Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Improved SERS Activity of non-stoichiometric Copper Sulfide Nanostructures Related to Charge-Transfer Resonance

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Supplementary Material

The EF value can be calculated by the following formula: EF = (I_{SERS} / N_{SERS}) / (I_{normal} / N_{normal}). Where I_{SERS} is the intensity of the Raman spectrum of R6G molecules adsorbed on the substrate. N_{SERS} is the total number of R6G molecules adsorbed on the substrate surface under the laser spot. I_{normal} is the intensity of the normal Raman spectrum of R6G powder. N_{normal} is the number of molecules of the R6G powder under the laser spot. As shown in Figure S3, taking the 613 cm^{-1} peak as an example, the measured values of I_{normal} and I_{SERS} are 489 and 519 counts. It is known that the density of R6G powder is about 0.99 g/cm^3, the radius of the confocal laser beam is 0.5 μm, the penetration depth of the confocal laser beam is about 2 μm, and the volume of R6G dropped on the substrate is 10 μL. Here, we assume that the R6G moleculars are uniformly distributed on the substrate after drying.

$N_{SERS} = N_A \times 0.25\pi\ \mu m^2 \times (10\ \mu L \times 10^{-7}\ M) / (25\ mm^2) = 1.89 \times 10^4$

$N_{normal} = N_A \times (0.99\ g/cm^3 \times 0.25\ \mu m^2 \times 2\ \mu m)/479\ g/mol = 6.22 \times 10^8$

It can be estimated that the values of N_{SERS} and N_{normal} are about 1.89×10^4 and 6.22×10^8. Thus, the EF value of 613 cm^{-1} was calculated to be 3.5×10^4.

Table S1. component analysis for (1) the as-synthesized samples and annealed samples at (2) 200 ^oC, (3) 250 ^oC, (4) 300 ^oC, and (5) 350 ^oC extrapolated from XRD results.

	CuS	$Cu_{7.2}S_4$	$CuSO_4$
(1)	100 %	0 %	0 %
(2)	100 %	0 %	0 %
(3)	43 %	24 %	33 %
(4)	7 %	40 %	53 %
(5)	0 %	0 %	100 %

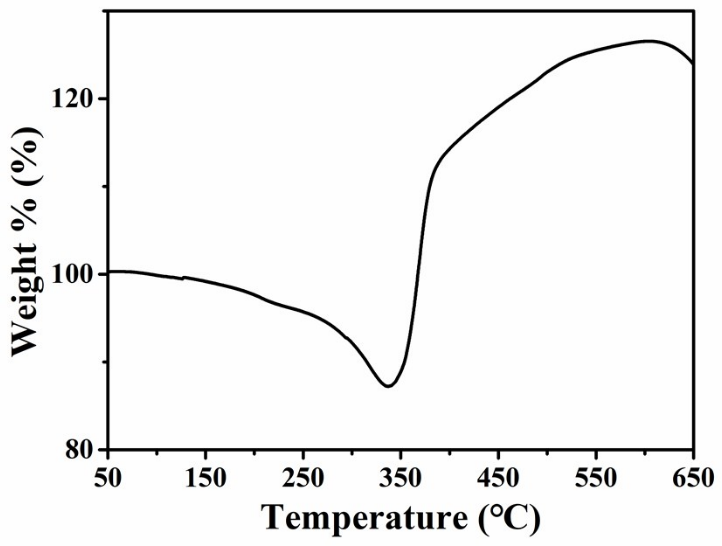

Figure S1. The thermogravimetric curve of CuS.

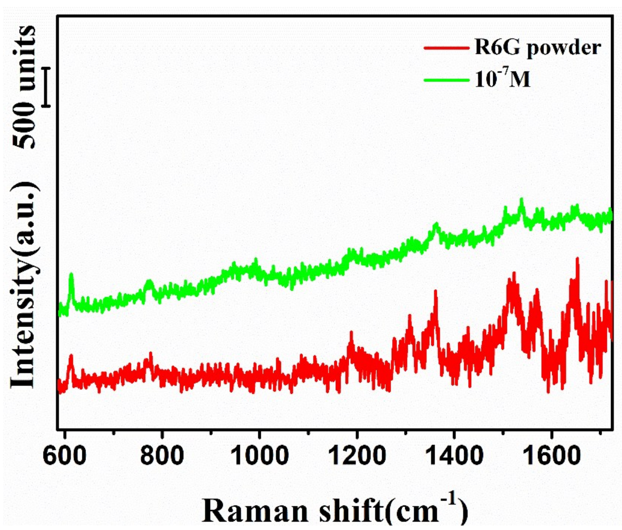

Figure S2. SERS spectra of 10^{-7} M R6G adsorbed on annealed sample at 300 ^oC and Raman spectrum of R6G powder.

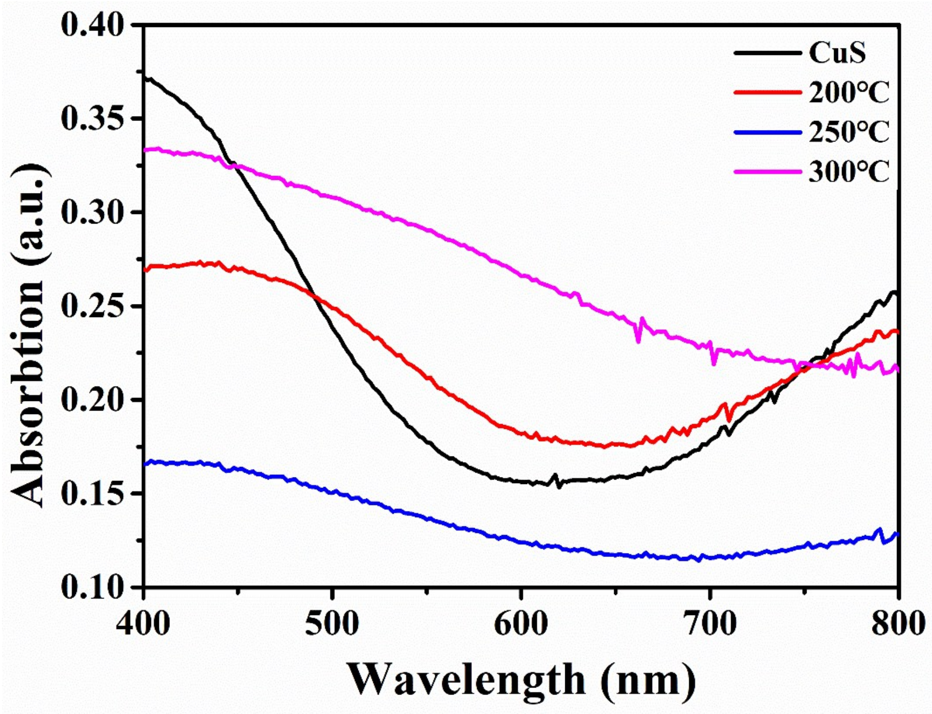

Figure S3. UV-Vis absorption spectra of (a) the as-synthesized samples and annealed samples at (b) 200 ^{o}C, (c) 250 ^{o}C, and (d) 300 ^{o}C.

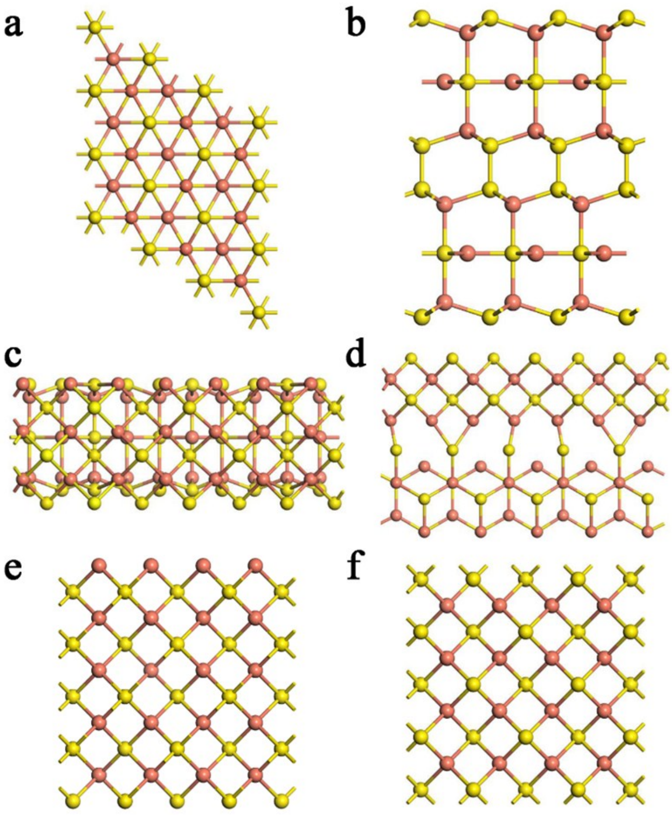

Figure S4. The top and side images of the structures: (a)(b) CuS; (c)(d) $Cu_{2-x}S$ and (e)(f) $Cu_{7.2}S_4$.