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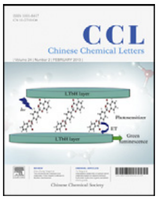

Original article

A facile route for shape-selective synthesis of silica nanostructures using poly-L-lysine as template

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ABSTRACT

A facile method for the shape-selective synthesis of silica nanostructures using a reverse-microemulsion-mediated template (RMMT) technique is reported. In this method, positive poly-L-lysine (PLL) is selected as template due to its configuration diversity. By adjusting pH and concentration, PLL demonstrates various secondary structures containing random coil, α-helix and β-sheet, which result in the formation of silica nanorods, silica nanospheres and silica nanotubes in the reverse-microemulsion system, respectively. Thus, the shape-selective synthesis of silica nanostructures might be achieved by using PLL as structural template in the reverse-microemulsion system.

1. Introduction

Recently, the synthesis of various morphological nanostructures has generated a great deal of interest and efforts in nanotechnology, since they have fascination geometries, chemical and physical properties, and numerous potential applications [1]. In particular, silica nanomaterials have some advantages such as biocompatibility and easy surface modification [2]. Thus, silica nanostructures, especially with particular shape and structure, can be applied to a wide range of areas, including catalysis [3], nanoscale electronic devices [4], bioseparation and biosensing [5], targeted thrombolysis [6], and controlled release [7]. Up to now, the methods for preparation of most silica nanostructures with various sizes, shapes, and structures, were mainly focused on the use of templates. Several soft templates, such as surfactants [8], polypeptides [9] and block copolymers [10], have been recently employed to form well-defined silica nanotubes. Meanwhile, some inorganic materials, including calcium carbonate [11] and gold nanorods [12], have been used as hard template to synthesize silica nanorods or nanotubes. Moreover, hollow and mesoporous silica nanospheres have also been synthesized by polymeric micelles and poly-L-lysine (PLL) as template [13–16]. Such template-directed methods can produce nanostructures with monodisperse diameters and lengths. However, the strict control of the distinctive geometry for silica nanostructures remains a great challenge with one template for potential applications.

Herein, we report a facile route for the shape-selective synthesis of silica nanostructures by using a reverse-microemulsion-mediated template (RMMT) technique. In this method, PLL is selected as structural template due to its configuration diversity. The shape-selective synthesis of silica nanostructures can be easily operated through controlling secondary structure of PLL.

2. Experimental

Poly-L-lysine (PLL) was purchased from Beijing Dingguo Inc. Tetraethyl orthosilicate (TEOS) and Triton-X 100 (TX-100) were obtained from Sigma Aldrich. Cyclohexane, *n*-hexanol and NH_4OH were purchased from Xilong Reagent Inc.

PLL was dissolved in aqueous solution with various pH values. Subsequently, the secondary structures of PLL were measured by the circular dichroism (CD) spectra. TEOS as monomer precursor product was directly used to prepare different morphological silica nanoparticles using water-in-oil microemulsion technique as previously reported [17]. Briefly, the microemulsion was prepared by mixing cyclohexane, TX-100, *n*-hexanol and water (15–20:3–5:3–5:1–3). An aqueous solution of PLL was then added into the mixture. In the presence of TEOS, a polymerization reaction was initiated by adding NH_4OH and the mixture was stirred for 24 h.

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Then the nanoparticles were isolated by ethanol, followed by centrifuging and washing with ethanol and water for several times to remove residual surfactant molecules. The morphology and diameter of the nanoparticles was measured by transmission electron microscopy (TEM).

3. Results and discussion

The overall procedure for synthesizing variously morphological silica nanostructures is illustrated in Scheme 1. Silica nanostructures were fabricated with PLL as template in a reverse microemulsion system. Rod-like, tubular and spherical reverse micelles were formed from surfactant and PLL in an aqueous solvent; the hydrolysis process occurred at the water/oil interface of the reverse micelles, producing variously morphological silica nanostructures. Under low pH condition, PLL showed random coil structure because of the electrostatic repulsion between the neighboring amine groups on the PLL chains. An aqueous solution of PLL (average MW 100,000) was added into a cyclohexane/TX-100/*n*-hexanol/water mixture at room temperature to form rod-like reverse micelles. TEOS was used as the silica precursor and introduced into the mixture. Silica was quickly formed at the water/oil interface of the rod-like reverse micelles after addition of aqueous NH_4OH. The repulsion between the neighboring amine groups could be decreased by increasing the pH value of the aqueous PLL solution, which induced the structure transition from random coil to α-helix of PLL. The morphology of reverse micelles thus tended to become nanospheres as a result of secondary structure transition of PLL, which result in the formation of silica nanospheres. The secondary structure of PLL also changed from α-helix to β-sheet, and thus the morphology of reverse micelles correspondingly transformed to nanotubes with increasing concentration of aqueous PLL at pH 11. Silica nanotubes were thus synthesized.

Here, we investigated structural transition of PLL as a function of concentration and pH through the CD measurements. Fig. 1a showed that three spectra for PLL at a concentration of 6 mg/mL, obtained at pH 1, 6.8 and 11. At pH 1, the CD spectrum demonstrated a positive absorption peak at 216 nm, indicating that PLL presented random coil structure. After adjusting pH value to 11, a negative absorption peak at 218 nm appeared in CD spectrum, which confirmed the β-sheet structure of PLL. While at pH 6.8, PLL showed a mixed structure of random coil and β-sheet. In addition, we also investigated structural transition of PLL (1 mg/mL) at pH 1, 6.8 and 11 (Fig. 1b). The CD spectrum at pH 1 was representative of random coil. While CD spectrum at pH 11 demonstrated two negative adsorption peaks at 206 nm and

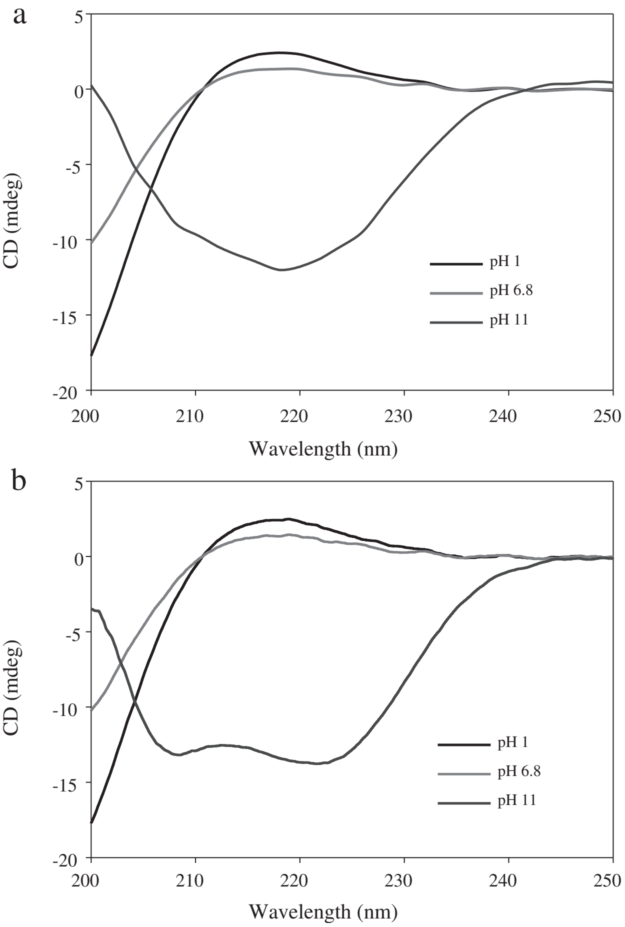
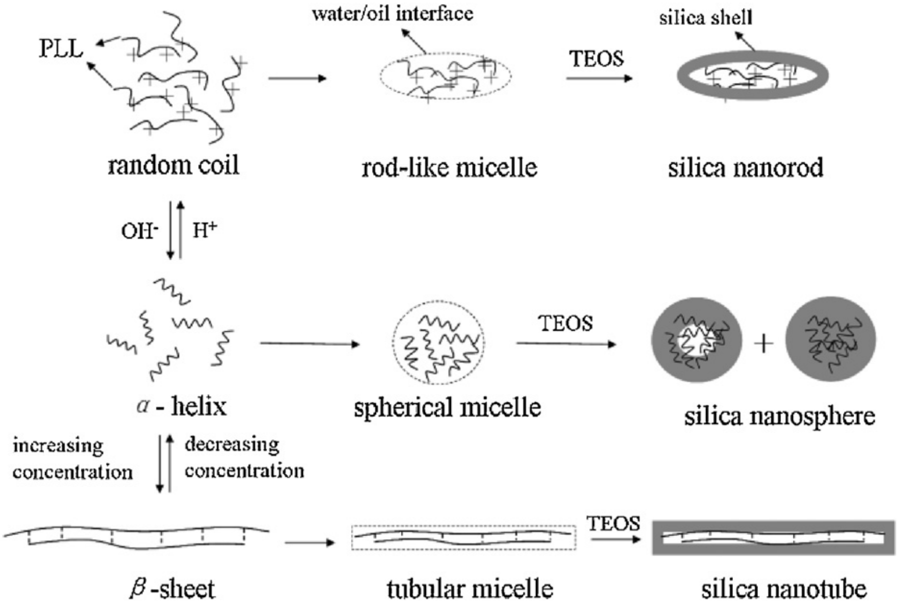


Fig. 1. CD spectra of 6 mg/mL (a) and 1 mg/mL (b) PLL solution under various pH values.



Scheme 1. Schematic illustration of shape-selective synthesis of silica nanostructures.