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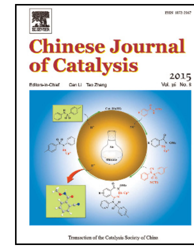

Article

Facet-dependent performance of Cu_2O nanocrystal for photocatalytic reduction of Cr(VI)

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Cu_2O octahedrons, rhombic dodecahedrons and cubes were prepared and evaluated for the reduction of hexavalent chromium under visible light irradiation. The specific activity of Cu_2O with different crystal planes followed the order {111} > {110} > {100}. The surface capping ligands of octahedral and rhombic dodecahedral Cu_2O have no blocking effect on their photocatalytic performance.

1. Introduction

Hexavalent chromium Cr(VI), which has high carcinogenicity and teratogenicity, is a common heavy metal pollutant with high stability in the natural environment. It is released in the effluents of various industrial activities, including electroplating, leather tanning, metal finishing, dyeing, textile production, and steel fabrication. The removal of Cr(VI) is of great importance and has stimulated the development of effective technology for wastewater treatment.

While recent innovative technology includes adsorption, ion exchange, membrane, separation, bioremediation, and chemical precipitation, photocatalysis is considered an attractive, efficient and clean strategy to reduce toxic Cr(VI) species to the less harmful Cr(III) species. Liu et al. [1] reported that more than 99.0% of Cr(VI) was removed in 5 h over α-Fe_2O_3 under visible light irradiation.

As an important p-type semiconductor with a direct band gap of 2.17 eV that is suitable for sunlight utilization, Cu_2O nanocrystals with different morphology have been successfully prepared and were demonstrated as useful for gas sensing, solar energy conversion, and use in lithium ion batteries and the photoactivated splitting of water into H_2 and O_2. Kuo et al. [2] reported a facile synthesis of Cu_2O nanocrystals with a systematic shape evolution. Sun et al. [3] investigated the crystal facet dependent effect of polyhedral Cu_2O microcrystals that exposed different index facets on the photodegradation of methyl orange. Li et al. [4] synthesized flower-like Cu_2O architectures with a high surface area and large pore volume, which exhibited high and stable photocatalytic activity for the reduction of Cr(VI).

The present work focused on comparing the activity for reducing Cr(VI) ions under visible light over Cu_2O cubes, octahedrons, and rhombic dodecahedrons, respectively, dominated by

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{100}, {111}, and {110} facets.

2. Experimental

2.1. Catalyst preparation

All chemical reagents in this work were analytical grade and used without further purification. Cubic, octahedral, and rhombic dodecahedral Cu_2O nanocrystals were prepared by reported wet chemical methods [5,6].

Cu_2O cubes (denoted as Cub) without a capping ligand were synthesized by adding 5.0 mL of NaOH aqueous solution (2.0 mol/L) into 50 mL of $CuCl_2$ aqueous solution (0.01 mol/L) under stirring. Then 5.0 mL ascorbic acid aqueous solution (0.6 mol/L) was added and the system was stirred for 5 h at 55 °C.

Octahedral (OctO) and rhombic dodecahedral (RhdO) Cu_2O nanocrystals capped with oleic acid were obtained as follows. 40 mL of $CuSO_4$ solution (1 mmol) was mixed with 20 mL absolute ethanol and 2.5 mL oleic acid for octahedron (4 mL oleic acid for rhombic dodecahedron). After heating to 100 °C, 10 mL of NaOH was added in 5 min, followed by adding 30 mL aqueous solution containing 3.42 g D-(+)-glucose under constant stirring for 1 h. The products from the round bottom flask were collected by centrifugation and washed with distilled water and absolute ethanol several times, and finally dried at 60 °C.

To remove the capping ligand oleic acid on the surface of the octahedral and rhombic dodecahedral Cu_2O nanocrystals, the samples OctO and RhdO were treated by a controlled oxidation treatment [7,8]. In a typical procedure, a mixed gas of propylene (8%), oxygen (4%), and argon (88%) with a total flow rate of 20 mL/min was fed to 0.2 g of Cu_2O loaded in a quartz tube (inner diameter of 15 mm). The temperature was programmed at a ramp rate of 5 °C/min to 215 °C and kept there for 30 min. The resulting octahedral and rhombic dodecahedral Cu_2O nanocrystals with clean surfaces were denoted as Oct and Rhd, respectively.

2.2. Characterization

The crystal phase of the as-prepared samples was characterized by a X-ray diffractometer (XRD, PANalytical X"pert PRO) using Cu K_α radiation (λ = 0.15406 nm) in the range of 20° to 80°. Microstructural analysis was performed using field emission scanning electron microscopy (FESEM, Hitachi S-4800). The BET surface area was determined using a Micromertitics Tristar 3000. FT-IR spectra were recorded on a Nicolet IS 5 spectrophotometer.

2.3. Photocatalytic experiments

In the photocatalytic experiment, 0.05 g of Cu_2O was suspended in 100 mL of Cr(VI) solution 40 mg/L. The pH value was adjusted to 5.0 by H_2SO_4 solution. After being kept in the dark for 50 min to attain adsorption equilibrium, the suspension with 7 vol% absolute methanol was irradiated with an 18 W LED white light lamp. A portion of the reaction solution was withdrawn every 5 to 10 min, which was centrifuged and analyzed for the Cr(VI) concentration by the 1,5-diphenylcarbazide method on a Tianjin UV-752B spectrophotometer.

3. Results and discussion

3.1. SEM observation

Figure 1 shows the SEM images of the Cu_2O cubes, octahedrons, and rhombic dodecahedrons with the sizes of a few hundred nm. Octahedral OctO and Oct with clean surfaces with eight {111} facets have almost the same morphology with the edge size of 400 to 800 nm, except that the flat surfaces of OctO become slightly coarse after cleaning off the capping oleic acid by propylene oxidation at 215 °C. These are shown in Fig. 1(a) and (b). Huang's group [7,8] adopted this method for the first time to remove the oleic acid capped on the surface of Cu_2O nanocrystals. Using SEM and XRD characterization, they found that the treatment had no effect on the morphology and structure of the Cu_2O nanocrystals other than getting rid of the capping agent, which was deduced from their XPS and IR spectra. Figure 1(c) shows rhombic dodecahedral Cu_2O nanocrystals RhdO with 12 exposed {110} facets which had 300 to 600 nm edges. Its counterpart Rhd with clean surfaces also has a similar shape and size to RhdO (not shown here). The edge lengths of the Cu_2O cubes with six {100} facets were 200 to 400 nm, as shown in Fig. 1(d).

3.2. XRD identification

Figure 2 shows the XRD patterns of the Cu_2O nanocrystals. All the diffraction peaks were indexed by the standard cubic structure of Cu_2O (JCPDS No. 05-0667). It is well known that Cu_2O is oxidized to CuO at temperatures higher than 150 °C. The fact that no peak other than those of Cu_2O was detected in the XRD patterns of Oct and Rhd indicated that the treatment at 215 °C for 0.5 h under the mixed C_3H_6 gas prevented the oxidation of Cu_2O into CuO.

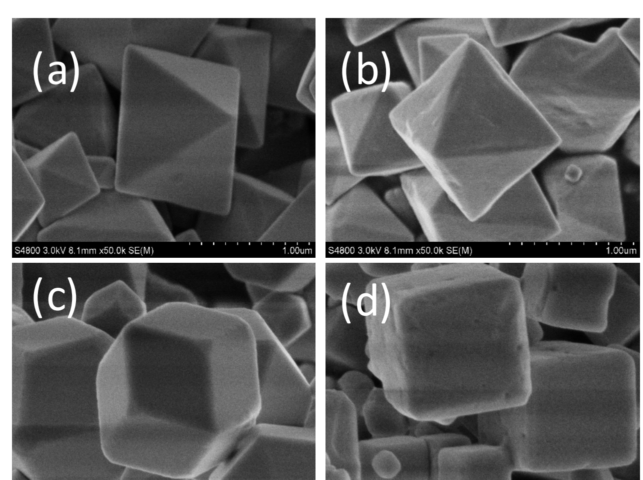

Fig. 1. SEM images of Cu_2O crystals. (a) OctO, octahedral Cu_2O prepared with oleic acid; (b) Oct, octahedral Cu_2O with clean surfaces; (c) RhdO, rhombic dodecahedral Cu_2O prepared with oleic acid; (d) Cub, cubic Cu_2O.