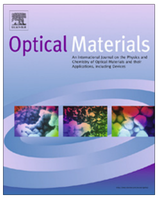
Optical Materials 36 (2014) 27–30

Contents lists available at SciVerse ScienceDirect

Optical Materials

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



Raman study of graphene/nanostructured oxides for optoelectronic applications

M. Khenfouch [a,b,*], M. Baïtoul [a,*], M. Maaza [b,c]

[a] University Sidi Mohamed Ben Abdellah, Faculty of Sciences Dhar el Mahraz, Laboratory of Solid State Physics, Research Group Polymers and Nanomaterials, P.O. Box 1796, Atlas Fez 30 000, Morocco
[b] iThemba LABS–National Research Foundation of South Africa, Old Faure Road, P.O. Box 722, Somerset West 7129, Western Cape Province, South Africa
[c] UNESCO–UNISA Africa Chair in Nanosciences–Nanotechnology, College of Graduate Studies, University of South Africa, Muckleneuk Ridge, P.O. Box 392, Pretoria, South Africa

ARTICLE INFO

Article history:
Available online 2 August 2013

Keywords:
Graphene
Raman scattering
ZnO nanorods
Fe_3O_4 nanorods
Semiconductor oxide
Optoelectronic

ABSTRACT

Recent progress on graphene/nanostructured oxide composites as advanced multifunctional nanonetwork is described, highlighting the importance of the interactions between graphene and the nanostructured materials and the beneficial role of graphene in their based composites for specific applications. In this work, we studied the interaction between graphene sheets and different nanostructured oxides for optoelectronic applications, including ZnO and Fe_3O_4 nanostructures in composites prepared via hydrothermal methods. Our results, obtained by a Raman spectroscopy with an excitation wavelength of 785 nm, show strong interactions in emerging from magnons generation, enhancing new light emission, sheets exfoliation and functionalization. These results were of particular importance in terms of understanding and knowing the origins of the emitted lights and the generated magnons as well as the structural properties of the elaborated nanocomposites. Scanning electron microscopy (SEM) and Transmission electron microscopy) TEM results were used to support and confirm Raman spectra based interpretations.

1. Introduction

Since the first report on its isolation, a single atomic plane of graphite has become an attractive area of research in physics, chemistry and materials science [1]. Graphene becomes a rising star with its exciting physical and chemical properties which make from it a promising nanostructure for future emerging technologies. In addition, this material offers a wide range of possibilities to synthesize graphene-based functional materials for various applications showing a strong ability to be a good base of multifunctional composites.

ZnO is a wide band gap semiconductor with an energy gap of 3.37 eV and a 60 meV binding energy of the free exciton, which permits excitonic emission at room temperature [2]. It has been used considerably for its catalytic, electrical, optoelectronic and photochemical properties [3,4]. Those properties become more and more important in the case of its nanostructured systems. One-dimensional ZnO nanorods have a lower threshold lasing-energy due to quantum effects. These results in a substantial density of states near band-edges and enhance radiative recombination due to carrier confinement [5], which leads to many optical and optoelectronic applications [6,7] including low-voltage and short wavelength electro-optical devices such as light emitting diodes; in addition to transparent electronics, chemical sensors and spin electronics [8,9].

Nanostructured Fe_3O_4 is the most thermodynamically stable iron oxide phase and is of particular interest because of its high resistance to corrosion, low processing cost and non-toxicity [10]. This multifunctional material has therefore been investigated extensively for a variety of applications including photo-catalysis [11], gas sensing [12], magnetic recording [13], drug delivery [14], tissue repair engineering [15], and magnetic resonance imaging [16] along with its use in lithium-ion batteries [13] spin electronic devices [17] and pigments [18]. In particular, the magnetic properties of Fe_3O_4 and its graphene based composites have attracted much interest over the past decades [19].

In this work, we studied the interactions of graphene with nanostructured oxide in our elaborated composite. ZnO/graphene composite were characterized for white light emitting diodes [20,21] and gas sensing applications [22]. Nanostructured Fe_3O_4/graphene composite was investigated by using Raman spectroscopy with an excitation wavelength of 785 nm; the powerful technique commonly used for phase identification and for degree of crystallinity analysis of this magnetic nanoparticulars. Additional

---

* Corresponding authors. Address: University Sidi Mohamed Ben Abdellah, Faculty of Sciences Dhar el Mahraz, Laboratory of Solid State Physics, Research Group Polymers and Nanomaterials, P.O. Box 1796, Atlas Fez 30 000, Morocco (M. Khenfouch). Tel.: +212 679786884.

E-mail addresses: khenfouch@yahoo.fr (M. Khenfouch), baitoul@yahoo.fr (M. Baïtoul).

0925-3467/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.optmat.2013.07.004

information about the interaction between the components is provided by TEM and SEM images analysis.

2. Experimental setup

2.1. Preparation of Graphene nanopowder

The graphite and ZnO precursors used in this work were purchased from Sigma–Aldrich. We synthesized the graphene powder using a modified Hummers method which involved graphite exfoliation in the presence of strong acids and oxidants. The obtained solution was reduced with hydrazine followed by heat treatment, and then the resultant graphene powder was dispersed in water.

2.2. Preparation of ZnO/Graphene composite

To synthesize ZnO nanorods, an equi-molar aqueous solution of 0.1 M zinc nitrate ($Zn(NO_3)_2$) and hexamethylenetetramine ($C_6H_{12}N_4$, HMT) with 0.001 M NaOH was prepared using deionised water and subsequently mixed with graphene solution. Normal glass slide substrates introduced so as to sit in the middle of the reactive solution, on the underside of its glass slide, at a tilt angle of 80° to the horizontal. This mixture was heated at a constant temperature of 90 °C in an oven for 24 h.

2.3. Preparation of Fe_3O_4/Graphene composite

To synthesize this composite, we prepared a mixture of graphene, $FeSO4{\cdot}7H_2O$ and $FeCl_3$ solution. The molar ratio $Fe^{3+}$and Fe^{2+} in was adjusted to 1.5:1. Under ultrasonic agitation, black precipitate was produced immediately by adding sodium hydroxide (NaOH). The Obtained Fe_3O_4 precipitate was aged at 65 °C for 30 min in water bath. To purify the prepared Fe_3O_4 particles, the samples were washed repeatedly with deionized water and ethanol until pH level of 7 was reached. Particles were then dried in vacuum.

3. Results and discussion

3.1. ZnO/Graphene composite

3.1.1. SEM study

The obtained ZnO nanorods on graphene nanosheets were analyzed by SEM observations in our previous work [20]. Fig. 1 shows typical SEM images of ZnO nanorods arrays grown on graphene. From the high magnification image (A), it can be seen that high-density ZnO nanorods with well-defined hexagonal facets were relatively grown vertically with a coexistence of two different sizes. The diameter distribution was determined by measuring 639 nanorods from SEM images using photoshop CS5. This figure shows nanorods with a narrow sizes distribution centered at 300 and 1236 nm. The contact between ZnO rods and agglomerated graphene sheets is shown in image (B), whereas image (C) shows defects in some rods. The low-magnification image (D) shows high-density ZnO nanorods growing over a large area on the substrate. This wafer scale growth implied that this method is applicable to mass production of aligned ZnO nanorods arrays on graphene nanosheets.

3.1.2. Raman study

Raman scattering carried out on this nanocomposite was dominated by graphene vibrational modes for the excitation wavelength of 785 nm. To enhance ZnO vibrational modes we increased the laser power. As one of the simplest uniaxial crystals, ZnO with wurtzite structure belongs to the C46vPmc space group. For the perfect ZnO crystal, only the optical phonons at C point of the Brillouin zone are involved in first order Raman scattering. Group theory predicts the existence of the following optical modes:

$$\Gamma_{opt} = A_1 + 2B_1 + E_1 + 2E_2 \tag{1}$$

Raman spectra shown in Fig. 2 depict ZnO/few layered graphene (ZnO/FLG) peaks. These bands were analyzed further in our previous study [22]. The existence of such peaks is attributed to the good cristallinity of the elaborated ZnO nanorods in the presence of graphene. The G band originates from in-plane vibration of sp^2 carbon atoms and is a doubly degenerate (TO and LO) phonon mode (E_{2g} symmetry) at the Brillouin zone center. The D band at 1308 cm^{-1} may be attributed to any defects in graphene nanosheets. The high intensity ratio of the D to G band (I_D/I_G) indicated the defects existence on the graphene surface due to interaction with ZnO [20]. The grafting of ZnO on graphene was confirmed by the appearance of a new peak situated at 1870 cm^{-1} which is attributed to C–O vibration mode. This results in new optical transitions which explain the emission of the white light from this composite that can be used as an active layer of a Light emitting diode (LED) [20,21] as well as the fast variation for resistance for gas sensing application [22].

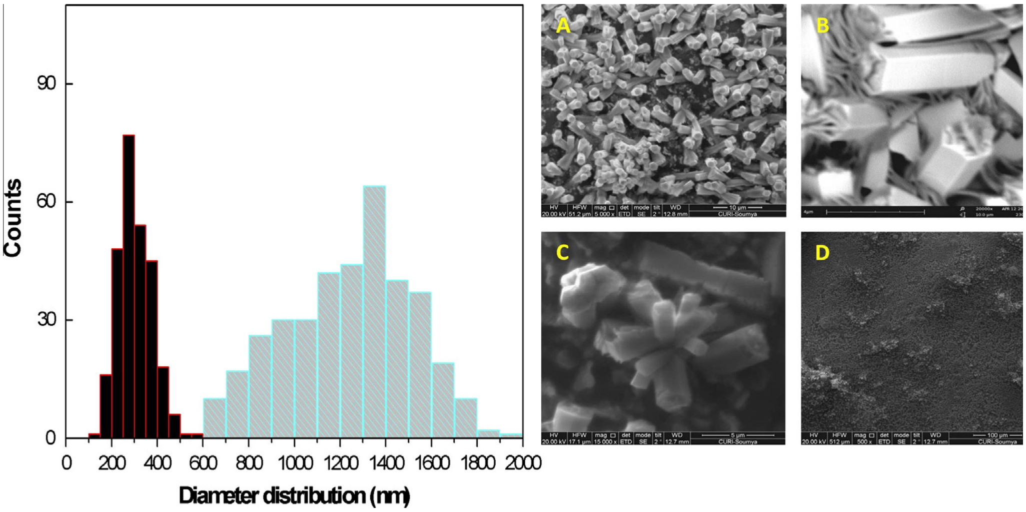


Fig. 1. SEM images and diameter distribution of FLG/ZnO show: the growth of ZnO macrorods on nanorods (A), contact of ZnO rods with agglomerated graphene sheets (B), defects on some rods (C) and the growth of FLG/ZnO in large area on a normal glass substrate.