

Supporting Information

Catalytic Degradation of Dye Molecules and *In-situ* SERS Monitoring by Peroxidase-like Au/CuS Composite

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1. The detailed XRD quantitative analysis for Au content in the Au/CuS composite

The reference intensity ratio method was employed for XRD quantitative analysis.

The following equation was used for calculation:

$$I/I_{cor} = kX/X_{cor}$$

where I is the intensity of the strongest diffraction peak of the unknown material; X is the mass fraction of unknown phase; cor is the abbreviation for corundum which serves as the standard phase; X_{cor} is the mass fraction of corundum; k is defined as I/I_{cor} value corresponding to the JCPDS card, which is the reference intensity ratio for a 50:50 mixture of an unknown phase and corundum. Based on this equation and the data in Table 1, the mass fraction of Au can be calculated to be 16.7%.

Table1. Constitute of the Au/CuS composite

Samples	Au	CuS
<i>k</i>	25.3	3.59
Intensity	4056	2865
Molar ratio	0.167	0.833

2. The size distribution histogram of the Au nanoparticles decorated on the surface of CuS nanoplates

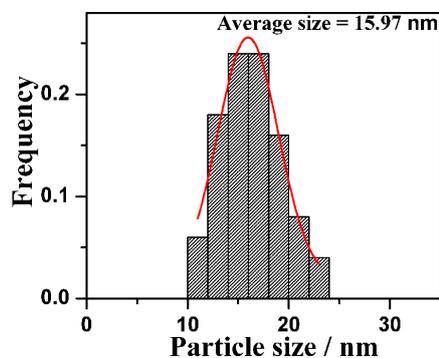


Figure S1. The size distribution histogram of Au nanoparticles based on 50 particles from the high-magnification image of TEM.

3. The normal Raman spectrum of 0.2 M R6G aqueous solution

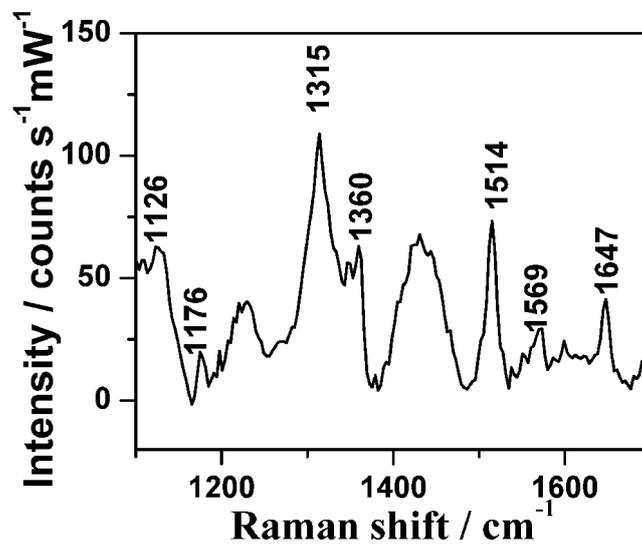


Figure S2. The normal Raman spectrum of 0.2 M R6G aqueous solution.

4. Enhancement factor (EF) calculation

The average SERS EF is calculated based on the formula:

$$EF = \frac{I_{SERS} N_0}{I_0 N_{SERS}}$$

where I_{SERS} and N_{SERS} are the peak intensity of Raman and probe molecule number under SERS conditions, respectively; I_0 and N_0 are the peak intensity of the normal Raman and probe molecule number measured with 0.2 M R6G aqueous solution.

$$N_0 = n_0 N_A = C_0 V_0 N_A;$$

$$N_{SERS} = n_{SERS} N_A = C_{SERS} V_{SERS} N_A$$

where n_0 and n_{SERS} are the amount of R6G molecules in the scattering volume; V_0 and V_{SERS} are the scattering volume ($V_0 = V_{SERS}$); C_0 and C_{SERS} are the concentration of R6G solution; N_A is Avogadro constant.

$$\text{So, } EF = \frac{I_{SERS} N_0}{I_0 N_{SERS}} = \frac{I_{SERS} C_0 V_0 N_A}{I_0 C_{SERS} V_{SERS} N_A} = \frac{I_{SERS} C_0}{I_0 C_{SERS}} = (520 \times 0.2) / (411 \times 1 \times 10^{-6}) = 2.53 \times 10^5$$

5. The intensities of the main Raman vibrations of R6G aqueous solution (1×10^{-6} M) for 150 spots

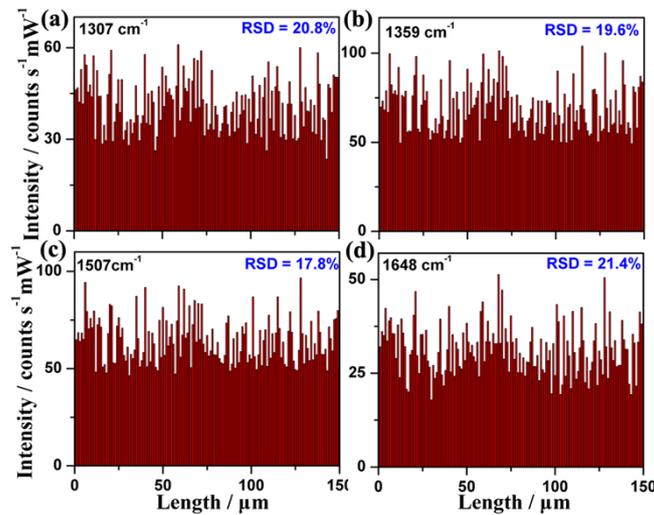


Figure S3. The intensities of the main Raman vibrations of R6G aqueous solution (1×10^{-6} M) for 150 spots

6. Fluorescence intensities of the terephthalic acid (TA) assay hydrogen peroxide solution with and without the addition of Au/CuS catalysts

To verify the $\text{OH}\cdot$ was generated in this process, TA was served as photoluminescence probing, which was widely used in the detection of $\text{OH}\cdot$. TA could react with $\text{OH}\cdot$ to yield a strong fluorescent product 2-hydroxy terephthalic acid (TAOH). The PL intensity enhanced about 9 times after adding Au/CuS catalysts, which strongly suggested that a high amount of $\text{HO}\cdot$ was generated in the catalytic reaction.

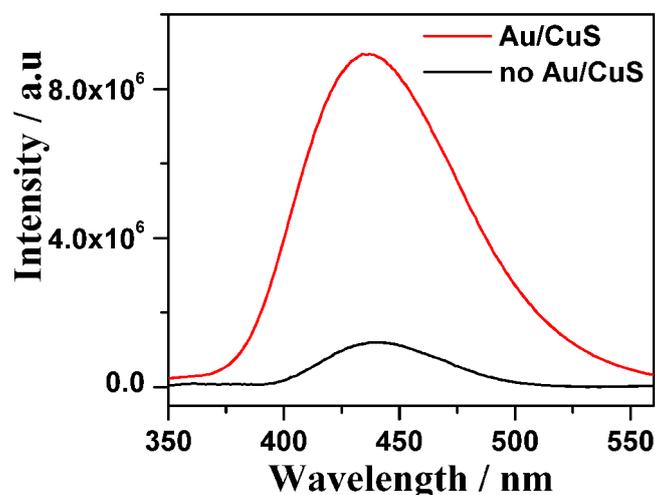


Figure S4. Fluorescence spectra of the TA assay hydrogen peroxide solution with and without the addition of Au/CuS catalysts.

7. The relationship between peak intensity and concentration of R6G molecules

The work curves of peak intensity and concentration of R6G were obtained, it is found that the intensity and concentration presents linear relationship for all the four characteristic peaks in the range of $1 \times 10^{-7} - 2 \times 10^{-5}$ M.

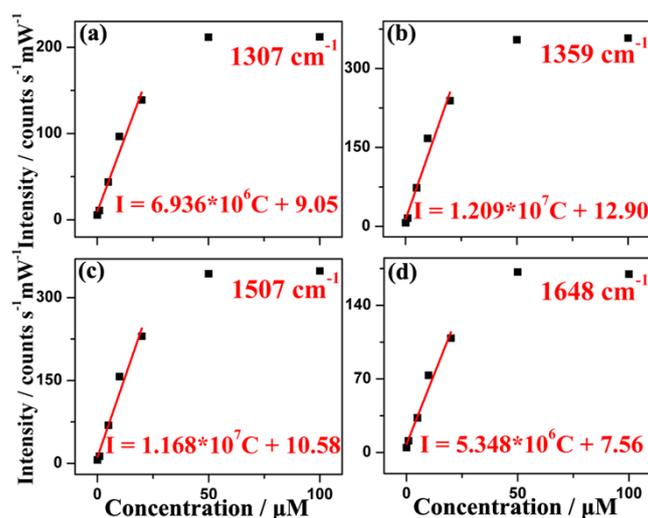


Figure S5. The work curves of Raman peak intensity and concentration of R6G at (a) 1307 cm⁻¹, (b) 1359 cm⁻¹, (c) 1507 cm⁻¹, (d) 1648 cm⁻¹.

8. The detailed calculation for the real and imaginary parts of dielectric constant of CuS nanoplates

Figure S6(a) shows the UV-Vis spectra of CuS nanoplates dispersed in deionized water with different concentrations. It is observed that there is a linear relationship between concentration and absorbance (Figure S6(b)), which can be expressed as $A = 322.196C + 0.05433$. It is known that the absorbance also can be denoted as $A = \alpha bC$ (α is absorption coefficient, b is the length of light path, which is equal to the width of

cuvette cell of 1 cm, C is molar concentration), so the value of α is corresponding to the slop of the straight line, which is 30931.2 cm^{-1} .

Absorption coefficient (α) also relates to the photon energy, which is used to measure the optical band gap (E_g). For the direct band gap semiconductor (CuS), the optical band gap can be characterized by the following expression: $h\nu = C_\alpha (h\nu - E_g)^\gamma$, where C_α is the constant, h is the Planck's constant, ν is the frequency and $\gamma = 1/2$ [1]. The functional dependence of $(\alpha h\nu)^2$ versus $(h\nu)$ with the concentration of $6 \times 10^{-3} \text{ M}$ is shown in Figure S6(c). Here, the band gap of CuS is determined by the extrapolation of the linear region on the energy axis ($h\nu$).

A correlation between refractive index (n) and optical band gap (E_g) has significant bearing on the band structure of semiconductors and would be useful in finding an acceptable n value of the unknown material from this relation. In the present work, n of CuS could be calculated using the Moss formula based on an atomic mode [2, 3]:

$n^4 = K/E_g$, where K is a constant with a value of 108 eV.

Absorption coefficient α is also related to the extinction coefficient (k):

$k = \alpha\lambda/4\pi$, so the extinction k could be calculated as 0.1255.

For further analysis of the optical data of CuS substrate, the following relations have been used to calculate the dielectric constant [4]:

$$\varepsilon = (n - ik)^2 = \varepsilon_1 - i\varepsilon_2$$

$$\varepsilon_1 = n^2 - k^2$$

$$\varepsilon_2 = 2nk$$

where ε is the dielectric constant, ε_1 and ε_2 are the real and imaginary parts of the dielectric constant, respectively.

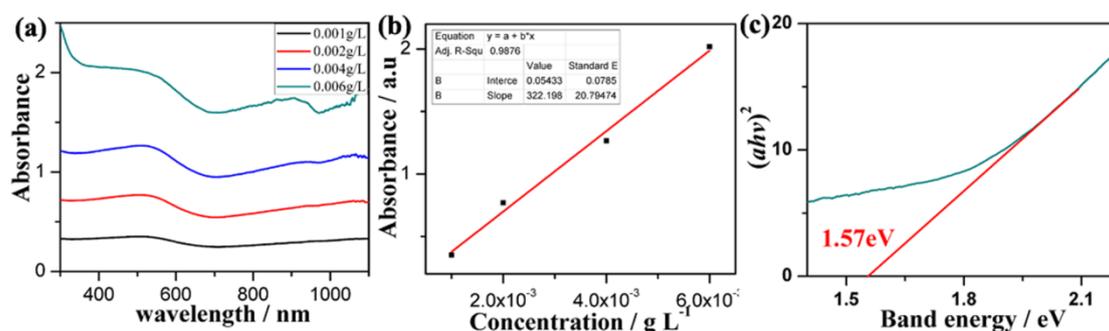


Figure S6. (a) Absorbance spectra of CuS nanoparticles dispersed in deionized water with different concentrations; (b) the linear relationship between concentration and absorbance at 510 nm; (c) plot of $(ahv)^2$ versus the photon energy (hv) for CuS nanoparticles.

References:

- (S1) M. Ali Yildirim and A. Ateş, *Opt. Commun.*, 2010, **283**, 1370.
- (S2) L. Hannachi and N. Bouarissa, *Physica B: Condensed Matter*, 2009, **404**, 3650.
- (S3) Y. Akaltun, M. A. Yildirim, A. Ates, *Opt. Commun.*, 2011, **284**, 2307.
- (S4) S. Kasap, C. Peter, Springer handbook of electronic and photonic materials Springer, 2007, chapter 3, pp 44-47.