Applied Surface Science 400 (2017) 129–138

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Photocatalytic and electrochemical performance of three-Dimensional reduced graphene Oxide/WS_2/Mg-doped ZnO composites

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ARTICLE INFO

Article history:
Received 27 September 2016
Received in revised form
18 November 2016
Accepted 17 December 2016
Available online 21 December 2016

Keyword:
Reduced graphene oxide
WS_2 nanosheet
Synergistic effect
Photocatalytic properties
Electrochemical performance

ABSTRACT

To improve the dispersion of reduced graphene oxide and enhance the photocatalytic property of reduced graphene oxide/Mg-doped ZnO composites (rGMZ), the reduced graphene oxide/WS_2/Mg-doped ZnO composites (rGWMZ) were prepared by electrostatic self-assembly and coprecipitation methods. The effects of mass ratio of WS_2 nanosheets to reduced graphene oxide (WS_2/rGO wt.%) and calcination temperature on the photocatalytic and electrochemical property of rGWMZ composites were investigated. Experimental results showed that the photocatalytic efficiency of rGWMZ composites is three-fold compared with that of rGMZ composites when the WS_2/rGO wt.% is 20.8% and calcination temperature is 500 °C, in which the degradation ratio Rhodamin B (RhB) can reach 95% within 15 min under the UV light and 90% within 90 min under simulated solar light. In addition, the rGWMZ show larger capacitance and smaller resistance than rGMZ. The enhancement for photocatalytic activity and electrochemical performance of rGWMZ is ascribed to improving the specific surface area, electrical conductivity and electronic storage capability because of the synergistic effect of rGO and WS_2 nanosheets.

1. Introduction

ZnO materials as a semiconductor metal oxides have been widely applied in photocatalytic field due to its wide direct bandgap (~3.37 eV), large exciton binding energy about 60 meV at room temperature, chemical stability and non-toxicity. However, the intrinsic ZnO materials can only absorb the ultraviolet light (about 5% of sunlight) and own high recombination rate of photogenerated carriers, thus limiting their wide practical application. Recently, many effective solutions have been applied to improve the photocatalytic efficiency of ZnO photocatalysts [1–6]. The photocatalytic activity of ZnO can be improved by Mg doping because of tuable electronic band gap of ZnO by varying the Mg^{2+} doping concentration and more oxygen vacancies or zinc vacancies due to ZnO atructural instability [7–9]. However, there still exists high recombination rate of photoelectron–hole pairs in Mg doping ZnO material due to the poor electrical conductivity and serious agglomeration. Graphene carrier is a very valid way to prevent the agglomeration of ZnO nanostructure and provide the conductive platform owing to its large surface area and high electrical conductivity [10–15]. However, graphene prefer to self-restack and poor compatibility with other nanomaterials. Hence, their intrinsically unique physical properties are not fully exploited as carriers for preparing high-performance photocatalysts [16]. Compared with graphene, reduced graphene oxide with many carboxyl, epoxy and hydroxyl groups reveals very good dispersion and strong interaction with nanocatalyst. Moreover, these functional groups disturb the surface structure of rGO offering more active sites [17,18]. But, this also reduce the conductivity of rGO due to the collapse of surface structure, resulting in decreasing the enhance effect [19]. In order to overcome this problem, composite catalytic carrier, assembled with rGO and other nanomaterial, has been widely researched.For example, 1D carbon nanotubes are deposited on rGO improving the dispersion and preventing the curling of rGO. Most importantly, the effective synergistic effect between rGO and nanostructures can enhance their electron transfer rate significantly [20,21]. Based on the 1D material/rGO composite catalytic carrier, 2D Layered material assembled with rGO has attracted widespread attention. Layered WS_2 owns unique nature open bandgap, distinctive physicochemical properties, native vacancy defects and low electrical conductivity [22]. Constructing 3D reduced graphene oxide/WS_2 sheet can alleviate the agglomeration of rGO and produce effective synergistic effect improving their electrical conductivity [23]. For example, Konda

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http://dx.doi.org/10.1016/j.apsusc.2016.12.138
0169-4332/

Shiva et al. employed synergistic interactions between reduced graphene oxide and layered WS_2 to improve the overall performance of Li-ion batteries [24]. Ke-Jing Huang et al. prepared layer tungsten sulfide-graphene nanocomposite with excellent electrochemical performances [25].

Inspired by these features, we firstly constructed the reduced graphene oxide/WS_2 catalyzer carrier by electrostatic attraction, then obtained the 3D rGWMZ by constant temperature coprecipitation method. The rGWMZ exhibits enhancement photocatalytic activity because of the effective synergistic effect between WS_2 nanosheets and reduced graphene oxide. Moreover, the enhancing photocatalytic activity mechanism of rGWMZ has been discussed in detail.

2. Experimental

2.1. Prepartion of rGWMZ composites

All the chemical used in synthesis have been used as received from chemical suppliers without any further purification and processing. The reduced graphene oxide was prepared by modified Hummers methods. The WS_2 nanosheets solution was prepared by the mechanical shear exfoliation method, referring to the previous reports [26]. The rGWMZ composites were performed typically as follows: 15 mL rGO solution (0.8 g L^{-1}) was sonicated for 15 mins, and then 2 mL WS_2 solution (1.25 g/L) was slowly added to the above rGO solution, forming the WS_2/rGO solution. Under vigorous stirring, 5.49 g $ZnC_2O_4{\cdot}2H_2O$ and 0.54 g $MgC_2O_4{\cdot}2H_2O$ (the molar ratio of Mg to Zn is 1:10) were dissolved in the WS_2/rGO solution. Subsequently, 100 mL oxalic acid solution (0.25 mol/L) was dropwise added to the aforesaid solution, and the solution was evaporated under 80 °C. After dried at 80 °C for 24 h, the resultant product (rGWMZ20.8 precursor) was annealed at 500 °C for 2 h under the protection of nitrogen gas. The achieved samples are recorded as rGWMZ20.8.

When the mass ratio of WS_2/rGO are 10.4 wt.%, 31.2 wt.% and 41.6 wt.%, the resultant hybrids are named as rGWMZ10.4, rGWMZ31.2 and rGWMZ41.6, respectively. Furthermore, the rGWMZ20.8 precursor was calcined at 400 °C and 600 °C, respectively. As a comparison, the reduced graphene oxide/magnesium-doped zinc oxide, the WS_2/magnesium-doped zinc oxide and the reduced graphene oxide/WS_2/zinc oxide calcined at 500 °C under the same conditions, labeled as rGMZ, WMZ and rGWZ.

2.2. Characterization

TG-DTA was performed by a NETZSCH STA 409 thermal analyzer under nitrogen atmosphere. X-ray diffraction (XRD) measurement was performed using Philips PW1710 diffractometer with Cu Ka1 radiation. Scanning electron microscopy (SEM) observations was carried out with S-4800 field emission scanning electron microscope. Transmission electron microscopy (TEM) analyses and element mapping images were conducted on a JEM-3010 transmission electron microscope. The Brunauer-Emmett-Teller (BET) surface areas were determined using a nitrogen adsorption analyzer (ASAP2020HD88). The Raman spectroscopy was executed by Renishaw inVia. Fluorescence spectra measurements and quantum yield were characterized on a Hitachi F4500 fluorescence spectrophotometer and the wavelength of excitation is 320 nm. UV–vis diffuse reflection spectra were recorded on TU-1901 spectrophotometer.

RhB was used as model dye to evaluate the photocatalytic activity of rGWMZ composites. The typical experiments can refer to our previous reports [11]. The cyclic voltammetry (CV) and AC impedance (EIS) spectras were performed with CHI 660 electrochenmical workstation, with the scan voltage range from −0.1 V to 0.8 V and scan rate of 2 mV/s. The working electrode was glassy carbon electrod coated 10 μL mixed liquor, which is composed of 5 mg sample, 950 μL absolute ethyl alcohol and 50 μL Nafion. Carbon stick electrode as the counter electrode and saturated calomel electrode. The electrolyte of CV test was 0.5 mol/L dilute sulphuric acid solution and in EIS test was 1 mol/L sodium sulfate solution. The electron spin resonance (ESR) spectra were obtained by using X-band JEOL JES-FA200 spectrometer. The captured agent of hydroxyl radical (·OH) in water is 5, 5-dimethyl-1-pyrroline-N-oxide (DMPO), and the microwave frequency is 9072.418 MHz.

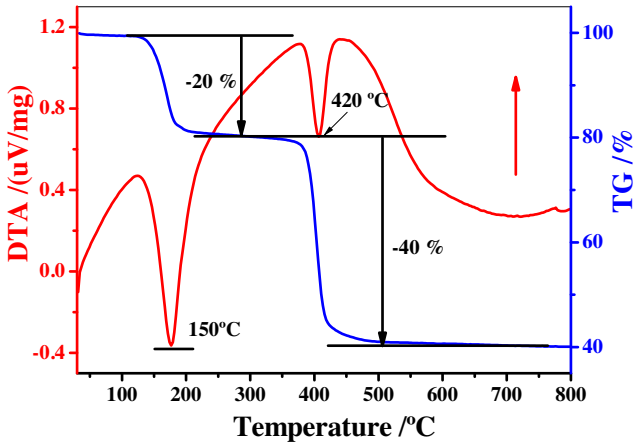

Fig. 1. TG-DTA images of rGWMZ20.8 precursor.

3. Results and discussion

3.1. Structure and morphology of rGWMZ composites

In order to consider the effect of annealed temperature on the structure of material, TG-DTA is used to analyse the thermal decomposition of rGWMZ20.8 precursor under nitrogen atmosphere, and the corresponding result is shown in Fig. 1. The DTA curve shows a strong endothermic peak is observed at around 150 °C, and there is 20% mass loss in the TG curve, originating from the loss of crystal water in zinc oxalate dihydrate crystallization. The endothermic peak at 420 °C, correspond to the weight loss of 40% in TG curve, is attributed to the thermal decomposition of zinc oxalate ($ZnC_2O_4 = ZnO + CO\uparrow + CO_2\uparrow$). There was no sign change in TG curve above 500 °C, while there is an exothermic peak at about 780 °C, indicating that the crystalline phase of residue is highly stable from 500 °C to 750 °C. According to above result, we choose the annealed temperature are 400 °C, 500 °C and 600 °C, respectively.

Fig. 2a illustrates the effect of the mass ratio of WS_2 to rGO on XRD patterns of resultant smaples. It is obvious that the diffraction peaks of all samples display in same position, which are attributed to (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) planes of hexagonal wurtzite ZnO (JCPDS NO.36-1451), respectively. Fig. 2b is the XRD patterns of rGWMZ20.8 precursor annealed at different temperature. The diffraction peaks of rGWMZ20.8 precursor are in accordance with JCPDS card (NO. 25-1029) for zinc oxalate dihydrate. After annealed, the diffraction peaks of samples are corresponding hexagonal wurtzite ZnO, and the intensity of diffraction peaks increase as increasing the annealed temperature. No diffraction peaks of rGO, carbon and WS_2 are observed, which may because their content is too low.

The morphology of different samples was examined by using SEM. As shown in Fig. 3, we find that the rGO (Fig. 3a) and rGO/WS_2 carriers (Fig. 3b) present very different morphologies. Pure rGO exhibits huge flake with seriously stacking, while the rGO/WS_2 car-