

# Study on the fluorescence quenching of ZnO by graphene oxide\*

LI Ji-tao (理记涛)<sup>1\*\*</sup>, YANG Jing (杨静)<sup>1</sup>, ZHOU Si-hua (周思华)<sup>1</sup>, WANG Shao-hui (王少辉)<sup>1</sup>, LIU Kui-li (刘奎立)<sup>1</sup>, and XU Chun-xiang (徐春祥)<sup>2</sup>

1. School of Physics and Telecommunications Engineering, Zhoukou Normal University, Zhoukou 466001, China

2. State Key Laboratory of Bioelectronics, School of Biological Science and Medical Engineering, Southeast University, Nanjing 210096, China

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Zinc oxide (ZnO) microrod arrays were synthesized on Si substrate by a vapor phase transport (VPT) method in a tube furnace. The obtained ZnO microrods are characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The photoluminescence (PL) measurement indicates that the ZnO microrods have a strong ultraviolet (UV) emission centered at ~391 nm and a defect-related emission centered at ~530 nm. After the microrods were coated with graphene oxide (GO), the PL intensity of the hybrid microstructure is quenched compared with that of the bare one at the same excitation condition, and the PL intensity changes with the concentration of the GO. The fluorescence quenching mechanism is also discussed in this work.

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In the past decades, zinc oxide (ZnO) has been extensively studied for its potential applications in various fields<sup>[1,2]</sup>. Among various ZnO micro/nanostructures, the one dimensional ZnO, such as ZnO nanowires or microrods, is considered as one of the most promising candidates in the field of semiconductor micro/nanostructures because of its higher surface-to-volume ratio and stronger dependence of electrical conductance on the amount of adsorbates<sup>[3,4]</sup>. Besides, the chemically synthesized ZnO has unique optical properties, such as high photoluminescence (PL) efficiency and size-dependent PL wavelength<sup>[5]</sup>. So, the control of exciton states in ZnO is essential for the fabrication of devices, such as light-emitting diodes (LEDs)<sup>[6]</sup>, lasers<sup>[7]</sup> and solar cells<sup>[8]</sup>. Generally, the excitonic responses of ZnO can be controlled via the charge and energy transfer at the interface between ZnO nanocrystals and the surrounding environment due to the large surface-to-volume ratios of the nanocrystals<sup>[9]</sup>. Drastic changes in the optical responses of nanocrystals are anticipated by controlling the nano-scale-localized energy transfer at the interface through surface modification.

Another material of graphene, a two-dimensional sheet of covalently bonded carbon atoms, has recently attracted tremendous attention due to its unique electrical and optical properties since its discovery in 2004<sup>[10]</sup>.

Graphene has a very high carrier mobility and remarkable electroconductivity, mechanical flexibility, strong thermal/chemical stability and optical transparency<sup>[10,11]</sup>. Previous studies indicate that the combination of ZnO and graphene has many benefits due to the composites can offer additional functionality to graphene and improve the properties of the host material ZnO<sup>[12,13]</sup>. ZnO-graphene hybrid architectures composed of regular arrays of ZnO nanorods formed on few-layer graphene films exhibit good optical transmittance and structural stability<sup>[14]</sup>.

In this paper, the graphene/ZnO microrods composite was fabricated by dipping ZnO microrods into graphene oxide (GO) solution, and PL properties of ZnO microrod array and the composite are compared. The quenched PL intensity is found in the graphene/ZnO composite, and PL intensity of the composite changes with the concentration of GO. On basis of the experimental observation, the fluorescence quenching mechanism is also discussed.

The ZnO microrod array was synthesized by a vapor phase transport (VPT) method. Briefly, a mixture of ZnO and graphite powders with absolute mass ratio of 1:1 was filled into a quartz boat as source materials, and the Si substrate was covered on the quartz boat, which was inserted into a horizontal tube furnace. Then the furnace was heated to 1 050 °C and maintained at this tempera-

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\*\* E-mail: lijitao8@126.com

ture. After growing for 45 min, the ZnO microrods were obtained on the Si substrate. The GO was prepared from natural graphite powder by a modified Hummers procedure<sup>[15]</sup>. Approximate 3 g graphite powder was added to 12 mL concentrated H<sub>2</sub>SO<sub>4</sub>, and then the mixture was kept at 80 °C for 5 h. After sonication at room temperature, the solution was filtered using a 200 nm porous filter to retrieve the pre-oxidized graphite powder. To exfoliate the pre-oxidized graphite powder into monolayer graphene sheets, 2 g pre-oxidized graphite powder and 15 g KMnO<sub>4</sub> were added into 120 mL H<sub>2</sub>SO<sub>4</sub> solution, and the mixture solution was stirred for 2 h, keeping the beaker in an ice-water bath to ensure the temperature remained below 10 °C. Then, 120 mL H<sub>2</sub>O<sub>2</sub> aqueous solution with weight percentage of 30% was added to the above liquid, and the mixture was stirred for 2 h at room temperature. Finally, the resulting suspension was filtered and washed with 10% HCl and distilled water in sequence. The obtained GO was dispersed in distilled water to form a stable brown solution. The graphene/ZnO microrods hybrid microstructure was produced by dipping ZnO microrods into the GO solution and dried in air.

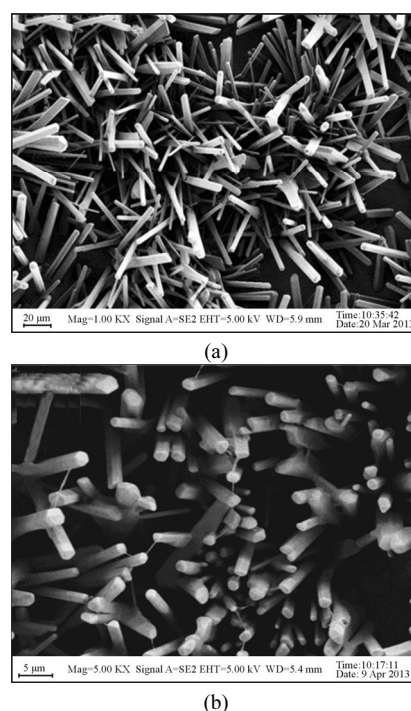
The morphology and structure of the samples were characterized by scanning electron microscope (SEM), X-ray diffraction (XRD) and Raman spectroscopy. For the PL measurements, the samples were excited by a 325 nm femtosecond (fs) pulse laser. The spectra were collected by an optical multichannel analyzer (Acton SP2500i) at room temperature.

The fabricated ZnO microrod array and the graphene/ZnO microrods hybrid microstructure were first characterized by SEM, as shown in Fig.1. From Fig.1(a), it can be seen that the as-synthesized ZnO microrods exhibit hexagonal cross-section with diameter of the microrod about several micrometers. Fig.1(b) shows the enlarged SEM image of the ZnO microrods after being dipped in the GO solution. It can be seen clearly that the ZnO microrods are coated with GO, and there are still GO trace on the microrod surface and between microrods. The existence of GO on the ZnO microrods can be further confirmed by Raman spectrum.

The XRD pattern of the as-synthesized ZnO microrods shown in Fig.2(a) reveals the high orientation of the ZnO microrods grown along the [0002] direction. The XRD pattern can be well indexed to the hexagonal ZnO, which is consistent with those in the standard diffraction pattern of wurtzite ZnO (JCPDS card No. 36-1451). The intensity of the ZnO (0002) peak is much stronger than other ZnO peaks, indicating that the (0002) plane might be the primary face of the microrods.

In order to further confirm the existence of GO in the hybrid microstructure, Raman spectrum of the graphene/ZnO microrods hybrid microstructure was collected as shown in Fig.2(b). The strong scattering peak at 438 cm<sup>-1</sup> corresponds to the typical optical modes of E<sub>2</sub>

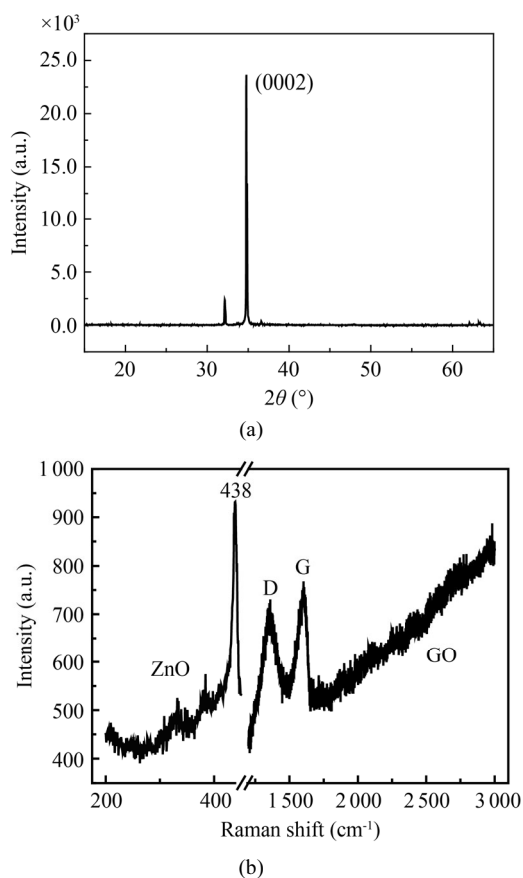
(high) of wurtzite ZnO, which is consistent with the XRD results. Besides, the Raman spectrum also shows two characteristic peaks of GO, i.e. the G band located at 1 580 cm<sup>-1</sup> and the D band located at 1 357 cm<sup>-1</sup>. Also, the intensity ratio of D mode to G mode ( $I_D/I_G$ ) is about 0.95, suggesting that more sp<sup>2</sup> domains are formed in the synthesized GO.



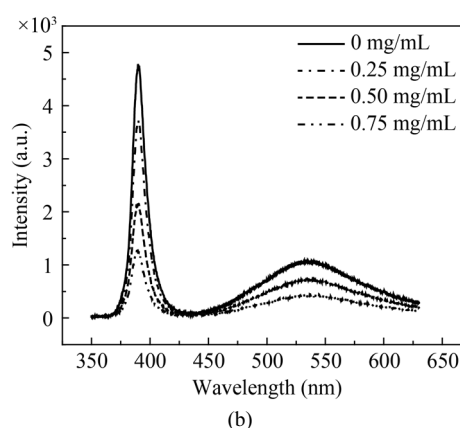
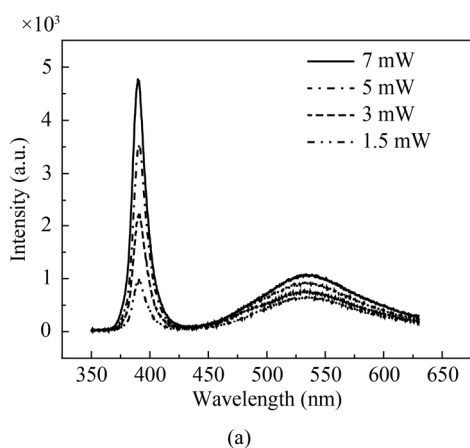
**Fig.1 SEM images of (a) ZnO microrod array and (b) graphene/ZnO microrods hybrid microstructure**

To investigate the optical properties of the ZnO microrods and the hybrid microstructure, the room temperature PL spectrum was measured under 325 nm fs laser excitation. As shown in Fig.3(a), the PL spectra of the ZnO microrod array exhibit an ultraviolet (UV) emission centered at ~391 nm and a defect-related emission centered at ~530 nm. The UV emission corresponds to the near band edge (NBE) emission of ZnO, and can be attributed to the recombination of free excitons, while the defect-related emission has been widely debated and considered usually to be corresponding to oxygen vacancies<sup>[16]</sup>. While, after the microrods were coated with GO, the fluorescence spectra describe an obvious quenching process of ZnO, as shown in Fig.3(b), which gives the PL spectra of hybrid microstructure at the same excitation power of 7 mW but with different GO concentrations from 0 mg/mL to 0.75 mg/mL. It can be seen clearly that the PL intensity of the hybrid microstructure decreases gradually as the GO concentration increases. We believe that the decreased PL intensity originates from the interaction between the ZnO microrods and the GO sheets on its surface. The interaction between the excited ZnO and the GO sheets results in an additional pathway for the disappearance of the charge carriers, and

the ability of ZnO to transfer photo-generated electrons to GO has been demonstrated previously from the quenching of ZnO emission<sup>[17]</sup>. In this present experiment, the emission quenching represents the interfacial charge-transfer processes of the excited ZnO to GO. Actually, in heterogeneous photocatalysis by semiconductor materials, such as TiO<sub>2</sub>, ZnO and ZnS, the charge recombination is often an important problem<sup>[18-20]</sup>. Thus the composition fabricated in this experiment should be possible to improve the photo-induced charge separation and then improve the photocatalysis performance.



**Fig.2 (a) XRD pattern of the ZnO microrod array and (b) Raman spectrum of the graphene/ZnO microrods hybrid microstructure**



**Fig.3 (a) Excitation power dependent PL spectra of the bare ZnO microrod array; (b) PL spectra of the graphene/ZnO microrods hybrid microstructure at excitation power of 7 mW with different GO concentrations**

In summary, hexagonal wurtzite ZnO was fabricated by a VPT method, and the graphene/ZnO microrods hybrid microstructure was obtained by a repeatable route. The PL spectra of the pure ZnO exhibit an UV emission corresponding to the NBE emission of ZnO and a defect-related emission. After the microrods were coated with GO, the PL intensity of the hybrid microstructure is quenched compared with that of the bare ZnO. The fluorescence quenching mechanism is discussed and implied an interfacial charge-transfer process of the excited ZnO to the GO, which can benefit the heterogeneous photocatalysis of semiconductor materials.

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