

Polymer Communication

# One-step preparation of organosilica@chitosan crosslinked nanospheres

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## Abstract

A one-step way to prepare organosilica@chitosan crosslinked nanospheres was developed through self-assembly of amphiphilic copolymers synthesized by concurrent grafting polymerization and sol–gel reaction. The core ‘organosilica’ was formed by hydrolysis and condensation of an alkyloxosilane-3-(trimethoxysilyl) propyl methacrylate (TMSPM) that was simultaneously polymerized using chitosan/*tert*-butyl hydroperoxide (TBHP) as redox-pair initiator. The well-defined nanospheres had adjustable sizes below 100 nm, and had not harmful residues impeding medical applications. This synthesis method simplified the preparation of silica@polymer spheres by eliminating the previous core-forming step, and could apply many water-soluble biopolymers containing –NH<sub>2</sub> groups as the shell materials.

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## 1. Introduction

Inorganic–organic core–shell nanospheres have attracted a great deal of attention because of their potential applications in cosmetics, inks, paints, optics and electronics [1,2]. In these studies, silica is the material most often selected as core. The silica-polymer core–shell (silica@polymer) nanospheres have been fabricated by several methods: (a) surface-initiated polymerizations initiated by functional groups on cores, such as –OH, –NH<sub>2</sub>, –CH=CH<sub>2</sub>, and –R–Br, etc. [3]; (b) layer-by-layer adsorption technique, of which oppositely charged species were alternatively deposited on charged cores [4]; and (c) in situ emulsion and dispersion polymerizations employed to directly entrap inorganic nanospheres in the reaction media [5,6]. Despite the success of these approaches, there are still some drawbacks, such as tedious multiple-step syntheses [3,4], necessity of suitable surfactants [4] and very low surface grafting efficiency or encapsulation efficiency [3,5].

Among the various shell polymers, biocompatible and biodegradable polymers [7] have recently been covalently bonded to silica for applications in the biomedical areas, such as passivation of prosthetic devices and implants, and coating of drug-delivery devices [8]. However, these reported

biodegradable shell polymers were limited in aliphatic polyesters, and the use of metal catalysts in most syntheses of biodegradable polyesters resulted in metallic residues impeding medical applications [9]. Therefore, we intended to develop a facile pathway, by which silica core could be covalently covered with suitable polysaccharides and proteins.

Chitosan is a versatile bio-polysaccharide widely applied in medical and pharmaceutical fields. Many hybrids of chitosan and silica have been prepared for applications such as protein chips, heterogeneous catalysis, gene deliveries, and biomedical scaffolds [10–12]. However, silica@chitosan crosslinked nanospheres have not been reported. In this communication, we reported a facile and bottom-up method to synthesize organosilica@chitosan crosslinked nanospheres. The core ‘organosilica’, different from the silica derived from tetraethoxy silane, was developed by hydrolysis and condensation of an alkyloxosilane: 3-(trimethoxysilyl)propyl methacrylate (TMSPM) that was simultaneously polymerized using a *tert*-butyl hydroperoxide (TBHP)/amino group (–NH<sub>2</sub>) initiation system. TBHP/–NH<sub>2</sub> system has been reported as an efficient redox pair, which can generate radicals on the nitrogen atom of –NH<sub>2</sub> at low temperatures [13]. Although some copolymers have been prepared using this redox pair [14,15], the work presented here is the first one employing it to develop hybrid nanospheres.

## 2. Experimental part

Chitosan (medium molecular weight, 77% deacetylation determined by an elemental analysis), acetic acid,

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3-(trimethoxysilyl) propyl methacrylate (TMSPM), and *tert*-butyl hydroperoxide (TBHP, 70% solution in water) were all purchased from Aldrich, and used as received. Freshly deionized and distilled water was used as the dispersion medium.

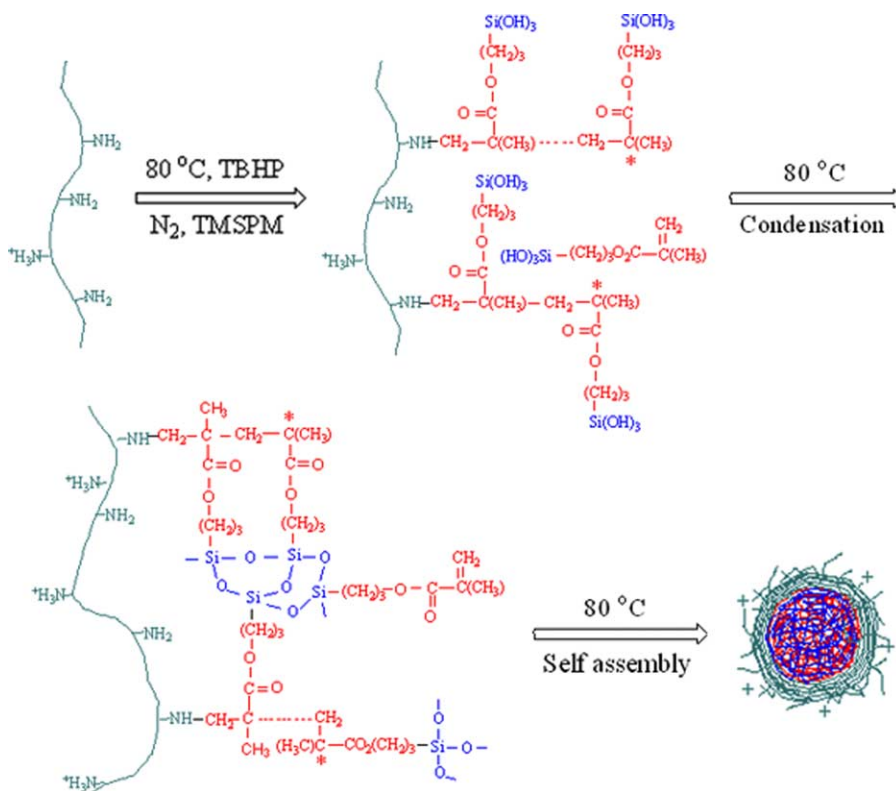
A typical synthesis of organosilica@chitosan crosslinked spheres was described as follows. In a flask equipped with a condenser and a nitrogen inlet, stirred chitosan solution (0.5 wt%, 100 mL) containing acetic acid (0.6 wt%) was purged with nitrogen for 30 min. About 2 mL TMSPM monomer was added at 80 °C and dissolved into water in 5 min. Then 1 mL 20 mM TBHP aqueous solution was added in one time. The mixture was stirred for 4 h under nitrogen. Finally, stable latex was obtained. The organosilica@chitosan hybrid nanospheres were carefully purified by repeated centrifugation, followed by decantation and resuspending in acetic acid solution (0.6 wt%). This procedure was repeated until conductivity of the supernatant was equal to that of the solution used.

The  $\zeta$ -potential of obtained nanospheres was measured with a Brookhaven Zeta Plus Analyzer. FTIR spectra were recorded on an IR spectrometer (Perkin–Elmer, System 2000). The nanosphere morphology was observed under a scanning electron microscope (SEM) (Leica Cambridge Ltd, Stereoscan 440), and their core–shell structures were studied with a transmission electron microscope (TEM) (Philips, CM-20) at an accelerating voltage of 120 kV. Thermogravimetric (TG) curves were recorded by a thermal analyzer Netzsch TGA/DSC (STA 449 C Jupiter), with a heating rate of 10 °C/min and air atmosphere.

### 3. Results and discussion

The one-step synthesis process of organosilica@chitosan crosslinked nanospheres can be described as follows (Scheme 1). In the acidic aqueous solution of chitosan, TMSPM was quickly hydrolyzed into silanols and dispersed into aqueous phase. After TBHP was added, radicals generated on the N atom of chitosan  $-\text{NH}_2$  groups, and the silanols with active vinyl groups were grafted onto chitosan chains. With the poly(vinyl silanol) side chains increasing, in situ condensation between adjacent Si–OH groups preferentially proceeded and microgels formed. As a result of the local gelation, the hydrophobicity of poly(propyl methacrylate) side chains became dominant and the amphiphilic copolymers self-assembled into core–shell sphere with chitosan as shell and organosilica as core. In practice, the transparent solution changed into translucent latex in about 30 min. This period was longer than the time for normal initiation of radical polymerization and shorter than the time for normal gelation of silanols. The fully reacted latex was stable over several months. However, when the reaction was stopped in 1 h, the latex agglomerated during storage. It was due to the large quantity of unpolymerized silanols and uncondensed Si–OH groups. The  $\zeta$ -potential of the stable latex was measured with 1 mM NaCl solution as the dilution fluid. A highly positive  $\zeta$ -potential value +68 was obtained, confirming the presence of chitosan on the sphere shells.

The obtained stable latex was dried and characterized by FTIR spectrometer. In the obtained FTIR spectra (Fig. 1), the absorption of TMSPM C=C at  $1639\text{ cm}^{-1}$  clearly decreased



Scheme 1. Schematic description of the development of organosilica@chitosan crosslinked nanospheres.

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