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Preparation and characterization of Graphene/Nickel Oxide nanorods composite

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ABSTRACT

Graphene-based nanocomposites are newly emerged materials with a wide range of applications such as in supercapacitors electrode. The high conductivity and ability for passing electric current, makes Graphene an appropriate new item to be used in cells. Electroactive transition metal oxides, owing fast reversible redox pairs, are used to store electrical charge. Furthermore, the Graphene/NiO nanocomposites can be used to improve the electrochemical properties of NiO. Here we report a new and facile route for synthesizing Graphene/NiO nanorods composite (GNC). High-quality few-layer Graphene/NiO nanorod composite (GNC) is synthesized via solvothermal method. Solution phase exfoliation of graphite is investigated in N-Methyl-Pyrrolidone (NMP). The existence of few-layer graphene is confirmed by Raman spectroscopy while presence of NiO is demonstrated by UV-Vis spectroscopy (UV) and X-ray diffraction (XRD) pattern. The Field Emission Scanning Electron Microscopy (FESEM) and X-ray diffraction (XRD) pattern also provide proof of GNC on graphene. Images indicate NiO nanorods with average diameter of 35 nm and 100 nm lengths, deposited on graphene.

Keywords: *Composite; NiO; Nanorods; Graphene; Solvothermal.*

INTRODUCTION

Graphene, a single 2D carbon sheet with the same structure as the distinct layers in graphite, has become a sparkling growth star on the horizon of materials science due to its extraordinary thermal, electrical, and mechanical properties [1,2]. One possible method for bringing these superior properties of graphene to application could be combining graphene sheets in a composite material [3-5]. Some graphene/inorganic nanoparticles composites show superior properties, which can be applied in emission displays, batteries, supercapacitors, sensors and catalysis [6-13]. Different characteristics of Nano-sized substances make supercapacitors an appropriate energy storage candidate [14].

The electrodes are usually materials with high active surface, such as porous carbon and metal oxides, which have the ability to perform oxidation-reduction reactions [15]. In spite of the small capacity, carbon compositions are considered to have very high electrical conductivity [16]. Electroactive transition metal oxides, which have a very fast reversible redox pairs, are used to stockpile electrical charges. Due to its ability to pass electric current and conductivity, graphene has become a new item to use in cells [17]. Considerable efforts have been focused on the synthesis of Nanoscale NiO and its composites [15,18-20], Due to their potential applications in secondary batteries and electrochemical capacitors [21]. Graphene, which has a superior conductivity comparable to that of carbon nanotubes, can be considered as a low-cost choice to carbon nanotubes in nanocomposite synthesis [22]. Composite electrodes with transition metal oxides enhance the capacity of supercapacitors impressively. In supercapacitors the electrodes need to compose with high electrical conductive material due to the low electrical conductivity of transition metal oxides, e.g. NiO, the best candidate for this objective is Graphene [23]. A dispersion of graphene in ethanol was obtained using solvent exchange from N-Methyl-Pyrrolidone (NMP) that enables extensive application of dispersed graphene [24]. Herein, Graphene/NiO nanorods Composite (GNC) are synthesized by a facile route. First we synthesized graphene by exfoliating the graphite powder in an organic solvent, N-Methyl-Pyrrolidone (NMP), and then Graphene/NiO nanorods Composite (GNC) was synthesized by a solvothermal method.

EXPERIMENTAL

GNC is prepared by solvothermal method in following steps: (i) to produce graphene suspension, 100 mg micron-sized Graphite powder(Merck, 99.9%) was mixed in 100 ml N-Methyl-Pyrrolidone (NMP, Merck), then placed in the ultrasonic bath (40%)for 24 h, centrifuged with 8000 rpm for 15 min twice, in order to separate solid and liquid phases. Then the residual sediments of solid graphite in NMP, was removed. (ii) 0.237 g ($NiCl_2 \cdot 6H_2O$), 0.063 g ($Na_2C_2O_4$) and 0.45 g of

Poly Ethylene Glycol (P-EG) were dissolved in the mixture of 9 ml of deionized water and 15 ml of Ethylene Glycol (EG). The solution was homogenized for 115 minutes by a magnetic stirrer. The products of the two steps were heated in Teflon-coated steel autoclave (with the volume of 50 ml) at temperature of 180 °C for 12 h. (iii) the product then centrifuged and washed with the mixture of deionized water and ethanol, for several times, then dried at 60 °C in oven. (iv) finally the powder was calcinated at 400 °C in oven for 2h and GNC was prepared.

RESULTS AND DISCUSSION

To characterize the synthesized Graphene, the suspension first filtered by PVDF paper (200 nm: pore size), then the remaining graphene powder on paper was heated to evaporate NMP under the condition of 550 mmHg vacuum at 180 °C for 10 h. To confirm the existence of graphene and characterize its structure, Raman spectroscopy was used. Figure 1 shows the main graphene peaks of the product. Peaks at 1590 cm^{-1} and 2700 cm^{-1}indicate sigma bonds (Graphite like structure) and interstitial disorders in graphene sheets, respectively.
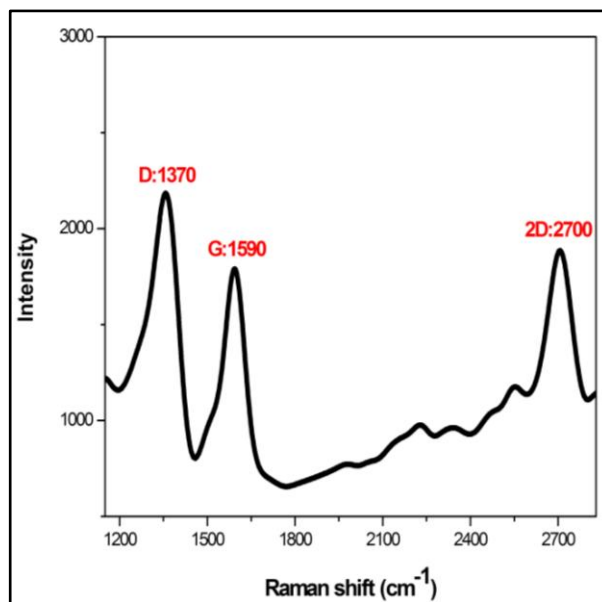

Fig. 1. Raman spectroscopy of graphene in NMP[1]

For characterizing NiO and GNC; UV, XRD and SEM was used. UV-Vis spectrum of NiO nanorods is shown in Figure 2. A strong absorption in the UV region is observed at a wavelength smaller than 475 nm (Figure 2a), which should be attributed to band gap absorption of NiO nanoparticles, assembling the NiO nanorods. The optical band gap for the absorption peak can be obtained by extrapolating the linear portion of the $[ah\acute{u}]^2$Vs($h\acute{u}$)curve to zero (Figure 2b).
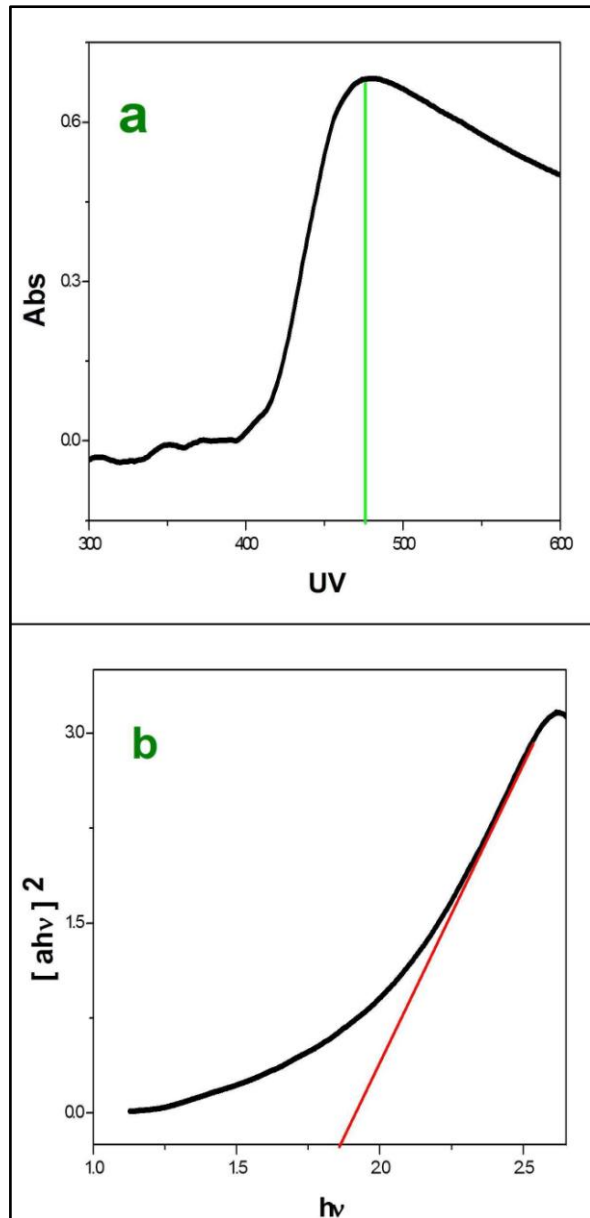

Fig. 2. UV of NiO, a: absorption, b: band gap.

The value of band gap of the NiO nanorod is about 1.85 eV, which is smaller than the value of bulk material (4.0 eV) [25]. It is well known that Nano scale sized semiconductors show a blue shift in their spectra due to the quantum confinement effects. However, the as-obtained samples have a band gap smaller than of the bulk. This effect is likely due to the chemical defects or vacancies presence in the intergranular regions, generating new energy level to reduce the band gap energy [26,27].

In Figure 3b, all diffraction peaks of as-annealed samples are perfectly consistent with NiO cubic structure and could be indexed as (111), (200), and (220) crystal planes (Card No.S NiO: 47-1049 & G: 79-1473). The average crystalline size and crystallinity of the obtained GNC and NiO nanoparticles are calculated, using Debye–Sherrer equation, to be 15.2nm & 60% and 86.4nm & 77%, respectively. GNC peaks shows less intensities in comparison with of NiO (Figure 3a). This reduction is duo to the London bands between graphene sheets and NiO nanorods. GNC peaks reduction (380,280,200) shown by XRD spectra, indicates the formation of Graphene/Nickel Oxide nanocomposite, while there is no additional peak indicating new sigma bonds, which shows graphene is bonded with NiO nanorods through London bonds. Graphene peak in GNC XRD pattern is not sharp, which could be duo to the existence of a few amount of graphene in the composite.

The morphology of the graphene/nickel oxide Nanorods composite is investigated by SEM. Figure 4 shows that the rod-like nickel oxides with diameter of about 35 nm and length up to 100 nm are obtained. The surface of these rod-like nickel oxides are not smooth, but rough, which could be a result of the degradation of organic groups and phase transformation. This image is evidence that shows the rod-like morphology is preserved in the calcination process.
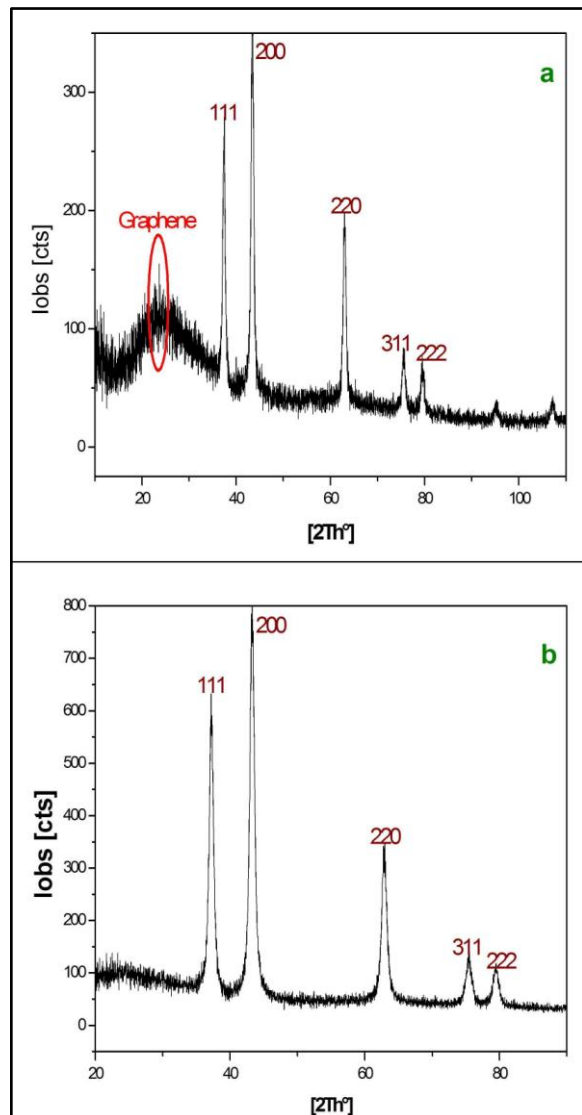
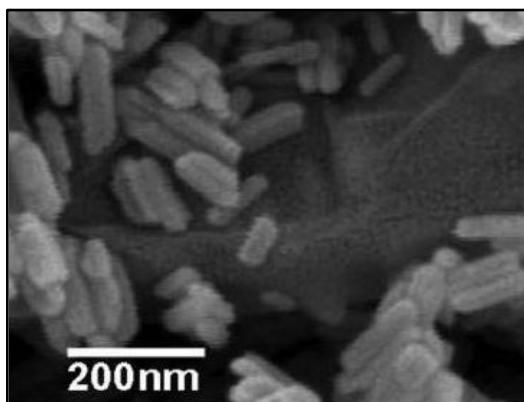**Fig. 3.** XRD spectroscopy, a: GNC & b: NiO.

Fig. 4. SEM image of GNC

CONCLUSIONS

We have used, for the first time, synthesis of GNC via solvothermal method. According to the literature [28], the peaks in Raman spectrum indicates the presence of graphene sheets. SEM image showed the formation of NiO nanorods/Graphene composite. Nano-sized rods with the length of about 100 nm were obtained. Peak intensity reduction in XRD pattern indicates the formation of NiO/Graphene nanocomposite, while there is no additional peak which indicates the existence of new sigma bonds. Nano-rod shaped NiO, duo to having a high specific surface and hence, acceleration in oxidation-reduction process, could be a more suitable candidate than the other kind of Nano shaped NiO. The optical absorption band gap of the NiO nanorod is determined to be 1.85 eV. This method is simple, fast, and low-cost for the preparing graphene/NiO Nanorods composite. The results show the importance of employing NiO nanorods in supercapacitors, with their optimal charge and decharge properties, compared with NiO nanoparticles. Therefore, this composite is quite appropriate to be used in supercapacitor electrodes as energy storage [17]. Composition of electrodes with transition element oxides lead to high increase in the capacity of supercapacitors.

ACKNOWLEDGMENTS

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