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Synthesis of flake shaped carbonyl iron/reduced graphene oxide/polyvinyl pyrrolidone ternary nanocomposites and their microwave absorbing properties

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Ternary composites of flake shaped carbonyl iron/reduced graphene oxide/polyvinyl pyrrolidone (CI/rGO/PVP) were synthesized via the assembly of positively charged CI and negatively charged graphene oxide (GO) with subsequent chemical reduction and PVP nanoparticles decoration. The preparation of such ternary composites was confirmed by various characterization methods including ξ-potential, scanning electron microscope (SEM), transmission electron microscope (TEM), energy dispersive X-ray spectrometer (EDS), RAMAN scattering spectroscopy, and X-ray diffraction (XRD). The influence of PVP concentration on the morphology and microwave absorbing property of CI/rGO/PVP composites was studied systematically. The hysteresis loops of pristine flake shaped CI, binary intermediate products and ternary final composites were measured by vibrating sample magnetometer (VSM) to illustrate their statics magnetism characteristics. The microwave absorbing properties of nanocomposites were calculated based on the analysis of electromagnetic parameters measured by vector network analyzer (VNA). According to the relative complex permittivity and relative permeability, dielectric loss of the ternary composites is mainly attributed to the orientational and interfacial polarization, while magnetic loss is prominently ascribed to eddy current loss, natural resonance, exchange resonance and hysteresis loss. The reflection loss (RL) calculation based on transmission line theories demonstrates that as-synthesized composites possess excellent microwave absorbing properties and the product with moderate PVP concentration shows an ultra-wide low reflection (RL < −10 dB) band from 4.2 to 18 GHz with a coating thickness of 2.5 mm. The synergetic effect between dielectric and magnetic constituents with novel ternary nanostructure leads to their enhanced microwave absorbing properties. Furthermore, the addition of rGO with much lower density than CI reduces the density of composites, which makes the CI/rGO/PVP ternary composites a very promising material in microwave absorbing application.

1. Introduction

With the growing of electromagnetic applications such as wireless communication, integrated electronic devices and military equipments, intensive attentions have been drawn to topics like preventing electromagnetic pollution, reducing electromagnetic interference and enhancing military camouflage [1–3], *etc.* Microwave absorbing materials (MAMs) can solve these problems by attenuating electromagnetic waves through energy conversion or interference. To date, magnetic materials based MAMs have been widely investigated, including Ni [4], Co [5], cobalt-zinc ferrites [6], barium hexagonal ferrites [7,8], Fe_3O_4 [9], carbonyl iron (CI) [10]. Among these materials, CI is a highly desirable magnetic absorbing material due to its strong magnetic loss originating from magnetic domain resonance, natural resonance, eddy current loss and magnetic hysteresis loss. More importantly, its magnetic properties can be tuned by morphology, shape and size. Recent research [11] has showed that flake shaped CI creates planar anisotropy which significantly improves the Snoek's limit, which leads to the increase

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of permeability and resonance frequency at the same time [12]. In addition, such flake morphology can avoid skin effect at high frequency [13]. Thus, flake shaped CI is believed to be a better candidate for the MAM than conventional CI.

Although magnetic based MAMs have many advantages for potential applications in microwave absorbing, there still are numerous significant limitations. Firstly, pure magnetic materials show predominantly magnetic loss and very low dielectric loss. Secondly, the complex permeability and complex permittivity of magnetic materials are out of balance, which results in an impedance mismatch. These two limitations of magnetic materials hamper the further improvement of their microwave absorbing properties. Moreover, traditional magnetic materials always possess high density, which heavily hinder their use in practical application. Coupling magnetic materials with lighter dielectric constituent is one of the most effective methods to conquer these limits. Thereby, a large amount of effort has been devoted in fabricating novel synergistic composites to try to obtain MAMs with strong absorption capability, wide operating frequency regime, low thickness and light weight [2,9,14–18].

Graphene, a two-dimensional one-atom-thick planar sheet of sp^2 bonded carbon atoms [19], has a series of prominent intrinsic chemical and physical features [20], which gives it a promising prospect in MAMs [21]. However, the lack of surface functionalities and excessive high conductivity [22] reduce its efficacy. In comparison, tunable conductivity, residual defects and organic groups [23] makes it convenient to manipulate the permittivity of chemically reduced graphene oxide (rGO). Together with CI, rGO can be used to construct complementary dielectric/magnetic microwave absorbing composites. rGO has been reported to be produced in bulk through a chemical oxidation and reduction process using graphite as a raw material [24,25]. Furthermore, the assembly of CI with rGO can decrease the material's density by partially replacing heavy metal carbonyl with much lighter carbon based nanosheets.

It is well-known that Polyvinyl pyrrolidone (PVP) possess a well-defined structure with *N*-vinylpyrrolidone monomers connected as a long chain is water-soluble and nontoxic [26]. In recent literature, rGO modified by PVP has been widely studied in electrode modification [27,28] and electrochemical sensing [29]. From the perspective of microwave absorbing property, grafting of nano-scaled PVP particles on rGO surface can introduce interfacial polarization and moderate the conductivity of rGO sheet, which enhances the capability of electromagnetic attenuation and improves the impedance match.

Till now, to the best of our knowledge, there is few report about the carbonyl iron/reduced graphene oxide/polyvinyl pyrrolidone (CI/rGO/PVP) composites for microwave absorbing application. In this work, we proposed a facile way to synthesize ternary composites of CI/rGO/PVP, which possess a novel configuration: flake shaped CI particles act as magnetic core that are assembled with wrinkled rGO layer, which is decorated by PVP nanoparticles. The fabrication procedure of such ternary composites is shown in Fig. 1, which can be divided into following steps: (1) activation of flake shaped CI particles utilizing *para*-aminobenzoic acid (PABA), (2) assembly of activated CI with graphene oxide (GO) through attractive electronic force, (3) simultaneous chemical reduction and PVP grafting with assistant of L-ascorbic acid (L-AA) [30]. The microwave absorbing mechanism of as-prepared ternary composites is also depicted in Fig. 1.

2. Experimental

2.1. Materials

Graphite powders (average diameter of 45 μm) were purchased from Macklin. PVP (K30), L-AA, PABA, Methanol, $NaNO_3$, H_2SO_4 (98%), $KMnO_4$, H_2O_2 (3%), HCl (35%) were all obtained from Sinopharm Chemical Reagent Co. Ltd. (China). Flake shaped CI powders were provided by Nanjing University (China), which were fabricated by mechanical milling method. All the chemical reagents were analytical grade and used directly without further purification. Deionized water was used for all experiments.

2.2. Preparation

2.2.1. Activation of flake shaped CI

Flake shaped CI powders (10 g) and PABA (2 g) were added in methanol (100 ml), followed by 1 h sonication (KQ-300, Kunshan, China) and mechanical stirring at 200 rpm, simultaneously. Then, excess PABA was removed by washing with methanol and water in turn.

2.2.2. Preparation of GO dispersion

GO dispersion was prepared using modified Hummer's method [24] from graphite powder. The detailed description is in Supporting Information (SI 1).

2.2.3. Assembly of CI with GO

The activated flake shaped CI powder (10 g) and water (100 ml) were added into a 250 ml beaker and sonicated for 1 h in a sonication bath. GO dispersion (10 ml) with the concentration of 4 mg/ml was dropwise added into the mixture under simultaneous sonication and constant mechanical stirring at 200 rpm for 1 h. The excess GO was removed by centrifugation at 1000 rpm for 25 min. The precipitation at the bottom of centrifuge tubes was collected and labeled as carbonyl iron/graphene oxide (CI/GO) and re-dispersed in 100 ml of water via sonication for further use.

2.2.4. Reduction of GO layers and PVP grafting

L-AA solution (10 ml) with the concentration of 8 mg/ml and PVP solution (10 ml) with different concentrations were added into as-prepared mixture. According to the concentration of PVP solution, the final products were named as carbonyl iron/reduced graphene oxide (CI/rGO, 0 mg/ml), P_1 (2 mg/ml), P_2 (4 mg/ml), P_3 (8 mg/ml) respectively. All the mixtures were sonicated for 10 min at room temperature, and heated up subsequently to 80 °C in water bath for 4 h. After that, magnetic decantation was used to collect the magnetic precipitates from the obtained black dispersion, which was dried in a vacuum oven at 40 °C for 24 h.

2.3. Characterization

ξ-potential of CI, activated CI, GO, CI/GO, CI/rGO, P_1, P_2, P_3 was measured on a Zetasizer (Nano-ZS90, Malvern). The chemical composition of fabricated materials was analyzed by field emission scanning electron microscopy (FE-SEM, Ultra55, Carl Zeiss) equipped with energy dispersive spectrometer (EDS, X-MAX 50, Oxford Instrument). The morphological study of CI, GO, CI/GO, CI/rGO, P_1, P_2, P_3 was performed on scanning electron microscope (SEM, FEI-XL30 FEG) and transmission electron microscope (TEM, FEI-G2 20). RAMAN scattering spectroscopy was used to study the transition between GO and rGO on a micro-raman spectroscope (XploRA, Horiba JobinYvon) equipped with a 532 nm laser beam. X-ray diffraction (XRD) patterns were measured using Xradiation (D8A Advance, BRUKER). Magnetism measurement was performed on vibrating sample magnetometer (VSM, MPMS (SQUID, Quantum Design) at 300 K. Microwave absorption properties were investigated by measuring the electromagnetic parameters over 2–18 GHz using a vector network analyzer (VNA, Agilent N5242A). The samples used for electromagnetic measurements were