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Key synthesis of magnetic Janus nanoparticles using a modified facile method

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ABSTRACT

Inorganic/organic poly(methylmethacrylate-acrylic acid-divinylbenzene) iron oxide Janus magnetic nanoparticles (P(MMA-AA-DVB)/Fe_3O_4) with strong magnetic domains and unique surface functionalities were prepared using a solvothermal process. The P(MMA-AA-DVB) nanoparticles were prepared via soap-free emulsion polymerization and used as a precursor for preparing Janus nanoparticles. The morphology and magnetic properties of the magnetic Janus nanoparticles formed were characterized using a laser particle size analyzer, transmission electron microscopy, Fourier transform infrared spectroscopy, vibrating sample magnetometry, and thermogravimetric analysis. The synthesized P(MMA-AA-DVB)/Fe_3O_4 magnetic Janus nanoparticles were characterized by a Janus structure and possessed a stable asymmetric morphology after being dually functionalized. The particle size, magnetic content, and magnetic domain of the P(MMA-AA-DVB)/Fe_3O_4 magnetic Janus nanoparticles were 200 nm, 40%, and 25 emu/g, respectively. The formation mechanism of the Janus nanoparticles was also investigated, and the results revealed that the reduction of Fe^{3+} ions and growth of Fe_3O_4 took place on the surface of the P(MMA-AA-DVB) polymeric precursor particles. The size of the Janus particles could be controlled by narrowing the size distribution of the P(MMA-AA-DVB) precursor nanoparticles.

1. Introduction

Recent advances in particle synthesis have enabled the generation of geometrically anisotropic Janus particles with high uniformity. Janus particles have both hydrophilic and hydrophobic faces. These particles, similar to molecular surfactants, could potentially function as effective stabilizers for various multiphase systems such as emulsions and foams (Kumar, Park, Tu, & Lee, 2013). The quest for new smart materials with embedded engineered properties and desired functionalities has driven scientists to explore the domain of nanotechnology over the past 20 years (Fathi, Mozafari, & Mohebbi, 2012). In fact, a wide variety of techniques have been developed to produce nanoparticles comprised of both polymers and inorganic materials such as ceramics, metals, oxides, and salts (López-Quintela, Tojo, Blanco, Garcı′a Rio, & Leis, 2004; Rozenberg & Tenne, 2008). Much progress has been made in recent years through the use of microfluidics and microparticles with controlled shape and functionality (Dendukuri, Pregibon, Collins, Hatton, & Doyle, 2006; Nie, Li, Seo, Xu, & Kumacheva, 2006; Serra & Chang, 2008; Sung et al., 2008). At the nanoscale, shape manipulation is known to be much more challenging (Jun, Choi, & Cheon, 2006). One approach to achieve this objective is to prepare particles having either an anisotropic structure or an anisotropic distribution of functional groups. The simplest case of an anisotropic structure can be achieved by dividing the nanoparticles into two distinct parts, each made of a different material or bearing different functional groups (de gennes, 1992a). Recent theoretical studies have demonstrated that the use of spherical particles with region-selective surface modifications (anisotropic surface chemistry) could be a promising route to develop materials with complex shapes and properties (Hong, Cacciuto, Luijten, & Granick, 2006; Iacovella, Horsch, Zhang, & Glotzer, 2005). Spherical beads that enable chemical surface segregation could be used either as dual-functionalized beads or have one hydrophilic and one hydrophobic hemisphere (Schwartz, Contescu, & Putyera, 2004). Various methods have been developed to prepare particles with a

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specific dissymmetrical structure that are called "Janus" particles (de Gennes, 1992b; Fan et al., 2013; Zhang et al., 2013). Moreover, Golestanian, Liverpool, and Ajdari (2007) noted that a special distribution of the active group could lead to unusual physicochemical properties. Several synthetic routes have been exploited to synthesize Janus particles (Perro et al., 2005; Walther & Müller, 2008). Inorganic–organic hybrid Janus particles have attracted much attention due to their multi functions, which are achieved by combining the different properties of these two distinct materials such as the mechanical strength, high modulus, thermal stability of the inorganic component, and the facile processability of polymeric part. Due to these novel properties, research in this area has recently been focused on organic–inorganic hybrid particles (Chen, Yang, Wang, Tan, & Chen, 2008; Laine, 2005; Ohnuma et al., 2009). Methods to synthesize microscale particles have already been developed (Cayre, Paunov, & Velev, 2003).

In this paper, we synthesize nanoscaled, asymmetrically dual-functionalized P(MMA-AA-DVB)/Fe_3O_4 magnetic Janus nanoparticles using a modified facile method. The novelty of the work reported here consists of three points: (i) our method is based on a limited coalescence process, which implies that almost all of the introduced iron oxide particles are adsorbed at the surface of polymeric precursor particles, thus increasing the efficiency of the method; (ii) magnetic Janus nanoparticles with average sizes of 200 nm have been obtained, which offers the possibility of creating materials with a higher level of integrated functionality; and (iii) the synthesized particles exhibit a higher effective content of magnetite in the final magnetic Janus nanoparticles. The size of the magnetic Janus nanoparticles can be controlled by narrowing the size distribution of the P(MMA-AA-DVB) precursor nanoparticles. Indeed, the synthesized magnetic Janus nanoparticles possess pronounced structural anisotropy with tunable surface properties and a higher effective content of magnetite.

2. Experimental

2.1. Materials

Analytical grade ferric chloride ($FeCl_3{\cdot}6H_2O$) was purchased from Tianjin Hongyan Chemical Reagent Factory. Sodium acetate (NaAc) and acrylic acid (AA) were purchased from Fu Chen Chemical Reagent, Tianjin. Trisodium citrate (Na_3Cit) was obtained from Guangzhou Jin Hua Da Chemical Reagent Co., Ltd. Divinylbenzene (DVB) and methylmethacrylate (MMA) were purchased from Fu Yu Chemical Reagent Co., Ltd., Tianjin. Ethylene glycol (EG) was purchased from Jin Shan Hua Shi Chengdu Chemical. Potassium peroxy sulfate (KPS) was obtained from Sinopharm Chemical Reagent Co., Ltd., Shanghai. All the reagents were of analytical grade and used without any further treatment.

2.2. Synthesis of P(MMA-AA-DVB) nanoparticles

P(MMA-AA-DVB) nanoparticles were prepared through soap-free emulsion polymerization with MMA and AA as monomers, DVB as the cross-linker, and KPS as the initiator (Liu, Yang, & Wang, 2007). The synthesis process was as follows: 6 g of MMA, 0.25 g AA, and DVB were added to 80 mL of water in a 150-mL round bottom flask that was properly assembled for heating and attached to a reflux. The amounts of DVB used for the preparation of the precursor particles P-1, P-2, and P-3 are listed in Table 1. The reaction mixture was heated from ambient temperature to 100 °C. KPS was added as the initiator and was prepared by adding 0.05 g to 20 mL of deionized water. The polymerization system was maintained under reflux for an additional 3 h.

Table 1
Formula amounts of cross linkers (DVB) for the preparation of the precursor nanoparticles.

Sample	P-1	P-2	P-3
DVB added (g)	0.90	0.94	1.20

After polymerization, the resultant P(MMA-AA-DVB) nanoparticles were dried in a vacuum oven at room temperature until achieving constant weight.

2.3. Synthesis of P(MMA-AA-DVB)/Fe_3O_4 magnetic Janus nanoparticles

A solvothermal process was used for the preparation of the P(MMA-AA-DVB)/Fe_3O_4 magnetic Janus nanoparticles in the presence of the as-synthesized P(MMA-AA-DVB) nanoparticles (Deng et al., 2005; Liu et al., 2009). First, 0.8 g of P(MMA-AA-DVB) nanoparticles (P-1), 2 g of $FeCl_3{\cdot}6H_2O$, 0.48 g of Na_3Cit, and 3.21 g of NaAc were dispersed in 66.7 mL of EG under ultrasonic irradiation and vigorous magnetic stirring for 30 min until the $FeCl_3{\cdot}6H_2O$ was dissolved completely. The resultant dispersion was transferred to a 100-mL Teflon-lined stainless-steel autoclave and was heated at 200 °C for 10 h. The autoclave was then carefully cooled to room temperature. The as-prepared black products of P(MMA-AA-DVB)/Fe_3O_4 magnetic Janus nanoparticles were dispersed in deionized water in a 200-mL beaker, and the beaker was then placed on an external magnet. After the black material

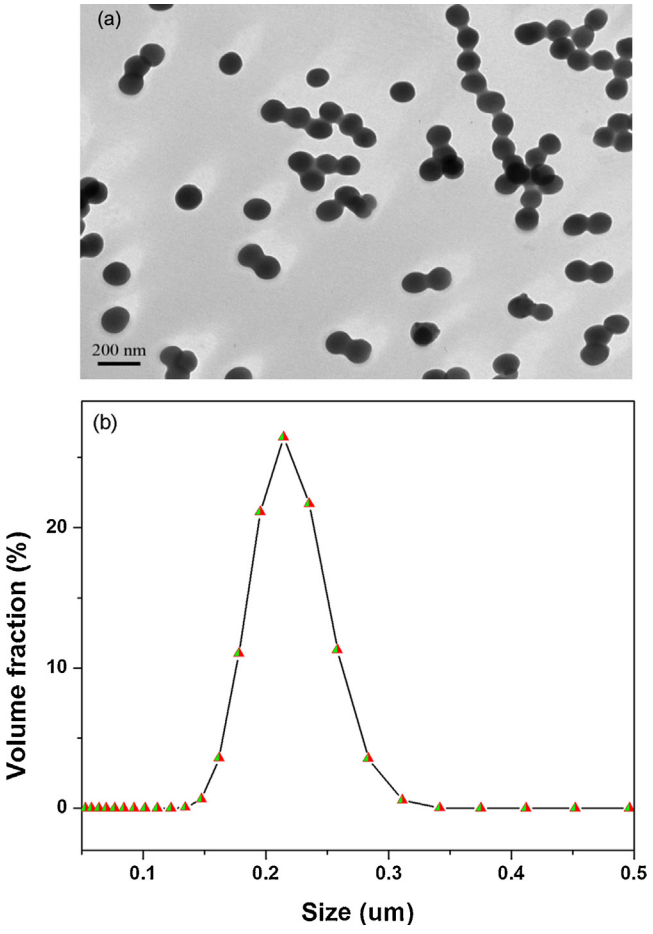

Fig. 1. (a) TEM image and (b) particle size distribution of P(MMA-AA-DVB) nanoparticles (P-1).

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