Composites Science and Technology 137 (2016) 118–129

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: http://www.elsevier.com/locate/compscitech

Preparation and electrorheological behavior of anisotropic titanium oxide/polyaniline core/shell nanocomposite

Xiaoli Tian [a, b], Kai He [a, b], Chengwei Wang [a, b], Qingkun Wen [a, b], Baoxiang Wang [a, b, *], Shoushan Yu [a, b], Chuncheng Hao [a, b], Kezheng Chen [a, **], Qingquan Lei [a, b]

[a] College of Materials Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, PR China
[b] State Key Laboratory of Electrical Insulation and Power Equipment, Xi'an Jiaotong University, Xi'an 710049, PR China

ARTICLE INFO

Article history:
Received 30 July 2016
Received in revised form
27 October 2016
Accepted 28 October 2016
Available online 1 November 2016

Keywords:
Smart materials
Nano composites
Mechanical properties
Electrorheological fluid

ABSTRACT

Anisotropic titanium oxide/polyaniline core/shell nanocomposite was synthesized via a three-step method, and its electrorheological (ER) properties under external applied electric field were researched. Firstly, monodispersed amorphous titanium oxide nanospheres were prepared by a controlled hydrolysis method and then anisotropic titanium oxide peanut-like nanospheres was obtained by using weak acid to etch the monodispersed titanium oxide sphere. At last, the surface of anisotropic TiO_2 was coated with polyaniline (PANI) through an *in-situ* polymerization method. Then the influence factors on the preparation of anisotropic TiO_2/polyaniline core/shell structure nanoparticles were discussed deeply, including different kinds and amounts of acid, the amount of aniline, and so on. The morphology and structure of the samples were characterized by scanning electron microscopy, transmission electron microscopy, zeta potential analysis and X-ray powder diffraction, respectively. The electrorheological behaviors of the anisotropic TiO_2/polyaniline composite particles are characterized using a rotational rheometer, which shown a good ER activity.

1. Introduction

The electrorheological (ER) fluid is a kind of intelligent materials whose rheological characters can be changed reversibly according to the external applied electric field [1–14]. An electrorheological system mostly composed of solid particles, and insulating carrier medium. The solid particles can be metallic oxide, inorganic, organic, and organic/inorganic composites [15–19]. For a variety of materials which used for ER solid particles, the electrical conductivity is a key parameter that needs to be satisfied with the semiconducting. In order to meet the conditions, researchers prepared many composites. The reason for that is because the electrical conductivity of composites is much more controllable than single material. Generally, the whole ER system is colloids, suspensions, and emulsions. Because of this nature of the ER fluid, make it has the application in varied control equipments, such as dampers and actuators controlled. But, ER system have several limitations such as easily electrical breakdown at high electrical field, low stability, and low shear strength, which largely restrict it's industry application [20–24]. To overcome these limitations, various types of materials have been introduced as ER dispersed materials. For instance, polymer/inorganic composite were used because of their high polarization ability attributed to the difference in chemical and physical structure.

At present, Titanium dioxide (TiO_2) has been becomes one of the most extensively researched semiconducting materials. Titanium oxide has many peculiar properties such as a wide band gap of 3.2 eV, low cost, chemical stability, etc. [25]. It also can be used in many fields, especially in photo catalysis, lithium-ion batteries, and solar energy [26]. As we all known, there is a great relationship between material performance and its morphology and structure. So, many people have done many words to synthesis novel structures of TiO_2. Recently, the research focuses on the one-dimensional nanotube and nanowire, two-dimensional nanosheets, hierarchical structures, hollow or porous structure, etc. [27–29] Among the conducting polymers, polyaniline (PANI) have a good prospect because it possess a lot of advantages, such as cheap raw materials, simple synthesis processes, controllable conductivity, good environmental stability and process ability. At present,

* Corresponding author. College of Materials Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, PR China.
** Corresponding author.
E-mail addresses: bxwang@qust.edu.cn (B. Wang), kchen@qust.edu.cn (K. Chen).

http://dx.doi.org/10.1016/j.compscitech.2016.10.026
0266-3538/

soft or hard templates were used to achieve PANI nanostructure. The combination of high dielectric TiO_2 and good conductive PANI with complex structure may provide high ER activity and application.

In addition, core-shell particles are an interesting design for ER materials, especially for better ER performance. Considering the dielectric TiO_2 and conducting polymers, the dielectric effects of core particles can be combined with the electrical properties of conducting shell layers. Therefore, anisotropic structured particles may provide high dielectric response, which is beneficial to the enhancement of ER activity. So, in this work, we prepared a kind composite that is made up of conducting polymers-PANI and semiconducting inorganic oxide-TiO_2, which also combine the advantage of core-shell and anisotropic structure. The prepared anisotropic TiO_2/polyaniline core/shell particles were dispersed in silicone oil and their electro-responsive ER properties were tested at various electric field strengths.

2. Experimental section

2.1. Synthesis of the monodispersed titanium oxide nanospheres

Monodispersed titanium oxide spherical particles were prepared by controlled hydrolysis of tetrabutyl titanate (TBT, $[CH_3(CH_2)_3O]_4Ti$, 98% purity) in ethanol. Firstly, 0.5 mL of 0.1 M aqueous potassium chloride was added into 100 mL ethanol, and then stirred 30 min. Secondly, 2 mL of TBT was added to above solution at ambient temperature. The solution was stirred strongly using a magnetic stirrer for about 10 min until a white precipitate appeared. Thirdly, the suspension was aged in a static condition for 24 h in a closed container at room temperature. The powder deposited at the bottom of the vessel was collected and washed it with ethanol and de-ionic water for several times, then dried at 50 °C in air.

2.2. Synthesis of anisotropic peanut-like titanium oxide particles

0.2 g as-obtained monodispersed TiO_2 spherical particles were dispersed in 50 mL deionized water with sonicating 0.5 h. Then different amounts (i.e. 1 g, 2 g, 5 g) of glacial acetic acid (GAA) was added into the above solution and continue stirred for 6 h. Subsequently, the products were separated by centrifugation, washed with deionized water until the pH of the solution was nearly 7. The product of anisotropic peanut-like titanium oxide was dispersed in 30 mL deionized water.

2.3. Synthesis of anisotropic TiO_2/PANI nanocomposites

30 mL as-obtained anisotropic titanium oxide solution was mixed with 1.5 mL aniline (An), 0.3 g CTAB and 1.8 g of glacial acetic acid at ice bath. The solution was mixed completely using a magnetic stirrer for about 2 h to form a uniform suspension at ice temperature. Then, 10 mL deionized water was mixed with 0.5537 g ammonium persulfate (APS). After mixing for about 10 min at ice temperature, APS solution was added into the above titanium oxide/An solution, continuously, stirred for about 30 min. The final product was centrifuged and washed with deionized water and ethanol for several times, then dried at 50 °C.

2.4. Characterization

The morphology of the obtained particles was observed by field emission scanning electron microscopy (FESEM, JEOL JSM-6700F). Transmission electron microscopy (TEM) images were recorded with HITACHI H-2650 high-resolution transmission electron microscopes. The accelerating voltage was 200 kV in each case. For the TEM measurements, small amounts of sample in ethanol was given an ultrasonic treatment for 5 min and then dropped onto a copper grid covered by a carbon film. Powder X-ray diffraction patterns were recorded on Rigaku D-MAX 2500/PC X-ray diffractometer with CuKα irradiation ($\lambda = 1.54178$ Å) and $2\theta = 4-80°$. The Zeta potential was investigated by the size and Zeta potential analyzer (Malvern Zetasizer Nano, UK).

The ER suspensions of anisotropic TiO_2/PANI nanocomposites were obtained as following: Before the preparation of ER fluid, the as-obtained sample was further immersed in aqueous NH_3 solution for over night. Finally, the TiO_2/PANI nanocomposities for the ER fluids was obtained by filtering, washing and drying. The obtained anisotropic TiO_2/PANI nanocomposites were dried in a vacuum oven at 80 °C for 12 h. The dried anisotropic TiO_2/PANI then was dispersed into silicone oil (Tian Jin Bodi chemical limited company, Tian Jin, China; dielectric constant $\varepsilon = 2.72-2.78$, viscosity $\eta = 486.5 \pm 24.3$ mPa s, and specific density $\rho = 0.966-0.974$ g cm^{-3} at 25 °C) to form the ER fluids (20 wt% particle concentration, w/w). The ER properties of suspensions were measured by an electrorheometer (HAAKE RheoStress 6000, Thermo Scientific, Germany) with a parallel plate system (PP ER35, the gap between plates was 1.0 mm), and WYZ-020 DC high-voltage generator (voltage 0–5 kV, current 0–1 mA). The steady flow curves of shear stress–shear rate were measured by the controlled shear rate (CSR) mode within 0.05–500 s^{-1} at room temperature. Before each measurement, The suspensions were presheared for 60 s at 300 s^{-1} and then applied electric fields. The yield stress was approximately obtained with the maximum shear stress at the low shear rate region. A dielectric study was carried out by using a Novocontrol broadband dielectric spectrometer at the frequency range of 0.1–10^6 Hz (Novolcontrol Technologies GmbH & Co. KG). All experiments were performed at 25 °C.

3. Results and discussion

3.1. The morphology of monodispersed titanium oxide nanospheres

The morphology of the titanium oxide nanospheres is shown by SEM images in Fig. 1(a) and (b). It was found that the titanium oxide nanospheres synthesized by the controlled hydrolysis are nearly monodispersed. Their size distribution are uniform and their surface is smooth. The diameter of nanospheres is about 400–500 nm.

3.2. The influence of different kinds and quantities of acid on the formation of anisotropic peanut-like titanium oxide particles

As-obtained monodispersed titanium oxide nanospheres can be dissolved completely in strong acid (HCl, HNO_3, etc.). It was found that the smooth monodispersed nanospheres have disappeared after reacting with strong acid. In order to obtain the anisotropic peanut-like titanium oxide, a weak acidic acid as a solvent need to be used to etch the titanium oxide spheres, such as glacial acetic acid and critic acid etc. The SEM images of anisotropic titanium oxide obtained by using different kinds of weak acid are shown in Fig. 2: (a and b) glacial acetic acid; (c and d) oleic acid. Moreover, anisotropic titanium oxide peanut-like particles can be obtained by using weak acid. Compared the SEM images as shown in Fig. 2a–d, they have obvious differences. Although under the existence of oleic acid, anisotropic titanium oxide peanut-like particles can be formed. There, however, are much more pieces or irregular particles in Fig. 2c and d. In Fig. 2a and b, anisotropic TiO_2 can be obtained and their peanut-like shape is clear, which means that GAA is much better than the using of oleic acid.

In order to investigate the influence of acid amounts on the