Facile synthesis of RGO/NiO composites and their excellent electromagnetic wave absorption properties

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ABSTRACT

Reduced graphene oxide/NiO composite (RGO/NiO) was synthesized by a facile pyrolyzation process. The NiO nanoparticles with a small size of about 10–50 nm are uniformly dispersed onto the thin graphene nanosheets. The as-prepared RGO/NiO composite shows excellent microwave absorbability. The obtained composite with a coating layer thickness of 3.5 mm exhibits a maximum absorption of −55.5 dB at 10.6 GHz. And in particular, the product with a coating layer thickness of only 3.0 mm possesses a bandwidth of 6.7 GHz (from frequency of 10.2 to 16.9 GHz) corresponding to reflection loss at −10 dB (90% absorption). Thus, the as-prepared RGO/NiO composite is a very promising EM wave absorbing material as lightweight and high-performance.

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1. Introduction

In recent years, a mass of severe electromagnetic (EM) radiation is generated by the increasingly using of wireless communication tools, local area networks, personal digital assistants and so on. Those radiations are highly harmful to people's living environments [1,2]. Therefore, many researchers are paying great attentions to develop high performance wave absorption materials. Besides the strong absorption characteristics, the excellent wave absorbents also require light weight, small thickness, wide absorption frequency range and so on [3,4]. According to previous studies, carbon based composite materials are good candidates for EM wave absorption materials [5,6]. Graphene, a new kind of carbon based materials, are used in many areas such as field effect transistors [7], supercapacitors [8,9], lithium ion batteries [10], chemical sensors [11] and so on. Furthermore, reduced graphene oxide (RGO) and their composites can also be used as wave absorption materials [12,13]. For examples, many researchers are devoted to prepare RGO and magnetic Fe_3O_4 composites with lightweight and

high-efficiency wave absorption performance due to the reasons of dielectric loss, magnetic loss and impedance match characteristics [14–21]. Besides, the composites of RGO incorporated with other semiconductor nanoparticles such as Ni [22], Fe [23], Co_3O_4 [24], α-Fe_2O_3 [25], hematite [26], γ-Fe_2O_3 [27], V_2O_5 [28] are also received good wave absorption properties because of the dielectric loss and impedance match. However, as far as we know, the binary composite of RGO and NiO can never be reported as wave absorbent, although it was used as supercapacitors [29], Li ion battery [30], DSSC [31] and so on.

In this paper, the binary RGO/NiO composite prepared by pyrolyzation method is reported. First, we synthesized the precursors of graphene oxide and Ni^{2+} by freeze drying method. Then, the mixtures were calcined in a tube furnace with the atmosphere of flowing argon. The obtained RGO/NiO composite displayed a greatly enhanced microwave absorption property in the range of 2–18 GHz. The maximum reflection loss of the composites can reach −55.5 dB at 10.6 GHz. And the absorption bandwidth with the reflection loss below −10 dB (90% absorption) is 6.7 GHz (from frequency of 10.2 to 16.9 GHz) with a thickness of 3.0 mm. Moreover, the addition amount of the composite into the paraffin matrix is only 8 wt%, which established a lightweight system for wave absorption materials. Thus, the as-prepared RGO/NiO composite was a candidate for lightweight and high-performance EM wave absorbing material.

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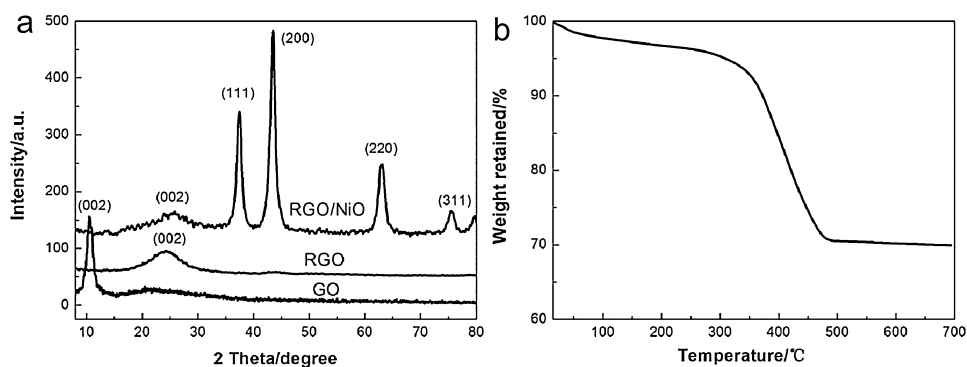anjx@163.com (A. Xie).

Fig. 1. (a) XRD patterns of GO, RGO and RGO/NiO composite, respectively. (b) TG analyze of RGO/NiO composite at a heating rate of $10\,°C\,min^{-1}$ in air.

2. Experimental

2.1. Materials

Graphite powder (325 mesh) purchased from Qingdao Huatai Lubricant Sealing S&T Co. Ltd. Concentrated sulfuric acid (H_2SO_4), hydrochloric acid (HCl), potassium permanganate ($KMnO_4$), sodium nitrate ($NaNO_3$), hydrogen peroxide (H_2O_2) were obtained from Chemical Shanghai Reagent Co. Nickel acetate ($Ni(COOH)_2\cdot4H_2O$) was purchased from Aladdin Chemical Reagent Co. All the reagents used for experiments were of analytical grade and used directly without further purification. DI water was used in all the process of aqueous solution preparations and washings.

2.2. Synthesis

Graphite oxide was synthesized from natural graphite powder using a modified Hummers' method [8,32]. To prepare suspensions of graphene oxide (GO), the graphite oxide was bath sonicated (KQ 800KDV, Kunshan, China) in water for 1 h to give a brown colloidal solution and then centrifuged (TG16-WS,changsha, China) at 4000 rpm for 20 min to remove any unexfoliated materials.

RGO/NiO composite was synthesized in a facile pyrolyzation process. In details, 0.2 mmol $Ni(COOH)_2\cdot4H_2O$ were dispersed into 25 mL 4 mg mL^{-1} GO solution with vigorous stirring. Then the mixture was sonicated for at least 1 h in order to make the Ni^{2+} fully interact with GO nanosheets. After, it was freeze dried under vacuum. The freeze dried mixture was then calcined in a tube furnace (OTF-1200X, Hefei, China) at 500 °C for 2 h with the heating and cooling rate were also 3 °C min^{-1}. During all calcination process, the atmosphere was flowing argon. The obtained product was collected and for further characterization.

2.3. Characterization

As synthesized GO, reduced graphene oxide (RGO) and RGO/NiO composite were characterized by X-ray diffraction (XRD) using a DX-2700 X-ray diffractometer equipped with Cu $K\alpha$ sealed tube (λ = 1.5406 Å). The samples were scanned in the range between 8° and 80° with a step size of 0.02°. Scanning electron microscopy (SEM) images were performed on a Hitachi S-4800 scanning electron microscope. X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB-MKII spectrometer (VG Co., U.K.) with Al Kr X-ray radiation as the X-ray source for excitation. High resolution transmission electron microscopy (HRTEM) image on Cu grid was obtained using a JEM 2100 microscope and an accelerating voltage of 100 kV. The thermogravimetric (TG) analysis of the composite was performed on a Q2000 thermogravimetric analyzer at a heating rate of 10 °C min^{-1} in air.

2.4. Electromagnetic parameters measurements

The electromagnetic parameters of RGO/NiO composite sample was measured in a VNA, AV3629D vector network analyzer in the range of 2–18 GHz after a full two-port calibration (SHORT–OPEN–LOAD–THRU). The measured sample was prepared by uniformly mixing 8 wt% of the sample with a paraffin matrix. The mixture was then pressed into toroidal shaped sample with an outer diameter of 7.00 mm and inner diameter of 3.04 mm.

3. Results and discussion

Fig. 1a shows the XRD patterns of GO, RGO, and the RGO/NiO composite. It can be seen that the feature diffraction peak of GO appears at 10.51 (0 0 2) as the AB stacking order with a layer-to-layer distance (d-spacing) of 0.849 nm [33]. And the RGO shows a very broad diffraction peak at 2θ of ca. 25.0°, which means that GO have been transformed to reduced GO [34]. Several characteristic peaks ((1 1 1), (2 0 0), (2 2 0) and (3 1 1)) can be observed for NiO (JCPDS: 65-2901) from the XRD pattern of the RGO/NiO composite, confirming the formation of NiO nanocrystals with face-centered-cubic structure [35]. Notably, a small and broadened peak for the RGO appears in the composite indicating that the as-prepared product is composed of NiO and RGO.

We use TG analysis to clarify the weight ratio of NiO nanoparticles in the as-prepared composite and the result is shown in Fig. 1b. The weight loss process can be divided into two processes. The slight weight loss below 300 °C is ascribed to the loss of absorbed water from the product. Then, a significant weight loss occurs between 300 °C and 500 °C indicating the removal of non-reduced oxygen-containing functional groups and the pyrolysis of graphene. We also draw a conclusion that the mass loading of NiO nanoparticles to the composite is about 69 wt%.

The element component of RGO/NiO composite is identified by XPS technique. Fig. 2a shows general XPS survey for RGO/NiO composite. It reveals that the composite is completely composed of Ni, O and C three elements. No other elemental signals are detected in the general XPS spectrum. The strong C 1s peak arises from the graphene in the sample. In Fig. 2b, Ni 2p3/2 at 854.2 eV and Ni 2p1/2 at 872.1 eV, typical of the Ni phase of NiO [36], the result is consistent with the XRD. Fig. 2d shows C 1s region of the pure GO, four different peaks centered at 284.8, 286.8, 287.6, and 289.4 eV are observed, corresponding to C—C in aromatic rings, C—O, C=O, and C—C=O groups, respectively. After the composite of RGO and NiO is formed, the peak intensity of C—O decreases dramatically (Fig. 2c) indicating that most of GO is reduced.

The SEM image of RGO/NiO composite is shown in Fig. 3a .Uniform distribution of the NiO nanoparticles throughout the surface of graphene nanosheets is clearly visible. This is also evident from the TEM image shown in Fig. 3c. From those pictures and the
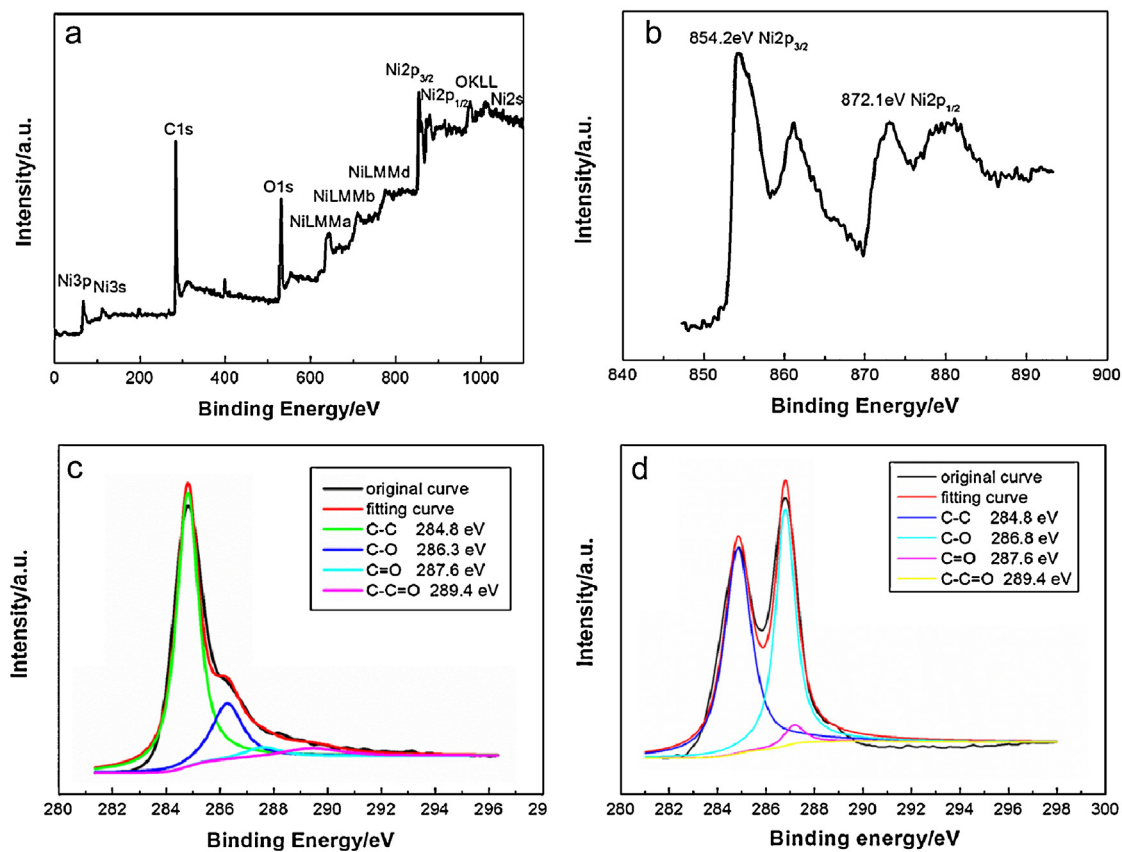
Fig. 2. (a) XPS survey, (b) Ni 2p region, (c) C 1s region of RGO/NiO composite and (d) C 1s region of GO.
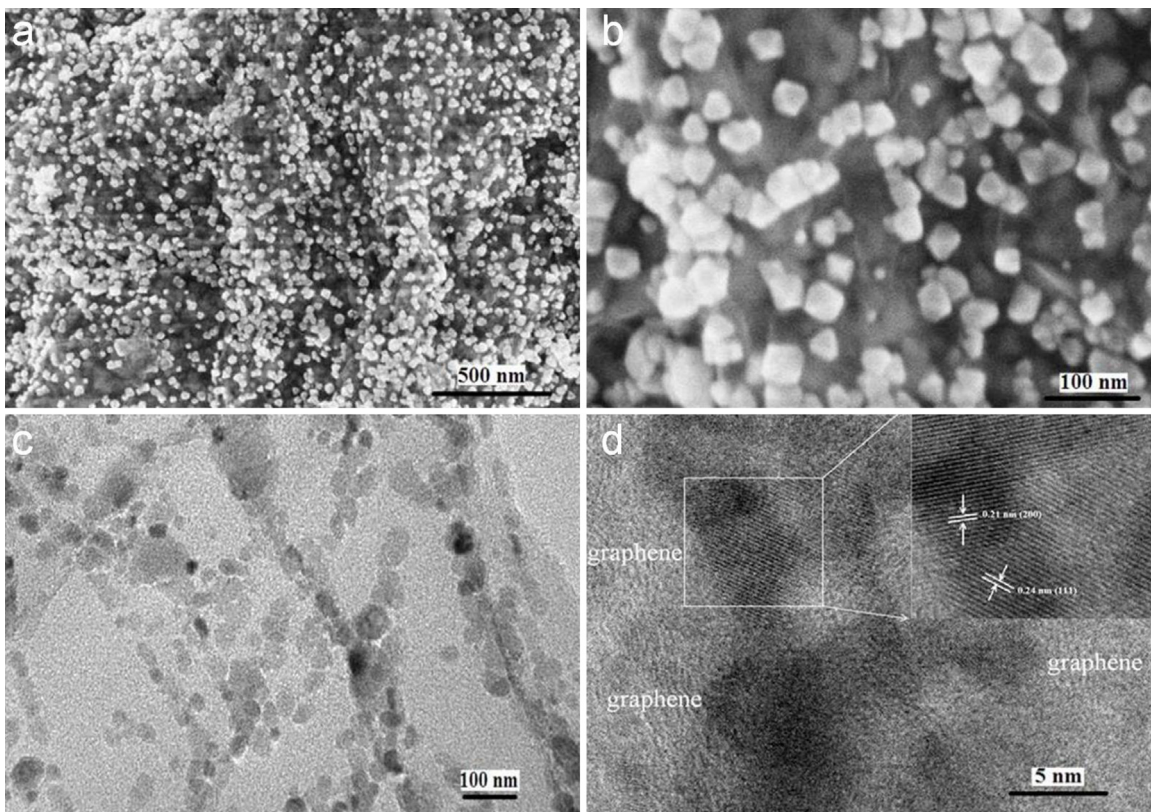

Fig. 3. (a) SEM image, (b) magnified SEM image, (c) TEM image, (d) HRTEM image of RGO/NiO composite.
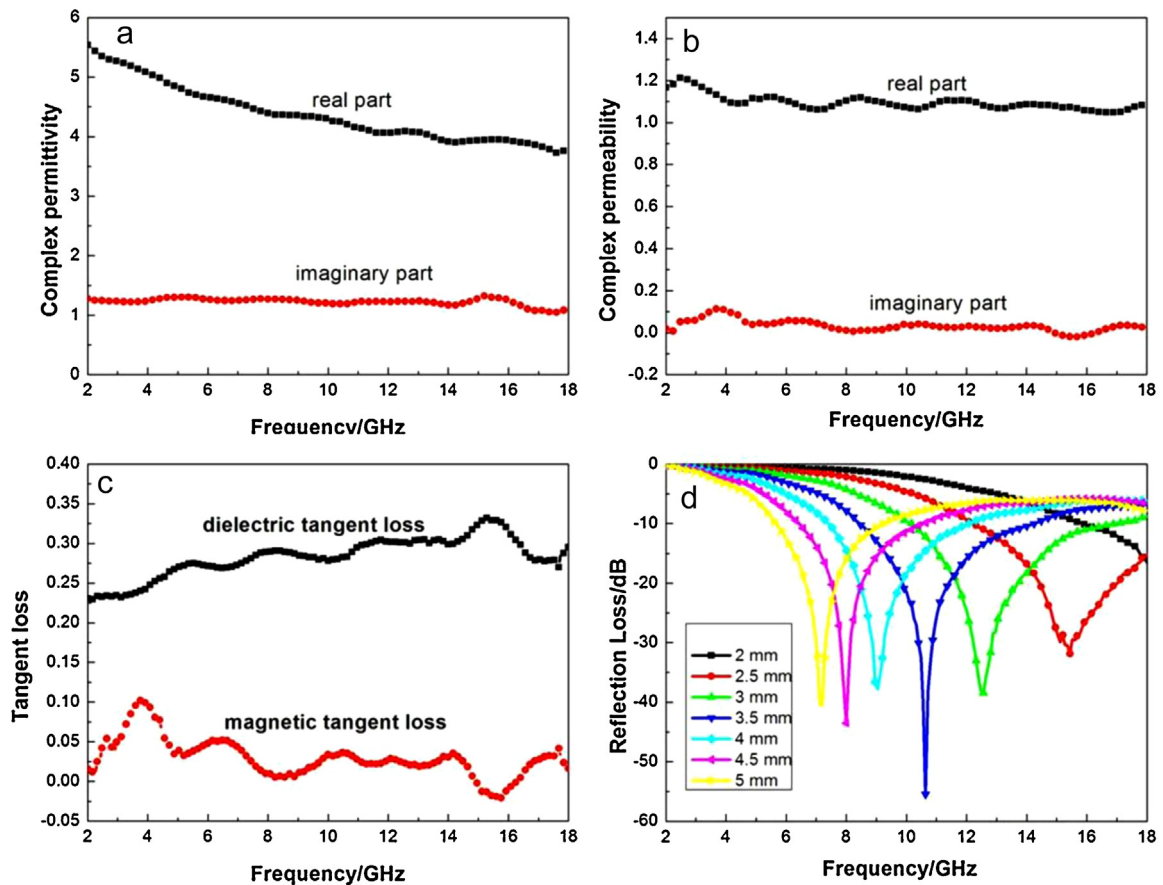
Fig. 4. (a) Frequency dependence of (a) the complex relative dielectric permittivity, (b) the complex relative magnetic permeability, (c) the loss tangent and(d) the reflection loss of RGO/NiO composite.

magnified SEM image in Fig. 3b, we can see the diameter of the NiO nanoparticles is ranged from 10 nm to 50 nm. Fig. 3d presents a HRTEM image of the RGO/NiO composite, in which the NiO nanoparticles are well crystallized. The crystal lattice fringes with d-spacing of 0.21 nm and 0.24 nm can be assigned to the (2 0 0) and (1 1 1) plane of the NiO [37], which is in accordance with the XRD results.

We investigate the electromagnetic parameters (complex permittivity and permeability) of RGO/NiO composite to reveal their microwave absorbing properties, shown in Fig. 4a–c. Fig. 4a shows the real part (ε') and imaginary part (ε'') of complex permittivity in the frequency range of 2–18 GHz. It can be found that the values of ε' and ε'' are in the range of 3.75–5.54 and 1.1–1.28, respectively. Both the ε' and ε'' values decrease with increasing frequency in 2–18 GHz, which may be related to a resonance behavior that is reported before [5,38,39]. We demonstrate the real part of permeability (μ'') and imaginary part of permeability (μ'') of the composite in the frequency range of 2–18 GHz, shown in Fig. 4b. It reveals that the values of μ' are in the range of 1–1.2 with several small fluctuations and the μ'' values are near to 0 over 2–18 GHz. The calculated dielectric tangent loss ($\tan \delta_E = \varepsilon''/\varepsilon'$) and magnetic tangent loss ($\tan \delta_M = \mu''/\mu'$) are shown in Fig. 4c. It reveals that the values of the magnetic loss are lower than those of the dielectric loss in frequencies ranging from 2 to 18 GHz, suggesting that the composite is mainly dependent on the dielectric loss. Due to the small size of NiO nanoparticles, it is very easy to cause the increase of the dipoles. Therefore, the dipole polarizations are existed in the composite, which will contribute to dielectric loss. In addition, at the interfaces of RGO and NiO would form many defects, which could serve as polarized centers. This phenomenon also lead to

dielectric loss [24]. Compared to pure RGO (Fig. S1), the composite has much lower ε' and ε'', which is very useful to impendence match theory. Because too high permittivity of absorber is harmful to the impedance match and results in strong reflection and weak absorption [25,28]. Therefore, impending match characteristic is another factor to influence the composite's wave absorption property.

To reveal the microwave absorption properties of the composites, the reflection loss (RL) values are calculated according to the transmission line theory as follows:

$$Z_{in} = Z_0 \left(\frac{\mu_r}{\varepsilon_r}\right)^{1/2} \tan h \left[j \left(\frac{2\pi f d}{c}\right) (\mu_r \varepsilon_r)^{1/2} \right] \qquad (1)$$

$$RL = 20 \log \left| \frac{(Z_{in} - Z_0)}{(Z_{in} + Z_0)} \right| \qquad (2)$$

where Z_{in} is the input impedance of the absorber, Z_0 is the intrinsic impedance of free space. μ_r and ε_r are the relative complex permeability and permittivity of the absorber medium, f is the frequency of electromagnetic wave, d is the coating thickness, c is the velocity of light. The calculated results are shown in Fig. 4d. The EM absorption properties of RGO/NiO composite is significantly enhanced. It can be clearly seen that a coating layer thickness of 3.5 mm exhibits a maximum absorption of −55.5 dB at 10.6 GHz. The bandwidth of RL values below −10 dB (90% of EM wave absorption) is 6.7 GHz (from frequency of 10.2 to 16.9 GHz). The enhanced wave absorption properties of RGO/NiO composite are contributed to the compensatory properties of graphene and small sized NiO nanoparticles. Thus, the RGO/NiO composite is a promising wave absorption material as lightweight and high performance.

4. Conclusions

In summary, a RGO/NiO composite with a prominently excellent microwave absorption properties has been successfully synthesized in a facile pyrolyzation way. The formation of small sized (10–50 nm) NiO nanoparticles in the RGO nanosheets results in greatly dielectric loss and impending match characteristic, therefore not only a larger wave absorption value (the maximum absorption value of −55.5 dB) but also a wider absorption band (6.7 GHz according to lower than −10 dB) in frequency range of 2–18 GHz have been obtained. These results show that the as-prepared RGO/NiO composite is a great potential EM wave absorbing material with lightweight and high-efficiency of practical applications.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apsusc.2014.06.172.

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