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Mesoporous silica-coating of gold nanorods by a templated method

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Abstract

Mesoporous silica with tunable morphology, pore architecture and crystallinity was successfully coated on gold nanorods by a template method based on the self-assembly of anionic surfactants with inorganic precursors. Varying the molar ratio of acid to surfactant or the volume ratio of ethanol to water resulted in products with different shapes, ranging from rods to spherical particles. A phase transformation of the mesoporous silica shell from 2D hexagonal to 3D cubic occurred due to an increased acid/surfactant ratio. Increasing the proportion of ethanol also gradually caused the disappear of 2D hexagonal symmetry of silica. The charge density matching relationship and solution polarity induced by varied reaction composition are believed to be the driving forces for the change of morphology and mesostructure.

Keywords: B. Electron microscopy; B. Nanocomposites; B. X-ray methods; Mesoporous silica-coating of Au nanorods; Morphological changes

1. Introduction

Since first synthesized by Mobil scientists in 1992 [1,2], surfactant-templated mesoporous silica materials have shown great perspective as catalysts [3], adsorbents [4], nanoreactors, and drug carriers [5,6], due to their high surface area, tunable pore size and controllable mesostructure [7–9]. Reaction conditions, especially pH of solution [10], composition of the acidic media [11], and amount of alcohol [12], are believed to have crucial impacts on the morphology, porosity and size of surfactant-templated mesoporous silica. By tuning reaction conditions, mesoporous silica nanostructures with diverse shapes and mesostructural symmetries have been prepared [13–17].

In the past decade, the synthesis of mesostructured silica coated gold nanorods (Au@MS) has been greatly developed. By combining the unique optical and physical properties of gold and the ordered structure of mesoporous silica, Au@MS nanostructures have opened new possibilities in optics, biomedicine, biosensing and catalysis [18–20]. Currently, to easily and precisely coat Au nanorods (AuNRs) with silica shell of desired morphology and mesostructure is still a big challenge, and the template method with anionic surfactant, despite of being a powerful way to prepare mesoporous silica, has yet hardly been applied on Au surface.

Herein, we successfully coated mesoporous silica on gold nanorods by a template method. The mesoporous silicate shells with different morphology, pore architecture and crystallinity were fabricated by tuning the molar ratio of reaction mixture. The effects of molar ratio of HCl/surfactant and volume ratio of ethanol/water were particularly investigated, which resulted in both morphology and mesostructure of the silica shell were dramatically changed.

2. Experimental

Gold nanorods (AuNRs) were first prepared using a seed-mediated growth procedure as described in reference [18]. Au@MS nanoparticles were prepared via a template method. For a typical process [21], the as-synthesized AuNRs (0.90 nM, 3 mL) were washed twice with water and then centrifuged at 11,500 rpm for 15 min. After the AuNRs were dispersed in 2 mL water, 20 mg (0.062 mmol) of N-miristoyl-L-alanine sodium salt (C_{14}-L-AlaS) was dissolved in the above solution. When the solution became

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transparent, 74 μL of 0.1 mol/L aqueous HCl was added under stirring. An hour later, a mixture of tetraethylorthosilicate (TEOS, 38.5 mg), 3-aminopropyltrimethoxysilane (APS, 6.86 mg) and anhydrous ethanol (39 mg) was added into the solution under stirring at room temperature. In this process, anionic surfactant C_{14}-L-AlaS and partially neutralized free amino acid N-acyl-L-alanine formed layers around the AuNRs, which served as template. APS was served as co-structure-directing agent, which co-condensed with TEOS to form mesoporous structure in the resultant silica shell. The molar ratio of C_{14}-L-AlaS/HCl/APS/TEOS/H_2O in this case is 1.0: 0.14: 0.43: 3: 1795. By varying the molar ratio of HCl/C_{14}-L-AlaS and the volume ratio of ethanol/H_2O, mesoporous silica shells with different morphology and symmetry can be readily fabricated. The reaction mixture was kept at room temperature for 2 h and at 80 °C for another 15 h under static conditions. The product was cooled to room temperature and washed three times with ethanol.

Synthesized nanoparticles were characterized by TEM, SEM, SAXRD, and WAXRD measurements. Transmission electron microscopy (TEM) characterization was operated with a Tecnai

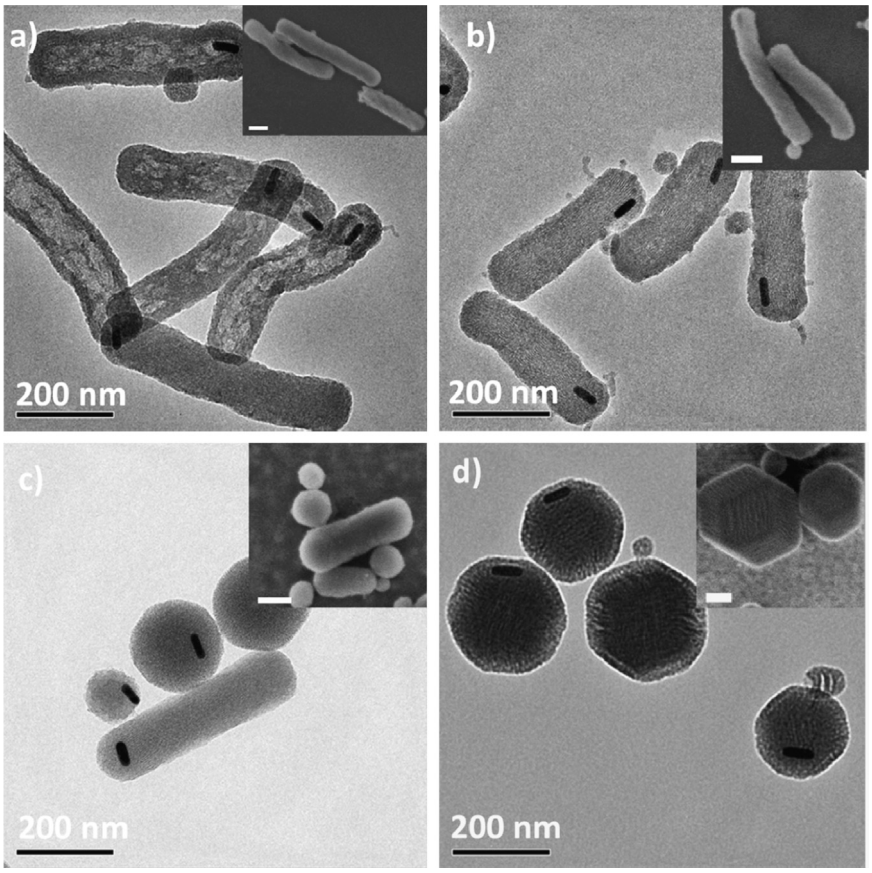

Fig. 1. TEM images of (a) S1, (b) S2, (c) S3 and (d) S4 synthesized with the HCl/C_{14}-L-AlaS molar ratios of 0.06, 0.14, 0.20 and 0.30, respectively. SEM images of S1–S4 (inset in a–d), the scale length is 100 nm.

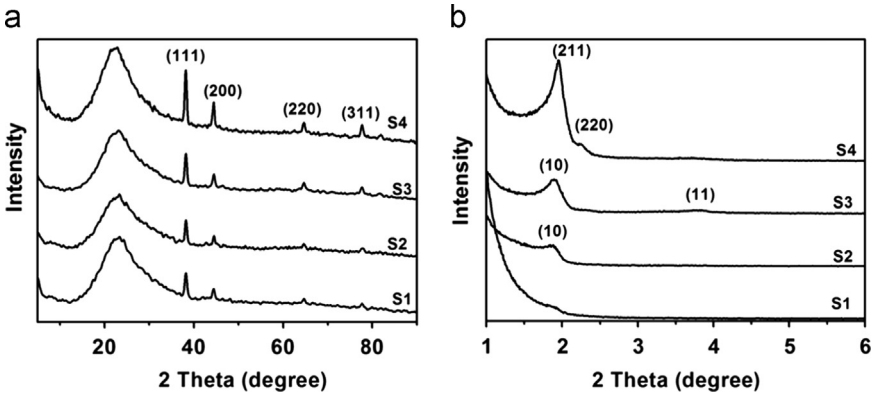

Fig. 2. (a) Wide-angle XRD patterns and (b) small-angle XRD patterns of S1, S2, S3 and S4. Wide-angle XRD patterns indicate the face-centered cubic phase of Au and small angle XRD patterns can clearly represent the microscopic structure of mesoporous silica of S1–S4.