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Preparation of silica nanoparticle-armored polyaniline microspheres in a Pickering emulsion

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Abstract

Silica nanoparticle-armored polyaniline microspheres (SNAPMs) were synthesized in a Pickering emulsion for the first time. The products were characterized by SEM, XRD and FTIR. The FTIR results showed that the silica nanoparticles were attached to the surfaces of the polyaniline microspheres by a hydrogen bonding action. The SEM results showed that the amount of the silica nanoparticles added in the emulsion had a distinct effect on the morphology and size of the SNAPMs. A mechanism for the formation of the SNAPMs was discussed. The route reported here may be used for the preparation of other composite nanostructures.

Keywords: Pickering emulsion; Armored microspheres; Silica nanoparticles; Polyaniline

1. Introduction

About a century ago, Pickering found that when some fine solid powders were mixed with water and oily solvent (for example, toluene or kerosene), solid-stabilized emulsion (often referred to as Pickering emulsion) could be obtained even though there were no surfactants used [1,2]. The fine solid powders situated at the surface of the droplets formed a spherical shell and impeded the coalescence when two droplets approached [3,4]. In a long period of time, the applications of Pickering emulsion were mainly limited to food, cosmetics and oil-recovery industries. Pickering emulsions are currently going through a renaissance. For example, Pickering emulsion is proved to be a feasible medium for the synthesis of various nanostructures. Velev and co-workers reported that polystyrene latex particles could be used to self-assemble into supracolloidal structures at the liquid–liquid interface of Pickering emulsion droplets [5]. Gu et al. prepared Ag–Fe_3O_4 heterodimers nanostructures based on a Fe_3O_4 nanoparticle-stabilized Pickering emulsion [6]. Noble et al. synthesized hairy colloidsomes in an emulsion solely stabilized by SU-8 photoresist epoxy resin microrods [7]. In a previous work, we synthesized nanostructures such as polyaniline nanofibers, polyaniline/nano-CeO_2 composites and CdS hollow nanospheres by simply changing the kinds of the nanoparticles used as the stabilizers for the Pickering emulsion [8–10].

Silica nanoparticles are relatively easy to be prepared by Stöber method, chemical vapor deposition or sol–gel route [11,12]. The preparation, stability and theological behaviors of the Pickering emulsion stabilized by silica nanoparticles have been profoundly studied in the pioneering work of Binks and co-workers [4,13]; however, there were rare reports on the synthesis of nanostructures based on the silica nanoparticle-stabilized Pickering emulsions.

In this work, novel silica nanoparticle-armored polyaniline microspheres (SNAPMs) were prepared in a silica nanoparticle-stabilized Pickering emulsion for the first time. The products were characterized by Scanning Electron Microcopy (SEM), Fourier Transformation Infrared Spectrum (FTIR) and X-ray Diffraction (XRD). The mechanism for the formation of the SNAPMs was discussed.

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2. Experimental

2.1. Materials

All reagents are of analytical grade. Ammonium peroxydisulfate, aniline, toluene, ethyl alcohol, acetone and hydrochloric acid were purchased from the Xi'an Reagents Company. Tetraethyl orthosilicate was purchased from the Tianjin Kernel Reagents Center. Aniline was distilled twice under reduced pressure before use, and the other reagents were used without further purification.

2.2. Synthesis of silica nanoparticles

Silica nanoparticles were prepared via an improved Stöber method. In a typical procedure, 1 mL of tetraethyl orthosilicate was added into 10 mL of ethyl alcohol under sonication. After 5 min, 10 mL of 25% ammonium hydroxide and 10 mL of ethyl alcohol were added into the reaction mixture synchronously. Sonication was continued for a further 50 min to get a white turbid suspension. Cycled water was used to maintain the temperature of the sonication bath at 24 °C. After reaction, the reaction mixture was centrifuged. The separated silica particles were washed with water and ethyl alcohol respectively. The washed silica particles were collected and dried under vacuum at 50 °C for 4 h.

2.3. Synthesis of silica nanoparticle-armored polyaniline microspheres (SNAPMs)

0.4 g of silica nanoparticles was dispersed in 50 mL of water using sonication for 3 min. 0.2 mL of aniline was dissolved in 1 mL of toluene, and subsequently this was mixed with the silica dispersion. A stable Pickering emulsion was generated via sonication for 3 min. Then 0.1 g of ammonium peroxydisulfate and 1 mL of 2 mol/L hydrochloric acid were added into the Pickering emulsion under magnetic agitation. The system was polymerized at 10 °C for 5 h under agitation. After a reaction, the mixture was centrifuged. The precipitates were washed with water and acetone for three times respectively, and dried at 45 °C under vacuum for 8 h.

For comparison, the experiments were also carried out by changing the amount of the silica nanoparticles added in the reaction mixture, while maintaining the other conditions.

2.4. Characterization

The type of Pickering emulsion was inferred by observing what happened when a drop of each emulsion was added to a volume of either pure oil or pure water. Water continuous (oil continuous) emulsions were dispersed in water (oil) and remained as drops in oil (water).

The SEM images of the products were collected by a Hitachi S-2700 scanning electron microscope. The FTIR spectra were obtained with a Nicolet Avatar 360 FTIR spectrometer in the 4000–400 cm^{-1} range with 32 scans. The samples were prepared into KBr pellets. The XRD traces were obtained by a Rigaku D/MAX-3C X-ray diffraction meter, using Cu Kα radiation with 40 kV and 20 mA at a 0.2° scan rate (in 2θ).

3. Results and discussion

3.1. Characterization results

The SEM images show that the silica nanoparticles prepared were perfect spheres having an average diameter of about 120 nm (see Fig. S1, Supplementary Material). The silica spheres had good monodispersity with a standard deviation of 7.2%. The results of XRD measurements showed that the silica nanoparticles were amorphous.

Fig. 1 shows the SEM image of the silica nanoparticle-armored polyaniline microspheres (SNAPMs) synthesized in the Pickering emulsion solely stabilized by silica nanoparticles. The diameters of the SNAPMs ranged from 2 μm to 6 μm. The silica nanoparticles were attached to the surfaces of the polyaniline microspheres. To the best of our knowledge, there were no reports on this kind of silica/polyaniline composite nanostructures till now.

Fig. 2 shows the FTIR spectra of the SNAPMs and pure polyaniline. The characteristic peaks of the emeraldine salt form of polyaniline at 1571 cm^{-1} (C═C stretching mode of the quinoid rings), 1471 cm^{-1} (C═C stretching mode of benzenoid rings), 1289 cm^{-1} (C–N stretching mode) and 1121 cm^{-1} (N═Q═N, where Q represents the quinoid ring) appear in the FTIR spectrum of the SNAPMs (see Fig. 2b), showing the formation of polyaniline. The peaks of polyaniline in the SNAPMs shift to the lower wavenumbers comparing to the corresponding peaks of pure polyaniline (at 1584, 1474, 1295 and 1131 cm^{-1} respectively, see Fig. 2a), indicating the formation of hydrogen bonds between the hydroxyl groups on the surface of silica nanoparticles and the imine groups in the polyaniline molecular chains.

3.2. Formation mechanism of the SNAPMs

The results of the emulsion type tests showed that the Pickering emulsions in this work were of oil-in-water type. When silica nanoparticles, toluene (containing aniline) and water (containing ammonium peroxydisulfate) were mixed under sonication, the organic solution was dispersed in the water phase, while silica nanoparticles assembled

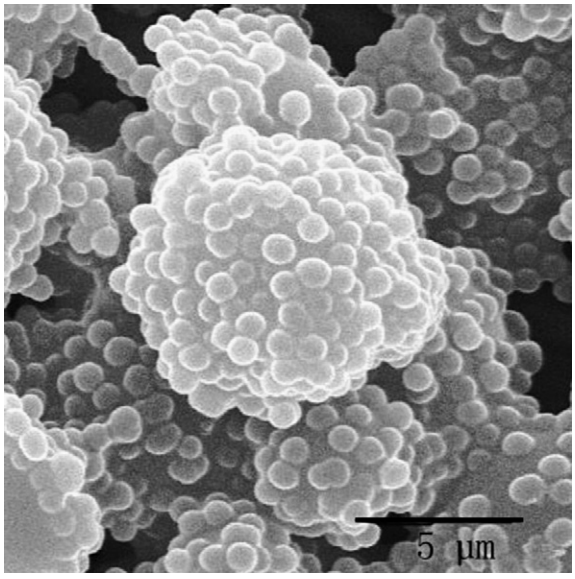

Fig. 1. SEM image of the as-prepared SNAPMs.