Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

pH-Responsive reversible self-assembly of gold nanoparticles into nanovesicles

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Experimental section

Materials

Chloroauric acid tetrahydrate ($HAuCl_4•4H_2O$) and oleylamine (OL) were purchased from Sinopharm Chemical Reagent. Rhodamine B (RhB) was purchased from Beijing Yinghai Fine Chemical Plant. Tert-butylamine borane complex (TBAB) and 4-mercaptobenzoic acid (4-MPA) were purchased from J&K Scientific Ltd.. Toluene, ethanol, petroleum ether, sodium hydroxide, and hydrochloric acid were purchased from Beijing Chemical Plant. All the reagents were used without further purification.

Synthesis of Au NPs

Au NPs were synthesized according to a previous report.[1] Typically, $HAuCl_4•4H_2O$ (100 mg) was dissolved in a mixture of toluene (10 mL) and OL (10 mL) at 25℃ to obtain an orange solution. Under vigorous stirring, a reducing agent solution containing TBAB (43.5 mg), OL (1 mL) and toluene (1 mL) was injected into the aforementioned solution of $HAuCl_4$. After addition of ethanol, Au NPs were collected and washed twice with toluene and ethanol. Finally, Au NPs were dispersed in 6 mL of toluene.

Surface modification and self-assembly of Au NPs

Surface modification of Au NPs was performed by a ligand exchange method. In a centrifuge tube (10 mL), 4-MPA (25 μL, 6 mM) was added in an ethanol solution of

Au NPs (25 μL Au NPs dispersed in 2 mL ethanol). The mixture was treated with ultrasound for 30 min. Then, 6 mL of petroleum ether was added to precipitate Au NPs. After centrifugation, the MPA modified Au NPs were collected.

Self-assembly of Au NPs modified by 4-MPA was conducted by ultrasonic treatment. As-obtained Au NPs were dispersed in deionized water (2 mL) and then the solution was treated with ultrasound for 30 min.

Characterization

Transmission electron microscopic (TEM) and high resolution TEM (HRTEM) images were obtained with a JEOL-2100F microscope with an accelerating voltage of 200 kV. UV-Vis absorption spectra and fluorescence spectra were collected by using a UV-3900 and F-4600 spectrophotometer, respectively. Fourier transform infrared (FTIR) spectra were recorded on a Perkin Elmer GX spectrophotometer scanning from 4000-400 cm^{-1} with a resolution of 4 cm^{-1}.

Cycling test on reversible assembly and disassembly of Au NVs

NaOH (1M) aqueous solution were added in the solution of vesicles with a volume ratio of 0.005:1 to disassociate the Au NVs. HCl aqueous solution (2M) was added in with the same volume ratio to recover the vesicular structure. After ultrasound treatment for 10 min, 1 mL aliquot was removed and analyzed on a UV-Vis spectrophotometer.

Release of RhB encapsulated in Au NVs

RhB was used as a model molecule to test the controlled release performance of Au NVs induced by pH stimuli. RhB was dissolved in deionized water and 4-MBA modified Au NPs was added in. Subsequently, the mixed solution was sonicated. The formed vesicle solution was centrifugated to remove the supernatant and the residual sediment was washed with deionized water. The final products were dispersed in water and the solution was kept stationarily for several hours before fluorescent tests. Finally, a certain volume of NaOH (5mM) was added in this solution at 2 min intervals to trigger the release of RhB. For the second release, the experimental procedure was the same as that mentioned above. It should be noted that new RhB needs to be added in the solution again.

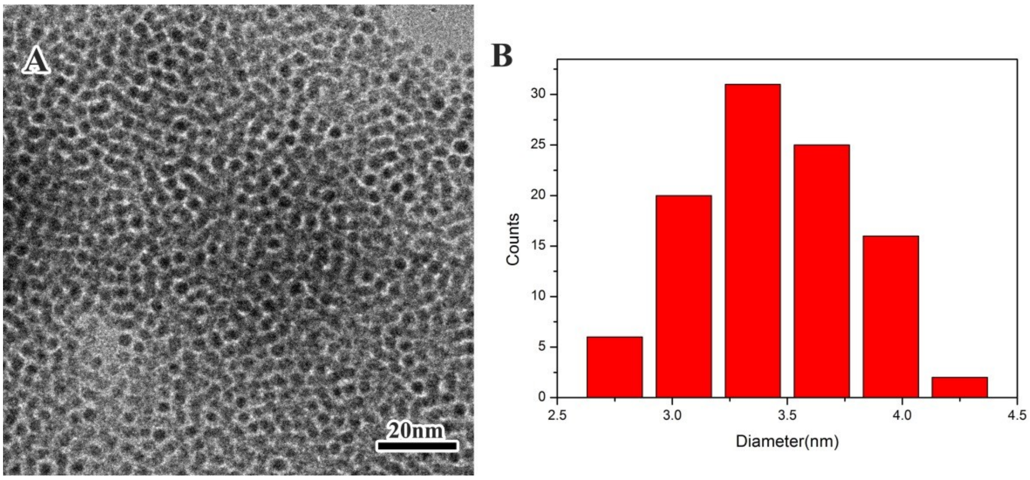

Fig. S1 TEM image (A) and size distribution (B) of Au NPs capped with OL (3.4 ± 0.3 nm).

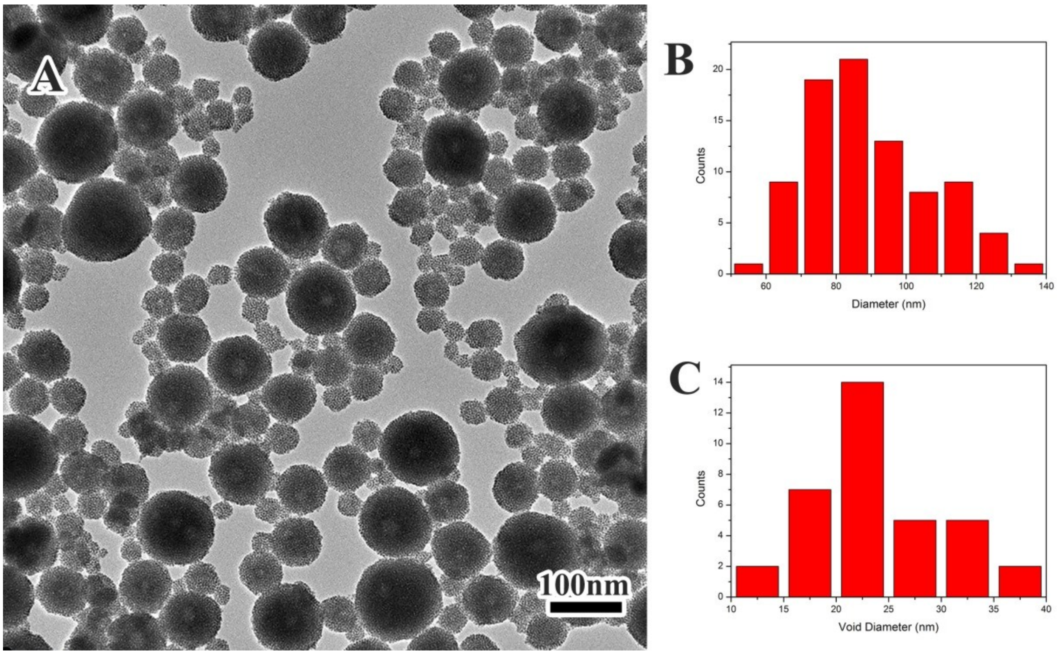

Fig. S2 (A) TEM image of self-assembled Au NVs and size distributions of (B) vesicles (89.2 ± 16.8 nm) and (C) voids in NVs (23.4 ± 6.5 nm).

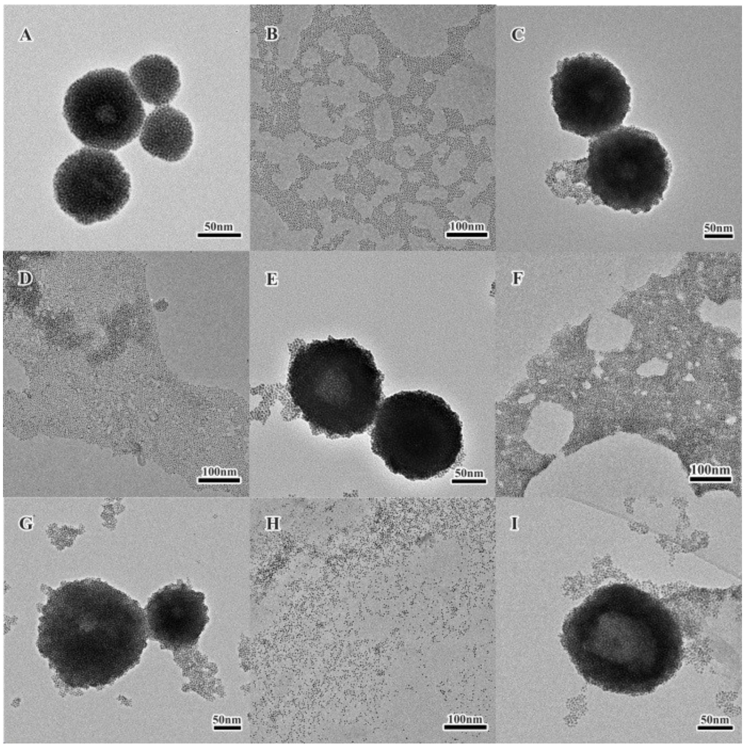

Fig. S3 TEM images of reversible changes on morphology induced by NaOH and HCl. (A) 1st, assembly; (2) 1st, disassembly; (C) 2nd, assembly; (D) 2nd, disassembly; (E) 3rd, assembly; (F) 3rd, disassembly; (G) 4th, assembly; (H) 4th, disassembly; (I) 5th,assembly.

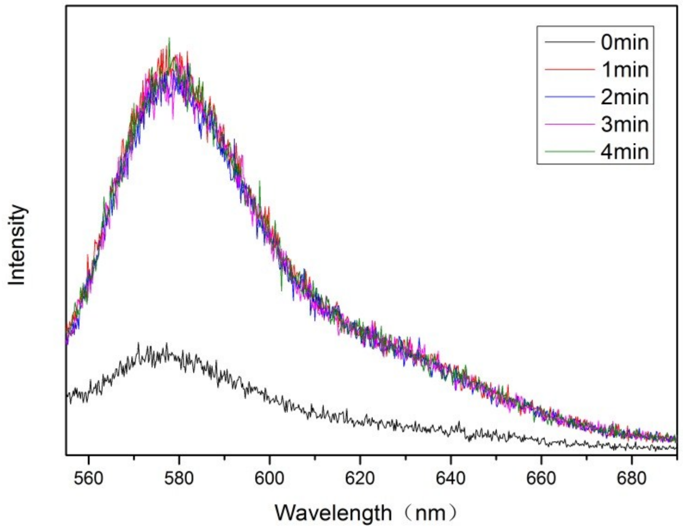

Fig. S4 Fluorescence emission spectra of RhB released from Au NVs after addition of a certain amount of NaOH over time.

Reference:

1. S. Peng, Y. M. Lee, C. Wang, H. F. Yin, S. Dai, S. H. Sun, *Nano Res*, 2008, **1**, 229.