The effect of different exposed facets on the photoelectrocatalytic degradation of o-chlorophenol using p-type Cu₂O crystals

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ABSTRACT

Although it is known that the efficacy of photoelectrocatalysts is enhanced by increasing the amount of high energy surface exposed, the development of a universal synthesis method with both superior activity and simplicity is needed for scalable applications. We herein controllably fabricated cuprous oxide (Cu₂O) micro crystals with different morphologies, evolving from cubes, cuboctahedra, truncated octahedra and finally to octahedra on indium tin oxide (ITO) glass substrates, by a facile electrochemical deposition method. The structures of facet-engineered Cu₂O samples and the underlying mechanism for the morphology evolution were investigated. The separation of photogenerated hole-electron pairs on Cu₂O crystals with different exposed facets was characterized by measuring the photocurrent densities with chopped illumination, which increased with the increased concentrations of PVP: the octahedral Cu₂O crystals, with the highest proportion of {111} facets exposed, exhibited the lowest electro-hole recombination in contrast to the cubes, cuboctahedra, and truncated octahedra, respectively. The photoelectrocatalytic degradation efficiency of the o-chlorophenol (2-CP) pollutant under sunlight irradiation with Cu₂O-coated photocathode was further investigated to reveal the effect of different exposed facets. Due to the increased number of surface active sites available for degradation reactions, the octahedral Cu₂O microcrystals presented higher photoelectrocatalytic activity compared to other shapes. Active oxygen species detected by electron spin-resonance (ESR) spectrometry implied that abundant superoxide radicals (O₂^{•−}) were the dominant active radicals in the degradation.

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1. Introduction

As a promising technology, photoelectrocatalytic degradation has attracted increasing attention for its ability to efficiently decompose refractory organic pollutants that cannot be eliminated biologically, due to its convenience, environmental compatibility, cost-effectiveness, versatility and safety [1–7]. Photoelectrocatalysis, as an enhanced photocatalytic technique, holds great promise for effective wastewater purification by decreasing the recombination of photogenerated electron-hole pairs via applying a bias potential. Thus, the degradation efficiency of organic contaminants

could be improved, and the toxic and refractory intermediates generated during electrochemical oxidation could be decomposed by photocatalysis-induced radicals. However, in conventional photoelectrocatalytic degradation, most of the studies have focused on the improvement of photocatalysts [1,8] or anodic electrode materials [2–5,7,9], while few studies have paid attention to cathodic electrode materials that also substantially influence both reaction selectivity and efficiency [6]. The reason is that some critical challenges still remain in the application of active cathodes for photoelectrocatalytic water treatment, including the low efficiency of photo-electric conversion under natural sunlight, short service life, high cost, secondary contamination, etc. Thus, cathodic electrode materials with high photoelectrocatalytic performance, low cost and no toxicity are greatly desired.

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As a typical p-type semi-conductive metal oxide, cuprous oxide (Cu_2O) is a promising material as photocathode because of its attractive photoelectric properties and environmentally friendly features [10,11], such as the natural abundance of copper, low cost of production, high sunlight irradiation absorption coefficient with a direct band gap of about 2.0 eV [12], high absorptivity and photostability [13]. The synthesis of Cu_2O micro or nanostructures with controllable morphologies has been developed [14,15], including nanocubes [15,16], octahedra [15,16], polyhedral morphology [17], hollow structures [18] and nanowires [19], and many growth mechanisms have been proposed. These Cu_2O microcrystals were generally synthesized by hydrothermal methods in the presence of different capping reagents (e.g., surfactant [20], ascorbic acid or hydrazine hydrate [16], and acetic acid [17]). The photodegradation of organic pollutants in a suspended catalyst system would cause several problems, such as difficulty in the recovery of photocatalysts, easy agglomeration and decreased active surface, low efficiency and the risk of secondary pollution. Therefore, fabrication and immobilization of Cu_2O crystals on a solid support is essential and practical for photoelectrocatalytic applications. Another core issue during photoelectrode design is to improve the relatively low efficiency of photocatalytic materials, either through controlling the morphology and structure of semiconductors or constructing heterostructured films. Among these strategies, the development of faceted micro and nano-materials for photocatalytic reactions has attracted worldwide research interest, due to the inherent necessity of constructing photocatalysts in a controllable manner. Several semiconductors with different exposed facets have been investigated, such as TiO_2 , Ag_3PO_4 , BiOCl etc. Due to the changes in surface characteristics and the possible spatial separation of photogenerated charge carriers, significantly improved photocatalytic activities were achieved by this strategy. For example, {001} facets of anatase TiO_2 showed higher activity than {101} facets [21,22]. The facet-dependent photocatalytic performance of ZnO was also explored in detail, and the results showed that the photocatalytic performance was dependent on the crystal facet exposed in the order {0001} > {1011} > {1010} [23]. Similarly, octahedral Cu_2O with exposed {111} crystal planes exhibited much better photoactivities and stabilities than Cu_2O with {100} and {110} facets [17,24]. Therefore, developing Cu_2O crystals with specific facets is highly desirable for enhancing the photoelectrocatalytic efficiency. Although the application of Cu_2O microcrystals on ITO glass substrates in photocatalytic degradation of dye pollutants has been studied [13], it is still challenging to controllably deposit facet-dependent engineered Cu_2O microcrystals on solid substrates and to compare how the different exposed facets influence the photoelectrocatalytic performance for organic pollutant degradation.

This research aims to fabricate Cu_2O photocathodes with different exposed facets and further investigate photoelectrocatalytic pollutant degradation, using o-chlorophenol (2-CP) as a model pollutant. In consideration of the inexpensive apparatus required, high purity of deposits, easy control of film thickness, and low fabrication temperature, electrodeposition was used for the fabrication of semiconductor microcrystal films on conducting substrates. The dominant facets of Cu_2O were rationally controlled by adjusting the electrodeposition time and polyvinylpyrrolidone (PVP) concentration. Subsequently, a photoelectrocatalytic cell was constructed with Cu_2O films on ITO glass substrates as the photocathode and a platinum (Pt) wire as the anode. The possible underlying mechanism for the efficient photoelectrocatalytic performance of Cu_2O was also discussed and proposed, revealing the effect of different exposed facets as well as the dominant active radicals.

2. Experimental

2.1. Materials

ITO glass was purchased from Shenzhen Crystal Glass Technology Co. Ltd. (10 cm × 10 cm, thickness 1.0 mm). The titanium sheet was obtained from Beijing Hengli Titanium Industry & Trade Co., Ltd. (3 cm × 6 cm, thickness 0.5 mm). The custom-built quartz reactor was made by Beijing Kailida quartz-glass instrument factory (3.5 cm × 3.5 cm × 7.0 cm).

Other chemicals including copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), sodium sulfate (Na_2SO_4), polyvinylpyrrolidone (PVP), and o-chlorophenol (2-CP) were purchased from Sinopharm Chemical Reagent Co. Ltd., with analytical grade purity. pH regulation was performed using either NaOH or H_2SO_4 (guaranteed grade). All the aqueous solutions were prepared with Milli-Q water having a resistivity of 18.2 M Ω .

2.2. Preparation of cathodes

The Cu_2O thin films were grown on ITO glass substrates using a simple electrodeposition method. A three-electrode system was used for the growth, including an ITO glass substrate (10.0 cm × 2.0 cm) used as the working electrode, an Ag/AgCl (Sat. 4 M KCl) reference electrode and a counter electrode made of titanium sheet. The electrodeposition process was conducted using an EG&G model 263A electrochemical workstation (Princeton Applied Research, USA).

Prior to the deposition, the ITO glass substrates (10.0 cm × 2.0 cm) were cleaned ultrasonically in aqueous detergent solution, distilled water, acetone and ethanol for 15 min respectively. Then, the substrates were rinsed with Milli-Q water and dried in a vacuum drying oven at 40 °C. Subsequently, the substrates were immersed into the electrolyte to be used as the working electrode in a custom-built electrolytic cell, and the distance between the working electrode and counter electrode was controlled at 10 cm. The electrolyte used for Cu_2O thin film deposition consisted of 20 mM $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and different concentrations of PVP (A.R.) (0, 0.2, 0.4, 0.8, 1.6, 2.4 and 8.0 mM respectively). Cu_2O microcrystals were galvanostatically electrodeposited on ITO glass substrates under a current of 0.8 mA, with electrodeposition times of 15, 30, 60 and 90 min respectively and growth temperature kept at room temperature.

Finally, the resulting ITO glass substrates were rinsed with abundant Milli-Q water to remove unwanted debris or precipitates (e.g., adsorbed PVP, Cu^{2+} and SO_4^{2-}), and dried in a vacuum drying oven at 40 °C. The electrodeposition area of every sample was kept at 6.0 cm × 2.0 cm and the deposited amount of Cu_2O was quantified using a balance (Mettler Toledo XS104).

2.3. Characterization

The surface morphology of the Cu_2O thin films was characterized in detail by a field-emission scanning electron microscope (SEM, Hitachi, S-3000N, Tokyo, Japan). X-ray powder diffraction (XRD) measurements of the samples were performed to characterize the surface composition of Cu_2O particles with an X'Pert PRO Powder diffractometer (PAN analytical Co.), using Ni-filtered Cu K α radiation from 5° to 80° (in 2 θ). X-ray photoelectron spectroscopy (XPS) analysis was performed with a Thermo Scientific ESCALAB 250Xi X-ray photoelectron spectrometer. High resolution transmission electron microscopy (HRTEM) was carried out in a JEM-2100F instrument (JEOL, Japan). The ITO glass substrate modified by Cu_2O microcrystals was cut into small pieces first and then analyzed by SEM, XRD and XPS. The HRTEM sample was obtained by scratching off a portion of the Cu_2O composite from the Cu_2O

photocathode surface, followed by ultrasonication in ethanol solution for 5 min. Two droplets of the well-dispersed ethanol solution were deposited on the carbon-coated copper grid. The HRTEM sample was ready to be analyzed after being dried overnight.

To evaluate the photoelectrocatalytic activity of facet-dependent Cu_2O films as photocathodes, the linear sweep current-voltage method was used under 150 W chopped illumination with an intensity of 100 mW cm^{-2} in 0.1 M Na_2SO_4 at a pH of 6.0. The photocurrent was measured from -0.4 V to 0 V versus the Ag/AgCl reference electrode and the scan rate was 5 mV/s with chopped illumination periods of 30 s, so the dark and light current could be monitored simultaneously.

2.4. Chemical Degradation

A 150 W xenon lamp (LHX150, Spectrum: 200–1800 nm, Zolix Instruments Co., Ltd.) was selected as the light source and a three-electrode system was used for the photoelectrocatalytic reactions. One piece of ITO glass substrate coated with Cu_2O microcrystals ($6.0 \text{ cm} \times 2.0 \text{ cm}$) was taken as the working electrode (cathode), the reference electrode was Ag/AgCl (Sat. 4 M KCl) and a platinum wire 72 mm in length and 1.5 mm in diameter was used as the counter electrode (anode). The three electrodes were directly inserted into the custom-built quartz reactor containing 80 mL 2 ppm 2-CP and 1 mM Na_2SO_4 solution, and then the reactor was placed at a distance of 20 cm from the lamp. The opening of the reactor was sealed with a polyethylene film to prevent the loss of water because of vaporization. During illumination, about 1 mL of reactive solution was sampled at regular time intervals (0, 5, 10, 15, 30, 60, 90 and 120 min) and filtered with a $0.45 \mu\text{m}$ membrane. Compared with the total reaction volume, the effect of the sampled volumes was considered to have negligible influence on the original concentration of 2-CP. All electrochemical experiments were performed with an EG&G model 263A workstation (Princeton Applied Research, USA).

2.5. Analytical Methods

The pH was measured using a 9165 BN pH electrode connected to an Orion–828 pH analyzer (Orion Research, Inc., Beverly, MA).

The concentrations of 2-CP were measured with a high performance liquid chromatography (HPLC) system (1260, Agilent Technology) equipped with a C-18 column (Agilent Technology) and two detectors connected in series, namely a diode array detector (Waters 996) and a fluorescence detector (Waters 474). The mobile phase consisted of 1% acetic acid and methanol (30:70, V/V) at a flow rate of 1 mL/min and a column temperature of 25°C .

3. Results and Discussion

3.1. Structures of Cu_2O semiconductors

Fig. 1a shows the X-ray diffraction (XRD) patterns for the deposited films obtained from 20 mM $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ with different PVP concentrations (0 mM, 0.2 mM, 2.4 mM and 8.0 mM). All the diffraction peaks can be indexed to cuprite Cu_2O (JCPDS NO. 03-065-3288). Four characteristic peaks appeared at 29.632° , 36.504° , 42.402° , and 61.521° , which correspond to the {110}, {111}, {200}, and {220} lattice planes of Cu_2O . The absence of diffraction peaks of other copper species in the XRD patterns confirmed the formation of pure Cu_2O on the ITO glass substrates. As shown in Fig. 1b, the diffraction intensity ratio of (111)/(200) exhibited an obvious increase with the shape evolution from cubes to octahedra under the same electrodeposition time. Also, with the same PVP concentration, the diffraction intensity ratio of (111)/(200) increased with increasing electrodeposition time. That means that the relative proportions of {111} facets increased with the PVP concentration and electrodeposition time until it reached a plateau with octahedral Cu_2O particles.

The highly dispersed nanoparticles on supports with larger surface areas have unique properties with advantages for catalytic activity [25]. Fig. 2 presents the scanning electron microscopy (SEM) images of Cu_2O microcrystals with different morphologies on the ITO glass substrates. The high-magnification view in the inset of each image shows that the films mainly consisted of polyhedral Cu_2O semiconductor crystals with different facets exposed. SEM observation revealed that all particles displayed perfect shapes and were evenly distributed on isolated spots of the ITO glass without obvious aggregations, which would result in the crystalline facets of the microcrystals being exposed to the fullest extent. The PVP concentration was a key factor directing the

Fig. 1. XRD patterns measured as the shape of the Cu_2O microcrystals evolved from cubes through truncated cubes, cuboctahedra, truncated octahedra and finally to octahedra (a) and the corresponding intensity ratio of (111)/(200) with different electrodeposition times (b).

Fig. 2. SEM images of the Cu_2O thin films with different PVP concentrations at 90 min electrodeposition time: (a) 0 mM (cubes), (b) 0.2 mM (cuboctahedra), (c) 2.4 mM (truncated octahedra) and (d) 8.0 mM (octahedra). The insets show high magnification views.

morphology evolution of the Cu_2O , from cubes (0 mM), cuboctahedra (0.2 mM), truncated octahedra (2.4 mM) to octahedra (8 mM) respectively. Furthermore, the size of Cu_2O semiconductor crystals decreased gradually from $\sim 4.0 \mu\text{m}$ to $\sim 2.0 \mu\text{m}$ as the PVP concentration was increased, and the film density was increased accordingly (Fig. 2a–d). On the contrary, with extended deposition time, the particle size increased from $\sim 1.5 \mu\text{m}$ to $\sim 3.0 \mu\text{m}$ under

the same PVP concentration (0.2 mM), and the distribution of microcrystals over the whole deposition area became denser (Fig. 3).

Similar to the functions of other surfactants [26], the mechanism for the shape control of Cu_2O crystals could be understood in terms of the preferential adsorption of PVP onto the crystal planes with the highest surface energy, which decreased

Fig. 3. SEM images of Cu_2O thin films with different electrodeposition times: 15 min (a), 30 min (b), 60 min (c) and 90 min (d) at 0.2 mM PVP.

the growth rate [15]. When the electrodeposition process began, electrochemical reactions could occur on the cathode under the constant current of -0.8 mA, and Cu_2O crystal nuclei formed on the surface of ITO glass substrate as follows:

In general, once the nuclei form, the growth rates vary along different crystallographic directions and the lowest growth direction determines the final morphology of the crystals. If adsorbed PVP additives are absent during the electrodeposition process (0 mM PVP), the final crystals display cubic shapes with dominant {100} exposed facets. Moreover, {111} crystal planes should have the highest surface energy due to the exposure of 'Cu' atoms with dangling bonds [15]. To minimize the total surface energy, the introduced PVP would prefer to be adsorbed onto the higher energy {111} surfaces. As the amount of PVP increased, the ratio of {111} facets gradually increased in the Cu_2O semiconductors. In the presence of a sufficient amount of PVP (8.0 mM), the growth rate of {111} crystal planes was slow enough for the formation of Cu_2O octahedra composed of high-energy {111} facets. The exposed facet for the Cu_2O octahedra was further confirmed by HRTEM images as shown in Fig. 4. The lattice spacing of 0.25 nm corresponds to the {111} plane of Cu_2O . If higher than 8.0 mM PVP was added, the adsorbed amount on the {111} facets reached saturation, and the {100} facets began to adsorb PVP molecules to further reduce the growth rate along the {100} direction. The octahedral shapes composed of all {111} crystal planes would disappear gradually [27].

In addition to affecting the growth anisotropy, PVP also reduced the nucleation rate and the subsequent growth rate of nuclei. At the beginning of the electrodeposition, nuclei can form quickly at the most active sites on the ITO glass substrate in an additive-free electrolyte solution. However, when PVP was added, the substrate became more homogenous and thereby more sites were suitable for nucleation, resulting in the formation of more Cu_2O semiconductor crystals. Therefore, as the amount of PVP increased, the distribution density of Cu_2O crystals on the ITO glass substrates gradually increased and the size gradually decreased. By the PVP-assisted electrodeposition method, Cu_2O films composed of uniform and dispersed microcrystalline particles could reliably be prepared.

3.2. Photoelectrochemical properties of Cu_2O semiconductors

Fig. 5 shows that the average deposited amounts of Cu_2O with different PVP concentrations at the same electrodeposition time (90 min) were similar to each other, about 0.18–0.19 mg/cm^2 . The

Fig. 5. The average deposition amount of Cu_2O with different PVP concentrations at 90 min electrodeposition time.

linear sweep current-voltage (I - V) plots of the different fabricated Cu_2O photocathodes are presented in Fig. 6. There was a trend that the photocurrent density of Cu_2O semiconductor electrodes in Fig. 6 increased with increasing PVP concentration under the same potential. The values in Fig. 6d were obviously higher than the others, and the sample produced a photocurrent of 0.04 mA/cm^2 at -0.4 V versus the Ag/AgCl reference electrode. Based on the similar deposited amounts of Cu_2O (Fig. 5), the higher performance probably can be attributed to the fact that only {111} crystalline surfaces were exposed for Fig. 6d sample; in addition, the microcrystals were distributed nearly isolated on the surface of the support (Fig. 1d), which would expose as many active sites on the Cu_2O particles as possible. It has been reported that the catalytic activity of Cu_2O nanoparticles was dependent on the crystallographic surface orientation, and Cu_2O exposing {111} facets showed improved ability for photodegradation of pollutants compared with other exposed facets [17,24]. Thus, we suspect that the electron mobility in the {111} direction of Cu_2O was significantly higher than in other directions. Higher electron/hole separation in some preferred crystal orientations has been reported previously [21–23,28,29], and these researchers found that the exposed facets with highest surface energy showed the highest photocatalytic activity under light irradiation.

Stability and reusability of photoelectrocatalysts are also very critical issues for practical applications. As to the photocathodes' stability under illumination, the insets of Fig. 6 show photocurrent stability measurements on different Cu_2O semiconductors held at -0.4 V vs. Ag/AgCl under chopped illumination periods of 30 s with a 150 W lamp. All samples showed no significant loss of activity, with more than 95% photocurrent density remaining after 5 min illumination. Compared with the powder catalysts, the Cu_2O

Fig. 4. A low-magnification TEM image of a Cu_2O nanocrystal (a) and a high-resolution TEM image of a Cu_2O octahedral microcrystal (b).

Fig. 6. The photoelectrochemical response of Cu_2O -deposited electrodes with different exposed facets under chopped illumination. Electrodeposition process of all electrodes is 90 min and with different PVP concentrations of (a) 0 mM (cubes), (b) 0.2 mM (cuboctahedra), (c) 2.4 mM (truncated octahedra) and (d) 8.0 mM (octahedra). Current-potential characteristics were detected in 0.1 M Na_2SO_4 of pH 6.0 under simulated 150 W solar irradiation. The insets show the photoelectrochemical stability tests for the electrodes under 30 s illumination and dark periods at a constant potential of -0.4 V vs. Ag/AgCl in 0.1 M Na_2SO_4 .

semiconductors grew directly on the solid substrates, so that they were firmly adhered on the carriers and easily recycled.

3.3. Photoelectrocatalytic degradation of 2-CP

To demonstrate the potential application of the as-deposited Cu_2O semiconductor films and the relationship between the exposed crystallographic facets and their photoelectrocatalytic properties, the degradation ability of Cu_2O photocathodes with different shapes (including cubes, cuboctahedra, truncated octahedra and octahedra) was investigated. Fig. 7 shows the electrocatalytic and photoelectrocatalytic degradation rates of o-chlorophenol (2-CP) for different samples obtained by electrodeposition of 90 min. The area of the Cu_2O films was about $6.0\text{ cm} \times 2.0\text{ cm}$ for all samples. All Cu_2O cathodes could enhance the electrolysis with or without sunlight illumination compared with a pure ITO glass substrate without any electrodeposited Cu_2O (curve marked with "ITO-glass" in Fig. 7a and 7b). For all crystal shapes, the as-prepared Cu_2O semiconductors on ITO glass substrates have excellent photoelectrocatalytic activity for the degradation of 2-CP solution under sunlight (Fig. 7b & 7d) compared with the absence of sunlight illumination (Fig. 7a & 7c). The electrodegradation efficiency of the octahedral Cu_2O cathode was only about 18.6% even under -0.4 V bias potential (Fig. 7c), while the degradation efficiency could achieve 42.9% under light illumination alone (Fig. 7d). When both illumination (sunlight) and bias potential (-0.4 V) were applied, due to synergetic effects, the photoelectrocatalytic efficiency of octahedral Cu_2O photocathode could reach 82.9% after 2 h treatment.

The degradation ability of 2-CP by the obtained Cu_2O semiconductors with different shapes on ITO substrates followed the sequence of octahedra > truncated octahedra > cuboctahedra > cubes under the same bias potential of -0.4 V . When the morphology converted from cubes to octahedra, the

electrodegradation efficiency increased from 10.3% to 18.6% as shown in Fig. 7a, and the corresponding photoelectrodegradation efficiency increased from 49.1% to 82.9% (Fig. 7b). The different Cu_2O shapes are determined by the crystallographic planes parallel to the facets. Considering their crystalline structures and similar amounts of deposited Cu_2O , it can be concluded that the photoelectrocatalytic degradation ability toward 2-CP had an intimate relationship with the increasing exposure of $\{111\}$ facets. When the proportion of exposed $\{111\}$ facets increased (from cubes to octahedra), the crystal sizes decreased and the distribution densities increased on the ITO glass substrates. The electronic structure, bonding, and surface energy of the $\{111\}$ facet-predominated Cu_2O crystals are different from those of other crystallographic planes, providing its high chemical reactivity. Thus, more molecules of 2-CP were readily adsorbed on the cathode and eventually degraded. Furthermore, the $\{111\}$ surfaces possess active 'Cu' atoms, which tend to interact with negatively charged 2-CP (i.e. Cl^-). Thus, the geometries with greater exposed $\{111\}$ surface areas would adsorb more 2-CP, especially at the initial stage. This coincides with the preferential adsorption of PVP on $\{111\}$ planes.

In recent years, many researchers have paid attention to photoelectrocatalytic mechanisms for the degradation of the organic pollutants [30–35], fundamentally aiming to enhance photogenerated electron/hole separation by application of a potential bias. More importantly, in the photoelectrocatalytic system, by an applied potential bias, the formation of radicals can be controlled on the electrodes. For example, by using a negative applied voltage, electrons can accumulate in the Cu_2O electrode. The electrons trapped by the semiconductor surface are easily transferred to the adsorbed O_2 to form $\text{O}_2^{\bullet-}$, which has been considered as an essential radical for the photodegradation of aromatic compounds over TiO_2 [30]. In this study, the ESR spin-trap technique (with DMPO) was used to detect the nature of the

Fig. 7. Application of the Cu_2O -coated electrodes for the degradation of 2-CP: (a) electrocatalysis and (b) photoelectrocatalysis of 2-CP using five different electrodes at constant bias potential of -0.4V (versus Ag/AgCl); (c) electrocatalysis and (d) photoelectrocatalysis of 2-CP using the same electrode (fabricated with octahedral Cu_2O crystals) with different applied bias potential.

reactive radical species generated in Cu_2O photocatalytic suspensions, and the result is shown in Fig. 8. As expected, strong signals of superoxide radical ions $\text{O}_2^{\bullet-}$ were detected in the reaction solutions.

According to the influential factors for the degradation efficiency, a possible photoelectron-catalytic degradation mechanism was suggested as follows. With a direct band gap of 2.0eV , the Cu_2O octahedral microcrystals on the ITO glass substrate had high absorption ability for visible light. Electrons of the valence band of Cu_2O could be excited to the conduction band, leaving positive holes on the electrode surfaces (Equation (2)). The photo-generated electrons accumulated on the Cu_2O working electrode of to produce superoxide radical ions $\text{O}_2^{\bullet-}$ (Equation (3)) and further oxidize the pollutants into

inorganic or nontoxic materials (Equation (4)).

Our experimental results indicate that the degradation reaction of 2-CP is mainly initiated by the reaction between the $\text{O}_2^{\bullet-}$ ion and pollutant radical anion.

4. Conclusions

In summary, a photoelectrocatalytic cell was constructed and applied to the aqueous degradation of refractory organic pollutant degradation. Cu_2O , a p-type semiconductor with a narrow band gap of 2.0eV , has been successfully fabricated with wide range of morphologies from cuboctahedra, truncated octahedra and to octahedra on the ITO glass substrates, by a PVP-tuning electrodeposition method. The preferential adsorption of the non-ionic surfactant (PVP) on the $\{111\}$ facets of Cu_2O semiconductors made it possible to delicately control the morphologies of Cu_2O semiconductors, and the octahedral Cu_2O with the highest proportion of $\{111\}$ facets exhibited the most effective photo-generated electron-hole separation. 2-CP photoelectrocatalytic degradation results demonstrated that the high proportion of exposed $\{111\}$ facets and the plentiful superoxide radicals generated with the assistance of O_2 should be responsible for the higher photoelectrocatalytic degradation efficiency. Photocurrent stability measurements showed that the Cu_2O semiconductor crystals were firmly adhered on the carriers and easily recycled. Thus, due to its high activity, great stability, low cost and no

Fig. 8. DMPO spin-trapping ESR spectra.

toxicity, the Cu₂O-based photocathode has great potential as an efficient photoelectrocatalyst for scalable water purification. Further, compared with powder photocatalysts, such semiconductors on a solid support were easily collected for recycling and maintained their high activity. Therefore, the reported method offers an environmentally friendly and efficient strategy to design photoelectrocatalytic systems for decomposing various organic pollutants in wastewaters.

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