Al^{3+}-directed electrostatic self-assembly and their surface plasmon resonance properties of Au nanocrystals

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Electronic Supplementary Information

Experimental details

Materials. Hydrogen tetrachloroaurate trihydrate ($HAuCl_4 \cdot 3H_2O$), rhodamine (R6G), and bis(p-sulfonatophenyl)phenylphosphine (BSPP) were obtained from Sigma-Aldrich. Other analytical grade reagents came from Guangdong Guanghua Chemical Reagent Co., such as sodium citrate ($Na_3C_6H_5O_7$) and aluminium chloride ($AlCl_3$). All the reagents were used without further purification. Milli-Q water (> 18.0 MΩ cm) was used to prepare all aqueous solutions.

Synthesis of Au nanoparticles (NPs). In a typical procedure for the preparation of Au NPs,[1] 40 mL of 2.5×10^{-4} M $HAuCl_4$ solution was heated and kept boiling and vigorous stirring for 30 min in an oil bath. Subsequently, 4 mL of 1% $Na_3C_6H_5O_7$ solution was introduced into the above solution quickly. After stirring 20 min, the color of the boiled solution changed to ruby red, indicating the formation of the Au NPs. Finally, the Au NPs growth was quenched by ice-cold ultrapure water.

Al^{3+}-directed electrostatic self-assembly of the Au NPs. In a typical procedure for the Al^{3+}-directed electrostatic self-assembly of the Au NPs, the as-prepared Au NPs solution was centrifuged two times at 8500 rpm for 15 min and the precipitate was dilute with ultrapure water to 20 mL. The freshly prepared Au NPs solution was then mixed with excess BSPP (with the final concentration of 0.3 mg/mL) and stirred overnight to form BSPP-capped Au NPs with negative charge. The resulting mixture was centrifuged at 8500 rpm for 15 min and redispersed in ultrapure water. The concentration of the BSPP-capped Au NPs was estimated ca. 1.35×10^{-9} M. Finally, 0.5 mL of the BSPP-capped Au NPs solution diluted into 2 mL was added different concentrations of $AlCl_3$ solution for obtaining different Au NPs self-assemblies through firstly shaking for a little while and then static for 5 min.

Instrumentation. Transmission electron microscopy (TEM) studies were performed by using a Hitachi H-7500 microscope operated at 80 kV. UV-visible (UV-vis) absorption spectrum was acquired with a Hewlett-Packard 8452 diode array spectrometer (U-3010). SERS spectra were acquired using a confocal microprobe Raman system (LabRAM Aramis, France) operated with a He-Ne laser (632.8 nm). The SERS samples were prepared according to the following procedure: (1) 500 μL of BSPP-capped Au NPs or NAs solutions were concentrated into 100 μL by centrifugation at 8500 rpm for 15 min, (2) 100 μL 2 mM R6G solutions were then introduced into the as-prepared BSPP-capped Au NPs or NAs solutions and diluted into 2 mL with Milli-Q water (the final concentration of R6G was 0.1 mM), (3) finally, 20 μL of the resulting mixtures were dropped into cleaned ITO glass for the SERS measurements. The SERS data were acquired for 10 s and 2 times.

References

1. G. Frens, *Nat Phys Sci*, 1973, **241**, 20.

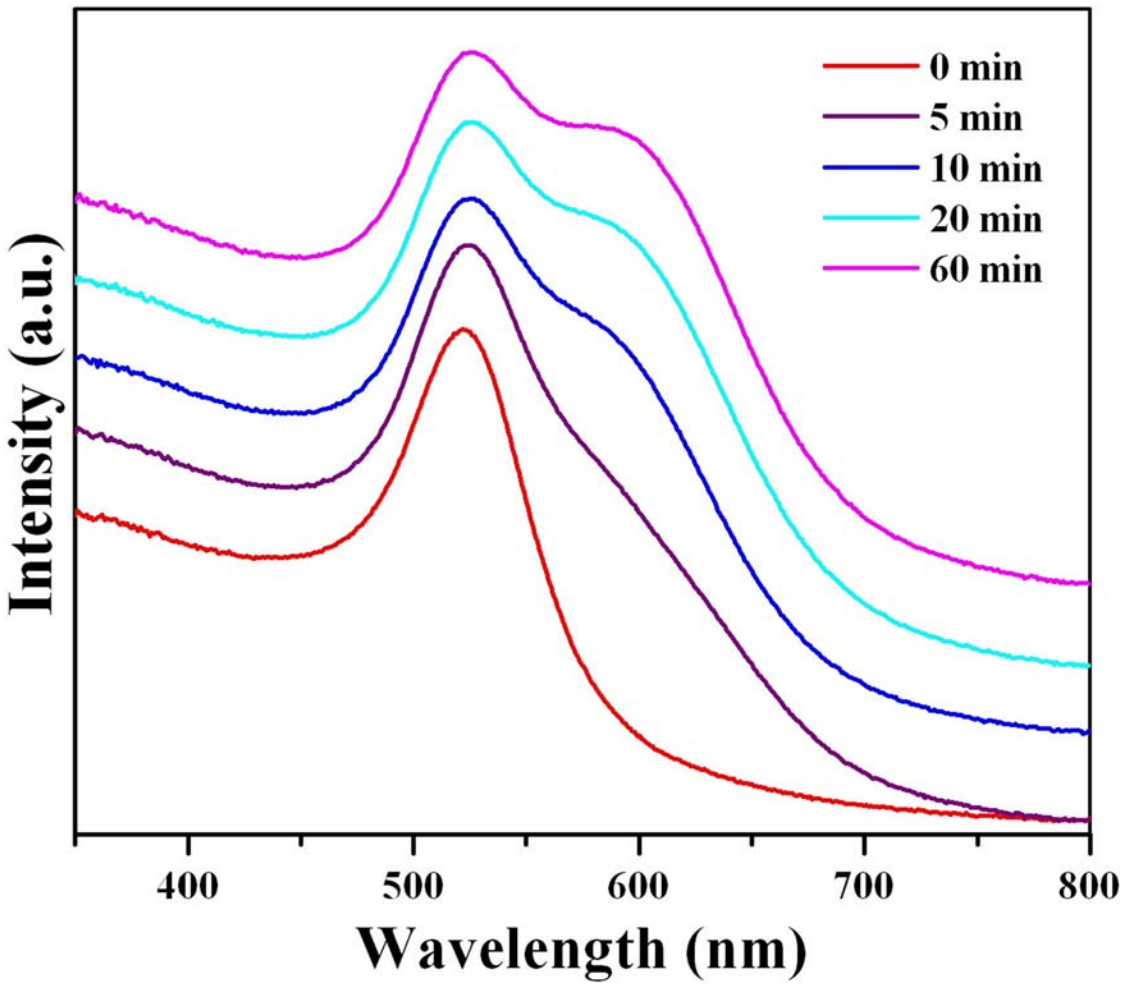

Fig. S1 UV-visible absorption spectra of the Au NPs and nanoassemblies solutions with different assembly time in the presence of 14 μL 2×10^{-4} M Al^{3+} solution, respectively.

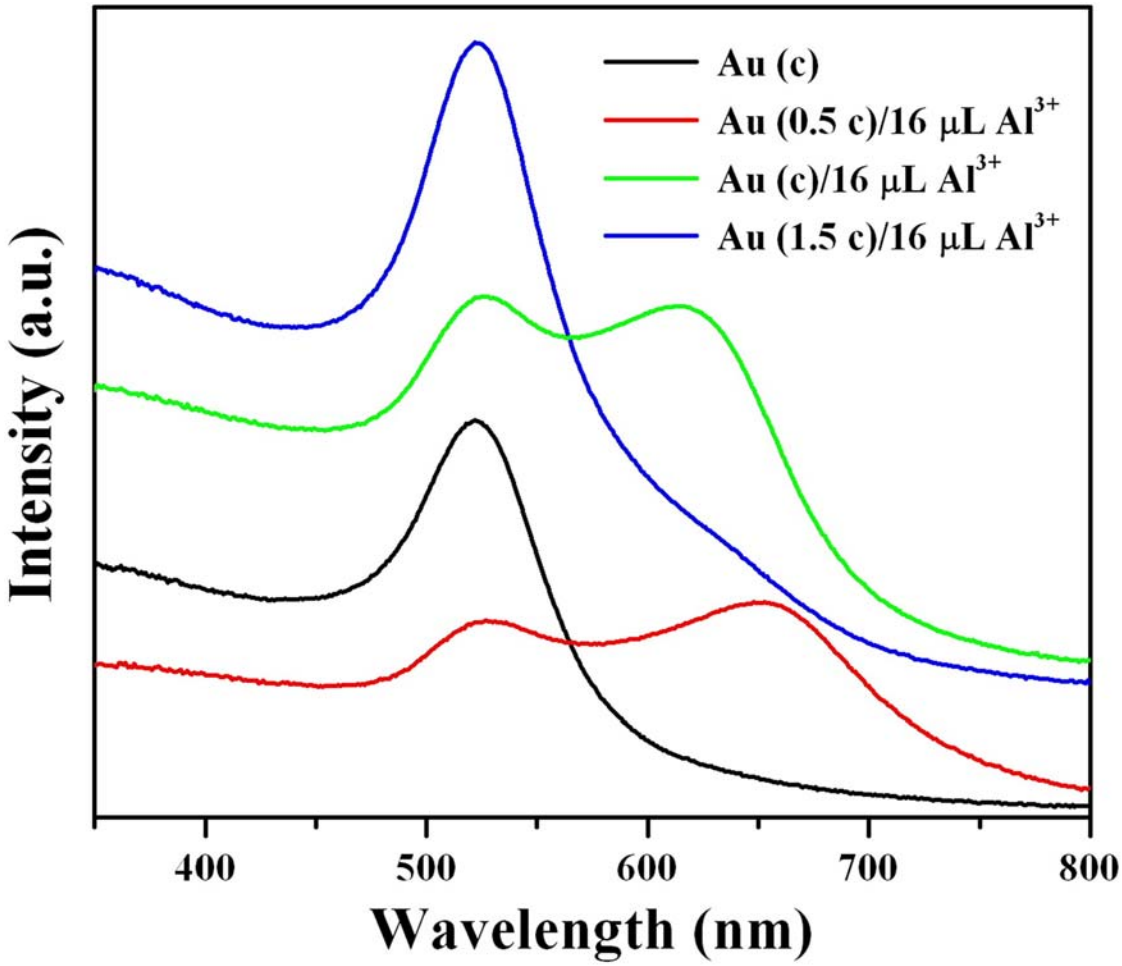

Fig. S2 UV-visible absorption spectra of the Au NPs and nanoassemblies solutions with different Au NPs concentration in the presence of 16 μL 2×10^{-4} M Al^{3+} solution for 5 min, respectively.