Supporting Information

Wafer-scale fabrication of Cu/Graphene double-nanocaps array for surface-enhanced Raman scattering substrates

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Experimental Methods

Fabrication of Cu/graphene double-nanocaps on glass substrates

The fabrication of the Cu/graphene double-nanocap began with the regular arrangement of around 250 nm diameter polystyrene spheres (PSS) from Sphere Scientific Co., Ltd. onto a glass substrate via the reported method (*J. Mater. Chem.* 2011, *21* (1), 40-56). In brief, a droplet of PSS suspension (2.5 wt.% in water, surfactant free) was dropped on the substrates fixed on a spin coater. The rotating speed was held at ~1500 revolutions per minute (rpm) for 5 min and a PSS monolayer with an area of about 2 cm^2 was uniformly formed on the substrate by a self-assembly process. Thereafter, the sample was placed in the evaporation apparatus and the chamber pressure was reduced to less than 2×10^{-4} Pa prior to the deposition of Cu from pure elemental target. The as-obtained PSS/Cu samples were placed in the quartz tube and the graphene was grown on Cu double-nanocap via CVD process in

H_2 (50 SCCM) at desired temperature (300~1000 ^oC). H_2 was introduced into the CVD furnace to remove metal oxides and other impurities. The growth of graphene lasted 30 min, afterwards, the quartz tube was cooled down to room temperature (10 ^oC/min). The bare Cu nanocaps array was prepared in similar manner but without the annealing process.

Finite-difference time-domain (FDTD) simulations.

The FDTD simulation was used to calculate the electric field distributions of the local electric field distributions of Cu nanocap array in this work and randomly distributed Cu nanoparticles in previous research under the excitation of 532 nm. The size of the Cu nanocaps was set to be 125 nm for inner radius and 165 nm for outer radius. The spacing was 15 nm. The sizes and gaps for randomly distributed Cu nanoparticles in previous research were derived from the SEM image of the sample (Figure 2a in ref. 2). The surrounding medium of the model structure was set to be air. All simulations were performed in Lumerical FDTD Solutions.

Characterizations

Scanning electron microscope (SEM) images were acquired on a JEOL JSM-6700F scanning electron microscope and transmission electron microscope (TEM) images on a JEM-2100F. X-ray photoelectron spectroscopic (XPS) measurement of the samples was carried out on a PHI 1600 ESCA system. Raman spectra were obtained using a RENISHAW RM2000 Raman System. The as-obtained Cu/graphene double-nanocap substrates were immersed in 1 mL R6G ethanol solutions (from 10^{-3} to 10^{-10} M) for 1

h, taken out and washed to remove the residues with ethanol then dried in air. The excitation laser wavelength was 532 nm, accumulated time is 20 s, and laser power is 2 mW. In each cycle test for the reusability, the substrate was washed before being re-immersed in 10^{-3} M R6G solution.

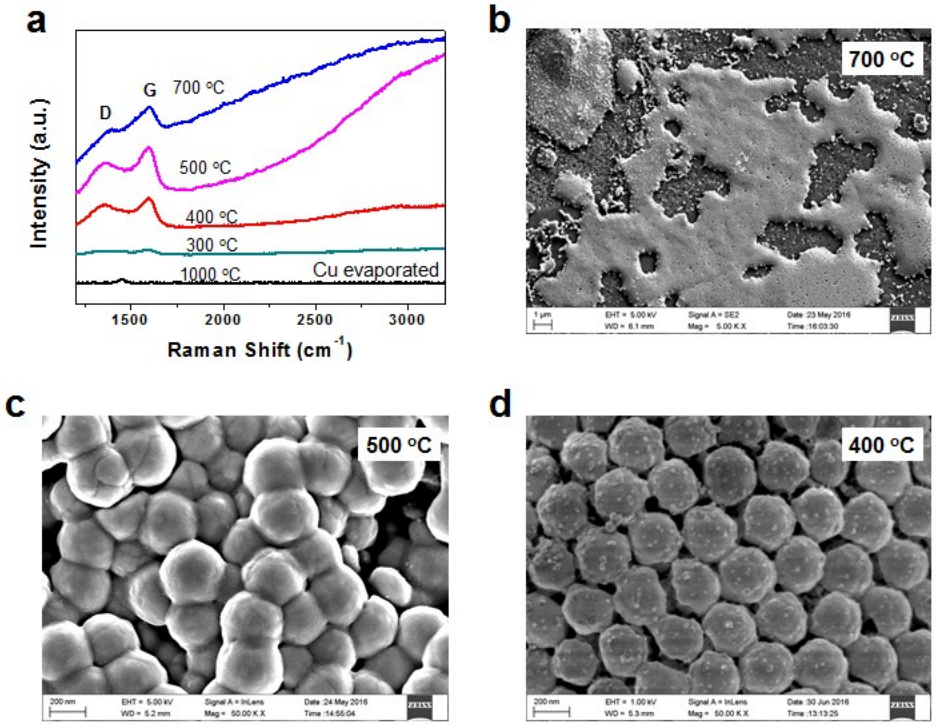

Figure S1. (a) Raman spectra of Cu/graphene shell samples obtained at different temperatures via CVD process. SEM images of samples obtained at (b) 700 °C with completely collapsed hemispherical shape, (c) 500 °C with partially collapsed and fused hemispherical shape, and (d) 400 °C with almost intact hemispherical shape.

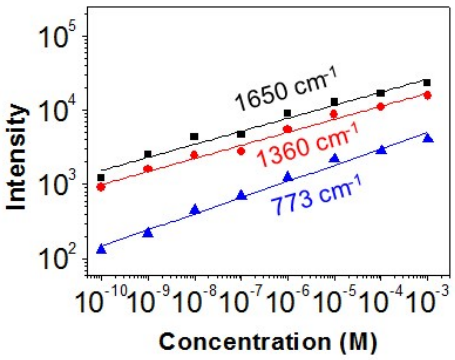

Figure S2. The Raman intensity of R6G peaks at 773 cm^{-1}, 1360 $cm^{-1}$and 1650 cm^{-1} on Cu/graphene double-nanocaps substrate, as a function of the molecular concentration, in log scale.

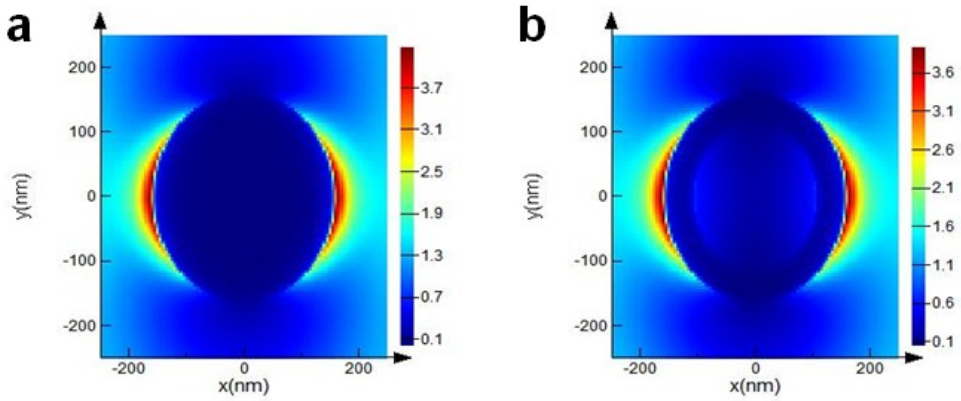

Figure S3. FDTD simulation for electromagnetic field distributions of (a) a solid Cu nanoparticle and (b) a hollow Cu nanocap.

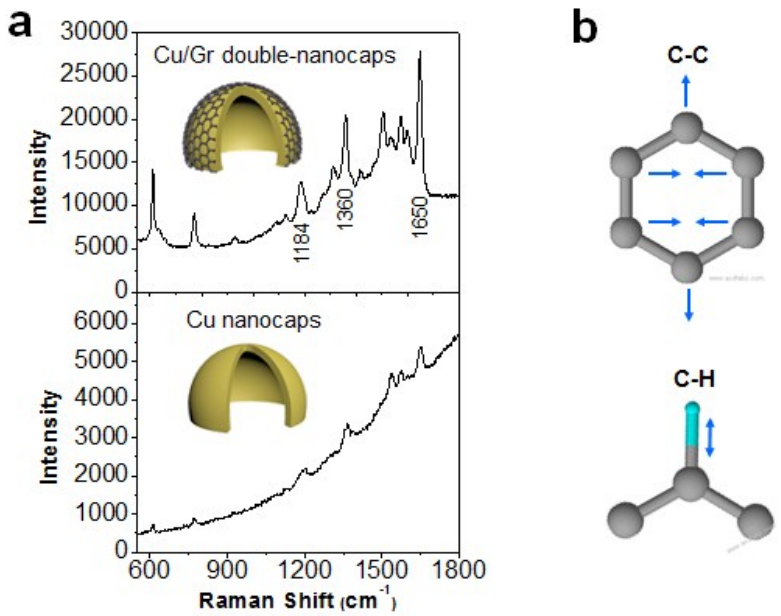

Figure S4. (a) The intensity of the fingerprint vibrational bands of R6G on Cu nanocaps substrate with and without graphene. (b) Schematic of C-C vibration mode and C-H vibration mode of R6G molecules.

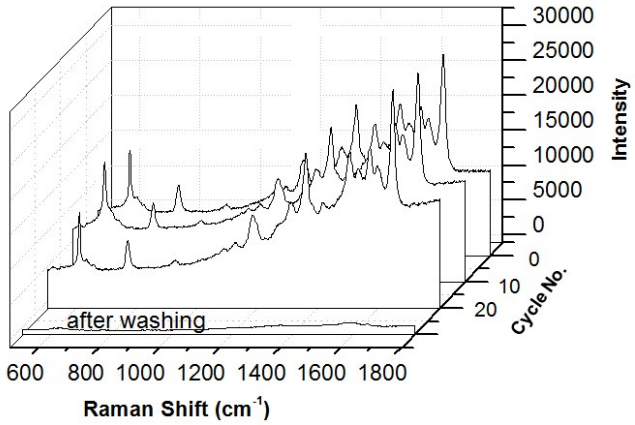

Figure S5. Reusability of the Cu/graphene double-nanocaps substrate for 20 cycles (for each recycle, the substrate was washed clean and then used for the detection of R6G solution).

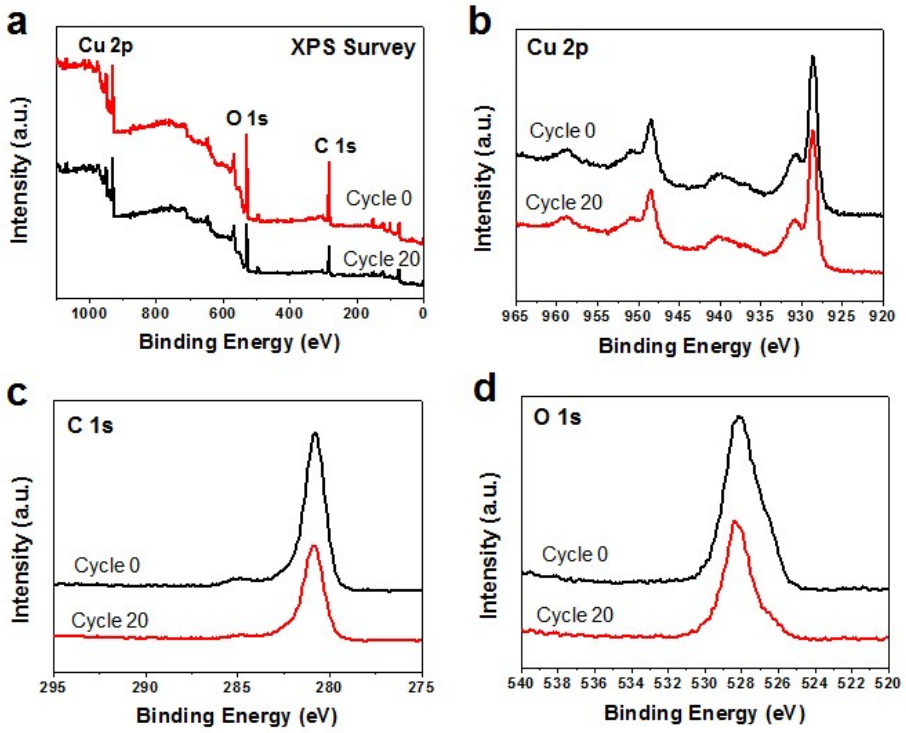

Figure S6. XPS spectra for the Cu/graphene double-nanocaps substrate before and after reusability tests.