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Shape transformation of silver nanospheres to silver nanoplates induced by redox reaction of hydrogen peroxide

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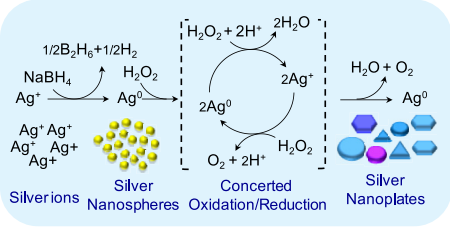
HIGHLIGHTS

- Rapid shape transformation of silver nanospheres to nanoplates by H_2O_2.
- Structural change completes in 2 min with a yellow-to-blue color change.
- Selective fabrication of silver nanoplates by tuning PVP and H_2O_2 concentrations.
- In this process, citrate ion is poisonous as it inhibits the shape transformation.
- Concentrated PVP delays the transformation by forming stable complex with Ag^+.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper we demonstrate a simple and rapid shape transformation of silver nanospheres (AgNSs) to silver nanoplates (AgNPls) using the oxidation and reduction capabilities of hydrogen peroxide. AgNPls having tunable surface plasmon resonance across the visible region with average size of 40–100 nm and thickness of 10–15 nm can be fabricated within 2 min simply by adding H_2O_2 into a colloid of AgNSs with average particle size of 7 nm. The efficiency of H_2O_2 as a shape-transforming agent depends strongly on its concentration, pH of the AgNS colloid, and the employed stabilizers. H_2O_2 oxidizes AgNSs to silver ions while concertedly reduces silver ions to silver atom necessary for the growth of AgNPls. The shape transformation reaction was conducted at a relatively low concentration of H_2O_2 in order to minimize the oxidative dissolution while facilitating kinetically controlled growth of AgNPls under a near neutral pH. Polyvinyl-pyrrolidone is an effective steric stabilizer preventing aggregation while assisting the growth of AgNPls. Trisodium citrate inhibits the formation of AgNPls under the H_2O_2 reduction as it forms a stable complex with silver ions capable of withstanding the weakly reducing power of H_2O_2. After a complete consumption of AgNSs, large nanoplates grows with an expense of smaller nanoplates. The growth continues until H_2O_2 is exhausted. A high concentration H_2O_2 promotes catalytic decomposition of H_2O_2 on the surface of AgNSs and oxidative dissolution of AgNSs without a formation of AgNPls.

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1. Introduction

In the past decade, two-dimensional silver nanoplates and nanoprisms of various sizes and shapes (triangular, truncated triangular, hexagonal, and round disk) have gained substantial interests due to their tunable size- and shape-dependent optical properties. Silver nanoplates of specific morphologies show potential applications as SERS substrates [1], chemical and biological sensors [2,3], catalysts [4–6], surface-enhanced fluorescence probes [7,8], and building blocks for complex nanophotonic devices and circuits [9–11]. The optical activity of the silver nanoplates could be selectively tuned across the visible to the NIR regions by manipulating the degree of anisotropy [12–16]. To meet the demand of morphologically controlled nanostructures, many synthetic methods were developed for the fabrication of silver nanoplates including photochemical processes [17–26], hard and soft template processes [27], thermochemical reductions [28–31], electrochemical techniques [32], and sonochemical methods [33]. Due to the demanding for nanomaterials with specific properties for dedicated applications, developments of novel techniques for creating functional nanostructures with desired morphologies and properties are constantly required.

Recently, efficient seed mediation approaches for preparations of anisotropic silver nanoplates and nanosheets were developed [34–41]. These thermal methods exploit the shape selective oxidative etching of H_2O_2 to selectively destroy unstable silver seeds while preserving those with planar twinned defects pivotal for the formation and growth of the anisotropic nanoplates. The nanoplates were then developed from the morphologically selected seeds under a controlled environment containing additional metal ions, reducing agents, and surface protecting agents. Trisodium citrate (TSC) was a proven essential ingredient for the formation and growth of silver nanoplates although it might be replaceable by di- and tri-carboxylate compounds with two nearest carboxylate groups separated by two or three carbon atoms [36,41]. TSC facilitates the lateral growth of the anisotropic nanoplates by preferentially binding onto the flat Ag{111} facets [32,36,41–45]. Polyvinylpyrrolidone (PVP) was normally employed as a secondary ligand as it promotes the formation of uniform nanoplates by preventing aggregation of nanoparticles. PVP promotes the thickness increment of nanoplates by preferentially binding onto the Ag {100} facets [41,43]. However, it is replaceable by polymers containing hydroxyl group such as polyethylene glycol and polyvinyl alcohol. A successive lateral and vertical growth of silver nanoplates capable of increasing the edge length for more than 100 times and increasing plate thickness for nearly 40 times of the original seeds utilizing TSC and PVP had been demonstrated [14,41].

The efficient catalytic decomposition of H_2O_2 by silver metals is well-known. The decomposition of concentrated H_2O_2 on silver metal is extremely violent with a release of intense heat, water vapor, and oxygen gas [46,47]. Despite its strong oxidizing property, H_2O_2 possesses a weakly reducing capability. There were few reports on using the reducing capability of H_2O_2 for synthesizing complex metal nanostructures [48–51]. One of the benefits of H_2O_2 is its benign nature as it finally decomposes to water and oxygen gas whether it functions as an oxidizing or a reducing agent.

Recently, the capability of H_2O_2 for transforming starch-stabilized silver nanospheres to nanoprisms with controllable LSPR wavelengths has been demonstrated [52]. The role of H_2O_2 as a mild reducing agent was clearly explained with corroborated experimental evidences. The mechanism of the shape transformation process was thoroughly analyzed from spectroscopic data of the colloids using the multivariate curve resolution–alternative least squares (MCR–ALS) analysis. The chemometric results corroborated the visual observation that the nanoplates developed with the expense of the nanospheres. Moreover, the successive growth of the large nanoplates persists with the expense of the small nanoplates [53]. However, soluble starch employed as the stabilizer for the silver nanoplate fabrication in our previous investigation is not as conventional as PVP and trisodium citrate. This contribution further explores the oxidation/reduction capabilities of H_2O_2 for the fabrication of silver nanoplates (AgNPls) from PVP-, citrate-, or PVP/citrate-stabilized AgNSs. The stabilization mechanism, the concentration of the stabilizer, pH of the AgNS seed solution, and the concentration of H_2O_2 are expected to be critical parameters for the selective fabrication of two-dimensional silver nanostructures utilizing H_2O_2 chemistry.

This paper is different from previous reports involving the usage of H_2O_2 for the synthesis of silver nanoplates as they utilized only the oxidizing capability of H_2O_2 for the selective etching of silver nanostructures [36,40,41,52]. Additional silver ions, strong reducing agent, and trisodium citrate were not necessary for the synthesis of AgNPls utilizing our approach. We employed just a sufficient amount of $NaBH_4$ for silver nanosphere preparation only to ensure the complete reduction of Ag^+ to Ag^0 without leaving the residual amount of unreacted reducing agent. Moreover, H_2O_2 were the principal shape-controlling reagent in our study, not the mixture of H_2O_2 and $NaBH_4$ as previously reported [41]. H_2O_2 was subsequently added into a colloid of AgNSs to trigger the shape transformation process in order to deliberately separate the nucleation of silver seeds and growth of the silver nanoplates. In addition, the amount of H_2O_2 required for the shape transformation was minimized as the H_2O_2-oxidation was not competing with the $NaBH_4$-reduction. Our approach can selectively fabricate silver nanoplate with various color e.g. red, pink, and violet. The ability to selectively control the LSPR property of silver nanoplates extends the range of applications and broadens the exploration of this functional materials in the fields of colorimetric sensor especially those in medical applications [54] and chemical sensors [55].

2. Experimental

Silver nitrate ($AgNO_3$), sodium borohydride ($NaBH_4$), soluble starch, trisodium citrate dihydrate, and hydrogen peroxide (H_2O_2 30% w/w) were purchased from Merck. All chemicals were analytical reagent (AR) grade and were used as received. All glassware and magnetic stir bars were rinsed with 6 M nitric acid, cleaned with detergent, and thoroughly rinsed with de-ionized (DI) water prior to use.

Four types of AgNS colloid prepared by a $NaBH_4$-reduction were employed for the shape transformation: (A) non-stabilized, (B) PVP-stabilized, (C) TSC-stabilized, and (D) PVP/TSC-stabilized AgNSs. Briefly, a solution of $AgNO_3$ (0.232 mM, 20 mL), with and without an addition of TSC and/or PVP, was reacted with an ice-cool $NaBH_4$ solution (68.7 mM, 97.3 μL) under a vigorous stir. The yellow colloids of AgNSs were stable without any sign of precipitation for at least 48 h. Before the shape transformation operation, the colloids were aged for 1 h in order to ensure a complete decomposition of residual $NaBH_4$, as indicated by an insignificant change of UV–visible spectra after an addition of a dilute solution of $AgNO_3$. The shape transformation of AgNSs to AgNPls was accomplished simply by adding a pre-determined volume of H_2O_2 solution (979 mM, 0–379 μL) into a colloid of AgNSs under a vigorous stir. A desired mole ratio R of $[H_2O_2]$:$[AgNO_3]$ was achieved by adjusting the volume of H_2O_2 solution. A series of color changes from yellow to red, pink, purple, blue, and magenta was visually observed depending on the amount of added H_2O_2 (see Electronic Supplementary Materials, Videos V1–V4). The color change indicates the decomposition of AgNSs with a concomitant formation and growth of AgNPls. The reaction is spontaneous and completed