

Supplementary Material (ESI) for RSC Advances
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Supporting Information

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

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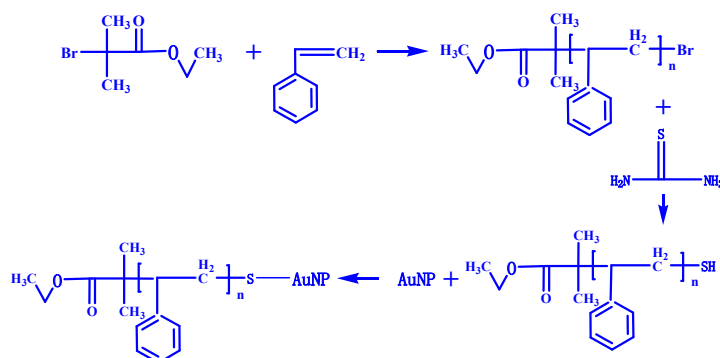
Chemicals and Materials.

Styrene (CP, purchased from Sinopharm Chemical Reagent Co., Ltd.) was washed with 5% NaOH aqueous solution, dried over anhydrous MgSO₄, and distilled under reduced pressure. CuBr (CP, purchased from Sinopharm Chemical Reagent Co., Ltd.) was soaked with dilute sulfuric (1.0 mol/L) and purified by washing with glacial acetic acid and ethanol three times after steeping in dilute sulfuric acid and drying in a vacuum oven at 100 °C. Tetrahydrofuran (THF, AR grade, Sinopharm Chemical Reagent Co., Ltd.) and cyclohexanon (AR grade, Sinopharm Chemical Reagent Co., Ltd.) were distillation under reduced pressure. H₂AuCl₄·4H₂O (Sinopharm Chemical Reagent Co., Ltd.), Sodium citrate (Na₃C₆H₅O₇, Sinopharm Chemical Reagent Co., Ltd., AR 96%) were used without further purification. Sulfoarea (GC), ethyl 2-Bromoisobutyrate (GC), *N, N, N', N', N''*-Pentamethyldiethylenetriamine (PMDETA, GC) was purchased from TCI (Shanghai) and were used as received. Glacial acetic acid (AR grade), ethanol (AR grade), toluene (AR grade), sulfuric acid (AR grade), ammonia chloride (AR grade), MgSO₄ (AR grade), NaOH (AR grade) and methanol (AR grade) were all purchased from Sinopharm Chemical Reagent Co., Ltd. High purity N₂ was obtain from Yingshang Jiang Shanghai Chemical., Ltd. All the solvents were distilled under reduced pressure before use.

Self-Assembly of AuNP Janus Film at Liquid-Liquid Interface.

AuNPs Janus film by self-assembly of AuNP at Liquid-liquid interface is depicted

structurally in Scheme S1. Firstly, ATRP initiator of 0.19 mL Ethyl 2-bromoisobutyrate, 21.6 mL styrene monomer, 19.4 mL Cyclohexanon were added into a Schlenk flask. After stirring for 60 min under N₂ atmosphere and reduced pressure at 0 °C three times, a mixture of 0.26 mL PMDETA and 0.18 mg CuBr was introduced to the Schlenk flask. The ATRP polymerization was conducted at 110 °C for 8 h under N₂ atmosphere and stopped by exposure to air. The mixture was diluted with THF and passed through a neutral alumina column (200–300 mesh) to remove the impurities from their preparations of synthetic. The substrates were washed with water/methanol and dried under reduced pressure at 60 °C.¹



Scheme S1. AuNPs Janus film by self-assembly of AuNP at Liquid-liquid interface depicted structurally with chemical structural formula.

Secondly, Thiol-terminated polystyrene (PS-SH) was synthesized by reaction of thiourea with the bromide-terminated polymer. Functionalization of polymer chain end from bromine to thiol was carried out by reacting the bromine terminated 1.0 g PS with 0.2 g thiourea in 30 mL THF solution by stirring 2.0 h was heated at 100 °C under argon flow for 24 h, followed by treatment with aqueous of 0.13 g/ml NaOH. Then, two drops dilute sulfuric acid were added and the mixture was stirred at room temperature for an additional 5.0 h. the solution was washed with water/methanol and dried under reduced pressure at 60 °C. The substrates were stored at room temperature.²

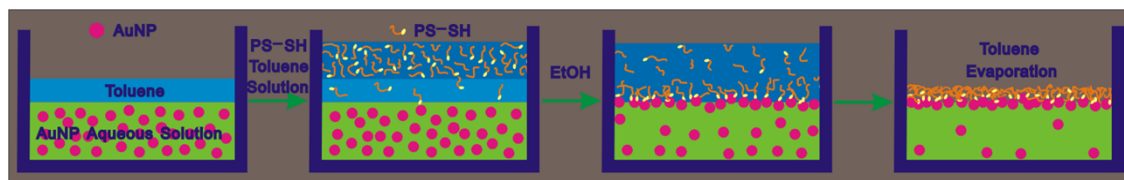


Figure S1. Schematic representation of the AuNP nanoparticle Janus film formation at liquid-liquid interface

Figure S1 shows a schematic representation the corresponding experiment images

of the steps involved in preparing the AuNP nanoparticle Janus film formation at liquid–liquid interface. Firstly, sodium citrate was added into 100 ml stirred boiling water which was refluxed for 8.0 min. An aqueous solution of 1.0 mL 0.024 mol/L HAuCl₄ was added quickly. Reflux was continued for another 6.0 min until a red solution was observed.

Then, the 10.0 mL, 0.1% colloidal particles were dispersed in 40.0 mL water, and added 0.005 g PS–SH into 10.0 ml toluene under stirring. After phase separation due to 10.0 ml toluene was dropped into colloidal solution, slowly dropped PS–SH solution into it. 10.0 min later, 20.0 mL ethanol was added into the dispersion drop by drop. At last, the Janus film of AuNP appears. The films with PS on one side and AuNP on the other side were collected.

Characterization.

Field emission transmission electron microscopy (FETEM) images were obtained on a JEM–200CX TEM (JEOL, Japan) equipped with a Model GATAN782 CCD camera at an operating voltage of 120 kV. In order to prepare FETEM specimens, polymer/AuNP film was deposited onto a carbon–coated copper grid.

Field emission scanning electron microscopy (FESEM) images were obtained on a JSM–6700F SEM (JEOL, Japan) at an operating voltage of 15.0 kV. In order to prepare FESEM specimens, polymer/AuNP film was deposited onto a silicon wafer.

Ultraviolet–visible (UV–vis) spectra were obtained with an Agilent 8453 spectrophotometer (Agilent technologies, CA, USA) equipped with an automatic sampling system.

The FT–IR spectra were measured by an American Nicolet FT–IR 380 spectrometer by dispersing the sample in potassium bromide.

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. The slit (ex/em) width was 3.0 nm/3.0 nm. The sensitivities of the equipment were chosen high. The enhanced light spectra of excitation and emission were recorded in range of 220–900 nm at $\lambda_{em}=636.0$ nm and $\lambda_{ex}=599.0$ nm, respectively. The enhanced light spectra were recorded in range of 220–900 nm with synchronous scanning at $\Delta\lambda=\lambda_{ex} - \lambda_{em}=57.0$ nm.

Preparation of AuNPs

Figure S2a shows that UV–vis absorption spectra of the gold colloid series synthesized with different amounts of reductants (Sodium citrate: 1 ml, 2 ml, 3 ml, 4 ml, 5 ml). Figure S2a inset shows that the absorption peaks with the proportioning of the sample. Absorption peak of gold colloids becomes blue shift, then red shift with adding reductants. The wavelength of absorption peak of gold colloids is the shortest as the adding 3 ml sodium citrate. It suggests that the size of nanoparticles firstly become smaller and then grow up with adding reductants.

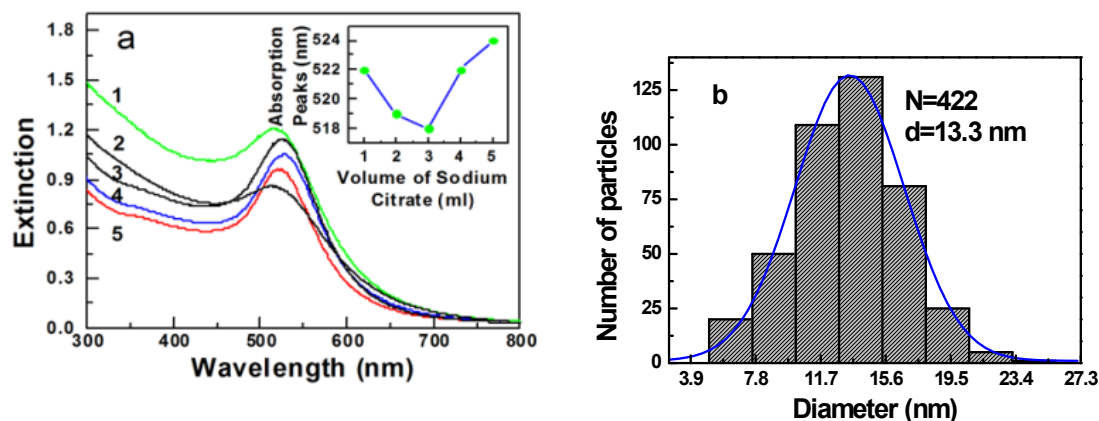


Figure S2 (a) UV–vis extinction spectra of the gold colloid series synthesized with different amounts of reductant (Inset: Absorption peaks.). (b) Different sizes of the percentage of gold particles. (HAuCl₄: 0.024 mol/L, sodium citrate: 0.034 mol/L)

According to literature³, the optimal volume ratio of sodium citrate and HAuCl₄ for preparation of small diameter gold nanoparticles is 3:1. Therefore, if the addition of sodium citrate is less than this ratio, less citrate ion adsorbs on the surface of the gold particles. The surface potential difference becomes lower. This is easy to lead the particle size become larger. As the excess amount of trisodium citrate to the acid chloride of gold (Ratio of more than 3:1), the positive Na⁺ of system easily neutralizes negative charge on citrate ion adsorbed on the surface of gold nanoparticles, resulting in gold nanoparticle size increase. Accordingly, sodium citrate is both trisodium citrate reductions and stabilizing agent.

Figure S2b is the different size of the percentage of choosing gold particles. The numbers of gold nanoparticle between 10.2 nm to 12.8 nm, 12.8 nm to 15.4 nm and 15.4 nm to 18 nm account for about 25.7%, 30.9% and 19.1%, respectively.

References

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