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Highly Efficient Visible-Light Plasmonic Photocatalyst Ag@AgBr

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Photocatalysts that are active under sunlight are extremely important in connection with removing organic pollutants in the environment. Desirable photocatalysts are those that can carry out complete decomposition of organic pollutants at low levels.[1] The most extensively studied photocatalyst, TiO_2, has a large band gap (i.e., 3.2 eV for anatase and 3.0 eV for rutile) and hence absorbs only the UV light, which accounts for only 4 % of the total sunlight, to generate charge carriers for promoting the surface redox reactions. Due to this inherent property of TiO_2, its practical applications are rather limited. To effectively utilize the visible light that constitutes 43 % of the total sunlight, it is important to find a photocatalyst that is active and efficient under visible light. Much effort has been devoted to developing "second-generation" TiO_2[2] and other narrow band gap semiconductors[3] that can absorb visible light. Photocatalysts active under visible light are not necessarily limited to semiconductors with a narrow band gap, but can include semiconductors with a large band gap that can work synergetically with nanoparticles of a noble metal.

Nanoparticles of noble metals exhibit unique optical properties that arise from the collective oscillation of the conduction electrons upon interaction with electromagnetic radiation, namely, the localized surface plasmon resonance (SPR).[4,5] For an ensemble of isolated nanoparticles, the shape, the amplitude, and the frequency of the maximum absorbance of the surface plasmon absorption band depend on the effective dielectric constant of the surrounding medium as well as their morphology and size distribution.[6–9] SPR can dramatically amplify the absorption of visible light and is therefore important in developing efficient visible-light photocatalysts.[10,11] Chen et al. have utilized SPR to develop Au/ZrO_2 and Au/SiO_2 plasmonic photocatalysts[10] with efficient photocatalytic activity under visible-light illumination. Silver nanoparticles also have an efficient plasmon resonance in the visible region and have been used in developing plasmonic photocatalysts.[11,12] Awazu et al.[11] showed that TiO_2 deposited on nanoparticles consisting of a silver core covered with a silica (SiO_2) shell exhibits enhanced photocatalytic activity under UV illumination. Recently, we have developed a new plasmonic photocatalyst, Ag@AgCl, which has silver nanoparticles deposited directly onto the surface of AgCl particles,[12] which is highly efficient and stable under visible-light illumination. Herein, we describe the synthesis and characterization of an analogous plasmonic photocatalyst, Ag@AgBr, which is more efficient than Ag@AgCl under visible-light illumination.

Silver bromide, which has a band gap of 2.6 eV, is a photosensitive compound extensively used as a source material in photographic films. Recently, AgBr has been used as an absorption layer for enhancing the efficiency of a photocatalyst. Hu et al.[13] demonstrated that $Ag/AgBr/TiO_2$ prepared by the deposition–precipitation method is photoactive in destroying bacteria under visible light, and Ag^0 species on the surface of the catalyst probably enhance the electron-hole separation and interfacial charge transfer. Gholami et al.[14] fabricated the visible-light photocatalyst, apatite-coated $Ag/AgBr/TiO_2$, for the destruction of bacteria. The photocatalyst Ag@AgBr described in this work is based on SPR, which dramatically amplifies the absorption of visible light and makes Ag@AgBr an efficient visible-light photocatalyst.

Our synthesis and characterization of Ag@AgBr are described in detail in the Supporting Information. A powder X-ray diffraction (XRD) pattern (Figure 1) of the as-prepared Ag@AgBr sample (for experimental details, see the Experimental Section) shows the coexistence of Ag (JCPDS

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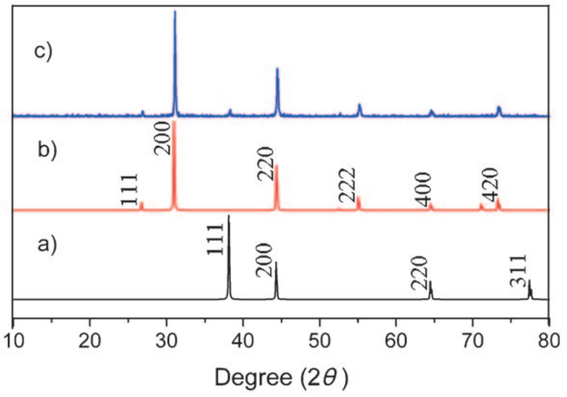

Figure 1. XRD patterns of a) Ag, b) AgBr, c) as-prepared Ag@AgBr.

file: 65-2871) and AgBr (JCPDS file: 6-438). The phase of Ag is cubic in the space group $Fm\bar{3}m$ with lattice constants $a=4.0861$ Å, and that of AgBr is also cubic in the space group $Fm\bar{3}m$ and lattice constants $a=5.7745$ Å. Scanning electron microscopy (SEM) images of the Ag@AgBr product (Figure 2) show that silver nanoparticles with a diameter in the range of 0.05–0.38 μm are formed on the surface of AgBr particles with diameters in the range of 0.33–1.5 μm. The UV/Vis diffuse reflectance spectra of Ag@AgBr, AgBr, and N-doped TiO_2 (used as our reference photocatalyst) are compared in Figure 3. In contrast to the case of AgBr and N-doped TiO_2, Ag@AgBr has a strong absorption in the visible region, which is almost as strong as that in the UV region due to the plasmon resonance of silver nanoparticles deposited on AgBr particles. For light with a wavelength much greater than the diameter of a silver nanoparticle, the electromagnetic field across the entire silver nanoparticle is essentially uniform. As the electromagnetic field oscillates, the weakly bound electrons of the silver nanoparticle respond collectively, giving rise to a plasmon state. When the incident light frequency matches the plasmon oscillation frequency, light is absorbed, resulting in a surface plasmon absorption. The nanoparticles deposited on AgBr have a large number of different shapes and diameters so that their plasmon oscillations cover a wide range of frequencies,[15,16] and hence Ag@AgBr can absorb in a wide range of visible light and UV.

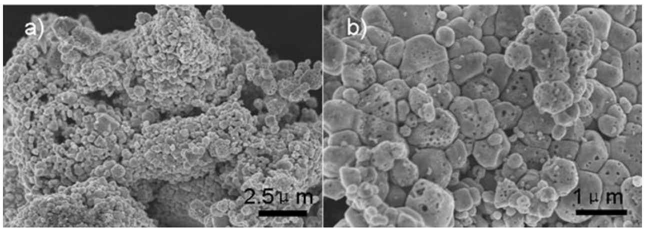

Figure 2. SEM images of a typical as-prepared Ag@AgBr sample: a) low resolution and b) high resolution.

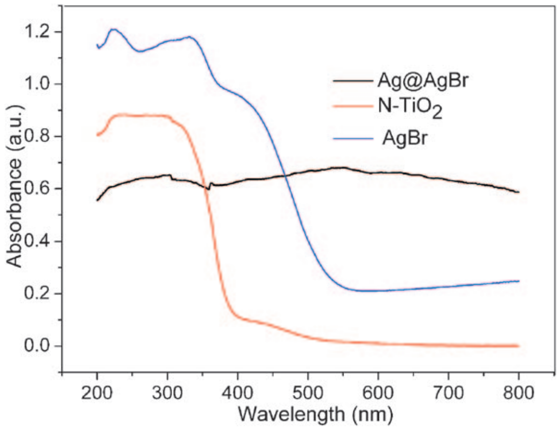

Figure 3. UV/Vis diffuse reflectance spectra of Ag@AgBr, AgBr, and N-doped TiO_2.

The photooxidation activity of Ag@AgBr was evaluated by photocatalytic decomposition of isopropyl alcohol (IPA). Figure 4 shows the photocatalytic decomposition (versus time) of IPA over Ag@AgBr under visible-light irradiation ($\lambda \geq 400$ nm). CO_2 is the final product in the photocatalytic oxidation of organic contaminants.[17] It is striking that about 40 % of the IPA is oxidized to CO_2 after irradiating the IPA solution over Ag@AgBr for only 5 min. For comparison, IPA decomposition over N-doped TiO_2 was also carried out under the same conditions (Figure 4); N-doped TiO_2 was found to be inactive. In experiments either without irradiation or without the photocatalyst, no generated CO_2 was detected.

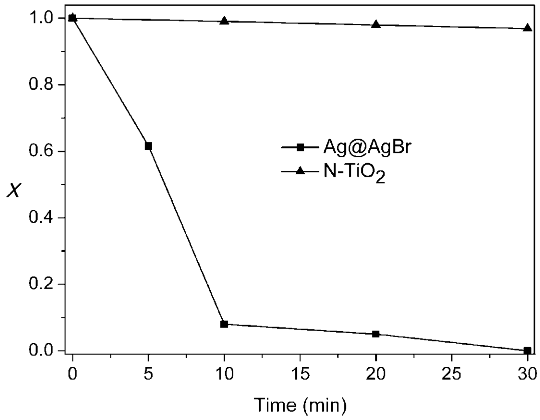

Figure 4. Mole fraction x of IPA that remains unoxidized as a function of irradiation time t over Ag/AgBr, N-doped TiO_2 under visible-light irradiation ($\lambda \geq 400$ nm).

Figure 5 shows how the solution of methylic orange (MO) over Ag@AgBr changes its color as a function of the irradiation time with visible light ($\lambda \geq 400$ nm). The results of MO decomposition over Ag@AgCl and N-doped TiO_2 are also given in Figure 5 for comparison. The decomposition of MO dye over Ag@AgBr is completed after irradiation for

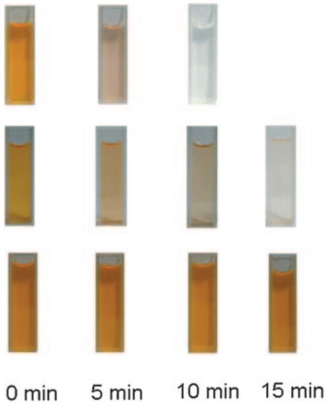

Figure 5. Colors of the MO solution over catalysts Ag@AgBr, Ag@AgCl and N-TiO_2 as a function of the irradiation time (in min) with visible light ($\lambda \geq 400$ nm).

10 min, but that over Ag@AgCl takes 15 min. The bleaching of MO over N-TiO_2 is slow. Provided that the bleaching reaction follows a pseudo-first-order reaction, the rate of MO-dye decomposition over Ag@AgBr is about 0.2 mg$\,min^{-1}$, which is faster than that over Ag@AgCl by a factor of 1.5. In decomposition experiments in the dark with Ag@AgBr and under full arc light irradiation without Ag@AgBr, the MO concentration remains unchanged as a function of the irradiation time, thereby demonstrating that Ag@AgBr is a photocatalyst active under visible light. The repeated MO-bleaching experiment on Ag@AgBr, similar to that for Ag@AgCl,[12] revealed that Ag@AgBr is stable for repeated MO bleaching. The stability of Ag@AgBr under light irradiation can be attributed to the fact that a photon is absorbed by the silver nanoparticles, and an electron separated from an absorbed photon remains in the nanoparticles rather than being transferred to the Ag^+ ions of the AgBr lattice. In general, photo-generated electrons are expected to be trapped by O_2 molecules in the solution to form superoxide ions (O_2^-) and other reactive oxygen species.[18]

Compared with Ag@AgCl,[12] Ag@AgBr has a weaker absorption in visible light, and the oxidization ability of Br^0 is weaker than Cl^0. Nevertheless, Ag@AgBr is more photocatalytically active than Ag@AgCl by a factor of 1.5. This apparently puzzling observation can be explained by considering the three steps involving the photocatalytic reaction of Ag@AgX (X=Cl, Br): 1) the light-absorption to generate an electron and a hole, 2) the combination of a photo-generated hole with X^- to form X^0 (i.e., 349 vs. 324 kJ$\,mol^{-1}$),[19] and 3) the oxidation by X^0. The electron affinity of Br^0 is lower than that of Cl^0, which makes it easier for Br^- than for Cl^- to combine with a hole. Thus, our experimental observation indicates that the rate-determining step of the photocatalytic reaction is the step in which a hole combines with X^- to form X^0.[20] In addition, the higher photocatalytic efficiency of AgBr compared with that of AgCl may also arise from the fact that AgBr has a smaller band gap than AgCl.

In summary, the plasmonic photocatalyst Ag@AgBr is efficient and stable under visible light. Ag@AgBr can absorb in a wide range of visible light and UV because the nanoparticles on AgBr have a large number of different shapes and diameters. Despite the fact that Br^0 has a lower oxidizing power than Cl^0, Ag@AgBr is a more efficient photocatalyst than Ag@AgCl, because the rate-determining step of photooxidation is the step in which a hole combines with X^- to form X^0 (X=Cl, Br) and because Cl^0 has a higher electron affinity than Br^0.

Experimental Section

Ag_2MoO_4 was prepared as described elsewhere.[12] AgBr was synthesized by the ion-exchange reaction between Ag_2MoO_4 and HBr. Ag_2MoO_4 was sonicated in concentrated HBr until the completion of the ion-exchange process.[22] This process yields MoO_3, which is dissolved in excess HBr, and AgBr, which is precipitated. The AgBr precipitate was collected and washed with deionized water. The resulting AgBr was irradiated by using the 300W Xe arc lamp (providing visible light $\lambda \geq 300$ nm). Then the resulting precipitate, which has silver NPs deposited on AgBr particles (see below), was washed and dried in air. The crystal structure of the Ag@AgBr sample was examined by XRD (Bruker AXS D8), its morphology by SEM (Hitachi S-4800 microscopy), and its diffuse reflectance by UV/Vis spectroscopy (UV-2550, Shimadzu). A reference photocatalyst, N-doped TiO_2, was prepared by nitridation of commercially available TiO_2 powder (with a surface area of 50 $m^2\,g^{-1}$) at 773 K for 10 h under NH_3 flow (flow rate of 350 mL$\,min^{-1}$).[21] The activities of the photocatalysts Ag/AgBr were evaluated by examining the decomposition of isopropyl alcohol (IPA) and the degradation of MO dye. The photocatalytic decomposition of IPA was performed with 0.2 g of the powdered photocatalyst placed at the bottom of a Pyrex glass cell (200 mL) at room temperature in a gas-closed system, the reaction solution consisted of IPA (7 mL), and deionized water (70 mL). The photocatalytic degradation of MO dye was carried out with 0.2 g of the powdered photocatalyst suspended in a 100 mL solution of MO dye prepared by dissolving MO powder (20 mg) in distilled water (1 L) 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 a UV cutoff filter (providing visible light $\lambda \geq 400$ nm). CO_2 was detected by gas chromatograph (Varian, CP-3800) with a flame ionization detector equipped with a methanizer, and the degradation of MO dye was monitored by UV/Vis spectroscopy (UV-7502PC, Xinmao, Shanghai).

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