



Preparation of magnetic poly(styrene-co-acrylic acid) microspheres with adsorption of protein



X.Y. Liu^a, S.W. Zheng^a, R.Y. Hong^{a,b,c,*}, Y.Q. Wang^c, W.G. Feng^d

^a College of Chemistry, Chemical Engineering and Materials Science & Key Laboratory of Organic Synthesis of Jiangsu Province, Soochow University, Suzhou 215123, China

^b College of Chemistry and Chemical Engineering, Fuzhou University, Fuzhou 350002, China

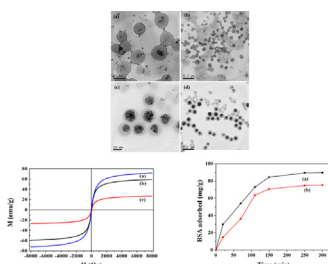
^c Key Laboratory of Environmental Materials and Engineering of Jiangsu Province, Yangzhou University, Yangzhou 225002, China

^d Suzhou Nanocomp Inc., Suzhou New District, Suzhou 215011, China

HIGHLIGHTS

- Poly(St-AA)/Fe₃O₄ microspheres were prepared via miniemulsion copolymerization.
- The effect of crosslinker on the final particle morphology was studied.
- The adsorbed weight of BSA at different adsorption time and pH were investigated.
- The adsorbed weight of BSA was increased with the content of AA.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 16 July 2013

Received in revised form

14 November 2013

Accepted 19 November 2013

Available online 8 December 2013

Keywords:

Poly(styrene-acrylic acid) microspheres

Magnetic microspheres

Magnetic separation

Protein adsorption

ABSTRACT

Monodisperse cross-linked superparamagnetic poly(St-AA)/Fe₃O₄ microspheres with carboxyl group on the surface were prepared via miniemulsion copolymerization. The morphology, composition, magnetic properties, and crystalline structure of the magnetic microspheres were characterized by transmission electron microscopy, vibrating sample magnetometer, X-ray diffraction, Fourier transform infrared spectroscopy and thermogravimetric analysis methods, respectively. The effect of crosslinker during polymerization on the particle morphology was studied. The relationship between the adsorbed weight of bovine serum albumin (BSA) on microspheres and adsorption time and pH was also investigated. Moreover, poly(St-AA)/Fe₃O₄ microspheres displayed excellent adsorption capabilities on BSA and the adsorbed weight of BSA was improved with the increasing AA content in the poly(St-AA)/Fe₃O₄ microspheres.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, the synthesis of functional magnetic nanoparticles (MNPs) has been intensively pursued for their biological application, such as magneto-thermal therapy [1], magnetofection [2], magnetic separation [3], drug delivery and *in vivo* medical

imaging [4–7]. On the basis of the different kinds of MNPs, composite microspheres consisting of an iron oxide core and a polymer shell have attracted more attention for their unique magnetic responsivity [8], good stability and chemically modifiable surface [9]. At the same time, the polymer shell can protect the naked MNPs from oxidation and to magnetically isolate individual particles. Furthermore, polymer shell with abundant functional groups, such as amino, hydroxyl, carboxyl, and thiol groups, are suited to further fictionalization by the attachment of various biological molecules [3,10,11].

Several methods in literature have been proposed to prepare magnetic polymer particles including dispersion polymerization

* Corresponding author at: College of Chemistry, Chemical Engineering and Materials Science & Key Laboratory of Organic Synthesis of Jiangsu Province, Soochow University, Suzhou 215123, China. Tel.: +86 512 6588 2057; fax: +86 512 6588 2057.

E-mail address: rhong@suda.edu.cn (R.Y. Hong).

[12–14], suspension polymerization [15–17], and emulsion polymerization [18–21]. Magnetic materials impregnated into the polymer microspheres by *in situ* formation [22,14,23], core–shell process [24], or copolymerization [25], have also been disclosed. Despite the success of these approaches, with respect to the synthetic methods or the properties of the particles produced, there are still some limitations, such as the poor magnetic response, irregular core/shell structures, low dispersibility, and the use of large amounts of toxic organic solvents, have not yet been well solved, resulting in poor practical application. Furthermore, the flexible strategy to control monodispersity, diameter and narrow size distribution is also crucial to their application.

Herein, we report a flexible and facile synthesis of well-defined magnetic poly(styrene-co-acrylic acid) microspheres with functional carboxyl groups on the surface and high saturation magnetization. First, oleic acid modified superparamagnetic nanoparticles were synthesized through the precipitation of iron oxide in alkaline solution and dispersed into heptanes. Then, the dispersion was miniemulsified into water using sodium dodecyl sulfate (SDS). Subsequently, the magnetite drop was mixed with monomer. Polymerization generated polymer particles with magnetite fully encapsulated. Carboxylic acid-functionalized polymer microspheres were successfully synthesized. The functional polymer shell abundant with carboxyl groups was easily covalently conjugate with various biological molecules. Bovine serum albumin (BSA) was utilized as a model protein to investigate the adsorbed capability of the magnetic microspheres. The effects of weight ratio of DVB to monomer and AA to monomer were also studied.

2. Experimental

2.1. Materials

Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), aqueous ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$), oleic acid were all of analytical grade. Styrene (St), acrylic acid (AA), sodium dodecyl sulfate (SDS) were obtained from National Pharmaceutical Group Corp. (China) and used without further purification. Divinylbenzene (DVB) was obtained from Sigma–Aldrich Co Ltd. Azobisisobutyronitrile (AIBN) was recrystallized in ethanol before use. Bovine serum albumin (BSA) was purchased from Shenggong Biotechnology Co Ltd. (Shanghai, China). Other chemical reagents were of analytical grade and used without further purification.

2.2. Preparation of oleic acid-coated Fe_3O_4 magnetic fluid

The preparation procedure of oleic acid-coated Fe_3O_4 magnetic fluid was previously published [26]. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ dissolved in deionized water was put into a three-neck equipped with a mechanical stirrer under Ar protection. After the mixture was stirred vigorously, some dosage of ammonium hydroxide was added rapidly into the solution. Then some oleic acid was added and the suspension was heated for 1 h. The MNPs modified by oleic acid were transferred *in situ* into the heptanes and stable colloid organic magnetic fluid with a magnetite weight content of 50% was obtained.

2.3. Preparation of poly(St-AA)/ Fe_3O_4 magnetic microspheres

The desired amount of 50 wt% magnetic fluid was added into a three-necked flask with aqueous solution containing 0.5 g SDS with continuous stirring. The mixture was treated by ultrasound for 15 min with 600 W protected by ice-water bath to obtain mag-mini-emulsion. Then, 2 mL St, 2 mL AA and 0.8 mL DVB were added into this mag-mini-emulsion with a mechanical stirrer for 2 h to obtain St/AA mag-mini-emulsion. After the reaction system was

Table 1
Synthesis magnetic microspheres.

Sample (no.)	Magnetic fluid (ml)	St (ml)	AA (ml)	DVB (ml)
1	0	2	2	0.8
2	5	2	2	0
3	5	2	2	0.8
4	5	2	1	0.6
5	5	2	2	0.8
6	5	2	4	1.2

All experiments carry out 70 °C for 24 h.

heated to 70 °C, 0.05 g AIBN were first added to initiate the polymerization and 0.05 g AIBN after 3 h, which was run under a mechanical stirrer at 200 rpm for 24 h Ar gas continuously passed through the flask. After the reaction completed, the resulting magnetic polymeric particles were magnetically separated after the addition of ethanol, and then washed 5 times with 50 mL of ethanol, and finally kept into deionized water at 5 °C. The recipe for preparation of microsphere is given in Table 1.

2.4. Protein adsorption

A protein, BSA was used as an example to test the load capacity of the as-prepared poly(St-AA)/ Fe_3O_4 microspheres. The mixture of a certain amount of magnetic microspheres and 10 mL BSA solution with 0.1 M PBS as solvent was stirred at 37 °C for 2 h. Then the microspheres were magnetically separated and the supernatant was analyzed using UV-visible spectroscopy (Hitachi U-3410) with the absorbance at 280 nm to determinate the concentration of BSA, based on calibration curves.

The amount of protein adsorbed per unit weight of polymer (q_e : g protein/g polymer) was calculated using the follow Eq.:

$$q_e = \frac{(C_0 - C_e)V}{W}$$

where V is the volume of buffer solution (L), C_0 is the initial protein concentration, C_e is the protein concentration at adsorption equilibrium (g/L), and W is the weight of the adsorbent (g).

2.5. Characterization

XRD analysis were performed on an X-ray diffractometer (D/Max-IIIC, Japan) using Cu- α radiation ($\lambda = 1.5406 \text{ \AA}$). Distances between peaks were compared to the JCDPS 5-0664 of International Center for Diffraction Data to determine crystalline structures. Fourier transform infrared spectroscopy (FT-IR) analysis of the samples was taken on a Nicolet Avatar 360 Fourier transform

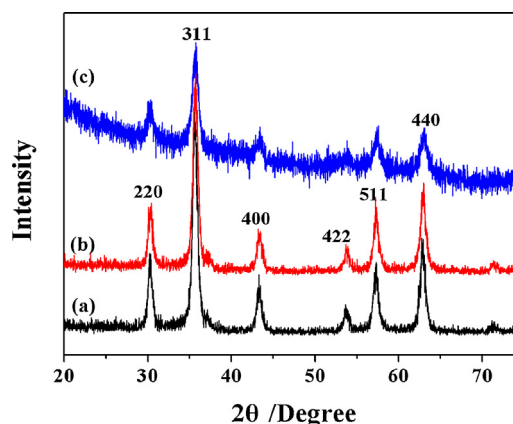


Fig. 1. Powder X-ray diffraction (XRD) patterns of (a) pure Fe_3O_4 MNPs, (b) oleic acid-coated Fe_3O_4 MNPs and (c) sample 5 (poly(St-AA)/ Fe_3O_4).

Download English Version:

<https://daneshyari.com/en/article/593017>

Download Persian Version:

<https://daneshyari.com/article/593017>

[Daneshyari.com](https://daneshyari.com)