

## **Electronic Supplementary Information (ESI)**

# **Covalently-capped seed-mediated growth: a unique approach towards hierarchical growth of gold nanocrystals**

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### **MATERIALS AND METHODS**

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## Chemicals

Cetyltrimethylammonium bromide (CTAB), 6-Mercaptohexanol (MCH), 11-Mercaptoundecanol (MCU), 1-Nonanethiol (1-NT), 11-Mercaptoundecanoic acid (MUA), 3-Mercaptopropionic acid (MPA), Cysteamine, Methoxy-poly(ethylene glycol)-thiol (PEG-SH), hydrogen tetrachloroaurate (III) trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ), ascorbic acid (AA), sodium borohydride ( $\text{NaBH}_4$ ) and silver nitrate ( $\text{AgNO}_3$ ) were purchased from Sigma–Aldrich. All reagents were used as received.

## Preparation of spherical Au seeds

The Au-seeds were prepared according to the Frens method.<sup>1</sup> Briefly, 100 mL of  $2.5 \times 10^{-4}$  M  $\text{HAuCl}_4$  solution was heated to  $120^\circ\text{C}$  in oil bath under vigorous stirring for 30 min. Subsequently, 1% sodium citrate solution (1 ml and 5 ml for 40 nm and 18 nm particles, respectively) was added into above solution with continuous boiling. After 20 min, the color of the boiled solution changed into ruby red, indicating the formation of Au NPs in the solution.

## Preparation of cubic Au seeds

Cubic gold NPs were prepared using a seeded growth method reported by Sau and Murphy with slight modification.<sup>2</sup> Briefly, the seeds were synthesized by the addition of a freshly prepared, ice-cold aqueous  $\text{NaBH}_4$  solution (0.01 M, 0.6 mL) into an aqueous mixture composed of  $\text{HAuCl}_4$  (0.01 M, 0.25 mL) and CTAB (0.1 M, 7.5 mL), followed by rapid inversion mixing for 2 min. The resultant seed solution was kept at room temperature for 1 h before use. The nanocubes were prepared by two step growth process. The growth solution in the first step was prepared by the sequential addition of CTAB (0.1 M, 6.4 mL),  $\text{HAuCl}_4$  (0.01 M, 0.8 mL), and ascorbic acid (0.1 M, 3.8 mL) into water (32 mL). 0.02 mL of the seed solution (diluted 10 times) was then added into the growth solution. The resultant solution was mixed by gentle inversion for 10 s and then left undisturbed overnight. The growth solution in the second step was prepared by mixing  $2.5 \times 10^{-4}$  M  $\text{HAuCl}_4$ , 0.01 M CTAB and  $5.5 \times 10^{-4}$  M Ascorbic Acid (AA) in 10 mL of water, then 3 mL of AuNPs solution in the first

step was added in the mixture, and kept at 30 °C in water bath for at least 6 hours.

#### **MCH, MCU, 1-NT, Cysteamine and PEG-SH modified Au-seeds**

Au seeds were modified with –SH containing capping agents (MCH or MCU or 1-NT) by replacing non-covalently bonded capping agents (e.g. citrate or CTAB). In brief, 20 mL of the original Au NPs (spherical or cubic seeds) were centrifuged (8000g, 20 min). The recovered nanocrystals were dispersed in DMF (20 mL). Then a solution of thiolated ligands (100 mg) in DMF (2 mL) was added into 20 mL of Au NPs (spherical or cubic seeds) in DMF maintaining a concentration of the ligands as 34 mM. After the solution was stirred for 24h, nanocrystals were recovered by centrifugation (8000g, 20 min) followed by redispersion in water for further use.

#### **MUA and MPA modified Au-seeds**

20 ml as-prepared Au NPs were centrifuged (8000g, 20 min) to remove the excess sodium citrate. After the supernatant had been removed, the precipitate was re-dispersed in ethanol. During the purification process, a small amount of water remained (~5%, v/v). Then 2 ml ethanolic solution (5mM) of MUA (or MPA) was added into the ethanolic suspension of Au NPs and left overnight.

#### **Growth of Au nanostructures using different Au seeds**

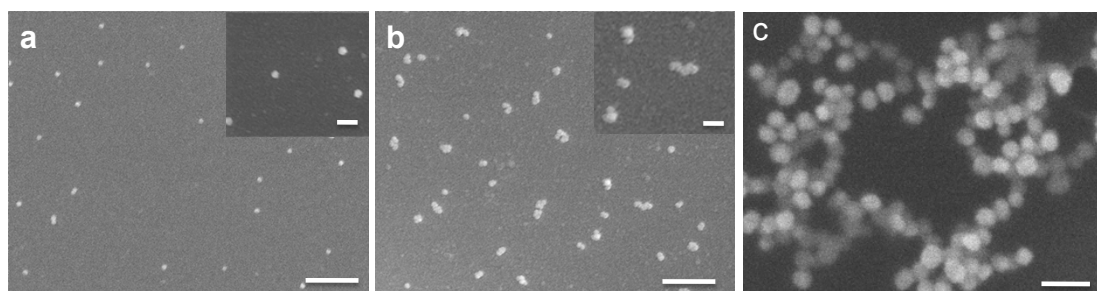
The growth solution was prepared by mixing  $2.5 \times 10^{-4}$  M HAuCl<sub>4</sub>, 0.01 M CTAB and  $5.5 \times 10^{-4}$  M AA. For the growth of different Au-seeds, 10 ml of growth solution was mixed with a fixed amount of Au-seed solution in a plastic tube by gentle inversion for 3 s and kept at 30 °C in water bath for 6 hours. .

#### **Characterizations**

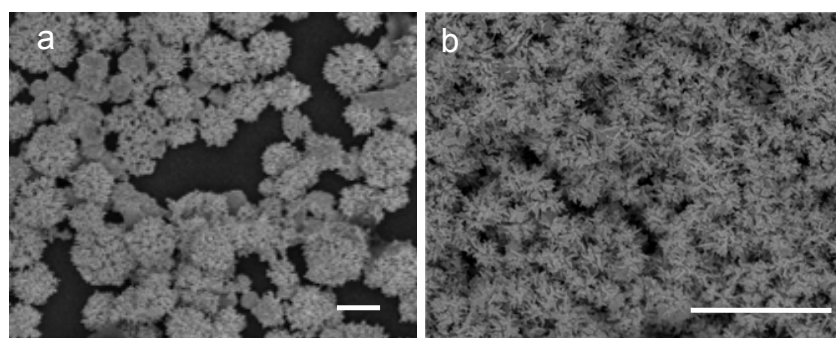
Field-emission scanning electron microscopy (FE-SEM) was performed on the JEOL instrument (JSM-6700F) at an acceleration voltage of 5 kV and a working distance between 7 and 8 mm. Raman spectra were collected using a Renishaw inVia confocal Raman spectrometer with 50× objective lens in the range of 500–2000 cm<sup>-1</sup> with one

accumulation and 10 s exposure time. A 632.8 nm wavelength HeNe laser (0.085 mW at the sample surface) was used to excite the sample.

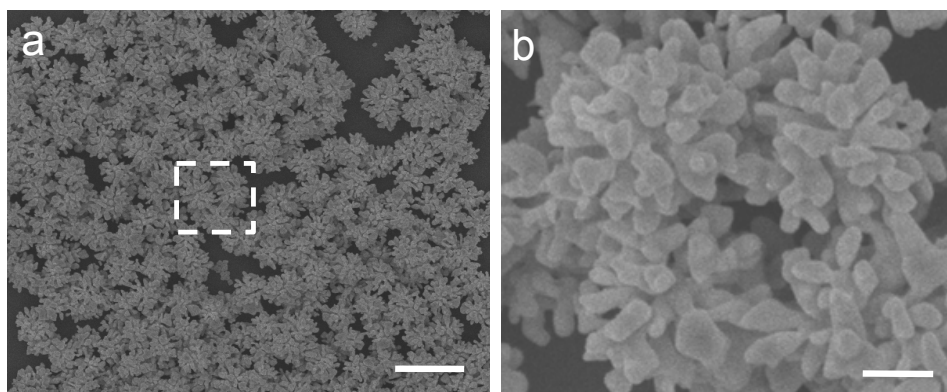
## Figures



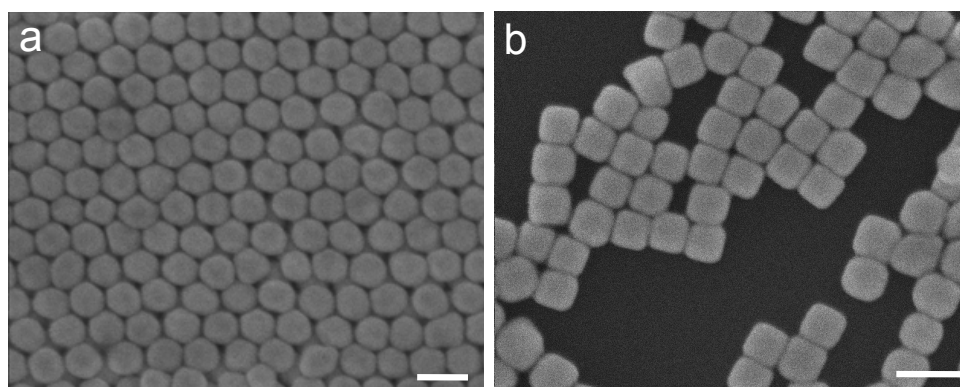
**Fig. S1** SEM images of (a) as prepared 18 nm Au NPs synthesized from citrate reduction and (b,c) the nanostructures obtained after modification by MCH and MUA, respectively. The scale bars in (a) and (b) represent 250 nm whereas those in the insets and (c) are 50 nm.



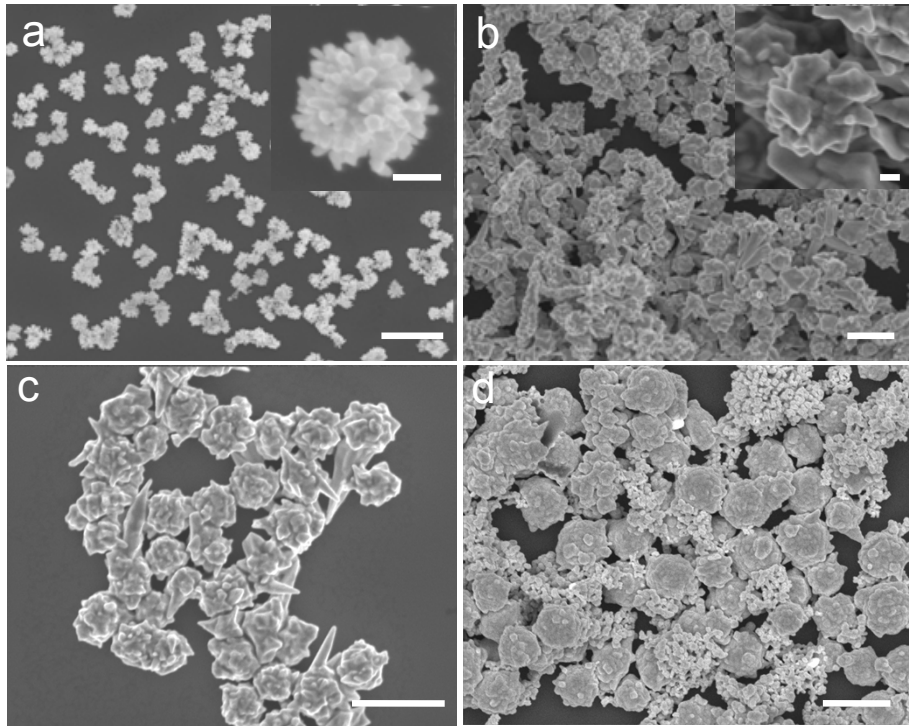
**Fig. S2** SEM images of hierarchical Au nanostructures obtained from the growth of (a) 5 mM and (b) 70 mM MCH modified 18 nm spherical seeds. The scale bars represent 1 μm.



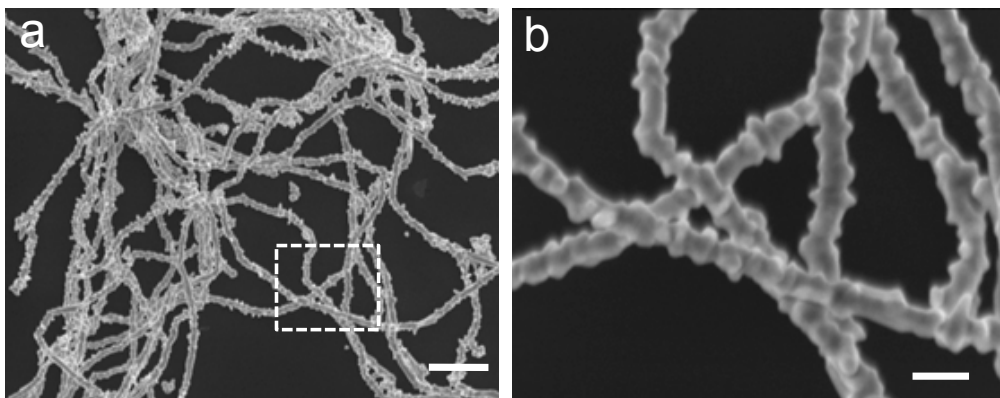
**Fig. S3** SEM images of hierarchical Au nanostructures obtained from the growth of MCH modified 40 nm cubic Au seeds. The scale bars in the images are 2  $\mu\text{m}$  and 200 nm, respectively.



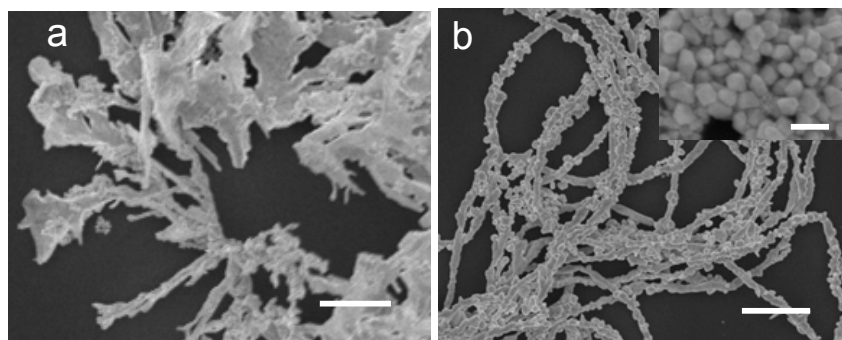
**Fig. S4** SEM images of Au nanostructures obtained from the growth of non-covalently modified 18 nm spherical (a) and 40 nm cubic seeds (b). The shapes of seeds are maintained throughout the growth process. The scale bars represent 100 nm.



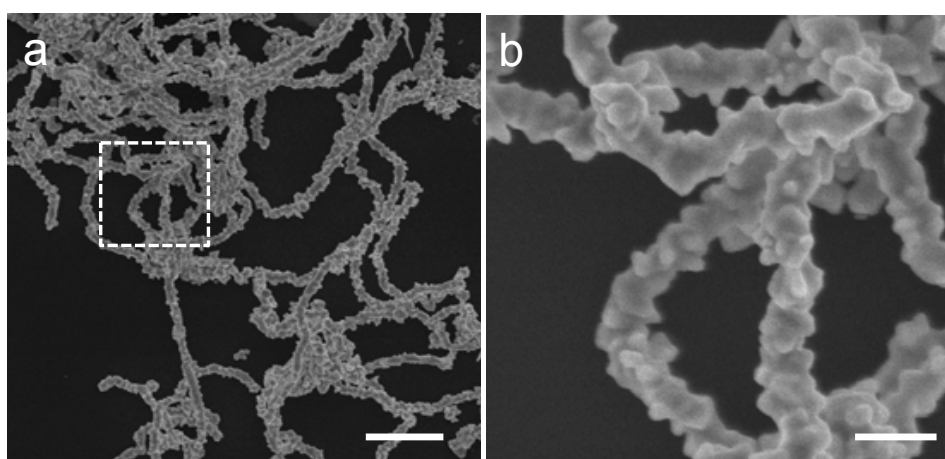
**Fig. S5.** SEM images of hierarchical Au nanostructures obtained from the growth of mercaptoundecanol (a), 1- nonanethiol (b), cysteamine (c) and PEG-SH (d) modified spherical Au seeds. The scale bars in the figures and insets are 1  $\mu\text{m}$  and 100 nm, respectively.



**Fig. S6** SEM images of hierarchical Au nanowires obtained from growth of MUA modified 18 nm Au seeds. The scale bars are 1  $\mu\text{m}$  and 200 nm, respectively



**Fig. S7** SEM images of nanostructures obtained from the growth of (a) 1mM and (b) 20 mM of MUA modified 40 nm Au seeds. Inset of (b) shows some agglomerated spherical seeds were present as impurities along with the nanowires. The scale bars in the figures and inset are 1  $\mu\text{m}$  and 100 nm, respectively.



**Fig. S8** SEM images of hierarchical Au nanowires obtained from growth of 3-mercaptopropionic acid-modified 40 nm Au seeds. The scale bars are 1  $\mu\text{m}$  and 200 nm, respectively

$$\text{Apparent Enhancement Factors (AEF)} = I_{\text{SERS}} [C_{\text{NRS}}] / I_{\text{NRS}} [C_{\text{SERS}}]$$

where  $C_{\text{NRS}}$  is the concentration of R6G deposited on bare silicon substrate,  $C_{\text{SERS}}$  is the concentration of the adsorbed molecules on the surface of Au nanostructures, and  $I_{\text{NRS}}$  and  $I_{\text{SERS}}$  are the peak intensities corresponding to the peak at  $1510 \text{ cm}^{-1}$  in normal Raman spectra and SERS spectra measured from baseline, respectively.

## References

1. G. Frens, *Nature Phys. Sci.*, 1973, **241**, 20-22.
2. T. K. Sau and C. J. Murphy, *J. Am. Chem. Soc.*, 2004, **126**, 8648-8649.