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Surface-sulfurized Ag_2O nanoparticles with stable full-solar-spectrum photocatalytic activity

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ABSTRACT

Ag_2O has attracted much recent attention, because of its high photocatalytic activity in the ultraviolet (UV)-visible region. However, there have been few reports on the near-infrared (NIR) photocatalytic activity of Ag_2O. This paper reports the high NIR photocatalytic activity of Ag_2O nanoparticles. Ag_2O is unsuitable for application in full-solar-spectrum photocatalysis, because it is unstable under UV irradiation. A surface sulfurization process was carried out to address this issue. Specifically, a layer of $Ag_2S_2O_7$ nanoparticles was grown on the surface of the Ag_2O nanoparticles, to improve the stability of the Ag_2O photocatalyst and enhance its photocatalytic activity in the UV, visible and NIR regions. The $Ag_2O/Ag_2S_2O_7$ heterostructure is a stable and efficient full-solar-spectrum photocatalyst. It has potential application in the photodegradation of organic pollutants, and more generally in environmental engineering where full utilization of the solar spectrum is required.

1. Introduction

Photocatalysts can convert sunlight into chemical energy, for use in the remediation of environmental pollutants and in the production of solar fuels. Photocatalysts therefore offer a "green" technology applicable to environmental and energy-related problems [1–7]. Semiconductors are commonly used as photocatalysts, because solar irradiation can generate free electrons and holes in semiconductors to degrade organic pollutants. The wide bandgaps of photocatalytic semiconductors such as TiO_2, ZnO and ZnS limit their excitation windows to the ultraviolet (UV) or near UV regions, which therefore limits their efficient use of solar energy.[1,3,4,7–13]. UV wavelengths account for approximately 5% of the solar spectrum, compared with approximately 48% and 54% for visible (Vis) and near-infrared (NIR) (~54%) wavelengths, respectively [2,14–22].

Much research attention has been given to visible-light-active photocatalysts. Studies on visible-light-active photocatalysts have largely focused on broadening the photocatalytic activity of TiO_2 from the UV to Vis regions. This has been achieved by doping cations or anions into TiO_2

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[4,9,13,23–25], integrating semiconductors with narrow bandgaps into TiO_2 [2,6,14,15,20,26–31], and assembling visible-light-active semiconductor nanoparticles onto TiO_2 nanostructures [2,3,12,32–40].

Photocatalysts with NIR activity have also been intensely studied, in attempt to more efficiently utilize the solar spectrum [2,14–19,21,22,41]. Semiconductor nanomaterials with narrow bandgaps or hybrid semiconductor nanostructures with NIR, Vis-NIR and UV-Vis-NIR activity have been reported. Five design principles have generally been followed in attempts to prepare efficient photocatalysts with UV-Vis-NIR activity covering the full solar spectrum: (1) light conversion based on up-conversion luminescence of rare earth materials [17,19,22] or carbon quantum dots [15,42,43], to convert NIR to Vis and UV wavelengths, and subsequently transfer this energy to UV- and Vis-light-active photocatalysts; (2) designing heterostructures with quantum dot-semiconductor hybrid nanostructures to achieve appropriate band alignment [18,21]; (3) modifying the electronic structures of traditional UV-Vis-driven photocatalysts to achieve NIR-active photocatalysts [2,14,16,41]; (4) designing surface plasmonic nanoparticles which effectively separate electron-hole pairs at the interface, as a consequence of their intimate contact with the bulk semiconductor [44–46]; (5) investigating semiconductors with narrow bandgaps and UV-Vis-NIR broad-spectrum activity [14,20]. The last principle is based on the intrinsic NIR photocatalytic activity of semiconductors, and will likely be beneficial in the design and construction of full-solar-spectrum photocatalysts.

Silver oxide (Ag_2O) is a brown powder with a simple cubic crystalline lattice and a lattice parameter of 0.472 nm. Ag_2O has been widely applied in industry [30,47–49]. The bandgap energy of Ag_2O is reported to be 1.2 eV, and the energy level of the conduction band (CB) edge to be +0.2 eV versus the standard hydrogen electrode (SHE) [5,50,51]. Ag_2O is a photosensitive material, so is seldom used as a photocatalytic material, except as a co-catalyst [28,29,37,52–54]. NIR-active photocatalysts based on Ag_2O nanoparticles and Ag_2O/TiO_2 composites were recently reported [32, 55]. The narrow bandgap of Ag_2O makes it easily reduced by photo-induced electrons. Thus, these Ag_2O-based photocatalysts are unsuitable for UV wavelengths and thus full-solar-spectrum applications. We previously demonstrated that a Ag_2O/TiO_2 nanobelt heterostructure was an efficient UV-Vis photocatalyst, but had low stability because of the photosensitivity of Ag_2O [5,53]. Ag_2O can be transformed into $Ag_2S_2O_7$ through a sulfur doping process similar to vulcanization. The resulting $Ag_2O/Ag_2S_2O_7/TiO_2$ nanobelt heterostructure was stable and exhibited high photocatalytic activity under UV and Vis irradiation [53].

Ag_2O is a narrow-bandgap semiconductor, but has received little attention as a NIR photocatalyst [32,55]. In the current study, Ag_2O nanoparticles are shown to have high NIR photocatalytic activity and good UV and Vis photocatalytic activity. Under UV and Vis irradiation, Ag_2O nanoparticles can lose their photocatalytic activity due to the photo-reduction of Ag_2O. To overcome this problem, a surface sulfurization process is used to grow a layer of $Ag_2S_2O_7$ on the surface of Ag_2O nanoparticles, to form heterostructured nanoparticles. The heterojunction between $Ag_2S_2O_7$ and Ag_2O promotes the UV-Vis-NIR photocatalytic activity of the resulting hybrid photocatalyst, and improves its stability compared with that of Ag_2O. The resulting stable full-solar-spectrum photocatalyst has potential in the photodegradation of organic pollutants in wastewater treatment [32,55].

2. Experimental

2.1. Materials

Sodium hydroxide (NaOH), silver nitrate ($AgNO_3$) and sodium sulfide (Na_2S) were purchased from China National Medicines Corporation Ltd. All chemicals were used as received without further purification. Deionized water was used throughout all experiments.

2.2. Synthesis of Ag_2O and S-doped Ag_2O nanoparticles

In a typical procedure, 0.29 g of $AgNO_3$ was dissolved in 100 mL of deionized water, which was stirred magnetically for 30 min. 0.2 mol·L^{-1} of NaOH solution was added dropwise to the above solution under magnetic stirring until the pH reached 14. The resulting suspension was incubated in the dark for 12 h. The brown-black product was separated by centrifugation, and subsequently washed several times with deionized water. Drying at 50 °C in an oven for 12 h yielded the Ag_2O nanoparticles.

0.1 g of Ag_2O nanoparticles was dispersed in 50 mL of distilled water, which was stirred magnetically for 30 min. 10.77 mL or 43.10 mL of aqueous Na_2S solution (0.01 mol·L^{-1}) was slowly added to the above Ag_2O suspension, to give oxygen: sulfur molar ratios of 1:4 or 1:1, respectively. The resulting mixture was stirred magnetically for 2 h. The S-doped Ag_2O nanoparticles were then separated by centrifugation, washed several times with deionized water, and dried at 50 °C in an oven for 12 h.

2.3. Characterization

X-ray powder diffraction (XRD) patterns of the Ag_2O and S-doped Ag_2O samples were recorded using a Bruker D8 Advance powder X-ray diffractometer, using Cu K_α radiation with a wavelength (λ) of 0.15406 nm. A Hitachi S-4800 field-emission scanning electron microscope (FE-SEM) was used to characterize the morphology and particle size of the Ag_2O and S-doped Ag_2O samples. Chemical compositions were investigated using energy-dispersive X-ray spectroscopy (EDS) attached to a transmission electron microscope (TEM). High-resolution TEM (HRTEM) and scanning transmission electron microscopy (STEM) images were acquired using a JOEL JEM 2100 microscope. UV-Vis-NIR diffuse reflectance spectra (DRS) were recorded using a UV-VIS-NIR spectrophotometer (UV-3600, Shimadzu), with an integrating sphere attachment and $BaSO_4$ as a reflectance standard. Photoluminescence (PL) spectra were recorded using a FLS920 fluorescence spectrometer, at an excitation wavelength of 380 nm. X-ray photoelectron (XPS) spectra were recorded using an ESCALAB