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Short communication

Synthesis of novel Ag/Ag_2O heterostructures with solar full spectrum (UV, visible and near-infrared) light-driven photocatalytic activity and enhanced photoelectrochemical performance

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ABSTRACT

Here we report the facile synthesis of Ag/Ag_2O heterostructures, which exhibit excellent solar full spectrum (UV, visible and near-infrared) photocatalytic activity and an enhanced photoelectrochemical (PEC) performance under irradiation of near-infrared light. The improved photocatalytic property and PEC performance originated from the synergistic effect on the narrow band gap of Ag_2O, plasmon enhancement of metallic Ag in-situ reduced from Ag_2O, and metal-semiconductor (Ag-Ag_2O) Mott-Schottky heterojunction.

1. Introduction

In the past decades, more and more attention has been focused on solar energy utilization [1–3]. Nevertheless, there are two major factors restricting the practical application of photocatalysis, that is, the relatively low charge separation efficiency and extremely insufficient utilization of solar light, especially the visible/near-infrared (NIR) region [4]. Therefore, many approaches have been developed to extend the spectral response of photocatalyst to visible light region [5–7]. Nevertheless, the NIR light, which accounts for >50% of the solar energy, still cannot be used [8]. Until recent years, a few NIR photocatalysts, such as up-conversion materials and $Cu_2(OH)PO_4$, have been investigated [9]. At present, most photocatalysts only possess UV, Vis, UV–Vis, or NIR photocatalytic activity, separately [10]. Therefore, searching for a semiconductor photocatalyst utilizing full spectrum of solar light remains an urgent challenge.

As a promising Ag-based photocatalyst, Ag_2O has presented an excellent visible photocatalytic property due to its appropriate bandgap (1.3–1.5 eV) [11]. Yet its application range is regrettably narrowed due to its photosensitive and unstable properties under light irradiation, which can be readily photoreduced to form metallic Ag and O_2, resulting the decrease of photocatalytic activity [12]. If this problem is solved, such a narrow bandgap of Ag_2O is especially helpful to realize NIR, even solar full-spectrum driven photocatalysis.

Here, we present a solar full spectrum photocatalyst comprised of Ag/Ag_2O heterostructures with a small portion of metallic Ag. Ag_2O can absorb from UV to NIR light according to its narrow bandgap. The metallic Ag photoreduction from the Ag_2O can enhance the optical absorption of Ag_2O to improve the photocatalytic activity due to the SPR effect. Metal-semiconductor Mott-Schottky (M-S) heterojunctions are formed to promote charge transfer from Ag_2O to Ag, leading to the concentration of electrons onto Ag under built-in electric fields. Moreover, the coexistence of Ag_2O and Ag can well maintain the photocatalytic stability of Ag_2O.

2. Experimental

Ag/Ag_2O heterostructures were synthesized by a coprecipitation photo-reduction method. $AgNO_3$ (0.005 mol) was dissolved in 50 mL water. Then, NaOH solution (50 mL, 0.05 M) was dropped to the above $AgNO_3$ solution, and the final PH is 14. The obtained samples were washed with deionized water. The above samples were added to the ethanol, then were illuminated with a 300 W ultraviolet lamp for 1 h, and then dried in a vacuum oven at 70 °C for 12 h. By controlling the illumination time for 20 min and 40 min, the obtained low ratio Ag of Ag/Ag_2O heterostructures were labeled as Ag-1 and Ag-2, respectively. Pure Ag_2O nanoparticles were also synthesized by a same fashion without the photoreduction method.

The photocatalytic activity of the Ag/Ag_2O heterostructures (1 g/L) was investigated by the photodegradation of methyl orange (MO, 20 mg/L). 300 W mercury lamp with filter glasses to filter visible light

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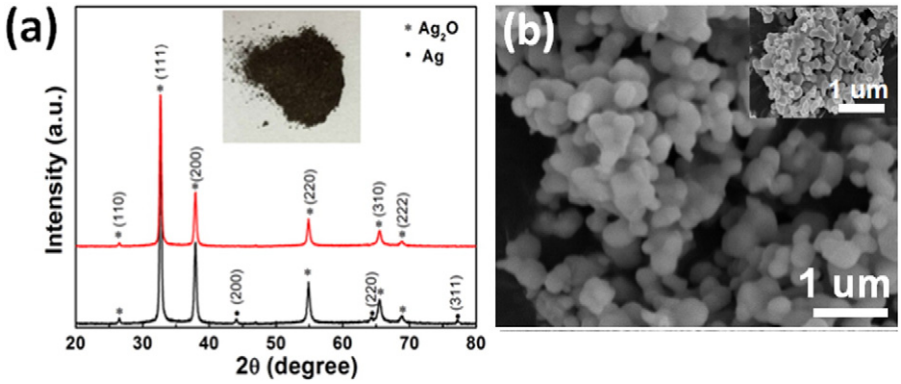

Fig. 1. (a) XRD spectrum of Ag/Ag_2O heterostructures (black line) and Ag_2O nanoparticles (red line). Powder of Ag/Ag_2O heterostructures is shown in the up inset; (b) SEM image of Ag/Ag_2O heterostructures. SEM image of Ag nanoparticles is shown in the upright inset.

of $\lambda > 365$ nm, 350 W Xe arc lamp with filter glasses to filter UV light of $\lambda < 400$ nm and NIR light of $\lambda > 780$ nm, 250 W infrared lamp with filter glasses to filter UV and visible light of $\lambda < 780$ nm were used as the UV, visible, and NIR light source for photocatalysis, separately. Photocurrent density, CV and Dynamic EIS curves were measured in a three-electrode electrochemical cell in the 0.1 M Na_2SO_4 electrolyte, in which Pt foil and $Hg/Hg_2Cl_2/KCl$ (saturated) electrode were used as the counter and reference electrodes, respectively. The I-t and CV curves were measured under a NIR light irradiation (740 nm, 100 mW/cm^2) with light ON-OFF switches.

3. Results and discussion

Ag/Ag_2O heterostructures synthesized by the co-precipitation photo-reduction method appear as dark-brown powders (inset in Fig. 1a). For Ag/Ag_2O heterostructures (black line in Fig. 1a), the peaks are attributed to the cubic phases of Ag_2O (JCPDS 43-0997) [13,14]. Additional three slight diffraction peaks can be indexed to the crystal planes of Ag^0 (JCPDS 04-0783) [15]. For Ag_2O nanoparticles (red line in Fig. 1a), all the peaks can be assigned to Ag_2O, and no extra peaks, such as Ag^0, are found.

Fig. 1b shows the SEM images of the Ag/Ag_2O heterostructures. The diameter of nanoparticles is about 200–500 nm. No obvious difference of size and morphology between Ag_2O nanoparticles and Ag/Ag_2O heterostructures can be observed under SEM conditions (inset in Fig. 1b). TEM image of the Ag/Ag_2O heterostructures (Fig. S1a) also confirm the morphology of particles, which appear as an aggregation of crystals. HR-TEM investigation (Fig. S1b) shows the metal Ag^0 on the Ag_2O nanoparticles, which reveals the resolved lattice fringes of cubic Ag_2O (111) planes with a spacing of 0.27 nm and metal Ag^0 (100) planes with a spacing of 0.281 nm [16,17].

Fig. S2 shows UV–Vis-NIR absorption spectra of the Ag/Ag_2O heterostructures, which reveals a strong and broad absorption from UV to NIR region, thus suggesting the enhanced photocatalytic activity in the solar broad spectrum region [18]. The Ag_2O nanoparticles also exhibit a remarkable absorption in the visible and NIR light region. P25 only shows strong absorption in the UV region. Compared to the Ag_2O nanoparticle, the small red shift from the Ag/Ag_2O heterostructure is attributed to the SPR effect of the small portion of Ag in the heterostructure, which can not only affect the intensity but also broaden the absorption region. The optical bandgap of Ag/Ag_2O heterostructures is estimated from the plot of $(\alpha h\nu)^2$ versus $h\nu$, which is converted according the Kubelka-Munk function from the UV–Vis-NIR absorption spectrum (Fig. S3), where α is the absorbance coefficient and $h\nu$ is the photon energy. Then the estimated band gap (E_g) of Ag/Ag_2O heterostructures is 1.35 eV.

High-resolution XPS spectra of elemental Ag and O are shown in Fig. S4, respectively. As shown in Fig. S4a, the peak at 531.4 eV is assigned to the lattice oxygen, along with two shoulders at 529.6 eV and 533.0 eV correspond to hydroxyl groups (—OH) and adsorbed O_2 on the surface of the sample, respectively [19]. The XPS spectrum of Ag 3d possesses two strong peaks at the binding energies of 368.2 eV for Ag 3d5/2 and 374.3 eV for Ag 3d3/2 orbitals of Ag^+ ions, respectively (Fig. S4b), while two weak peaks observed at 368.8 eV and 374.5 eV can be assigned to the Ag 3d5/2 and Ag 3d3/2 orbitals of Ag^0 [12,20]. This clearly demonstrates that there are a small portion of metallic Ag^0 in Ag/Ag_2O heterostructures, which is in good agreement with the XRD results.

The photocatalytic degradation of MO over Ag/Ag_2O heterostructures was studies under UV, visible and NIR light irradiation. Before the photocatalysis, the solution including MO and photocatalysts was stirred in the dark for the adsorption equilibrium. These results highlight that the samples by themselves exhibit no absorption on MO in the dark (Fig. 2). As shown in Fig. 2a, P25 only has UV light photocatalytic property. The Ag/Ag_2O heterostructures exhibit an enhanced full-spectra photodegradation efficiency. Around 84%, 78%, and 88% of MO

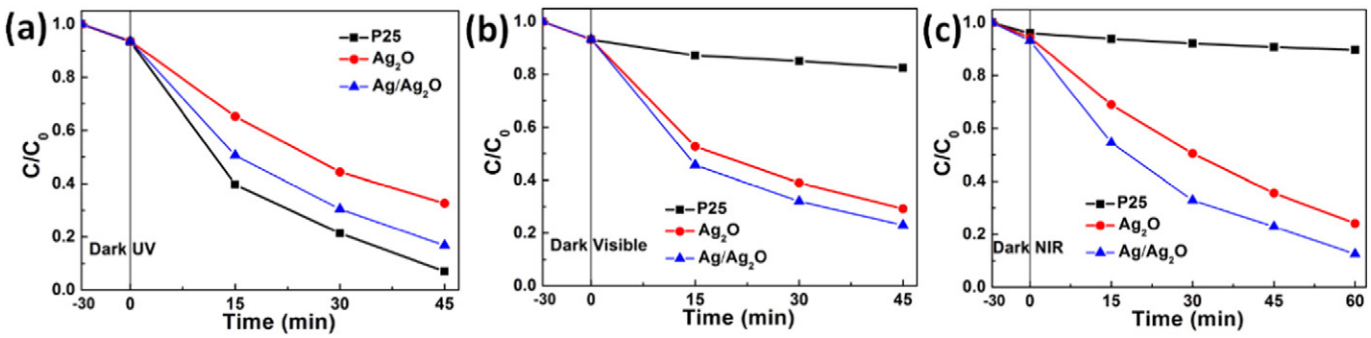

Fig. 2. Photocatalytic degradation of MO in the presence of the samples under (a) UV, (b) visible and (c) NIR light irradiation.