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In-situ growth of zinc tungstate nanorods on graphene for enhanced photocatalytic performance

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ABSTRACT

Graphene–zinc tungstate (G–$ZnWO_4$) hybrid photocatalysts were prepared by an in-situ growth method in which the reduction of graphene oxide (GO) and the growth of $ZnWO_4$ crystals occurred simultaneously. The materials were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, UV–vis diffuse reflectance spectroscopy and X-ray photoelectron spectroscopy. The photocatalytic activity was investigated by the degradation of dye methylene blue (MB). An enhancement in the photocatalytic activity was observed for G–$ZnWO_4$ hybrids compared with pure $ZnWO_4$ under UV light. This improvement was attributed to the following two reasons: increased migration efficiency of photo-induced electrons and increased adsorption activity for dye molecules. The effect of the amount of graphene on the photocatalytic activity was also investigated. Results showed that there was an optimum amount of 2%.

1. Introduction

Semiconductor photocatalysis has attracted widespread attention for the removal of organic pollutants or energy conversion in recent years [1–4]. Generally, titania is one of the most investigated photocatalyst due to its good properties. In the most recently years, tungstates have also received increasing attentions in the photocatalytic degradation of organic pollutants [5–8]. It is well known that Bi_2WO_6 is one of the most common tungstates, which shows high photocatalytic activity for organic pollutants degradation. Zinc tungstate ($ZnWO_4$) is another tungstate which has been applied for degradation of organic pollutants [9–13]. However, the high recombination rates of photoinduced electron–hole pairs and low quantum efficiency have hindered the practical application of $ZnWO_4$ in pollutants degradation. There are several methods to improve the photocatalytic activity of $ZnWO_4$ such as doping with metal ions, coupling with other semiconductors and so on [14–16].

In the past several years, graphene has drawn much attention due to its remarkable properties such as large surface area and high carrier mobility [17–20]. Therefore, it can be serving as an ideal support material for semiconductor photocatalysts, which would show improved photocatalytic activity for the following two reasons. Firstly, a hybrid of graphene-semiconductor would show enhanced adsorption activity. Secondly, the graphene can help to reduce the recombination rate of photogenerated electron–hole pairs. There are many works investigated on the preparation and properties of graphene based hybrid materials [21–24], and they found that the hybrid photocatalyst shows enhanced photocatalytic activity for water splitting and organic pollutants degradation. However, there is no work focused on the preparation and photocatalytic properties of graphene–$ZnWO_4$ (GZW) hybrid material. Our purpose is to find a convenient method to prepare graphene based tungstate hybrid photocatalyst with high photocatalytic properties.

In the present work, we found a simple one-pot way to prepare GZW hybrid photocatalyst. Then, we studied their UV light responsive photocatalytic activity on decomposition of methylene blue (MB) in aqueous solution. Furthermore, we investigated the influence of graphene content on the photocatalytic activity of as-prepared hybrid photocatalyst. This new hybrid photocatalyst is

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anticipated to provide a new material in the environment remediation.

2. Material and methods

2.1. Preparation of the GZW hybrid photocatalyst

The graphene oxide (GO) was prepared by a modified Hummers method as reported in our previous papers [25]. The GZW hybrid photocatalysts were prepared by a one-pot solvothermal method as follows: first of all, definite amount of GO was added to 80 mL ultrapure water and then it was sonicated for 1 h. On other hand, 0.594 g $Zn(NO_3)_2 \cdot 6H_2O$ and 0.66 g $Na_2WO_4 \cdot 2H_2O$ were dissolved into 80 mL ultrapure water and sonicated for 30 min. Afterwards, the precipitate was centrifuged and washed by ultrawater for several times before it was added into the above GO suspension. At last, the suspension was adjusted to pH 10 and sealed into a teflon-lined autoclave and maintained at 180 °C for 24 h. Subsequently, the autoclave was cooled to room temperature naturally. The resulted samples were collected, washed with ultrapure water and ethanol for several times and dried at 60 °C under vacuum. In our experiment, four samples with initial GO weight of 1.0%, 2% and 5%, 10% were prepared. The four samples were defined as GZW-1, GZW-2, GZW-3, and GZW-4, respectively. For comparison, pure $ZnWO_4$ was also prepared by the same method just without the addition of GO.

2.2. Characterization

The phase structure properties were determined by X-ray diffractometer (XRD, XD-3A, Shimadzu Corporation, Japan) using graphite monochromatic copper radiation (Cu–Kα) at 40 kV, 30 mA over the 2θ range 10–70°. The morphologies were characterized by scanning electron microscope (SEM, Hitachi, S-4800) and transmission electron microscope (TEM, JEOL, JEM-2100). The X-ray photoelectron spectroscopy (XPS) measurement was carried out on VG ESCALAB MK-II electron spectrometer. UV–vis diffuse reflectance spectra (DRS) of the obtained samples were carried on a UV–vis spectrophotometer (Shimadzu, UV3600). The concentration of MB in irradiation process was also analyzed using the UV–vis spectrophotometer (Shimadzu, UV3600). The photoluminescence spectra were measured by a fluorescence spectrophotometer (Hitachi, F-7000).

2.3. Photocatalytic experiment

In order to investigate the photocatalytic activity of as-prepared GZW samples, degradation experiments of MB were conducted under UV light irradiation. 0.1 g samples was dispersed into a 200 mL MB aqueous solution, whose initial dye concentration was 10 mg L^{-1}. Then, the suspension was irradiated with an 18 W UV lamp (centered at 254 nm) under continuous stirring. Before the irradiation, the suspension was maintained in the dark for 0.5 h to reach complete adsorption–desorption equilibrium. The blank experiment without catalysts was also investigated, and the value can be neglected with less than 2% of conversion after 2 h illumination.

The formation of hydroxyl radicals in the photocatalytic process was investigated by photoluminescence technology using terephthalic acid as a probe molecule. The terephthalic acid can react with hydroxyl radicals to produce highly fluorescent 2-hydroxyterephthalic acid [26]. The process was similar with the photocatalytic experiment just with the MB solution replaced by 3 mM terephthalic acid (dissolved in 10 mM NaOH aqueous solution).

3. Results and discussion

3.1. Characterization of as-prepared samples

The XRD patterns of pure $ZnWO_4$ and GZWs photocatalysts are shown in Fig. 1. From the figure, it can be seen that the diffraction peaks of the pure $ZnWO_4$ are in good agreement with the monoclinic wolframite tungstate structure according to the standard card (JCPDS no. 73-0554). It can also be seen that the crystal phase of GZWs does not change after the compositing of graphene. No diffraction peaks of graphene oxide are detected in the plot of the GZWs, which indicates the reduction of graphene oxide to graphene. The diffraction peaks of graphite are not detected too, which illustrates the graphene sheets are separated efficiently with little aggregation.

Fig. 2 shows the SEM images of pure $ZnWO_4$ and GZWs photocatalysts. It can be seen from Fig. 2(a) that the obtained pure $ZnWO_4$ has a rod-like shape with a diameter of 30–40 nm and a length of 300–400 nm. The rod like nanostructured $ZnWO_4$ with similar diameter and length are also found in the GZW samples (Fig. 2(b)–(e)). The $ZnWO_4$ nanorods are randomly distributed on the graphene sheets. The typical TEM image of GZW-2 also shows the same distribution of $ZnWO_4$ nanorods on the graphene sheets, which can be seen in Fig. 2(f). The GZW samples show a mass of wrinkles both on the edge of graphene sheets and on the interlayer sheets. The layered structure of the graphene sheets in the GZW samples exhibits a much rougher surface, which would provide more active site for the adsorption of organic pollutants and help to enhance the photocatalytic activity of $ZnWO_4$. This intimate interaction of graphene and $ZnWO_4$ enables the electron transfer from photo-excited $ZnWO_4$ to graphene during the photocatalysis process. Furthermore, we can see that the area of graphene without deposition of $ZnWO_4$ nanorods increases with the increase in initial GO weight.

The optical properties of as-prepared GZW samples were investigated by DRS, and the results are shown in Fig. 3. From the DRS data we can see that the GZW samples show similar absorption and identical band gap energy with pure $ZnWO_4$. However, the absorption intensities of GZW samples are all higher than that of pure $ZnWO_4$ both in the UV and visible light region. Furthermore, we found that the absorption intensity of as-prepared hybrid samples enhance with the increase of the graphene amount. This increasing of absorption intensity can be ascribed to the addition of black graphite-like materials. It also illustrates that the GO in GZW samples has been well deoxygenated and reduced to graphene [27].

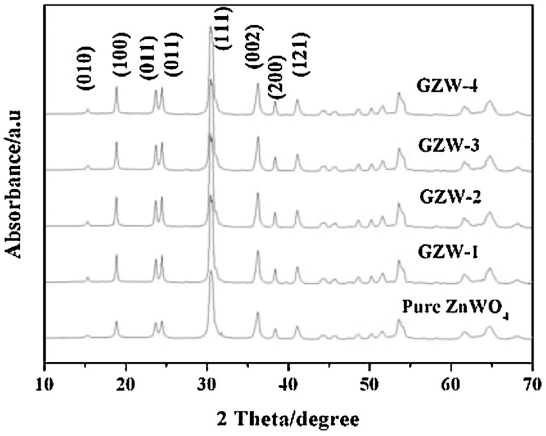

Fig. 1. XRD patterns of different samples.