



# A new method for an efficient porous carbon/Fe<sub>3</sub>O<sub>4</sub> composite based electromagnetic wave absorber derived from a specially designed polyimide

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## ABSTRACT

A new strategy was developed for the fabrication of the honeycomb-like porous carbon (HPC) material, involving a liquid-liquid phase separation process and a pyrolysis process. First of all, a novel polyimide containing benzothiazole moieties was designed and synthesized as the carbon precursor. Due to the high glass-transition temperature ( $T_g$ , 404 °C) and the low initial thermal decomposition temperature (394 °C) of this specially designed polyimide, the pore structure formed during the phase separation process was well maintained in the following pyrolysis process. As determined by SEM, the product has a honeycomb-like pore structure with a high uniformity. XRD and Raman spectra manifested the resulting carbon material possessed a disordered graphite structure, which can greatly contribute to its EM wave dissipation ability. After modifying HPC with Fe<sub>3</sub>O<sub>4</sub> nanoparticles, the nanocomposites (HPC/Fe<sub>3</sub>O<sub>4</sub>) achieved an excellent EM wave absorption performance. At the absorber thickness of 5.5 mm, a minimum reflection loss (RL) value of  $-20.1$  dB was achieved. Moreover, with the variation of the absorber thickness from 1.3 to 5.0 mm, the minimum RL curves in  $Ku$  band were all lower than  $-10$  dB. These results demonstrated the polyimide could be an excellent precursor for the synthesis of porous carbon materials with controllable morphology. Additionally, HPC/Fe<sub>3</sub>O<sub>4</sub> could be a promising material for applications in the field of EM wave absorption.

## 1. Introduction

With the rapid development of information technology, electromagnetic (EM) wave in gigahertz range has been extensively applied to the commercial and military electronic devices, such as satellite broadcasting, mobile telephone systems and military radar, which tremendously disturbs the EM environment and does harm to human health at the same time [1,2]. To address this issue, numerous efforts have been already made to exploit high-efficiency EM wave absorbing materials with tiny thickness, light weight, high thermal stability, wide bandwidth and strong absorption.

Among the absorbing materials exploited, carbon-based absorbing materials (carbon fibers, carbon nanotubes, carbon black, graphene, porous carbon) have attracted considerable attentions in the past few years due to their advantages in high dielectric loss, low density, high conductivity, outstanding thermal and chemical stability [3–7]. However, comparing with the nonporous carbon materials (carbon fibers, carbon nanotubes, carbon black, graphene), carbon materials with porous or hollow microstructure have been proved effectively to meet the increasing demands [8–11]. Thus, many efforts have been directed

toward the development of the porous carbon materials with excellent EM wave absorption performance [12–17]. Song et al. investigated a highly ordered porous carbon (HOPC) with SiO<sub>2</sub> colloidal templates and phenol resin [18]. The HOPC/wax composites displaced a reflection loss of  $-18$  dB at 13 GHz with an effective bandwidth of 4.5 GHz (11.7–16.2 GHz), when the filler loading reached to 5 wt. %. Meng et al. prepared porous hybridizing nanotubes structure of amorphous carbon interspersed among Fe<sub>3</sub>O<sub>4</sub> (C@ Fe<sub>3</sub>O<sub>4</sub>) with a 200 nm diameter and 70 nm thickness. The C@ Fe<sub>3</sub>O<sub>4</sub> hybrid with porous structure showed a strong absorbency for EM wave at low frequency area ( $-45$  dB at 6.18 GHz, with 3.4 mm thickness) [19]. These carbon materials have shown good reflection loss value, however, carbon materials derived from these methods often have complicated complex preparation process and high environmental cost. To solve these problems, one of the most promising methods, which obtains the porous carbon structure from the polymer template, has attracted great attentions from all over the world recently. Bhuwania et al. introduced sol-gel cross-linking via organic-alkoxy silanes (vinyltrimethoxysilane) to partially restrict the substructure collapse of polyimide (PI) fibers during pyrolysis [20]. Koh et al. applied a one-pot technique to crosslink the polymer precursors to

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protect the porous morphology of the membranes from thermally induced structural rearrangement during carbonization [21]. The key issue of this method is to restrict the collapse of the porous morphology during pyrolysis. Generally, polymer precursor with high glass transition temperature ( $T_g$ ) and low decomposition temperature ( $T_d$ ) can stay in solid state during the carbonization process [22]. However, it is hard to develop such materials since the material with high  $T_g$  often possess high  $T_d$  at the same time. In our lately work, PAN was utilized as a desired porous carbon precursor. The stabilization process of polyacrylonitrile (PAN) could induce the cyan groups in the side chain to form the cross-linked structure, affording robust network to maintain the hole-structure during the carbonization process [23]. Polyimide, as a kind of high thermostable polymer, has been widely used as the carbon precursor. However, the hole-structure changes a lot during the carbonization, which makes it difficult to control the pore structure [24].

In the present work, benzothiazole moieties with a high rigidity were incorporated into the polyimide (PI) backbone. Due to the rigidity and strong electron-withdrawing property of benzothiazole, the synthesized PI might possess both high glass transition temperature and relatively low thermal decomposition temperature. By the phase-inversion method, the porous PI membrane was prepared facilely and handily. After carbonization, a honeycomb-like porous carbon membrane was obtained. To the best of our knowledge, the attenuation of EM wave was implemented in two parts: dielectric loss and magnetic loss. Generally, the material with unilateral dielectric loss or magnetic loss can't attain satisfying EM wave absorbing performance, attributing to the poor matching between the complex permittivity and the complex permeability. In order to improve the absorbing performances, HPC/Fe<sub>3</sub>O<sub>4</sub> nanoparticles composites (HPC/Fe<sub>3</sub>O<sub>4</sub>) were synthesized by an in-situ synthesis method. Combining the Fe<sub>3</sub>O<sub>4</sub> nanoparticles with the porous carbon would not only provide good impedance matching, but also generate magnetic resonance and loss in the composites. For the excellent impedance matching condition and enhanced EM wave attenuation ability, HPC/Fe<sub>3</sub>O<sub>4</sub> showed excellent EM wave attenuation performance.

## 2. Methods

### 2.1. Synthesis of 6, 6'-Oxybis (benzothiazol-2-amine) (OBBTA)

As shown in Fig. S1a, the diamine monomer OBBTA was synthesized in two steps, which involves the preparation of 4, 4'-Oxydiphenylbis (thiourea) from 4, 4'-Oxydiamiline (4, 4'-ODA) and its cyclization at bromine catalysis. At first, 4, 4'-ODA (10.012 g, 0.05 mol) and ammonium thiocyanate (9.1344 g, 0.12 mol) was added to 200 mL glacial acetic acid, respectively, yielding yellow light brown solution which was stirred at room temperature for 2 h. Secondly, a mixture of bromine (17.58 g, 0.11 mol) and glacial acetic acid (30 mL) was added drop by drop via the constant pressure addition funnel with stirring at a water bath so that the temperature can be kept at 16–20 °C. As the bromine mixture added, orange solid precipitated from the solution. The orange slurry was stirred for another 1 h after all the mixture added. The orange acidic solid was collected by vacuum filtration and was dissolved in hot water. After removing undissolved impurity, the obtained filter was neutralized to neutral by sodium carbonate aqueous solution with white solid precipitating from the solution. Later, the crude diamine was recrystallized from N,N-Dimethylformamide/water mixed solution for 3–5 times to get the pure light-yellow solid, and the yield of OBBTA was 57%. Comparing with the reported procedure [25], our procedure can be achieved by a consecutive step. In addition, acetic acid was served as solvent and catalyst tremendously shorting the reaction time.

<sup>1</sup>H NMR spectrum (DMSO-*d*<sub>6</sub>) of OBBTA monomer are shown in Fig. S1b,  $\delta$ 7.37 (s, 4H, NH<sub>2</sub>),  $\delta$ 7.33 (d, 2H, phenyl),  $\delta$ 7.29 (d, 2H, phenyl),  $\delta$ 6.88 (q, 2H, phenyl), which demonstrated the successful synthesis of OBBTA. FT-IR spectrum of OBBTA monomer are shown in Fig. S2a, the

absorption bands at 3440 and 3280 cm<sup>-1</sup> are corresponding to amino (-NH<sub>2</sub>) stretching, and the characteristic C=N absorption appear at 1640 cm<sup>-1</sup>. Fig. S2b show the mass spectrum of OBBTA monomer, and significant molecular ion peak is obtained at 314.

### 2.2. Synthesis of honeycomb-like porous carbon (HPC)

To obtain poly (amic acid) (PAA) precursor solution, the above-mentioned OBBTA (1.5 mmol) was completely dissolved in N,N-Dimethylacetamide (DMAc) in a three-necked flask equipped with a mechanical stirrer, a calcium chloride tube and argon source. Then equimolar 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) was slowly added. The mixture was stirred for 10 h at room temperature to form a viscous solution of PAA, and the solid content of PAA solution was maintained at 18 wt.%. Then the solution was casted on a glass plate with a doctor blade at room temperature, and the resulting casting solution was immersed into the coagulating bath immediately. The coagulating bath used for phase inversion was H<sub>2</sub>O. After the phase inversion process, the resulting porous PAA membrane was dried at room temperature for 24 h and imidized at 180 °C, 260 °C and 340 °C in that order for 1 h each under vacuum. The porous PI was observed after the thermal imidization reaction completed. Lastly, it was carbonized in a tube furnace under a flowing argon gas atmosphere with a proper heating procedure (20 °C to 1000 °C, 1 °C min<sup>-1</sup>; 1000 °C, 1 h; 1000 °C to 20 °C, 5 °C min<sup>-1</sup>). Then the honeycomb-like porous carbon (HPC) was obtained by grinding the porous carbon membrane into powder. Scheme 1a shows the change of the PI's chemical structure in this process.

### 2.3. Synthesis of HPC/Fe<sub>3</sub>O<sub>4</sub> nanoparticle composites

According to the method that has been reported in our previous study, the Fe<sub>3</sub>O<sub>4</sub> nanoparticles were synthesized using a coprecipitation reaction. With the protection of argon gas, FeCl<sub>3</sub>·6H<sub>2</sub>O (0.1352 g, 0.5 mmol) and FeCl<sub>2</sub>·4H<sub>2</sub>O (0.0497 g, 0.25 mmol) were added to a 100 mL suspension of the obtained HPC (2.3 mg mL<sup>-1</sup>, in water). With a rapidly stirring, the mixture was heated to 70 °C in a water bath. Subsequently, NH<sub>3</sub>·H<sub>2</sub>O was added to adjust the mixture's pH value to 10. After that, the mixture was held at 70 °C for 1 h. Then the product was collected by centrifugation (3000 rpm for 5 min), and washed with water and ethanol repeatedly for several times. The product was dried in a vacuum oven at 50 °C for 12 h. Eventually the HPC/Fe<sub>3</sub>O<sub>4</sub> nanoparticles composites (HPC/Fe<sub>3</sub>O<sub>4</sub>) was obtained. Scheme 1b shows the synthetic routine of HPC/Fe<sub>3</sub>O<sub>4</sub>.

### 2.4. Characterization

Fourier transform infrared spectra (FT-IR) were obtained on an OPUS spectrometer with a mixture of KBr and sample (weight ratio sample/KBr = 1:100). <sup>1</sup>H NMR spectra were measured at 300 MHz on an AV300. X-ray powder diffraction (XRD) was performed on a PANalytical B.V. Empyrean system (Cu K $\alpha$ ) in the scattering range of 10–80°. Scanning electron microscopy (SEM) images were obtained on a FEI Nano 450 field emission SEM system and samples were platinum coated. Inherent viscosities were measured at 0.5 g dL<sup>-1</sup> concentration of PAA in DMAc using an Ubbelohde capillary viscometer at 25 °C. The thermal property of synthesized materials was detected by thermogravimetric analysis (TGA) (PerkinElmer TGA-7) and differential scanning calorimetry (DSC) (Mettler Toledo DSC 821e). The magnetic properties were measured by a Lake-shore 7410 vibrating sample magnetometer (VSM). The relative permeability and permittivity was obtained on an Agilent N5244A PNA-X network analyzer in the EM wave frequency range of 2–18 GHz for the calculation of reflection loss (RL) by the coaxial reflection/transmission method based on NRW method. For EM wave measurement, the synthesized absorber was uniformly dispersed into paraffin wax with the weight ratio of 40 wt. % and then pressed into a ring with an outer diameter of 7.00 mm, an

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