Microwave assisted synthesis of reduced graphene oxide incorporated MOF-derived ZnO composites for photocatalytic application

Guang Zhu^{*}, Xuelian Li, Hongyan Wang, Li Zhang^{*}

*Anhui Key Laboratory of Spin Electron and Nanomaterials, Suzhou University,
Suzhou, 234000, P. R. China;*

Abstract:

Metal-organic frameworks (MOF) have been arousing a great interest due to their excellent properties. In this work, reduced graphene oxide (RGO) incorporated MOF-derived ZnO composites have been prepared via the microwave assisted method and used as photocatalysts for the photocatalytic degradation of methylene blue (MB). The results indicate that as-prepared composite with 1.5 wt.% RGO shows an optimal photocatalytic performance and the photocatalytic activity is 1.78 times of that using pure ZnO. The photocatalytic performance improvement can be attributed to RGO being able to enhance light absorption, separate the photogenerated electrons and suppression of charge carriers recombination.

Keywords: Reduced graphene oxide; MOF-derived ZnO; composites; photocatalysis; recombination

^{*} Corresponding author. Tel.: +86 557 3681973; E-mail address: guangzhu@ahsztc.edu.cn

^{*} Corresponding author. Tel.: +86 557 2871006; E-mail address: zhelisuzh@163.com

1. Introduction

Over the past decades, metal oxide semiconductors based photodegradation have received increasing attention for their promising application to energy generation and environmental purification [1-4]. It is well known that the photocatalytic performance strongly depends on the morphology of the as-prepared materials. Recently, the porous structured metal oxide photocatalysts, such as ZnO, TiO₂, SnO₂ and CeO₂, have been prepared and used to enhance photocatalytic performance due to large surface area and higher electron transport of organic pollutants[5,6]. Despite the above process has been achieved, the conventional chemistry methods such as self-assembly and templated growth can prepare the porous structures but with primarily nonporous shells[7,8]. Therefore, the design and fabrication of porous metal oxides with high photocatalytic performance are still very challenging.

Metal-organic frameworks (MOFs) with high specific surface areas and tunable porous sizes have attracted considerable attention due to their potential applications in sensors, catalysis, separation, gas storage, electrochemical and photochemical devices[9-24]. Recently, many researches have demonstrated that metal oxides with porous structure (such as TiO₂ and ZnO) can be easily prepared via simple heat treatments of MOFs precursors under a variety of atmospheric gaseous conditions as photocatalysts to enhance the photocatalytic performance[25,26]. Although the photocatalytic performance can be improved for the metal oxides with porous structure. However, the as-prepared porous metal oxides with large bandgap means that only ultraviolet light in the solar spectrum is useful for the photocatalytic effect, which limits the development of photocatalysis [27-29].

In this work, a simple and fast microwave-assisted method has been employed to synthesize reduced graphene oxide (RGO) incorporated MOF-derived ZnO composites, in which the MOF-derived ZnO is prepared using simple heat treatments of MOFs precursors under air atmosphere condition. The photocatalytic activity of as-prepared composites has been investigated through degradation of methylene blue (MB) under visible light irradiation. The results show that as-prepared composite with 1.5 wt.% RGO shows an optimal photocatalytic performance and the photocatalytic activity is 1.37 times of that using pure MOF-derived ZnO. The photocatalytic performance improvement can be attributed to RGO being able to enhance light absorption, separate the photogenerated electrons and suppression of charge carriers recombination.

2. Experimental

The zeolitic imidazolate framework-8 (ZIF-8) crystals was prepared in a typical procedure[30]. The as-prepared ZIF-8 was subsequently thermally treated at 600 °C under air atmosphere condition with a heating rate of 2 °C/min. After reaching 600 °C, the sample was allowed to cool to room temperature and collected. The graphene oxide (GO) was prepared by using a modified Hummers method. The preparation of GO is as follows: graphite powder was put into an 80 °C solution of concentrated nitric acid and sulfuric acid and kept for 5 h. The mixture was cooled to room temperature and diluted with deionized (DI) water. Then, the reaction vessel was immersed in an ice bath, and potassium permanganate was added slowly. Successively, the mixture was stirred and left for 2 h. Then, after the dilution with DI water, 30% H₂O₂ was added to the mixture. RGO incorporated MOF-derived ZnO

composites were prepared via microwave-assisted reduction of GO in MOF-derived ZnO suspensions using a microwave system. In brief, 16 mg as-prepared MOF-derived ZnO was added into 20 mL GO solution, and then the solution was put into an automated focused microwave system (Explorer-48, CEM Co.) and treated at 150 °C with microwave irradiation power of 150 W for 10 min. In this work, as-synthesized RGO incorporated MOF-derived ZnO composites with 0, 0.5, 1.0, 1.5 and 2 wt.% RGO, named as RMZ-0, RMZ-1, RMZ-2, RMZ-3, and RMZ-4, respectively.

The morphology and structure of as-prepared samples were characterized by the field emission scanning electronic microscopy (FESEM, Hitachi 4800) and JEOL-2010 high-resolution transmission electron microscope (HRTEM), respectively. The UV-vis absorption spectra of as-prepared samples were detected using a UV-vis spectrophotometer (Hitachi U-3900). Photoluminescence (PL) spectra were recorded on a HORIBA Jobin Yvon fluoromax-4 fluorescence spectrophotometer, using the 350 nm excitation line of a Xe lamp as light source. Brunauer-Emmett-Teller (BET) surface area was measured by ASAP 2020 Accelerated Surface Area and Porosimetry System (Micrometitics, Norcross, GA).

The photocatalytic activities of as-prepared samples were evaluated via decomposing methylene blue (MB) dye solution at room temperature. The concentration of MB and photocatalyst were set as 10 mg/L and 1 g/L, respectively. The photocatalytic degradation process was observed by the change of the absorbance maximum in optical absorption spectra of MB dye. Prior to irradiation, the suspensions were magnetically stirred in the dark for 30 min to establish an adsorption/desorption equilibrium. The dispersions were kept under constant air-equilibrated conditions before and during irradiation. A 300 W Xe lamp with a

420 nm cutoff filter was employed as a irradiation source, and located 10 cm away from the reactor to trigger the photocatalytic reaction.

3. Results and discussion

Figure 1 a shows the FESEM image of as-prepared MOF-derived ZnO (RMF-0). It can be observed that as-prepared ZnO particles have a average diameter of ca 200 nm and are monodisperse. The FESEM image of as-prepared RMF-3 composite is shown in Figure 1 b. Compared with pure ZnO, It is clearly observed that the surface of curled RGO nanosheets is packed densely by ZnO particles, which indicates a good combination between ZnO and RGO. The composition of as-prepared RMF-3 composite is identified by energy dispersive X-ray spectroscopy (EDS) linked to FESEM, as shown inset in Figure 1 b. The results display that the main elements such as C, Zn and O are present with no unexpected elements being observed, indicating the purity of as-prepared samples.

The high-resolution transmission electron microscope (HRTEM) images of as-prepared RMF-3 composite are shown in Figure 2. It can be observed that some as-prepared ZnO particles are attached onto the surface of RGO sheets (as shown in Figure 2 a). The RGO sheets act as bridges for the connection between different ZnO particles, which is beneficial for the separation of photo-generated carriers, and enhances the photocatalytic performance. Figure 2 b displays the high-magnification HRTEM images of as-prepared RMF-3 composite. The crystallites connecting to the RGO have a lattice fringe of 0.28 nm which is ascribed to the (100) plane of ZnO (JCPDS 36-1451).

The XRD patterns of as-prepared samples are shown in Figure S1. It can be observed that as-prepared composites have the same crystalline wurtzite-structure of ZnO, which demonstrates that the presence of RGO does not result in the development of new crystal orientations or changes in preferential orientations of ZnO. It is noted that no typical diffraction peaks of carbon species are observed, which may be due to the low amount and relatively low diffraction intensity of RGO in the composites.

Figure 3 a shows the UV-vis absorption spectra of as-prepared RMZ-0, RMZ-1, RMZ-2, RMZ-3, and RMZ-4 composites. Compared with the absorption edge of as-prepared pure ZnO (RMF-0), there is not a obvious change for the composites. The band gaps of the RMF-0 and composites obtained from the absorption edge (ca 390 nm) are about 3.18 eV. However, compared with pure ZnO, the visible light absorption of ZnO/RGO composites gradually increases with the increase of RGO amount content in the composites, which can be due to the presence of the black RGO[31,32]. The increased light absorption can enhance the number of photo-generated electrons and holes to participate in the photocatalytic reaction and improve the photocatalytic performance. Figure 3 b shows the photoluminescence (PL) emission spectra of as-prepared RMZ-0, RMZ-1, RMZ-2, RMZ-3, and RMZ-4 composites. Compared with pure ZnO (RMZ-0), the introduction of RGO in the composites can decrease excitonic PL intensity, which indicates that the recombination of photo-induced electrons and holes in ZnO can be effectively inhibited in the composites, leading to a enhanced photocatalytic performance. However, it is noted that RMZ-4 exhibits a significant increase of intensity compared to that of RMZ-2 and RMZ-3 composites, which is because that the excessive RGO

on ZnO can act as a kind of recombination center instead of providing an electron pathway[33].

The photocatalytic degradation of MB under visible light irradiation is used to evaluate the photocatalytic performance of as-prepared composites. Figure 4 shows the photocatalytic performance of as-prepared ZIF-8, RMZ-0, RMZ-1, RMZ-2, RMZ-3, and RMZ-4 composites under visible light irradiation, respectively. The inset indicates the absorption spectrum of MB using RMZ-3 composite with reaction time under light radiation, which indicates that the MB content decreases with the increase of the light irradiation time. It is observed that the photocatalytic activity of as-prepared ZIF-8 (29%) is lower than that of pure ZnO (RMZ-0) (46%). Moreover, When RGO amount is increased, the degradation efficiency is increased, and reaches a maximum value of 82% for RMZ-3 composite. The enhanced photocatalytic activity can be due to increased visible light absorption (as shown in Figure 3 a) and surface area. The BET surface area of as-prepared pure ZnO ($53.6 \text{ m}^2\text{g}^{-1}$) is lower than that of RMZ-3 composite ($61.3 \text{ m}^2\text{g}^{-1}$) due to loading ROG with higher surface area. However, the photocatalytic performance will decrease with the further increase of RGO loading due to the formation of the light harvesting competition and the recombination centers from the excessive RGO[31,33]. The stability of as-prepared RMZ-3 composite as catalyst is also discussed (as shown in Figure S2). It can be seen that the photocatalytic activity of composite do not decrease conspicuously after six successive cycles of degradation tests, indicating that the composite is fairly stability.

4. Conclusions

In summarized, RGO incorporated MOF-derived ZnO composites have been prepared for the photocatalytic degradation of MB under visible light irradiation. The

results indicate that the photocatalytic activity of as-prepared composites is superior to that of pure ZnO, and as-prepared RMZ-3 composite achieves a maximum degradation efficiency of 82%. The enhanced photocatalytic performance is ascribed to the effects of the enhanced light absorption, separate the photogenerated electrons and suppression of charge carriers recombination resulting from the interaction between ZnO and RGO.

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Figure Captions:

Figure 1 FESEM images of (a) as-prepared pure MOF-derived ZnO (RMF-0), and (b) RMF-3 composite. The inset is EDX spectrum of as-prepared RMF-3 composite.

Figure 2 (a) low-magnification HRTEM images and (b) high-magnification HRTEM images of as-prepared RMF-3 composite.

Figure 3 (a) UV-vis absorption spectra and (b) Room-temperature PL emission spectra of as-prepared composites.

Figure 4 Photocatalytic degradation of MB in the presence of as-prepared ZIF-8 and composites under visible light irradiation, and the inset is UV-vis absorption spectra of degradation MB solution over RMZ-3 under light irradiation.

Figure 1

Figure 2

Figure 3

Figure 4