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Facile Preparation of Crosslinked Polymeric Nanocapsules via Combination of Surface-Initiated Atom Transfer Radical Polymerization and Ultraviolet Irradiated Crosslinking Techniques

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Abstract A facile approach for the preparation of crosslinked polymeric nanocapsules was developed by the combination of the surface-initiated atom transfer radical polymerization and ultraviolet irradiation crosslinking techniques. The well-defined polystyrene grafted silica nanoparticles were prepared via the SI-ATRP of styrene from functionalized silica nanoparticles. Then the grafted polystyrene chains were crosslinked with ultraviolet irradiation. The cross-linked polystyrene nanocapsules with diameter of 20–50 nm were achieved after the etching of the silica nanoparticle templates with hydrofluoric acid. The strategy developed was confirmed with Fourier transform infrared, thermogravimetric analysis, and transmission electron microscopy.

Keywords Crosslinked polymeric nanocapsules · Template · Surface-initiated atom transfer radical polymerization · Ultraviolet irradiation

Introduction

In recent years, significant progress has been made in the design and fabrication of polymeric micro- and nanocapsules, which have attracted great attention because of a variety of applications such as delivery vesicles for drugs, dyes, or inks; micro-containers for artificial cells and catalysis; protection shield for proteins, enzymes, or DNA; probing single-cell signaling, and so on [1–5].

A large number of physical and chemical strategies have been developed for the preparation of polymeric micro- and nanocapsules. Compared with the other methods such as micelle formation [6, 7], interfacial polymerization [8, 9], and emulsion polymerization [10, 11], the template methods via layer-by-layer technique [12–14] or surface polymerization technique showed the most efficiency in the precise controlling of the inner diameters of the micro- and nanocapsules. The composition of the capsule via the layer-by-layer technique is restricted as polyelectrolytes. Comparatively, the template methods via the polymerization on the surfaces of the templates could extend the polymers or monomers used [15–17] and morphologies of the capsules [18, 19]. After Mandal et al. [15] reported the preparation of the poly(benzyl methacrylate) (PBzMA) microcapsules via the SI-ATRP of benzyl methacrylate on silica microparticles (about 3 μm), the surface-initiated controlled/"living" radical polymerization (C/LRP) technique has attracted more and more attention due to the control over the thicknesses of the shell of the polymeric micro- and nanocapsules [20–23]. In the methods, the polymer chains grafted had been crosslinked with the crosslinkers to improve the stability of the capsules before the etching of the templates. Fu et al. [24] developed the ultraviolet irradiated crosslinking of the polystyrene blocks as solid state in which another poly(methyl methacrylate) (PMMA) layer was needed to avoid the inter-particle linkage.

In the present work, we develop a strategy for the preparation of the crosslinked polymeric nanocapsules based on the widely used sacrificial silica nanoparticle templates via the combination of the surface-initiated atom transfer radical polymerization (SI-ATRP) technique and ultraviolet irradiated crosslinking techniques (Scheme 1).

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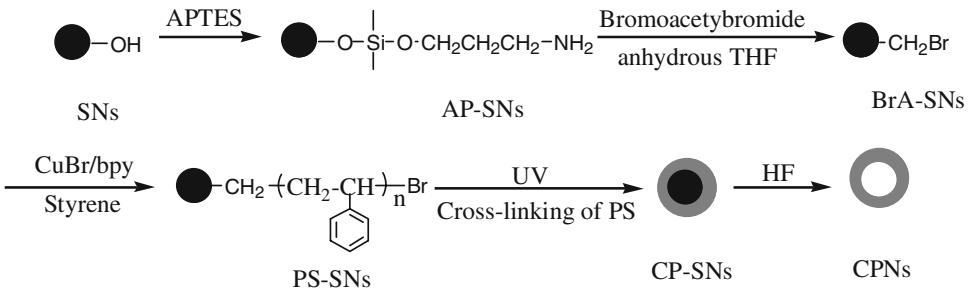
Scheme 1 Schematic illustration of steps for the crosslinked polymeric nanocapsules (CPNs)



The protecting shell was not needed in the strategy developed because the ultraviolet irradiated crosslinking was conducted in the dispersion.

Experimental Section

Materials and Reagents

Silica nanoparticles with average particle size of 10 nm were MN1P obtained from Zhoushan Mingri Nano-materials Co. Ltd., Zhejiang, China. They were dried in vacuum at 110 °C for 48 h before use.

γ-Aminopropyltriethoxysilane (APTES) (Gaizhou Chemical Industrial Co. Ltd., Liaoning, China) was used as received. Bromoacetylbromide was analytical reagent grade and purchased from Acros Organics (Phillipsburg, New Jersey, USA). Cu(I)Br (Tianjin Chemical Co., Tianjin, China) was analytical reagent grade and purified by stirring in glacial acetic acid, filtered, washed with ethanol, and dried. 2,2′-bipyridine (bpy) (A.R., 97.0%) provided by Tianjin Chemical Co., China, was recrystallized twice from acetone. Hexamethylene diisocyanate (HDI) was used as received from Aldrich. Styrene (St, analytical reagent, Tianjin Chemicals Co. Ltd., China) was dried over CaH_2 and distilled under reduced pressure. Triethylamine (TEA) and tetrahydrofuran (THF) were dried by CaH_2 overnight, and then distilled under reduced pressure before use.

Toluene, dimethylformamide (DMF), tetrahydrofuran (THF), ethanol, hydrofluoric acid, and other solvents used were all of analytical reagent grade and obtained from Tianjin Chemical Co., Tianjin, China, and were used without further purification. Distilled water was used throughout.

Polystyrene Grafted Silica Nanoparticles (PS-SNs)

The preparation procedure of the crosslinked polymeric nanocapsules (CPNs) is shown schematically as Scheme 1. The bromo-acetyl modified silica nanoparticles (BrA-SNs) used as the macroinitiators in the surface-initiated atom transfer radical polymerization (SI-ATRP) of styrene were prepared with the same procedures as reported previously [25].

The SI-ATRP of styrene (St) from the BrA-SN macroinitiators was accomplished by the following procedure (Scheme 1): BrA-SN 0.5 g, the monomer (St) 15 mL, 215 mg (1.5 mmol) of CuBr, and 470 mg (3 mmol) of bpy were added into a dry round-bottom flask. The mixture was irradiated with ultrasonic vibrations for 30 min, bubbling with nitrogen (N_2). The reaction proceeded at 90 °C for 10 h with magnetic stirring. N_2 was bubbled throughout the polymerization period. The products, polystyrene grafted silica nanoparticles (PS-SNs), were separated by centrifugation and subjected to intense washing by toluene. Ultrasonication was used in combination with above solvents to remove the impurities, and then dried in vacuum at 40 °C.

Crosslinked Polystyrene Nanocapsules

The dispersion of polystyrene grafted silica nanoparticles (PS-SNs) in dimethylformamide (0.02 g/mL) was irradiated at a distance of about 5 cm for 6 h with a 300 W mercury UV lamp having a maximum emission wavelength at 365 nm. The crosslinked polystyrene grafted silica nanoparticles (CP-SNs) were collected by centrifugation and washed thoroughly with THF. Then the CP-SNs obtained were resuspended in DMF (10 mL) and 24% aqueous HF solution (10 mL) was added. The mixture was stirred at room temperature for 10 h. The resulting products, crosslinked polystyrene nanocapsules (CPNs), were collected by centrifugation, washed thoroughly with THF, and dried under vacuum.

Analysis and Characterization

Elemental analysis (EA) of C, N, and H was performed on Elementar vario EL instrument (Elementar Analysensysteme GmbH, Munich, German). Bruker IFS 66 v/s infrared spectrometer (Bruker, Karlsruhe, Germany) was used for the Fourier transform infrared (FT-IR) spectroscopy analysis in the range of 400–4000 cm^{-1} with the resolution of 4 cm^{-1}. The KBr pellet technique was adopted to prepare

the sample for recording the IR spectra. Thermogravimetric analysis (TGA) was performed with a Perkin-Elmer TGA-7 system (Norwalk, CT, USA) at a scan rate of 10 °C min to 800 °C in N_2 atmosphere. The morphologies of the polymer grafted silica nanoparticles and the polymeric nanocapsules were characterized with a JEM-1200 EX/S transmission electron microscope (TEM) (JEOL, Tokyo, Japan). The samples were dispersed in toluene (PS-SNs) and dimethylformamide (CPNs) in an ultrasonic bath for 5 min, and then deposited on a copper grid covered with a perforated carbon film.

Results and Discussion

The bromo-acetyl modified silica nanoparticles (BrA-SNs), by the bromoacetylation of the surface amino groups of the aminopropyl modified silica nanoparticles (AP-SNs) with bromoacetylbromide (Scheme 1), were used as the macroinitiators in the surface-initiated atom transfer radical polymerization (SI-ATRP) of styrene, using CuBr/2,2′-bipyridine as the catalyst system. After the SI-ATRP of styrene, the PS-SNs, were separated by centrifugation and subjected to intense washing by toluene, and to remove soluble ungrafted polymers. The percentage of grafting (PG, mass ratio of the grafted polymer to silica nanoparticles) of the PS-SNs was found to be 61% according to the TGA analysis (Fig. 1).

The surface polystyrene shells of the PS-SNs were crosslinked by exposing with UV irradiation. It could be seen from TGA curve that the organic proportion of the cross-linked polystyrene grafted silica nanoparticles (CP-SNs) was less than that of the polystyrene grafted silica nanoparticles (PS-SNs), the percentage of grafting of the crosslinked polymer is about 12.5% (Fig. 1). It might be due to the photo-decomposition of polystyrene grafted during the ultraviolet irradiated crosslinking process [26].

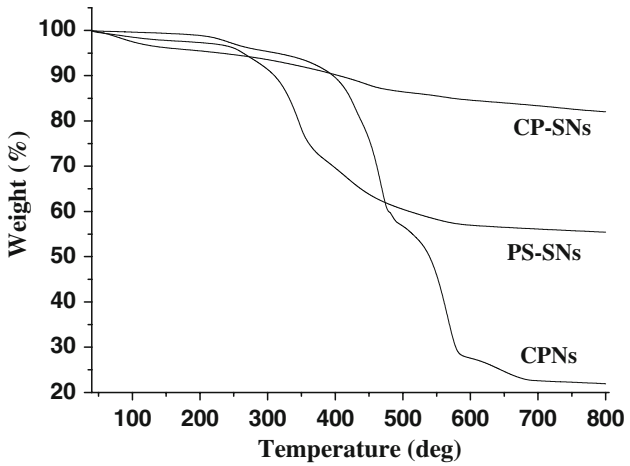


Fig. 1 TGA curves of the nanocomposites and nanocapsule

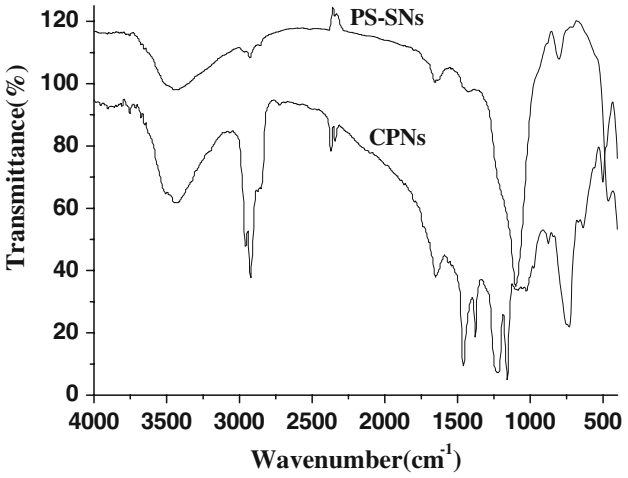


Fig. 2 FT-IR spectra polystyrene grafted silica nanoparticles and crosslinked polymeric nanocapsules

Subsequently the crosslinked polymer grafted silica nanoparticles (CP-SNs) were dispersed in DMF. The suspension was stirred for 10 h at room temperature after HF was added. To validate the complete etching of the silica templates, the FTIR technique was used. In the FTIR spectrum of the products treated with HF, the absorption bands at 1105 cm^{-1} of the Si–O–Si symmetric stretching mode and $\delta_{Si\text{-}O}$ at 464 cm^{-1} disappeared (Fig. 2). It indicated that the silica nanoparticle templates encapsulated in the crosslinked polymer shell had been etched completely. The TGA analysis of the crosslinked polymeric nanocapsules (CPNs) showed a weight loss of about 78% at 800 °C (Fig. 1). The residue might be some carbonized products.

The hollow structure of the crosslinked polymeric nanocapsules (CPNs) obtained could be observed in the TEM analysis (Fig. 3c). The inner diameter of nanocapsules was 20–50 nm which was larger than the sizes of the primary particles (10–20 nm). It might be caused by the fact that the primary particles themselves formed large aggregates due to van der Vaals interparticle attraction and the aggregation was kept somehow during the preparation of the functionalized silica nanoparticles as well as the following polymerization and purification processes [27, 28], as shown in Fig. 3a and b. The collapse of the crosslinked polymeric shells during the etching in DMF maybe due to the lower crosslinking degree [29] and the osmotic pressure between the inner and outer of the nanocapsules.

Conclusions

The crosslinked polymeric nanocapsules (CPNs) with inner diameter of 20–50 nm were successfully prepared via the

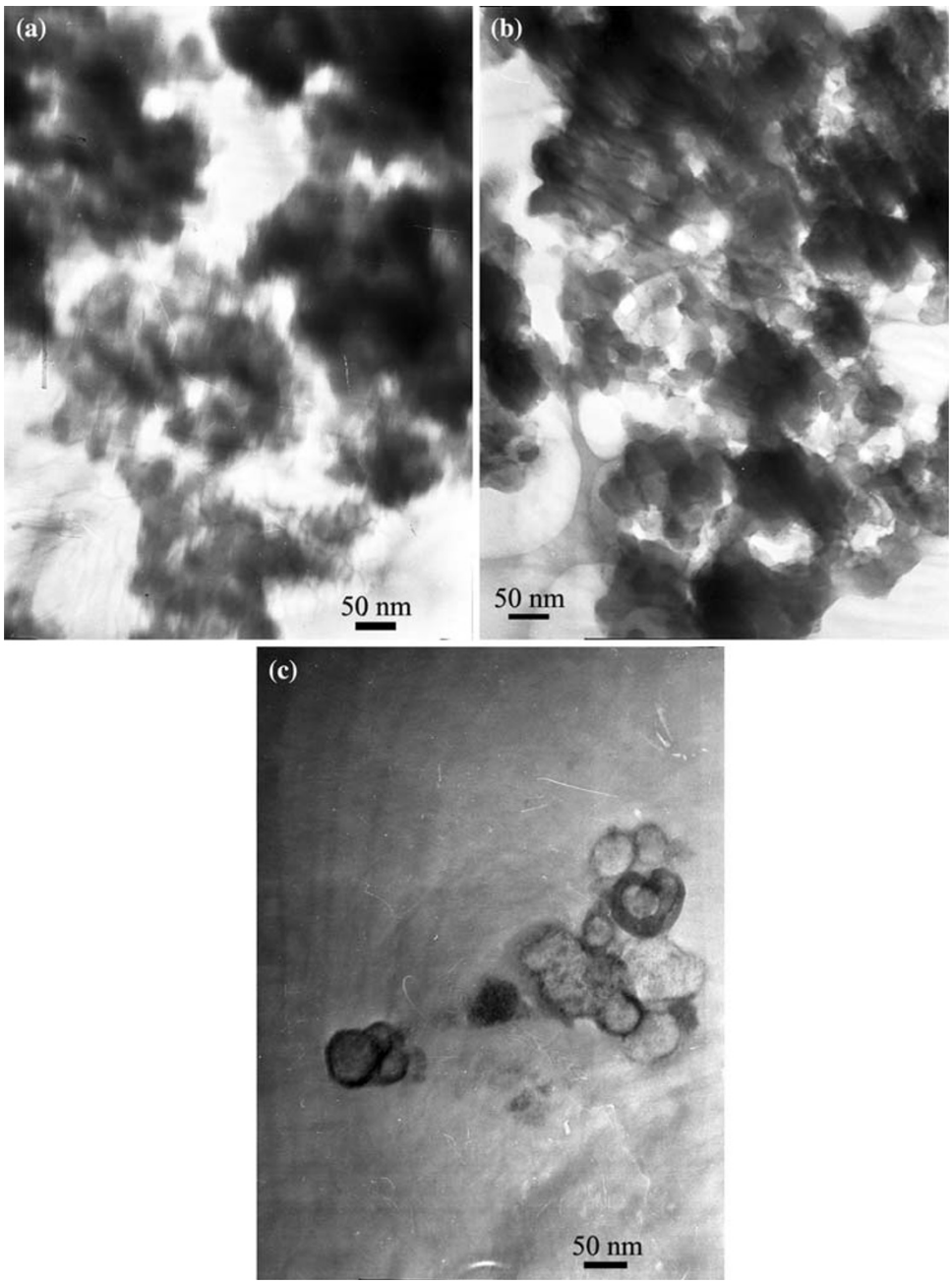


Fig. 3 TEM images of the nanocomposites and nanocapsule

combination of the surface-initiated atom transfer radical polymerization (SI-ATRP) technique and ultraviolet irradiated crosslinking techniques. Functionalized silica nanoparticles (BrA-SNs) were used as the macroinitiators for the SI-ATRP and the sacrificial silica nanoparticle templates. The strategy developed is expected to be extended to other polymers to prepare various crosslinked polymeric nanocapsules.

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