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Three-dimensional $Ag_2O/WO_3{\cdot}0.33H_2O$ heterostructures for improving photocatalytic activity

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ABSTRACT

Three-dimensional $Ag_2O/WO_3{\cdot}0.33H_2O$ heterostructures were fabricated by loading Ag_2O nanoparticles on $WO_3{\cdot}0.33H_2O$ 3D networks via a simple chemical precipitation method. The $Ag_2O/WO_3{\cdot}0.33H_2O$ heterostructures exhibited much enhanced photocatalytic activity for the degradation of methylene blue (MB) under simulated solar light irradiation. The optimal molar ratio of Ag_2O and $WO_3{\cdot}0.33H_2O$ is 1:2. The outstanding photocatalytic activity of the $Ag_2O/WO_3{\cdot}0.33H_2O$ can be attributed to its large surface area of the three-dimensional networks, the enhanced sunlight absorption and the prevention of electrons–holes combination from the heterostructures. The experiment result demonstrates that wide band gap semiconductor ($WO_3{\cdot}0.33H_2O$) modified by narrow band gap metal oxide (Ag_2O) with 3D architecture will be an effective route to enhance its photocatalytic activity.

1. Introduction

In the past few decades, environmental problems such as air and water pollution have become a block for economic development and human health, which also provide impetus for sustained fundamental and applied researches into the area of environmental remediation [1–3]. Semiconductor such as TiO_2, with the band gap of 3.2 eV, has found potential application in photocatalysis in the recent years [4–6]. Hydrate WO_3 ($WO_3{\cdot}0.33H_2O$) has been reported with the same band gap energy as TiO_2 (3.2 eV), which can be regarded as another potential photocatalytic material in the ultraviolet spectral range [7]. However, a major factor affecting the photocatalytic efficiency of $WO_3{\cdot}0.33H_2O$ is its narrow absorption spectral range, for only about 3–5% of the total solar irradiance can be absorbed by pure $WO_3{\cdot}0.33H_2O$ nanoparticles. Another limitation in achieving high photocatalytic efficiency for $WO_3{\cdot}0.33H_2O$ is the recombination of photo-generated electron–hole pairs. In addition, as the photocatalytic activity strongly relies on the structures of catalysts, it is important to improve the nanostructures of catalysts to realize high specific area and easy microchannels.

To address these problems, rationally designed photocatalytic systems should allow efficient charge separation, enhancement of light absorption to utilize efficient solar light [8–10], and structure optimization to achieve high specific area and easy microchannels [11–13]. Heterogeneous photocatalysis has been considered as a cost-effective alternate for solving the charge separation, transport, and enhancement of light absorption problems [14–16]. The novel photocatalysts of Ag_2O hybridized with semiconductor are recognized as a promising photocatalytic system, such as Ag_2O/TiO_2, Ag_2O/ZnO, and Ag_2O/Bi_2WO_6 [17–19]. First, Ag_2O, a brown powder possessing a small band gap (ca. 1.2 eV), has been demonstrated to be sensitive to the visible light. Moreover, the deposition of Ag_2O nanoparticles (NPS) onto TiO_2 photocatalyst surfaces has been found to be able to impede efficiently the recombination of photoinduced charge carriers [20,21]. On the other hand, many studies have found that the three-dimensional (3D) hierarchical nanoarchitectures are highly desirable materials due to their high surface-to-volume ratio, high organic pollutant adsorption, and excellent incident light scattering within the structures and easy microchannels [22]. However, studies on the $WO_3{\cdot}0.33H_2O$ and semiconductor heterogeneous system are few, and $Ag_2O/WO_3{\cdot}0.33H_2O$ three-dimensional (3D) heterostructures have not been designed and prepared yet. Therefore, in this paper, we attempted to investigate the photocatalytic performance of $Ag_2O/WO_3{\cdot}0.33H_2O$ nanonetworks under visible-light irradiation. It is a new kind of photocatalysts besides TiO_2.

2. Experimental

2.1. Synthesis of $Ag_2O/WO_3{\cdot}0.33H_2O$ nanonetworks

The preparation of $WO_3{\cdot}0.33H_2O$ nanonetworks has been reported in the previous paper [7]. The $Ag_2O/WO_3{\cdot}0.33H_2O$

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heterostructure catalyst with molar ratio ($R = Ag_2O/WO_3{\cdot}0.33H_2O$) of 1:1 was obtained by the chemical precipitation method. Typically, 0.05 g of $WO_3{\cdot}0.33H_2O$ networks were dissolved into 15 mL distilled water, then 0.1 mol/L $AgNO_3$ solution (4 mL) and 0.5 mol/L glucose ($C_6H_{12}O_6$) solution (4 mL) were added into the beaker. The mixture was vigorously stirred for 3 h. Finally, about 0.1 g sample was obtained by washing and centrifugation process. By changing the amount of $AgNO_3$ and $C_6H_{12}O_6$, $Ag_2O/WO_3{\cdot}0.33H_2O$ with different molar ratio (R = 1:4, 1:2, 1:1, and 2:1), different samples were obtained.

2.2. Photocatalytic degradation

The degradation of methylene blue (MB) was performed in a beaker in exposure to a simulated sunlight at room temperature. Forty milligrams of the $Ag_2O/WO_3{\cdot}0.33H_2O$ catalyst were dispersed in 80 mL of 10 mg/L MB aqueous solution. Prior to illumination, the suspensions were magnetically stirred in the dark for 30 min to ensure the establishment of adsorption–desorption equilibrium of MB on the surface of the catalyst. Then, the measurement of photocatalytic reactivity was carried out using a simulated sunlight instrument (CH-XM-500 W) with intensity of 100 mW/cm^2. At a given intervals, 3 mL of the suspension was extracted and then centrifuged at a rate of 2000 rpm for 2 min to remove the catalyst. The concentration change of MB was then determined by using a UV–vis–NIR spectrophotometer (Shimadzu UV-3600).

2.3. Characterization

The structure and morphology of the as-prepared products were characterized with X-ray diffraction (XRD-6000, Shimadzu, with Cu Kα radiation), filed emission scanning electron microscopy (FESEM, FEI Nova 400), and transmission electron microscope (TEM, JEOL-4000EX).

3. Results and discussion

Fig. 1a shows SEM image of $WO_3{\cdot}0.33H_2O$ networks synthesized by 0.4 mmol Na_2WO_4 and 0.4 mmol $CaCl_2$ at temperature of 180 °C for 24 h at pH 3.3, from which we can see uniform networks with the average diameter 5 μm, indicating high specific area of such 3D nanostructure. Fig. 1b presents XRD patterns of the $Ag_2O/WO_3{\cdot}0.33H_2O$ (network) catalysts with R = 0:1, 1:4, 1:2, 1:1, and 2:1. The sample with R = 0:1 exhibits pure orthorhombic phase of $WO_3{\cdot}0.33H_2O$, while the rest of the samples show both orthorhombic $WO_3{\cdot}0.33H_2O$ and hexagonal Ag_2O phases, and the XRD patterns match the JCPDS file No. 35-0270 for $WO_3{\cdot}0.33H_2O$ and 19-1155 for Ag_2O, respectively.

The morphologies of the $Ag_2O/WO_3{\cdot}0.33H_2O$ network heterostructures with different R values are shown by SEM and TEM images in Fig. 2. With R value increasing, more Ag_2O nanoparticles with sizes ranging from 10 to 15 nm are distributed uniformly onto the surface of $WO_3{\cdot}0.33H_2O$ networks. However, Ag_2O nanoparticles flock together and unevenly load when R value increases to 2:1.

To evaluate the photocatalytic degradation ability of these samples, we examined the photodegradation of MB in aqueous solution under the simulated sunlight. As the previous research has found out that the MB molecules are also sensitized by visible light [23], it is necessary to examine the decomposition of MB in aqueous solution (the same concentration) without photocatalyst under the simulated sunlight. The experiment results show that about 10% of MB has been decomposed after 2 h. Namely, about 90% of MB molecules need to be decomposed by photocatalyst. Forty milligrams of the $Ag_2O/WO_3{\cdot}0.33H_2O$ catalysts were dispersed in 80 mL of 10 mg/L MB aqueous solution. The comparative experiment results of photocatalytic activity of these samples with different R values for 120 min are shown in Fig. 3. It can be seen that with increasing amount of the Ag_2O NPs on $WO_3{\cdot}0.33H_2O$ networks, the photodegradation efficiency increases correspondingly, except for the excessive loading of Ag_2O nanoparticles. The $Ag_2O/WO_3{\cdot}0.33H_2O$ samples with R = 1:2 exhibit the highest activity for MB degradation. When the R value is more than 1:2 (R = 1:1, 2:1), the $Ag_2O/WO_3{\cdot}0.33H_2O$ samples show a lower photodegradation efficiency, which is even lower than that of the pure $WO_3{\cdot}0.33H_2O$ powder (R = 0). It is proved that $Ag_2O/WO_3{\cdot}0.33H_2O$ heterostructures with proper Ag_2O loading is essential for the achievement of excellent photocatalytic activity.

Stability of the photocatalyst is a key factor for its recycle use and long term efficiency. Therefore, the stability of the as-synthesized photocatalyst is studied by recycle tests. The recycle test is performed four times on the $Ag_2O/WO_3{\cdot}0.33H_2O$ catalyst with R = 1:2 and the results are compared in Fig. 4. It is revealed that the activity of the photocatalyst remains almost constant, which shows that the $Ag_2O/WO_3{\cdot}0.33H_2O$ heterostructure is a stable photocatalyst.

Due to the narrow band gap of Ag_2O (1.2 eV), the heterostructures can absorb the light ranging from the UV light to visible light. In addition, the heterostructure is favorable for electrons transfer when the electron acquires energy from the sunlight due to the step-like band gap. Moreover, from the BET (Brunauer-Emmett–Teller) result and UV–vis absorption spectra of the $WO_3{\cdot}0.33H_2O$ network structures [7], we know that the 3D hierarchical structures possess large specific surface area and can enhance incident light scattering within the structures. Meanwhile, the hierarchical structure catalysts can provide microchannels for reactant diffusion and more reaction active sites

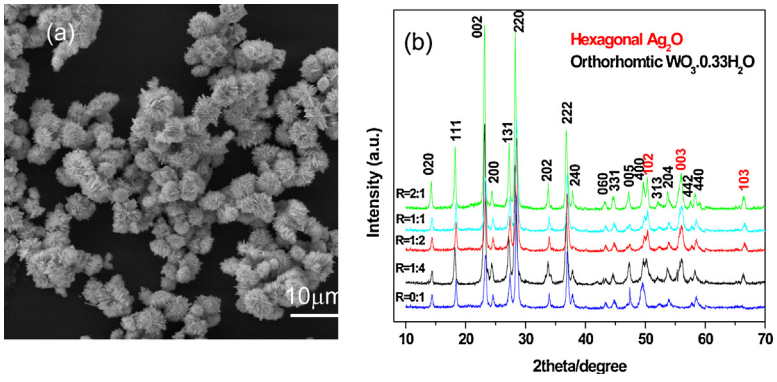

Fig. 1. SEM image of $WO_3{\cdot}0.33H_2O$ sample (a) and XRD patterns (b) of the $Ag_2O/WO_3{\cdot}0.33H_2O$ samples with R = 0:1, 1:4, 1:2, 1:1, and 2:1.