Recycling valuable silver from waste generated in diverse nanotemplate reactions

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ABSTRACT The shape-controlled silver nanostructures have been widely used for template synthesis of metal nanostructures with desired morphologies and compositions for specific applications by galvanic replacement reaction, while the silver is sacrificed as oxidized to silver ion and abandoned as by-products. In view of the broad application prospect of the obtained metal nanostructures, the cost and environment problems after the template reactions should be taken into account for the large scale production in the future. To solve this problem, we conceptually demonstrate that the wasted AgCl generated from the template reactions can be easily recycled for the synthesis of valuable Ag nanowires. As representative examples, the average recovery of silver can be about 69.8%–84.6% after the template synthesis of Au/Pt nanostructures. The resynthesized Ag nanowires show uniform size distribution and excellent physical and chemical properties for the fabrication of transparent electrode and template synthesis.

Keywords: silver nanostructures, templating synthesis, metal nanostructures, waste, recycling, silver nanowires

INTRODUCTION

Metal nanomaterials with well-defined structures have received increasing attention in recent years due to their fascinating performance in various fields such as optoelectronics, catalysis, sensing, biomedicine and so on [1–5]. In order to tailor their properties for specific applications, many studies have been focused on fabricating metal nanostructures with controlled parameters especially the shape and composition [6–10]. Compared with the solid sample, the porous or hollow metal nanostructures are lower in density and higher in surface area and proved to be more economically viable and efficient in properties (e.g., catalysis and sensing) [11,12]. Among various methods, the template-directed synthesis has been demonstrated as

the most straightforward and commonly used method for the synthesis of porous or hollow metal nanostructures because of its easy scalability and high structural controllability [13,14]. Despite the advantages, the templates during the reactions are always etched out and wasted. In view of the broad application prospect of the obtained metal nanostructures, the cost and environmental problems after the template reactions should be taken into account for the large scale production in the future especially when the templates are expensive or toxic [15].

Silver nanostructures as templates for the synthesis of multifunctional porous metal nanostructures (such as Au nanostructures) were firstly reported by Xia's group [9,16], and since then the template synthesis using silver nanostructures as templates has been successfully extended to be a particularly effective and versatile synthesis strategy due to the easy control of the composition, internal structure, and morphology of the resultant nanostructures [17–27]. However, when considering the cost and wide applications of electronics, surface plasmonics, surface-enhanced Raman scattering spectroscopy (SERS) and chemical sensing for the silver itself [28], it will be a waste when the silver nanostructures are sacrificed after the template synthesis which usually transform to AgCl precipitate and are abandoned as by-products. Although the element of silver has high price as a noble metal, how to deal with the by-products of AgCl during the experiments has always been ignored over the past years.

Herein, we first report a general strategy for synthesis of Ag nanowires (NWs) by recycling the valuable silver from wasted AgCl solid generated in diverse nanotemplate reactions (e.g., template synthesis of Au/Pt hollow nanostructures) (Scheme 1). This strategy can make the wasted AgCl

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Scheme 1 Illustration of recycling the valuable silver from wasted AgCl solid generated in diverse nanotemplate reactions to synthesize Ag NWs.

into valuable silver nanostructures and pave the way for the large-scale production of multiple metal nanostructures that were template synthesized from silver nanostructures with much less cost and waste. Compared with the content of the sacrificed silver during the template reactions, the average recovery of the silver recycled for the synthesis of Ag NWs can be about 69.8%–84.6%. In addition, the reproduced Ag NWs show uniform size distribution with diameter of ~44 nm and are still with excellent physical and chemical properties for the fabrication of transparent electrode and various template syntheses.

EXPERIMENTAL SECTION

Materials

AgNO₃, ethylene glycol, glycerol, HAuCl₄·4H₂O, H₂PtCl₆·6H₂O, poly(vinyl pyrrolidone) (PVP, $M_w \approx 40,000$), Na₃CA, NaBH₄, Na₂S, L-ascorbic acid, NaCl, ammonium hydroxide (28 wt.%) and hydrazine hydrate (85 wt.%) were all purchased from Shanghai Chemical Reagent Co. Ltd. All chemicals were of analytical grade and were used as received without further purification except the ethylene glycol (EG) which was refluxed at 140°C for 3–5 h.

Instruments

Transmission electron microscopy (TEM) were carried out on a commercial JEOL-7650 transmission electron microscope operated at an accelerating voltage of 100 kV. Scanning electron microscopy (SEM) was carried out on a Zeiss Supra 40 field-emission scanning microscope operated at 5 kV. The X-ray diffraction patterns (XRD) were measured on a Philips X'Pert Pro Super X-ray diffractometer equipped with graphite-monochromatized Cu K α radiation. UV-vis spectra were recorded on

UV-2501PC/2550 at room temperature (Shimadzu Corporation, Japan). The content of element silver was measured by inductively coupled plasma (ICP) mass spectrometry (Plasma Quad 3, America).

Synthesis of Ag nanocubes

In a typical synthesis, 12 mL EG was heated at 150°C in a 25 mL glass vial. After about 20 min, 3 mL and 1 mL EG solutions containing AgNO₃ (48 mg mL⁻¹) and PVP ($M_w \approx 40,000$) (20 mg mL⁻¹) were sequentially injected and stirred for 9 min, and then 0.16 mL EG solution containing Na₂S (3 mmol L⁻¹) was quickly injected. After 10–15 min, the color of the solution changed to opalescent ruddy-brown and concurrently became opaque indicating the formation of Ag nanocubes [29].

Synthesis of Ag NWs

In a typical synthesis, 5.86 g PVP was added to 190 mL of glycerol in a 500 mL three-necked, round bottle flask and heated at 110°C to get a homogeneous solution. After cooling to room temperature, 1.58 g AgNO₃ was added to the solution. Then the solution was heated from room temperature to 210°C in 30 min with slow stirring. When the temperature reached at about 60°C, NaCl solution (59 mg of NaCl dissolving in 0.5 mL of deionized water and 10 mL of glycerol) was added to the flask. The heating stopped immediately as soon as the temperature reached at 210°C, and 200 mL deionized water was added to the solution. The solution was kept undisturbed for 24 h to remove Ag nanoparticles from the NWs [30].

Synthesis of Ag nanoplates

In a typical synthesis, the silver seeds were firstly synthesized as follows: 110 mL of aqueous solution containing

AgNO_3 (0.11 mmol L^{-1}) and Na_3CA (2.05 mmol L^{-1}) was prepared. Under magnetic stirring, 3 mL aqueous solution containing 5 mmol L^{-1} NaBH_4 was added to the solution in one go and the mixture was stirred for 10 min. This seed solution was then aged at room temperature for 5 h prior to future use. Then silver nanoplates were synthesized as follows: 92.5 mL of deionized water was mixed with 10 mL aqueous AgNO_3 (5 mmol L^{-1}), 7.5 mL aqueous PVP (0.7 mmol L^{-1} in terms of the repeating unit), 7.5 mL aqueous Na_3CA (30 mmol L^{-1}), and 6.4 mL of the as-prepared seed solution, followed by dropping into 62.5 mL aqueous L-ascorbic acid (1 mmol L^{-1}) under magnetic stirring. After 15 min, the colour of the solution became unchanged indicating the formation of nanoplates [31].

Synthesis of Au/Pt nanostructures

All the Ag nanostructures were centrifuged and washed with water for twice and then dispersed into deionized water containing 1 mg mL^{-1} PVP (the concentration of the Ag nanostructures were about 0.05 mg mL^{-1}) and were heated to boiling for 10 min with vigorous stirring, then different volumes of 1 mmol L^{-1} HAuCl_4 and 0.2 mL (1 mmol L^{-1}) H_2PtCl_6 (the molar ratio of Au/Pt to Ag was 1:3 and 1:4) were dropped to the solutions at the rate of 45 mL h^{-1} . After another 10 min, the color of the solution became stable, indicating the formation of Au/Pt nanostructures [23,32–35].

Recycle the silver after the template synthesis

In a typical process, (0.6 mL) ammonium hydroxide (28 wt.%) was dropped to 10 mL deionized water containing the products until the AgCl (0.034 g) was fully dissolved to the transparent Tollens' Reagent and centrifuged from the valuable metal nanostructures, then (0.2 mL) hydrazine hydrate (85 wt.%) was added to the solution of the separated Tollens' Reagent to get the Ag particles. After centrifugation, (0.1 mL) HNO_3 (65 wt.%) was added to Ag precipitate in 25 mL round-bottom flask to form AgNO_3 and dried at 80°C for the further application of synthesis Ag NWs.

Synthesis of Ag NWs from recycled silver

The silver NWs were synthesized by a modified polyol process. Typically, 0.125 g PVP was added to 8 mL glycerol in a round-bottom flask and heated to 100°C until the PVP was fully dissolved. After cooling to room temperature, 40 mg AgNO_3 was added and then 2 mL glycerol containing 4 mg NaCl dissolved in 50 μL deionized water was added. The solution was then heated at 180°C for 5 h for the growth of Ag NWs [30,36].

RESULTS AND DISCUSSION

As chemical template, Ag nanostructures [28] have been widely studied for the synthesis of metal nanostructures with well-controlled sizes and shapes because the physicochemical properties of the metals are strongly dependent on their size, shape, and morphology [37]. Three kinds of Ag nanostructures that are nanocubes (NCs), NWs and nanoplates (NPs) were selected as templates to synthesize Au/Pt nanostructures for the study of recycling AgCl to the valuable Ag NWs in the practice.

The gold and platinum hollow nanostructures with wide applications in sensing and catalysts are commonly synthesized using Ag nanostructures as templates by the galvanic replacement reactions because of the more positive reduction potential of the $\text{AuCl}_4^-/\text{Au}$ ($\text{PtCl}_6^{2-}/\text{Pt}$) than AgCl/Ag . After the galvanic replacement reactions, silver was oxidized to Ag^+ and quickly reacted with Cl^- to form the precipitate of AgCl. Figs 1a, d and g are the typical TEM images of the Ag NCs, NWs and NPs synthesized according to previous reports [29–31]. For the synthesis of hollow metal nanostructures, the templates of silver nanostructures were first added to the boiling water for ten minutes with vigorous stirring to form a homogeneous suspension, and then the desired noble metal salts (e.g., HAuCl_4 and H_2PtCl_6) were titrated to the solution at the rate of 45 mL h^{-1} . Using the Ag NCs as a template, the Au and Pt nanocages (NCAs) were synthesized as shown in Figs 1b and c through the galvanic replacement reactions [23,32]. Besides, the Au, Pt nanotubes (NTs) and Au nanorings (NRs) (Figs 1e, f and h) were also synthesized using the Ag NWs and NPs as templates [33–35]. As shown by the TEM and SEM images (Figs S1a–h), the most component of silver was etched away and translated to the Pt or Au porous and hollow nanostructures, which were also characterized by XRD patterns (Fig. S2). The change of the UV-vis absorption spectra and color of the suspension between the silver and metal (Au/Pt) nanostructures shown in Supplementary information (Fig. S3) indicates the different optical properties of the products. The amounts of the Ag nanostructures before and after different template reactions were recorded by the inductively coupled plasma mass spectrometry (ICP) as shown in Supplementary information (Table S1). Different from the previous reports, AgCl produced in the experiments was collected and Fig. 1i shows the typical AgCl suspension recycled for the synthesis of Ag NWs.

Synthesis of Ag NWs has been extensively studied because of the excellent electrical conductivity and mechanical robustness for wider applications of electronics [28,36,38–40]. In the most synthesis strategies, AgNO_3 was

Figure 1 (a–c) TEM images of the Ag NCs, Au NCAs and Pt NCAs. (d–f) TEM images of the Ag NWs, Au NTs and Pt NTs. (g, h) TEM images of the Ag NPs and Au NRs. (i) Digital photograph of the AgCl suspension recycled from the template synthesis. The scale bar in (a–h) is 100 nm.

reported as the most commonly used precursor for the synthesis of Ag NWs. Based on the previous reports [30,36], we synthesized Ag NWs using the AgCl precipitate as the starting precursor with several chemical transformation processes introduced. Although it seems more complicated and unnecessary for the synthesis of Ag NWs, this strategy actually resolves the problem existing in the template synthesis that AgCl usually is washed away using saturated NaCl solution and abandoned as by-product. The typical process for the synthesis of Ag NWs and the chemical transformation processes can be described as follows:

Figs 2a and S4a show the typical XRD pattern of AgCl that was separated from the products after the template reactions of synthesis metal nanostructures by precipitation process. According to the Reactions (1–3), the ammonium hydroxide was added to the AgCl suspension to form silver-ammonia solution, then it was reduced to silver particles (Figs 2b and S4b) by adding the appropriate amount of hydrazine hydrate as reducing agent, and AgNO_3 (Figs 2c and S4c) was formed by adding concentrated HNO_3 to the centrifuged silver particles. Finally, the Ag NWs can be easily synthesized by a modified polyol method as described in Reaction (4) (the details are given in the experiment part).

However, the by-product of AgCl produced after the template reactions cannot be fully separated through the precipitation process from the products owing to the sedimentation and adsorbing with the porous products. To overcome this problem, we first centrifuged the products and AgCl together to remove the impurities such as the unreacted noble metal salts in the solution, and then added the

Figure 2 XRD patterns of the recycled (a) AgCl after the template reactions; (b) Ag; (c) AgNO₃.

dilute solution of ammonium hydroxide to the precipitate to dissolve AgCl from the products. It has been reported [41] that the ammonium hydroxide solution can etch Ag to silver-ammonia solution when exposed to the oxygen, which might involve the dealloying process that does not exist when using the saturated sodium chloride solution to wash the precipitate of AgCl as previous reports. In this report, we bubbled nitrogen to the suspension of the precipitate to avoid the attack of the oxygen. Figs 3a–c are typical TEM images and UV-vis spectra of Ag NWs before and after the immersion of ammonium hydroxide for two hours and show that only the end places of the Ag NWs were slightly etched with little change of the UV-vis absorption peak, which might be caused by the pre-oxidation of the Ag NWs during the synthesis or transferring process. In addition, the impact of the ammonium hydroxide solution on the metal nanostructures of Au NTs has also been studied. The TEM images and UV-vis spectra shown in Figs

3d–e indicate that there is almost no change in both morphology and UV-vis absorption peaks of the Au NTs even after the immersion of ammonium hydroxide solution for two hours. These results indicate that the employing of ammonium hydroxide solution to improve the recycle ratios of silver during the recycling process has almost no impact on the products when avoiding the exposure to oxygen.

Fig. 4a shows the *in-situ* process for the synthesis of Ag NWs from solid AgCl. Firstly, ammonium hydroxide was added to the AgCl suspension to form clear silver-ammonia solution, then it was reduced to silver particles by adding appropriate amount of hydrazine hydrate as reducing agent, and finally AgNO₃ was formed by adding the concentrated HNO₃ to the centrifuged silver particles. The Ag NWs can be easily obtained by a modified polyol method heated at 180°C for 5 h. TEM and XRD characterization show that with the addition of NaCl, some AgCl nanoparticles still exist in the products observed (Fig. S5),

Figure 3 TEM images of Ag NWs before (a) and after (b) immersing with ammonium hydroxide; (c) UV-vis spectra of the Ag NWs before and after immersion in solution of ammonium hydroxide; (d) and (e) TEM images of Au NTs before and after immersion with ammonium hydroxide; (f) UV-vis spectra of the Au NTs before and after immersion in solution of ammonium hydroxide.

Figure 4 (a) The *in-situ* process for the synthesis of Ag NWs from wasted AgCl. (b) SEM image of the Ag NWs, the inset is the TEM image of the Ag NWs. (c) XRD pattern of the Ag NWs. (d) Recycle ratios of different reaction systems. A: AgNO₃ + NaCl, B: Ag NCs + HAuCl₄, C: Ag NCs + H₂PtCl₆, D: Ag NPs + HAuCl₄, E: Ag NWs + HAuCl₄, F: Ag NWs + H₂PtCl₆.

which can be easily washed away with dilute solution of ammonium hydroxide. Figs 4b and the inset show the typical SEM and TEM images of the purified Ag NWs suggesting the uniform size of NWs (~44 nm in diameter with fifty NWs statistic in Fig. S6). Fig. 4c is the XRD pattern of the resynthesized Ag NWs, showing good agreement with the standard literature data of silver (JCPDF card number: 04-0783) without any impurities. Before each synthesis process, the content of the silver was first confirmed by ICP to ensure that the raw material with appropriate ratios ($m(\text{AgNO}_3):m(\text{NaCl}):m(\text{PVP}):V(\text{glycol}) = 40 \text{ mg}:4 \text{ mg}:125 \text{ mg}:8 \text{ mL}$) in the synthesis process. The recycling rate of the different systems for template synthesis was characterized by the ICP as shown in Fig. 4d. Compared with silver (100%) that was etched out during the template reactions, the relative contents of the recycled silver were about 95.6%, 75.1%, 69.8%, 84.6%, 70.4%, 73.3% for different systems of synthesis AgCl (AgNO₃ + NaCl), Au NCAs (Ag NCs + HAuCl₄), Pt NCAs (Ag NCs + H₂PtCl₆), Au NRs (Ag NPs + HAuCl₄), Au NTs (Ag NWs + HAuCl₄), and Pt NTs (Ag NWs + H₂PtCl₆). More than ten pots of the same template reactions were carried out to recycle silver for one-pot synthesis of Ag NWs, in view of that one pot of the template reaction had much less silver. Besides, collecting silver from more experiments at the same conditions also avoids the statistics deviation for the same template reactions. The reason for the high recycle ratio of the system for the synthesis of AgCl was that the reaction was only carried out in 10 mL aqueous solution with 33.5 mg AgCl, meaning that

much less AgCl was dissolved in the solution and less centrifugation process. The loss in yield (about 15–30%) during each recycle process was mainly caused by the separation steps and the partial dissolution of AgCl in the reaction solution that could not fully precipitated by centrifugation as more aqueous solution (about 800 mL for 33.5 mg AgCl) were involved in the reactions.

Recent studies of transparent electrodes revealed that silver NWs have led the way for the brittle indium tin oxides (ITO) replacement due to their intriguing electrical and optical properties. To verify the electrical performance of the Ag NWs reproduced in this report, the flexible transparent electrode was fabricated by spray-coating method according to the previous report [42]. Besides, the silver NWs as unique templates for synthesizing one dimensional (1D) metal nanostructures with novel functionalities have also been performed. Fig. 5a depicts the strategy for the quality evaluation of the reproduced Ag NWs. For the fabrication of transparent electrode, the Ag NWs were first dispersed in ethanol solution and then spray-coated on a flexible polyethylene terephthalate (PET) substrate that anchored on a 140°C hotplate using a commercial airbrush (HD-130). Fig. 5b shows the representative SEM image, indicating the uniformity of silver nanowire networks. The optical transmittance and sheet resistance were measured with an average value of 85% and 30 Ω/sq for five different spray coated films as shown in Fig. 5c. As unique templates for 1D nanostructures, Ag NWs reproduced from the template synthesis were reused to template synthesize the core-shell

Figure 5 (a) Schematic illustration of the Ag NWs used for transparent electrodes and template synthesis. (b) SEM image of the Ag NW networks fabricated by spray-coating. (c) The transmittance spectra of five different Ag NW transparent electrode films. The inset is the sheet resistance of one film tested by a four-probe meter. (d–f) TEM images of the Ag@SiO₂ nanocables, Au and Pt NTs synthesized using the recycled Ag NWs as templates.

structure of Ag@SiO₂ nanocables [41] (Fig. 5d) and hollow nanostructures of Au/Pt NTs (Figs 5e–f) with uniform morphologies. These results indicate that the Ag NWs reproduced from the template synthesis have both good physical and chemical properties for the electrodes fabrication and template synthesis.

CONCLUSIONS

In summary, we reported a general strategy to recycle valuable silver from wasted AgCl solid generated in diverse nanotemplate reactions. Remarkably, the by-product of AgCl for the synthesis of Ag NWs can be transferred to AgNO₃ by several chemical transformations. To improve the recycle ratio of the silver, ammonium hydroxide was used to dissolve the AgCl that cannot be fully separated from the porous and hollow metal nanostructures by centrifugation. The resynthesized Ag NWs show uniform size distribution with excellent physical and chemical properties, which can be used for the fabrication of transparent electrode and various template syntheses. Moreover, the present work will pave the way for the large scale production of multiple metal nanostructures that are template synthesized from silver nanostructures with much less cost and waste.

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- Conflict of interest** The authors declare that they have no conflict of interest.
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多种纳米模板反应中高价值银的回收与重复利用

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摘要 利用银纳米材料的反应活性, 通过模板反应可以制备形貌和结构可控的多种金属纳米结构, 然而, 在模板反应过程中, 银纳米模板剂通常被氧化成银离子作为副产物被遗弃. 考虑到金属纳米结构具有的广泛应用前景, 以银为模板剂大规模制备各种金属纳米结构过程中的成本和环境问题必须予以关注. 为了解决这个问题, 我们对此类模板反应过程中所产生的废弃副产物氯化银进行了回收, 并以此为原料成功的制备出高质量的银纳米线. 以模板反应制备金/铂纳米结构为例, 银的平均回收率可达到69.8%~84.6%. 此外, 利用废弃副产物重新合成的银纳米线具有均一的尺寸分布, 在模板反应和制备透明导电电极方面表现出优异的化学和物理性能.