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Article

Facet-dependent performance of Cu₂O nanocrystal for photocatalytic reduction of Cr(VI)

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ABSTRACT

Cu₂O octahedrons, rhombic dodecahedrons and cubes were prepared and evaluated for the reduction of hexavalent chromium under visible light irradiation. The specific activity of Cu₂O with different crystal planes followed the order {111} > {110} > {100}. The surface capping ligands of octahedral and rhombic dodecahedral Cu₂O have no blocking effect on their photocatalytic performance.

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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 -Fe₂O₃ 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, Cu₂O 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 H₂ and O₂. Kuo et al. [2] reported a facile synthesis of Cu₂O nanocrystals with a systematic shape evolution. Sun et al. [3] investigated the crystal facet dependent effect of polyhedral Cu₂O microcrystals that exposed different index facets on the photodegradation of methyl orange. Li et al. [4] synthesized flower-like Cu₂O 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 Cu₂O 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 $\text{Cu } K_\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) 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 Micromeritics 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 ana-

lyzed 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 .

Fig. 2. XRD patterns of Cu_2O crystals with different morphology.

3.3. FT-IR analysis

To examine the effect of the mild oxidation for removing the surface capping oleic acid, the as-prepared OctO and Oct were characterized by FT-IR. The results obtained are the same as reported by Huang's group [7,8]: no band around 2900 cm^{-1} corresponding to the vibration of C–H appeared, showing that the oxidation treatment had removed the surface oleic acid. IR spectroscopy has long been utilized as a powerful tool to provide supplementary information on the nature of copper oxides: the absorption peak at 610 cm^{-1} was attributed to the stretching of $\text{Cu(I)}\text{--O}$ and the band at $\sim 530\text{ cm}^{-1}$ to the vibration of $\text{Cu(II)}\text{--O}$ [9,10]. We further compared the absorption features of OctO and Oct in the range of $400\text{--}1000\text{ cm}^{-1}$. This is shown in Fig. 3. Both OctO and Oct displayed only one absorption peak at 605 cm^{-1} , which excluded the existence of CuO . Thus, IR characterization confirmed that OctO and Oct were of the cuprous oxide phase.

3.4. Photocatalytic activity

Figure 4(a) shows the catalytic performance for reducing Cr(VI) under visible light over the Cu_2O nanocrystals without a capping agent. The Cu_2O nanocrystals catalyzed the process,

Fig. 3. FT-IR spectra of octahedral Cu_2O prepared without (Oct) and with (OctO) oleic acid.

Fig. 4. Photocatalytic reduction of Cr(VI) over Cu_2O nanocrystals under visible light.

reducing 40% Cr(VI) in 3 h, as compared to that only 10% Cr(VI) was reduced under the same condition without the catalysts. From the data up to 100 min, the first order rate constant k for the Cu_2O samples with different morphology were obtained and shown in Fig. 5. The catalytic activity for the reduction of Cr(VI) was ranked as: rhombic dodecahedron > octahedron > cube, i.e., facets $\{110\} > \{111\} > \{100\}$.

To evaluate the effect of the capping oleic acid on the performance of the catalysts, octahedral and rhombic dodecahedral Cu_2O nanocrystals before and after the mild oxidation treatment in the mixed C_3H_6 gas were used to reduce Cr(VI) under the same condition with visible light irradiation. OctO and Oct gave a similar kinetic behavior in 100 min, as shown in

Fig. 5. First order rate constants for the photocatalytic reduction of Cr(VI) over Cu_2O with different morphology.

Fig. 4(b), with almost the same rate constant (Fig. 5). The situation of RhdO and Rhd was the same as the Cu₂O octahedrons. Hua et al. [11] reported a surface blocking effect exerted by the capping ligand on the reduction behavior of H₂ and CO over Cu₂O nanocrystals. They found that different capping ligands gave different reduction temperatures. Unlike their findings for the gas reaction, our experimental results that the OctO and Oct, and RhdO and Rhd samples have the same rate constant showed that there was no blocking effect by the capping oleic acid on the surfaces of octahedral and rhombic dodecahedral Cu₂O on their catalytic performance in the aqueous system. It was shown recently that the vertices and edges of Cu₂O nanocrystals experienced erosion due to slight dissolution after several weeks in water [12]. The capping oleic acid can act as a protecting agent to slow down the dissolution of Cu₂O in a weak acid solution or the oxidation by holes formed by light absorption [13]. Thus an apparent activity at a long reaction time that was higher than the actual one could be produced by these Cu₂O nanocrystals capped with oleic acid, as shown in Fig. 4(b).

The crystal structure, grain size, surface area, and morphology of the catalyst will affect the photocatalytic activity. In order to explore the factors determining the performance of the samples, the use of the photocatalytic activity per unit surface area, the specific activity, is more reasonable. The specific surface areas S_{BET} of cubic, octahedral, and rhombic dodecahedral Cu₂O determined by the BET method were 2.85, 0.65, and 0.96 m²/g, respectively. Their specific rate constants k' , defined as k/S_{BET} , for the photocatalytic reduction of Cr(VI) were calculated and shown in Fig. 5. The results clearly showed that the specific activity of the Cu₂O nanocrystals depended on the exposed crystal planes and can be ranked as {111} > {110} > {100}.

Recent theoretical investigations have shown that there are differences between the different facets of Cu₂O crystals. While the {111} crystal plane of Cu₂O octahedrons has both coordination unsaturated Cu and coordination saturated Cu [14,15], the {110} crystal plane of Cu₂O rhombic dodecahedrons only has coordination saturated Cu and the {100} crystal plane of Cu₂O cubes has coordination unsaturated O. Therefore, the Cu₂O

{111} and {110} facets would have a higher energy compared to the {100} plane with 100% terminal oxygen. As a result, the {111} and {110} facets with the higher surface energy would be expected to be more easily photoexcited to produce electrons and holes and have a higher photocatalytic activity than the {100} facets [16]. As to comparing the {111} and {110} facets of Cu₂O, it would be reasonable that the former with unsaturated Cu gives a better catalytic result because coordination unsaturated sites usually act as the active sites, which would benefit photo-generated electrons and holes migration to the surface and reduce the electron-hole recombination probability. More work is needed to elucidate the factors determining the facet dependent performance of metal oxide nanocrystals.

4. Conclusions

We systematically investigated the catalytic performance of Cu₂O cubes, octahedrons, and rhombic dodecahedrons with well-defined shape for the catalytic reduction of Cr(VI) under visible light irradiation. There was no surface blocking effect exerted by the capping ligand on their reduction performance of Cr(VI) in aqueous solution. The photocatalytic specific activity over the Cu₂O nanocrystals dominated by different facets followed the order {111} > {110} > {100}.

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Graphical Abstract

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Facet-dependent performance of Cu₂O nanocrystal for photocatalytic reduction of Cr(VI)

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Catalysis by Cu₂O nanocrystals with different morphology for the photoreduction of Cr(VI) showed that the surface capping ligands of octahedral and rhombic dodecahedral Cu₂O have no blocking effect and the activity of different facets was ranked {111} > {110} > {100}.

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不同晶面Cu₂O光催化还原Cr(VI)的性能

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摘要: Cr(VI)具有高毒性和强诱变致癌性, 且能稳定存在于自然界中, 对人类和自然环境危害极大. 而容易沉淀和吸附在固体上的Cr(III)毒性较小, 约为Cr(VI)的千分之一. 因此, 将Cr(VI)还原为Cr(III)是处理含铬废水的有效途径. 光催化还原是一种环境友好的新型技术, 基于可见光的催化还原处理含Cr(VI)废水能够在常温常压下进行, 具有经济、高效、清洁和无二次污染等特点而受到广泛关注. 采用适宜的晶面生长控制剂, 调变不同晶面的相对生长速率, 可制得暴露不同晶面、具有多种形貌的Cu₂O. 将这些具有不同晶面的Cu₂O用于光催化氧化降解有机污染物的研究表明, Cu₂O的光催化氧化性能与其所暴露的晶面密切相关, 其表面残留的用作晶面生长控制剂的表面活性剂对其催化性能有重要影响. 相对而言, 将Cu₂O用于光催化还原Cr(VI)的研究较少, 关于晶面导向剂油酸对其光催化还原Cr(VI)性能的影响尚未见报道.

本文采用液相法, 首先合成了仅暴露Cu₂O{100}晶面的立方体(Cub), 进而通过控制晶面导向剂油酸的用量, 制得仅外露Cu₂O{111}晶面的八面体(OctO)和仅暴露Cu₂O{110}晶面的十二面体(RhdO), 继而再将OctO和RhdO在C₃H₆-O₂等混合气中于215 °C处理30 min, 通过此温和氧化除去表面油酸, 获得了具有洁净表面的八面体(Oct)和十二面体(Rhd)的Cu₂O. 采用X射线衍射(XRD)、扫描电镜(SEM)和傅里叶变换红外光谱(FT-IR)等技术对其物性特征进行了表征. 在LED可见光辐照下, 对比评价了具有不同晶面的Cu₂O光催化还原Cr(VI)的性能, 研究了暴露晶面及晶面导向剂油酸等对Cu₂O光催化还原Cr(VI)的影响.

XRD研究表明, 采用液相法及温和氧化处理可制得纯相的Cu₂O, 其XRD图中无Cu及CuO等杂峰出现. SEM观测结果表明, 所得Cu₂O样品形貌均一性较好, 采用丙烯选择氧化去除表面油酸后, Cu₂O的形貌无明显改变, 仅其外表面略有粗化. FT-IR分析进一步说明, 去除表面油酸后, 其物相仍为Cu₂O, 没有出现CuO的红外特征吸收.

动力学研究结果显示, Cu₂O光催化还原Cr(VI)具有准一级反应动力学特征, 晶面导向剂油酸的存在能够在一定程度上减缓光腐蚀和酸腐蚀, 有助于较长时间内保持Cu₂O光催化还原活性, 而对Cu₂O光催化速率没有影响. 以单位比表面积速率常数为比活性指标, 不同晶面Cu₂O光催化还原Cr(VI)的活性次序为{111} > {110} > {100}. Cu₂O不同晶面的原子配位情况差异明显, 且{100}晶面的表面能较低, 由此可较好解释具有不同晶面Cu₂O光催化还原Cr(VI)活性的不同. 八面体Cu₂O的{111}面上同时存在配位饱和与配位不饱和Cu, 而菱形十二面体Cu₂O的{110}面上只有配位饱和Cu, 立方体Cu₂O的{100}面上只有配位不饱和O. 相对于Cu₂O的{100}晶面, 具有更高表面自由能的{111}和{110}晶面易于产生光生电子-空穴对, 从而表现出较{100}晶面更高的光催化活性. 而Cu₂O{111}晶面表现出更高光催化活性的原因可能是: Cu₂O{111}晶面上存在的不饱和Cu可作为活性位点, 在某种程度上有利于光生电子-空穴对分离, 减少光生电子-空穴对复合, 从而提高光催化还原速率.

关键词: 六价铬; 晶面; 光催化; 可见光; 氧化亚铜

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