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Spontaneous assembly and synchronous scan spectra of gold nanoparticles monolayers Janus film with thiol–terminated polystyrene

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This communication presents a facile methodology for preparing ordering hydrophilic metal nanoparticles into a gold nanoparticles monolayers Janus film (top face solvent–phobic polystyrene and bottom face solvent–philic nanoparticles) with thiol–terminated polystyrene. It also reveals the enhanced light source spectrum properties of gold nanoparticles monolayers Janus film.

The assembly of nanoparticles with an asymmetric, hybrid structure into two– or hierarchical structures is of considerable interest due to their already widespread and potential applications in electronic, optical devices and sensing devices.[1] Gold nanoparticles can be controlled using polymers ligands on the nanoparticle size, shape, and surface functionality, which in turn affect the nanoparticle's performance.[2] For example, upon aggregation, the surface plasmon resonance for each GNP becomes delocalized, altering the optical properties.[3] The gold nanoparticles show selective and efficient destruction of cancerous cells due to the significant thermo–plasmonic effect of nanostructures.[4]

A novel assembly procedure to form close packed 2–dimensional nanoparticle films with high regularity by converting nanoparticle repulsive force into van der Waals interactions through in situ coating of nanoparticles on the interface with alkane-thiols was presented.[5] However, the alkane-thiols terminated single nanoparticle facilely rolls over under Brownian motion due to the size and quality of alkane chain are very small. In order to obtain the homogeneous and bulk monolayer film of nanoparticles, polymer-thiols are suggested to fix gold nanoparticles to form the Janus film (top face solvent–phobic polystyrene and bottom face solvent–philic nanoparticles) on the interface.[6] As we known, Janus substance has different assembly behaviours and properties due to its many categories and a variety of shapes.[7] Many efforts have been devoted to the investigation of Janus substance over the past few years, focusing both on novel preparation strategies and on theory of simulation.[8]

In the past years, many experimental work and theoretical calculations have been reported concerning the fluorescent properties of gold nanoparticles.[9] However, the quantum efficiency of such AuNPs is very low, limiting the widespread use of fluorescence properties in biosensing.[10] In recently, functionalizing AuNPs becomes a powerful tool to drive the assembly of groupings with optical properties thanks to their large absorption and scattering cross sections at visible plasmon resonance frequencies.[11] Synchronous scan spectra have received intense attention due to its high sensitivity and simplicity during recent years. It has successfully analyzed complicated multi-component samples when they have severely overlapping emission and/or excitation spectra that limit the ability of single-wavelength fluorescence measurement.[12] Therefore, the functionalizing AuNPs can be utilized by synchronous scan spectra to enlarge its tremendous scope for applications.

In order to obtain the homogeneous and bulk monolayer film of nanoparticles in this communication, polymerthiols are suggested to form Janus film on the interface with gold nanoparticles. A facile methodology for preparing ordering hydrophilic metal nanoparticles into a gold nanoparticles monolayers Janus film with thiol–terminated polystyrene at the interface of toluene and water is presented. The synchronous scan spectra show the enhanced light source spectrum properties of gold nanoparticles monolayers Janus film. The destabilized gold nanoparticles due to the addition of alcohol are adsorbed into an interface where the surface of entrapped Au nanoparticle was in situ coated with the thiol–terminated polystyrene present in a transition toluene layer.

Fig. 1 Schematic representation of the AuNP nanoparticle Janus film formation at liquid–liquid interface and the synchronous scan spectra obtained.

Schematic representation of the AuNP nanoparticle Janus film formation at liquid–liquid interface and the synchronous scan spectra obtained is shown in Fig. 1. Gold nanoparticles monolayers Janus film with thiol–terminated polystyrene (PS–SH) was facilely prepared. The destabilized gold nanoparticles due to the addition of alcohol are adsorbed into an interface where the surface of entrapped Au nanoparticle was in situ coated with the thiol–terminated polystyrene consisting in a transition toluene layer. The synchronous scan spectra show the enhanced light source spectrum properties of gold nanoparticles monolayers Janus film. The surface enhanced spectra characteristics of the AuNP–PS asymmetric particles films are of interest in the fields of optical devices and sensing devices.

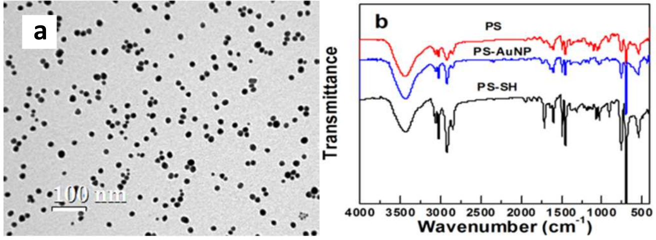
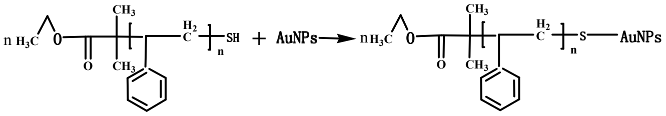


Fig. 2 TEM image of the gold colloid (a) and IR spectra of PS, PS–SH and PS–AuNP (b).

We chose large AuNPs for this work due to the larger colloids will resulting in stronger enhancement in light source spectrum than that from smaller colloids.[13] Fig. 2a is the TEM image of the AuNP in colloid with 3.0 ml of sodium citrate solution (0.034 mol / L). As can be seen from the TEM photograph, the gold particle dispersion and the particle shape are uniform. The average size of AuNP is about 11.0–15.0 nm (**ESI†**, Fig. S2). The preparation of AuNPs is presented with different amounts of reductant (**ESI†**) .

Polystyrene mentioned above in this communication was synthesized by atom transfer radical polymerization (ATRP). Then thiol–terminated polystyrene was synthesized by reaction of thiourea with the bromide–terminated polymer (**ESI†**). Fig. 2b shows IR spectra of PS and PS–SH. The peak at wave number of 3600 cm^{-1} is the N–H bond absorption peaks; the peak at wave number of 3080–2920 cm^{-1} is benzene ring absorption peaks; the peaks at wave number of 1600 cm^{-1}, 1492 cm^{-1} and 1462 cm^{-1} are benzene ring skeleton vibration absorption peaks; the peaks at wave number of 756 cm^{-1} and 696 cm^{-1} suggest that the reaction product with mono–substituted at the benzene ring. Therefore the resulting product was confirmed that PS was the successful synthesized. The IR spectra of the particles and of PS–SH are similar, which indicates that the thiol is indeed part of the composite.[14]

As can be seen from Fig. 2b, all the absorption peaks on the IR spectra of PS–Au and PS present peculiar peaks; it means that the polymer obtained is polystyrene. The intensity of absorption peak of the obtained product becomes lower compared to that of PS, which indicates that the polystyrene was thiolated gold nanoparticles.



Scheme 1. AuNPs Janus film by self–assembly of AuNP at liquid−liquid interface depicted structurally with chemical structural formula.

AuNPs Janus film by self–assembly of AuNP at liquid−liquid interface is depicted structurally in Scheme 1 (**ESI†**). Due to the ethanol addition, the driving force for the entrapment of gold nanoparticles at the interface is at the hexane/water interface.[15] Reincke and his colleagues suggested this process on the basis of a thermodynamic evaluation of the charged nanoparticles self–assembly at the water/oil interface.[16] With the addition of ethanol, the electrostatic repulsive force between nanoparticles was weak; the entrapped nanoparticle would result in the irreversible aggregate of nanoparticles at the interface. Meanwhile, hydrophilic thiol–terminated of polystyrene prone to interface from toluene extend to aqueous phase, resulting in gold nanoparticles reaction with the styrene-thiol groups in the oil phase and water. This prevents the entrapped nanoparticles aggregating. Therefore, the decrease of electrostatic repulsive force leads to the formation of a close–packed nanoparticle film by counteracting the van der Waals interaction. Because of the attracting force among the trapped nanoparticles as there is polystyrene-thiol in the toluene layer, the density of nanoparticles at the interface increase. After toluene evaporation, the repulsive force disappears and the distance between nanoparticle gets closer. The monlayer gold nanoparticles film was obtained (**ESI†**). In this process, the interface allows the half surface gold nanoparticles reacts with the thiol–terminated of polystyrene and the other half do not participate in the reaction.

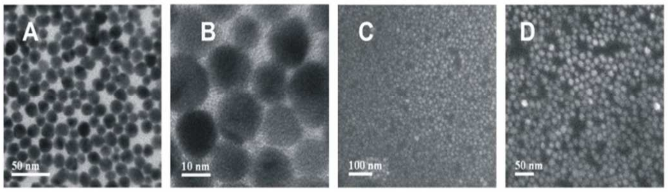


Fig. 3 TEM (A, B) and SEM (C, D) images of the Au–PS asymmetric particles films. The average diameter of the Au nanoparticles is about 13.0 nm.

Although it is possible to assemble nanoparticles into monolayers on the interfaces, void areas between the nanoparticle aggregates appearances. It is due to the broad size distribution and competitive electrostatic repulsion against long–range van der Waals interactions.[5]

Field emission transmission electron microscopy (FETEM) and scanning electron microscopy (FESEM) images were obtained on a JEM–200CX TEM and JSM–6700F SEM, respectively (**ESI†**). Fig. 3 shows FETEM (A, B) and FESEM (C, D) images of the Au–PS asymmetric particles films. There is monolayer of nanoparticles with lots of voids as polystyrene-thiolated was added (Fig. 3A and C). As previously reported, the film with close–packed gold nanoparticles in the TEM images coexists with large void areas.[5] However, Fig. 3B and D shows a corresponding enlarged in FETEM and FESEM images, presenting the monolayer nature. As shown in the TEM image, nanoparticles are in direct contact with each other. Fig. 3B and D show close and ordered–nanoparticle films if without taking into account the void area.

The synchronous scan spectra were performed at room temperature on a RF–5301PC Spectrofluorophotometer (Shimadzu Corporation, Japan) equipped with a 150 W Xenon lamp, a recorder and dual monochromators (**ESI†**). The sample was adjusted under the condition of 45°–angle geometry in the direction of light. The enhanced light spectra of excitation were obtained at the wavelength of 636 nm and the enhanced light spectrum of emission at the wavelength of 515 nm. The enhanced light spectra of the Au–PS asymmetric particles Janus films are shown in Fig. 4a. The maximum enhanced spectra intensity of excitation and emission are at the wavelength of 598 nm and 637 nm, respectively. This similar result on AgNPs was also demonstrated by Lukomska J et al.[13]

The enhanced light spectra of excitation and emission are overlap. In order to eliminate the interference influence of adjacent peaks and obtain the sharp, simple and precise value of enhanced light spectra intensity, the synchronous scan spectrometry always is made.

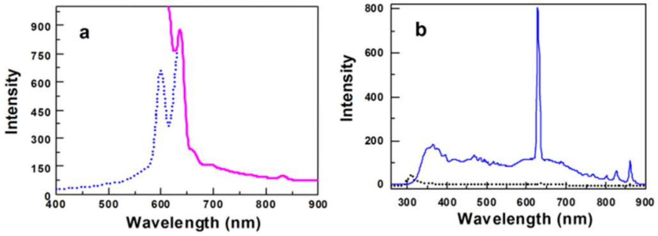


Fig. 4 (a) Enhanced light spectra of excitation (dot line, λem=636 nm) and emission (solid line λex=599 nm) spectra of the Au–PS asymmetric particles films on the quartz glass; (b) Synchronous scan spectra of the Au–PS asymmetric particles films on the quartz glass (solid line) and quartz glass (dot line, Δλ=57 nm).

The enhanced light spectra of the Au–PS asymmetric particles films on the quartz glass and quartz glass is shown in Fig. 4b. The surface light spectrum peaks of quartz glass are slight. However, the nanoparticle films on a quartz substrate prepared in the presence of PS–Au shows a sharp enhanced light peak centred at the wavelength of 634 nm. It is due to the large surface plasmon characteristics of these films[5].

In conclusions, we present a facile methodology for preparing ordering metal nanoparticles into a gold nanoparticles monolayers Janus film. AuNPs and PS–SH were obtained firstly. Then the gold nanoparticles react with the polystyrene-thiols groups at interface between the oil phase and water due to the hydrophilic polystyrene extending to aqueous phase from toluene. Due to the addition of alcohol, the destabilized gold nanoparticles are adsorbed into an interface where the surface of entrapped Au nanoparticle was in situ coated with the thiol–terminated polystyrene consisting in a transition toluene layer. After toluene evaporation, the monolayer gold nanoparticles film was obtained. The neatly arranged gold particles have been observed by TEM and SEM on this nanoparticles Janus film. Due to introduction of functional polystyrene-thiols and orderly nanoparticles, the synchronous scan spectra show the enhanced light source spectrum properties of gold nanoparticles monolayers Janus film. It is expected that there would be facile preparation of this Janus film, and tremendous scope for applications of this ordering and surface functionalizing, such as in electronic, optical and sensing devices.

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Notes and references

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