ARTICLE

Supplementary Information

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Table 1 The oxidation-reduction potential (ORP) of the electrolyte solution

No.	Metal ion containing in the electrolyte	Concentration of the metal ion	ORP / V
1	Cu^{2+}-Au^{3+}	0.001mM Cu^{2+} and 0.0015mM Au^{3+}	0.10
2	Au^{3+}-Ag^+	0.001mM Au^{3+} and 0.001mM Ag^+	0.21

Materials: Positive photoresist (AZ MiR (TM) 701) and the developer are purchased from AZ Electronic Materials. Hexamethyldisilazane (AR 99%, HMDS) is purchased from Macklin, China. Tetrachloroauric (Ⅲ) acid tetrahydrate (HAuCl₄·4H₂O), Copper(II) chloride dihydrate (CuCl₂), Sodium sulfite (Na₂SO₃), Dipotassium hydrogen phosphate (K₂HPO₄), Ethylenediaminetetra acetic acid (EDTA) and Rhodamine 6G (R6G) are both purchased from Sinopharm Chemical Reagent Co., Ltd. All the silicon are chemically cleaned and heated to remove the contamination and moisture on the wafer surface and all prepare process are carried out on the Clean Booth Station.

Prepare method: The fabrication procedure for the Cu-Au alloy arrays are described in Figure S1. Firstly, the AZ photoresist thin films are coated on the wafer, before that a liquid adhesion promoter (HMDS) is spin-coated on the silicon to promote the adhesion of the photoresist to the wafer. The photoresist is exposed in a UV mask aligner (MJB 3, SUSS MicroTec) with the main wavelength of 365 nm in the soft contact mode and after being developed, the photoresist pattern are obtained. Subsequently, a dry etching with XeF₂ vapor is adopted to etch the silicon

isotropically with the etching rates as large as 1-2 μm/min. After etching, the photoresist is removed from the substrate and the highly ordered Si pillar arrays with the diameter and height of each pillar of about 3 μm are obtained. At last, silicon arrays are immersed into the electrolyte solution, which are prepared by HAuCl₄ and CuCl₂ precursor electrolytes with the molar ratio of Cu^{2+}:Au^{3+} (1:0.2-3), and the HAuCl₄ electrolyte is prepared by HAuCl₄ (1 g/L), Na₂SO₃ (16 g/L), K₂HPO₄ (0.3 g/L) and EDTA (0.5 g/L), while the CuCl₂ electrolyte is prepared by CuCl₂ (1.2 g/L), Na₂SO₃ (16 g/L), K₂HPO₄ (0.3 g/L) and EDTA (0.5 g/L), respectively. Because this ordered surface profile exhibits superhydrophobic properties with the contact angle (CA) is about 109.3°, the flower-like dendritic Cu-Au alloy can be mostly reduced and assembled upon the top surface of the silicon pillar, due to the favorable restrictive contact caused by the air pockets trapped inside structural gaps, as seen the S2 in the supporting information. The morphologies of Cu-Au alloy have been tailored by controlling the nucleation and growth processes through careful regulation of reaction rate via changing the applied voltage, concentration and reaction time.
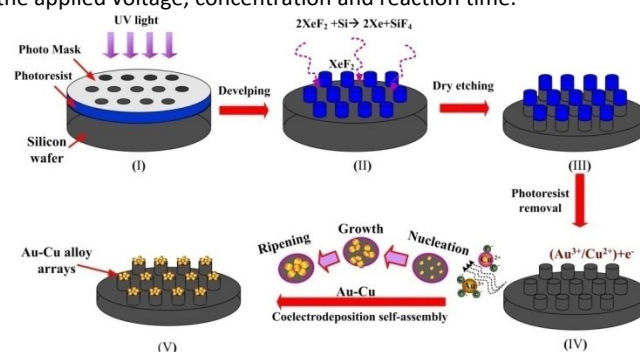

Figure S1. Schematic fabrication procedure for the highly ordered Cu-Au alloy arrays. (I) photoresist thin films are coated on the silicon wafer and exposed in a UV mask aligner. (II) photoresist pattern are etched by XeF₂ vapor. (III) The photoresist is removed from the substrate and (IV) highly ordered Si pillar arrays are obtained. (V) Hierarchical Cu-Au alloys with controllable morphologies are fabricated by coelectrodeposition and self-assembly.

Performance characterization: The composition and morphology of the Cu-Au alloy arrays are characterized in details by energy dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM) and scanning electron microscope (SEM).

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Furthermore, the effects of composition and morphology on the SERS properties with R6G as the probe molecule are demonstrated by using a HORIBA Jobin Yvon LabRAM HR Evolution cofocal microprobe Raman spectrometer with the 532 nm He-Ne Laser line at room temperature. Samples for SERS are dipped into the Rhodamine 6G (R6G) aqueous solution for 10hours, followed by thorough rinsing in deionized water and absolute ethyl alcohol to remove the unbound R6G molecules and dry before SERS measurement. The electric field spatial distribution of the Cu-Au alloy arrays is simulated theoretically by three dimensional finite-difference time-domain (3D FDTD) simulations (Lumerical FDTD Solution, Inc., Canada). The total field/scattered-field plane wave source with the wavelength of 532 nm is selected and the polarization direction is parallel to the horizontal direction.
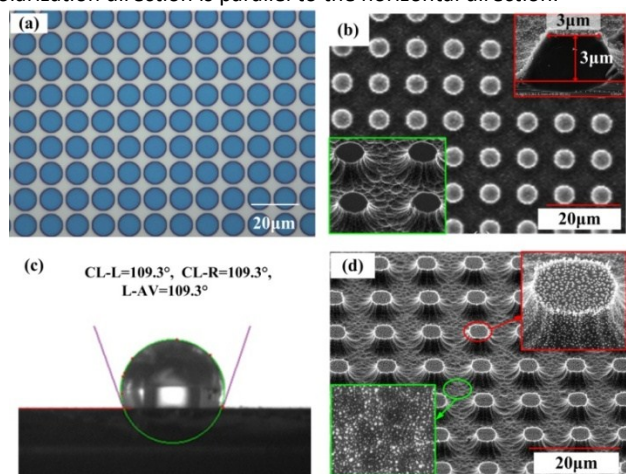

Figure S2. Microscopy images of the as-prepared Si pillar arrays and Cu-Au alloy arrays. (a) The optical microscopy image of the photoresist thin film pattern, (b) the SEM top views of the Si pillar arrays, (c) the contact angle (CA) of the Si pillar arrays and (d) the SEM top views of the Cu-Au alloy arrays.
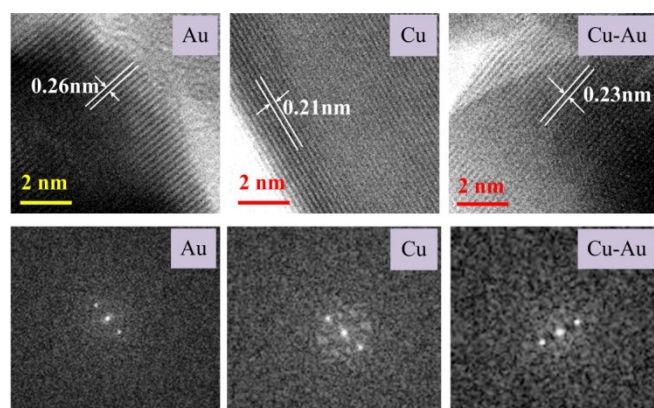

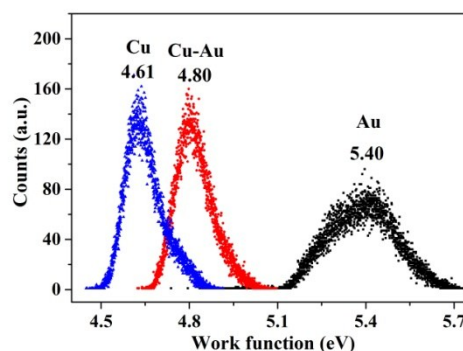**Figure S3.** the HRTEM images of Au, Cu, and Cu-Au alloy, respectively.

Figure S4. the work function of Au, Cu, and Cu-Au alloy measured by a Atomic Force Microscope (AFM), respectively.