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Composite Semiconductor $H_2WO_4{\cdot}H_2O/AgCl$ as an Efficient and Stable Photocatalyst under Visible Light

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The removal of hazardous organic materials from water has become a serious issue,[1–3] because an effective treatment of wastewater is crucial in the face of increasing population/industrial activity and decreasing energy resources. Traditional methods of wastewater treatment have several disadvantages.[4] The photocatalytic decomposition of water pollutants under visible light is an attractive alternative because it utilizes solar energy and does not produce secondary waste products, owing to the fact that organic wastes are decomposed into harmless chemicals such as H_2O, CO_2 and mineral acids.[5–7] The conventional TiO_2 photocatalyst possesses excellent activities and stabilities, but requires UV light (only 4% of the solar spectrum) for effective photocatalysis thereby severely limiting its practical utility. It is highly desirable to develop a photocatalyst that can harness visible light in high efficiency under normal sunlight conditions. In the past, factors controlling photocatalysis have been explored so as to develop photocatalysts active in the visible light, which include phase/morphological control, doping, surface sensitization, noble-metal loading and use of composite materials.[8–15] Composite semiconductors can reduce the recombination of photogenerated electrons and holes,[16,17] so that they are often employed as photocatalysts to increase the lifetime of the charge carriers and enhance the quantum yield.[18]

Silver chloride AgCl has a direct bandgap of 5.6 eV and an indirect bandgap of 3.25 eV.[19] However, grains of AgCl are photosensitive because of their point ionic defects and electron traps.[20] On absorbing a photon, an AgCl particle generates an electron and a hole and the photo-generated electron combines with an Ag^+ ion to form an Ag^0 atom, so that repeated absorption of photons leads to a cluster of silver atoms within an AgCl particle. Despite its photosensitivity, AgCl can be made a stable and efficient photocatalyst under ultraviolet and visible light if photo-generated electrons are prevented from combining with Ag^+ ions and if photo-generated holes are combined with Cl^- ions to form Cl^0 atoms. These requirements are met by a new photocatalyst Ag@AgCl, in which silver nanoparticles are formed on the surface of AgCl powder particles.[21] An alternative way of meeting the requirements is to prepare a composite semiconductor system in which AgCl particles are formed on the surface of another semiconductor with a smaller band gap (SBG) such that the conduction band (CB) bottom and the valence band (VB) top of the SBG semiconductor lie below the CB bottom and VB top of AgCl, respectively (Figure 1). For such a system, photons may be absorbed in both AgCl and the SBG semiconductor forming electrons and holes. However, an electron at the CB bottom of AgCl would migrate to that of the SBG semiconductor, hence being prevented from combining with an Ag^+ ion, whereas a hole at the VB top of AgCl would remain there. In contrast, a hole at the VB top of the SBG semiconductor would migrate to that of AgCl, but an electron at the CB bottom of the SBG semiconductor would remain there (Figure 1).

The holes at the VB top of AgCl will combine with Cl^- ions to form Cl^0 atoms. Since the Cl^0 atoms are radicals with strong oxidation power, they can oxidize organic compounds hence becoming Cl^- ions again. The photo-generated electrons are expected to be trapped by the O_2 in the solution to form superoxide ions (O_2^-) and other reactive oxygen species.[22] The band gaps of $WO_3{\cdot}xH_2O$ ($x=0$, 1, 2) are

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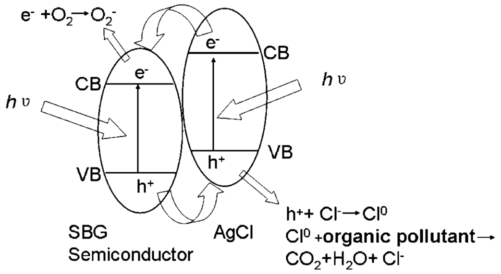

Figure 1. Schematic diagram showing the CB bottom and VB top of the SBG semiconductor and AgCl, the separation of the photo-generated electron and hole, and the reactions that the photo-generated electron and hole may induce.

smaller than that of AgCl, and have been widely used as photocatalysts.[23,24] As shown in the supporting information, empirical calculations predict that the CB bottom and the VB top of $H_2WO_4{\cdot}H_2O$ lie below the CB bottom and VB top of AgCl, respectively. This prompted us to search for such a composite semiconductor and led us to synthesize a new photocatalyst efficient and stable under visible light, i.e., $H_2WO_4{\cdot}H_2O$ with AgCl particle formed on the surface of $H_2WO_4{\cdot}H_2O$, which will be referred to as $H_2WO_4{\cdot}H_2O$/AgCl for convenience. The $H_2WO_4{\cdot}H_2O$/AgCl was fabricated by the ion exchange process between Ag_2WO_4 and HCl, as described in the experimental section.

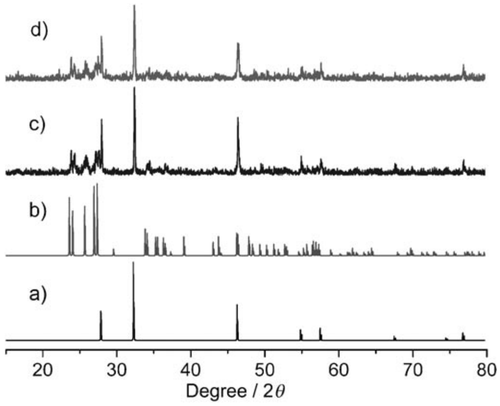

Figure 2. XRD patterns of a) AgCl, b) $H_2WO_4{\cdot}H_2O$, c) as-prepared $H_2WO_4{\cdot}H_2O$/AgCl, and d) $H_2WO_4{\cdot}H_2O$/AgCl used for ten consecutive photo-oxidation experiments with the solution of methylene orange dye under visible-light irradiation.

A powder X-ray diffraction (XRD) pattern (Figure 2) of the as prepared $H_2WO_4{\cdot}H_2O$/AgCl sample shows the coexistence of $H_2WO_4{\cdot}H_2O$ (JCPDS file: 18-1420) and AgCl (JCPDS file: 31-1238). The phase of AgCl is cubic with lattice constants $a = 5.5491$ Å, and the phase of $H_2WO_4{\cdot}H_2O$ is monoclinic with the space group *P*2*m* and the lattice constants $a = 7.5$ Å, $b = 6.93$ Å and $c = 3.7$ Å. The crystal structure of $H_2WO_4{\cdot}H_2O$ is not known, although its powder diffraction pattern has been reported. The scanning electron microscopy (SEM) images of Figure 3 show the morphology of the as-prepared $H_2WO_4{\cdot}H_2O$/AgCl sample; AgCl particles are formed on the surface of $H_2WO_4{\cdot}H_2O$. The shape of AgCl is cubic with its size varying between 100–450 nm. $H_2WO_4{\cdot}H_2O$ exhibits dendritic structures with length 2–5 μm along the trunk and its side branches of about 0.4–2.5 μm (Figure 3a,b). All the dendrites of $H_2WO_4{\cdot}H_2O$ consist of nanorods (Figure 3c), which are similar in shape to the nanorods of Ag_2WO_4 (Figure 3d).

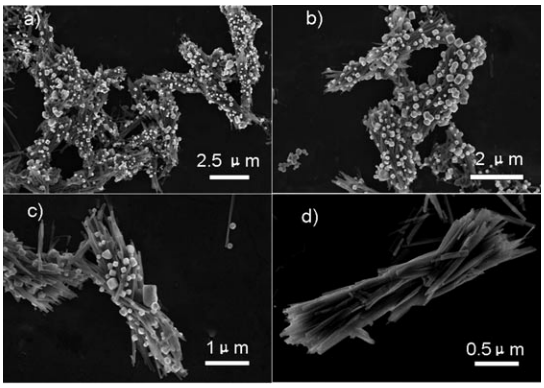

Figure 3. Representative SEM images of a–c) $H_2WO_4{\cdot}H_2O$/AgCl and d) Ag_2WO_4.

The UV/Vis diffuse reflectance spectra of $H_2WO_4{\cdot}H_2O$/AgCl, $H_2WO_4{\cdot}H_2O$, AgCl and N-doped TiO_2 are presented in Figure 4. AgCl, N-doped TiO_2 and $H_2WO_4{\cdot}H_2O$ have strong absorption in the UV region, but do not in the visible region, although $H_2WO_4{\cdot}H_2O$ exhibits weak absorption in the visible region. From the absorption edge of $H_2WO_4{\cdot}H_2O$ (425 nm), the band gap of $H_2WO_4{\cdot}H_2O$ is estimated to be 2.92 eV. In contrast, the as-grown $H_2WO_4{\cdot}H_2O$/AgCl samples have strong adsorption in the UV as well as in the visible region. Since neither $H_2WO_4{\cdot}H_2O$ nor AgCl absorbs strongly in the visible region, it is probable that the electronic states associated with the interface between $H_2WO_4{\cdot}H_2O$ and AgCl particles are responsible for the strong absorption of $H_2WO_4{\cdot}H_2O$/AgCl in the visible region.

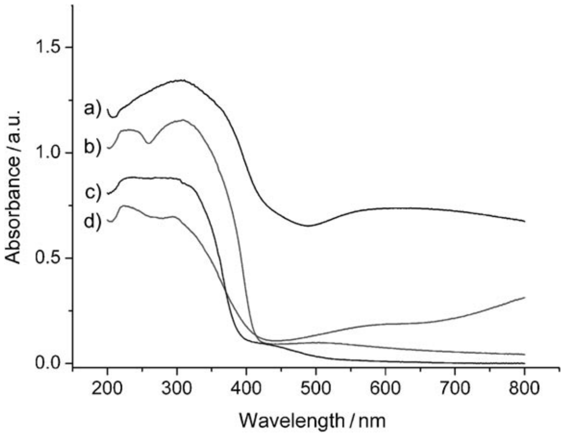

Figure 4. UV/Vis diffuse reflectance spectra of a) $H_2WO_4{\cdot}H_2O$/AgCl, b) AgCl, c) N-doped TiO_2 and d) $H_2WO_4{\cdot}H_2O$.

The photocatalytic activity of $H_2WO_4{\cdot}H_2O/AgCl$ under visible light was examined by probing the photocatalytic decomposition of isopropyl alcohol (IPA) over $H_2WO_4{\cdot}H_2O/AgCl$ under visible-light irradiation ($\lambda \geq 400$ nm) as a function of irradiation time (Figure 5a). CO_2 is the final product in the photocatalytic oxidation of organic contaminants.[25] Nearly half the amount of IPA is photocatalytically oxidized to CO_2 after only 5 min of irradiation, and almost 95 % of IPA after 10 min of irradiation. Our experiments were also performed a) without irradiation, but with $H_2WO_4{\cdot}H_2O/AgCl$ and b) with irradiation, but in the absence of the photocatalyst. In both cases, no CO_2 was generated, which shows that $H_2WO_4{\cdot}H_2O/AgCl$ is a visible-light photocatalyst. The decomposition experiments of IPA over the reference photocatalysts $H_2WO_4{\cdot}H_2O$ and N-doped TiO_2 under the same conditions show that they are not photocatalytic (Figure 4a).

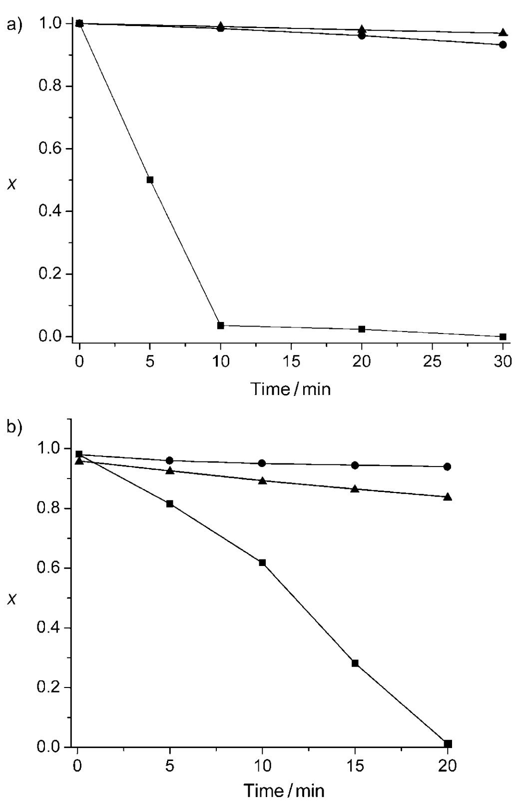

Figure 5. Mole fraction x of a) IPA and b) MO dye that remains unoxidized as a function of irradiation time t over $H_2WO_4{\cdot}H_2O/AgCl$ (■), N-doped TiO_2 (▲) and $H_2WO_4{\cdot}H_2O$ (●) under visible-light irradiation ($\lambda \geq 400$ nm).

Results of the photocatalytic decompositions of methylene orange (MO) dye over $H_2WO_4{\cdot}H_2O/AgCl$, $H_2WO_4{\cdot}H_2O$ and N-doped TiO_2 under visible light irradiation ($\lambda \geq 400$ nm) as a function of irradiation time are compared in Figure 5b. Prior to light irradiation, the solution of MO dye was kept in the dark for 30 min to obtain equilibrium adsorption states. The MO dye concentration is slightly reduced while the MO solution is kept in the dark, so that the mole fraction x of the MO dye in the solution is slightly smaller than 1 at $t=0$. As the irradiation time t increases, the decomposition of MO dye progresses steadily, and the decomposition over the $H_2WO_4{\cdot}H_2O/AgCl$ catalyst is completed in 20 min after visible-light irradiation. Provided that the bleaching reaction follows a pseudo-first-order reaction, the rate of the MO-dye decomposition over $H_2WO_4{\cdot}H_2O/AgCl$ is estimated to be ~0.100 mg min^{-1}, faster than that over N-doped TiO_2 ($\approx$0.016 mg min^{-1}) by a factor of six, faster than that over $H_2WO_4{\cdot}H_2O$ ($\approx$0.006 mg min^{-1}) by a factor of 17, but slower than that over Ag@AgCl ($\approx$0.133 mg min^{-1}).[21] The latter can be attributed to the fact that the visible-light adsorption by $H_2WO_4{\cdot}H_2O/AgCl$ is weaker than that by Ag@AgCl. Though not shown, other organic dyes, such as Rhodamine B and methylene blue, are also quickly bleached by $H_2WO_4{\cdot}H_2O/AgCl$ under visible-light irradiation. To show that the MO-dye decomposition over $H_2WO_4{\cdot}H_2O/AgCl$ is not caused by catalysis nor by photolysis, we carried out the decomposition experiment a) in the dark with $H_2WO_4{\cdot}H_2O/AgCl$ (catalysis) and b) under full arc-light (i.e., UV and visible) irradiation without $H_2WO_4{\cdot}H_2O/AgCl$ (photolysis). In both cases, the MO concentration remained unchanged as a function of the irradiation time thereby demonstrating that $H_2WO_4{\cdot}H_2O/AgCl$ is a photocatalyst active under visible light.

For practical purposes, a photocatalyst should be stable under repeated applications. N-doped TiO_2 and sulfide photocatalysts sometimes suffer from the instability under repeated use.[26,27] The stability of the photocatalyst $H_2WO_4{\cdot}H_2O/AgCl$ was tested by repeatedly performing MO bleaching experiments. As summarized in Figure 6, MO dye is quickly bleached after every injection of the solution of MO dye. In addition, as compared in Figure 2, the XRD pattern of the $H_2WO_4{\cdot}H_2O/AgCl$ sample at the end of the repeated bleaching experiment is almost identical with that of the as-prepared sample. It should be pointed out that our $H_2WO_4{\cdot}H_2O/AgCl$ photo-oxidation experiments, also carried

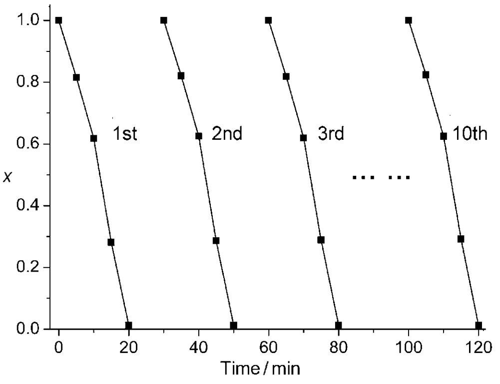

Figure 6. Irradiation–time dependence of the mole fraction x of the MO dye that remains in the MO solution over $H_2WO_4{\cdot}H_2O/AgCl$ during repeated photooxidation experiments under visible light.

out under full Xe arc light (i.e., including UV and visible light), led to the same result. Thus, $H_2WO_4{\cdot}H_2O$/AgCl is a photocatalyst effective and stable under both UV and visible light.

In summary, the composite semiconductor $H_2WO_4{\cdot}H_2O$/AgCl is an efficient and stable photocatalyst under visible light. This arises from the facts that the conduction band (CB) bottom and the valence band (VB) of $H_2WO_4{\cdot}H_2O$ lie below the CB bottom and the VB top of AgCl, respectively, and that $H_2WO_4{\cdot}H_2O$/AgCl absorbs strongly in the visible region. Studies on other composite semiconductors based on silver halides are in progress.

Experimental Section

Ag_2WO_4 was prepared by the methods used for the preparation of Ag_2MoO_4 described in our early report.[21] In the typical process, an aqueous solution of $AgNO_3$ and that of Na_2WO_4 were prepared in advance. 10 mL of 0.2 M $AgNO_3$ solution was mixed with 10 mL of 0.1 M Na_2WO_4 solution, and the pH value of the mixed solution was adjusted to 6.0 by adding dilute HNO_3 solution. The resulting solution was stirred for about 0.5 h, transferred into a special Teflon autoclave, and then heated at 180 °C for 1 h under microwave radiation, which led to the precipitation of Ag_2WO_4. The Ag_2WO_4 precipitate was collected and 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. $H_2WO_4{\cdot}H_2O$/AgCl was synthesized by the ion exchange reaction between Ag_2WO_4 and concentrated HCl while sonicating the solution until the completion of the ion exchange process. The precipitate was collected, washed with deionized water and dried in air. The crystal structure of the $H_2WO_4{\cdot}H_2O$/AgCl sample was examined by using X-ray diffraction (XRD, Bruker AXS D8), its morphology by scanning electron microscopy (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 $50\,m^2g$) at 773 K for 10 h under NH_3 flow (flow rate of $350\,mL\,min^{-1}$).[28] Another reference photocatalyst, $H_2WO_4{\cdot}H_2O$, was prepared using the method reported in the literature.[29] The activities of the photocatalysts $H_2WO_4{\cdot}H_2O$/AgCl were evaluated by studying the decomposition of IPA and the degradation of MO dye. The photocatalytic decompositions of IPA was performed with 0.2 g of the powdered photocatalyst placed at the bottom of a Pyrex glass cell (200 mL) containing 7 mL IPA and 70 mL deionized water at room temperature in a gas-closed system. 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 20 mg of MO powder in 1 L of distilled water in a Pyrex glass cell at room temperature under air. The optical system for detecting the catalytic reaction included a 300W Xe arc lamp (focused through a shutter window) with UV cutoff filter (providing visible light $\lambda \geq 400$ nm). CO_2 was detected by gas chromatograph (Varian, CP-3800, U. S.) 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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