A facile approach to control the metal superstructure architecture by organic thin films

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Experimental section

A. Chemicals and materials.

3-Aminopropyltriethoxysilane (APTES, 98%, Alfa Aesar), anhydrous toluene (99.8%), $AgNO_3$ (99.8%), NH_4OH (25%), H_2O_2, acetic anhydride (98.5%), concentrated sulfuric acid anhydrous ethanol, ethyl acetate and $NaBH_4$ were obtained from Sinopharm Chemical Reagent Co. (Shanghai, China). Poly(acrylic acid) (PAA solution, average Mw ~100,000, 35 wt. % in H2O, Aldrich) and Polyethylenimine (PEI, branched average Mw ~25,000, Aldrich). All were used as received without further purification.

N-doped, (100)-oriented silicon wafers solid substrates were used. The silicon wafers were cut into ca. 15 × 15 mm^2 pieces and cleaned in a mixture of H_2O_2/H_2SO_4 (1:3, v/v) at 80 °C ("piranha solution") for 2 h, washed thoroughly with Milli-Qgrade water, and dried in a stream of N_2 before APTES deposition. (Caution: Piranha solution reacts violently with organic matter!). Deionized water used in the preparation of chemical solutions and in the cleaning of the experimental apparatus was produced by a Millipore Water Purification System.

B. Preparations and modifications of APTES, APTES/PAA, APTES/PAA/PEI films.

APTES films were prepared as described before.[1] A freshly prepared OH-terminated silicon substrate, which was treated with fresh piranha solution, was immersed in a 5% APTES anhydrous toluene solution and sonicated for appropriate time. Then, APTES molecules were attached to the silicon wafers via silanization reaction. After the deposition, solid substrates were sonicated twice in toluene for 10 min to remove loosely physisorbed APTES and sonicated two times in acetic anhydride and deionized water for 10 min, and then dried by the use of a stream of N_2 before use. All glass reaction vessels were passivated twice by the use of vaporized HMDS at 100 °C before use to minimize the formation of APTES films.

The APTES/PAA substrates were prepared by wet chemical assembly. APTES/PAA substrate: APTES-functionalized silicon substrates were submerged in PAA(1.0mg/mL) aqueous solution for 30min, then thorough rinsing with water (Milli-Q), substrates were dried under a stream of nitrogen. APTES/PAA/PEI substrate: submerging APTES-functionalized substrate in previous PAA(1.0mg/mL) aqueous solution for 30min, then the positively charged electrolyte-modified substrates were immersed in the PEI solution (1.0mg/mL) for 30 min, finally thorough rinsing with water (Milli-Q), substrates were dried under a stream of nitrogen.

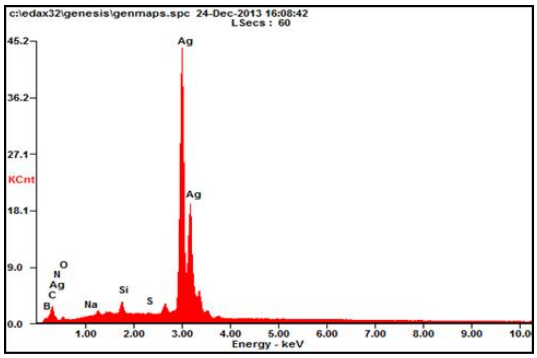
C. Ag Superstructure Preparation.

The as-prepared organic brushes were immersed in the slightly alkaline Tollens reagent (0.01M, 10mL) for appropriate time, the positively charged $[Ag(NH_3)_2]^+$ was adsorbed to the organic thin film via ion-exchange and electrostatic interaction. After rinsing with an amount of water to wash away unstable adsorption ions, the substrate was treated with a freshly prepared ice aqueous solution of $NaBH_4$ for 10 min to fabricate silver superstructures.

Characterizations.

Atomic force microscopy (AFM) images were taken by a multimode AFM (Being Nano-Instruments, Ltd.) operating in the tapping mode using silicon cantilevers (spring constant: 3~40 Nm^{-1}, resonant frequency: 75−300 kHz). The scanning electron microscopy (SEM) images, which were obtained by using the field emission scanning

electron microscope (SU-70) equipped with an energy dispersive X-ray system, were used for determining the morphologies of the Ag superstructures. X-ray diffraction (XRD) was carried out on a Rigaku D/max-RA X-ray diffraction meter using Cu Kα radiation (λ= 1.5418 Å). Static water contact angles were measured at room temperature using the sessile drop method and image analysis of the drop profile. The instrument (OCA-20, Dataphysics) used a charge-coupled device (CCD) camera and an image analysis processor.



Element	*Wt%*	*At%*
BK	01.34	09.68
CK	01.55	10.06
NK	00.46	02.54
OK	01.01	04.92
NaK	00.05	00.17
SiK	01.51	04.17
SK	00.33	00.80
AgL	93.75	67.66
Matrix	Correction	ZAF

Fig. S1 EDS analysis of Ag superstructures (S30)

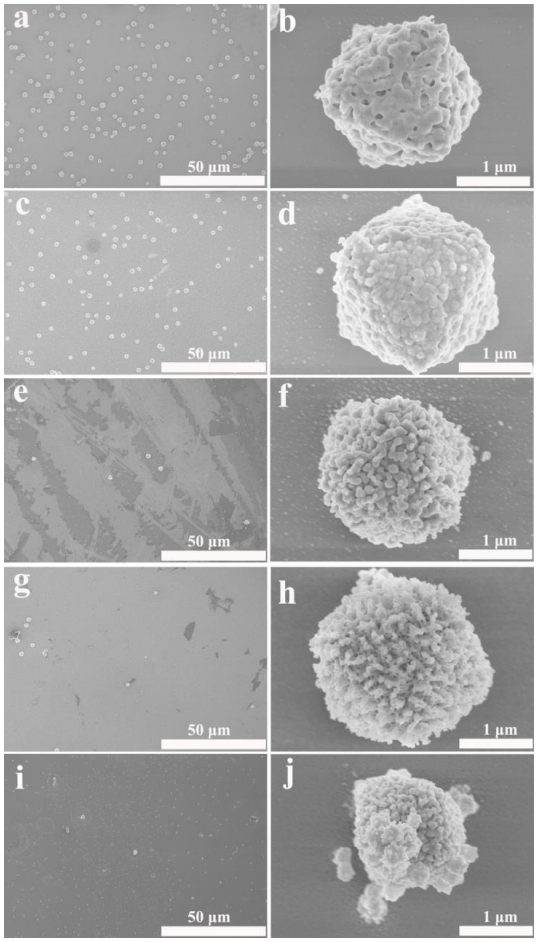


Fig. S2 Low- and high-magnification SEM images of Ag superstructures on APTES film with different thickness. The reaction time of APTES with silicon wafer: (a, b) 15 min, (c, d) 60 min, (e, f) 120 min, (g, h) 240 min and (i, j) 360 min.

References

[1] Yanqiong Yang, Wenqin Wang, Tao Chen, and Zhong-Ren Chen. Simultaneous Synthesis and Assembly of Silver Nanoparticles to Three-Demensional Superstructures for Sensitive Surface-Enhanced Raman Spectroscopy Detection. ACS Appl. Mater. Interfaces 2014, 6, 21468-21473.