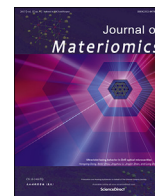




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## Hierarchically structured 2D silver sheets with fractal network

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### ABSTRACT

Oriented attachment can be used as a good synthetic route to make highly anisotropic nanostructures including nanorod, nanowire, nanoplate, and nanosheets. In a typical growth of anisotropic nanostructures, coalescence and reshaping after attachment make dense nanostructures. In this report, we show the formation of Ag sheets having fractal network by oriented attachment at low reaction temperature of 30 °C. The synthesized Ag sheets exhibited good crystalline nature despite of their network structure and low synthetic temperature. We also investigated the effect of reaction conditions for the formation of the Ag sheets. In addition, using the Ag sheets as a sacrificial template, we could make hollow Au sheets via galvanic replacement.

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### 1. Introduction

In recent past, many researches have been devoted to rational design and construction of anisotropic nanomaterials [1–4]. The intrinsic properties of these materials can be tailored by tuning their size and morphology. For instance, particle shapes such as stars, rods, wires, cubes, and plates, were successfully synthesized for a variety of applications including sensing, imaging, surface-enhanced Raman scattering (SERS), and medical device fabrications [5–15]. Recently, solution-based procedures for the preparation of anisotropic metal nanostructures are very promising because of their versatility in controlling the precise morphologies, and thus maneuvering their properties. In the previous syntheses of highly anisotropic metal nanostructures, it was demonstrated that slowing down the decomposition or reduction rate of a metal precursors was favorable for the anisotropic growth of nanostructures [16]. This growth model is termed as kinetically controlled growth which is based on slowing down the growth kinetics by using a weak reducing agent, selective adhesion of capping ligands to a particular crystal facet of a growing

nanocrystals [17–19]. However, recent studies clearly reveal that this mechanism could not provide sufficient explanation in many systems [7,10,11,13,20]. Alternatively, Penn and Banfield proposed an aggregation based crystal growth mechanism, known as “oriented attachment” [21–23]. This phenomenon suggests that adjacent nanoparticles can spontaneously aggregate and further grow into large crystals through an oriented attachment mechanism; thereby providing a promising route for the fabrication of anisotropic nanostructures. Recent studies show that a variety of well-defined metal nanostructures could be constructed via oriented attachment. Typical examples include coral, dendrite, flowers, and disk-like shapes [24–27]. In these systems, the bigger particles are grown from self-assembly of small primary nanoparticles, in which the adjacent nanoparticles are self-assembled by sharing a common crystallographic orientation and docking of these particles at a planar interface.

Fabricating nanostructures using bottom-up synthetic routes especially with unusual shapes is very promising due to their remarkable ability to control optical and chemical properties. Among them silver (Ag) nanoplates with controllable size, thickness, and aspect ratio are very attractive because of their unique structure, high anisotropy, and optical properties [18,28–30]. Ag nanoplates with triangular [30], hexagonal [31], and disk shapes [27] have been reported previously, but it is still of great interest in designing Ag plates having unreported morphologies.

In this work we first report the synthesis of hierarchically

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structured highly anisotropic 2D Ag sheets with fractal network in an aqueous-phase at mild reaction conditions. These Ag sheets were synthesized by reacting  $\text{Ag}^+$  with polyethyleneimine (PEI) in the presence of urea at reaction temperature of 30 °C. In the present synthesis, PEI serves as both reducing and stabilizing agent, while urea acts as an organic additive to control the anisotropic growth of 2D Ag sheets. We investigated the detailed growth mechanism to see the structural and morphological evolution of the Ag sheets. The electron microscopy investigation reveals that these Ag sheets with an average diameter of  $12.6 \pm 1.8 \mu\text{m}$  were synthesized by progressive attachment of small Ag nanoparticles via oriented attachment and fusion between nanoparticles during growth to form perfectly ordered single crystalline 2D fractal network. We performed control experiments to study the influence of reaction conditions including pH of the solution, temperature, type of ligand, and precursor concentration. Furthermore, we use these Ag sheets as a sacrificial template to produce gold (Au) sheets with hollow network structure for the first time.

## 2. Experimental details

### 2.1. Chemicals and materials

Branched polyethyleneimine (PEI, MW = 750,000, 50 wt% solution in water), linear polyethyleneimine (LPEI, MW = 25,000), polyvinylpyrrolidone (PVP, MW = 55,000), silver nitrate ( $\text{AgNO}_3$ , purity  $\geq 99\%$ ), Chloroauric acid ( $\text{HAuCl}_4$ , purity  $\geq 99\%$ ), and urea (purity 99–100%) were purchased from Aldrich and used without further purification. Water was purified by ion-exchange (deionized, DI water).

### 2.2. Synthesis of Ag sheets

In a typical synthesis, PEI (2.5 mg) and 0.3 g of urea was dissolved in deionized water (5 mL) and heated to 30 °C under magnetic stirring at 400 rpm, and 15  $\mu\text{L}$  of 1 M aqueous  $\text{AgNO}_3$  solution was added to the reaction solution using a pipette. The resulting mixture was heated and stirred for 16 h and cooled to room temperature.

### 2.3. Synthesis of Au sheets via galvanic replacement reaction

The 2.0 mL of as-synthesized Ag sheets were re-dispersed in 3 mL of DI water, and 1.0 mL of an aqueous  $\text{HAuCl}_4$  solution (1 mM) was added to the reaction solution at 30 °C. The resulting mixture was heated and stirred for 4 h and cooled to room temperature.

### 2.4. Characterization

The morphology and composition of the sample were recorded by scanning electron microscopy (SEM, LEO SUPRA 55) and energy dispersive X-ray spectroscopy (EDS, INCA, Oxford Company). Transmission electron microscopy (TEM) images were captured using a JEM-2100 F microscope operated at 200 kV. The UV–vis spectra were recorded using a Jasco UV–vis spectrophotometer. The powder X-ray diffraction (XRD) patterns were obtained using a Rigaku D-MAX/A diffractometer at 35 kV and 35 mA. X-ray photoelectron spectroscopy (XPS) measurements were conducted using a Thermo Scientific K-Alpha spectrometer with an Al K $\alpha$  X-ray source. Thermal gravimetric analysis (TGA) was performed using a TGA Q5000 IR thermal analyzer.

## 3. Results and discussion

### 3.1. Synthesis and characterization of Ag sheets

The hierarchically structured highly anisotropic 2D Ag sheets with fractal network were synthesized in an aqueous-phase containing  $\text{AgNO}_3$ , PEI, and urea at mild reaction temperature of 30 °C for 16 h. In the present synthesis, PEI acts as both reducing and stabilizing agent, as reported previously [32]. The color of reaction solution changed from light pink to dark reddish pink after several hours into the reaction, indicating the formation of Ag sheets (Fig. S1). Fig. 1 shows typical TEM and SEM images of the product, revealing the formation of Ag sheets with an average diameter of  $12.7 \pm 1.8 \mu\text{m}$  and thickness of about 38 nm. SEM and high resolution SEM (HRSEM) images reveal that the Ag sheets were composed of fractal network structures in inner space and bounded by dense plate-like structures on the edges (Fig. 1(b) and (c)). Selected area electron diffraction (SAED) patterns taken by directing the electron beam perpendicular to the flat faces of the Ag sheet exhibited diffraction spots with a six-fold rotational symmetry, indicating that the Ag sheet is a single crystal and the top and bottom faces of the Ag sheet was enclosed by (111) habit planes (inset of Fig. 1(a)) [26,33].

The XRD patterns taken from the product show the presence of diffraction peak at 38.1° which can be assigned to (111) crystal plane of face-centered cubic (fcc) silver (Fig. S2(a),  $Fm\bar{3}m$ ,  $a = 4.086 \text{ \AA}$ , Joint Committee on Powder Diffraction Standards (JCPDS) file no. 04–0783). This result indicates the preferred orientation of Ag sheets along (111) face, well matched with TEM observations [27]. The XPS core level spectrum shows two distinct peaks at 368.2 and 374.2 eV corresponding to the binding energies of metallic Ag 3d<sub>5/2</sub> and Ag 3d<sub>3/2</sub>, respectively, thus confirming the metallic structure of the Ag sheets (Fig. S2(b)). EDS data of the Ag sheets also confirmed the presence of Ag as major element (Fig. S2(c)). These results confirmed the formation of highly anisotropic Ag sheets with fractal network and their preferred orientation along (111) plane. The percentage yield of the Ag sheets was calculated using TGA in a nitrogen atmosphere at a heating rate of 10 °C/min. The PEI stabilized Ag sheets showed around 12% weight loss at a temperature of as high as 500 °C, while PEI and urea showed around 100% weight loss at the same temperature (Fig. S3). Based on the calculation using TGA data, we could conclude that the percentage yield of the Ag sheets came out to be around 84%.

### 3.2. Growth mechanism of Ag sheets

In typical syntheses of nanoparticles, monomer attachment on the surface of seed particles is a main growth factor [21,34]. Recently, however, there have been some reports that the size and morphology of anisotropic nanostructures could be modulated by particle attachment and fusion via oriented attachment. We investigated the detailed morphological evolution of the Ag sheets by taking samples at various reaction stages and then analyzing them by TEM and UV–vis absorption spectroscopy. Fig. 2 shows typical TEM and high-resolution TEM (HRTEM) images of the products sampled at 5 min to 16 h, respectively. The average size and size distributions of these products are presented in Fig. S4. At  $t = 5$  min, small Ag nanoparticles with sizes around 13 nm were found (Fig. 2(a)). At  $t = 10$  min, we observed peanut-shaped or elongated nanoparticles around 25 nm in size (Fig. 2(c)), and after 10 min, 33 nm-sized aggregates composed of small Ag nanoparticles were found (Fig. 2(e)). The HRTEM image of these nanoparticles show lattice fringes with an interplanar distance of 2.3 Å, which corresponds to (111) crystal plane of metallic Ag (Fig. 2(b), (d), and (f)) [35]. At  $t = 30$  min, the size of

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