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Hierarchical composites of polypyrrole/graphene oxide synthesized by *in situ* intercalation polymerization for high efficiency and broadband responses of electromagnetic absorption

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ABSTRACT

Hierarchical graphene oxide/polypyrrole composites were fabricated by initiating an *in situ* intercalation polymerization of pyrrole into the interlayers of graphite oxide. It was interesting that a chemical hybridizing group of HN—CO could be verified inside the graphene oxide layers during the exfoliation of graphite oxide, resulting in a new kind of graphene oxide based composites with highly crumpled structures. This intercalation compounding technique made the composite display much stronger polarization, leading to notable enhancement in electromagnetic loss with broadband responses. As an example of the 2.96 mm thickness sample, the rock-bottom on the reflection loss curve was low to −58.1 dB at 12.4 GHz and the bandwidth below −10.0 dB could be as wide as 6.2 GHz, which was remarkable superior to those of the pure graphite oxide as well as other hybrids of graphene oxide that had ever been reported. The improvement in absorbing capacity arose from the unsymmetrical groups generated from the chemical hybridization, which could lead to multi-scaled polarization relaxations. In addition, the three-dimensional intercalated network would lead to synergistically benefit of impedance matching and interfacial relaxation loss. These results provided a new strategy to prepare graphene-like composites for functional design such as high-efficient microwave absorbent.

1. Introduction

Recently, increasing efforts have been made for the design of microwave absorbing materials due to the growing problem of electromagnetic (EM) interference and pollution in personal digital assistants, industry and military affairs [1–5]. So far, various nanostructures have been developed for microwave absorption, such as carbon nanotubes (CNTs) [6], graphene [7], conducting polymers [8–10] and Fe_3O_4 contained nanomaterials [11]. One of the typical profiles to improve the microwave absorption was to introduce abundant and multi-scaled interfaces leading to more polarization relaxation [12]. The nano-effect and special nanostructures could also make a significant improvement in microwave absorption, bringing about unique EM loss mechanism [13].

Graphene oxide (GO), as a derivative of graphene, exhibited various excellent performance, such as unique two-dimensional structure, low density and high specific surface area [14]. More importantly, the surface of GO was rich in various functional groups, which could which could make GO be well dispersed in water and easily react with other materials [15]. All these advantages arose GO a good choice for the design of lightweight microwave absorbing materials. Recently, it has been found that the crumpling of graphene could be well controlled and significantly affect the optical [16] and energy storage [17] properties. Accordingly, crumpling polarization units of graphene were also considered to be beneficial to the improvement of EM properties due to the polarization relaxation effect. Wang et al. studied the microwave absorption of chemical reduction of GO (rGO) [18]. It had been found that rGO presented improved EM loss compared to that of graphite due to the special oxide-containing groups and defects

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that would cause further polarization relaxation. However, the minimum reflection loss (RL) of rGO was only −6.9 dB at 7 GHz. Great efforts were still needed to improve the microwave absorption of GO.

One of the effective methods was to combine GO with conducting polymers, which might bring about extra interfaces or hybrid interactions and take advantages of their excellent structural and functional properties. Wu et al. [19] developed a three-dimensional (3D) rGO/poly (3,4-ethylenedioxythiophene) architecture. The EM absorption bandwidth of the hybrid (below −10 dB) could reach 5 GHz. They also put forward a two-step method preparing rGO/polypyrrole (PPy) aerogels with EM absorption bandwidth of 6.76 GHz [10]. However, among these methods, the synthesize process were all relative complex. Although the EM loss of composites could be further enhanced by adding magnetic nanoparticles due to dielectric/magnetic matching with multiple losses [20,21], the introduction of magnetic nanoparticles more or less limited the practical applications of the composites. As far as is known, few work has involved with the microwave absorption of conducting polymer intercalated into graphene oxide, which might introduce more intercalated hybrid groups and wrinkles.

Herein, Graphite oxide (GtO), which presented an even larger interlayer spacing, was chosen to be intercalated by PPy. Highly crumpled structure of GO hybrid has been achieved by a relative simple intercalation polymerization of pyrrole. More importantly, the composites exhibited broadband response and multi-scaled polarization relaxations, leading to an effective improvement in EM loss. The PPy/GO composites showed an optimal RL value of −58.1 dB (12.4 GHz) and the absorption bandwidth (90% absorption) could be up to 6.2 GHz under a thickness of 2.96 mm.

2. Experimental

2.1. Materials

Natural graphite (2.6 μm) was purchased from Aladdin Industrial Inc. (China). Pyrrole (Py, Kelong Chemical, China) was distilled under reduced pressure and stored below 0 °C. Other chemicals, such as ammonium peroxydisulfate (APS, $(NH_4)_2S_2O_8$), $NaNO_3$, H_2SO_4, $KMnO_4$, H_2O_2 (30% solutions), $Na_2S_2O_2 \cdot H_2O_2$, NaOH, 36% hydrochloric acid (HCl) were analytical grade, and were used as received without further purification. The graphite oxide (GtO) was obtained using an improved Hummers' method [14]. All experiments were carried out using deionized water.

2.2. Preparation of PPy/GO and PPy/rGO

The polypyrrole/graphene oxide composite (PPy/GO) was synthesized using an in-situ intercalation polymerization of Py in-site the GtO according to our previous work [20,21]. Thus, 2 mmol of Py (0.2 ml) and 20 ml 1 N HCl aqueous solution was mixed and stirred for 30 min under 0–5 °C. Then 1 wt % GtO to Py was added into the above cooled solution. After mechanical stirring (300 rpm) for 4 h and mild sonication (40 KHz, ultrasonic bath) for 1 h under ice bath, 1.6 mmol of APS dissolved in 10 ml 1 N HCl aqueous solution was then slowly added into the above cooled solution with a slow stirring. The mixture was kept for polymerization at 0–5 °C for 16 h. The precipitate was washed with deionized water and ethanol for three times, and was dried in a freeze-drying system. The product was denoted as PPy/GO.

Reduction process was carried out for the preparation of PPy/rGO. 10 ml $Na_2S_2O_2 \cdot H_2O_2$ (12.5 mg/L) and 40 ml NaOH (50 mg/L) solutions were added into the resulting PPy/GO aqueous solution (400 mg/L). After mechanical stirring (300 rpm) for 1 h under 60 °C. The product was washed with deionized water and ethanol for three times, and was dried in a freeze-drying system. Then a 24 h redope process using HCl solutions was carried out. The final product was denoted as PPy/rGO.

2.3. Characterizations

The morphologies were observed on a field emission scanning electron microscopy (FE-SEM, JEOL, JSM-7001F) and a transmission electron microscopy (TEM, JEOL, JEM-2100F). X-ray diffraction (XRD) analyses were carried out on a Philips X'Pert PRO X-ray diffractometer with a CuKα radiation. Fourier transform infrared (FTIR) spectra with a resolution of 2 cm^{-1} were recorded on a Nicolet 6700 spectrometer (Thermo Fisher Scientific, US). The Raman spectra for the samples were obtained on a Laser Raman spectroscopy (InVia, RENISHAW) using a 514 nm argon ion laser. X-ray photoelectron spectroscopy (XPS, VG Microtech, ESCA 2000) analysis was used to measure the chemical composition of the samples. The complex permeability and permittivity were measured on a vector network analyzer (AV3618, CETC, China) in the frequency of 2–18 GHz. The samples were mixed with wax and prepared as the toroidal shape with an outer diameter of 7.0 mm, an inner diameter of 3.04 mm and a thickness of 3.0 mm. The mass ratios of the samples to wax were set to be 3:7.

3. Results and discussion

3.1. Morphology and XRD study of PPy intercalated GO composites

The morphologies of GtO, PPy/GO and PPy/rGO were characterized by FE-SEM (See Supplementary data, Fig. S1) and FE-TEM. As shown in Fig. 1(a)–(c) and Fig. S1, for PPy/GO and PPy/rGO, sandwich like PPy/graphene composites with highly crumpled and intercalated structures were formed after the intercalation compounding. These 3D highly crumpled structures were actually unique from both our previous work [22,23] and others work [19–21,24] on graphene/polymer hybrids, which might be due to the interlayer chain movement of PPy and the hybrid interactions between PPy and GO. Comparisons of the HR-TEM images of PPy/GO and PPy/rGO were given in Fig. 1(d) and (e). It was obvious that after reduction, the lattice structure of GO became more distorted for PPy/rGO compared with that of PPy/GO. The XRD pattern of GtO was illustrated in Fig. 1(f). The sharp characteristic peak for the (001) plane of GtO could be observed at $2\theta = 10°$, indicating the d-spacing of 0.878 nm [24]. However, the relative intensity of this peak for PPy/GO sharply decreased and a new broad peak appeared at $2\theta = 23.5°$, which further depicted the separation of the GtO layers into few-layered GO [25]. For PPy/rGO, only one broad peak at $2\theta = 25°$ could be observed, which illustrated further disorganization in the composites. This phenomenon agreed well with the HR-TEM results.

3.2. Structural analysis of PPy intercalated GO composites

In order to have a deeply understand of the unique intercalated structure of sandwich like PPy/graphene composites, detailed structural analysis were carried out. Evidence for the structural differences among these four samples were given in Fig. 2. For GtO (shown in Fig. 2(a)), the vibrational bands at about 1730, 1630, 1059 cm^{-1} were due to the C═O, C═C and C─O stretching vibrations in GtO, respectively [26]. However, the vibrational bands at 1730 cm^{-1} disappeared in the spectrum of PPy/GO. What was more, in the spectrum of PPy/GO, the vibrational band at about 1553 cm^{-1} attributed to C─C stretching vibrations on pyrrole rings exhibited 12 cm^{-1} red shifts to 1541 cm^{-1} and the band at about 1193 cm^{-1}