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Electronic Supplementary Information

Electrochemical Synthesis of Fractal Bimetallic Cu/Ag Nanodendrites for Efficient Surface Enhanced Raman Spectroscopy **

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Experimental details

Materials

$CuSO_4 \cdot 5H_2O$ (Aldrich, 97%), $AgNO_3$•6H2O, 4-mercaptobenzoic acid (4-MBA) and an isoporous membrane (polycarbonate, hydrophilic, 0.22 μm, 47 mm, white, Millipore Corporation, Australia) were purchased from Sigma Aldrich. Graphite was purchased from Qingdao, China. Sodium phosphate dibasic anhydrous (Na_2HPO_4, 99.5%), sodium phosphate monobasic monohydrate ($NaH_2PO_4\,H_2O$, 99.5%), sodium chloride (NaCl, 99.6%), sulfuric acid (98%), hydrogen peroxide (30%), sulfuric acid H_2SO4 (98%), qualitative filter paper (whatman, Thickness: 0.2 ± 0.01 mm, Material: Cotton Pulp) were purchased from Fisher Scientific. Millipore water (18 MΩ) was used in all experiments. All chemicals were of reagent grade and used as received.

Synthesis of graphene and preparation of graphene paper by filtration

The graphene naonosheet was synthesized from graphite according to the modified Hummer's method. [1] Graphenes were prepared with the reduction of graphene oxide using L-ascorbic.[2] The details about synthesis and characterization of graphene were reported in a previous publication.[3] Graphene paper was prepared by vacuum filtration. 5 ml graphene (1 mg ml^{-1}) was vacuum on an isoporous membrane (polycarbonate, hydrophilic, 0.22 μm, 47 mm, white, Millipore Corporation, Australia) using a vacuum filtration unit (RZ6, Vacuubrand Inc., USA).

Electrodeposition of fractal Cu/Ag on filter paper and graphene paper

The experimental set-up consisted of a cylindrical watch glass with the filter (or graphene) paper in the bottom of the watch glass. The graphene paper was soaked with the electrolyte solutions ($CuSO_4$, $AgNO_3$). The anode was a copper ring of 4 cm diameter and the centrally located cathode was a copper wire. Electrochemical deposition of copper and silver was carried out using 10 mM $CuSO_4$ and 10 mM $AgNO_3$, respectively. The bimetallic copper/silver was electrodeposited with different atom ratio of copper to silver.

The voltage used to grow the nanodendrites was determined using the cyclic voltammograms in a solution containing 10 mM $CuSO_4$ and $AgNO_3$, respectively.[4] The standard electrochemical deposition was achieved under a constant voltage condition at 4.0 V. The overpotential was the electrochemical driving force in the constant potential mode, significantly affecting the nucleation and growth kinetics.

The dendritic nature of the deposit was achieved via a diffusion limited aggregation (DLA) process. Metal deposition was a process of nucleation and crystal growth. [5] The pattern was mainly affected by the structure character which determines the number of the crystal nucleus.

Characterization

Powder X-ray diffraction (XRD) patterns were obtained using X'Pert Powder Instrument (The Analytical X-ray Company). The operating voltage was set as 40 mV and current was 30 mA. The diffraction angle started with 10° and ended at 90°. The morphology and structure were examined using ZEISS Supra 55VP scanning electron microscope (SEM) (ZEISS, Oberkochen, Germany) and energy-dispersive X-ray spectroscopic (EDX) elemental distribution was determined by ZEISS Supra 55VP scanning electron microscope.

SERS Measurements

Raman spectra were recorded using a confocal Raman microscope (Renishaw plc, Gloucestershire, UK) equipped a 785 nm, 633 nm and 514.5 nm laser and a thermo-electrical cooled CCD detector using 10 seconds exposure time. Spectral data was acquired using 20 s exposure time, 5% power together with 4 cm^{-1} spectral resolution. The Raman sample was prepared by dropping one drop of diluted solution on the SERS substrates (Cu, Ag, or Cu/Ag) which were supported by SiO_2/Si substrate. After liquid evaporated, the samples were used for Raman tests. All Raman spectra in comparison were obtained under the same conditions if not specially pointed out.

We used the SERS peak at 1590 cm^{-1} of 4-mercaptobenzoic acid (4-MBA) molecule to compute the SERS enhancement factor (EF) using the following equation

$$EF = (I_{SERS} \times N_{bulk})/(I_{bulk} \times N_{SERS}) \qquad (1)$$

where I_{SERS} and I_{bulk} are the intensities of the same band for the SERS and ordinary spectra from a bulk sample, N_{bulk} and N_{SERS} are the numbers of bulk molecules probed for a bulk sample and those molecules probed in SERS, respectively. For determining the number of molecules probed in SERS, we assumed that the surface was covered by a complete monolayer of MBA molecules.

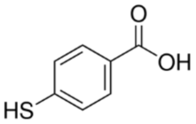
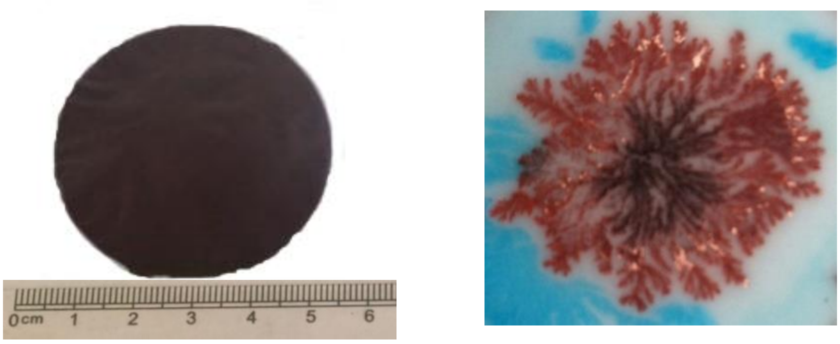
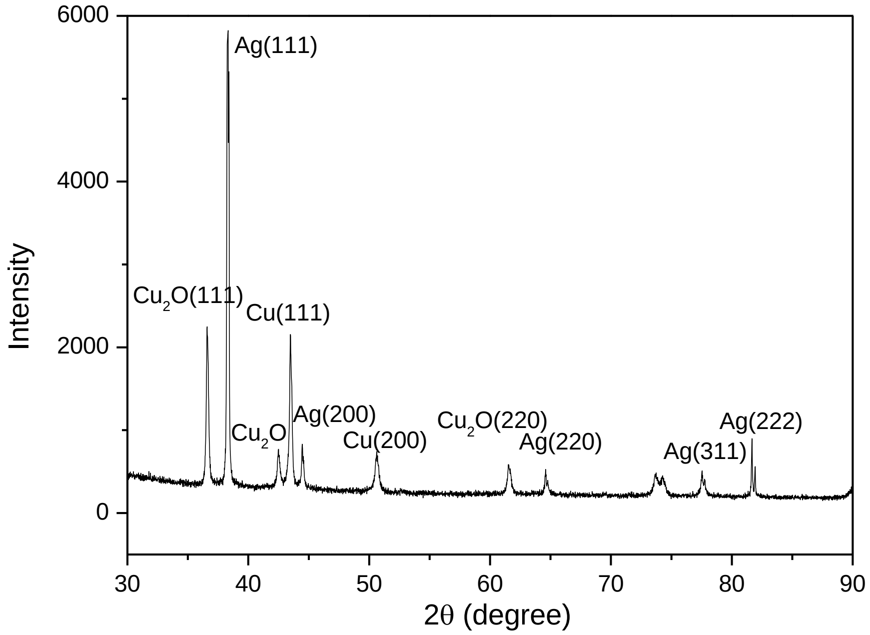


Fig. S1 The structure of 4-mercaptobenzoic acid

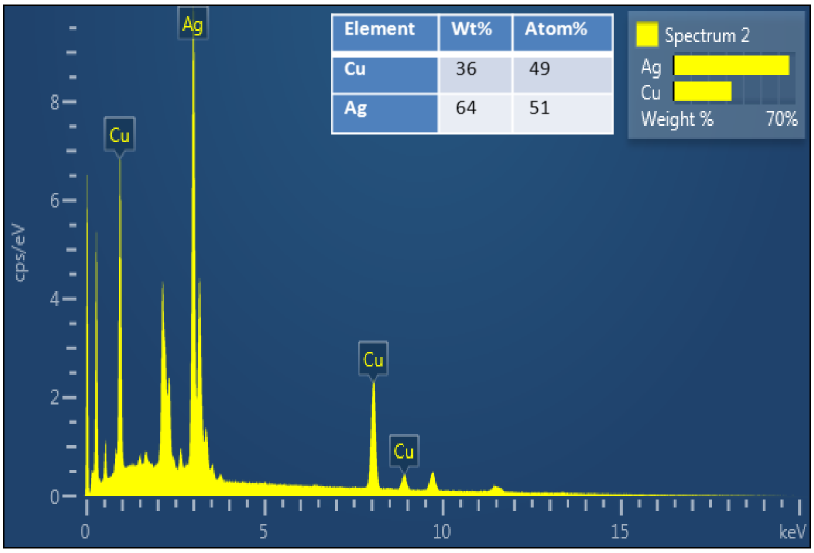


(a) (b)

Fig. S2 (a) Digital photograph of a 10μm-thick graphene paper by vacuum filtration of a graphene dispersion through an isoporous membrane. (b) Digital photograph of fractal Cu electrodeposited on filter paper.



(a)



Element	Wt%	Atom%
Cu	36	49
Ag	64	51

(b)

Fig. S3 XRD and EDX patterns of Cu/Ag@G dendrities (atom ratio of Ag to Cu is 1:1).

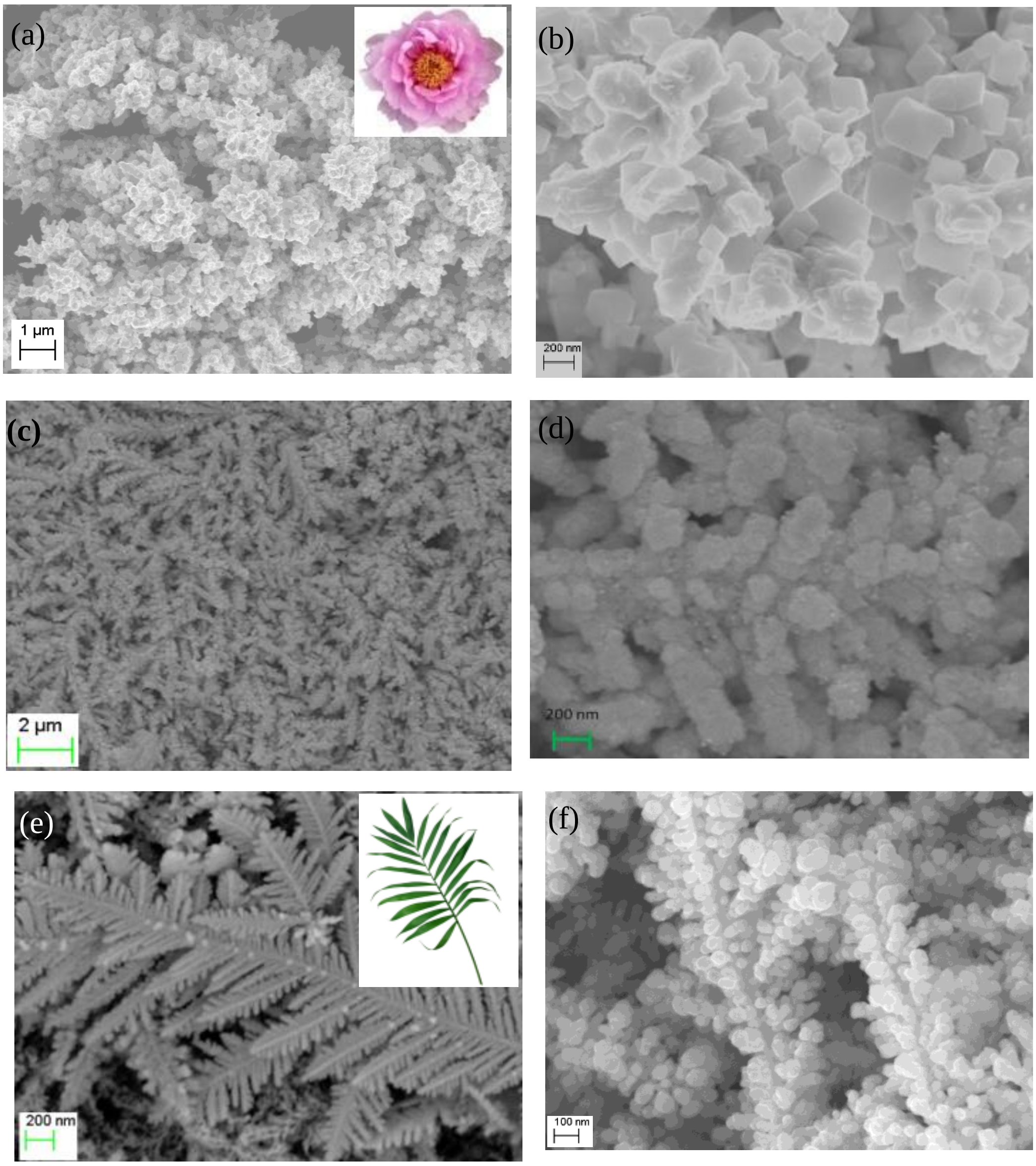


Fig. S4 SEM images of Cu@G and Cu/Ag@G with different atom ratio of Cu to Ag prepared at a potential of 4.0 V. (a) (b) Cu@G (inset, flower), (c)(d) Cu/Ag@G (Cu:Ag=2:1), (e)(f) Cu/Ag@G (Cu:Ag=1:1)

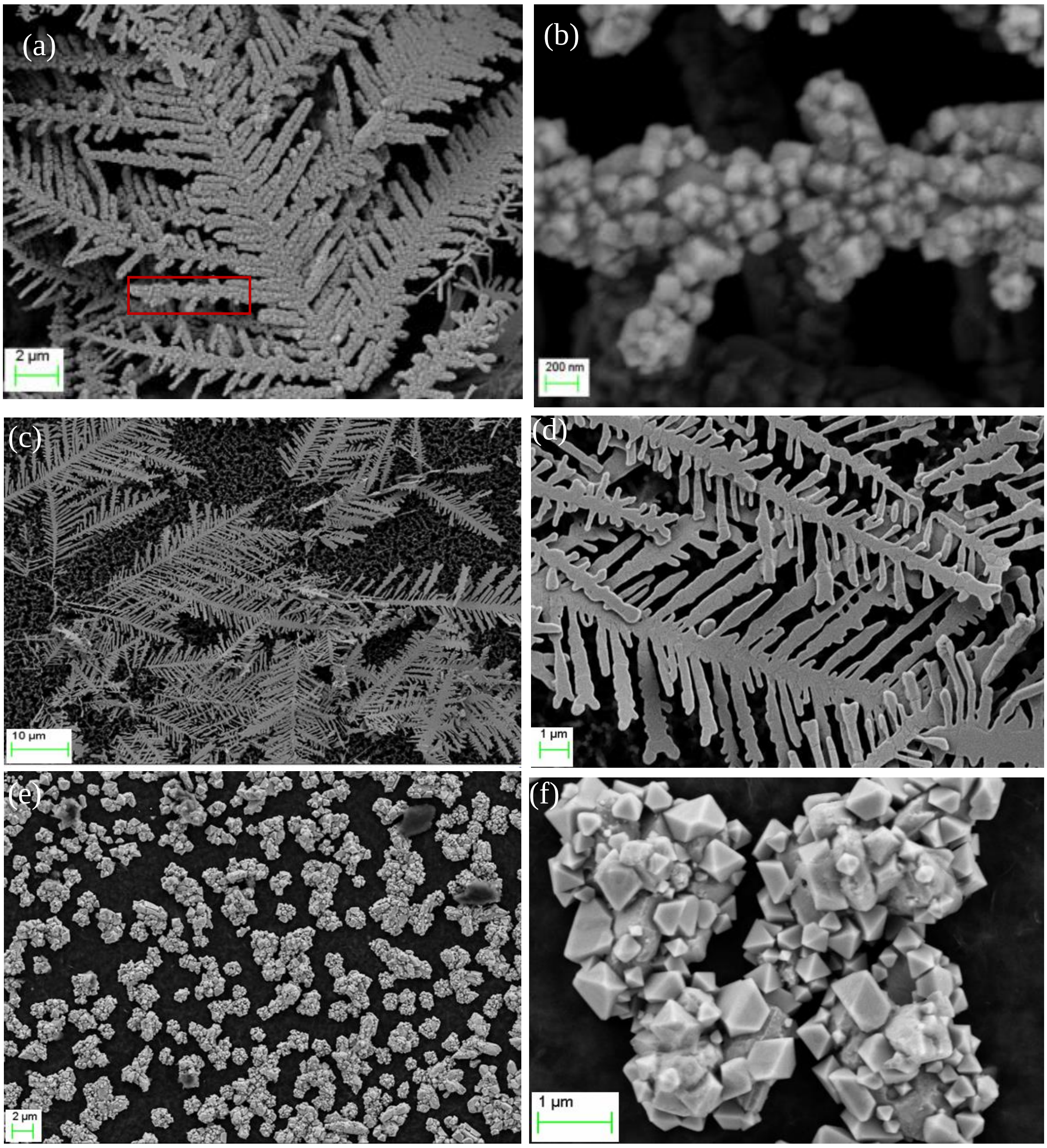


Fig. S5 SEM images of (a) (b)Cu/Ag@G with atom ratio of Cu to Ag (1:2) and (c)(d) Ag@G (e)(f) Cu@G deposited at 5.0 V

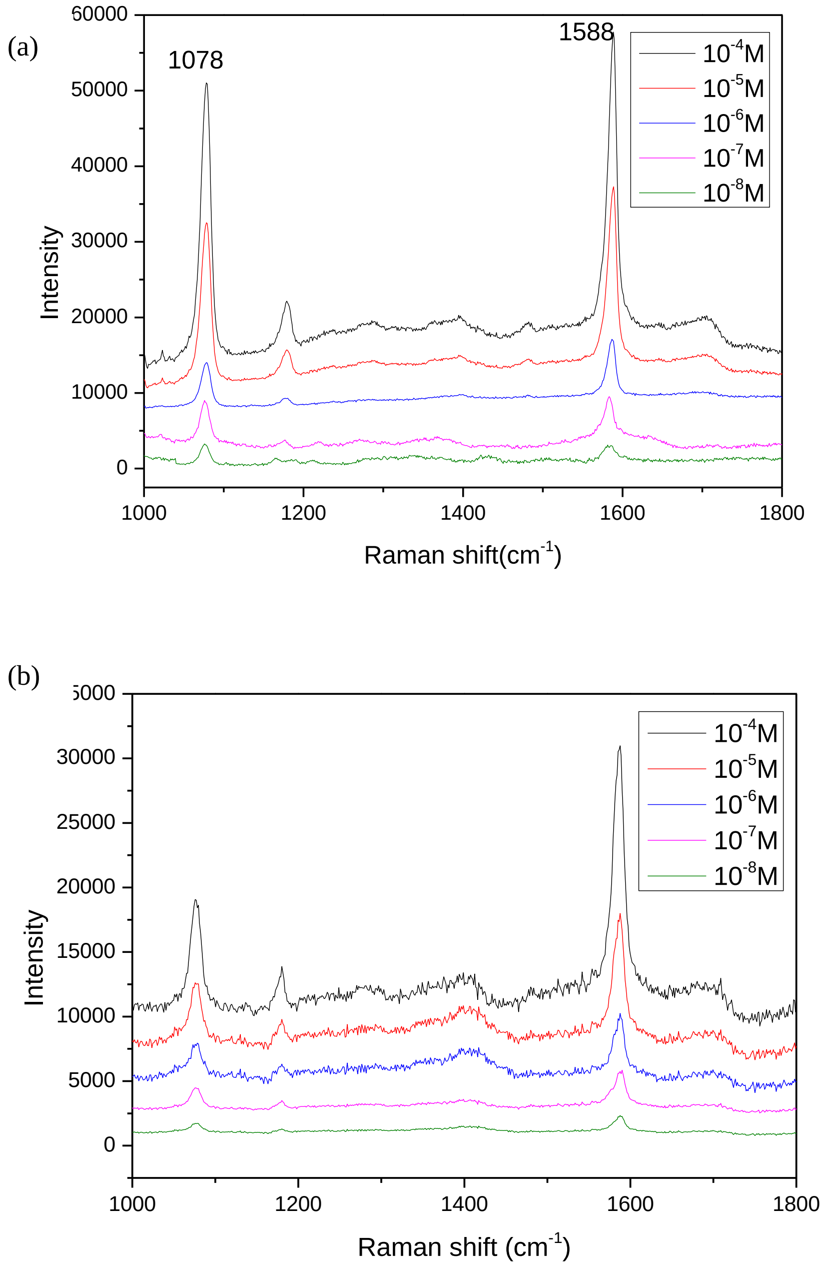


Fig. S6 SERS spectra of 4-MBA with different concentration on Cu/Ag@G (1:1) obtained using different wavelength laser (a) 633 nm and (b) 514nm .

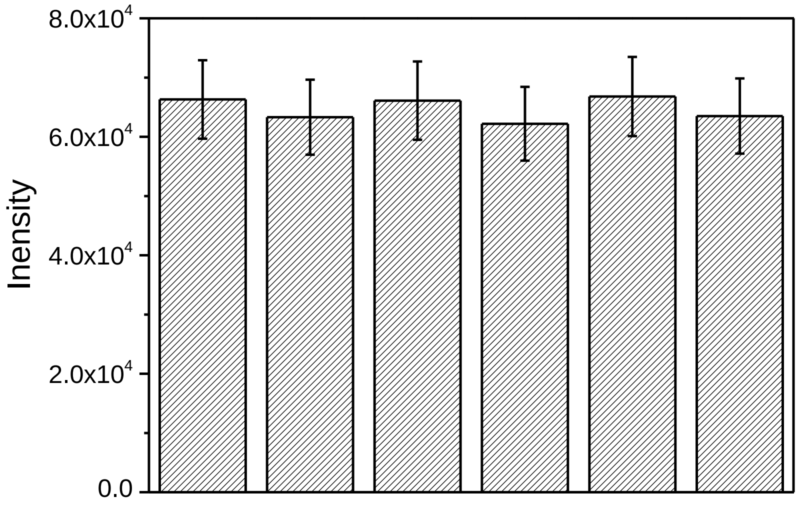


Fig. S7 Standard deviations to the SERS measurements tested at different spots. SERS Intensity of 4-MBA (10^{-4} M) at 1590 cm^{-1} peak on Cu/Ag@G

References

1. S. William, J. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.
2. J. Zhang, H. Yang, G. Shen, P. Cheng, J. Zhang and S. Guo, *Chem. Commun.*, 2010, **46**, 1112-1114.
3. D. Li, J. Liu, C. J. Barrow and W. Yang, *Chem. Commun.*, 2014, **50**, 8197-8200.
4. Y. Kang and F. Chen, *J. Appl. Electrochem.*, 2013, **43**, 667-677.
5. J. Ustarroz, J. A. Hammons, T. Altantzis, A. Hubin, S. Bals and H. Terryn, *J. Am. Chem. Soc.*, 2013, **135**, 11550-11561.