Controlled synthesis of 2D Au nanostructure assembly with the assistance of sulfonated polyaniline nanotubes

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Abstract

A wet chemical approach is used successfully to produce nanostructured Au material by the reduction of sulfonated polyaniline (SPANI) nanotubes. The Au nanostructures obtained are composed of single crystal Au nanoplates, which are aggregated layer-by-layer into stacks or edge-on-face into clusters at various conditions. The Au nanoplate diameter and thickness can be conveniently controlled in the range of 100 nm to 2\,\mu m and 10 to 30 nm, respectively, with no accompanying single Au nanoparticles being observed. The formation of the Au nanostructures was controlled by the degradation of SPANI. The gradually and slowly released segments of SPANI served as the reductant during the growth of the 2D Au nanostructures.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Recently, nanostructured materials have received significant scientific and technological interest due to their potential applications in electronics [1–3], catalysis [4–6], and bioassay [7, 8]. These applications are attributed to their unique electronic, magnetic, catalytic and mechanical properties [9, 10]. Moreover, their physical and chemical properties are dominated by their architectural parameters, such as size, shape and composition [11]. Much effort has been focused on the synthesis of shape-controlled metal nanostructured materials, such as 1D [12], 2D [13–22], faceted and branched metal nanocrystals [23, 24]. The assembly of such shape-controlled nanoparticles, for example, spheres, rods, and plates, is a key step for their application in nanodevices. Nanostructured materials stabilized by surfactant will spontaneously orientate in the 2D or 3D direction [25].

Scheme 1. The chemical structure of SPANI.

Routine approaches to assemble nanoparticles can be achieved by modifying the inter-particle interactions [26].

Herein, we report novel assemblies of complex 2D nanostructured Au synthesized by a facile wet chemical approach using SPANI nanotubes. The 2D nanostructured Au materials are composed of single Au (111) nanoplates, with a thickness of 10–30 nm, and form stack-like or cluster-like self-assemblies under appropriate conditions. It is different from the self-assemblies of the separable nanoparticles formed by the inter-nanoparticle interaction in that the 2D nanostructured
Au assemblies are composed of inseparable single Au nanoplates interconnected via steps between layers. To date, the novel assembly of nanostructured Au has not been reported. The growth of the 2D nanostructured Au assemblies was monitored. It is found that the degradation of SPANI dominates the growth of the 2D nanostructured Au.

2. Experimental section

Unless otherwise stated, the chemicals and reagents were purchased from Sigma-Aldrich. Aniline was redistilled before use, and the purified water was obtained by passing distilled water through an ultrapure water system (Beijing Liyuan Digital Instruments).

The self-assembly approach [27] has successfully been used to synthesize PANI nanotubes. Herein, the SPANI nanotubes were typically obtained by co-polymerization of aniline and o-aminobenzenesulfonic acid in aqueous solution. Briefly, a 1:1 molar ratio of aniline and o-aminobenzenesulfonic acid (0.005 mol) was mixed and stirred in 100 ml of phosphate buffer solution (PBS) (pH 4.0) for 30 min in an ice bath. Next, 0.005 mol of ammonium persulfate was added to the solution. The solution was stirred for 3 min, and aged in a refrigerator at 4 °C for at least 24 h. Then, the mixture obtained was rinsed with deionized water and methanol until the eluting solution became colourless, and was then dried in a vacuum oven at 80 °C. The de-doping of SPANI nanotubes was obtained by dialysing with 1 M NH₃·H₂O [28].

To synthesize 2D Au nanostructures, 5.6 mg SPANI and various amounts of HAuCl₄ were mixed in 3 ml of deionized water and stirred for 24 h. The solution was centrifuged at 3000 rpm for 10 min to collect the precipitates. The precipitates were re-dispersed in ethanol and centrifuged.

The chemical composition of SPANI was determined by the Elementar Varioel Apparatus.

The morphology of the SPANI nanotubes and nanostructured Au was observed with SEM and TEM. A drop of ethanol solution containing SPANI or Au nanostructures was placed on a carbon-coated copper grid, and imaged by a JEOL 2000 transmission microscope operating at 200 kV, and several drops of ethanol solution containing SPANI nanotubes or nanostructured Au was slowly evaporated on an indium–tin-oxide (ITO) glass slide, and imaged by an XL30 ESEM FEM scanning electron microscope operating at 20 kV. The sample was previously sputtered with a 20 nm thickness of Au prior to the measurements of the SPANI nanotubes images.
Controlled synthesis of 2D Au nanostructure assembly with the assistance of sulfonated polyaniline nanotubes

Figure 3. (A) SEM image of Au stack-like nanostructured assemblies at low magnification, the mass ratio of SPANI nanotubes and HAuCl₄ is 5.6:12. (B) A profile image of nanostack assembly, the average thickness of single Au nanoplates is 15 nm; (C) EDX analysis reveals that the Au nanostack assemblies obtained coexist with less SPANI.

The UV–vis spectrum was collected on a CARY500 UV/vis/near IR spectrophotometer. And the RT-IR spectrum was recorded on a Nicolet FTIR 520 FT Spectrophotometer.

Electrochemical investigation was carried out with a CH Instrument using a conventional three-electrode configuration; a KCl-saturated Ag|AgCl electrode was used as a reference electrode, and a platinum wire was used as a counter electrode. An ITO glass slide was immersed in the reaction solution of SPANI and HAuCl₄ for 24 h, and covered with SPANI nanotubes. This slide was rinsed with water and methanol, dried at 50 °C, and was used as a working electrode. The electrolyte was 0.5 M Na₂SO₄ solution, and the pH was adjusted by dilute H₂SO₄ solution.

3. Results and discussions

The chemical structure of SPANI was calculated from the chemical composition of SPANI obtained from the element analysis results, and is shown as follows (scheme 1).

Herein, o-aminobenzenesulfonic acid serves as a template for the micelle with aniline oligomers during the formation of SPANI nanotubes [27]; on the other hand, o-aminobenzenesulfonic acid is oxidized, and becomes one part of the SPANI chain.

The SPANI cannot be resolved by water and ethanol, and always aggregates in the water. The microscopic observations (figures 1(A) and (B)) reveal that most of the SPANI obtained are formed in nanotubes with a length of 1–2 µm, 100 nm outer diameter, and 50 nm inner diameter.

Figure 1(C) presents a typical FTIR spectrum of SPANI, the broad peaks at 1582 and 1498 cm⁻¹ correspond to quinoid and benzenoid rings, respectively, which confirm the emeraldine structure of as-synthesized SPANI. The bands at 1302, 1240 and 823.6 cm⁻¹ originate from the vibrations of C–N bonds in the quinoid and benzenoid rings, and from the in-plane and out-of-plane C–H bending, respectively. The peak at 1040 cm⁻¹, assigned to S=O stretching, confirms the presence of the sulfonate group in the polymer. The S–O stretching band can be seen at about 700 cm⁻¹, and the C–S stretching vibration is at 612 cm⁻¹ [29].

The electrode potential of SPANI is strongly affected by the pH of the solution (as seen in figure 2), and its redox potential is measured as −0.173–0.027 V versus NHE in the acidic solution (pH1 ~ 4), which is much lower than that of AuCl₄⁻/Au⁺ (0.99 V versus NHE), thus the SPANI can serve as a reductant in the synthesis of Au nanosheets.

Figure 3(A) shows that 2D Au nanostructures obtained from the reaction of SPANI nanotubes and HAuCl₄ have a mass ratio of 5.6:12. Most of the 2D Au nanostructures form
hexagonally shaped plates at low magnification, and those plates are about 1–2 µm in diameter and about 10–20 nm in thickness (figure 3(B)). The chemical composition of the Au nanoplates obtained was further determined by EDX. The EDX spectrum of the precipitate obtained shows a strong peak which corresponds to the Au component (as shown in figure 3(C)), and faint peaks that correspond to C, N, and O elements, indicating that these Au nanoplates are composed of an almost pure metallic Au, the SPANI is hardly seen on the surface of these Au nanoplates.

Interestingly, most of these nanoplates obtained can form stack-like nanostructured assemblies with several (figure 4(A)) or tens of layers (figure 4(B)). The results from the transmission electron microscopy (TEM) measurements confirm that those Au nanoplates form at least 16 stacked layers (as seen in figure 4(C)). The TEM image shows that the edges of the Au plates are clear-cut. The selected area electron diffraction (SAED) pattern reveals a hexagonal symmetry structure (figure 4(D)), demonstrating that Au nanoplates grow along the (111) facet.

Our result is different from previously reported 2D Au nanostructures, such as nanoprisms, nanoplates or nanosheets, which can be randomly overlapped, or self-assembly stacked layer-by-layer [15–22]. The individual Ag or Au 2D nanostructures are separable. However, in our case, the Au nanoplates are inseparable. SEM images show that there are irregular steps on the surface of the Au nanoplates (figure 5(A)). These steps are parallel to the plane of the Au nanoplate, and a new Au nanoplate generates and grows epitaxially from the steps. The Au nanoplates are interconnected via steps to form the stack-like Au nanostructured assemblies. Background scanning electron microscope (BSEM) images clearly show that these Au nanoplates form cascade structures (figure 5(B)), the upper layer and the lower layer are parallel.

It is worth mentioning that the mass ratio of SPANI nanotubes and HAuCl₄ has a dramatic effect on the
Controlled synthesis of 2D Au nanostructure assembly with the assistance of sulfonated polyaniline nanotubes

Figure 6. (A) SEM image of cluster-like Au nanostructured assemblies at low magnification, the mass ratio of SPANI nanotubes and HAuCl₄ is 5.6:2.5. Top-left inset: zoomed SEM image showing a typical Au nanocluster assembly, the steps are labelled with arrows; bottom-right inset: zoomed SEM image showing a profile of Au nanocluster assembly, the thickness of the Au nanoplates is almost 25 nm; (B) TEM image showing the Au nanocluster assemblies, and a zoomed TEM image of an Au nanocluster assembly is inset.

Figure 7 shows the nanostructured Au synthesized with the de-doped SPANI nanotubes. The mass ratio of SPANI and HAuCl₄ is 5.6:12. Obviously, most of Au nanostructures are presented as particles, and less Au nanoplates are produced. It seems that the nanostructure and the redox state of SPANI affect the shape of the Au nanostructures.

As shown in scheme 2, the protonated acid, HAuCl₄ is a good dopant for SPANI, just as HCl is. However, HAuCl₄ is different from HCl in that HAuCl₄ is a strong oxidant.
Figure 9. TEM images of Au nanostack assemblies growing in the period of (A) 10 min, (B) 20 min, (F) and (G) 1 h, (H) 2 h, and (I) 4 h. The mass ratio of SPANI nanotubes and HAuCl₄ is 5.6:12.

for SPANI. Neoh et al [30] reported the oxidation–reduction interactions between PANI and Au (III) ions in the acid solution. It is believable that the reduction of Au (III) to Au (0) by PANI results in the degradation of PANI and the release of soluble product. Because the redox potential of HAuCl₄ is higher than that of SPANI in the acid solution, HAuCl₄ can oxidize SPANI. In order to make sure that HAuCl₄ can degrade SPANI just as it does PANI, a control experiment was carried out. The acid solution, HCl or HAuCl₄, with the same ratio to SPANI, was mixed with SPANI nanotubes for 24 h respectively. After discarding the insoluble precipitate, the filtrate containing the soluble product was collected and characterized by UV–vis spectrum (figure 8). Since the absorbance of UV–vis spectrum for the soluble product is stronger, the concentration of the soluble product in the filtrate is higher. Obviously, the filtrate from the reaction solution mixed with HAuCl₄ has a higher concentration of soluble product than that with HCl. Thus, it is reasonable to presume that HAuCl₄ can also degrade SPANI, and that the degraded SPANI releases the soluble product.

In order to understand the mechanism of the growth assembly of 2D Au nanostructures, the TEM images of these Au nanostructures during the whole process were collected. After the HAuCl₄ and SPANI nanotubes were mixed, the nanostructured Au was sampled from the reaction solution at different intervals (10 min, 20 min, 1 h, 2 h and 4 h). The sampled solution was centrifuged to remove the unreacted HAuCl₄ and placed on carbon-supported copper grid for TEM measurements.

Figure 9(A) shows that HAuCl₄ was reduced by SPANI and formed Au nanoparticles in a site on the surface of the SPANI nanotubes after HAuCl₄ and SPANI nanotubes were mixed for 10 min. The Au nanoparticles formed are irregular and their diameters are about 70–90 nm.

When HAuCl₄ and SPANI nanotubes were mixed for 20 min, more Au nanoparticles were attached onto the surface of the SPANI nanotubes (as seen in figure 9(B)), and the diameter of the Au nanoparticles increased from about 70–90 to about 80–200 nm. Some Au nanoparticles with a diameter of about 200 nm began to form stack-like nanostructured assemblies with irregular edges. Along these Au nanoparticles, Au nanoplates with a diameter of 200 nm can be seen.

When HAuCl₄ and SPANI nanotubes were mixed for 1 h, most of the Au nanoparticles were evolved into the stack-like nanostructured assemblies (figures 9(C) and (D)), and some were stripped off from the surface of the SPANI nanotubes (figure 9(D)).

When HAuCl₄ and SPANI nanotubes were mixed for 2 h, most of Au nanostructures were Au nanostack assemblies (figure 9(E)) and single Au nanoplates, and no Au nanoparticles were observed at this time. The edges of the Au nanoplates were still irregular, but the diameter of the Au nanoplates and the layers in the Au nanostack assemblies obviously increased. It is interesting that the Au nanostructures continue to grow, although few of the Au nanostructures were on the surface of the SPANI nanotubes in this period.
Obviously, SPANI nanotubes cannot promote the continuing growth of Au nanostructures at this stage. As discussed above, HAuCl₄ can degrade SPANI, and the degraded SPANI releases the soluble product, the SPANI oligomer, in the reaction solution. Obviously, it is reasonable to presume that the soluble SPANI oligomer acts as the effective reductant during the further growth of the 2D nanostack Au.

When HAuCl₄ and SPANI nanotubes were mixed for 4 h, all of the Au nanoplates finally formed hexagonal shapes (figure 9(F)). There was no increase in the diameter of the Au plates and the layers in the Au nanostack assemblies after more than 4 h of mixing. HAuCl₄ was depleted at this time, and the growth of the Au nanostack assemblies was terminated.

The whole process of the growth of the nanostructured Au materials can be summarized as follows. First, the Au nucleus is formed and grows on the surface of the SPANI. The Au nucleus evolves into nanoplates, and then stack-like nanostructured assemblies. At the same time, the SPANI nanoplates are gradually degraded and slowly release soluble SPANI segments, which ensure further growth of the Au nanoplates and nanostack assemblies until the HAuCl₄ is totally depleted.

On the other hand, the Au nanoparticles grow epitaxially along the Au(111) plane, and form hexagonal nanoplates when the Au nucleus is produced. However, the growth is imperfect, and some steps will appear on the Au(111) plane. It seems that the formation of steps may result from the crystal dislocation of single Au crystal nanoplates. Moreover, the step generated is a new active centre of growth for the Au nucleus, which will produce a new layer of Au nanoplate. The mass ratio of HAuCl₄ and SPANI will affect the orientation of the steps on the planes of the Au nanoplates. In the higher mass ratio of HAuCl₄ and SPANI (12:5.6), the steps are parallel to the Au nanoplates. The Au nanoplates generated from the steps are non-parallel, and form cluster-like Au nanostructured assemblies. In summary, the nanostructured Au materials, nanostack assemblies and nanocluster assemblies with ultra-thin single crystal structure have been synthesized using SPANI nanotubes via a facile wet chemical approach under mild conditions. This study reveals that the size and the thickness of the Au nanostructures are influenced by the mass ratio of SPANI nanotubes and HAuCl₄. The thickness of the obtained Au nanoplates can be easily controlled at about 10–30 nm. In the synthesis of the nanostructured Au, SPANI nanoplates are gradually degraded, and release the soluble reductant, which ensures further growth of the nanostructured Au.

Acknowledgments

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