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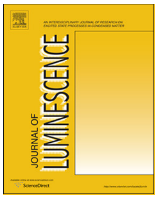

Facile synthesis and enhanced luminescence behavior of ZnO:Reduced graphene oxide(rGO) hybrid nanostructures

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ABSTRACT

The structural, electronic and luminescence behavior of ZnO nanorods and ZnO-reduced graphene oxide (ZnO:rGO) hybrid nanostructures have been studied using X-diffraction (XRD), Raman scattering, X-ray absorption near edge structure (XANES) spectroscopy and photoluminescence (PL) studies. XRD and Raman analyses reveal the formation of hybrid nanostructures composed of ZnO and rGO. The morphology and elemental composition of the grown nanostructures were investigated using FESEM and EDX measurements. The hybridization of rGO with ZnO provides an additional path way for the transfer of charge from the defect states of ZnO to rGO as evidenced from the increase in unoccupied density of states in the O-*K* edge XANES spectra and the enhanced UV, blue emissions as well as the suppressed visible emission in the PL spectra, respectively. Our systematic experimental investigations demonstrate the hybridization of rGO with ZnO is an effective approach to tailor the optical properties of ZnO and offers the prospective way for the fabrication of novel optoelectronic devices.

1. Introduction

ZnO is a promising semiconducting material because of its fascinating properties such as direct wide band gap (3.37 eV), high exciton binding energy (60 meV) at room temperature, high surface area, high mechanical strength, thermal stabilities, and high oscillator strength of excitonic transitions find applications in various technological devices including optoelectronics devices, solar cells, sensors, spintronic devices, photocatalysis, UV photodetectors and ultraviolet lasers [1–7]. The one-dimensional nanostructures such as nanorods, nanowires, nanotubes, nanoflowers, nanobelts have been attracted due to their remarkable physical and chemical properties that can be used in various electronic and optoelectronic devices [8,9]. The luminescent behavior in ultraviolet (UV) region is of great interest due to its potential applications in optical and optoelectronic devices such as UV lasers, UV photodetectos and UV light emitting diodes etc. Several synthesis routes have been employed for the growth of ZnO nanostructures including sol–gel [10], hydrothermal [11], co-precipitation [12], physical vapour deposition [5,13] techniques etc. Among the synthesis routes, hydrothermal technique is simple, low cost technique, large scale production and the shape, dimensions of ZnO nanostructures can be controlled by the growth parameters. However, the dangling bonds on the surfaces, impurities and large number of intrinsic defects in ZnO, such as Zn interstitials (Zn_i), oxygen vacancies (V_o), oxygen interstitials (O_i), and oxygen antisite (O_{Zn}) are act as electron trapping centers, which potentially quenches the luminescence efficiency in the ultraviolet region [1,14]. In order to obtain the high efficient UV emission, it is essential to enhance the radiative recombination centers and to reduce the defects in the ZnO nanostructures.

The hybrid nanostructures comprising of low-dimensional semiconducting nanostructures and 2D carbon based materials offer intriguing optoelectronic properties [15–18]. The hybridization of 2D carbon based materials with ZnO has been potentially investigated for the fabrication of supercapacitors, photocatalysis, photodetectors and solar cell applications [15,19–21]. Reduced graphene oxide (rGO), a 2D sp^2-hybridized carbon atoms composed of oxygen containing functional groups such as epoxy, hydroxyl and carboxylic groups in the basal planes as well as edges of graphene facilitate the chemical bonding between rGO and ZnO due to the plasmonic effect of graphene, similar to that of the surface plasmons induced by the metal nanoparticles [22,23]. Recently, an enhanced photoluminescence in ZnO nanostructures assisted by surface plasmon resonance of reduced graphene oxide nanoflakes have been proven an effective means to improve the efficiency of optoelectronic devices such as light emitters [16,24–27].

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Han et al. have reported the photoluminescence behavior of ZnO nanorods by capping with the reduced graphene oxide sheets and the observed enhanced UV emission is attributed to the interfacial charge transfer from ZnO nanorods to rGO [28]. Ding et al. have reported the photoluminescence behavior of ZnO nanorods coated with rGO and found that the intensity of UV emission is significantly increased [8]. However, none of the experimental reports dealing the alternation of local electronic structure of ZnO upon hybridization with the rGO sheets. Further, the correlation of local electronic structure of ZnO:rGO with its photoluminescence behavior has not been reported so far.

In the present study, we have highlighted the facile synthesis of ZnO:rGO hybrid nanostructures and investigated its electronic structural and photoluminescence behavior. Finally, a model which demonstrates the synergistic effects between ZnO and rGO via the interfacial charge transfer from the defect states that lies below the conduction band of ZnO to rGO, which could effectively stimulate the coupling of optical transition between ZnO nanorods (NRs) and the sp^2-hybridized carbon in the sp^3- matrix of graphene oxide nanoflakes is proposed.

2. Experimental details

2.1. Growth Mechanism of ZnO NRs

The growth of ZnO NRs structure by hydrothermal method consists of hydrolysis of zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) in water in the presence of hexamethylenetetramine ($C_6H_{12}N_4$) in deionized water and heating the solution constantly at 90 °C for 12 h. The set of chemical reactions (Eqs. (1)–(8)) driven the growth of ZnO NRs architecture is described below: [26]

$$C_6H_{12}N_4 + 6H_2O \leftrightarrow 6HCHO + 4NH_3 \rightarrow \quad (1)$$

$$NH_3 + H_2O \leftrightarrow NH_3.\ H_2O \rightarrow \quad (2)$$

$$NH_3.\ H_2O \leftrightarrow NH_4^+ + OH^- \rightarrow \quad (3)$$

$$Zn(NO_3)_2 \rightarrow Zn^{2+} + 2NO_3^- \rightarrow \quad (4)$$

$$Zn^{2+} + 2OH^- \leftrightarrow Zn(OH)_2 \rightarrow \quad (5)$$

$$Zn(OH)_2 \leftrightarrow ZnO + H_2O \rightarrow \quad (6)$$

$$Zn(OH)_2 + OH^- \leftrightarrow [Zn(OH)_4]^{2-} \rightarrow \quad (7)$$

$$[Zn(OH)_4]^{2-} \leftrightarrow ZnO + H_2O + OH^- \rightarrow \quad (8)$$

In the hydrothermal process, HMTA serves as a precursor for the growth of ZnO NRs and acts as a buffer layer for the release of OH^- ions. It initially hydrolyzed gradually with water and form formaldehyde and ammonia (NH_3). The NH_3 reacts with the water, producing OH^- ions and decomposition of zinc nitrate hexahydrate salts provides Zn^{2+} ions, which are required for the building blocks of ZnO NRs. The electrostatic interaction between the negatively charged, OH^- anions and positively charged, Zn^{2+}cations form an intermediate compound, $[Zn(OH)_4]^{2-}$, which play an important role in the crystal growth of ZnO by dehydration process.

2.2. Synthesis of ZnO NRs on Si substrate

ZnO NRs were synthesized by a simple hydrothermal method and then drop-casted onto the Si substrate. Before the deposition, the Si substrates of dimension of 1 cm^2 was successively rinsed with ethanol, acetone and distilled water using ultrasonic bath and then dried. Briefly, 0.2 M equimolar aqueous solution of zinc acetate dihydrate and hexamethylenetetramine solutions were admixed, and stirred at room temperature, and then subjected to the hydrothermal reaction at 90 °C for 12 h. The final product was then collected by filtration, washed with deionized water for three times and then annealed at 450 °C for 4 h to improve the crystallinity. The as-synthesized ZnO NRs powders were dispersed in ethanol with the concentration of 1 mg/ml and ultrasonicated for 30 min to produce uniform dispersion and subsequently drop-casted onto the clean Si substrate and then annealed at 500 °C in an air ambient.

2.3. Synthesis of reduced graphene oxide (rGO)

Graphene oxide was prepared by using modified Hummer's method [27]. Briefly, graphite powder (2 g) and $NaNO_3$ (2 g) was put into a solution of conc. H_2SO_4 (100 ml) in a beaker and stirred vigorously for 1 h with in an ice bath, whose temperature was maintained below 10 °C. 12 g $KMnO_4$ was gradually added to the above reaction mixture and continued the stirring for 30 mins. The ice bath was then removed and the solution was kept in continuous stirring for 3 h at room temperature. The suspension was then diluted with 250 ml of distilled water followed by addition of 30 ml of H_2O_2 (30%) to reduce the residual permanganate and manganese dioxide to colourless soluble manganese sulphate. The GO deposit was then centrifuged at 4000 rpm for 10 mins to eliminate the trace amount of un-exfoliated graphite particles and repeatedly washed with deionized water until the pH = 7 was achieved. To obtain reduced graphene oxide (rGO), the exfoliated GO solution of 1 g in 1000 ml was mixed with 1 ml of hydrazine monohydrate under constant stirring and then the mixture was heated at 150 °C for 24 h. The as-obtained black precipitate was further centrifuged at 10,000 rpm for 30 mins and the final product was collected from the centrifugation and then washed with the distilled water and dried in a hot air oven at 90 °C for 4 h.

2.4. Synthesis of ZnO:rGO hybrid nanostructure on Si substrate

ZnO NRs powder synthesized by using hydrothermal method, described in Section 2.2 and GO powder prepared from graphite powder using modified Hummer's method, described in Section 2.3 were admixed in the ethanol solution with the concentration of 1 mg/ml and 0.5 mg/ml respectively, and the admixed solution was stirred for 1 h and then drop casted onto the Si substrate. Finally, it annealed at 500 °C for 1 h in air ambient to enhance the chemical bonding of few layer reduced graphene oxide sheets with ZnO NRs.

2.5. Characterization

The structural studies of ZnO NRs and ZnO:rGO hybrid nanostructures have been performed by grazing incidence X-ray diffraction GIXRD measurements using a Inel Equinox 2000 × -ray diffractometer operating at 40 kV and a current of 30 mA with Cu K_α radiation of wavelength, 1.5406 Å. Raman analyses of the samples were carried out using WITech Alpha 300 RA spectrometer equipped with a 532 nm laser as an excitation source in the backscattering geometry. The morphology of ZnO and ZnO:rGO hybrid nanostructures were examined using field emission scanning electron microscope (FE-SEM; Carl Zeiss-Neon 40). The elemental composition of the samples was analyzed by energy-dispersive X-ray (EDX) spectroscopy using an EDX detector (INCA, Oxford). The chemical bonds and composition in the ZnO, ZnO:rGO nanostructures were investigated using a FTIR spectrometer (Bruker Tensor II) equipped with an attenuated total reflectance (ATR) diamond crystal in the range from 500 to 4000 cm^{-1} with a resolution of 4 cm^{-1}. X-ray absorption near-edge structure (XANES) measurements have been performed using SXAS beam line at Indus-2, Raja Ramanna Center for Advanced Technology, Indore. The room temperature photoluminescence (PL) measurements were recorded using WITech Alpha 300 RA spectrometer with laser excitation of 355 nm and power of 1 mW in the backscattering geometry.