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Photocatalysts

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

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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, TiO_2 was deposited on NPs consisting of a silver core covered with a silica (SiO_2) shell to prevent oxidation of Ag by direct contact with TiO_2. Under UV illumination, this plasmonic photocatalyst exhibits enhanced catalytic activity, which increases with decreasing thickness of the SiO_2 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 Ag^0 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 O_2 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 H_2 production from CH_3OH/H_2O solution.[21] In their study on the $AgBr/SiO_2$ photocatalyst, Kakuta et al.[21] observed that Ag^0 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 Ag^0 species, and the latter may catalyze H_2 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 Ag_2MoO_4 with HCl to form AgCl powder and then reducing some Ag^+ ions in the surface region of the AgCl particles to Ag^0 species (for details, see the Experimental Section). For convenience, these are referred to as Ag@AgCl particles.

The X-ray diffraction (XRD) pattern of the Ag@AgCl product clearly shows that the cubic phase of Ag with lattice constant $a = 4.0861$ Å (JCPDS file: 65-2871) coexists with the cubic phase of AgCl with lattice constant $a = 5.5491$ Å (JCPDS file: 31-1238; see Figure 1). Scanning electron microscopy (SEM) images of the Ag@AgCl product (Figure 2) reveal that silver NPs with diameters in the range of 20–150 nm are deposited on the surface of AgCl particles with diameters in the range of 0.2–1.3 μm. The UV/Vis diffuse-reflectance spectra of Ag@AgCl, AgCl, and N-doped TiO_2 (used as reference photocatalyst) are compared in Figure 3. In contrast to AgCl and N-doped TiO_2, Ag@AgCl has a strong adsorption in the visible region which is almost as strong as that in the UV region. This is attributed to the plasmon resonance of silver NPs deposited on AgCl particles.

To evaluate the photooxidation capability of Ag@AgCl, we examined the decomposition of methylic orange (MO) dye in solution over the Ag@AgCl sample under visible-light irradiation as a function of time (Figure 4). For comparison, we also carried out decomposition of the MO dye in solution over the N-doped TiO_2 reference photocatalyst under visible-

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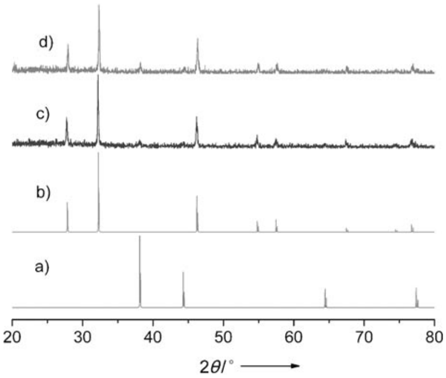

Figure 1. XRD patterns of a) Ag, b) AgCl, c) as-prepared Ag@AgCl, and d) Ag@AgCl used for ten consecutive photooxidation experiments with the solution of MO dye (see text for details) under visible-light irradiation.

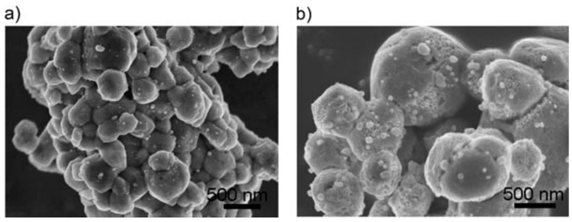

Figure 2. Typical SEM images of the as-prepared Ag@AgCl sample.

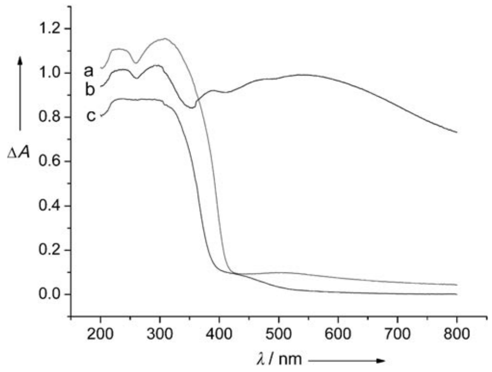

Figure 3. UV/Vis diffuse-reflectance spectra of a) AgCl, b) Ag@AgCl, and c) N-doped TiO_2.

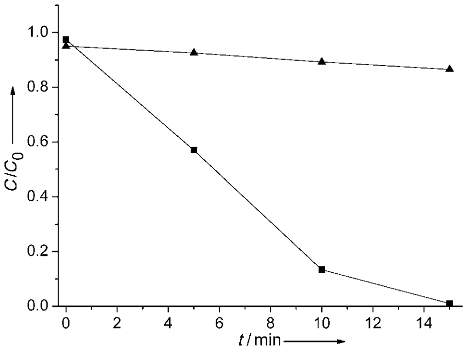

Figure 4. Photodecomposition of MO dye in solution $(20\ \mathrm{mg\,L})^{-1}$ over Ag@AgCl (■) and N-doped TiO_2 (▲) under visible-light irradiation ($\lambda \geq 400$ nm). C is the concentration of MO dye at time t, and C_0 that in the MO solution immediately before it is kept in the dark.

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 $\mathrm{mg\,min^{-1}}$, faster than that over N-doped TiO_2 (ca. 0.017 $\mathrm{mg\,min^{-1}}$) by a factor of eight. We found that other organic dyes such as rhodamine B and methylene blue are also quickly bleached by Ag@AgCl under visible-light irradiation. To show that the decomposition of MO dye over Ag@AgCl is neither caused by catalysis nor by photolysis, we carried out the decomposition experiment in the dark with Ag@AgCl (catalysis) and under full arc-light irradiation without Ag@AgCl (photolysis). In these experiments, the MO concentration remained unchanged as a function of time, that is, Ag@AgCl is a photocatalyst active under visible light.

For a photocatalyst to be useful, it should be stable under repeated application. The N-doped TiO_2 and sulfide photocatalysts sometimes suffer from instability under repeated use.[22,23] To test the repeatability of MO bleaching on Ag@AgCl, we carried out the bleaching experiment repeatedly ten times. As shown in Figure 5, the MO dye is quickly bleached after every injection of the MO solution, and the photocatalyst Ag@AgCl is stable under repeated application with nearly constant photodecomposition rate. The XRD pattern of the Ag@AgCl sample at the end of the repeated bleaching experiment is almost identical to that of the as-prepared sample (Figure 1). Our Ag@AgCl photooxidation experiments, also carried out under full Xe arc light including UV and visible light, led to the same result. Thus, Ag@AgCl is a photocatalyst active and stable under UV and visible light.

AgCl has a direct band gap of 5.6 eV and an indirect band gap of 3.25 eV.[24] Nevertheless, grains of AgCl are photosensitive due to their point ionic defects and electron traps.[25] It is of interest to consider how Ag@AgCl particles become a

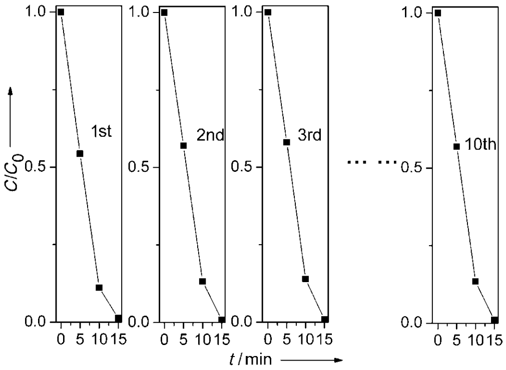

Figure 5. Irradiation–time dependence of the relative concentration C/C_0 of the MO dye in solution over Ag@AgCl during repeated photooxidation experiments under visible light.

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 Cl^0 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 O_2 in the solution to form superoxide ions (O_2^-) 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

Ag_2MoO_4 was prepared by a typical microwave-assisted hydrothermal reaction. Aqueous solutions of $AgNO_3$ and Na_2MoO_4 were prepared in advance. 10 mL of 0.2 M $AgNO_3$ solution was mixed with 10 mL of 0.1 M Na_2MoO_4 solution, and the pH value of the mixed solution was adjusted to 8.0 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 Ag_2MoO_4. The Ag_2MoO_4 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 Ag_2MoO_4 and HCl. Ag_2MoO_4 was sonicated in concentrated HCl until completion of the ion-exchange process. This process yields H_2MoO_4, 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 $\lambda \geq 400$ 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 TiO_2 reference photocatalyst was prepared by nitridation of commercially available TiO_2 powder (surface area $50\,m^2g^{-1}$) at 773 K for 10 h under NH_3 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 $\lambda \geq 400$ nm), and the degradation of MO dye was monitored by UV/Vis spectroscopy (UV-7502PC, Xinmao, Shanghai).

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