Materials Letters 129 (2014) 35–38

Contents lists available at ScienceDirect

Materials Letters

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

Synthesis and excellent microwave absorption properties of graphene/polypyrrole composites with Fe_3O_4 particles prepared via a co-precipitation method

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ARTICLE INFO

Article history:
Received 5 March 2014
Accepted 30 April 2014
Available online 9 May 2014

Keywords:
Carbon materials
Polymers
Dielectrics
Microwave absorption properties

ABSTRACT

The microwave absorption properties of the presented ternary composites are not satisfactory and the microwave absorption properties of the ternary composites composed of graphene, polypyrrole and Fe_3O_4 have never been reported. Herein, in order to expand the scope of microwave absorbers, the graphene/polypyrrole/Fe_3O_4 (GN/PPy/Fe_3O_4) composites were synthesized by a co-precipitation method. The microwave absorbability reveals that GN/PPy/Fe_3O_4 exhibits excellent microwave absorption properties and broad absorption bandwidths compared with GN, GN/PPy and GN/Fe_3O_4. The maximum reflection loss of GN/PPy/Fe_3O_4 is up to −56.9 dB at 6.6 GHz with a thickness of 5.3 mm and the absorption bandwidths exceeding −10 dB are more than 15.1 GHz with a thickness in the range of 3–7 mm. Furthermore, our strategy confirms that GN/PPy/Fe_3O_4 can be used as an attractive candidate for the new type of microwave absorbers.

1. Introduction

Microwave absorption materials have received considerable attention due to the rapid development of their applications. Excellent microwave absorption materials are required to be lightweight, with strong absorption and broad absorption bandwidths. Graphene (GN), a new carbon-based material with low density and high complex permittivity, can be used as a promising candidate for microwave absorbers. Nevertheless, GN is found to be non-magnetic; the microwave absorption properties which mostly contribute to dielectric loss and the impedance matching are out of balance [1]. One of the effective ways to solve the problem is to couple GN with magnetic constituents, such as Fe_3O_4 [2–4], Co_3O_4 [5] and $NiFe_2O_4$ [6]. Conducting polymers (CPs) with excellent physical and chemical properties can also be used as microwave absorbers [7,8]. Over the past decade, considerable attention has been paid to the microwave absorption properties of CPs [9–11]. Recently, the ternary composites of EG/PANI/CF [12], graphene/Fe_3O_4/PANI [13,14] and RGO-PPy-Co_3O_4 [15] have been studied due to their multi-functional electrical properties, but the microwave absorption properties and the absorption bandwidths are not satisfactory. To the best of our knowledge, the microwave absorption properties of GN/PPy/Fe_3O_4 have never been reported.

In this paper, the ternary composites of GN/PPy/Fe_3O_4 have been synthesized and the structure has been investigated. The maximum reflection loss of GN/PPy/Fe_3O_4 is up to −56.9 dB at 6.6 GHz with a thickness of 5.3 mm and the absorption bandwidths exceeding −10 dB are range from 2.9 to 18 GHz when the thicknesses vary from 3 to 7 mm.

2. Experimental

Graphene oxide (GO) was synthesized by the Hummers method [16]. The ternary composites of GN/PPy/Fe_3O_4 were prepared via a two-step method as follows: firstly, pyrrole monomer (0.1 mL) with H_2SO_4 (2 mL) and $(NH_4)_2S_2O_8$ (APS, 0.95 g) was dissolved in GO solution (50 mL) by sonication treatment, then the solution was cooled down to 0 °C and stirred for 12 h. The precipitates were washed with distilled water. Secondly, a solution of $FeCl_2 \cdot 4H_2O$ (0.2 g) and $FeCl_3 \cdot 6H_2O$ (0.27 g) was added to the precipitates, then 1 M NaOH solution was added to maintain the pH at 11. After 2 h, hydrazine (0.5 mL) was added and the temperature was raised to 90 °C with further stirring for 5 h. The resulting solution was cooled to room temperature, washed with distilled water several times and dried at 60 °C for 12 h.

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http://dx.doi.org/10.1016/j.matlet.2014.04.194
0167-577X/

XRD was identified by X-ray diffraction (D/max 2550 V, Cu Kα radiation). The chemical states were investigated by X-ray photoelectron spectroscopy (XPS, PHI 5300X). The morphology was characterized by a field emission transmission electron microscope (FETEM: Tecnai F30 G^2). The microwave parameters were measured by HP8753D vector network analyzer.

3. Results and discussion

The XRD pattern of GN/PPy/Fe_3O_4 is shown in Fig. 1a. It can be observed that the diffraction peaks at 2θ=30.2°, 35.6°, 43.3°, 53.6°, 57.3° and 62.9° can be assigned to the (220), (311), (400), (422), (511) and (440) planes of Fe_3O_4, which is similar to the standard pattern of Fe_3O_4 (JCPDS Card no. 19-0629). No obvious diffraction peaks for GN and PPy can be observe, which may be due to the relatively low diffraction intensity. The relatively weak intensity demonstrates that Fe_3O_4 particles are small. XPS spectra (Fig. 1b) indicate the presence of C, N, O and Fe elements in GN/PPy/Fe_3O_4. In Fig. 1c, N 1s XPS spectra of GN/PPy/Fe_3O_4 can be deconvoluted into three peaks, the peaks at 398.2, 399.7 and 401.3 eV are attributed to the quinoid imine (=N–), the benzenoid amine (–NH–) and the cationic nitrogen atoms ($-N^+-$), respectively, indicating the presence of PPy [17]. As shown in Fig. 1d, the core level binding energy at 711.1 and 724.5 eV are the characteristic doublets of Fe $2p_{3/2}$ and Fe $2p_{1/2}$, respectively. These results indicate the assembly of Fe_3O_4 particles on GN/PPy.

The morphology of the products is shown in Fig. 2. In Fig. 2a, it is clear that bare GN sheets are transparent and appear as silky waves, except for some wrinkles at the edges. After decoration with PPy, the surface of GN becomes rough and many PPy wrinkles cover GN sheets uniformly, as indicated by the red arrows in Fig. 2b. Because PPy is an amorphous material, the SAED pattern (inset in Fig. 2b) indicates that GN/PPy has no obvious crystalline character. As shown in Fig. 2c, large-scale Fe_3O_4 particles with a relatively uniform size are anchored on the surface of GN/PPy via a simple co-precipitation route. Furthermore, there are no large areas of GN/PPy that are not decorated with Fe_3O_4 particles. The considerably sharp ring-like feature of the corresponding SAED pattern (inset in Fig. 2c) indicates the crystalline nature of Fe_3O_4. As Fig. 2d shows, except many PPy wrinkles, Fe_3O_4 particles can also be seen in an orderly, dense and even manner. In order to verify the crystalline structure of Fe_3O_4 particles, HRTEM image of GN/PPy/Fe_3O_4 is presented in Fig. 2e. It is clear that the lattice fringe space of Fe_3O_4 particles is 0.253 nm (inset in Fig. 2e), corresponding to the (311) plane of Fe_3O_4, in agreement with the XRD analysis. The elemental maps of a single piece in Fig. 2f demonstrate a very homogeneous C, N and Fe elements distribution in GN/PPy/Fe_3O_4, which is consistent with the results of XPS.

In order to investigate that GN/PPy/Fe_3O_4 has excellent microwave absorption properties, the reflection loss (R_L) of GN, GN/PPy, GN/Fe_3O_4 and GN/PPy/Fe_3O_4 is calculated as follows:

$$R_L(\mathrm{dB}) = 20 \log \left| \frac{Z_{in}-1}{Z_{in}+1} \right| \quad (1)$$

$$Z_{in} = \sqrt{\mu_r/\varepsilon_r}\, \tanh\left[j(2\pi f d/c)\sqrt{\varepsilon_r \mu_r}\right] \quad (2)$$

where Z_{in} is the input impedance of the absorber, c is the velocity of electromagnetic waves in free space, f is the frequency and d is the layer thickness. In Fig. 3a, it can be observed that the maximum R_L of GN is only −8.9 dB at 9.5 GHz when the thickness is 2 mm. For GN/PPy in Fig. 3b, the maximum R_L values are less than −6.1 dB when the thickness ranges from 2 to 7 mm. As shown in Fig. 3c, the maximum R_L of GN/Fe_3O_4 is −19.1 dB at 13.7 GHz and the maximum R_L values obviously shift to the lower frequency ranges as the thickness of the absorbers increases. For GN/PPy/Fe_3O_4 in Fig. 3d, it is noted that there is one sharp and strong wave absorption peak at 15.6 GHz, the maximum R_L is up to

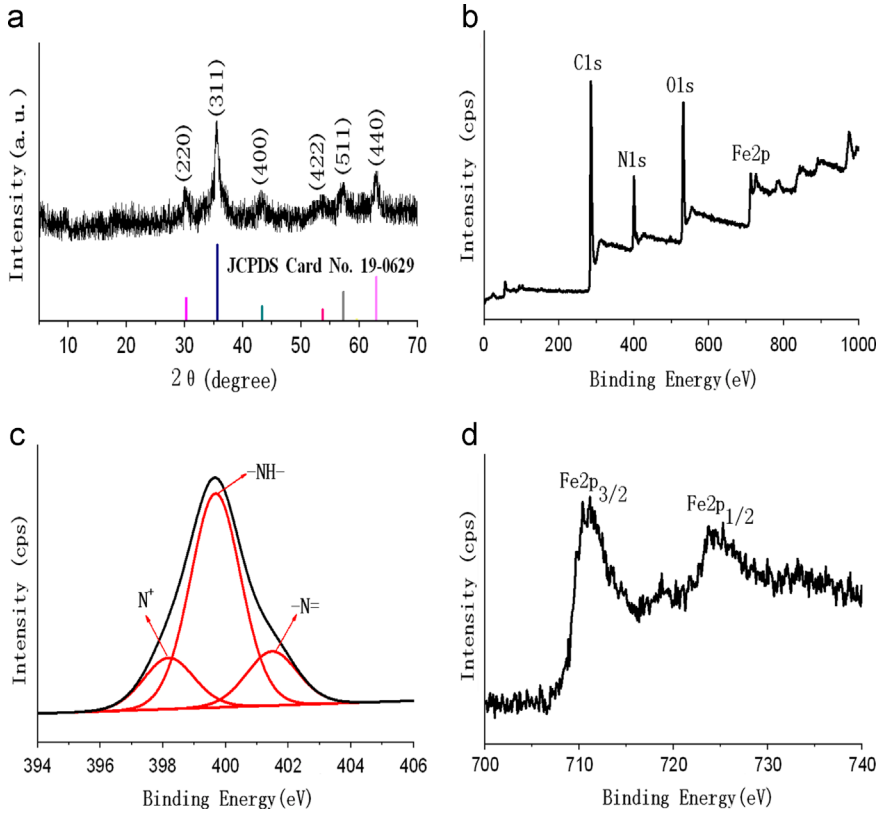

Fig. 1. XRD pattern (a), XPS spectrum (b), N 1s (c) and Fe 2p (d) spectra of GN/PPy/Fe_3O_4.