

## Supporting information for

# **Salt-induced size-selective separation, concentration, and preservation of zwitterion-modified gold nanoparticles**

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## **Experimental Section**

### **Materials and instruments**

2-(Dimethylamino) ethane thiol hydrochloride (purity > 95%) and sodium borohydride (purity > 96%) were purchased from Sigma-Aldrich. Chloroauric acid tetrahydrate, ether, acetone, Trisodium citrate dihydrate, acetic acid glacial, 1,3-propane sultone, sodium hydroxide, sodium perborate tetrahydrate, and anhydrous magnesium sulfate were obtained from domestic suppliers and were of analytical reagent grade. All the materials were used as supplied.

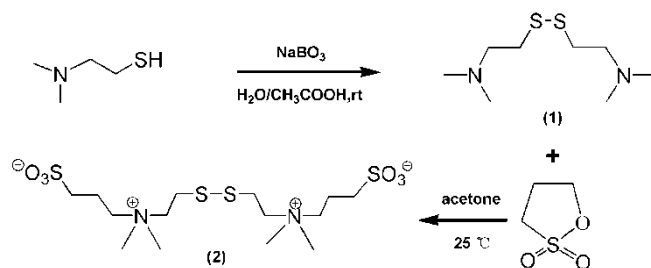
UV-vis absorption spectra were recorded on a UV-1800 UV-vis spectrophotometer (Shimadzu, Japan). Transmission electron microscopy (TEM) was performed on JEM-2100F and JEM-1230 transmission microscope (JEOL, Japan). NMR spectra were obtained at room temperature on an INOVA 400 spectrometer (Varian, America).

### **Synthesis of 4, 16 and 70 nm citrate capped Au nanoparticles<sup>1,2</sup>**

18.5 mL of H<sub>2</sub>O, 0.5 mL of  $1.0 \times 10^{-2}$  mol dm<sup>-3</sup> HAuCl<sub>4</sub>, and 0.5 mL of 0.01 mol dm<sup>-3</sup> sodium citrate were stirred in an ice-bath cooled three-necked flask for 5 min. Then, 0.5 mL of 0.1 mol dm<sup>-3</sup> NaBH<sub>4</sub> was added to the solution. The color changed from light yellow to orange, indicating the formation of the 4 nm Au NPs as determined by TEM image.

50 mL of 0.01% HAuCl<sub>4</sub> (by weight) was quickly heated to boiling while stirred vigorously. Then, 1 mL of 1% sodium citrate (by weight) was added and the color of the solution changed from light yellow to wine-red gradually. The solution was stirred for another 30 min and then cooled down to room temperature. These procedures generated the 16 nm Au NPs. The 70 nm Au NPs were prepared through similar procedures by decreasing the sodium citrate to 0.3 mL.

### **Synthesis of zwitterion disulfide and ligand exchange of citrate ion by zwitterion disulfide**

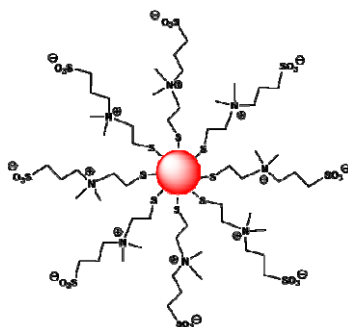


**Scheme S1** Synthesis of bis(2-dimethylaminoethyl)disulfide **1** and zwitterion disulfide **2**.

Zwitterions disulfide was synthesized according to reference 3, which was schematically shown in Scheme S1. 10 mmol (1.42 g) of 2-dimethylaminoethane thiol was oxidized to bis(2-dimethylaminoethyl) disulfide (**1**) in 70% v/v aqueous acetic acid by adding 20 mmol (3.07g) of sodium perborate. The reaction solution was stirred for 2 h at room temperature. Then, sodium hydroxides were gradually added and the disulfide was separated in the form of oil from the solution (at a pH of about 13). The oil was extracted with ether, which was dried over anhydrous  $\text{MgSO}_4$  and removed by reduced pressure distillation after  $\text{MgSO}_4$  was filtered. The final product **1** (colorless oil) was obtained, with a yield of 60%.

Then, the mixture of 3 mmol (0.63 g) product **1** and 6.6 mmol (0.81 g) propane sultone was stirred for 12 h in dry acetone (50 mL) at room temperature. The white precipitate formed was filtered, rinsed with dry acetone ( $3 \times 10$  mL), and then dried under vacuum at  $30^\circ\text{C}$ , with a yield of 70%.

$^1\text{H}$  NMR of **1** (in  $\text{CDCl}_3$  versus TMS, 400 MHz,  $\delta$ ): 2.2 (s, 12H, N ( $\text{CH}_3$ )<sub>2</sub>), 2.5-2.6 (t, 4H,  $\text{SCH}_2$ ), 2.8-2.9 (t, 4H,  $\text{CH}_2\text{N}$  ( $\text{CH}_3$ )<sub>2</sub>).  $^1\text{H}$  NMR of **2** (in  $\text{D}_2\text{O}$  versus TMS, 400 MHz  $\delta$ ): 2.2-2.3 (m, 4H,  $\text{CH}_2\text{CH}_2\text{SO}_3$ ), 2.9-3.0 (t, 4H,  $\text{SCH}_2$ ), 3.0-3.2 (t, 4H,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{SO}_3$ ), 3.2 (s, 12H, N ( $\text{CH}_3$ )<sub>2</sub>), 3.4-3.6 (m, 4H,  $\text{CH}_2\text{SO}_3$ ), 3.6-3.8 (m, 4H,  $\text{SCH}_2\text{CH}_2$ ).



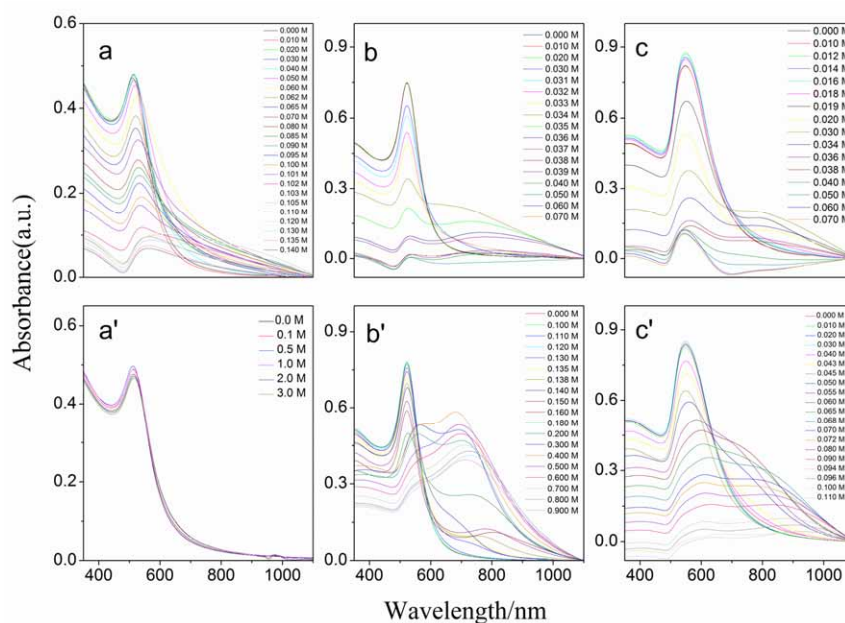
**Scheme S2** Schematic configuration of zwitterion-modified Au NP.

25  $\mu\text{L}$  of  $1 \times 10^{-2}$  mol  $\text{dm}^{-3}$  disulfide and 24 mL of citrate-capped Au NPs was continuously stirred for 12 h at the room temperature to allow sufficient ligand exchange of the citrate ion by zwitterion disulfide. At such a concentration, the molecule amount equals nearly 1 monolayer, 3 monolayers, and 12 monolayers on the

4, 16, and 70 nm Au NPs, respectively, which were calculated by knowing the zwitterion ligand molecule area ( $0.25 \text{ nm}^2$ )<sup>3</sup> and the total Au nanoparticle surfaces in the dispersions (evaluated from the feeding amount of HAuCl<sub>4</sub> and TEM-determined particle size). The final surface configuration of zwitterions on the surface of an Au NP was shown in Scheme S2.

### Critical coagulation concentrations of unmodified and zwitterion-modified Au NPs.

Varying amount NaCl was added into Au NP dispersions of equal volume in a series of vials. The dispersions were left undisturbed for 2 min and the time-dependent UV-vis spectra were then measured. All the UV-vis spectra for the three sized, both unmodified and zwitterion-modified Au NPs were shown in Fig. S1. As is seen, apart from a continuous decrease in intensity of the surface plasmon of isolated Au NPs (about 520 nm), a new broad peak starts to appear and gradually red-shifts for dispersions with NaCl concentration above a certain value. This broad peak, a sensitive indicator for particle aggregation, indicates the formation of Au NP aggregates. Therefore, the critical coagulation concentration, the lowest NaCl concentration that enables particle aggregation, can be determined from the UV-vis spectra.

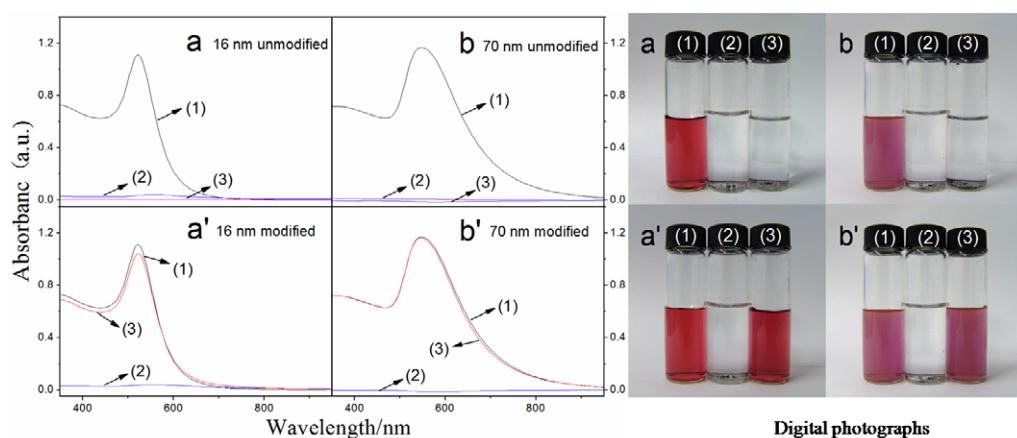


**Fig. S1** UV-vis spectra of unmodified (a, b, and c) and zwitterion-modified (a', b', and c') Au NPs upon the addition of varying amount of NaCl. a, a' : 4 nm; b, b': 16 nm; and c, c': 70 nm.

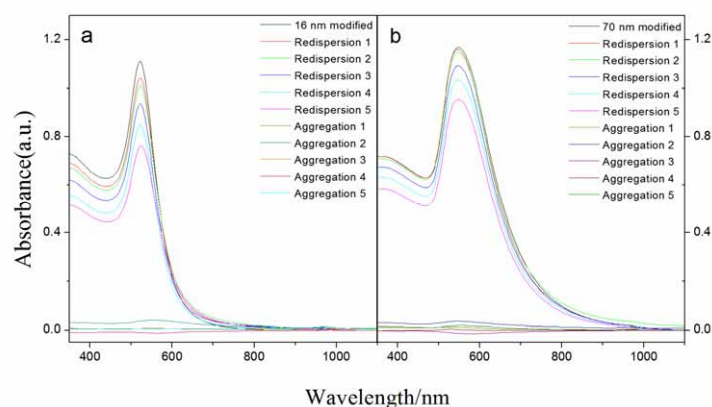
### Irreversible aggregation of unmodified Au NPs, reversible aggregation of zwitterion-modified Au NPs, and particle separation

Particle aggregation was initiated by adding NaCl into 6 mL of unmodified and

zwitterion-modified Au NP dispersions (final NaCl concentration of 0.5 and 0.09 mol dm<sup>-3</sup> for 16 and 70 nm Au NPs respectively). After leaving the dispersions undisturbed for 12 h, particle aggregates settled at the bottom of the bottle and were collected upon removing the clear colorless supernatant. The aggregates were then gently shaken in 6 mL of deionized water. Fig. S2 shows that the aggregates of unmodified Au NPs cannot be recovered into dispersions again (see curves (3) in panels a and b and bottles (3) in photographs a and b), while those of the zwitterion-modified Au NPs can be recovered into well dispersed dispersions (see curves (3) in panels a' and b' and bottles (3) in photographs a' and b').



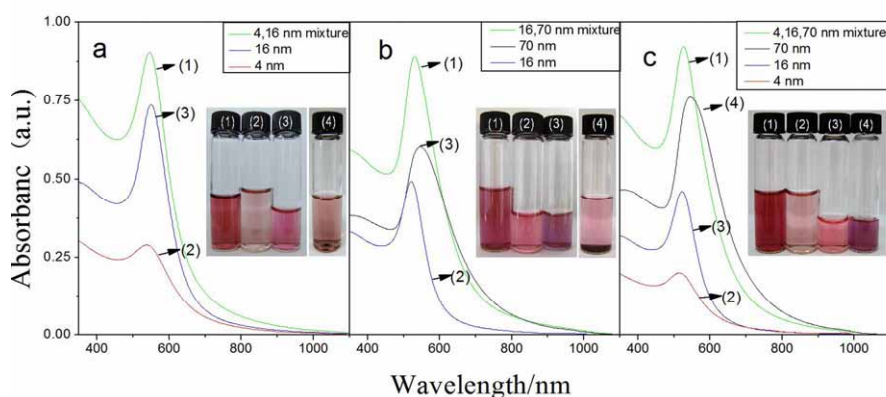
**Fig. S2** UV-vis spectra and digital photographs of original dispersions (curve (1) and bottle (1) in each panel and photograph), salt-induced, aggregated dispersions (curve (2) and bottle (2) in each panel and photograph), and redispersions of the shaken, aggregated dispersions (curve (3) and bottle (3) in each panel and photograph). a, a' : 16 nm and b, b' : 70 nm.



**Fig. S3** UV-vis spectra of the supernatants of aggregation and the redispersions for (a) 16 and (b) 70 nm zwitterion-modified Au NPs.

To further demonstrate the reversible aggregation property of zwitterion-modified Au NPs, the cycles of aggregation and redispersion were repeated. For time saving reason, the aggregates were separated and collected by centrifuging at 2000 rpm for 5 min after leaving the aggregated dispersions undisturbed for 3 h. Redispersion of the particle aggregates was easily realized by shaking them in deionized water. The next aggregation was achieved by adding equal amount of NaCl into the redispersions. The UV-vis spectra of the supernatants and the redispersions for 5 cycles of aggregation and dispersion were shown in Fig. S3. The integrated area of their surface Plasmon as a function of cycle number is shown in Fig. 1.

Particle separation is detailed in the text. Fig. S4 shows the UV-vis spectra and digital photographs of the binary and ternary mixtures before and after size-selective separation.



**Fig. S4** UV-vis spectra and digital photographs of (a) 4/16 and (b) 16/70 nm binary mixtures and (c) 4/16/70 nm ternary mixture before and after size-selective separation. The 4/16 and 16/70 nm binary mixtures were separated by adding 0.5 and 0.09 mol dm<sup>-3</sup> NaCl (final concentration), respectively, and the 4/16/70 nm ternary mixture by first adding 0.09 and then 0.5 mol dm<sup>-3</sup> NaCl (final concentration). The bottles labeled (4) in (a) and (b) show the particle aggregates which deposited at the bottom of the bottles after adding NaCl and leaving the mixtures undisturbed for 12 h.

## References

- (1) R. T. Tom, V. Suryanarayanan, P. G. Reddy, S. Baskaran, and T. Pradeep, *Langmuir*, 2004, **20**, 1909-1914.
- (2) G. Frens, *Nat. Phys. Sci.*, 1973, **241**, 20-22.
- (3) L. L. Rouhana, J. A. Jaber, and J. B. Schlenoff, *Langmuir*, 2007, **23**, 12799-12801.