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The effect of different exposed facets on the photoelectrocatalytic degradation of o-chlorophenol using p-type Cu_2O 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 (Cu_2O) 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 Cu_2O samples and the underlying mechanism for the morphology evolution were investigated. The separation of photogenerated hole-electron pairs on Cu_2O 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 Cu_2O 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 Cu_2O-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 Cu_2O microcrystals presented higher photoelectrocatalytic activity compared to other shapes. Active oxygen species detected by electron spin-resonance (ESR) spectrometry implied that abundant superoxide radicals ($O_2^{\bullet-}$) were the dominant active radicals in the degradation.

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 nanomaterials 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 ($CuSO_4.5H_2O$), 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 MΩ.

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 $CuSO_4.5H_2O$ 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 Kα radiation from 5° to 80° (in 2θ). 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