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Microwave absorption properties and infrared emissivities of ordered mesoporous C–TiO_2 nanocomposites with crystalline framework

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ABSTRACT

Ordered mesoporous C–TiO_2 nanocomposites with crystalline framework were prepared by the evaporation-induced triconstituent co-assembly method. The products were characterized by XRD, TEM, N_2 adsorption–desorption and TG. Their microwave absorption properties were investigated by mixing the product and epoxy resin. It is found that the peak with minimum reflection loss value moves to lower frequencies and the ordered mesoporous C–TiO_2 nanocomposite possesses an excellent microwave absorbing property with the maximum reflection loss of −25.4 dB and the bandwidth lower than −10 dB is 6.6 GHz. The attenuation of microwave can be attributed to dielectric loss and their absorption mechanism is discussed in detail. The mesoporous C–TiO_2 nanocomposites also exhibit a lower infrared emissivity in the wavelength from 8 to 14 μm than that of TiO_2-free powder.

1. Introduction

Since the first discovery of ordered mesoporous silicates in 1992, a window to new technological areas has been opened [1,2]. Ordered mesoporous materials have received steady growing interest because of their fascinating properties and various applications as compared with the bulk or microsized counterparts [3–6]. Recently, the synthesis of carbon-based composite with uniform mesopores and high surface area received significant attention because they may have the advantages of coupling the function of non-carbon phase with the rich properties of carbon and the new and unpredictable properties [7,8]. Zhao et al. [9–11] synthesized the ordered carbon/oxides nanocomposites using the evaporation-induced triconstituent co-assembly method. The degradation of rhodamine B and the electrocatalytic properties of the ordered C–TiO_2 nanocomposites were demonstrated in their reports. He et al. [12,13] synthesized OMC-Ni as a catalyst support which can easily yield a higher mass activity when the initial Ni content is around 10–15% and OMC-NiO with an excellent capacitance properties because of the presence of NiO nanocrystallites.

Microwaves have been widely used in both military and civil applications: radar, space technology, telecommunication, local area networks, personal digital assistant, etc. [14,15]. However, there are many problems caused by the increasing usage of microwave. In order to provide solution to electromagnetic interference (EMI) and electromagnetic compatibility (EMC), the absorbers of microwave are becoming very important, which have attracted much attention of many scientists [16–19]. Generally, magnetic metal particles are used for the microwave absorption materials. However, the high specific gravity and the difficult formulation have limited their practical applications. The nanoscale materials have attracted increasing interest in microwave absorbing and shielding materials in the high-frequency range due to their many unique chemical and physical properties [20,21]. Particularly, the unique structures and many excellent properties of carbon nanotubes (CNTs) have prompted intensive studies for electromagnetic wave absorbing [22–24]. Many efforts have been focused on the combination of organic polymers or carbon with inorganic nanocrystals or metal nanoparticles in order to yield new functional material which may combine the advantages of each component [25–27]. Mesoporous titania-based materials with a crystalline framework, high surface area and tunable pore size have received significant research attention due to the range of applications for such materials: photocatalysis [28–30], sensing fields [31,32], energy storage and conversion [33,34]. Recently, PAni/HCl/TiO_2 nanocomposite fabricated by using TiO_2 as a filler showed a large dielectric constant [35]. Phang et al. reported a novel hexanoic acid (HA) doped PAni micro/nanocomposite containing TiO_2 and Fe_3O_4 and PAni/HA/TiO_2/Fe_3O_4 with 40% of Fe_3O_4 achieved the best performance of microwave absorption (greater than 99.4% absorption) at high frequency [36]. TiO_2 shows excellent transparency and stability, so TiO_2 is also expected to improve the infrared absorbing

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performance, while not affecting the microwave absorbing performance of the material [37]. Ordered mesoporous carbon with TiO_2 as a dielectric filler could be an excellent microwave absorbing material, but few studies on their infrared emissivities and microwave absorbing behaviors have been carried out.

In this paper, ordered mesoporous C–TiO_2 nanocomposites with crystalline framework were synthesized by using a low-molecular-weight resol (phenol–formaldehyde, $M_w < 500$) as an organic precursor, less reactive metal alkoxide as an inorganic precursor, and amphiphilic triblock copolymer F127 as a template. Add amorphous components, such as carbon, into the mesostructured metal oxides framework, can form a glasslike phase; it is responsible for the stability of ordered mesostructures [10]. Moreover, the combination of ordered mesoporous structure and incorporation of TiO_2 may contribute to the better impedance matching, which can result in the improved microwave absorption in a wide band. We investigated the effect of annealing temperature on the crystalline state of TiO_2 and TiO_2/C ratio on the microwave adsorption performance of C–TiO_2 nanocomposites. Additionally, the infrared emissivities of C–TiO_2 nanocomposites were also investigated. The ordered mesoporous C–TiO_2 nanocomposites exhibit effective microwave adsorption performances and lower infrared emissivities in the wavelength from 8 to 14 μm.

2. Materials and methods

2.1. Materials

All the reagents were of analytical purity and used without further purification. Pluronic F127 (EO106PO70EO106, EO= ethylene oxide, PO=propylene oxide) was purchased from Sigma-Aldrich Corporation. Tetrabutyl titanate, phenol, formaldehyde, hydrofluoric acid, hydrochloric acid and ethanol were purchased from Sinopharm Chemical Reagent Limited Corporation. The resol precursor ($M_w < 500$) was prepared according to the procedure reported previously [38].

2.2. Synthesis

In a typical preparation, 2 g of Pluronic F127 was dissolved in 12 ml of absolute ethyl alcohol and stirred for 1 h at 40 °C as solution A. Meantime solution B was prepared from 1.5 ml of 37 wt% hydrochloric acid and 6 ml of absolute ethyl alcohol. Tetrabutyl titanate (3.4 g) was portioned slowly to solution B under vigorous stirring. After 1 h stirring, solution B and 2.5 g of 20 wt% resols' ethanolic solution were added in solution A. After being stirred for 2 h, the mixture was transferred into dishes. It took 24 h at room temperature to evaporate ethanol and 36 h at 70 °C in an oven to thermopolymerize. The as-made products, orange and transparent films, were scraped from the dishes. Calcination was carried out in a tubular furnace at 350 °C for 5 h and 500, 600 and 700 °C for 2 h under N_2 flow with a rate of 1 °C/min to remove the amphiphilic triblock copolymer templates and get mesoporous C–TiO_2 nanocomposites. We take the mesoporous nanocomposite C–TiO_2-x with x representing the heating temperature. Mesoporous nanocomposite C–TiO_2-350 was calcined at 350 °C for 5 h in air to burn off carbon and generate mesoporous titania material. The nanocomposites with different compositions in a wide range from 30 to 70 wt% TiO_2 were prepared by varying the mass ratios of resol to tetrabutyl titanate. The final products were labeled as MCyT$(10-y)$, where y represents the weight percentage of carbon content in the nanocomposites. Moreover, ordered mesoporous carbon (OMC-500) as a reference was prepared according to the previous report [39].

2.3. Characterization

The porous structures of the ordered mesoporous C–TiO_2 nanocomposites and mesoporous TiO_2 oxide were measured by N_2 adsorption–desorption isotherm using Micromeritics ASAP 2010 at 77 K. X-ray diffraction (XRD) patterns were recorded by a Bruker D8 ADVANCE diffractometer using Cu $K\alpha$ radiation (λ=0.154056 nm). Transmission electron microscopy (TEM, FEI Tecnai G^2) operating at 200 kV was applied to characterize the morphology of the mesoporous materials. Samples for TEM measurements were prepared by ultrasonically suspending the powder in ethanol and placing a drop of the suspension on a carbon film supported by Cu grids. Weight changes of the products were monitored using a Mettler Toledo TG-209-F1 analyzer (NETZSCH) from 25 to 950 °C under nitrogen or air with a heating rate of 5 °C min^{-1}. Energy dispersive X-ray spectrum (EDS) installed in FEI Tecnai G^2 system was also used to analyze the microzone composition of the samples.

2.4. Microwave adsorption measurement

The as-prepared powders were uniformly dispersed into the commercial epoxy resin and then pressed into toroidal-shaped samples with the outer diameter of 7.0 mm, the inner diameter of 3.04 mm and the thickness of 3.0 mm. Commercial epoxy resin [40,41] or paraffin [42,43] is often used as binder matrix in electromagnetic wave adsorption measurement. In order to study electromagnetic wave absorption properties systematically in our researches [44,45], we are familiar with commercial epoxy resin as binder matrix. The scattering parameters S_{11}, S_{21} of the samples with 40 wt% as-prepared powders were measured using a vector network analyzer (Agilent E8363A) by the coaxial reflection/transmission technique. The relative permittivity and permeability values were determined from the scattering parameters as measured in the frequency range 0.5–18 GHz. To reduce errors, all values were obtained by averaging over the data measured from three different toroids of each sample.

2.5. Infrared emissivity measurement

Aluminum sheet, previously degreased in diluted NaOH at 50 °C and then chemically polished in diluted HNO_3, was used as the substrate for the coatings, and EPDM dissolved in dimethylbenzene as the adhesive. The prepared powder was used as the filling and its weight ratio was set as 30% in the coating. The coating thickness was controlled at about 35 μm by the wire-wound rod coater (Tianjin Jingke Material Testing Machine Factory, China). Infrared emissivity value at the wavelength of 8–14 μm was measured by using IR-2 Infrared Emissometer (Shanghai Institute of Technological Physics of the Chinese Academy of Sciences). All values were obtained by averaging over the data measured from ten different regions of each coating.

3. Results and discussion

3.1. Preparation of mesoporous C–TiO_2 nanocomposites

Small-angle XRD patterns of mesoporous C–TiO_2 nanocomposites with different calcined temperatures are shown in Fig. 1a. After the calcination under an inert atmosphere (N_2) at 350 °C for 5 h, the small-angle XRD pattern becomes poorly resolved, and a well-resolved diffraction peak is observed, suggesting that the typical ordered mesostructure is retained. Sample MC5T5-500 show patterns with an intense diffraction peak (100) and two