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Supporting Materials

Employing cobalt sulfides/noble metal composites bi-functional ability for degradation and monitoring by SERS in real time

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1. The size distribution histogram of the Au nanoparticles decorated on the surface of CoS_2 and CoS.

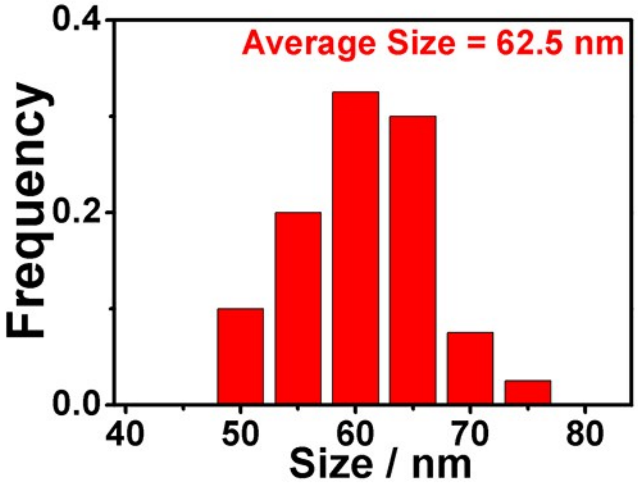

Figure S1. The size distribution histogram of Au nanoparticles measured on 250 particles from the SEM image of CoS_2/Au sample.

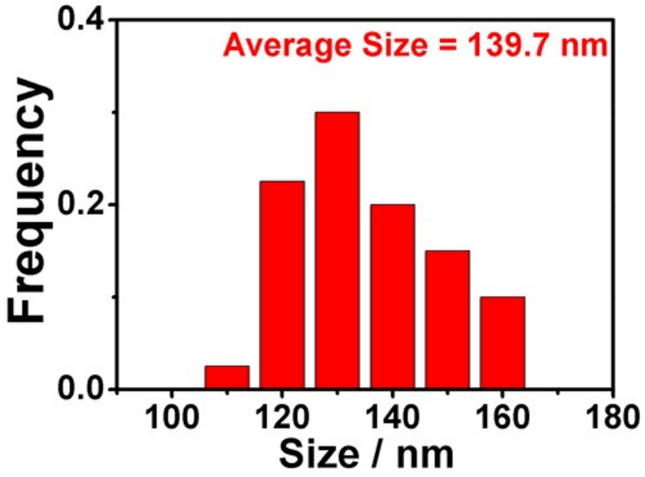

Figure S2. The size distribution of reduced Au nanoparticles with 250 particles measured from the SEM image of CoS/Au sample.

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

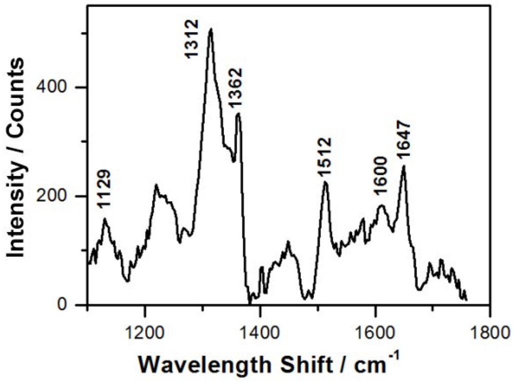

Figure S3. The normal Raman spectrum of 0.2 M R6G aqueous solution.

3. Contrast experiment of the catalytic oxidation process in the absence of CoS_2/Au (CoS/Au) catalyst or H_2O_2.

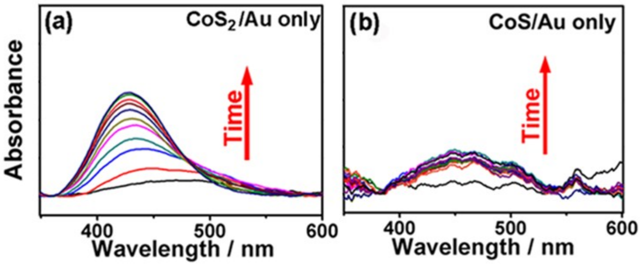

Figure S4. The UV-vis spectra of the catalytic oxidation process of OPD molecules without the addition of H_2O_2: (a) only CoS_2/Au and (b) only CoS/Au composite was added.

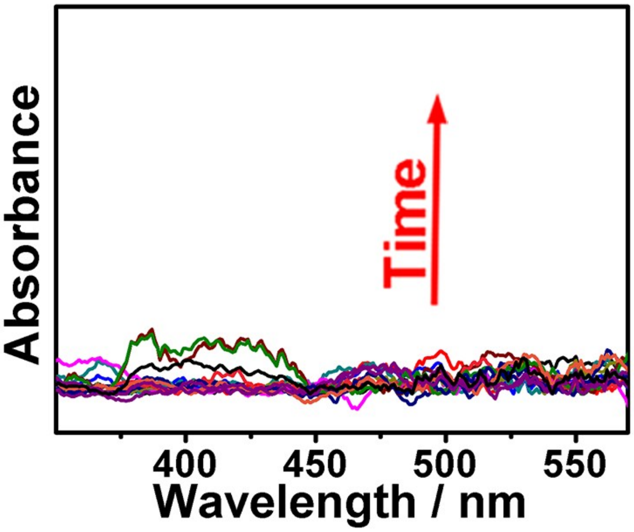

Figure S5. The UV-vis spectra of the catalytic oxidation process of OPD molecule with only H_2O_2 added.

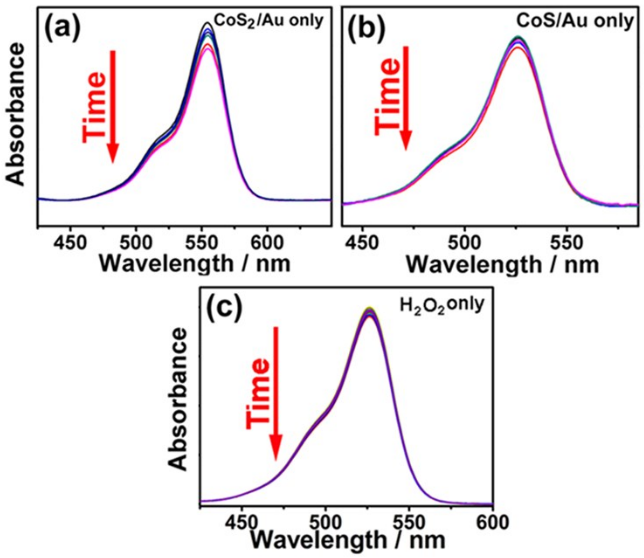

Figure S6. The UV-vis spectra of the degradation process of R6G molecules: (a) and (b) only the catalyst CoS_2/Au and CoS/Au was added without H_2O_2, and (c) only the H_2O_2 was added without catalysts.

4. The relationship between the peak intensity and concentration of R6G molecules.

The work curves of Raman signal intensity and concentration of R6G were obtained as follows: The substrates were fabricated with as-prepared CoS_2/Au or CoS/Au and the concentration of R6G solution varied from 1×10^{-7} M to 1×10^{-4} M. The vibration bands of R6G molecules at 1315, 1365, 1512 and 1654 cm^{-1} were chosen for analysis with CoS_2/Au substrate. The linear relationships are expressed as: $I = 4.63 \times 10^8 C_{R6G} + 100.1$, $I = 6.88 \times 10^8 C_{R6G} + 155.9$, $I = 6.59 \times 10^8 C_{R6G} + 147.2$, $I = 3.43 \times 10^8 C_{R6G} + 530.2$, respectively. The vibration bands of R6G molecules at 1312, 1357, 1513 and 1646 cm^{-1}

were chosen for analysis with CoS/Au substrate, and the linear relationships are expressed as: I = 1.95 × 10^8 C_{R6G} + 346.8, I = 2.26 × 10^8 C_{R6G} + 528.1, I = 3.05 × 10^8 C_{R6G} + 629.5, I = 1.57 × 10^7 C_{R6G} + 187.6 respectively. Each inset is the amplification of the linear part. And the concentration range of R6G is from 1×10^{-7} to 1×10^{-5} M. Based on these equations, the goodness of fit and standard deviation are provided in Tables S1 and S2.

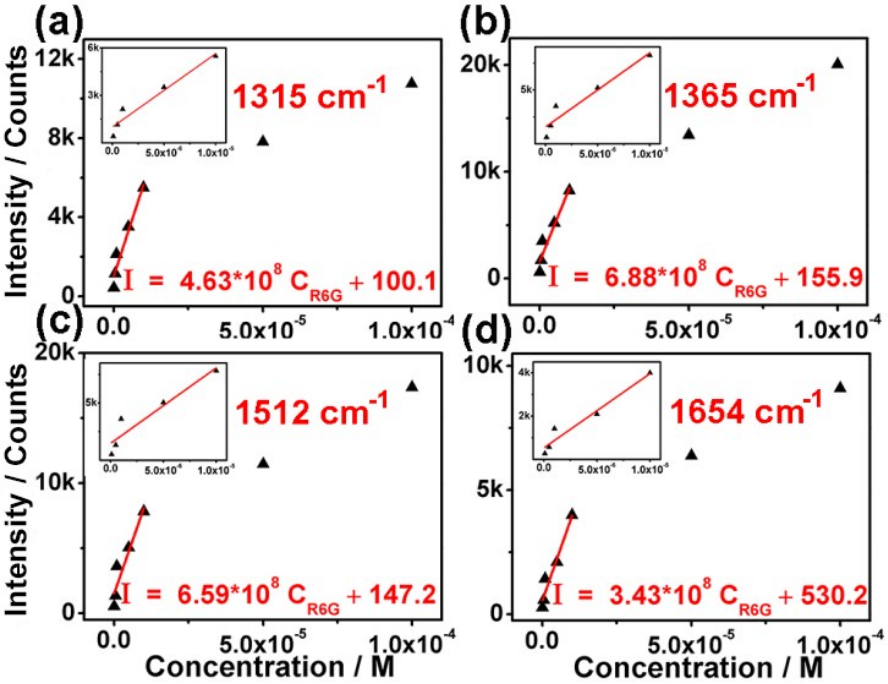

Figure S7. The work curves of Raman peak intensity and concentration of R6G at (a) 1315 cm^{-1}, (b) 1365 cm^{-1}, (c) 1512 cm^{-1}, and (d) 1654 cm^{-1} by employing CoS_2/Au as the substrate.

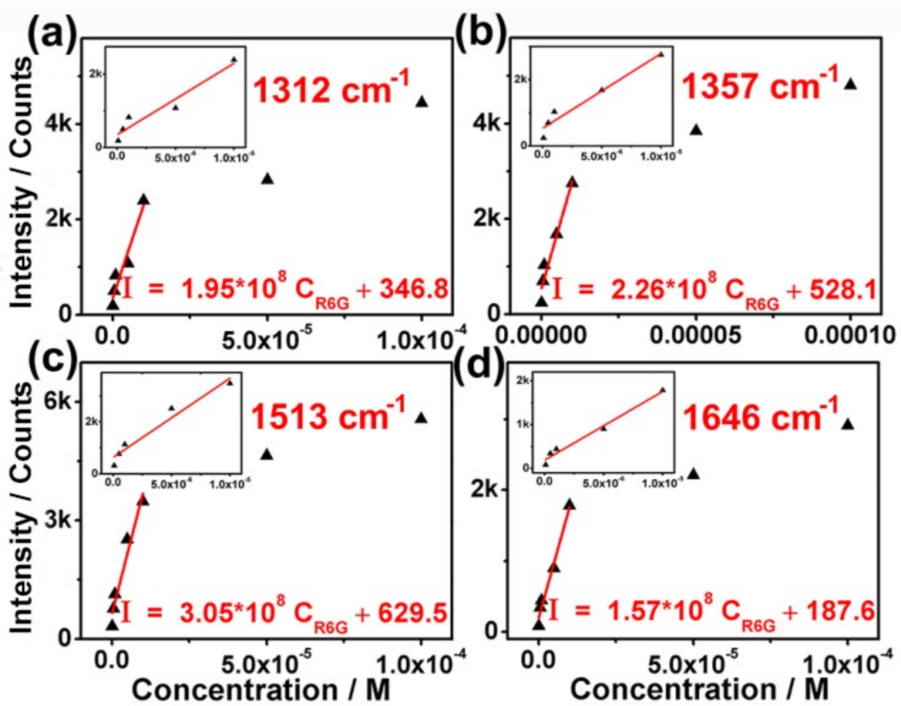

Figure S8. The work curves of Raman peak intensity and concentration of R6G at (a) 1312 cm^{-1}, (b) 1357 cm^{-1}, (c) 1513 cm^{-1}, and (d) 1646 cm^{-1} employing CoS/Au as the substrate.

Table S1. The correlation coefficient of fitting and standard deviation of SERS signals with the R6G concentration of 10^{-7}-10^{-5} M based on CoS_2/Au substrate.

Raman shift / cm^{-1}	1315	1365	1512	1654
R	0.97167	0.96177	0.94675	0.97511
SD	54.91721	95.39963	109.18789	37.98624

Table S2. The correlation coefficient of fitting and standard deviation of SERS signals with the R6G concentration of 10^{-7}-10^{-5} M based on CoS/Au substrate.

Raman shift / cm^{-1}	1312	1357	1513	1646
R	0.9673	0.97628	0.97633	0.98994
SD	24.89679	24.40512	32.90289	109.16683

Table S3. Comparison of the reaction rates in the degradation of R6G with peroxidase-like catalysts with previously reported catalysts.

Materials	Apparent rate constant, *k* / min^{-1}	Ref.
CoS_2/Au	0.215	This work
CoS/Au	0.239	This work
ZnO/UV	0.020	1
N-ZrO2/UVC	0.024	2
TiO2/methanol	0.009	3
Fe/titanates	0.261	4
LiFePO4	0.026	5
Fe/TiO2	0.106	6

References

1 K. Polychronopoulou, S. M. Aouadi, B. Sirota, D. S. Stone, L. Wang, P. Kohli, M. E. McCarroll, *J. Nanopar. Res.*, 2013, **16**, 2180.

2 H. Sudrajat, S. Babel, *Environ. Sci. Pollut. Res. Int.*, 2016, **23**, 10177-10188.

3 N. B. Bokhale, S. D. Bomble, R. R. Dalbhanjan, D. D. Mahale, S. P. Hinge, B. S. Banerjee, A. V. Mohod, P. R. Gogate, *Ultrason. Sonochem.*, 2014, **21**, 1797-1804.

4 Y. Z. Chen, N. Li, Y. Zhang, L. D. Zhang, *J. Colloid Interface Sci.*, 2014, **422**, 9-15.

5 Z. J. Li, G. Ali, H. J. Kim, S. H. Yoo, S. O. Cho, *Nanoscale Res. Lett.*, 2014, **9**, 276.

6 N. Demir, G. Gunduz, M. Dukkanci, *Environ. Sci. Pollut. Res.*, 2015, **22,** 3193-3201.