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Preparation, Properties and Application of Polyaniline Nanocomposites

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Based on the design of polyaniline structure, two different types of magnetic nanoparticles/polyaniline composites with electromagnetic absorption properties are prepared using the mechanical blending method based on protonic acid doping. Different sizes of FePt/PANI and Fe3O4/PANI composites with hollow structure are prepared by hard template method and mechanical blending method. The impact of the thickness of different shells on the absorbing property of composites is studied by adjusting the mass ratio of aniline/polystyrene. The research shows that the microspheres prepared with hollow structure have a fine morphology and uniform size and the average size is 1μm and 2μm respectively. With the increase of doping concentration, the minimum reflection loss peak shifts toward the low frequency and the corresponding matching thickness gradually becomes thicker. In addition, the loss mechanisms such as dielectric relaxation polarization, eddy current loss and interference cancellation play a major role in the electromagnetic wave absorption process of EG/PANI/Fe3O4 composites.

1. Introduction

In the preparation process of conductive PANI, it is necessary to make a reasonable selection of dopants according to the preparation process. In the application of conductive polymers, the amount of material loss is relatively large, and part of electromagnetic energy loss is large. Polyaniline is an absorbing material that can absorb electromagnetic waves. The preparation process of polyaniline nanocomposites is simple and it has high application value in the preparation of conductive PANI. In practical application, the chemical synthesis method is often used for the monomer polymerization of aniline to form PANI.
This paper mainly studies the preparation experiment and material processing manufacturing technique of polyaniline nanocomposites and analyzes the material properties and the application of electromagnetic wave absorption.

2. Literature review

A conductive polymer is a polymer that exhibits semiconductor or even conductor properties by chemical or electrochemical doping of a polymer backbone having a conjugated double bond (Riaz, 2016). It not only breaks the traditional concept that polymer materials can only act as insulators, but also makes important contributions to the improvement of low-dimensional solid-state electronics. This laid the foundation for molecular electronics (Liu et al., 2016).
Polyaniline is considered to be the most promising conductive polymer for practical applications (Pan et al., 2016). The button type secondary battery was prepared using polyaniline as an electrode material. Polyaniline has become a research hotspot in the field of conductive polymers. The history of polyaniline has been reviewed. The research is roughly divided into three phases: the debate about the nature of polyaniline, the development of organic semiconductors, and the hotspots of conductive polymer research (Ji et al., 2015).
Polyaniline is a kind of polymer compound which has special electrical and optical properties. After doping, it has electrical and electrochemical properties (Luo et al., 2016). After certain treatment, various equipments and materials with special functions can be produced. The electrical activity of polyaniline originates from the P-electron conjugated structure in the molecular chain. With the expansion of the P-electron system in the

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molecular chain, the P-bonded state and the P*-inverse-bonded state form a valence band and a conduction band, respectively. This non-localized P-electron conjugated structure is doped to form P-type and N-type conductive states. Compared with the doping mechanism of other conductive polymers to generate cationic vacancies under the action of oxidant, the number of electrons in the doping process of polyaniline does not change. The doped protonic acid is decomposed to produce H+ and the counter anion enters the backbone. This combines with the N atoms in the amine and imine groups to form a pole and a dipole delocalized into the P bond of the entire molecular chain. As a result, polyaniline exhibits higher conductivity. This unique doping mechanism makes the doping and dedoping of polyaniline completely reversible. The degree of doping is affected by factors such as pH and potential, and is manifested as a corresponding change in the appearance color. Polyaniline is therefore electrochemically active and electrochromic.

High quality polyaniline was synthesized by electrochemical method. Electrochemical preparation of polyaniline has been studied (Svenonius et al., 2016). Chemical oxidative polymerization and electrochemical polymerization are the most commonly used methods for polyaniline synthesis. In addition, there are vacuum evaporation, plasma polymerization, and photopolymerization (Zou et al., 2017).

The researchers studied the temperature dependence of room temperature conductivity and conductivity of LGS-PANI at different LGS levels (Guan et al., 2018). LGS-PANI may have the following structure: When the content is 11.4wt%, LGS is the template and the stretching chain structure is formed. When the LGS content is 48.2wt%, a double-stranded ordered structure is formed. When the LGS content is 69.5wt%, the proportion of LGS single-chain disordered packing increases. When the LGS content is high, it also contains the hydrogen bond between LGS and PANI (Franco-Orozco et al., 2017). The aqueous solution of PAN/PANMPS can be stably placed for more than two months under normal environmental conditions (Silvagomes et al., 2016). When (Anmol)/(AMPSmol=0.3:1), PAN/PAMPS has a PAMPS-doped PANI of a double-stranded coil structure and is deposited into a granular form. SEM analysis by scanning electron microscopy showed that the particle morphology formed by the deposition was well dispersed in the linear polymer matrix. The room temperature conductivity of PANI/PAMPS solid membrane and PANI/PAMPS solution was studied separately. The thermostability of PANI/PAMPS was studied using a thermogravimetric analyzer (Shima et al., 2017).

In summary, considering the conductivity, particle size and uniformity, dispersibility, conductivity stability and thermal stability of polyaniline composites, a suitable nanocomposite is selected as the conductive filler. Polyaniline is facilitated by the conversion of functional material phase structural materials, which has a new definition of the range of applications of polyaniline materials.

3. Method

3.1 Experimental

The reagents and instruments used in the test are shown in Tables 1 and 2 below.

Table 1: practical use of test sites

Reagent name	Reagent purity	Manufacturer
H2PtCl·6H2O	Analytically pure	Tianjin Guangfu Fine Chemical Research Institute
FeCl3·6H2O	Analytically pure	Yantai Shuang Shuang Chemical Industry Co., Ltd.
FeSO4·7H2O	Analytically pure	Baiyin Chemical Reagent Factory
NaOH	Analytically pure	Tianjin Da Mao Chemical Reagent Factory
Anhydrous ethanol	Analytically pure	Tianjin Fuyu Fine Chemical Co., Ltd.
Azo two isobutadiene	Analytically pure	Tianjin Da Mao Chemical Reagent Factory
aniline	Analytically pure	Tianjin Da Mao Chemical Reagent Factory
toluene	Analytically pure	Tianjin Da Mao Chemical Reagent Factory
hydrochloric acid	Analytically pure	BaiyinLiangyou Chemical Reagent Co., Ltd.

Fourier transform infrared spectrometer (FT-IR) is used to test the functional group contained in the sample. In the infrared absorption spectrum, the wave number (cm-1) is usually used as the abscissa and the transmittance (%) as the ordinate; test method: a small amount of powder sample and a certain amount of KBr are taken for the tablet ting after mixing and grinding uniformly, and then it is placed in an infrared spectrometer for testing. The phase and crystallinity of the sample are characterized by X-ray diffractometer (XRD). Test method: the powder sample to be tested is placed in the sample tank for tableting and then it is placed in CuKα (the tube voltage and tube current are 40 kV and 150 mA respectively; the generator power is

3000 W; the scanning range is 10° to 90°; and the scanning step is 100/min) as the radiation source of the X-ray diffractometer for the testing. The transmission electron microscopy (TEM) is used to analyze the structure and particle size of the sample. Test method: a small amount of the powder sample to be tested is taken for the ultrasonic dispersion in absolute ethanol. Then, one or two drops of the dispersed solution is dropped on 300 mesh copper net and it is dried at 40 °C in a vacuum oven. Finally, it is put in the transmission electron microscope for observation and analysis. The surface morphology of the sample is analyzed by scanning electron microscopy (SEM). Test method: a certain amount of powder sample to be tested with uniform dispersion is directly adhered to the conductive paste and the surface is gilt to enable it to be conductive. Finally, it is placed in a scanning electron microscope for observation and analysis.

Table 2: list of experimental apparatus and specifications

Instrument name	Instrument model	Manufacturer
Thermal type constant temperature heating magnetic stirrer	DF-101S	Zhengzhou Ya Rong Instrument Co., Ltd.
Electronic balance	FA2104N	Shanghai Precision Science Instrument Co., Ltd
Ultrasonic cleaner	KQ5200B	Kunshan Ultrasonic Instrument Co., Ltd.
Centrifuge	TGL-16G	Shanghai Anting Scientific Instrument Factory
Digital display intelligent temperature control magnetic stirrer	SZCL-A	Zhengzhou the Great Wall science and Trade Co., Ltd
Rotary evaporator	RE52-99	Shanghai Ya Rong biochemical instrument factory
Vacuum drying oven	DZF-6050	Shanghai Jinghong Experimental Equipment Co., Ltd
Quartz automatic double water distiller	1810-B	Jiangsu Jintan Zheng Ji Instrument Co., Ltd.
Refrigerator	BCD-181MLC	Hefei MeiLing Limited by Share Ltd

3.2 Polyaniline Nanocomposites

In recent years, magnetic nanoparticles/conductive polymer composites have been widely used in the field of electromagnetic wave absorption in military and civilian applications. Among conductive polymers, PANI is a good electrical loss type of absorbing material because of its low cost, simple preparation, low density and good environmental stability, which has received extensive attention. However, it is difficult for pure PANI to meet the requirements of absorbing bandwidth and performance of absorbing materials. Considering the electromagnetic matching requirement for good absorbing materials, many researchers combine magnetic nanoparticles with PANI to obtain the absorbing agent with good performance. For this reason, the alloys represented by Fe, Co, and Ni and their oxides have received extensive attention. Among magnetic materials, magnetic FePt nanoparticles have good chemical stability, which are an excellent magnetic loss type of absorbing material. The Fe3O4 nanoparticles have also received wide attention because of the simple preparation method, low cost and less magnetic loss. Li et al. prepared PANI/Mn0.8Zn0.2Fe2O4 nanocomposites by in-situ polymerization method and studied their absorbing properties in the range of 2 to 18 GHz. The results showes that its RLmin reached -20.6 dB at 14.4 GHz and its bandwidth of RL < -10 dB was up to 5.6 GHz. The bandwidth -5 Db<RL<-10 dB of core-shell BaTiO3/PANI composite is located in the range of 2000-6000 MHz and then the one-step method is used to prepare the magnetic FePt nanoparticles of uniform dispersion. The experimental flow is shown in Figure 1. Firstly, 0.2000 g of chloroplatinic acid (H2PtCl·6H2O) was added to 20.0 mL of ethanol and 0.2045 g of iron acetylacetonate was weighed and added to 30 mL of tetraethylene glycol, all of which was then added to a 100.0 mL three-necked flask. It was protected with nitrogen, heated to 80 °C, magnetically stirred for 30 min and kept for 30 min. After all the ethanol was evaporated, 0.2995 g of polyvinylpyrrolidone (PVP) was added and warmed up to 290 °C. Then, the reflux condensation was conducted for 3h and the heating device was removed. After cooling to room temperature, the black product was transferred into a centrifugal tube and the black FePt nanoparticles were obtained via the centrifugal separation of the centrifugal tube. Then, it was washed with absolute ethanol and then transferred to a rotary evaporator for rotary evaporation (constant temperature at 80 °C, rotation speed 50 r/min) until the liquid was evaporate. After that, the round bottom flask was removed and was dried at 40 °C in a vacuum oven for 48 h.

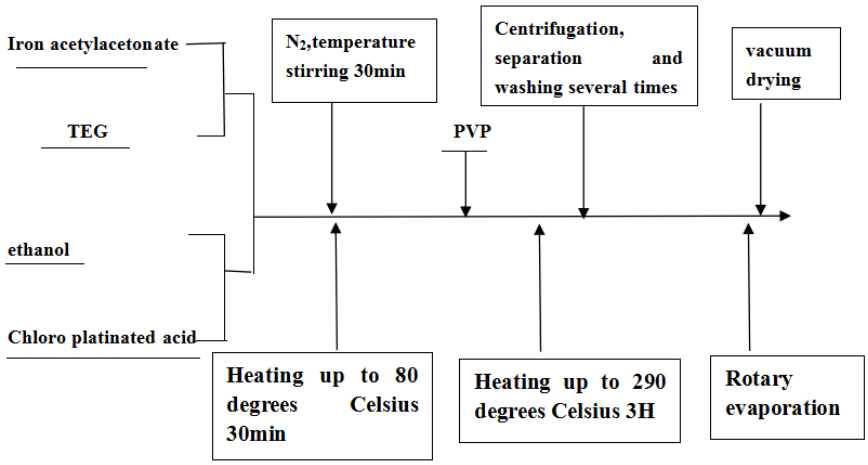

Figure 1: Flow chart of magnetic FEPT particles prepared by one-step method

Magnetic nanoparticles and PANI with hollow structure wwre composited by mechanical blending to prepare the magnetic nanoparticles/PANI binary composite. The basic process is as follows: a certain amount of magnetic nanoparticles and PANI microspheres were added to 50 mL of absolute ethanol for ultrasonic dispersion at room temperature for 30 min. Then, it was transferred to a three-necked flask and mechanically stirred at 25 °C for 3 h. After magnetic separation, the magnetic PANI-based binary composite with hollow structure can be obtained. Figure 2 is a schematic diagram showing the preparation process of 2 μm Fe3O4/PANI composite.

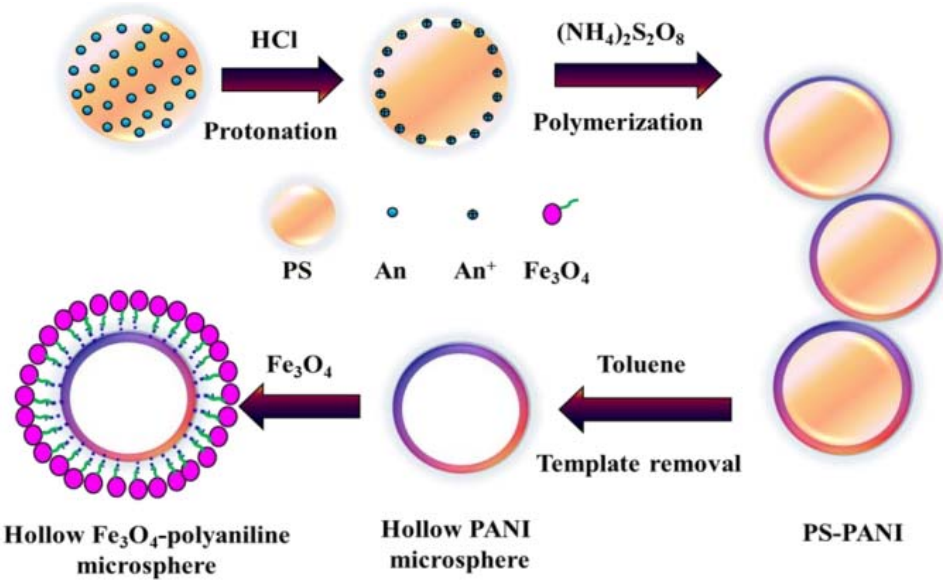

Figure 2: Experimental flow chart for preparation of hollow structure Fe3O4/PANI Composites

4. Result Analysis

The average particle size of PS template sphere is about 1 μm, with regular shape and uniform size. The PANI hollow sphere prepared using the PS sphere as a template has a uniform shape and size and the thickness of the PANI shell is also uniform at about 55 nm. In the TEM photograph of the FePt/PANI composite, FePt particles are loaded on the surface of the PANI hollow sphere, but the FePt particles loaded on the PANI are not uniformly dispersed. This phenomenon may be due to the partial agglomeration caused by the magnetic property of FePt. Due to the agglomeration of Fe3O4, it can be seen from the TEM

photograph of the Fe3O4/PANI composite in Figure 3 that a large quantity of Fe3O4 nanoparticles are loaded on the surface of PANI,and the agglomeration phenomenon is more obvious.

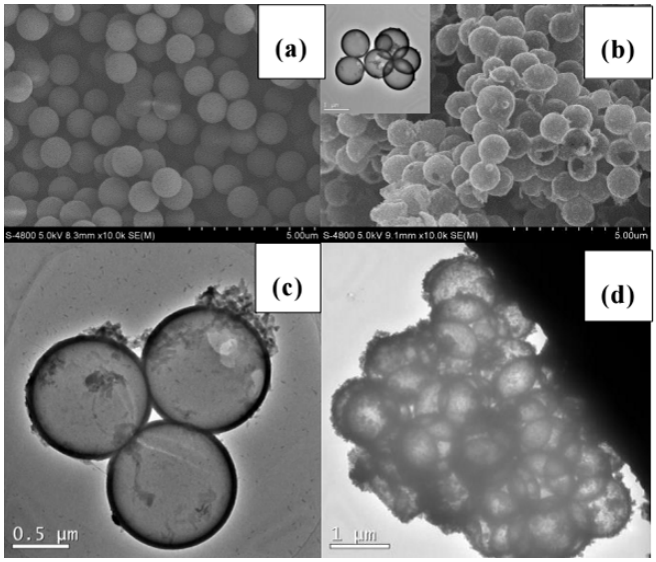

Figure 3: SEM((a)PS; (b) PANI; (c) FePt/PANI) and TEM photos; (d) Fe3O4/PANI) of different samples

The transmission electron micrographs of the PS template sphere and Fe3O4 are shown in Figure 4. It can be seen that the average particle size of monodisperse PS template sphere is about 2 μm with uniform morphology and size. The average particle size of the Fe3O4 nanoparticles in Figure 4b is around 10 nm.

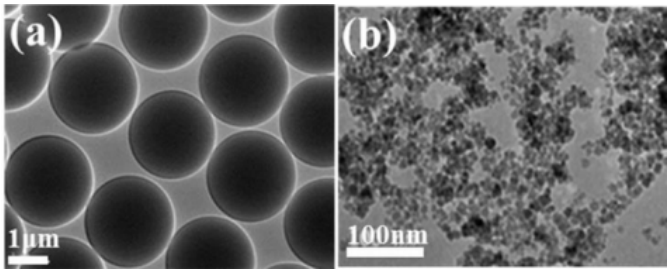

Figure 4 TEM photos of different samples

Comparing the photograph of the PS microspheres, it can be seen that PANI is successfully coated on the surface of the PS template and still maintained a good morphology of the template sphere, indicating that the PS/PANI core-shell structure is successfully obtained by in-situ polymerization. After the template removal by toluene, the sample remains good spherical structure and no collapse occurs. With the decrease of AN/PS mass ratio, the PANI shell thickness of the sample is 100 nm, 60 nm and 50 nm respectively.

5. Conclusion

The PANI microspheres with hollow structure and good dispersibility are successfully prepared by hard template method, whose average particle size is 1μm. Also, FEPT and Fe3O4 nanoparticles are prepared by one-step method and coprecipitation method. The FEPT/PANI and Fe3O4/PANI composites with hollow structure are obtained via mechanical blending, whose average particle size is 1μm. Compared with solid materials, the absorbing agent with hollow material has more reflection and scattering of electromagnetic waves, which enable them with good absorbing properties. At the same time, it can effectively buffer the thermal energy brought by electromagnetic wave conversion and the thermal stability is good. The loss mechanisms, such as natural resonance, eddy current loss and interference cancellation enable the magnetic nanoparticle/PANI binary composite to have good absorbing properties for X-band and Ku-band.

Due to the addition of different magnetic materials, the electromagnetic wave absorption properties of PANI-based composites are significantly different, which makes the FEPT/PANI and Fe3O4/PANI composite materials with hollow structure have potential application value in different frequency ranges.

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