Photocatalysts

Ag@AgCl: A Highly Efficient and Stable Photocatalyst Active under Visible Light**

Peng Wang, Baibiao Huang, * Xiaoyan Qin, Xiaoyang Zhang, Ying Dai, Jiyong Wei, and Myung-Hwan Whangbo

Dedicated to Professor Minhua Jiang

Nanoparticles (NPs) of noble metals can strongly absorb visible light because of their plasmon resonance,[1–4] which is greatly influenced by their morphology and size.[5–10] The phenomenon of plasmon resonance gives rise to important applications such as colorimetric sensors,[11,12] photovoltaic devices,[13,14] photochromic devices,[15] and photocatalysts.[16] Noble metal NPs exhibit characteristic optical and physical properties that are substantially different from those of the corresponding bulk materials.[17–19] In particular, silver NPs show efficient plasmon resonance in the visible region, which Awazu et al.[16] recently utilized to develop a plasmonic photocatalyst. In their study, TiO2 was deposited on NPs consisting of a silver core covered with a silica (SiO2) shell to prevent oxidation of Ag by direct contact with TiO2. Under UV illumination, this plasmonic photocatalyst exhibits enhanced catalytic activity, which increases with decreasing thickness of the SiO2 shell. To enhance the activity of a plasmonic photocatalyst, it is desirable to deposit silver NPs directly onto the surface of an active dielectric substrate without a protective shell, because the near-field effect of the NPs will be more strongly felt by the substrate. Herein we show that such a photocatalyst can be obtained from silver chloride by exploiting its photosensitivity, and the resulting plasmonic photocatalyst is highly efficient and stable under visible-light illumination.

Silver halides are photosensitive materials extensively used as source materials in photographic films. On absorbing a photon, a silver halide particle generates an electron and a hole, and subsequently the photogenerated electron combines with an Ag+ ion to form an Ag0 atom. Ultimately, a cluster of silver atoms is formed within a silver halide particle upon repeated absorption of photons. Due to this instability under sunlight, which provides the very basis for chemical photography, silver halides are seldom used as photocatalysts. Nevertheless, there have been reports that under UV/VIS illumination AgCl deposited on a conducting support photocatalyzes O2 production from water in the presence of a small excess of silver ions in solution,[20] and that under UV illumination AgBr dispersed on a silica support photocatalyzes H2 production from CH3OH/H2O solution.[21] In their study on the AgBr/SiO2 photocatalyst, Kakuta et al.[21] observed that Ag0 species are formed on AgBr in the early stage of the reaction, and AgBr is not destroyed under successive UV illumination. As suggested by Kakuta et al., electron–hole separation may occur smoothly in the presence of Ag0 species, and the latter may catalyze H2 production from alcohol radicals formed by photo-induced holes. If so, silver NPs formed on silver halide particles might be expected to be a stable photocatalyst under visible-light illumination due to their plasmon resonance. This expectation led us to prepare a new photocatalyst active and stable under visible light, namely, AgCl particles with silver NPs formed on their surface, by first treating Ag2MoO4 with HCl to form AgCl. Under UV illumination AgCl deposited on a conducting support photo-

---

[1] P. Wang, Prof. Dr. B. Huang, X. Qin, Prof. X. Zhang, Dr. J. Wei
State Key Lab of Crystal Materials
Shandong University, Jinan 250100 (China)
E-mail: bbhuang@sdu.edu.cn
Homepage: http://www.icm.sdu.edu.cn/index.php
Prof. Dr. Y. Dai
School of Physics, Shandong University
Prof. Dr. M.-H. Whangbo
Department of Chemistry, North Carolina State University
Raleigh, NC 27695-8204 (USA)

[2] This work was financially supported by the National Basic Research Program of China (973 Program, Grant 2007CB613302) and the National Natural Science Foundation of China under Grants 50721002 and 10774091. M.-H.W. is thankful for support by the Office of Basic Energy Sciences, Division of Materials Sciences, U.S. Department of Energy, under Grant DE-FG02-86ER45259.

[3] This work was financially supported by the National Basic Research Program of China (973 Program, Grant 2007CB613302) and the National Natural Science Foundation of China under Grants 50721002 and 10774091. M.-H.W. is thankful for support by the Office of Basic Energy Sciences, Division of Materials Sciences, U.S. Department of Energy, under Grant DE-FG02-86ER45259.

[4] This work was financially supported by the National Basic Research Program of China (973 Program, Grant 2007CB613302) and the National Natural Science Foundation of China under Grants 50721002 and 10774091. M.-H.W. is thankful for support by the Office of Basic Energy Sciences, Division of Materials Sciences, U.S. Department of Energy, under Grant DE-FG02-86ER45259.
light irradiation. Prior to irradiation, the MO solution over the catalyst was kept in the dark for 30 min to obtain the equilibrium adsorption state. The concentration of the MO solution slightly decreases while it is kept in the dark, so that the $C/C_0$ value is slightly smaller than 1 at $t=0$. As the irradiation time increases, the decomposition of MO dye progresses steadily, and decomposition over the Ag@AgCl catalyst is completed in 15 min of visible-light irradiation.

Provided that the bleaching reaction follows a pseudo-first-order reaction, the rate of the MO-dye decomposition over Ag@AgCl is estimated to be about 0.133 mg min$^{-1}$/C$_0$ ($\lambda \geq 400$ nm). C is the concentration of MO dye at time $t$, and $C_0$ that in the MO solution immediately before it is kept in the dark.

Figure 1. XRD patterns of a) Ag, b) AgCl, c) as-prepared Ag@AgCl, and d) Ag@AgCl used for ten consecutive photooxidation experiments with the solution of MO dye (see text for details) under visible-light irradiation.

Figure 2. Typical SEM images of the as-prepared Ag@AgCl sample.

Figure 3. UV/Vis diffuse-reflectance spectra of a) AgCl, b) Ag@AgCl, and c) N-doped TiO$_2$.

Figure 4. Photodecomposition of MO dye in solution (20 mg L$^{-1}$) over Ag@AgCl (●) and N-doped TiO$_2$ (▲) under visible-light irradiation ($\lambda \geq 400$ nm). C is the concentration of MO dye at time $t$, and $C_0$ that in the MO solution immediately before it is kept in the dark.

Figure 5. Irradiation–time dependence of the relative concentration $C/C_0$ of the MO dye in solution over Ag@AgCl during repeated photooxidation experiments under visible light.
stable and efficient photocatalyst under visible light. The surface of AgCl particles is most likely terminated by Cl⁻ ions, and is therefore negatively charged. Consequently, a silver NP deposited on the surface of an AgCl particle should polarize its electron distribution such that the regions of its negative and positive charges are far from and close to the Ag/AgCl interface, respectively. The localized surface plasmon state of a silver NP lies in the visible region, so absorption of visible light by the Ag/AgCl catalyst takes place at the silver NPs. Given the dipolar character of the surface plasmon state of a silver NP, an absorbed photon would be efficiently separated into an electron and a hole such that an electron is transferred to the surface of the NP farthest away from the Ag/AgCl interface, and a hole to the surface of the AgCl particle bearing the NP. Hole transfer to the AgCl surface corresponds to the oxidation of Cl⁻ ions to Cl²⁻ atoms. As chlorine atoms are reactive radical species, they should be able to oxidize MO dye and hence become reduced to chloride ions again. The stability of the Ag@AgCl photocatalyst under light irradiation arises most likely from the fact that a photon is absorbed by the silver NPs, and an electron separated from an absorbed photon remains in the NPs rather than being transferred to the Ag⁺ ions of the AgCl lattice. In general, photogenerated electrons are expected to be trapped by O₂ in the solution to form superoxide ions (O₂⁻) and other reactive oxygen species.[26]

In summary, the plasmonic photocatalyst Ag@AgCl described herein is efficient and stable under visible light. Plasmonic photocatalysts are promising candidates for the development of highly efficient and stable photocatalysts active under visible light. Work on Ag@AgBr and Ag@AgI is in progress.

**Experimental Section**

Ag₂MoO₄ was prepared by a typical microwave-assisted hydrothermal reaction. Aqueous solutions of AgNO₃ and Na₂MoO₄ were prepared in advance. 10 mL of 0.2 mol AgNO₃ solution and 1 mol Na₂MoO₄ solution, and the pH value of the mixed solution was adjusted to 8.5 by adding dilute NaOH solution. The resulting solution was stirred for about 0.5 h, transferred to a special teflon autoclave, and then heated at 180°C for 1 h under microwave irradiation, which leads to precipitation of Ag₂MoO₄. The Ag₂MoO₄ precipitate was collected, washed with deionized water until the pH value of the washing solution was about 7, and dried in air at 80°C for 8 h.

AgCl was synthesized by the ion-exchange reaction between Ag₂MoO₄ and HCl. Ag₂MoO₄ was sonicated in concentrated HCl until completion of the ion-exchange process. This process yields H₂MoO₄, which is dissolved in an excess of HCl, and AgCl, which is precipitated. The AgCl precipitate was collected, washed with deionized water and dried in air.

The AgCl powder was put into a solution of MO dye, which was then irradiated with a 300 W Xe arc lamp equipped with an ultraviolet cutoff filter to provide visible light with λ ≥ 400 nm. Then the resulting precipitate, which consists of silver NPs deposited on AgCl particles, was washed and dried in air. The crystal structure of the Ag@AgCl sample was examined by XRD (Bruker AXS D8), its morphology by SEM (Hitachi S-4800 microscope), and its diffuse reflectance by UV/Vis spectroscopy (UV-2550, Shimadzu).

The N-doped TiO₂ reference photocatalyst was prepared by nitration of commercially available TiO₂ powder (surface area 50 m² g⁻¹) at 773 K for 10 h under NH₃ flow (flow rate of 350 mL min⁻¹).[27]

Photocatalytic degradation of MO dye was carried out with 0.2 g of the powdered photocatalyst suspended in 100 mL of MO dye solution prepared by dissolving 20 mg of MO powder in 1.0 L of distilled water in a pyrex-glass cell at room temperature under air. The optical system for detecting the catalytic reaction included a 300 W Xe arc lamp (focused through a shutter window) with UV cutoff filter (providing visible light with λ ≥ 400 nm), and the degradation of MO dye was monitored by UV/Vis spectroscopy (UV-750PC, Xinnao, Shanghai).

Received: May 28, 2008
Revised: July 24, 2008
Published online: ■■ ■■, 2008

**Keywords:** heterogeneous catalysis · nanostructures · photocatalysts · photochemistry · silver

Ag@AgCl: A Highly Efficient and Stable Photocatalyst Active under Visible Light

Plasmonic photocatalyst Ag@AgCl, in which Ag nanoparticles are deposited on the surfaces of AgCl particles (SEM image depicted), was prepared by treating Ag₂MoO₄ with HCl to form AgCl powder and then reducing some Ag⁺ ions in the surface region of the AgCl particles to Ag⁰. This photocatalyst is highly efficient, for example in the degradation of organic dyes, and stable under visible light.