Electronic Supplemental Information

SERS-active silver nanoparticle assemblies on branched Cu_2O crystals through controlled galvanic replacement

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Experimental Section

Electrodeposition of branched Cu_2O crystals.

Cu_2O crystals were electrodeposited on ITO substrates according to previous reported methods.[1,2] Briefly, the branched Cu_2O crystals were electrodeposited from an 0.05 M $Cu(CH_3COO)_2$ aqueous solution under a constant potential of -0.15 V for 15 min in a standard three-electrode setup. ITO (10 Ω resistance) was used as working electrode. The counter electrode is a platinum wire. The reference electrode is an Ag/AgCl electrode in 4 M KCl solution. All ITO glass were rinsed and cleaned in ultrapure water, ethanol and acetone with sonication for at least three times before use.

Galvanic replacement reaction

The obtained Cu_2O crystals were immersed in a mixture of 0.05 M $AgNO_3$ aqueous solution and 0.05 M acid for Ag growth. Here, different acids (5-Sulfosalicylic acid,

citric acid, lactic acid, etc) were tried. Reaction time is strictly controlled to study the Ag morphology evolution during the galvanic replacement process. After reaction at a controlled time, the substrates were taken out from the $AgNO_3$ aqueous solution immediately and rinsed with water for several times. Then the subtrates were dried in air.

Characterization

Scanning electron microscopic (SEM) images were taken on a FEI Inspect SEM. The X-ray diffraction （XRD）measurements were carried out on a Shimadzu XRD-6000 diffract meter using fine line sealed Cu-Kα tube (λ= 1.5406 Å) X-rays. For SERS measurement, the silver nanoparticle assemblies-supported ITO substrates were immersed in RhB and MB aqueous solutions of different concentrations for 30 min, and then washed with deionized water thoroughly. The SERS spectra were recorded on a Renishaw In Via micro Raman spectroscopy system, using the TE air-cooled 576×400 CCD array in a confocal Raman system (wavelength: 633 nm; Power: 0.1 mW), with an 50X objective and acquisition time of 10 s.

Reference

1 C. M. McShane, K. S. Choi, *J. AM. CHEM. SOC*. 2009, **131**, 2561-2569.

2 M. J. Siegfried, K. S. Choi, *Angew. Chem*. 2008, **120**, 374-378.

Additional Figures:

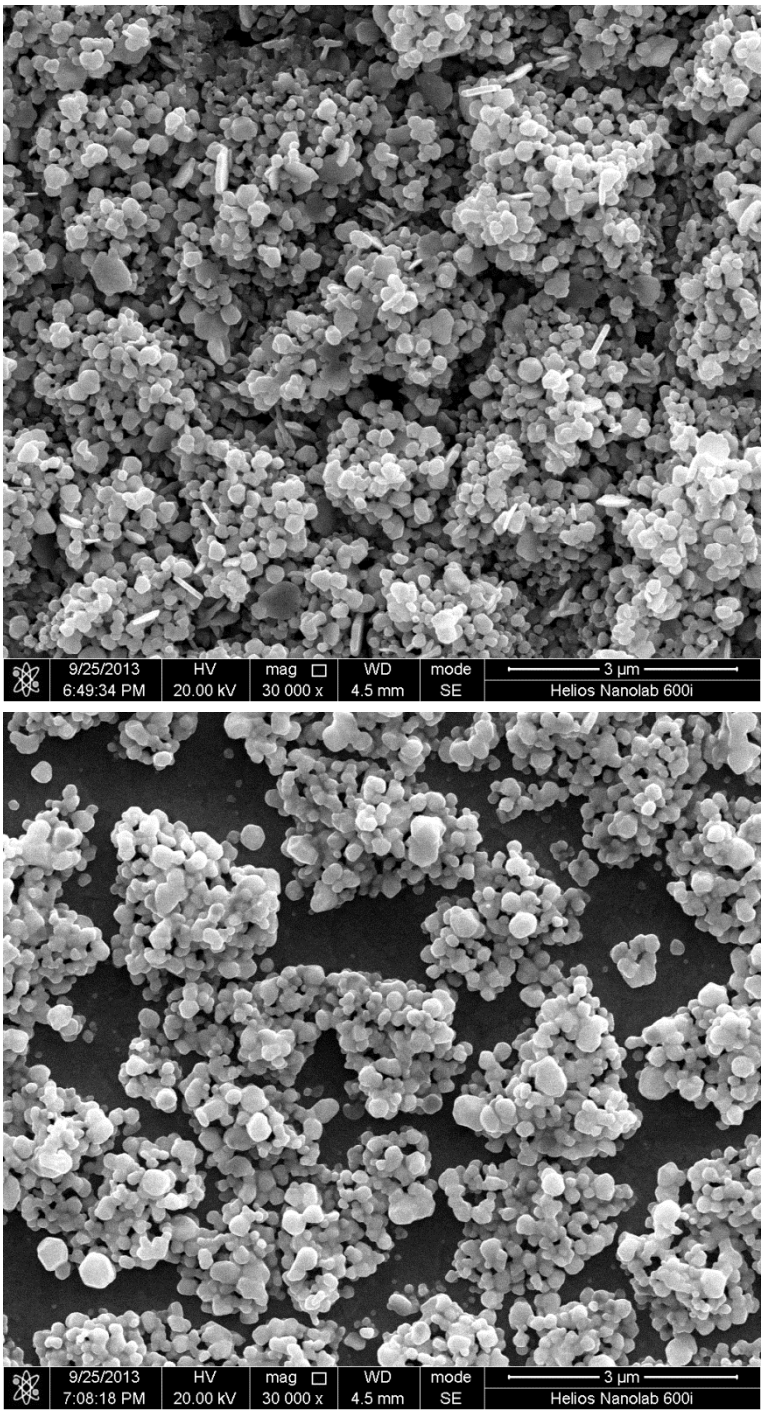

Fig. S1 SEM images of Ag nanoparticle assemblies obtained from galvanic replacement for (top) 5 min, and (down) 10 min. During the galvanic replacement process, 5-sulfosalicylic acid was used as the additive acid.

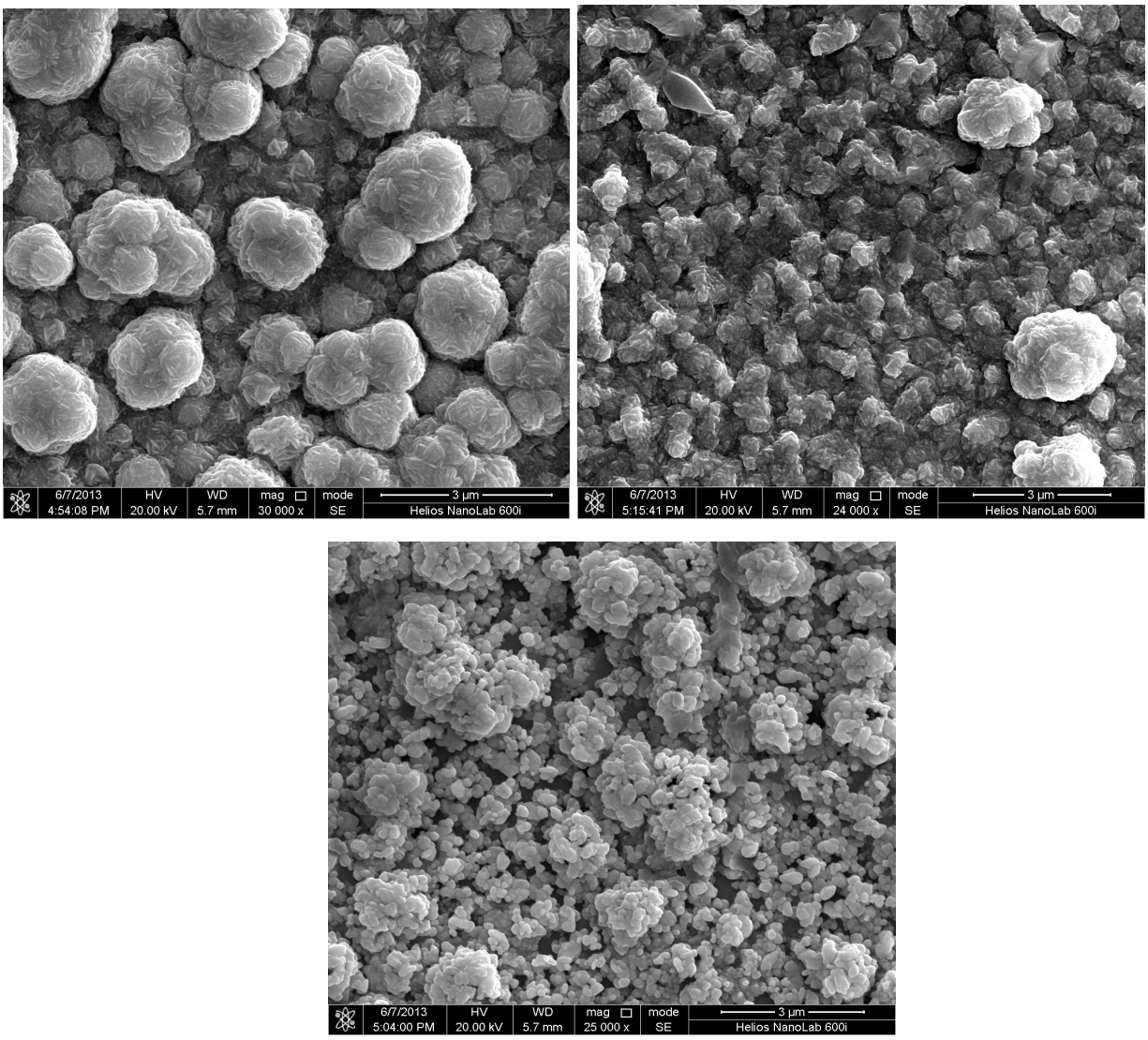

Fig. S2 SEM images of Ag nanoparticle assemblies obtained from galvanic replacement for 30 s. During the galvanic replacement process, citric acid (up, left), camphorsulfonic acid (up, right), and lactic acid (down) were used as the additive acid.

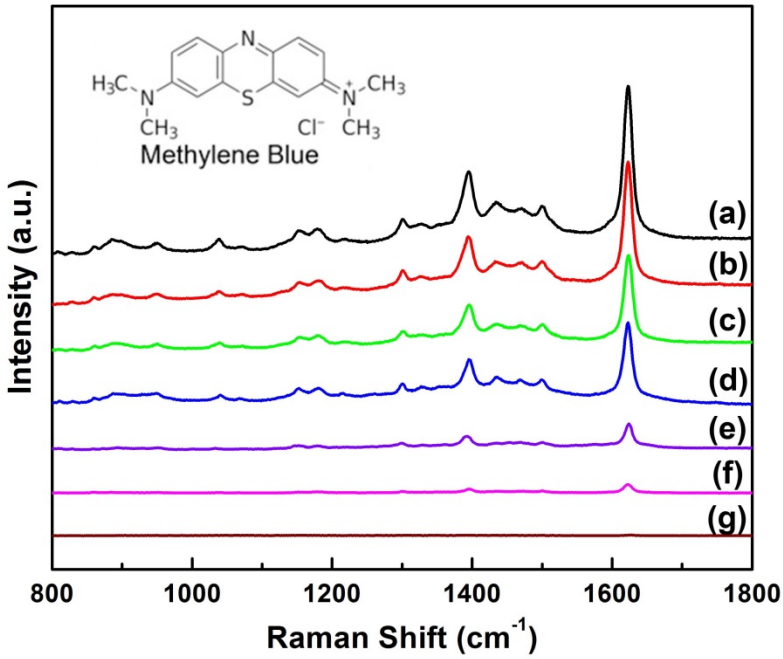

Fig. S3 SERS spectra of methylene blue (MB) of different concentrations measured on Ag nanoparticle assemblies obtained from galvanic replacement for 30 s (see Fig. 1e, f): (a) 10^{-4}, (b) 10^{-5}, (c) 10^{-6}, (d) 10^{-7}, (e) 10^{-8}, (f) 10^{-9}, (g) 10^{-10} mol/L.

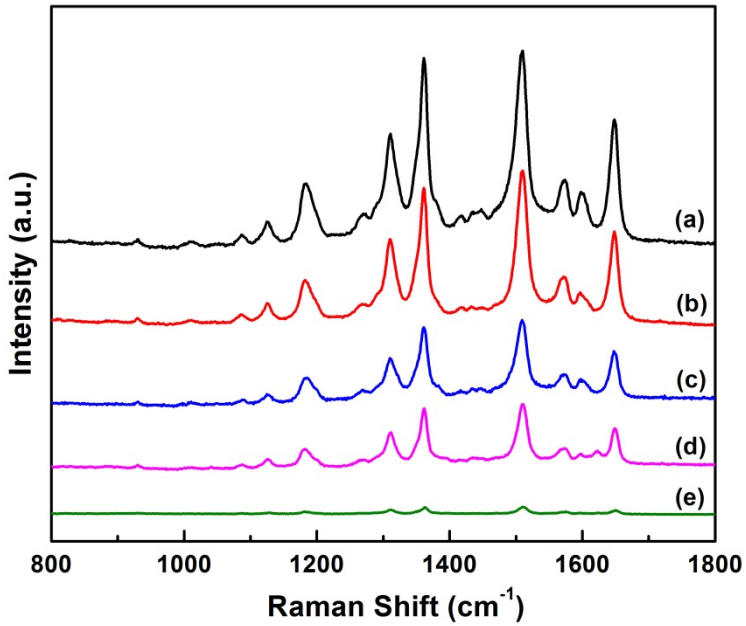

Fig. S4 SERS spectra of RhB of different concentrations measured on Ag nanoparticle assemblies obtained from galvanic replacement for 30 s: (a) 10^{-5}, (b) 10^{-6}, (c) 10^{-7}, (d) 10^{-8}, (e) 10^{-9} mol/L.

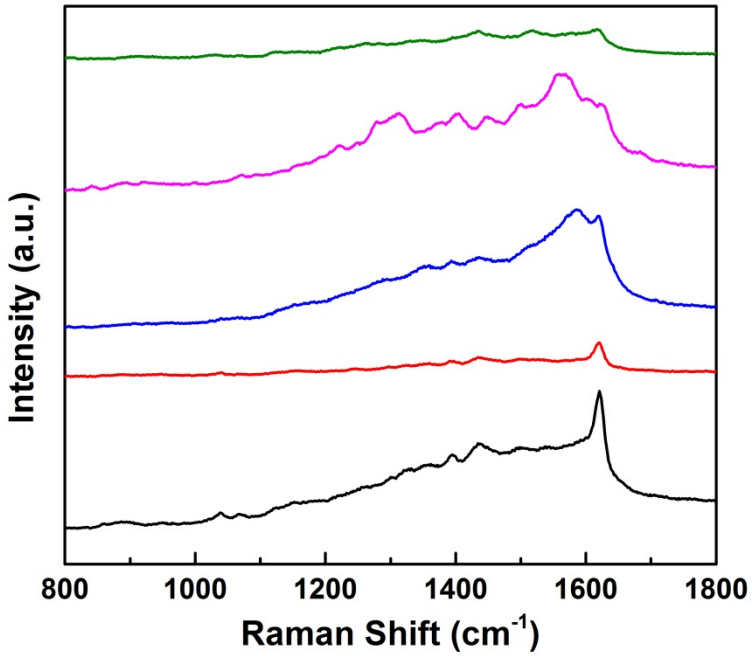

Fig. S5 SERS spectra of methylene blue (MB, 10^{-6} mol/L) taken from different sites on the Ag nanoparticle assemblies supported on Cu_2O crystals prepared using lactic acid as the additive acid.