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Controlled fabrication and tunable photoluminescence properties of Mn^{2+} doped graphene–ZnO composite

Xinglong Luan, Yihe Zhang [*], Wangshu Tong, Jiwu Shang, Qi An, Hongwei Huang

School of Materials Science and Technology, China University of Geosciences, Beijing 100083, China

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ABSTRACT

Graphene–ZnO composites (G–ZnO) with controlled morphology and photoluminescence property were synthesized by a mixed solvothermal method. Mixed solvent were composed by dimethyl sulfoxide and ethylene glycol. Fourier transform infrared spectroscopy, transmission electron microscopy and photoluminescence spectra were used to characterize G–ZnO. Graphene as a substrate can help the distribution and the dispersity of ZnO, and a possible model of the interaction between graphene oxide and ZnO particles is proposed. At the same time, graphene also reduce the size of ZnO particles to about 5 nm. Furthermore, Mn^{2+} ions dopes G–ZnO successfully by the mixed solvothermal synthesis and the doping of Mn^{2+} makes G–ZnO shift red from 465 nm to 548 nm and 554 nm in the emission spectrum. The changes of the emission spectrum by the adding of Mn^{2+} make G–ZnO have tunable photoluminescence spectrum which is desirable for practical applications.

1. Introduction

Quantum dots (QDs) are nanocrystals made of semiconductor materials which are small enough to exhibit quantum mechanical properties with strongly size-depending optical and electrical properties [1]. ZnO is a kind of large-band-gap semiconductors with unique physical properties and high chemical stability. The biocompatible ZnO can be used as non-resonant nonlinear optical probes for bioimaging applications in vitro [2]. However, like many other QDs [3,4], ZnO in nano size are easily aggregated and cannot disperse homogeneously without modification agent, which lead to the limitation of its application.

Graphene, a two-dimensional material composed of sp^2-bonded carbon atoms, has very high charge carrier mobility [5] and specific surface area [6]. Recently, researchers used graphene as a substrate to disperse QDs and even improve the QDs properties, such as photosensitivity and photoconductivity. Liwei Liu et al. [7] have found that the combination of graphene and CdSe QDs can improve their photosensitivity and photoconductivity in magnitudes. Graphene-QDs composites are considered ideal candidates for several applications including photocatalytic [8,9], supercapacitor [10], solar cell [11] and biosensing systems [12,13].

In this paper, we synthesized graphene–ZnO composites (G–ZnO) by mixed solvothermal method using graphene oxide by modified Hummer method and studied its morphologies and photoluminescence (PL) properties. We also proposed a hypothesis to explain the the interaction between ZnO and graphene oxide. Furthermore, Mn^{2+} doped G–ZnO were prepared referring to previous works [14–16]. The tunable photoluminescence spectrum and good dispersion of Mn^{2+} doped G–ZnO make it an ideal candidate for biological sensors.

2. Experimental

Graphite oxide (GO) was prepared by modified Hummer method [17] and G–ZnO composites were synthesized by mixed solvothermal method. In a typical synthesis of G–ZnO composites, 20 mg polyvinyl pyrrolidone (PVP) acting as capping agent was added to the mixed solvent (DMSO/EG = 1/3) with 20 mg GO and 100 mg $Zn(Ac)_2\cdot 2H_2O$ under ultrasound for 2 h. Then the resulted solution was transferred into a 100 mL Teflon-lined stainless steel autoclave, followed by solvothermal treatment at 160 °C for 6 h. After that, the precipitates were centrifuged and washed by absolute alcohol and distilled water for five times, followed by freeze-drying. Mn^{2+} doped G–ZnO composites were synthesized by adding certain amount of $MnCl_2\cdot H_2O$ in the same condition.

Fourier transform infrared spectra (FTIR, PerkinElmer Spectrum 100), X-ray photoelectron spectroscopy (XPS, Axis Ultra Kratos Analytical Ltd.), X-ray diffraction (XRD, Rigaku D/max-rA) and transmission electron microscopy (TEM, JEOL JEM2100F) were

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[*] Corresponding author. Tel.: +86 10 82323433.
E-mail address: zyh@cugb.edu.cn (Y. Zhang).

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carried out to characterize the structure and morphologies of the samples. Zeta potentials were tested by Zetasizer Nano ZS90 (Malvern). PL property was examined by F-7000 fluorescence spectrophotometer (Hitachi High Technologies, Inc.).

3. Results and discussion

3.1. Structure and morphology of G–ZnO

To demonstrate the changes of functional groups on the GO surface after the solvothermal treatment, the FTIR of GO and G–ZnO were shown in Fig. 1a. For GO, the stretching vibrations of O—H (around 3400 cm^{-1}), C═O (1733 cm^{-1}), aromatic C═C (1625 cm^{-1}), epoxy C—O (1224 cm^{-1}), and C—O (1067 cm^{-1}) are observed. For G–ZnO, the decrease of frequency of C═C (1625 to 1571 cm^{-1}) and increase of its intensity were observed due to the interaction between C═C double-bond. At the same time, the GO related stretching bands of carboxyl and epoxy groups, are not observed in G–ZnO, indicating the reduction of GO after solvothermal treatment.

XPS shows the reduction of GO during the mixed solvent treatment and the formation of G–ZnO. All of the peaks in Fig. 1b are ascribed to Zn, O, C elements. The peaks at 1044.8 and 1021.6 eV are attributed to Zn 2p1 and ZnO respectively. There's an obvious decrease of the C1s intensity of G–ZnO compared with the XPS result of GO. The C1s deconvolution spectra of GO and G–ZnO are shown in Fig. 1c and d. Peaks located at 284.8, 286.9 and 288.4 eV correspond to C—C, C—O, and carboxylic groups C═O, respectively. The decrease of C—O and C═O peaks indicates the reduction of GO, which shows the same result of FTIR.

XRD was also carried out to characterize the formation of G–ZnO. As shown in Fig. 2, GO shows a broad peak at 2θ = 9.5°, corresponding to an average interlayer space of ~0.93 nm. For G–ZnO, the broad peak around 24° corresponds to the fluffy stack of graphene [18] and the diffraction angles at 31.74, 34.37, 36.19, 47.46, 56.45, and 62.74 can be assigned to (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), and (1 0 3) crystal planes of zincite (ICSD#076641). All the results above conform that G–ZnO composites were prepared by the mixed solvent method.

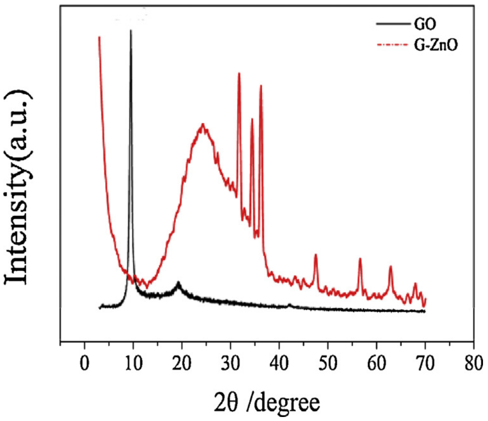

Fig. 2. XRD of G–ZnO and GO.

TEM is performed to clarify the morphology of G–ZnO. As shown in Fig. 3(a–c), the wrinkles of the sheets can be seen, which indicates the as prepared G–ZnO is easily dispersed. At the same time, ZnO disperse homogeneously on the sheets and the sizes of the ZnO are about 5 nm (Fig. 3c), while without GO, the sizes of the ZnO particles prepared under the same condition are much larger (Fig. 3d). Graphene oxide with big surface area and amount oxygen-containing groups has the interaction with Zn^{2+} leading to the good dispersion and small sizes of ZnO.

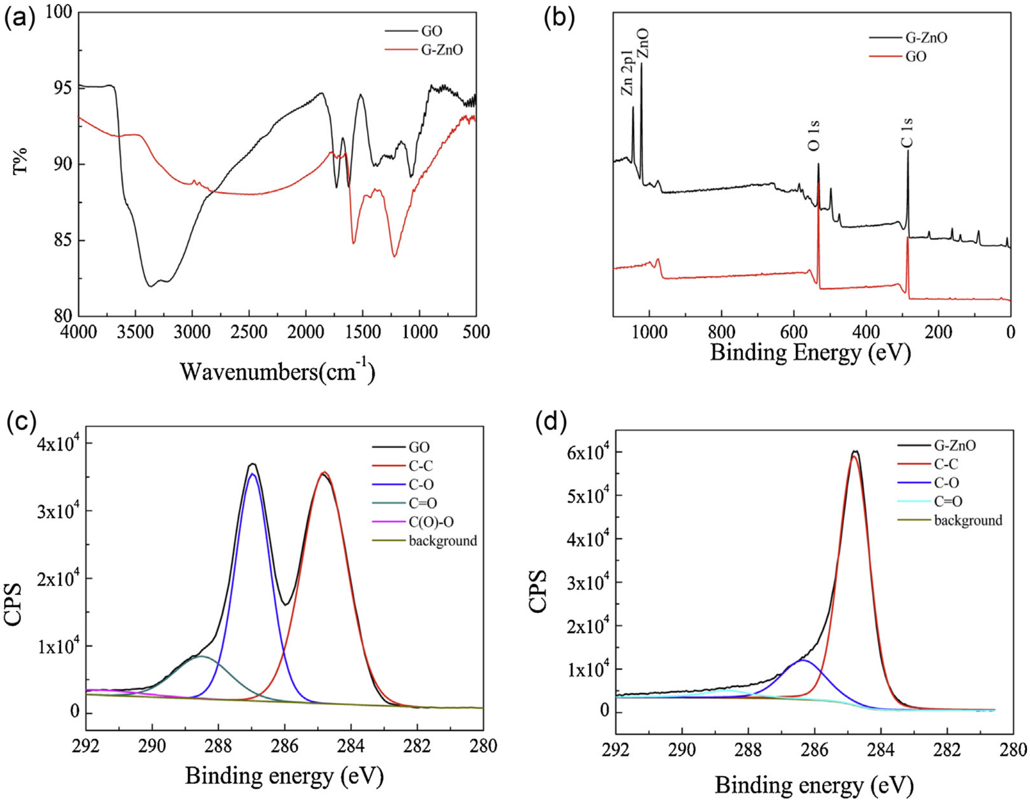

Fig. 1. FTIR of GO and G–ZnO (a), XPS of GO and G–ZnO (b) and the C1s deconvolution spectra of GO (c) and G–ZnO (d).