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Synthesis of PSS-capped triangular silver nanoplates with tunable SPR

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ABSTRACT

Poly(styrene-4-sulfonate) (PSS) was used as a capping agent to directly synthesize triangular silver nanoplates. The in-plane dipole surface plasmon resonance (SPR) peak of the resultant nanoplates can be tuned from ca. 580 nm to ca. 725 nm by decreasing the PSS concentration (C_{pss}) and is almost a linear function of C_{pss}.

1. Introduction

Silver nanostructures have received much focus recently due to their unique SPR properties and significant application prospects including biosensing and chemosensing. Silver nanostructures are also promising from their potential application as active substrates for surface-enhanced Raman scattering, near-field optical probes and biomedical imaging [1–9]. For triangular silver nanoplates, while there have been few reports with regards to their application [10], a number of diverse shape-controlled synthesis methods have been developed, including photo or thermally induced transformation, microemulsion and chemical reduction method [11–16]. In these synthesis methods, bis(p-sulfonatophenyl-l)phenylphosphine dehydrate dipotassium, trisodium citrate (TSC), cetyltrimethylammonium bromide, poly(vinyl pyrrolidone) often serve as capping agents to prevent aggregation of the triangular silver nanoplates. The electronegative polymer, poly(styrene-4-sulfonate) (PSS), is an excellent capping agent that can be used to modify nanoparticles functionally for biosensing and chemosensing applications [17,18]. While PSS has not yet been used to modify Ag triangular nanoplates, it is expected that PSS will extend greatly the applications of silver nanoplates. Herein, Ag triangular nanoplates were successfully fabricated directly using PSS as a capping agent in the aqueous phase at room temperature for the first time. Unexpectedly, the in-plane dipole SPR peak of the resultant silver nanoplates is almost a linear function of C_{pss}.

2. Experimental

2.1. Materials and reagents

PSS, trisodium citrate, $NaBH_4$, and H_2O_2 were obtained from Alfa-Aesar.

2.2. Preparation of triangular silver nanoplate

The silver nanoplates were synthesized by reducing $AgNO_3$ (0.1 mM, 50 mL) with $NaBH_4$ (70 mM, 300 (L) in the presence of TSC (30 mM, 3 mL), H_2O_2 (60 (L of 30 wt.%) and PSS (3 mL) under magnetic stirring at room temperature (about 25 °C) in the dark.

3. Results and discussion

In our experiments, a study was focused on the effect of PSS concentration on the synthesis process of nanoplates. The C_{pss} was altered from 5 mg/ml to zero, while keeping the other experimental conditions fixed. After some time, the mixed solution appeared with different colors, which varied with different concentrations of PSS, namely, blue for C_{pss} = 0, and then deepened gradually when C_{pss} was increased from 0.5 to 3 mg/ml, gray for C_{pss} = 4 mg/ml and pale yellowish green for C_{pss} = 5 mg/ml, respectively, as shown in Fig. 1. The color change occurred within 2 min in the absence of PSS, but was prolonged in the presence of PSS, probably because the capping of PSS extended the time taken for Ag^+ to diffuse into the Ag crystal nucleus [19].

The in-plane dipole SPR band has been shown to be a good indicator of general nanoplate architecture [20]. Therefore, the UV–vis spectra of these species provides a quick evaluation of the

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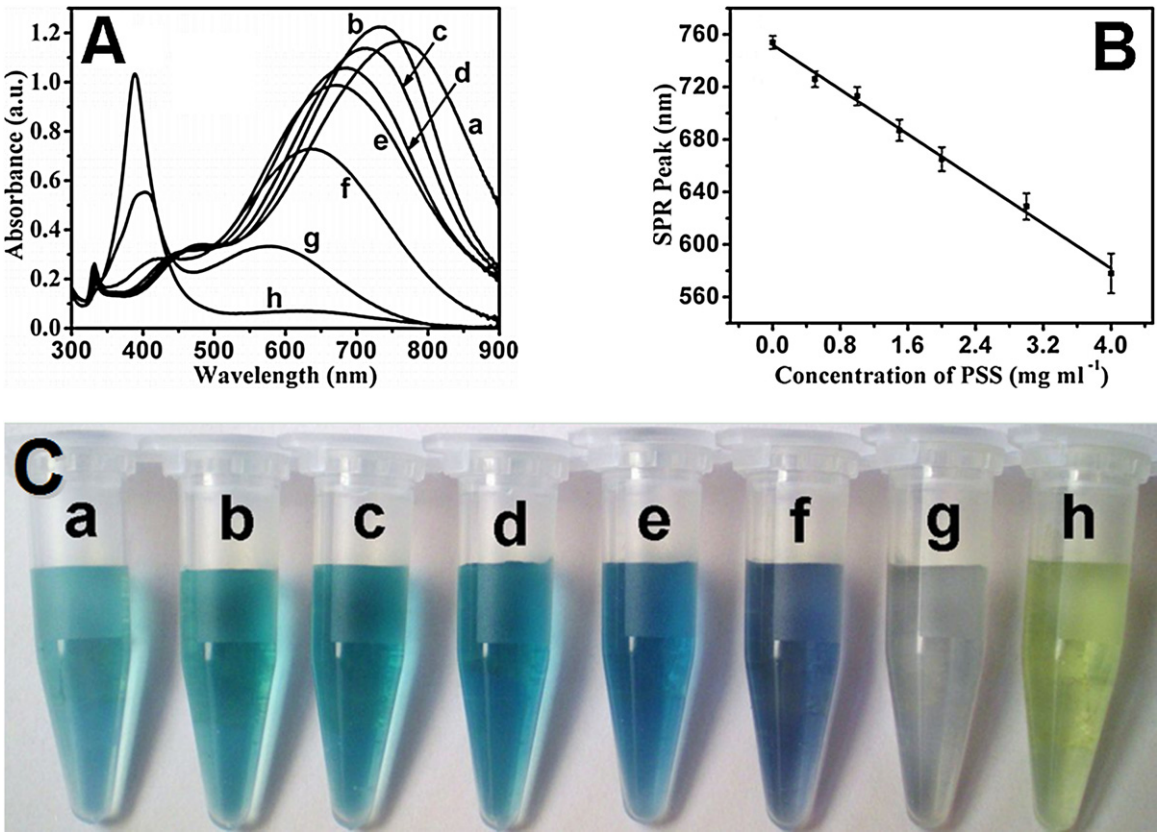

Fig. 1. (A) The UV–vis spectra of as-prepared silver nanoplates in different C_{pss}, from a to h, corresponding to 0, 0.5, 1, 1.5, 2, 3, 4, and 5 mg/ml, respectively. (B) The working curve of in-plane dipole SPR peaks of nanoplates vs. C_{pss} (0–4 mg/ml) added to the sample. (C) The photographs of as-prepared silver nanoplates in different C_{pss}, from a to h, corresponding to 0, 0.5, 1, 1.5, 2, 3, 4, and 5 mg/ml, respectively.

nanoplates formed. As shown in Fig. 1A, a–f, each spectrum of the as-prepared colloids exhibits three SPR bands located at approximately 755–630 nm, 470–415 nm and 330 nm, which are ascribed to the in-plane dipole, the in-plane quadrupole and the out-of-plane quadrupole resonance of the triangular silver nanoplates, respectively. These values are similar to those already reported for triangular nanoplates [21,22]. For Fig. 1A, g, the bands at 580 nm and 330 nm are attributed to the in-plane dipole and out-of-plane quadrupole SPR modes of the triangular silver nanoplates, respectively, while the band at 403 nm is considered to be due to the SPR signal for a mixture of Ag spherical nanoparticles and triangular nanoplates. For Fig. 1A, h, the SPR bands of the Ag triangular

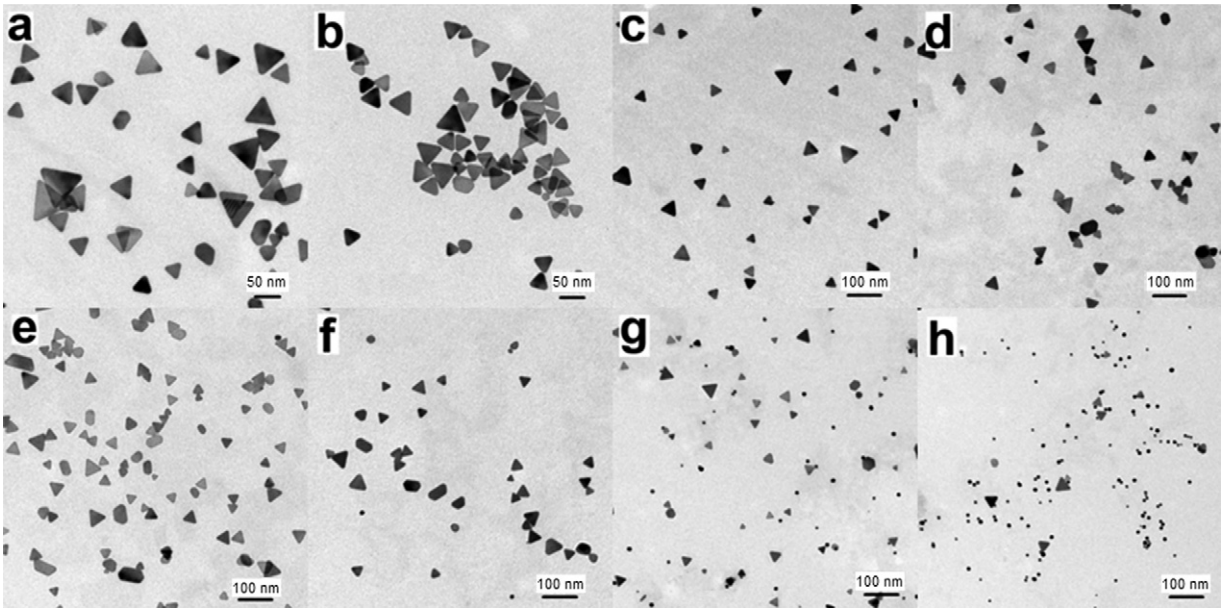

Fig. 2. TEM images of as-prepared silver nanoplates in different C_{pss}, from a to h, corresponding to 0, 0.5, 1, 1.5, 2, 3, 4, and 5 mg/ml, respectively.