Applied Surface Science 466 (2019) 401–410

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

Improving the intrinsic properties of rGO sheets by S-doping and the effects of rGO improvements on the photocatalytic performance of Cu_3Se_2/rGO nanocomposites

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ARTICLE INFO

Keywords:
S-doped rGO
Intrinsic properties of GO
Semiconductor/rGO nanocomposites
Photocatalytic performance
Type-II heterostructure

ABSTRACT

The effects of S-doping on intrinsic properties of graphene oxide (GO) sheets such as interlayer spacing, reduction level, and electrical resistance and the influence of these properties on the photocatalytic performance of rGO/Cu_3Se_2 nanocomposites were investigated. A simple chemical method was used to synthesize S-doped GO sheets and a cost-effective co-precipitation method was used to decorate of the NPs on S-doped GO (as S-doped GO/NPs nanocomposites) and undoped GO (as undoped GO/NPs nanocomposites) sheets. X-ray diffraction (XRD) patterns of the products indicated that GO sheets were changed into reduced GO (rGO) sheets during the synthesis process. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images showed more exfoliation for the S-doped rGO sheets in comparison to the undoped rGO. X-ray photoelectron spectroscopy (XPS) indicated that S-doping caused an improve reduction level of rGO. UV–vis results revealed that S-doped rGO/NPs nanocomposites had a band-gap value around 2.2 eV that was bigger than the band-gap value of the undoped rGO/NPs that was around 1.9 eV. Room temperature photoluminescence (PL) results indicated that, the electron-hole recombination rate of S-doped rGO/NPs nanocomposites was lower than the undoped rGO/NPs nanocomposites. The photocatalytic activity under visible light irradiation for degradation of methylene blue (MB) dye showed a significant enhancement photocatalytic performance for S-doped rGO/NPs nanocomposites in comparison to the photocatalytic activity of the undoped rGO/NPs nanocomposites. Brunauer–Emmett–Teller (BET) calculation indicated a specific surface area of 251.6 and 220.7 $m^2 g^{-1}$ for the S-doped and undoped rGO/NPs nanocomposites, respectively. In addition, photoresponse measurements under visible light source irradiation indicated that, the electrical conductivity of rGO as an intrinsic property of the rGO sheets was increased by S-doping. Finally, according to valence band (VB) edge spectroscopy results of the samples, it was understood that a type-II heterostructure was formed by S-doped rGO/NPs with pristine NPs that was another important factor for the enhancement photocatalytic performance of this sample.

1. Introduction

Increasing of the photocatalytic efficiency of a semiconductor under irradiation of the visible light spectrum is one of the hot topics in the recent years. Usually, the semiconductor should have a suitable band-gap value to absorb visible photons and the stability during the photocatalytic activity. It is known, the most important factor to enhance the photocatalytic performance of a semiconductor is to prevent recombination of electron-hole pairs, which were created by absorbed photons, in the semiconductor. One of the common methods to decrease recombination of electron-hole pairs in a semiconductor is to be made a heterojunction with another semiconductor [1,2]. Such heterojunction can cause to transfer of excited electrons, holes, or both from the semiconductor, which was interacted by photons, to another semiconductor. The second semiconductor is able to trap excited electrons and holes and then the electrons and holes can be transferred from this semiconductor toward the pollutants' molecules and the reduction-oxidation (redox) process of pollutants' molecules has happened that

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https://doi.org/10.1016/j.apsusc.2018.10.082
Received 20 July 2018; Received in revised form 28 September 2018; Accepted 9 October 2018

causes degradation of pollutants from wastewaters.

Recently, two-dimensional (2D) structures from carbon nanocomposite family like graphene and g-C_3N_4 have been used to improve the photocatalytic activity of semiconductors due to their interesting physical and chemical properties [3,4]. Graphene oxide (GO) and reduced graphene oxide (rGO) are also known as 2D structures with unique properties such as their functional electron sink properties, low density, large surface area, and high conductivity [5,6]. Therefore, recently several semiconducting nanostructures were decorated on GO and rGO to improve photoelectrochemical applications of semiconductors such as the photocatalytic performance, solar-cells, and water splitting [7–14]. It is known, the intrinsic properties of GO and rGO such as interlayer spacing, reduction level, textural property, and electrical resistance can be tuned by covering with oxygen atoms [5]. Therefore, if some of these oxygen groups can be substituted by the other atoms, then the physical and chemical properties of GO and rGO can be changed [15–17]. The best atom to substitute for oxygen atom in GO or rGO structure is sulfur element due to its similar chemical properties with oxygen element. Recently, several works have been reported about the effects of sulfur on physical and chemical properties of GO and rGO [18–26]. All these studies showed that intrinsic properties of GO or rGO were improved by S-doping significantly. However, few studies have been conducted on the effects of improvement of intrinsic properties of rGO on the photocatalytic performance of semiconductor/rGO nanocomposites.

More recently, copper selenide nanostructures have been of great interest to researchers as photocatalytic materials that work under visible light irradiation due to their suitable band-gap and tuning of the band-gap value by changing of stoichiometry (1.5–2.5 eV) or doping materials [27–32].

Therefore, here we present the effects of S-doped GO sheets on photocatalytic activity of rGO/Cu_3Se_2 nanocomposites. Na_2S was used as S-doping source in GO solutions to obtain S-doped GO sheets. Then, the Cu_3Se_2 NPs were decorated on these doped sheets by a co-precipitation method. The undoped and S-doped GO sheets were changed to undoped and S-doped rGO sheets during the synthesis process of products due to the presence of the reducing agent in the synthesis process. As a comparison study, the NPs were also decorated on the pristine GO sheets by the similar method. After that, the photocatalytic activity of these samples, as well as pristine NPs was examined to remove MB dye under visible light irradiation conditions. We believe that, current results could be led to present a method to enhance the photocatalytic performance of the semiconductor/rGO nanocomposites in the future. As far as we can tell, there is no such comparison study in the literature about the effects of S-doped GO on the photocatalytic performance of a semiconductor so far.

2. Experimental

2.1. Materials and synthesis process

In the first step, S-doped GO sheets were synthesized by a simple mixture of Na_2S and GO solutions. High purity GO powder sheets (GO 99.999%, US Research Nanomaterials, Inc.) was used as GO source that was included 6–10 layers. In this part, a GO solution was prepared and then it was ultrasonicated for 15 min. After that, the GO solution with 10 wt%/v concentration was mixed with a 0.29 mM of Na_2S under magnetic stirring at 80 °C for 30 min. Then, 5 mM of $Cu(NO_3)_2{\cdot}3H_2O$ (99.99%) as Cu source, 5 mM of Se powder as Se source, and 13 nM of $NaBH_4$ as a reducing agent were used to synthesize pristine NPs and decorated of the NPs on the pristine GO and S-doped GO sheets. Detailed synthesis process and some characterizations of the pristine NPs and undoped rGO/NPs nanocomposites were reported in our previous works [25,26].

2.2. Characterizations

The crystal phase of the products were investigated by X-ray powder diffraction (XRD, Philips, X'pert, system using Cu-K_α radiation and $\lambda = 0.154060$ nm), selected area electron diffraction (SAED, Hitachi H-7100), Fourier transform infrared spectrometry (FTIR, Perkin-Elmer System 2000 series spectrophotometer (USA) by the KBr method), and X-ray photoelectron spectroscopy (XPS, Thermofisher Scientific with Mg-Kα radiation as the excitation source and C-1s peak (285 eV) was used to calibrate as a reference). The morphology of the samples was studied by transmission electron microscopy (TEM, Hitachi H-7100) and field emission scanning electron microscopy (FESEM, TE-SCAN, MIRA3). UV–vis spectroscopy (Perkin-Elmer spectrometer) and room temperature photoluminescence (PL) (UniRam PL spectrometer) with a He–Cd laser as a light source with a power of 200 mW and an excitation wavelength of 325 nm were used to study optical properties of the products. Energy-dispersive X-ray spectroscopy (EDX), which was attached to the FESEM microscope, was applied to show the elemental mapping of the S-doped GO sheets. Specific surface area of the products was estimated by the linear portion ($P/P_o = 0.05$–0.2, pressure transducer ≈ 133 kPa) of the Brunauer–Emmett–Teller (BET) model using N_2 adsorption-desorption at liquid nitrogen temperature (77 K) (BElSORP Mini (Microtrac Bel Corp CO)). In addition, the Barrett-Joyner-Halenda (BJH) model was applied for calculation of pore diameter and pore volumes of the samples.

2.3. Preparation of the photocatalytic degradation samples

The photocatalytic activity of the samples was measured using the degradation of a solution of MB dye under the visible light irradiation. The conditions for the photocatalytic process were similar to our previous work that was used to exam the photocatalytic activity of Mg-doped ZnO/rGO nanocomposites [33]. The MB pollution was simulated by a solution of MB dye with a concentration of 10 mg/l. Here, 10 mg of the NPs and nanocomposites were dispersed in 30 ml of the pollution water. The mixed suspension was magnetically stirred for 30 min in the dark to reach an adsorption–desorption equilibrium. Under the ambient conditions and stirring, the mixed suspension was also exposed to the visible light source, which it was an LED with 50 W powers and 4300 LM. At certain time intervals, 2.5 ml of the mixed suspension was extracted and centrifugated to remove the photocatalyst. The degradation process was monitored by measuring the absorption of MB in the filtrate at 664 nm using a UV–vis absorption spectrometer.

2.4. Electrical and photocurrent measurements

Different powder samples were mixed into a solution of ethyl cellulose and alcohol and then some drops of α-terpineol were added to this solution. A drop-casting method was used to deposit powder solutions on the photoelectrode films, which was the glass/FTO/TiO_2(NPs) (TiO_2 past). Next, the films were dried in an oven at 100 °C for 30 min. An Au film (thickness ≈ 10 nm) was coated on FTO-glass by a sputter coater set-up (DSR, Nanostructured Coatings CO., Iran), which was used as a counter electrode. An electrolyte solution was prepared by a mixture of 0.5 M of KI and 0.05 M of I_2 in ethylene glycol. The illuminated area of the specimens and the distance between the films and the light source were 0.25 cm^2 and 5 cm, respectively. The photocurrent was determined over the ON and OFF duration of the light source by a key. The same LED, which was used for photocatalytic experiments, was applied as illumination source light for photocurrent measurements.