

In situ self-assembly synthesis of gold nanoparticle arrays on polystyrene microspheres and their surface plasmon resonance

Jian Gong · Xihong Zu · Wei Mu · Yulin Deng

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Abstract Gold (Au) nanoparticle arrays with tunable morphology and optical characteristics were synthesized by in situ self-assembly process that occurred on the surface of aniline-modified polystyrene (PS) microspheres. The method can be used to control the growth of both single and aggregated Au nanoparticle arrays on PS microsphere surface. This method could also be adapted for synthesis of other noble metals hybrid materials, which opens exciting opportunities for their practical applications.

Keywords Gold nanoparticle · Array · Polystyrene microsphere · Self-assembly · Morphology

Introduction

Core-shell-structured noble metal nanoparticles on polymer microspheres have received much attention due to their enhanced optical, electronic, and magnetic properties [1–3]. By introducing such nanoparticles on a polymeric bead surface, the composite microspheres have been used as a scattering contrast agent for medical imaging and optical encoding of biomolecules for sensors and immunoassays and other optical and electronic devices [4, 5]. Among these noble metal nanoparticles, gold (Au) nanoparticles have

attracted the most attention because of its unique electrical, optical, and biocompatible properties [6–9]. For example, Meredith and coworkers reported that, by coating poly(vinyl pyrrolidone)-stabilized Au nanoparticles on the surface of polystyrene (PS) beads using a solvent-controlled swelling-heteroaggregation technique, the composite material exhibits highly enhanced Raman signals of poly(vinyl pyrrolidone) capping molecules [4]. Jung and coworkers reported a porphyrin derivative based on Au@SiO₂ core/shell nanoparticles. The porphyrin-functionalized Au@SiO₂ nanoparticles were red in color and exhibited strong fluorescence emission [10]. Additionally, by changing the size, shape, composition, and the distance between the Au nanoparticles on a substrate, Au nanoparticles can efficiently convert the absorbed light into localized heat. Meanwhile the surface plasmon resonance can be tuned to near-infrared region, which can be exploited for selective laser photothermal therapy of cancer [11]. In order to fabricate morphology-controlled nanocomposites from polymer and metal nanoparticles for advanced applications, although many physical and chemical synthesis methods have been investigated to date, several challenges such as the aggregation of metal nanoparticles and a broad-size distribution have not been avoided completely [12, 13]. In most cases, the amount and the morphology of the Au nanoparticles are still far from well controlled [14, 15]. Because PS microsphere has high specific surface area, uniform distribution, and high colloidal stability in water, taking into account the advantages of PS and Au nanoparticles, the PS microspheres with Au nanoparticles have earned great attention, especially in its applications of biomedical imaging and biosensor [16, 17].

Incorporation of gold nanoparticles with polymers or inorganic materials has attracted increasing interest in improving the stability and biocompatibility to enhance the capability of immobilization. Among these materials, polyaniline (PANI)

J. Gong (✉) · X. Zu · W. Mu · Y. Deng
School of Chemical and Biomolecular Engineering,
Georgia Institute of Technology,
Atlanta, GA 30332-0620, USA
e-mail: gongj823@nenu.edu.cn

J. Gong
Key Laboratory of Polyoxometalate Science
of Ministry of Education, Department of Chemistry,
Northeast Normal University,
Changchun, Jilin 130024, People's Republic of China

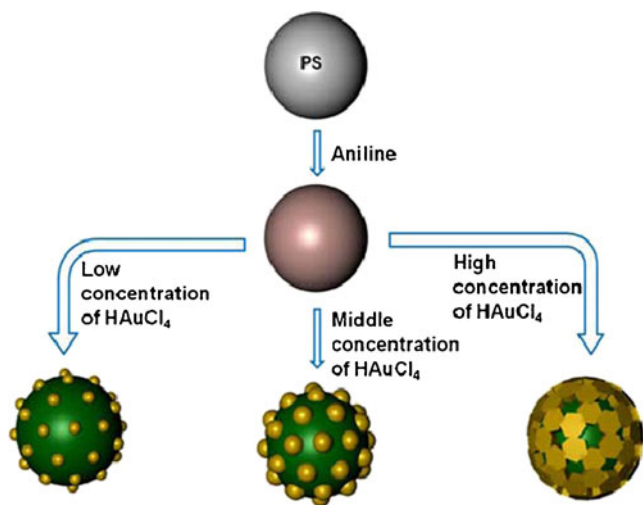
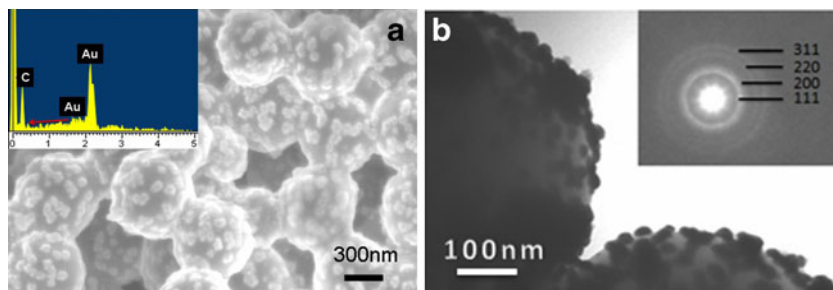


Fig. 1 Schematic illustration of the procedure for synthesizing the Au nanoparticle arrays on PS composite microspheres

has been proven particularly useful in the development of biosensors. Polystyrene latex spheres are a kind of functional polymer materials, which have many admirable properties such as biocompatibility, nontoxicity, high surface area, and chemical inertness. Taking into account the advantages of PS, PANI, and gold nanoparticles, the core–shell nanocomposite has been fabricated and was applied to assemble a glucose biosensor [16]. Gu et al. [17] used an adsorption method to load preprepared Au nanoparticles to PS latex surface. Shi et al. [18] used commercially available ion-exchange resins as a support for Au nanoparticles. Panigrahi and coworkers reported the direct deposition of Au NPs from chloroauric acid (HAuCl_4) followed by NaBH_4 reduction onto conventional polymer particles in water [19]. Liu et al. [20] studied the direct deposition of Au nanoparticles onto commercial polymer spheres in aqueous media by loading HAuCl_4 onto the PS latex surface followed by NaBH_4 reduction. Feng et al. [21] reported a method to prepare polyaniline/Au composite hollow spheres. In their study, monomer aniline was first introduced into the PS latex particles, and then was reduced by HAuCl_4 . The reduction product of Au nanoparticles was directly deposited on PS nanosphere surface to form Au core and PS/PANI shell composite particles. By dissolving the PS core, hollow Au/PANI spheres were prepared.

Fig. 2 SEM (a) and TEM (b) images of the Au nanoparticle arrays on the PS composite microspheres prepared with 15 mM of HAuCl_4 . The insets are the corresponding EDX and ED patterns



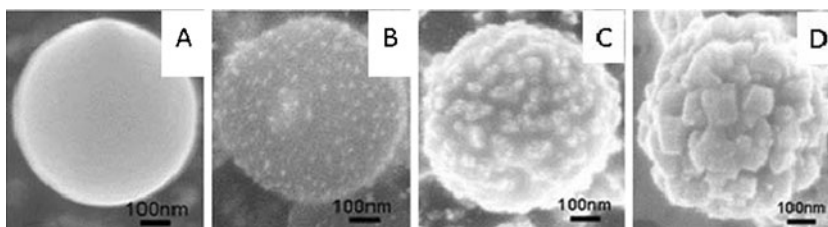
Although different methods have been developed to coat Au nanoparticles on polymer spheres, the amount and the morphology of the Au coating layer are far from well controlled. Herein, we studied a self-assembly process for synthesizing Au nanoparticle arrays on aniline-modified PS microspheres. One of the advantages of our method is that both the amount and morphology of Au nanoparticles on the surface of the PS composite microspheres can be tuned by simply varying the concentration of HAuCl_4 in the reaction system, and the coverage of Au nanoparticles on PS surface can be very high. For the first time, large cubic-shaped Au nanoparticle aggregate array on PS microsphere surface was obtained by using this method. It has been known that the surface roughness in the form of bumps, pits, ridges, valleys, etc. significantly amplifies the local electromagnetic field [22]. It can be seen from this report that our Au-coated PS composite microspheres can have either a relative smooth or a very rough surface. The possible formation mechanism of the Au nanoparticle arrays on the PS composite microspheres is also discussed. The optical property of such Au nanoparticles on PS surface was characterized by using ultraviolet–visible (UV–Vis) spectrometry.

Experiments

Instruments and reagent

All chemicals were analytical grade. Aniline was distilled twice under vacuum before use. The transmission electron microscopy (TEM) images were obtained using a JEOL JEM-100 CXII transmission electron microscopy with an acceleration voltage of 100 kV. The samples for TEM observations were prepared by dispersing onto a carbon-coated copper grid. The scanning electron microscopy (SEM) images were analyzed using LEO 1530 thermally assisted field emission scanning electron microscopy. Fourier transform infrared (FT-IR) spectrum was measured on a Magna-IR 550 spectrometer with a KBr pellet. The frequency range was 2000–400 cm^{-1} . The X-ray diffraction (XRD) was measured with X'Pert X-ray diffractometer using $\text{CuK}\alpha$ source. Scans were made from 10° to 80° (2θ) at the speed of 2°min^{-1} . UV–Vis diffuse reflectance spectrometry of the samples were obtained

Fig. 3 SEM images of aniline-swelled PS microspheres (a) and the Au nanoparticle arrays on the PS composite microspheres prepared with 8 mM (b), 15 mM (c), and 25 mM (d) of HAuCl₄ at higher magnification



with Beckman-DU-8B UV spectrophotometer in the range of 400–800 nm.

Preparation of PS nanoparticles

Surfactant-free emulsion polymerization was used for PS nanoparticle preparation. Styrene monomer (8 g) was added to 70 g of distilled water under stirring (600 rpm) for 15 min at 70 °C in a nitrogen atmosphere. An aqueous solution of initiator (2 mL of water containing 0.05 g of potassium persulfate) was added, and the reaction was held for 4 h. Finally, the emulsion was naturally cooled to ambient temperature, and the monodispersed PS colloid was obtained. The diameter of the PS nanoparticles was about 600 nm.

Preparation of the Au nanoparticle arrays on PS composite nanospheres

Aniline (0.02 mL) was added to 2 mL of water at 0 °C and under ultrasonic treatment for 2 min followed by the addition of 0.1 mL of the above PS nanoparticles solution. The mixture was stirred with ultrasonic assistance for 5 min at 0 °C to allow sufficient absorption of aniline into the PS nanoparticles. After 1 h at room temperature, the swelled PS nanoparticles were separated by centrifugation and washed with distilled water at least three times. HAuCl₄ solution

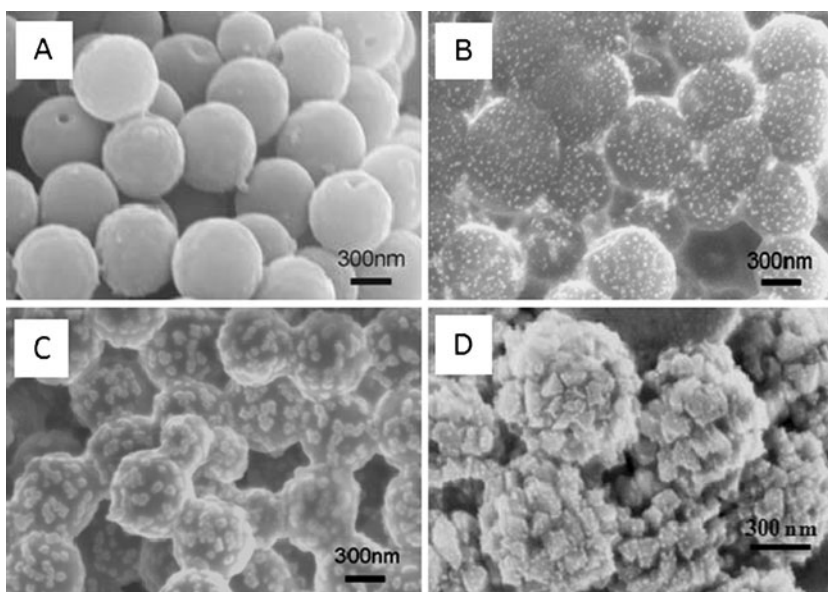
with different concentration (8, 15, and 25 mM, respectively) was prepared. Then 2 mL of HAuCl₄ solution was added into the modified PS nanoparticles. The mixture was stirred slowly and maintained at 0 °C for the first 5 h. After that, the polymerization was carried out for 12 h at room temperature. An olive suspension was obtained.

Results and discussion

The formation process of the Au nanoparticle arrays on the PS composite microspheres is described in Fig. 1. In our experiments, required amount of aniline monomer was added to the PS microspheres suspension in water and mixed. Because aniline has a higher affinity with PS polymer but water, it was absorbed by PS to form aniline-swelled PS microspheres. When these aniline-swelled PS microspheres were immersed in HAuCl₄ water solution, the oxidation–reduction reaction between aniline and HAuCl₄ happened on the surface of PS microspheres. As a result, aniline was oxidized to PANI, and Au³⁺ was reduced to Au nanoparticles which were enmeshed on the surface of the PS microspheres.

Figure 2 shows the typical SEM and TEM images of the Au nanoparticle arrays on the PS composite microspheres. The SEM image shows that a large Au nanoparticles array

Fig. 4 SEM images of aniline-swelled PS microspheres (a) and the Au nanoparticle arrays on the PS composite microspheres prepared with 8 mM (b), 15 mM (c), and 25 mM (d) of HAuCl₄ at lower magnification



was formed on the surface of the PS microspheres (Fig. 2a). The inset is a pattern of energy-dispersive X-ray analysis of the Au nanoparticle arrays on the PS composite microspheres, which reveals the presence of carbon, nitrogen (arrow), and gold, confirming the compositions of the aim products. From Fig. 2b, it can be clearly seen that many black dots exist, which indicates the presence of Au nanoparticles. The inset is the electron diffraction pattern of the Au nanoparticles, which confirms that the Au nanoparticles are polycrystallines.

Figure 3a is the PS microsphere after swelled with aniline but before reacted with HAuCl_4 , which clearly shows the shape of the PS microsphere does not change by absorbing aniline. The average diameter of the spheres is ca. 600 nm. Different from the swelled PS microspheres, the Au nanoparticle arrays on the PS–PANI microspheres surface showed an array of Au nanoparticles. The concentration of HAuCl_4 in the reaction system can affect the shape and pattern of Au nanoparticles on the surface of the PS microspheres. It is obvious from the SEM images that the content of Au nanoparticles on the surface of the PS microspheres increases with increasing the concentration of HAuCl_4 in reaction system (Fig. 3b–d). Meanwhile, we found that all microspheres after reacted with HAuCl_4 at different concentrations show Au nanoparticle array pattern on the surface. However, the size, shape, and amount of Au nanoparticles are different. For a low concentration of 8-mM HAuCl_4 reaction system (Fig. 3b), the resulting product shows uniformly distributed single Au nanoparticle array. The distance between any two single Au nanoparticles is about 50 nm. With increasing the concentration of HAuCl_4 to 15 mM (Fig. 3c), the array patten of Au nanoparticles was kept, but the single Au nanoparticles are replaced by aggregates of Au nanoparticles. When the concentration of HAuCl_4 was further increased to 25 mM (Fig. 3d), it was clearly seen that the single or aggregates of Au nanoparticles are replaced by bigger Au nanoparticles (~100 nm) or crystal with a cubic type of morphology which has not been reported in literature before. Because of the large and rough

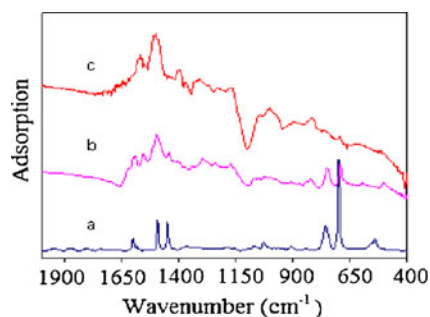


Fig. 5 FT-IR spectra of pure PS (a), the Au nanoparticle arrays on PS composite nanospheres (b), and above product immersed in THF for 24 h (c)

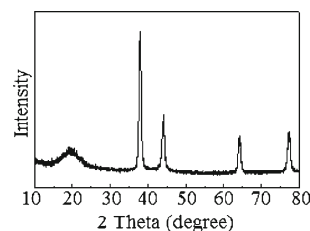


Fig. 6 XRD pattern of the Au nanoparticle arrays on the PS composite nanospheres

aggregates as well as high coverage of Au on the PS microspheres, this unique material may be more effective for Raman spectrum enhancement. The large area of this unique morphology was shown in Fig. 4. To the best of our knowledge, this is the first to be seen that cubic Au nanoparticles or crystal are arrayed on the surface of polymer. We deduce that the array of Au nanoparticles is related with the reduction of aniline in solid phase. In our reaction, the formation of polymerization of aniline is caused by oxidation of Au^{3+} in acidic solution. When the reaction is started, the Au^{3+} is diffused from solution to the microsphere surface to react with aniline. As a result, Au^{3+} is reduced into Au atom and forms a nucleus on the PS surface. Meanwhile, aniline is oxidized to polyaniline. The further reaction involves the diffusion of aniline to the Au nucleus site to participate the reaction. The aniline monomer in a small radial area around Au nucleus on the PS surface will diffuse to that particular nucleus to form an Au nanoparticle in that small area. As a result, an array pattern of Au is formed on the PS microsphere surface. It was also found that although the increase of concentration of HAuCl_4 will change the size of each Au crystal or aggregate, all the samples show a clear array pattern of Au on the PS microsphere surface (see Figs. 3 and 4).

The FT-IR spectra are shown in Fig. 5. The curve a is the characteristic absorption of pure PS, which shows the typical absorption peaks of PS latex particle at 1,600, 1,490, 1,450, 750, and 694 cm^{-1} [23]. In the spectrum of the Au

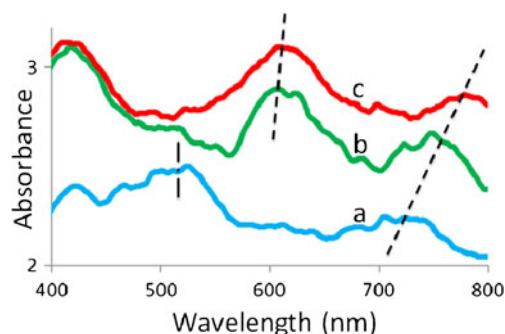


Fig. 7 UV-Vis diffuse reflectance spectrometry of the Au nanoparticle arrays on the PS composite microspheres prepared with 8 mM (curve a), 15 mM (curve b), and 25 mM (curve c) of HAuCl_4

nanoparticle arrays on the PS composite nanospheres (curve b), it is clearly seen that a new peak at $1,550\text{ cm}^{-1}$ and a group new peaks between $1,200\text{--}1,400\text{ cm}^{-1}$ appear. Because of the interference of PANI and PS peaks, the Au nanoparticle arrays on the PS composite nanospheres was immersed in tetrahydrofuran (THF) for 24 h before it was determined. As shown in the FT-IR spectra (curve c), the characteristic absorption peaks of PANI appear at $1,550$ and $1,490\text{ cm}^{-1}$ are corresponding to the C=C stretching vibration of quinoid and benzenoid rings, respectively. The peaks around $1,260\text{ cm}^{-1}$ attributes to the C–N stretching vibration with aromatic conjugation. The peak at $1,145\text{ cm}^{-1}$ assigned to the characteristic of Q=NH⁺–B (where Q and B denote quinoid ring and benzene ring, respectively) is also observed [24]. Two peaks (750 and 694 cm^{-1}) of PS that do not overlap with the peaks of PANI have completely disappeared in curve c. It is evident the PS is successfully removed after immersing the Au nanoparticle arrays on the PS composite nanospheres into THF.

XRD pattern of the Au nanoparticle arrays on the PS composite nanospheres shows a broad peak at $2\theta=20^\circ$ (Fig. 6), which is ascribed to the periodicity parallel of PANI chains or amorphous PS [25]. Meanwhile, four additional peaks at 38° , 43° , 65° , and 77° representing Bragg reflections from (111), (200), (220), and (311) planes of Au are observed [26], which indicate the existence of Au nanoparticles on the PS composite nanospheres.

It is well known that localized surface plasmon resonance excitation in metal nanoparticles can produce scattering spectra [27–29]. The peak position of plasmon resonance of metal nanoparticles will shift for different particle size, shape, and interparticle distance [4, 30]. Here, UV–Vis diffusion reflectance spectrometry of the Au nanoparticle arrays on the PS composite microspheres is shown in Fig. 7. For the UV–Vis spectrum of the smallest Au nanoparticle arrays on the PS–PANI microspheres, the plasmon resonance peak appears around 520 nm, and meantime a broad plasmon peak appears at longer wavelengths (ca. 725 nm) due to the aggregated Au nanoparticles, which is consistent with the early report [4]. With increasing the size of Au nanoparticles arrays on the PS composite microspheres, the plasmon resonance peaks are red-shifted as shown in Fig. 7 (dotted line). This significant red-shifting of the plasmon resonance peak can be attributed to intensified interparticle coupling resonance due to Au nanoparticles crowding on the PS microspheres [29].

Conclusion

In summary, we developed a new method that could in situ synthesize and control the Au nanoparticle arrays on PS composite microspheres. It was found that different amount

and morphologies of Au nanoparticles can be deposited on the nanospheres of polyaniline–polystyrene composite by reduction reaction between aniline and H₂AuO₄. The density and the shape of the Au nanoparticles strongly depend on the concentration of H₂AuCl₄ in the solution. Increasing the reactant concentration will increase the particle size of Au on the PS surface. The morphology of gold nanoparticles on the PS surface prepared at 25 mM H₂AuCl₄ is unique. At low H₂AuCl₄ concentration, a single Au nanoparticle array with a uniform distribution was founded. At high concentration of H₂AuCl₄, large cubic shape of Au nanoparticle aggregates was observed for the first time. These large Au aggregates also show an array pattern on PS latex surface. The morphology and size of the Au nanoparticles on the surface of the PS composite microspheres are tunable by changing the concentration of H₂AuCl₄ solution in the reaction system. This method provides a facile way for direct synthesis of noble metal nanoparticles-covered polymer microspheres which has potential applications in biosensing fields.

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