

## Supporting Information

### **Multilayered Core–satellite Nanoassemblies with Finely-Tunable Broadband Plasmon Resonances**

*Wei Xiong, Debabrata Sikdar, Lim Wei Yap, Malin Premaratne, Xinyong Li, and Wenlong Cheng\**

## 1. Experimental section

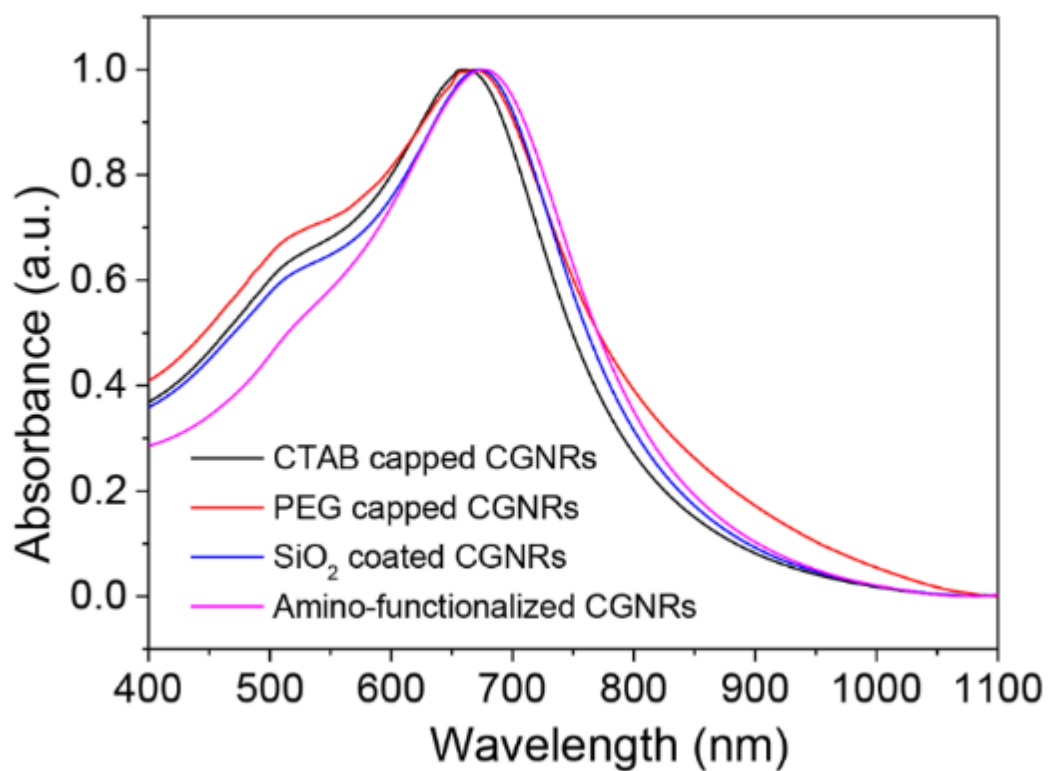
*Chemicals.* Gold (III) chloride trihydrate ( $\text{HAuCl}_4$ ), hexadecyltrimethylammonium bromide (CTAB), 5-bromosalicylic acid, silver nitrate ( $\text{AgNO}_3$ ), sodium borohydride ( $\text{NaBH}_4$ ), L-ascorbic acid (AA), Cetyltrimethylammonium chloride (CTAC, 25 wt.% in  $\text{H}_2\text{O}$ ), Polyvinylpyrrolidone (PVP), trisodium citrate, and Sodium dodecyl sulfate (SDS) were obtained from Sigma Aldrich.

*Synthesis of AuNPs:* 0.59 mL 25 mM  $\text{HAuCl}_4$  was diluted to 50 mL and heated to boiling. 1.75 mL 34 mM trisodium citrate solution was added for the reductant. 13 nm AuNPs were obtained after heating for 10 min. 30 nm AuNPs was synthesized by reducing the volume of trisodium citrate solution to 0.75 mL. For 3 nm AuNPs, 0.2 mL 25 mM  $\text{HAuCl}_4$  and 0.147 mL 34 mM trisodium citrate were added into 20 mL D.I. water with vigorous stirring. AuNPs were prepared by added 0.6 mL ice-cold 0.1 M  $\text{NaBH}_4$  solution.

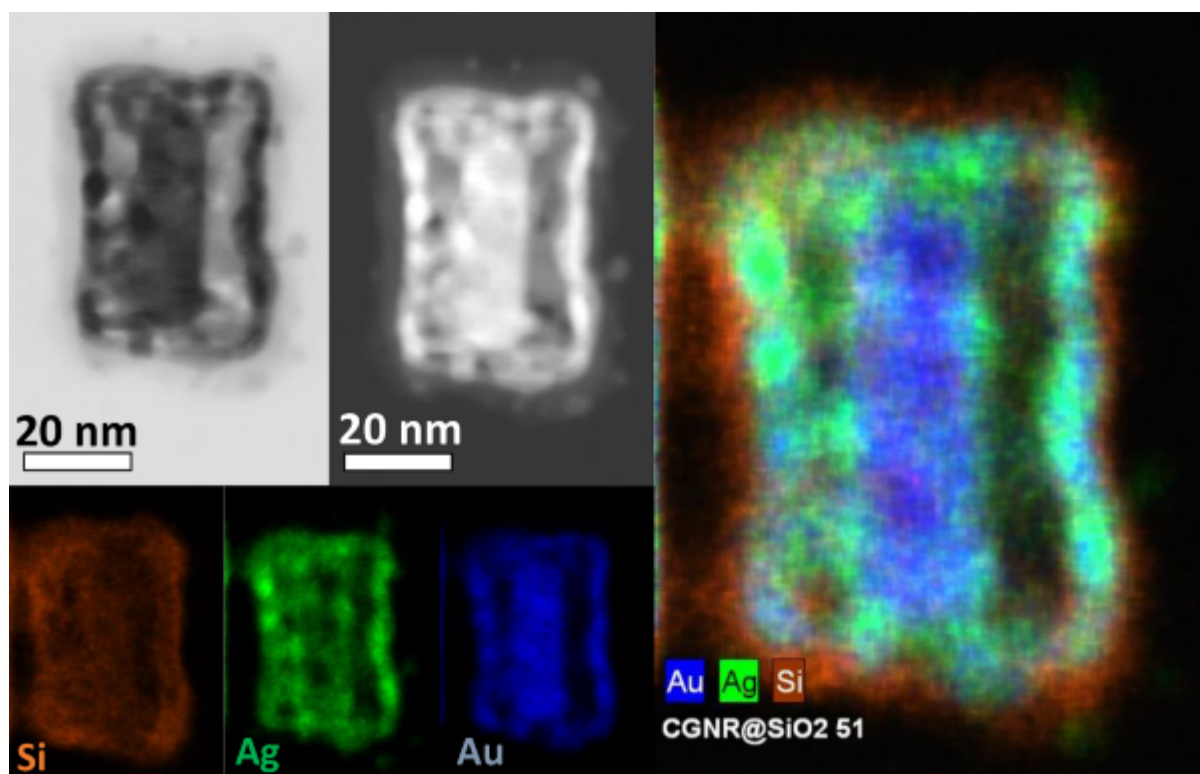
*Synthesis of CGNRs:* The CGNRs were synthesized as reported previously.<sup>[1]</sup> Firstly, to prepare gold nanorods (AuNRs),<sup>[2]</sup> 1.1 g 5-bromosalicylic acid was mixed with CTAB (250 mL, 0.1 M) solution and stirred at 65 °C until homogeneous solution formed. After the solution cool down to 30 °C,  $\text{AgNO}_3$  (12 mL, 4 mM) was added and kept undisturbed for 15 min, after which  $\text{HAuCl}_4$  (250 mL, 1 mM) were added. After 15 min of slow stirring (400 rpm), AA solution (1.6 mL 0.08 M) was added, and the solution was vigorously stirred for 30 s until it became colorless. Then 0.8 mL seed solution which was prepared by mixing CTAB (5.0 mL, 0.2 M) and  $\text{HAuCl}_4$  (5.0 mL, 0.5 mM) followed by adding ice-cold  $\text{NaBH}_4$  (0.6 mL, 0.01 M), was added and stirred for 30s. The resultant mixture was left undisturbed at 30 °C for 12h for AuNRs growth. The AuNRs were centrifuged at 7000 rpm for 1h and wash with DI water twice. The precipitates were redispersed in CTAC solution (50 mL, 80 mM) for silver coating. For silver coating,<sup>[3]</sup> 1 mL AuNRs in CTAC solution was mixed with CTAC solution (9 mL, 80 mM) and stirred at 65 °C, following by adding  $\text{AgNO}_3$  (1.0 mL, 10 mM) and AA

solution (0.5 mL, 100 mM). After stirring for 3 h at 1000 rpm, the resulted sample was isolated by centrifuged at 6000 rpm for 10 min and washed with DI water twice and gold@silver core-shell nanocubioids (AuNR@AgNCs) were obtained as the templates for CGNRs prepared via galvanic replacement reaction. In order to prepared CGNRs, 2 mL AuNR@AgNCs aqueous solution was mixed with CTAB (4 mL, 0.2 M) and PVP (2 mL, 2wt%) solution. After stirred at 90 °C for 2 min, H<sub>2</sub>AuCl<sub>4</sub> solution (3.4 mL, 0.5 mM) was added and stirred for another 10 min until dark blue color appeared. The product was wash with water twice and redispersed in 1 mL D.I. water for silica coating.

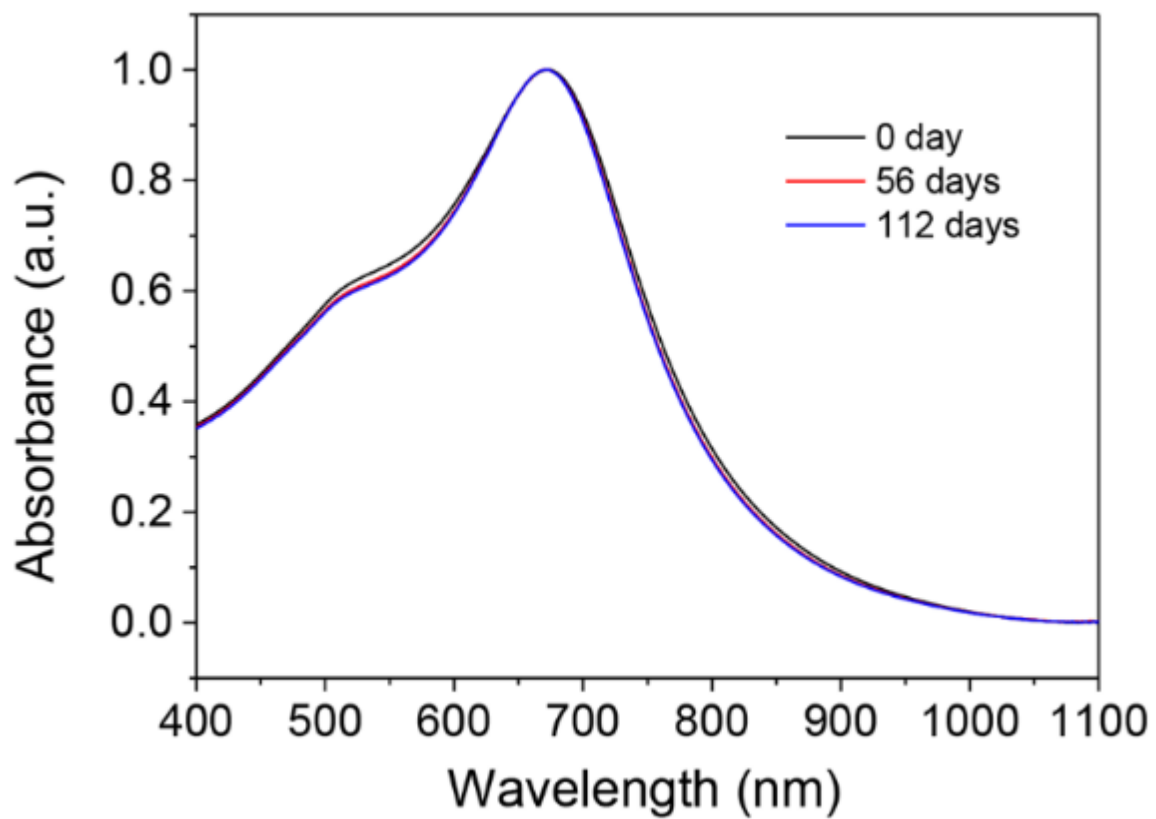
## 2. Results



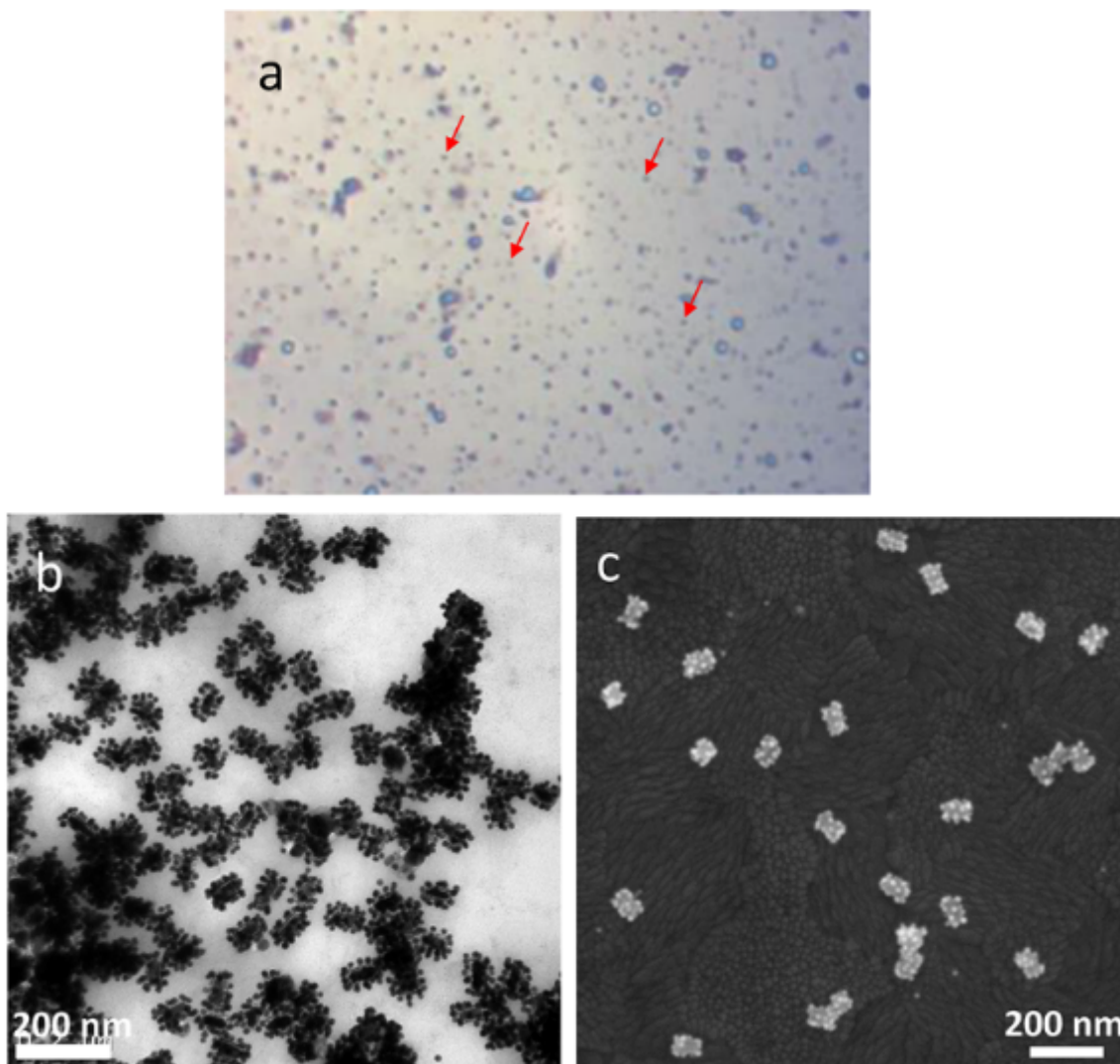
**Figure S1.** UV-vis spectra of CTAB-capped CGNRs, PEG-capped CGNRs, SiO<sub>2</sub> coated CGNRs and amino-functionalized CGNRs.



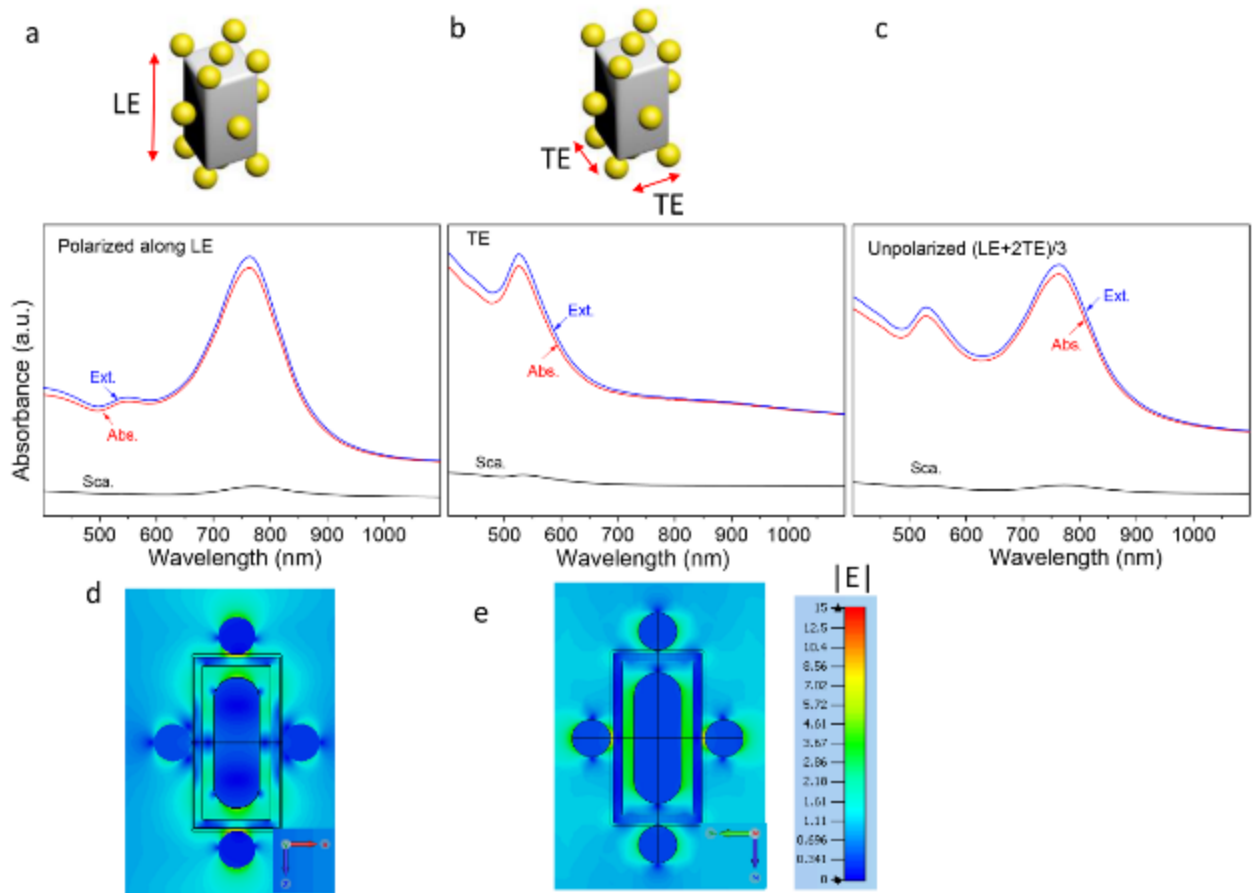
**Figure S2.** EDX mapping of CGNRs coated with silica shell.



**Figure S3.** UV-vis spectra of silica coated CGNRs obtained after 0, 56, 112 days.

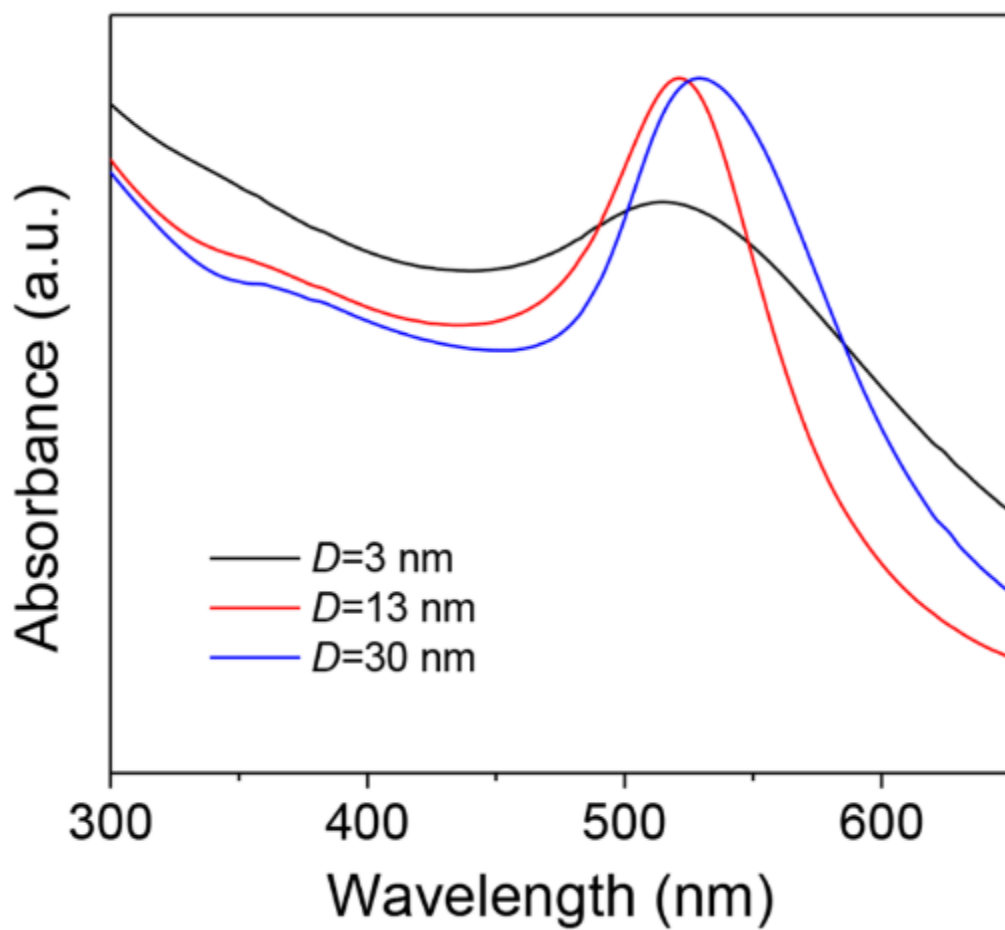


**Figure S4.** The optical microscope image (a), TEM (b) and SEM (c) of the MCS nanoassemblies sample ( $D=13$ ,  $T=1$ ,  $N=22$ ).

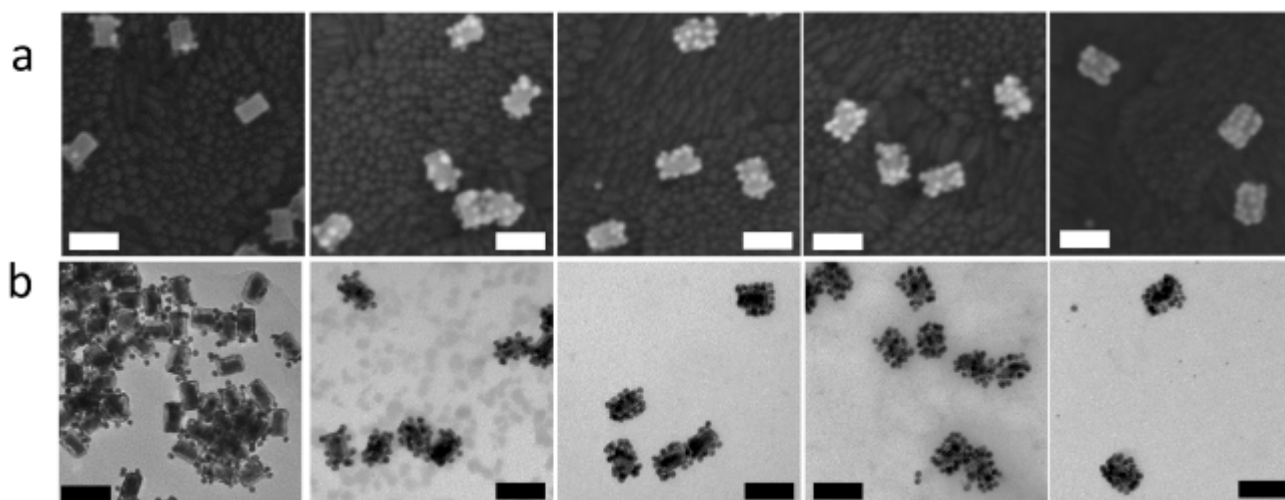


**Figure S5.** Extinction spectra of a MCS nanoassembly for incident light polarized along longitudinal edge (LE) (a) and transverse edge (TE) (b). (c) Optical response for unpolarised light calculated using a weighted average of LE and TE spectra, given by  $(LE+2TE)/3$ . Near-field distribution pattern of the E-field for LE (d) and TE (e) orientations of incident light polarization.

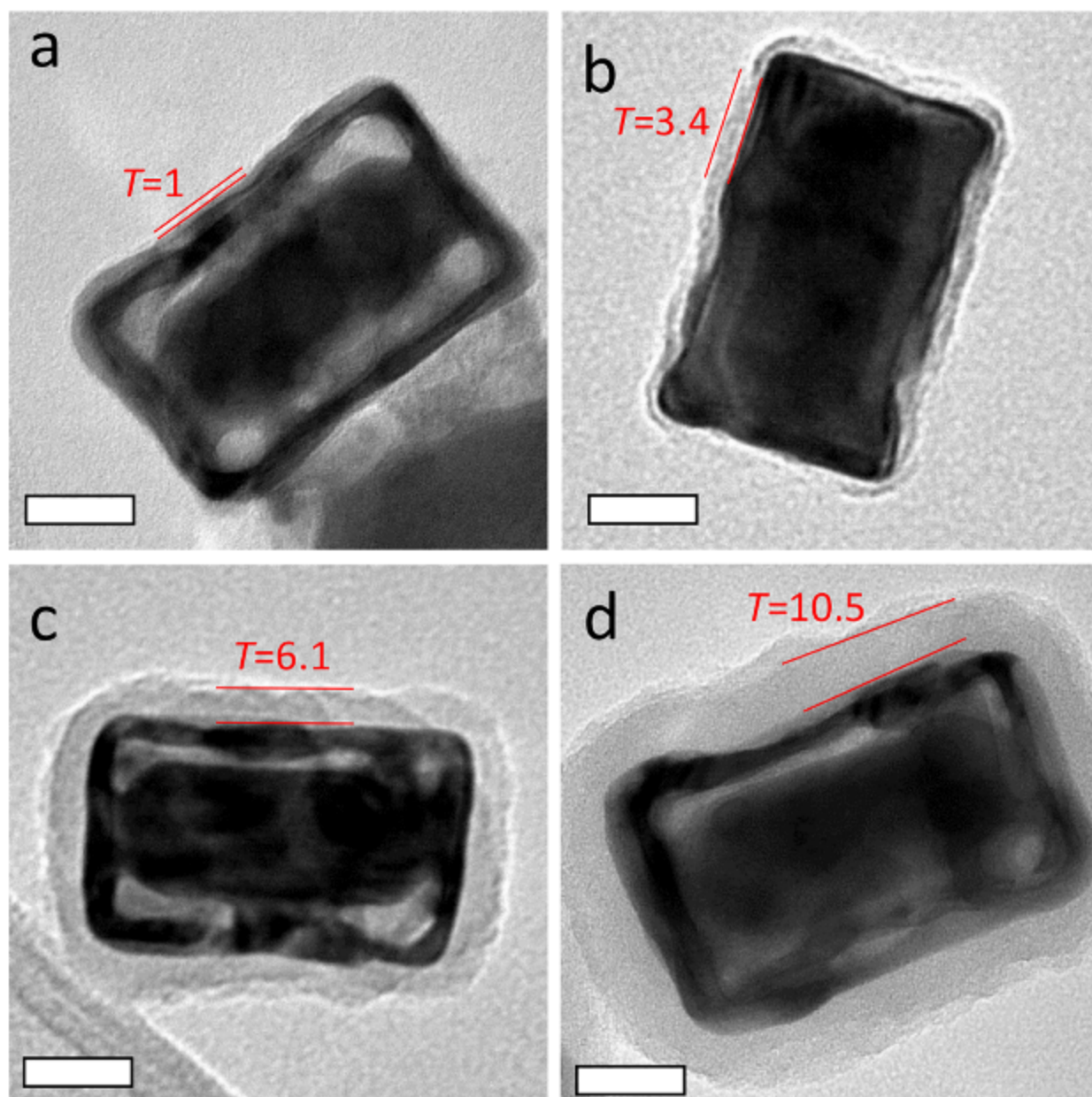




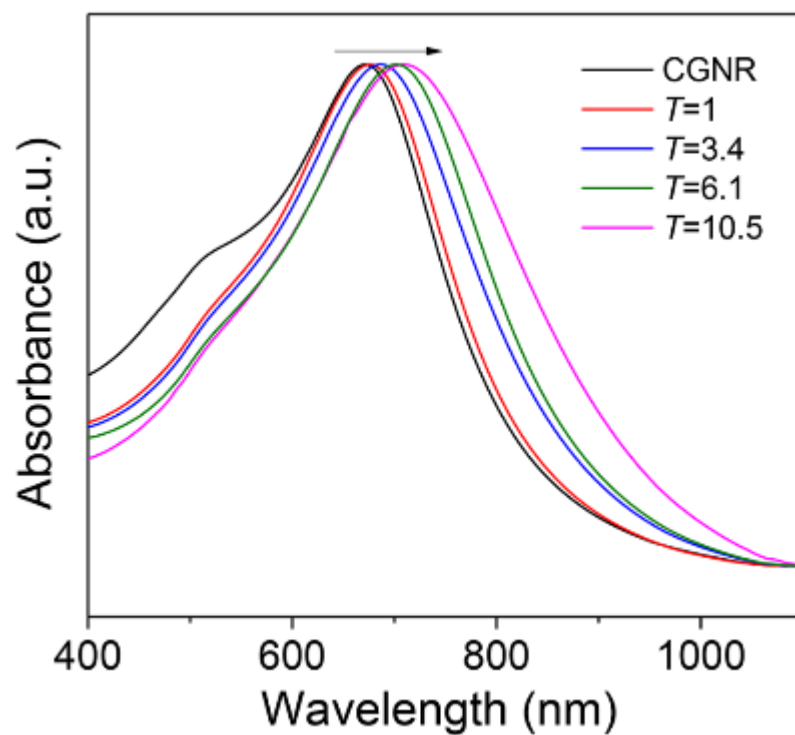
**Figure S6.** UV-vis spectra of AuNPs with diameters of 3, 13, and 30 nm.



**Figure S7.** SEM (a) and TEM (b) for the MCS nanoassemblies with different number of satellites per core (from left to right: 4, 9, 13, 18, 22). Scale bar: 100 nm.



**Figure S8.** TEM images of CGNRs coated with different thicknesses of silica-spacer layer for assembly: 1, 3.4, 6.1, and 10.5 nm. Scale bar: 20 nm.



**Figure S9.** UV-vis spectra of CGNRs coated with different thicknesses of silica-spacer layer for assembly: 1, 3.4, 6.1, and 10.5 nm.

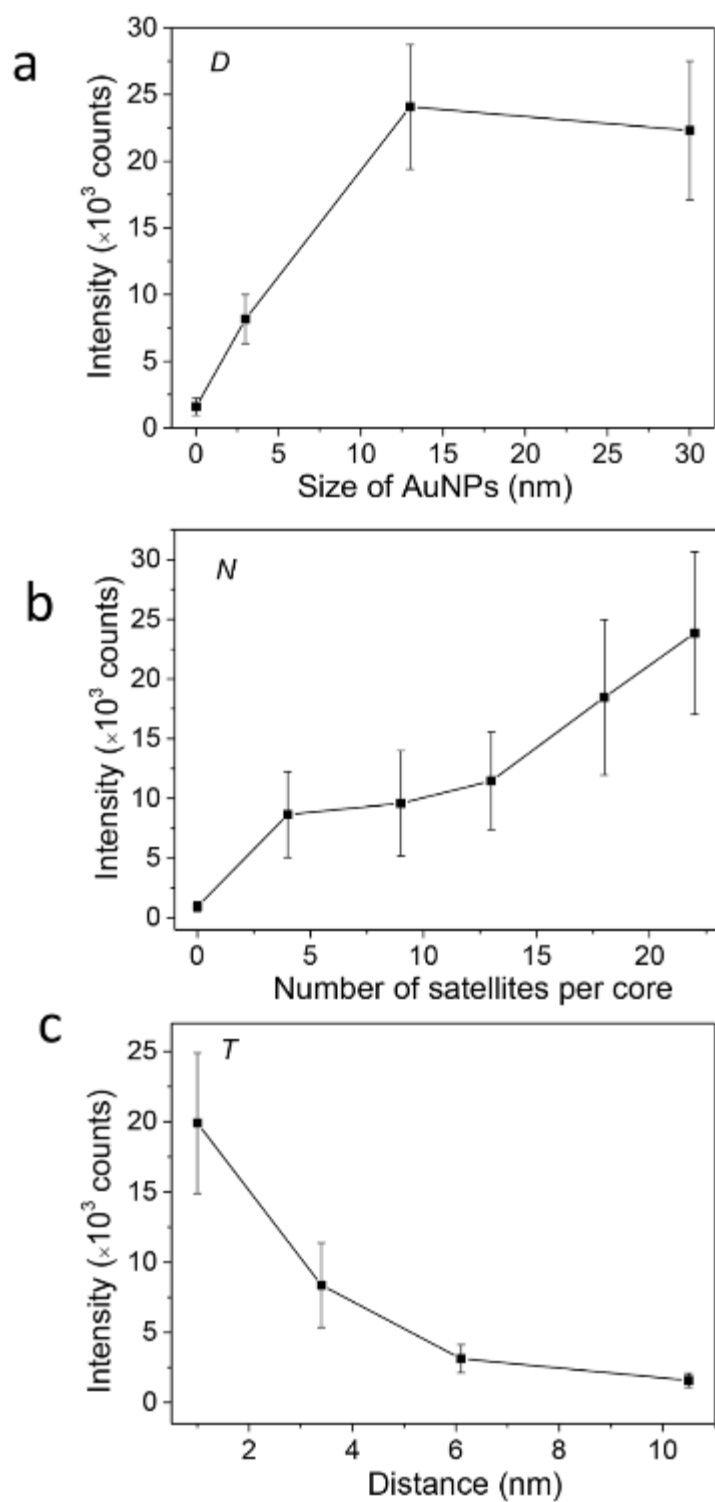


Figure S10. The intensity of Raman shift at  $1072\text{ cm}^{-1}$  of 4-ATP for the MCS nanoassemblies: (a) various sizes of AuNPs, (b) various number density of AuNPs, (c) different thicknesses of silica-spacer layer between cage and AuNPs.

### 3. Reference

- 1 Xiong, W.; Sikdar, D.; Walsh, M.; Si, K. J.; Tang, Y.; Chen, Y.; Mazid, R.; Weyland, M.; Rukhlenko, I. D.; Etheridge, J.; Premaratne, M.; Li, X.; Cheng, W. *Chem. Commun.* **2013**, *49*, 9630-9632.
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