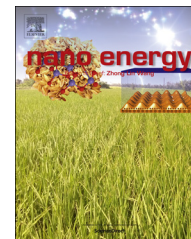




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COMMUNICATION

Facet-defined AgCl nanocrystals with surface-electronic-structure-dominated photoreactivities



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Abstract

The conventional understanding of facet effects on photocatalysts is that semiconductor micro/nanocrystals exposed with high-reactivity facets usually exhibit excellent photocatalytic activities. However, this point of view is being challenged in some circumstances. Herein, two types of facet-defined AgCl nanocrystals, AgCl nanocubes exposed with six {100} facets and AgCl octahedrons enclosed by eight {111} facets have been successfully prepared. The comparative studies of their photocatalytic properties reveal an unusual higher photoreactivity of AgCl nanocubes than that of AgCl octahedrons, although AgCl {100} facets have lower theoretical surface energy than the AgCl {111} facets. The further mechanism investigation suggests that the much decreased reduction potential of {111} facet would result in insufficient consumption of photo-excited electrons and hence depress the involvement of holes in photooxidation reactions. Consequently, the surface electronic structures dominate the photoreactivities of AgCl {111} and {100} facets. Our work reveals the true photoreactivities of AgCl {111} and {100} facets by direct experimental evidence, and the proposed mechanism will facilitate further development of highly efficient AgCl photocatalysts.

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Introduction

Heterogeneous photocatalysis has attracted wide attention due to its potential applications in the renewable energy and environmental fields [1-13]. The photocatalytic reaction is a catalytic process occurring on the surface of semiconductor materials under the light irradiation, in which the surface atomic and electronic structures of photocatalysts play significant roles in determining their photoreactivities [14-19]. The architecture tailoring of semiconductors with desirable shape and size is an effective strategy to adjust their surface states so as to improve the photoreactivities [20-24]. In particular, great efforts have been devoted to fabricating polyhedral micro/nanocrystals and investigating their facet-dependent properties [25-31]. The conventional understanding of facet effects on photocatalysts is that semiconductor micro/nanocrystals exposed with high-reactivity facets have high density of atomic steps, ledges, kinks and dangling bonds, and should exhibit excellent photocatalytic activities [32-36]. However, with intense studies, photoreactivities of some polyhedral semiconductors seemed inconsistent with their crystal facets activities, and researchers found that the surface atomic structure was not a sole factor determining the photocatalytic activities [25,37,38]. Other significant issues including surface electronic structure and specific surface areas of photocatalysts, as well as types of substrate molecules should also be taken into consideration [25,37-39]. Thus, the rational design of a polyhedral semiconductor with ideal photoreactivity need more comprehensive analysis besides considering surface atomic structure.

With trace amount of Ag(0) on its surface, AgCl exhibiting excellent photocatalytic performance under visible light irradiation is drawing significant attention [40-47]. {111} and {100} are two important candidates of exposed facets for AgCl nanocrystals, and the theoretical studies predicted that AgCl crystals exposed with {111} facets would exhibit higher photoreactivity than that enclosed by {100} facets due to their higher surface energy [48]. However, this proposal has not been directly verified by solid experimental data, and such comparative study is unexplored limited by unsuccessful fabrication of facet-defined AgCl nanocrystals using identical reaction system. Therefore, it is of great importance for the successful preparation of facet-defined AgCl nanocrystals exposed with {111} and {100} facets, respectively, and investigating their true photoreactivities and facet effects.

In this work, two kinds of facet-defined AgCl nanocrystals, AgCl nanocubes exposed with six {100} facets and AgCl octahedrons enclosed by eight {111} facets have been successfully prepared. Following the comparative study of their photoreactivities, it turns out that {100}-bound AgCl nanocubes exhibit higher photocatalytic oxidation activity than AgCl octahedrons exposed with {111} facets, although the theoretical calculations predict that the AgCl {111} facets have higher surface energy than the {100} facets. Further mechanism studies suggest that the much reduced reduction potential of {111} facet would result in rate-limiting consumption of photo-excited electrons and depress the involvement of holes in photooxidation reactions. Thus, it is the surface electronic structure that dominates the photoreactivity of AgCl {111} and {100} facets. Our work reveals the true photoreactivities of AgCl

{111} and {100} facets by direct experimental evidence, and the proposed mechanism will promote the development of high efficient AgCl photocatalysts.

Experimental

Preparation of AgCl nanocrystals

The AgCl polyhedra were prepared using a direct precipitation reaction. Typically, an amount of polyvinylpyrrolidone (PVP) (average MW 58,000, K29-32, Acros) and 26 mg NaCl were added to 12 mL dimethyl sulfoxide (DMSO), and then the solution was kept at 60 °C for 30 min under intensive magnetic stirring. After both PVP and NaCl were completely dissolved, 30 mL DMSO solution of CH₃COOAg (60 mg) was dropwise added to the above solution under intensive stirring, and then the mixture solution was kept for 1 h at 60 °C for an adequate precipitation process. At last, the as-prepared AgCl nanoparticles were collected by centrifugation and washed several times with ethanol to ensure the adsorbed ions removal, and then dried overnight at room temperature under vacuum condition. The processes of the preparation of AgCl octahedrons and cubes are nearly the same with only different amounts of PVP, corresponding to 350 mg and 970 mg, respectively. Moreover, when changing the reaction temperature to 30 °C, the AgCl octahedrons and cubes can also be obtained by adjusting the amount of added PVP, corresponding to 27 and 1080 mg.

Materials characterization

The morphologies of the samples were studied by a field-emission gun scanning electron microscope (FEI Quanta 400, 5 kV). Transmission electron microscopy (TEM) images and the corresponding selected area electron diffraction (SAED) patterns were characterized by an FEI Tian 80-300 microscope at 80 kV. The X-ray diffraction (XRD) spectra of the samples were recorded by a Rigaku Dmax 2200 X-ray diffractometer with Cu K α radiation ($\lambda=1.5416$ Å). Diffuse reflectance absorption spectra of AgCl-based photocatalysts were recorded in the range from 200 to 800 nm using a Hitachi U-3010 spectroscopy with BaSO₄ as reference. Specific surface areas were measured at 77 K by Brunauer-Emmett-Teller (BET) nitrogen adsorption-desorption (NOVA 2200e, Quantachrome, USA). X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) were measured on a PHI 5600 XPS system equipped with a monochromatic Al K α source and a He discharge lamp.

Photocatalytic experiment

Photocatalytic activities of the AgCl-based photocatalyst were evaluated by degradation of methyl orange (MO) and rhodamine B (Rh B) dyes under a 300 W Xe lamp with UV cutoff filter (providing visible light with $\lambda \geq 400$ nm). MO solution (100 mL, 10^{-4} mol L⁻¹) or Rh B solution (100 mL, 2×10^{-5} mol L⁻¹) containing 0.1 g of the AgCl-based photocatalysts was placed in a 200 mL cylindrical quartz vessel. Before the light was turned on, the solution was stirred in the dark for 30 min to ensure an adsorption/desorption

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