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Urchin-like polyaniline microspheres fabricated from self-assembly of polyaniline nanowires and their electro-responsive characteristics

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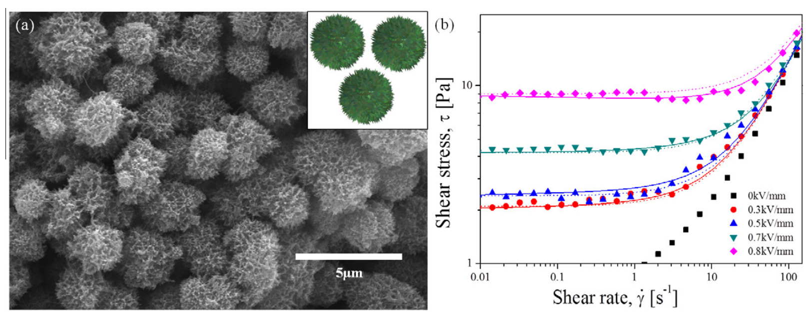
HIGHLIGHTS

- Micron-sized polyaniline beads with a porous sea urchin like appearance were synthesized.
- A self-assembly process from polyaniline nanowires was adopted.
- Typical electro-responsive characteristics were observed for sea urchin like polyaniline beads.

GRAPHICAL ABSTRACT



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ABSTRACT

Micron-sized PANI beads with a porous sea urchin like appearance, mean diameter of 2.5 μm and spherical shape, were synthesized by a self-assembly process from PANI nanowires. The nanowires were polymerized using ammonium persulfate as an oxidant in an aqueous solution. The structure of the urchin-like PANI microspheres was characterized by scanning electron microscopy, while the Brunauer–Emmett–Teller specific surface area of the urchin-like PANI microspheres was calculated from N_2 adsorption/desorption. The microspheres, which were dedoped to a low conductivity, were then applied to electro-responsive electrorheological (ER) materials dispersed in silicone oil with a volume fraction of 10%. The particulate structures of the ER fluid under an applied electric field were observed by optical microscopy. The ER properties of the ER fluid including the shear stress, shear viscosity and yield stress were examined using a rotational rheometer under an applied electric field.

1. Introduction

Electrorheological (ER) fluids in general are suspensions of electrically polarizable particles dispersed in insulating oil, such as mineral oil, silicone oil and hydrocarbon oil [1]. As important smart/intelligent materials, they exhibit tunable phase transition characteristics from a liquid-like to a solid-like state by connecting the dispersed particles in the direction of the external electric field [2–5]. These structural changes in the ER fluid induce a significant increase in shear stress and shear viscosity, which is fast and reversible. Because of these rheological properties, ER fluids can be used for a wide range of engineering applications including polishing, haptic, torque-transferring devices, such as torque transducers, dampers, and tactile interfaces [6–8]. A variety of materials have been used as polarizable particles in ER fluids including both organic solid particles, such as starch, cellulose and polyaniline (PANI), and inorganic solid particles, such as silica, zeolite and TiO_2 [9–15]. Among these materials, PANI, as a conducting polymer, has attracted considerable interest because of its low cost, easy synthesis, good optical and electrical properties [16]. The synthesis, characterization and application of PANI have been studied widely over the past three decades because of its potential use as a key material in a range of electrochemical devices [17].

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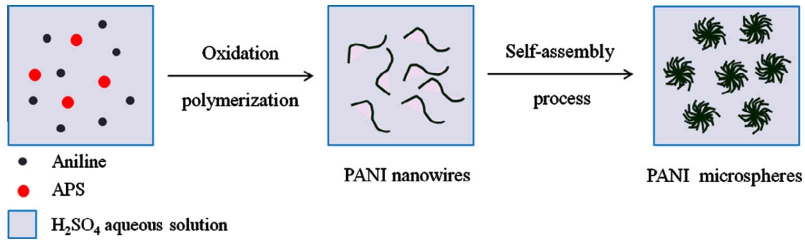

Fig. 1. Schematic process for synthesizing the urchin-like PANI microspheres.

The design and synthesis of PANI nanostructure have attracted considerable attention in nanoscience and nanotechnology because of their unique properties and potential applications [18–22]. A range of approaches, such as template methods, template-free methods and electrochemical methods, have been used widely for the fabrication of PANI nanostructures [23]. The morphology of PANI is strongly affected by the following: the nature and concentration of the dopant, oxidant and monomer, molar ratios of the dopant and oxidant to monomer; temperature; and polymerization methods [24–27]. A variety of PANI micro/nanostructures have been synthesized by changing these polymerization parameters. Self-assembly driven by various molecular interactions, such as hydrogen bonding, π–π stacking, and van der Waals interactions, is an effective strategy for producing nanostructures [28]. Herein, urchin-like PANI microspheres were produced from 1D nanowires synthesized by oxidation polymerization using a self-assembly process [17,23,29], and applied as ER materials. The ER properties of the particles dispersed in silicone oil were examined using a rotational rheometer at various electric field strengths. It can be also noted that various inorganic urchin-like ER particles have been also introduced recently [30–32].

2. Experimental section

2.1. Materials and synthesis method

Aniline (Mw: 93.13 g/mole, density: 1.02 g/ml, DC Chemical), ammonium persulfate (APS, Mw: 228.18 g/mole, density: 1.98 g/ml, Dae-Jung), sulfuric acid (Mw: 98.07 g/mole, density: 1.84 g/ml, OCI), and deionized water were used to obtain urchin-like PANI microspheres. Fig. 1 summarizes the polymerization process by an oxidative polymerization and self assembly process. An aniline solution was prepared by adding 2.4 ml of aniline to 57.6 ml of 5 M sulfuric acid. The APS solution was prepared by adding 3 g of APS to 60 ml of 5 M sulfuric acid. Subsequently, the aniline solution was cooled to −10 °C, and an APS solution was added to the aniline solution. After stirring for 30 s, the reaction was carried out for 24 h at −10 °C. The product was washed with deionized water until the filtrate was clear. The obtained PANI particles were dedoped by dropping a 1.0 M NaOH aqueous solution until the pH of the particle suspension reached 9.5. The resulting product was then washed several times with deionized water. The ER fluid was then fabricated by dispersing the dried PANI particles (10 vol%) in an insulating silicone oil with a kinematic viscosity of 50cS.

2.2. Characterization

The prepared PANI microspheres were observed by scanning electron microscopy (SEM, S-4300, Hitachi, Japan). The chemical structures of the particles were characterized by Fourier transform infrared (FT-IR, Perkin Elmer System 2000) spectroscopy in the range of 4000–700 cm^{-1}. Density of the synthesized PANI microspheres was measured by using a pycnometer (Accupyc 1330, Gas pycnometer, USA). The conductivity was measured using a standard four-probe method (MCP-T610, Mitsubishi chemical). The Brunauer–Emmett–Teller (BET, ASAP ZOZO) surface area was determined using nitrogen as the adsorbate. Optical microscopy (OM, BX-51, Olympus) was performed to observe the movement of particles in silicone oil dropped between a hand-made aluminum electrode. The ER properties of the urchin-like PANI microsphere-based ER fluid (10 vol%) was observed using a rotational rheometer (MCR 300, Physica) equipped with a high-voltage power supply (HCP 14-12500, fug) and CC17 geometry. A dielectric study was further carried out using a LCR meter (Agilent HP 4284A) over frequency range of 20–10^6 Hz.

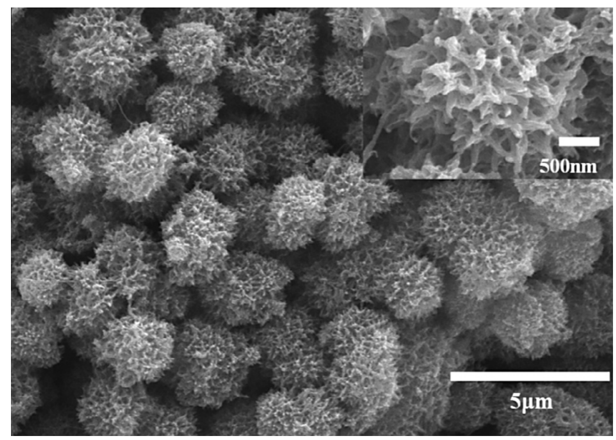

Fig. 2. SEM image of the dedoped urchin-like PANI microspheres.

3. Results and discussion

Fig. 2 shows images of the sea urchin-like PANI microspheres fabricated by a self-assembly process from PANI nanowires synthesized in the oxidation polymerization of aniline. The particles obtained were spherical with pores, and had a mean diameter of 2.5 μm. In high-magnification, the microspheres consisted of PANI nanowires, which were interconnected and entered into the microspheres. The density of the synthesized urchin-like PANI microspheres was 1.16 g/cm^3.

Fig. 3 is the FT-IR spectrum of the dedoped sea urchin-like PANI microspheres. The characteristic peak at 3456 cm^{-1} means the N—H bond of the first amine, and the peaks at 1579 and 1493 cm^{-1} were assigned to the C═C stretching vibration of the aromatic rings, respectively. The peak at 1304 cm^{-1} indicates the C—N stretching vibration of second aromatic amine. The peaks at 1142 and 823 cm^{-1} were assigned to the out-of-plane vibration in the 1–4 dis-substituted aromatic rings.

The BET technique was carried out to estimate the BET specific surface area and pore properties of the urchin-like PANI