Microscale Golden Candock Leaves Self-Aggregated on a Polymer Surface: Raman Scattering Enhancement and Superhydrophobicity

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Supporting Information

ABSTRACT: Gold nanoparticles (AuNP’s) prepared through a controllable synthesis and aggregation process are attractive for their unique properties that arise from their surface plasmon resonances (SPRs). However, aggregation-controlled AuNP’s on amorphous surfaces have not been well explored. In this study, we present a simple in situ synthesis method for preparing AuNP’s in which the AuNP’s self-aggregate into microscale Candock-leaf-like structures on a polyelectrolyte film (PEF) surface. In this approach, the PEF plays an important role in adsorbing and storing AuCl4− as well as in controlling the release speed of AuCl4− in the preparation process. The mechanism for forming these Candock-leaf-like structures has been illustrated by both the growth process of gold nanoparticles and the Ostwald ripening of the aggregations. AuNP’s with a unique structure exhibited significantly enhanced surface Raman scattering and strong superhydrophobicity.

INTRODUCTION

Gold nanoparticles (AuNP’s) have attracted much attention because of their unique optical properties that arise from their surface plasmon resonances (SPRs) and the intensive expectation of their applications in devices, sensors, imaging, and therapy.1–5 Much effort has been expended in synthesizing AuNP’s with controlled shape, size, and dimensionality.6–11 The AuNP’s, acting as nanoscale building blocks, can be assembled into various ordered micro/nanostructures that could show surface-enhanced Raman scattering (SERS)12 and superhydrophobic surfaces.13 Various hierarchical architectures composed of low-dimensional (D) AuNP’s have been extensively investigated, including 2D nanoplatelets, nanosheets and nanoribbons14–16 and 1D nanobelts, nanowires, nanorods, and nanotubes.17 The chemically driven assembly of AuNP’s is a relatively simple, low-cost method for fabricating hierarchical nanostructures.18 However, this approach involves at least two steps: (1) synthesizing AuNP’s in an aqueous solution with surfactants and (2) assembling AuNP’s into hierarchical nanostructures with the assistance of DNA19,20 or another special chemical interaction as a template.21–23 Furthermore, it is difficult to obtain nanostructures that could be aligned in order over a long range.

The in situ synthesis of AuNP’s with a polyelectrolyte film (PEF) is a promising approach to fabricating AuNP/polymer nanocomposites. The molecular architectures of PEF are easily controlled through adjustments of the synthesis conditions, which could provide controllable nanoreactors to tune the size and shape of nanoparticles precisely during the in situ synthesis process. For example, Chia et al. introduced amine groups into a polyelectrolyte multilayer for the in situ synthesis of size-controllable AuNP’s through photoreduction without any surfactant.24 However, the AuNP’s prepared by the traditional in situ synthesis approach are usually embedded in the polymer matrix, which prevents their self-assembly and further application as functional materials.

In this letter, we present a facile method for the in situ synthesis and self-aggregation of AuNP’s on the surface of PEF under surfactant-free conditions. The self-aggregation of AuNP’s with nanoscale thickness was achieved on the surface of a designed PEF, resulting in the unique microscale golden Candock leaf structures with well-defined morphology. To the best of our knowledge, there have been no reports on the self-aggregation of AuNP’s with morphologies similar to those that we demonstrate here. The growth process, structure, and morphology of golden Candock leaves were investigated by UV–vis extinction spectra, X-ray diffraction (XRD), and scanning and transmission electron microscopy (SEM and TEM). A reasonable formation mechanism for the novel assembly of AuNP’s was also proposed. Interestingly, this kind of unique golden Candock...
leaf structure exhibited a significant enhancement of Raman scattering and strong superhydrophobicity. Therefore, the approach described here could provide a great potential for preparing heterometal/polymer nanocomposites and thus their application as biological sensors.

## EXPERIMENTAL SECTION

### Materials and Sample Preparation

N,N-Dimethylamino-propyl acrylamide (DMAPAA) was purchased from Shenyang Wanbate Chemical Industry Co., Ltd. Methacrylic acid (MA) was purchased from Beijing Yili Fine Chemical Co., Ltd. Pentaerythritol triacrylate (PE-3A) was purchased from Kyoeisha Chemicals, Japan. Trihydrate gold(III) chloride was purchased from Shanghai July Chemical Co., Ltd. Ascorbic acid, rhodamine 6G (laser grade), and the benzil photosensitizer were purchased from Sigma-Aldrich. Photoinitiator 2-benzyl-2-(dimethylamino)-4'-morpholinobutyrophene was purchased from Acros. All chemicals were used without any further purification. The photosensitive resin was prepared by mixing DMAPAA (39 mg, 0.25 mmol), MA (53 mg, 0.61 mmol), and PE-3A (235 mg, 0.79 mmol), photoinitiator (3 mg), and photosensitizer (3 mg). After the liquid resin was stirred for 15 min, it was sandwiched between a pair of glass slides and polymerized under the irradiation of a high-voltage mercury lamp (power, 32.5 mW·cm⁻²; wavelength, 365 nm) for 3 min. Then the PEF was soaked in a gold(III) trihydrate aqueous solution (0.10 M) for 30 min at 40°C. After being washed with deionized water twice, the film was dried in air. The treated PEF was subsequently soaked in an ascorbic acid aqueous solution (0.10 M) at room temperature.

### Characterization

The extinction spectra of the PEF were recorded on a UV–vis spectrophotometer (UV-2550, Shimadzu) using a glass slide as a reference. XRD was measured with a polycrystalline X-ray diffractometer (Bruker D8 Focus), using a monochromatic Cu Kα X-ray beam. The nanostructures were characterized by SEM (Hitachi S-4300 FEG) and TEM (JEOL JEM-2100). The surface-enhanced Raman scattering measurements were performed on a micro-Raman spectrometer (Renishaw inVia) using rhodamine 6G (0.5 mM in ethanol) as the reference and a laser with the wavelength of 785 nm as the excitation source. Water contact angles were measured with contact angle instrument (JC-2000A, Shanghai Zhongchen Digital Technic Apparatus Co., Ltd.).

## RESULTS AND DISCUSSION

The procedure for our novel in situ synthesis and self-aggregation of AuNP’s on the surface of a polyelectrolyte film (PEF) is illustrated in Scheme 1. Our basic strategy for designing the PEF included the following two steps: (1) introducing an electrolyte monomer with an amine group to improve the capability to adsorb and store the AuCl₄⁻ anions inside the polymer matrix; (2) forming dense 3D polymer networks to control the release speed of the AuCl₄⁻ anions inside by increasing the amount of cross-linker in the photoresist. In practice, the PEF was obtained by photopolymerization with a modified photoresist. We prepared the photore sist by selecting N,N-dimethyaminopropyl acrylamide (DMAPAA) as the electrolyte monomer, pentaerythritol triacrylate (PE-3A) as the cross-linker, methacrylic acid (MA) as another monomer, 1 wt % benzyl as the photoinitiator, and 1 wt % 2-benzy l-2-(dimethylamino)-4’-morpholinobutyrophene as the photosensitizer. The PEF was obtained by polymerizing the liquid resin that was sandwiched between a pair of glass slides under the irradiation of a high-voltage mercury lamp. Then, we soaked the PEF in a 0.10 M H₂AuCl₄ aqueous solution for 30 min to adsorb enough AuCl₄⁻ anions into the prepared networks. The soaked PEF became slightly yellow with a broad absorption band around the wavelength of 323 nm, which indicated the adsorption of AuCl₄⁻. The broad absorption band shown in Figure 1a arose from the aggregations of AuCl₄⁻ anions in the polymer networks, as a result of the inhomogeneous distribution of amine groups in the PEF owing to the phase separation in the prepolymer system. The areas with amine groups adsorbed AuCl₄⁻ anions and acted as the sources of AuCl₄⁻ anions in the in situ synthesis of AuNP’s, as shown in Scheme 1.

During the evolution of the soaking time in a 1 M ascorbic acid aqueous solution, a band at around 550 nm was visible that could be assigned to the plasmon band of AuNP’s. The areas with amine groups adsorbed AuCl₄⁻ anions and acted as the sources of AuCl₄⁻ anions in the in situ synthesis of AuNP’s, as shown in Scheme 1.
provide seeds for the growth process of AuNP’s. Consequently, the growth and aggregation of AuNP’s were indicated by the appearance of the broadened and red-shifted plasmon band during the evolution of the soaking time. Furthermore, the growth of AuNP’s was assessed by X-ray diffraction (XRD). As shown in Figure 1b, a typical XRD pattern exhibited four characteristic diffraction peaks of a face-centered cubic (fcc) crystalline structure. These peaks could be assigned to the (111), (200), (220), and (311) planes of AuNP’s (ICSD: 52249). Then, the diameters of AuNP’s in the growth process were evaluated according to the Scherrer equation (calculation details in the Supporting Information). The results are shown in the inset of Figure 1b, where the average diameter is about 14 nm after soaking for 1 min. It increased rapidly to 21 nm at 2 min, and then remained at about 21 nm upon further increasing the soaking time.

The growth and aggregation processes of AuNP’s were directly visualized through a tracing observation by SEM images (Figure 2). The AuNP clusters were generated on the surface of PEF after being soaked in the ascorbic acid aqueous solution for 10 s (Figure 2a). The diameters of AuNP’s were almost less than 20 nm (inset of Figure 2a), forming AuNP clusters with sizes of 80–200 nm. AuNP clusters with an obvious nucleus in the center grew to 100–400 nm within 1 min (Figure 2b). Further reductions in size accelerated the growth of the AuNP clusters, resulting in the formation of microscale golden nanostructures with Candock-leaf-like morphology (Figure 2f) floating on the surface of the PEF. Moreover, the analysis of the energy-dispersive spectrum (EDS) indicated that the Candock leaves and the centered nuclei particles all consisted of Au elements (Figure S2). The sizes of these golden Candock leaves varied from about 400 nm to 1.5 μm.

TEM analysis also provides detailed information about golden Candock leaf nanostructures. The TEM image (Figure 3a) of the cross section of the nanocomposites further confirmed that a single layer of aggregated AuNP with a thickness of less than 30 nm was achieved. Furthermore, the TEM image of the golden nanostructure sliced layer distinctly shows that the golden Candock leaves are constructed from round-like assemblies of...
AuNP’s that were isolated by numerous gaps (Figure 3b). The characteristic rings in the corresponding electron diffraction (ED) pattern (inset of Figure 3b) were indexed to the (111), (200), (220) and (311) planes, which were allowed reflecting planes expected from the fcc Au28. Furthermore, the high-resolution TEM (HR-TEM) images shown in Figure 3c,d revealed that the apparent AuNP’s in the SEM images included both single-crystalline and polycrystalline phases. According to Ostwald ripening theory,29 larger structures are more stable because of the lower surface free energy. Therefore, AuNP’s from small structures could redissolve into the aqueous solution and then redeposit on the other AuNP’s to form larger polycrystalline AuNP’s.

On the basis of the experimental and analytical results, we proposed a reasonable mechanism to illustrating the whole process of forming microscale golden Candock leaves. As shown in Scheme 1, in the initial stage of the AuCl4− anions’ reduction process, the anions adsorbed on the PEF surface were reduced expeditiously to form gold seeds, which were discretely dispersed on the surface. When the external AuCl4− anions on the surface were exhausted, those anions inside the polymer matrix started to diffuse from the inside to the surface, which continually provided anions for the growth of gold seeds and resulted in the formation of both single-crystalline and polycrystalline AuNP’s. Figure 3a showed that only a few AuNP’s were synthesized inside the polymer matrix, suggesting a well-controlled release process. Although the final sizes of AuNP’s were only around 20 nm, the golden Candock leaf structures on the microscale could be achieved by Ostwald ripening. The observations from both TEM and SEM images clearly proved that the generation and growth of golden Candock leaves were mainly attributed to the self-aggregation process of AuNP’s.

A significant Raman scattering enhancement was observed from the unique golden Candock leaf structures. Figure 4 shows the Raman scattering spectra of rhodamine 6G (Rh6G) molecules on three different surfaces: the golden Candock leaf structures on the PEF, a sputtered gold film on the PEF, and a quartz plate. All samples were excited at a wavelength of 785 nm under an excitation intensity of 5.0 × 103 W/cm2. The obvious Raman bands of Rh6G molecules on the sputtered gold film were observed at 614 cm-1 for the ν(C−C−C) ring-in-plane bend, 771 cm-1 for the ν(C−H) out-of-plane bend, 1193 cm-1 for the ν(C−H) in-plane bend, and 1363, 1509, and 1650 cm-1 for ν(C−C) stretching vibrational mode, respectively.30 Surprisingly, the golden Candock leaf structures dramatically enhanced the intensity of Raman signals with an enhancement factor of more than five compared to that of the sputtered gold film. This strong Raman scattering enhancing effect could be attributed to the complicated morphology of the golden Candock leaves in which the edge thickness was less than 30 nm and the nanoscale gap between AuNP’s could construct strong plasmonic enhancing fields (Figure 3b).

Aside from the significant Raman scattering enhancement, the unique golden Candock leaf structures also exhibited excellent superhydrophobic behavior. Golden Candock leaves coated with n-dodecanethiol displayed superhydrophobicity with a maximum water contact angle (CA) of 155° as shown in Figure 5a. In contrast, the intrinsic water CA of PEF was only 30° (Figure 5b). It provided clear evidence that the formation of unique golden structures on the PEF surface efficiently improved the superhydrophobic properties of PEF. Moreover, the hydrophobicity of the golden Candock leaf structures greatly exceeded that of the sputtered gold film on PEF coated with n-dodecanethiol, on which the water CA was only 93°. The superhydrophobicity of the homogeneous golden Candock leaf structures should be attributed to the air traps generated in the interspaces of the golden Candock leaves, which suggests the morphology of the golden Candock leaves.

**CONCLUSIONS**

We successfully developed a facile method to prepare golden nanostructures through the in situ synthesis and self-assembly of AuNP’s on the surface of PEF under surfactant-free conditions. The golden nanostructures exhibited unique microscale golden Candock-leaf-like morphology with nanoscale thickness and were constructed by the self-aggregation of numerous single-crystalline and polycrystalline AuNP’s. The golden Candock leaves exhibited a 5-fold-higher Raman scattering enhancement compared to that of a sputtered gold film and strong superhydrophobicity of 155°, which would provide great potential for significant applications in molecular detection, biological sensing, and environmental monitoring.

**ASSOCIATED CONTENT**

Supporting Information. Calculation of the average sizes of AuNP’s by the Sherrer equation. Selected-area EDS of a candock-leaf-like structure. This material is available free of charge via the Internet at http://pubs.acs.org.

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