

Communications

H₂O₂-Assisted One-pot Synthesis of Silver Nanoplates Using Polymeric Materials

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The synthesis of plate-like silver nanomaterials, or silver nanoplates (AgNPLs), has been a highly fascinating issue for the past decade since the first photochemical synthesis of silver nanoprisms.^{1,2} To date, several other synthetic developments for AgNPLs have been also reported, such as ligand-assisted chemical reduction,³⁻⁵ and electrochemical,⁶ or sonochemical reactions.⁷ Among them, seed-mediated growth method is particularly attractive because it is capable of controlling the size of AgNPLs, and is highly reproducible. Despite its versatility, however, the method should suffer from major drawbacks such as (1) complicated multi-step procedures composed of (a) seed preparation and (b) its growth, and (2) essential time duration between those steps.⁸ To overcome these obstacles, recently a few one-step syntheses for AgNPLs have been reported.⁹⁻¹¹ Further development of more advanced one-step synthetic methods, however, is still substantially required.

Herein, we present a simple, convenient, and facile one-pot synthesis of AgNPLs using water-soluble polymers and hydrogen peroxide (H₂O₂) (Figure 1(a)). Importantly, the AgNPLs synthesized by this method are highly anisotropic and monodisperse with negligible number of impure spherical nanoparticles. Two main advantages of this method are important: (1) the shape control of the AgNPLs by polymers, and (2) enhanced monodispersity by H₂O₂.

The synthesis began with the preparation of the aqueous reaction mixture (5.65 mL) containing sodium citrate (4.42 mM), NaBH₄ (0.53 mM), polymer (22.1 mg/L), and H₂O₂ (18.4 mM). To investigate the effect of the polymer on the shape control, we employed 4 different types of water-soluble polymers: chitosan, poly(sodium 4-styrenesulfonate) (PSSS, M.W. = 1,000,000), polyvinylpyrrolidone (PVP, M.W. = 29,000), and Pluronic F108 (Figure 1(a)). To this mixture, an aqueous Ag⁺ solution (1.25 mM, 2 mL) was added drop by drop, resulting in color changes of the solution (colorless → yellow → purple → blue, see Supporting Information). Importantly, the color changes of the mixture indicate the formation of nanosized metallic silver materials, and their subsequent structural evolution, based on surface plasmon resonance. For example, the initial appearance of yellow is attributed to the formation of tiny isotropic silver nanoparticles, which further changed to blue owing to their growth

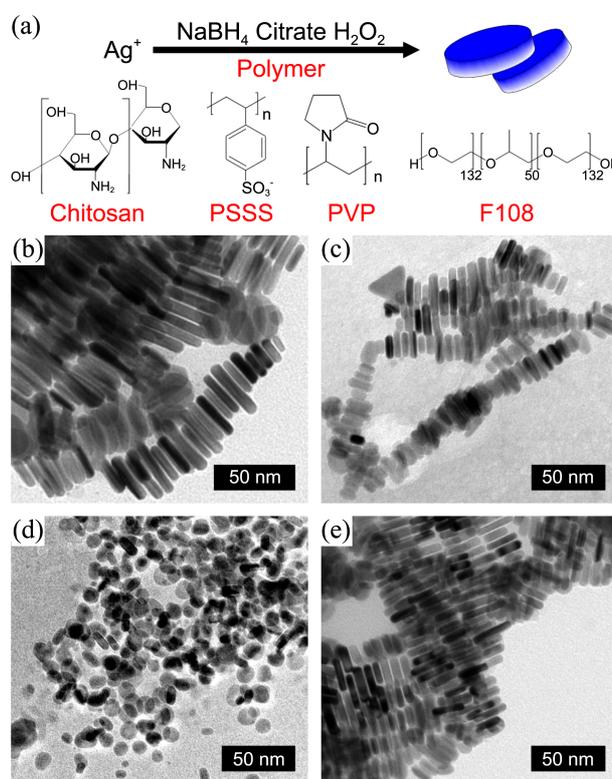


Figure 1. (a) A schematic illustration of the synthesis of AgNPLs. The molecular structures of polymers used for the synthesis are drawn. (b) A TEM image of the AgNPLs synthesized with chitosan, (c) PSSS, (d) PVP, and (e) F108.

into larger anisotropic nanoparticles with various shapes and sizes, depending on the polymers employed. For the size increase of the AgNPLs, the growth is allowed to take place for additional 48 h.

The structural properties of the synthesized AgNPLs with different polymers were analyzed by transmission electron microscopy (TEM). The AgNPLs synthesized with chitosan were about 50 nm in diameter and 5 nm in thickness (Figure 1(b)). The AgNPLs synthesized with PSSS were smaller (30 nm in diameter and 5 nm in thickness), indicating the size and shapes of the resultant AgNPLs can be controlled by the types of polymers employed (Figure 1(c)). The control of the

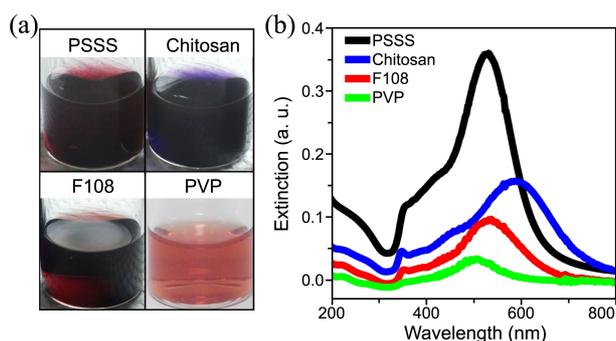


Figure 2. (a) Solutions containing the AgNPLs synthesized with PSSS, chitosan, F108, and PVP. (b) UV-vis spectra of the AgNPLs (Agilent 8453).

shapes and sizes of the AgNPLs was also clearly demonstrated with the AgNPLs synthesized with PVP, which were the smallest and thinnest (Figure 1(d)). We also obtained highly monodisperse AgNPLs with F108 (Figure 1(e)). Importantly, the isotropic spherical nanoparticles, the most common side product in the synthesis of AgNPLs, were rarely observed in all 4 cases, but were obtained in a majority without the polymers (data not shown), indicating the strong capability of the method to regulate the shape of the resultant nanoparticles. In fact, the essential role of the polymers to control the shape of the AgNPLs was also demonstrated in the seed-mediated growth method.⁵

In addition to the shape-directing role of the polymers, the function of H₂O₂ as an oxidant also contributed significantly to the high quality of the AgNPLs. Because H₂O₂ ‘kills’ the less protected isotropic nanoparticles preferentially at the early stage of the synthesis, only the remaining anisotropic nanoparticles grow into larger AgNPLs.^{8,9,11,12} In fact, we observed only isotropic spherical nanoparticles ($D < 5$ nm) without H₂O₂ (data not shown). Although this mechanistic explanation has not been spectroscopically evidenced, it has been still the most persuasive and rational proposal.⁸

As previously discussed above, the final AgNPL solutions exhibit distinctive colors depending on their shapes and sizes that were determined by the polymers (Figure 2(a)).¹³ The optical properties of the AgNPLs were further analyzed by obtaining their UV-vis spectra (Figure 2(b)). Three important analyses can be discussed. (1) All the spectra exhibit a local maximum extinction at ~350 nm, indicative of the transverse plasmon mode of the AgNPLs. (2) The larger the AgNPL is, the longer the wavelength at which the maximum extinction (from the longitudinal plasmon mode) takes place is. For example, the largest AgNPLs synthesized with chitosan (Figure 1(b)) exhibit the maximum extinction at ~600 nm, the longest wavelength among the 4 spectra. (3) PVP, the most popular polymer used for the synthesis of anisotropic silver nanomaterials including AgNPLs, unexpectedly does not show satisfactory results, in terms of yield and aniso-

tropy. For example, the AgNPLs synthesized with PVP exhibit the lowest maximum extinction which is partially associated with the low yield, and the very broad spectrum indicating the presence of non-uniform nanoparticles.

In conclusion, we have developed a simple, yet powerful method for the one-pot synthesis of AgNPLs using H₂O₂ and various polymers. The effect of H₂O₂ and polymers has been investigated and demonstrated to determine both the structural and corresponding optical properties of the AgNPLs. Considering the crucial roles of both H₂O₂ and polymers for the anisotropic growth of the AgNPLs, this work could be further extended to the synthesis of other types of anisotropic gold and silver nanomaterials.¹⁴⁻¹⁷

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Supporting Information. A short movie showing the synthesis of AgNPLs.

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