

## Supporting Information

### 3D-Gold superstructures grown on poly(acrylic acid) brush

Wenqin Wang,\* Guohong Ren, Wujin Cai

Faculty of materials science and chemical engineering, Ningbo University, Ningbo, China.

Tel: +8657487609987; E-mail: wqwang@126.com

## Experimental Section

### Materials:

Cetyltrimethylammonium bromide (CTAB),  $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$  (>99%),  $\text{AgNO}_3$  ( $\geq 99.8$ ),  $\text{NH}_4\text{OH}$  (25%), ascorbic acid (AA) and  $\text{NaBH}_4$  were obtained from Sinopharm Chemical Reagent Co. (Shanghai, China).  $\text{CuBr}$ , 2,2-dipyridine, sodium acrylate monomer and 4-aminothiophenol (4-ATP) were purchased from Sigma-Aldrich. All chemicals were used without further purification.

### Synthesis of Poly(acrylic acid) (PAA) brushes by atom transfer radical polymerization

A self-assembled monolayer of Silane initiator (11-(2-Bromo-2-methyl-propionyloxy)undecyltrichloro-silane) <sup>1</sup> was obtained by immersing Si substrates in a 0.1 vol% solution of initiator (5  $\mu\text{L}$ ) in anhydrous toluene (15 mL) for 1 h. Then, the substrates were washed with toluene, ethanol and deionized water, successively. The samples were finally dried in a stream of  $\text{N}_2$  and immediately transferred into the polymerization solution. In a nitrogen atmosphere,  $\text{CuBr}$  (5.74 mg, 0.04mmol) and 2,2-dipyridine (13.74mg, 0.088 mmol) were added to 1 mL of MeOH. Above mixture was sonicated for 2 min to form the organometallic catalyst: the  $\text{CuBr}/2,2$ -

dipyridine complex. Next, sodium acrylate monomer (1.88 g, 20 mmol) was added to the complex solution and deionized water (8 mL) was subsequently added into the solution with shaking. The polymerization solution was then transferred into flasks containing the sample substrates with immobilized initiator. The flasks were sealed with rubber septa and kept at room temperature under nitrogen. After the desired reaction time (30min and 2h), the substrates were removed from the polymerization solution and rinsed with deionized water. The as-prepared poly(sodium acrylate) (PNaAc) brushes were immersed into the diluted HCl aqueous solution (pH=2) overnight and subsequently thoroughly rinsed with deionized water.

### **Synthesis of PAA brush-Ag nanoparticles (NPs) composite film**

First, the  $[\text{Ag}(\text{NH}_3)_2]^+$  solution was prepared by adding diluted ammonia solution (1M) dropwise to the aqueous  $\text{AgNO}_3$  solution (0.01M, 10mL) until a transparent solution was obtained. The PAA brushes on the silicon wafers (1cm  $\times$  1cm) were then incubated with above  $[\text{Ag}(\text{NH}_3)_2]^+$  solution for 30min followed rinsing thoroughly with deionized water. Subsequently, the coordinated  $[\text{Ag}(\text{NH}_3)_2]^+$  ions along PAA chains were reduced in ice-cold aqueous  $\text{NaBH}_4$  solution (0.01 M, 20mL) for 7 h resulting in the formation of PAA brush-Ag NPs composite films.

### **Growth of gold superstructures on the PAA brushes**

Each PAA brush-Ag NPs composite film was immersed into the growth solution (50mL of 0.1M CTAB, 2mL of 0.01M  $\text{HAuCl}_4$ , 0.4mL of 0.1 M ascorbic acid) for desired time (15min, 30min, and 60min) at 30°C, and subsequently the as-formed film was thoroughly rinsed with deionized water.

### **Preparation of SERS-active substrate**

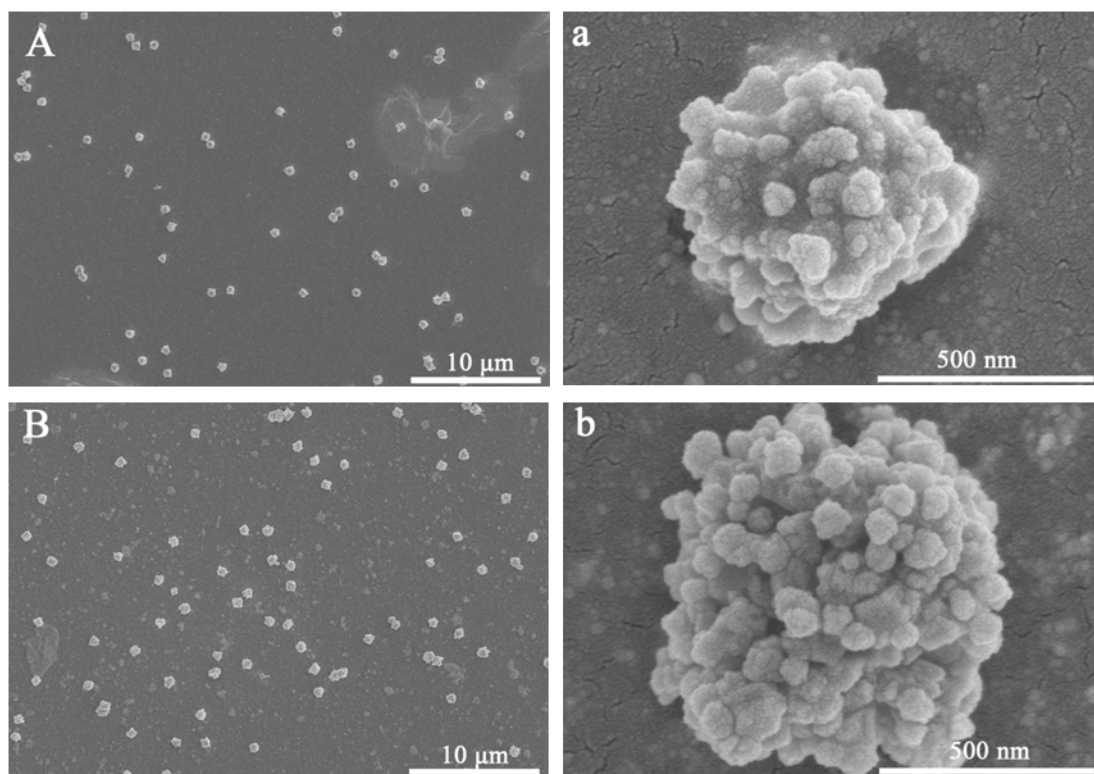
The PAA brush-gold composite films were dipped into a 4-ATP aqueous solution ( $10^{-5}\text{M}$ ) for 1h, rinsed with deionized water, and dried with high-purity flowing nitrogen before Raman examination.

### **Characterization:**

Scanning electron microscope (SEM, SU-70) was used to observe the morphologies of gold superstructures on the PAA brushes. The chemical information of the PAA brushes-gold composite film was characterized by X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD). X-ray diffraction (XRD, Rigaku D/max-1200) was used to characterize the gold superstructure. Raman spectra were carried out on HR800 microscope confocal Raman spectrometer employing an air-cooled He-Ne laser operating at 632.8 nm. The laser beam was focused on a spot with a diameter of approximately 1  $\mu\text{m}$  using 25 mW laser power.

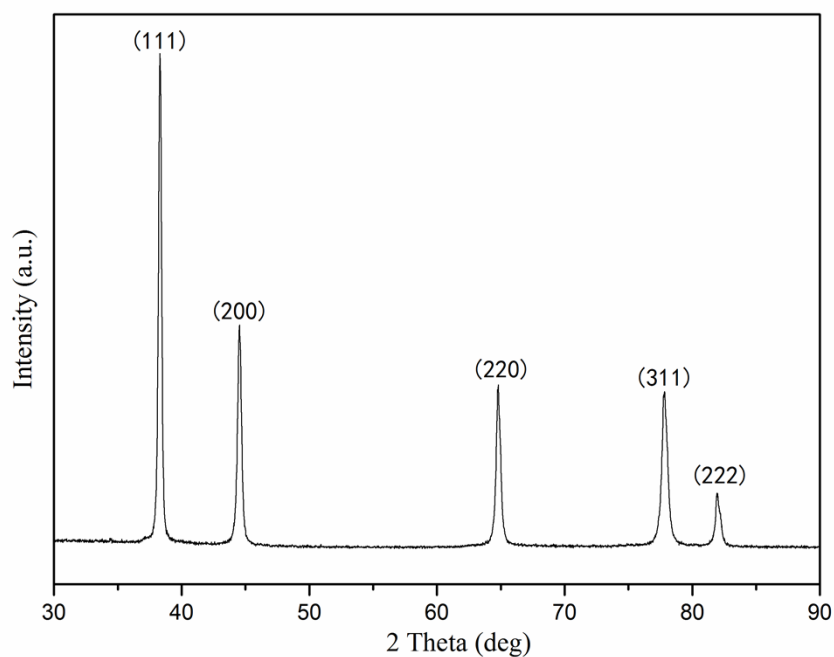
The SEM images of the as-prepared gold superstructures when the reaction time is less than 15 min

were shown in *Figure S1*. In combination with *Figure S1* and Figure 3 shown in the manuscript, it could be found that the morphology of gold superstructures gradually transformed into octahedron as growth time increasing.



**Figure S1.** Low- and high magnification SEM images of as-prepared gold octahedra for different growth times (A: 5min, B: 10min) on the PAA brush with 100 nm thickness.

We also used X-ray diffraction (XRD) to characterize the gold superstructures, and the XRD pattern of the Au superstructures was shown in **Figure S2**. It exhibited peaks at  $2\theta$  angles 37.9, 44.1, 64.3, 77.2, and 81.4 corresponding to the reflections of (111), (200), (220), (311), and (222) crystalline planes of the fcc structure of Au, indicating that the Au superstructures with crystallinity were formed on PAA brushes.

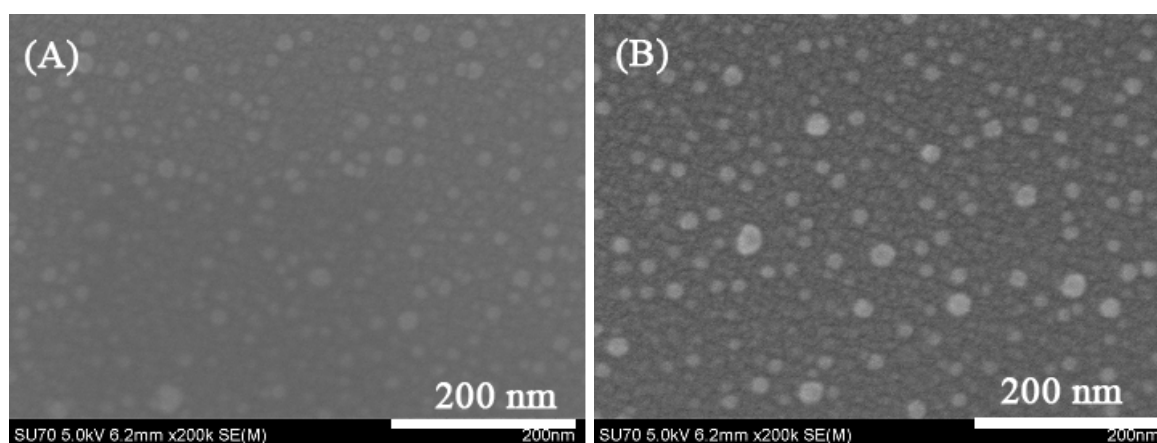


**Figure S2.** XRD pattern of gold superstructures on PAA brush.

Because the formation mechanism 3D gold superstructures is complex, as of now, unclear, another

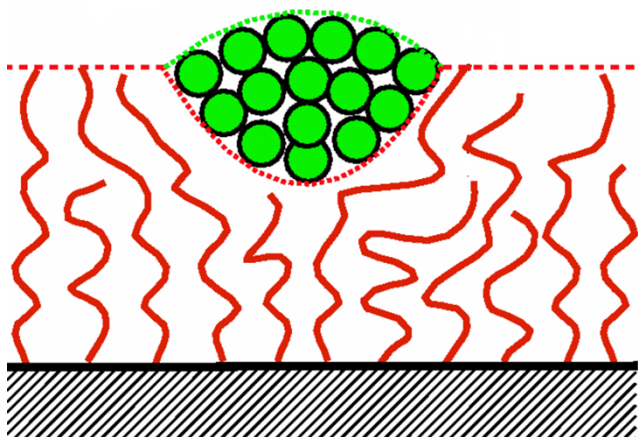
possible mechanism is hypothesized as following:

“Compared with the shorter PAA brush, the longer PAA brush can coordinate more  $[\text{Ag}(\text{NH}_3)_2]^+$  ions, which are reduced by  $\text{NaBH}_4$  resulting in *in-situ* formation of more silver NPs within polymer brush. Once the silver NPs were formed within PAA brush, complex internal interaction between polymer brush, silver NPs and solvent molecules determined the spatial distribution of the silver NPs within PAA brush. Shorter PAA brush limits the depth of silver NPs penetration and pushes particles towards its surface, which causes silver NPs are homogenously distributed over the brush surface. However, to longer PAA brush, loading of silver NPs is higher than that within shorter PAA brush, an amount of silver NPs should be attached within deeper regions of PAA brush. In this deeper region, van der Waals attraction between silver NPs trends to coalesce them into large aggregates and the penalty imposed by the brush in two lateral directions (parallel to substrate) results silver NPs aggregation to be anisotropic. That is, shorter brush will induce 2D ordering of silver NPs, and 3D ordering of silver NPs should be obtained on longer brush (ref 19, *Figure S4*). When 2D or 3D ordering of silver NPs on PAA brush were dipped into the growth solution, gold reduced by AA would be deposited on these silver NPs. At this stage, CTAB will further guide the growth of gold octahedra superstructure because the CTAB could act as a shape-control agent promoting reduction onto specific crystal faces while preventing reduction onto others.”



**Figure S3.** SEM images of Ag nanoseeds on the surfaces of the PAA brushes. (A) 30nm thickness, (B) 100 nm

thickness.



**Figure S4.** 3D ordering of silver nanoseeds within longer PAA brushes.

## References

1. K. Matyjaszewski, P. J. Miller, N. Shukla, B. Immaraporn, A. Gelman, B. B. Luokala, T. M. Siclovan, G. Kickelbick, T. Vallant, H. Hoffmann and T. Pakula, *Macromolecules*, 1999, **32**, 8716–8724.