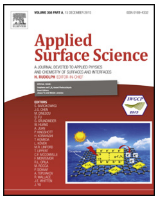
Applied Surface Science 358 (2015) 63–69

Contents lists available at ScienceDirect

Applied Surface Science

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



Effect of various amounts of graphene oxide on the degradation characteristics of the ZnSe/graphene nanocomposites

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ARTICLE INFO

Article history:
Received 20 June 2015
Received in revised form 23 August 2015
Accepted 25 August 2015
Available online 28 August 2015

Keywords:
ZnSe
Graphene
Methylene blue
Nanocomposites

ABSTRACT

In this work, the graphene oxide (GO) sheets were synthesized by modified Hummers and Offeman's method. The GO was mixed with ZnSe that was prepared using various amounts of N_2H_4 at a ratio of (0.25–2):1 to form precursors. The ZnSe/graphene nanocomposites were synthesized under hydrothermal conditions (180 °C; 12 h) from the previous precursor. Obtained ZnSe/graphene photocatalysts were characterized by X-ray diffraction analysis (XRD), Fourier transform infrared (FTIR) spectroscopy, UV–vis diffuse reflection spectroscopy, transmission electron microscope, scanning electron microscope, Raman spectra and X-ray photoelectron spectroscopy (XPS). Photocatalytic activity under visible light is evaluated in methylene blue (MB) dye degradation reaction in aqueous phase.

The results show that the formation of ZnSe/graphene nanocomposite is depend on ratio of the addition of GO to the amount of ZnSe–N_2H_4. The optimum degradation efficiency of the ZnSe/graphene nanocomposites on MB increases with increasing the ratio of the addition of GO to the amount of ZnSe–N_2H_4. When the amount of N_2H_4 increased from 5 ml to 7 ml, the ratio of the addition of GO to the amount of ZnSe–N_2H_4 increased from 1 to 1.25.

1. Introduction

The wastewater generated from textile industries generally contains a large number of organic dyes and hazardous wastage that create environmental pollution problems. Methylene blue (MB) is a heterocyclic organic dye, frequently used in dying cotton, wool and silk. MB can cause permanent injury to humans and animals on inhalation and ingestion. It is estimated that 30–40% of the used dyes originating from industrial sources are released into waste waters [1]. There are several techniques that have been developed to removal of dyes from the waste water, including physical adsorption [2,3], anaerobic treatment, membrane filtration, chemical oxidation [4], biological method [5], and photocatalytic degradation method and so on. Among them, the photocatalytic degradation method has much more attraction for its potential in utilizing solar energy for environmental purification [6–12]. Recently, photocatalysis using semiconductor nanoparticles (TiO_2) have opened a new door for the remediation of toxic organic pollutants owing to its stability, low cost and non-toxicity [13,14]. Titanium dioxide (TiO_2) is a wide band gap semiconductor (3.2 eV). The wide band gap of TiO_2 confines its application under visible light. The photocatalytic efficiency is also limited by the fast electron–hole recombination. To resolve these drawbacks, the development of photocatalysts that only use visible light for photocatalysis has already drawn great attention. The light absorption range of zinc selenide (ZnSe) falls in the visible light region. Compared with TiO_2, ZnSe has a wider range in which sunlight can be used for catalytic reactions. Recently, Qian et al. [15] discovered that the photocatalytic activity of ZnSe nanoribbons is higher than that of TiO_2 particles when used for the degradation of magenta acid dye under ultraviolet (UV) irradiation, indicating that ZnSe is an effective photocatalyst for the photocatalytic degradation of organic pollutants.

Nanostructured carbon materials (e.g. graphene) has emerged as high potential material and increasingly attracted attention, due to its specific properties, including excellent electron mobility, large specific surface area, flexible structure, high transparency and stability at room temperature [16]. When used to modify other materials, graphene can retard the recombination of electron-electron hole pairs that are photochemically or electrochemically generated; thus, graphene can increase the transfer of photo-generated charges and further increase the catalytic activity [17]. These properties are important features when dealing with the preparation and use of graphene-based materials and,

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http://dx.doi.org/10.1016/j.apsusc.2015.08.220
0169-4332/

for this reason, the combination of semiconductor and graphene maybe an ideal preference to achieve an enhanced charge separation processes. Thus far, many researchers have reported the graphene-based semiconductor nanocomposites composite exhibits enhanced photoactivity [18–24]. Among graphene-based semiconductor photocatalysts, graphene-based ZnSe nanocomposites were expected to provide improved photoactivity and promote extraordinary properties under visible-light irradiation. Chen et al. studied the photocatalytic activities of nitrogen-doped graphene/ZnSe nanocomposite (GN–ZnSe) under visible light. They have reported that the high photocatalytic activity of GN–ZnSe is attributed to promote charge collection and separation at the interfaces of GN/ZnSe and thus improves [25]. Liu et al. [26] reported that the as-prepared nanocomposites $ZnSe{\cdot}xN_2H_4$/GS and ZnSe/N-GS exhibit remarkably enhanced photocatalytic activities for methylene blue (MB) dye under visible light irradiation. Ullah et al. prepared ZnSe/graphene nanocomposites by utilizing one pot hydrothermal techniques. The photodegradation rates of organic dyes by the ZnSe/Graphene nanocomposites are found to be markedly high. Reused ZnSe/graphene showed excellent stability [27]. Zhou et al. fabricated setaria palmifolia-like, turfgrass-like and needle-like zinc selenide (ZnSe) nanograsses on graphene oxide sheets by a hydrothermal method. The results show that GO/ZnSe nanograsses have best field emission properties with a low turn-on electric field of $4.5\,V\mu m^{-1}$ and a high field enhancement factor of 2715 [28]. Zhang et al. demonstrated a facile route for the synthesis of ZnSe-reduced graphene oxide (rGO) nanocomposites as an electrode material for lithium ion batteries. The results show that the synergetic effects between ZnSe nanoparticles and graphene nanosheets make ZnSe-rGO nanocomposites exhibit high reversible capacity ($876\,mAh\,g^{-1}$ after 50 cycles), excellent cyclic performance and good rate capability ($778\,mAh\,g^{-1}$ after 400 cycles at $1000\,mAh\,g^{-1}$) [29]. To the best of our knowledge, the photodegradation of MB using GN/ZnSe was seldom addressed.

In the present work, we have prepared ZnSe/graphene nanocomposites by the hydrothermal method. The photocatalytic activity of as-prepared ZnSe/graphene nanocomposite was investigated by photodegradation of methylene blue (MB) under visible light irradiation. In this study, the $ZnSe–N_2H_4$ reacted with GO and formed GN–ZnSe nanocomposites. The formation of GN–ZnSe is determined by the ratio of $ZnSe–N_2H_4$ and GO. We report the effects of ratio of $ZnSe–N_2H_4$ and GO on degradation of methyl blue (MB) dye was investigated. This work may provide new insights for preparing highly photocatalytic activity ZnSe/graphene nanocomposite.

2. Experimental

In this work, the graphene oxide (GO) sheets were synthesized by modified Hummers and Offeman's method. Through this process, the natural graphite powder was exfoliated by strong oxidizing agent ($KMnO_4 + H_2O_2$). For obtaining ZnSe deposited on the surface of graphene. First, 5 ml of hydrazine (N_2H_4), 14 ml of Diethylenetriamine ($C_4H_{13}N_3$, DETA) and 16 ml of H_2O (volume ratio: 5:14:16) were mixed to form a solution. Then, zinc sulfate heptahydrate ($ZnSO_4{\cdot}7H_2O$) and sodium selenite (Na_2SeO_3) were added to the mixed solution (35 ml), and the solution was stirred. The uniformly mixed solution was transferred to a 50-ml Teflon stainless steel autoclave for a hydrothermal reaction for 12 h at 180 °C. After the hydrothermal reaction, white flocculates were obtained. The white flocculates were then collected via centrifugation and rinsed with ethanol. The precipitate was collected and vacuum-dried in an oven at 80 °C for 6 h. The dried product was a $ZnSe–N_2H_4$ nanopowder. $ZnSe–N_2H_4$with 5 ml of N_2H_4 is denoted by ZnSe (5 ml)–N_2H_4. In addition, $ZnSe–N_2H_4$ was also prepared with different amounts of N_2H_4 (4 ml, 5 ml, 6 ml, 7 ml and 8 ml). $ZnSe–N_2H_4$ prepared from *X* ml of N_2H_4, 14 ml of DETA and 16 ml H_2O is denoted by ZnSe (*X* ml)–N_2H_4.

Sixteen milligrams of dried graphene oxide (GO) and 16 mg of dried ZnSe (*X* ml)–N_2H_4 powder were collected and then placed into 16 ml of water for ultrasonic agitation. Then, the ZnSe solution was slowly added to the GO solution, which was magnetically stirred at 25 °C for 5 min. The uniformly mixed solution was then transferred to a 50-ml Teflon stainless steel autoclave for hydrothermal reaction for 12 h at 180 °C. The product was then collected through centrifugation and rinsed multiple times with water and ethanol. The precipitate was collected and dried in an oven at 70 °C until completely dry. The dried product was a ZnSe/graphene nanocomposite, which is denoted GN–*X* ml ZnSe. In addition, GO was mixed with ZnSe (*X* ml)–N_2H_4 at different weight ratios of (0.25–2):1. Then, the mixtures underwent a hydrothermal reaction in a Teflon stainless steel autoclave at 180 °C for 12 h, and ZnSe/graphene nanocomposites were obtained, which are denoted GN–*X* ml ZnSe (*Y*). For instance, GO was mixed with ZnSe (5 ml)–N_2H_4 at weight ratios of 1:1 which are denoted GN–5 ml ZnSe (1).

The ZnSe/GN was characterized by X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, UV–vis diffuse reflection spectroscopy, transmission electron microscope, scanning electron microscope, Raman spectra and X-ray photoelectron spectroscopy (XPS). Powder X-ray diffraction (XRD) analyzes was performed on a Bruker D8 Advance diffractometer with Cu K_α radiation. Fourier transform infrared (FT-IR) spectroscopy was performed in the wavelength range of $4000–400\,cm^{-1}$. X-ray photoelectron spectroscopy (XPS) measurements were performed using a PHI 5000 VersaProbe system. Raman spectra were collected by using the Horiba (TRIAX 550) Raman microscope, excited at room temperature with excitation laser wavelength of 488 nm. A 200 kV transmission electron microscope (TEM, JEOL JEM-2010) and scanning electron microscope (JEOL JSM-6510LV) were used for the observation of microstructure.

The methylene blue (MB) solution was 60 ml in volume with a concentration of 35 mg/l, pH value of 4, and GN–ZnSe photocatalyst of 10 mg for each test. The test solution was first stirred by magnetic stirrer for 0.5 h in dark. For photocatalytic degradation experiment, the photocatalytic reaction was started by the exposure to the visible light and then taken 4 ml out as sample for 1, 2, 3, 4, 5 and 6 h, respectively. The visible light is generated by a solar simulator under the one-sun global solar spectrum of air mass (AM) 1.5 (under $100\,mW\,cm^{-2}$). Each sample solution was analyzed by UV–vis spectrophotometer to monitor the concentration of MB left in the aqueous system by detecting the maximum absorption wavelength for MB at 663 nm. The intensity of the main absorption peak (663 nm) of the MB dye was considered as a measure of the residual MB dye concentration (C) and the initial concentration of dye was referred as (C_0).

3. Result and discussion

Fig. 1(a) and (b) shows the XRD spectra of the $ZnSe–N_2H_4$ and the annealed ZnSe nanocomposites. The presence of the spectrum in Fig. 1(a) could only be confirmed by some peaks corresponding to the peaks of $ZnSe–N_2H_4$. The other spectrum can be an organic-inorganic hybrid phase [30]. Fig. 1(b) shows the pattern of the hexagonal ZnSe phase, which exhibits a wurtzite structure (PDF 15-0105). This reveals that $ZnSe–N_2H_4$ can be formed after mixed solution of hydrazine, diethylenetriamine, zinc sulfate heptahydrate, and sodium selenite. Fig. 2(a)–(e) presents the XRD spectra of GN–4 ml ZnSe, GN–5 ml ZnSe, GN–6 ml ZnSe, GN–7 ml ZnSe, and GN–8 ml ZnSe nanocomposites, respectively. Fig. 2(a)–(e) also