytic activity of TiO_2 : (a) 0.67%; (b) 1.92%; (c) 3.24%; (d) 4.53%; (e) 6.78%; (f) 9.06%; (g) P25.

Fig. 7. Linear correlation between $\ln(C_0/C)$ and t for MB photocatalytic degradation over 4.53 wt.% $\text{Cu}_2\text{O}/\text{TiO}_2$.

obvious enhanced effect on the photocatalytic activity of the catalysts prepared. In addition, the photocatalytic activity of $\text{Cu}_2\text{O}/\text{TiO}_2$ decreased rapidly when copper species deposited content was higher than 4.53 wt.% (Fig. 6), which could be attributed to the fact that excess Cu_2O on TiO_2 surface may screen the photocatalyst from the irradiation source.

4. Conclusions

EK technology was developed for separation and reutilization of Cu resource from waste PCBs. In the EK process, $\text{Cu}_2\text{O}/\text{TiO}_2$ nanocomposites were prepared in the cathode compartment with nano- TiO_2 as catholyte. Cu could be leached and electro-reduced separately in nano-size on TiO_2 surface from the mixed system. The average size of Cu_2O was about 40 nm. This method is reliable and easy to carry out in a large scale. The deposited Cu_2O amount increased with the increase of EK preparation time, but the Cu_2O on the TiO_2 surface kept high dispersivity under different deposited amount.

Cu_2O on the TiO_2 surface could improve the photocatalytic efficiency remarkably due to their function to accelerate the rate of transferring electron to oxygen, resulting in a large number of holes which can degrade the organic compounds. The highest photocat-

alyst activity could be obtained when the Cu_2O deposited amount was 4.53 wt.%, which was prepared by 6 h EK treatment. In addition, it was found that the decomposition of MB followed the first-order kinetics with 4.53 wt.% $\text{Cu}_2\text{O}/\text{TiO}_2$ catalyst prepared.

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