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Communication

## Freezing the self-assembly process of gold nanocrystals†

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### †Electronic Supplementary information

#### 10 Experimental methods

##### Synthesis of gold nanoparticles (AuNPs)

AuNPs are synthesized using Turkevish method.<sup>1</sup> First, 110  $\mu\text{L}$  of  $\text{HAuCl}_4$  solution (sigma-484385) is added to 100 mL nanopure water (18.2  $\text{M}\Omega\text{-cm}$ ) to prepare 1mM  $\text{HAuCl}_4$  solution. The prepared solution is then boiled under vigorous stirring. 10 mL of sodium citrate (38.8 mM) is briefly preheated  
15 and added to the boiling  $\text{HAuCl}_4$  solution quickly. The solution becomes colorless before changing to violet and finally to ruby red. The resulting AuNPs are 32nm  $\pm$ 5 nm and they are used without any further modification.

##### Synthesis of gold nanorods (AuNRs)

AuNRs are synthesized using a seed-mediated approach.<sup>2,3</sup> Seed solution was prepared by adding 1 ml  
20 of an ice-cold solution of 10 mM sodium borohydride to 10 ml of 0.1 M cetyltrimethylammonium

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bromide (CTAB) and  $2.5 \times 10^{-4}$  M HAuCl<sub>4</sub> (aq.) solution under magnetic stirring at room temperature. The color of the solution changed from yellow to brown. Growth solution was prepared by mixing 95 ml of 0.1 M CTAB, 1 ml of 10 mM silver nitrate, 5 ml of 10 mM HAuCl<sub>4</sub>, and 0.55 ml of 0.1 M ascorbic acid in the same order. The solution was homogenized by gentle stirring. To the resulting colorless solution, 0.12 ml of freshly prepared seed solution was added and set aside in the dark for 14 h. The solution turned from colorless to violet brown with most of the color change happening in the first hour. Prior to use, AuNR solution is centrifuged at 13 000 rpm for 10 min to remove excess CTAB and redispersed in nanopure water. The pH of AuNR solution is then adjusted to 1.5 before use for self-assembly.

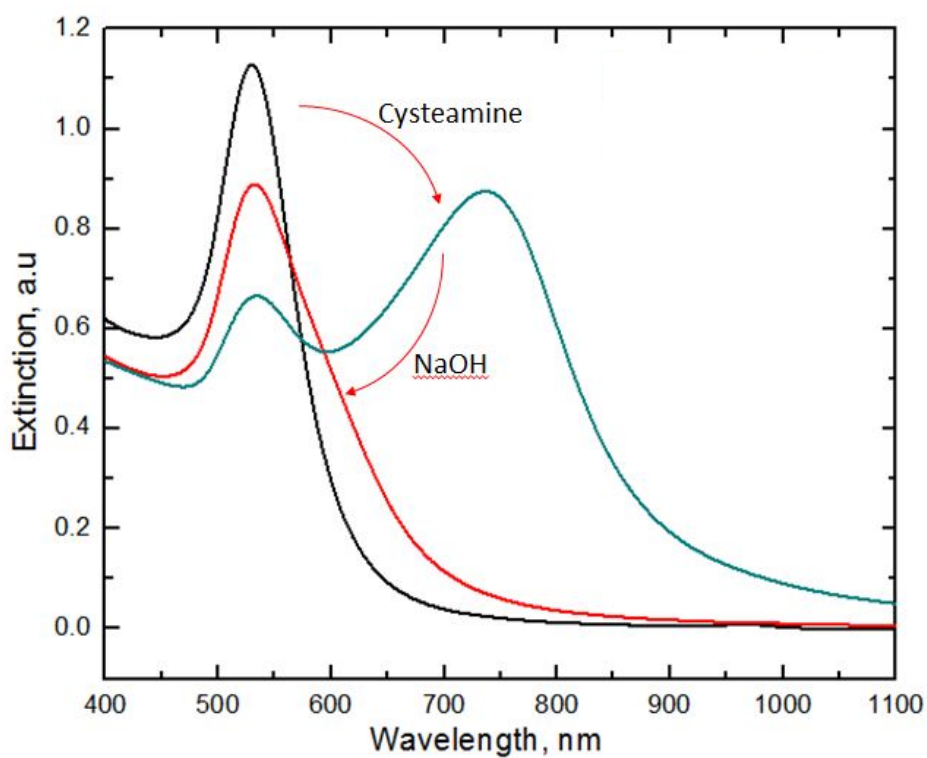
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### Characterization of AuNPs and AuNRs

The synthesis and assembly of AuNPs and AuNRs were monitored through their UV-visible extinction spectra collected using Shimadzu 1800 spectrophotometer. TEM images were obtained using a field emission transmission electron microscope (JEM-2100F, JEOL) operating at an accelerating voltage of 200 kV (Figure 2C, D). Cysteamine configurations on gold surface were studied through their Raman spectra collected using a Renishaw inVia confocal Raman spectrometer mounted on a Leica microscope with 50X objective (NA =0.90) in the range of 100 cm<sup>-1</sup>–3200 cm<sup>-1</sup>. A diode laser of 785 nm wavelength (0.5 mW) is used for sample excitation.

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## Figure S1



5 **Figure S1.** UV-visible extinction spectra showing the assembly of AuNRs by cysteamine cross-linkers and AuNR disassembly caused by NaOH treatment.

## References

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