Colloids and Surfaces A: Physicochem. Eng. Aspects 339 (2009) 100–105

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

# Controlling the heterocoagulation process for fabricating PS–$CoFe_2O_4$ nanocomposite particles

Yunxing Li, Dongping Yin, Zhaoqun Wang*, Bing Li, Gi Xue

*Department of Polymer Science and Engineering, College of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, PR China*

ARTICLE INFO

*Article history:*
Received 10 November 2008
Received in revised form
29 December 2008
Accepted 2 February 2009
Available online 10 February 2009

*Keywords:*
Heterocoagulation
Magnetic nanocomposite
Particle
Cobalt ferrite
Polystyrene

ABSTRACT

Most ordinary polystyrene (PS) microspheres without any surface modification and hard magnetic cobalt ferrite ($CoFe_2O_4$) nanoparticles were, respectively, used as large host particles and small guest particles in a heterocoagulation system. In order to achieve a regular heterocoagulation for fabricating PS–$CoFe_2O_4$ composite particles having tailored morphology, chief attention was focused on controlling over the heterocoagulation process instead of the surface modification of the polymer microspheres. A process was adopted, which included blending the two colloids at pH 1 and then, adjusting the pH value of the blending colloid to an optimal range of 2–4 under a suitable weight ratio of the two kinds of particles. The results of TEM, SEM, ζ-potential, TGA and magnetization measurements have confirmed the high density of coverage of the $CoFe_2O_4$ nanoparticles onto the surface of polystyrene particles.

## 1. Introduction

The composite microparticles with nanostructure often exhibit improved physical or chemical properties, novel functions and are therefore applied in more extensive fields compared with their single-component counterparts [1–3]. Magnetic polymer composite microspheres have been paid extensive attention as a potential functional material suitable for applications in many fields such as biomedicine, microelectronics, information technology, catalysis, coating, magnetic and electromagnetic interference shields, etc. [4–8]. Obviously, advantages deriving from composite hybridization can be made prominent by precise controlling over the structure and morphology such as nano-scale of the magnetic microdomain and narrow size distribution of the composites and so on [9].

Many works have been focused on preparation of magnetic composite particles and control of the structure. In brief, incorporating magnetic compounds with polymer to prepare different composite particles has been carried out by following three strategies. For one strategy, magnetic particles are prefabricated and then embedded in polymer during heterophase polymerizations [10–12], or by adsorbing, grafting polymer chains onto them [13,14]. Before the hybridization, a surface treatment or modification must be performed to purposively enhance affinity between the inorganic particles and the polymer. In the second procedure, magnetic compounds are synthesized via some reactions such as hydrolysis or thermolysis inside or onto pre-formed polymer particles to construct various structures [15–20]. For example, Ugelstad et al. made iron salts directly precipitate inside porous polystyrene particles to form composite particles with a number of magnetic domains [15,16]. Besides, magnetic compounds were synthesized in presence of the pre-formed functional polymer particles and directly precipitated onto their surface to form core–shell composite particles. Apparently, it is difficult to control over the loading yield and form intact magnetic shell so that the resulting particles have usually an uneven surface. The third method is to employ a regular coagulation between two kinds of pre-formed particles, i.e., so-called “heterocoagulation method”, which has become a broadly effective tool to build nanocomposites with tailored morphologies. It is induced with the aid of electrostatic interaction or other between two kinds of particles [21–25]. For instance, Sauzedde et al. [22] synthesized, respectively, $Fe_3O_4$ nanoparticles with negative charge and a series of polymer particles with cationic surface and then made the magnetic particles adsorb onto the polymer particle to form heterocoagulated particles. In order to improve the coagulation effect, cationic groups were introduced into the polymer particles by copolymerization of styrene and some monomers with amido groups such as *N*-isopropylacrylamide and aminoethyl methacrylate hydrochloride or even directly by using poly(*N*-isopropylacrylamide) particles. As a similar process, layer-by-layer (LbL) method based on the electrostatic action is often

---

* Corresponding author. Tel.: +86 25 8161 5138; fax: +86 25 8331 7761.
*E-mail address:* zqwang@nju.edu.cn (Z. Wang).

0927-7757/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.colsurfa.2009.02.001

applied to fabricate the magnetic composite microspheres [21,26]. In the main, these hybrid strategies rely on surface functionalization or modification in order to enhance physicochemical or chemical affinity of polymer and magnetic component. Recently, Wang and co-workers [27] proposed a facile, versatile heterocoagulation strategy based on colloid steric stabilization theory. Without any surface modification, large polystyrene particles and various nanoparticles can self-assemble rapidly to fabricate a series of functional nanocomposite particles.

Herein, most ordinary polystyrene (PS) microspheres without any surface modification and hard magnetic cobalt ferrite ($CoFe_2O_4$) nanoparticles are adopted, respectively, as large host particles and small guest particles in a heterocoagulation system. The PS–$CoFe_2O_4$ nanocomposite particles with uniform morphology are prepared via well controlling over the blend process to induce a regular heterocoagulation. Influence of pH value, weight ratio of the large and small particles on the heterocoagulation process, particle morphology and colloidal stability is investigated.

## 2. Experimental

### 2.1. Materials

Styrene (S) of industrial grade from Jinling Oil Chemical Corp. were purified by distillation under reduced pressure in a nitrogen atmosphere and then washed with 1N NaOH and water to remove polymerization inhibitor before used. Potassium persulfate (KPS) (Nanjing Chemical Reagent Co., AR) was purified by recrystallization from its aqueous solution. $CoCl_2 \cdot 6H_2O$, $HNO_3$ (Nanjing Chemical Reagent Co., AR), $FeCl_3 \cdot 6H_2O$ (Shanghai Jinshan Chemical Co., AR), NaOH (Jiangsu Huakang Chemical Reagent Co., AR), and $Fe(NO_3)_3 \cdot 9H_2O$ (Shanghai Pengzheng Chemical Co., CP) were used as received. Distilled deionized water was employed as polymerization medium and in other experiments.

### 2.2. Preparation of original particles with different size and characteristics

$CoFe_2O_4$ nanoparticles were prepared by hydrothermal coprecipitation method according to Ref. [28]. Aqueous solutions of $CoCl_2 \cdot 6H_2O$ and $FeCl_3 \cdot 6H_2O$ mixtures in an alkaline medium of NaOH were kept boiling for 30 min and then cooled down to room temperature. The separated coprecipitates were washed three times with $HNO_3$ solution and were boiled with a $Fe(NO_3)_3$ aqueous solution. After washed with $HNO_3$ solution, the resulting suspension was dialysed against in water for several days.

Monodisperse polystyrene particles were prepared by emulsifier-free emulsion polymerization. S of 10 g was added into water of 150 mL in a four-neck glass flask equipped with a condenser, mechanical stirrer and nitrogen inlet at 70 °C. After stirring for 10 min, KPS of 0.23 g dissolved in water of 10 mL was added into the system. The polymerization was carried out for 24 h.

### 2.3. Preparation of magnetic polymer composite particles

The magnetic nanoparticle colloid and the polymer particle emulsion were separately diluted with water for adjusting their solid contents to 1 wt.% and 5 wt.%, and their pH value were adjusted to suitable values with $HNO_3$ or NaOH aqueous solution. Then, the polymer emulsion was slowly dropped into magnetic colloid under stirring. After mixed fully by stirring, the pH of the dispersion was slowly adjusted to a certain value with 0.2 N NaOH and kept it for 10–20 min. The dispersion was centrifuged at 3000 rpm for 10 min to remove the unheterocoagulated free magnetic particles and the assembled particles were obtained finally.

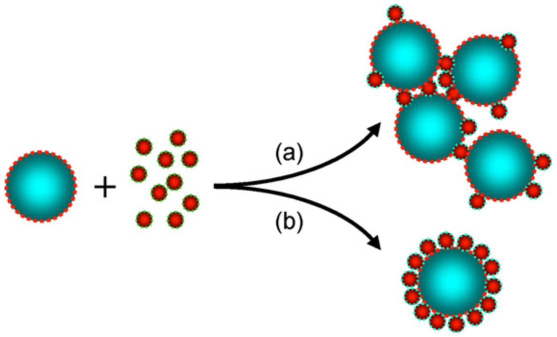
### 2.4. Analysis

$\zeta$-Potential and number-average diameter ($D_n$) of the PS particles, the $CoFe_2O_4$ nanoparticles and the assembled particles were measured by dynamic light-scattering spectroscopy with a model 90 PLUS particle size analyzer (Brookhaven Instruments Corp.) in water dispersion with different pH value at room temperature. Morphologies of the particles were observed by JEM-200CX transmission electron microscope (TEM, Japan JEOL Corp.) and scanning electron microscope (SEM, LEO 1530vp, German LEO Corp.). FTIR spectra of dried particles mixed in KBr pellets were measured by a FTIR spectrophotometer (VECTOR 22, German Bruker Corp.). Magnetization measurements of dried particles were performed at room temperature using vibrating sample magnetometer (VSM, VSM LS307-9309, USA Lakeshore Corp.). Thermal stability of the composite particles was investigated by a Pyris 1 TGA thermogravimetric analyzer (TGA, USA PerKinElmer Corp.) with nitrogen as pure gas at a flow rate of 100 mL/min and heating rate of 20 °C/min.

## 3. Results and discussion

As oppositely charged particles intermix together in a colloid system, disorder conglomeration should be apt to occur that leads to colloidal instability. But then, this conglomerating between the heterogeneous particles can be converted into an available result as long as the heterocoagulation proceeds under well control. The regular heterocoagulation means that the surface of all the relatively large particles in the system is completely covered with numerous small particles as shown in Scheme 1. It is obvious that the system would continuously maintain colloidal stability since both the newly assembled particle groups and the residual small particles in the system have same surface charge. So, the key to successfully assemble the two kinds of particles with opposite charges into composite particles having a distinct shape is how to impel them to the regular heterocoagulation illustrated in Scheme 1(b) and correspondingly, to avoid the phenomenon that the small guest particles may act as a "bridge" between two large particles to lead to a disorderly heterocoagulation as shown in Scheme 1(a). At least, the following two points are taken into account to be in favor of achieving the purpose. In initial, the two kinds of particles are effectively controlled to have similar surface charges and thus, they can stably coexist in same medium before the heterocoagulation process is started. Secondly, there are sufficient small guest particles to meet the need of covering all large particles during the heterocoagulation proceeds.

Fig. 1 shows TEM photographs of $CoFe_2O_4$ nanoparticles and PS particles having diameter of about 15 nm and 400 nm, respectively.



**Scheme 1.** Schematic representation of disorderly (a) and regular heterocoagulation (b) between small and large particles in a blending colloid.