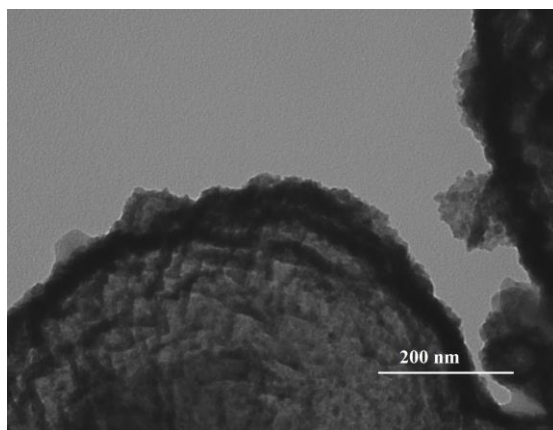


# A Green and General Strategy to Synthesize Ag/CdS Hollow Nanocomposites for Superior SERS Performance

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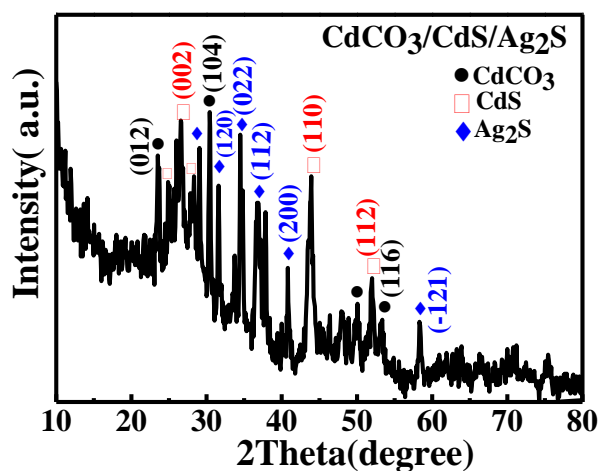
## Supporting Information



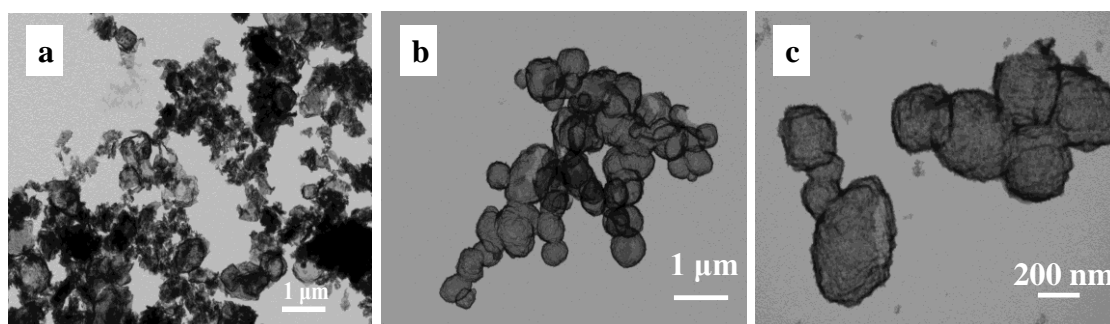
**Fig. S1** TEM image of CdS hollow nanosphere

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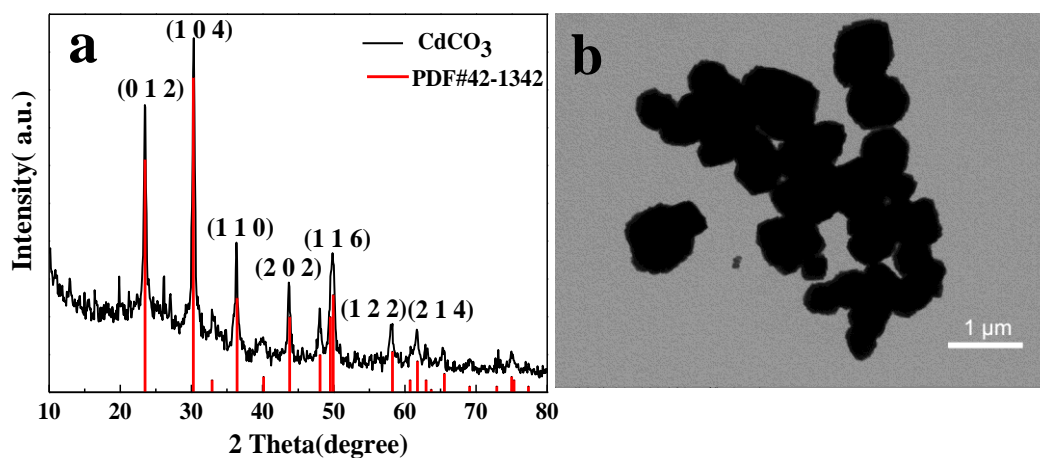
\* E-mail: songxy@sdu.edu.cn



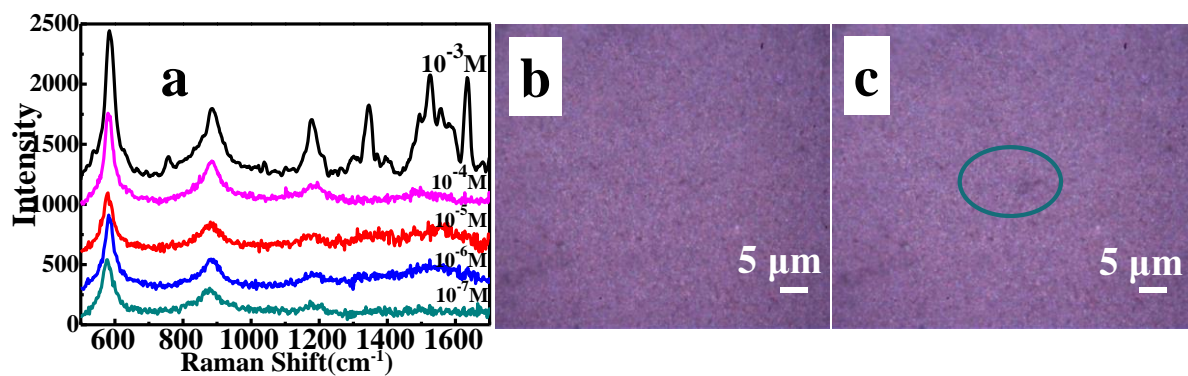
**Fig. S2** XRD patterns of CdCO<sub>3</sub>/CdS/Ag<sub>2</sub>S NCs at the sulfuration reaction time about 24 hours.



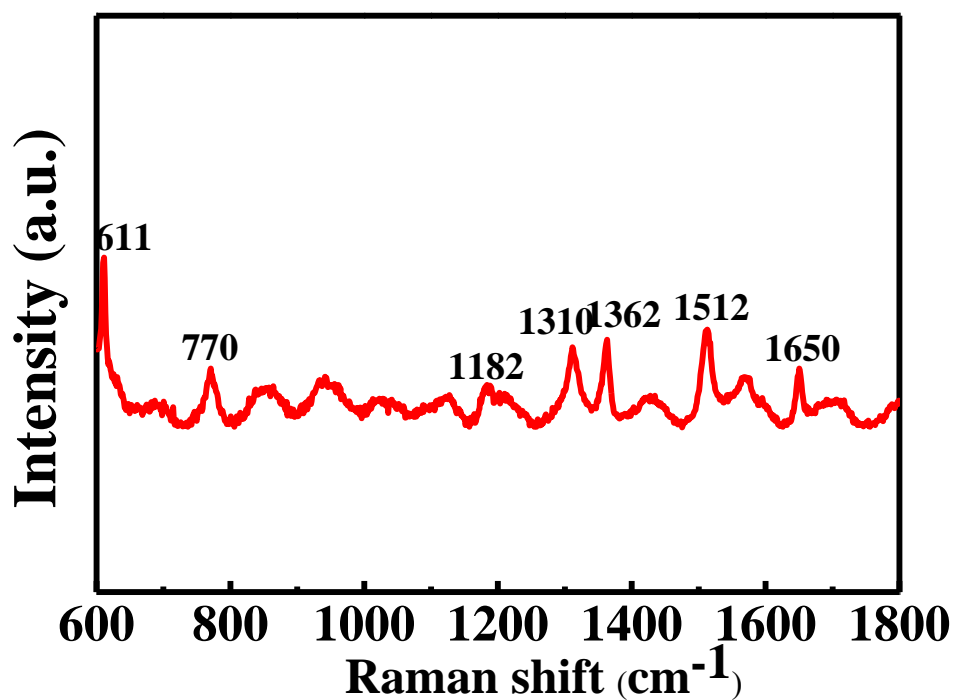
**Fig. S3** TEM images of CdS in different time of sulfur ion exchange: (a) 30 minutes, (b) 2 hours, (c) 24 hours.



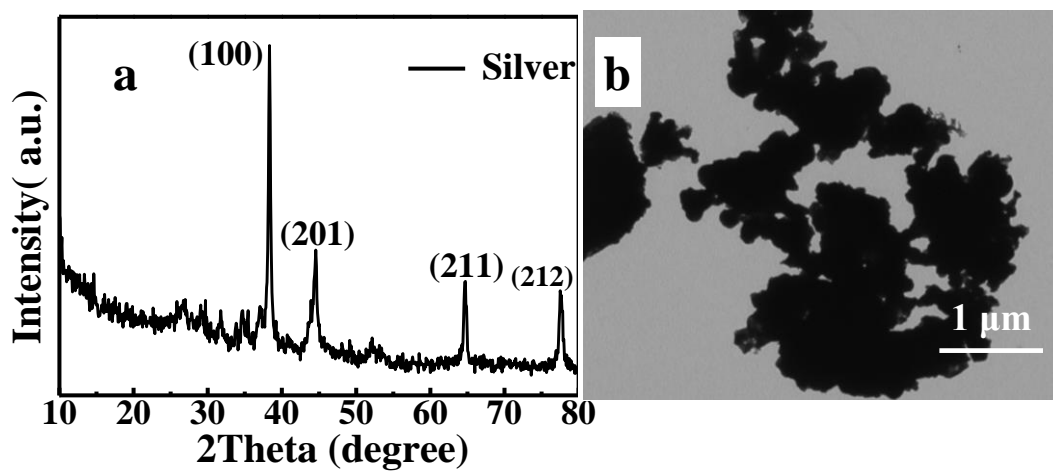
**Fig. S4** (a) XRD pattern of the sample after recycling, (b) TEM of the sample after recycling.



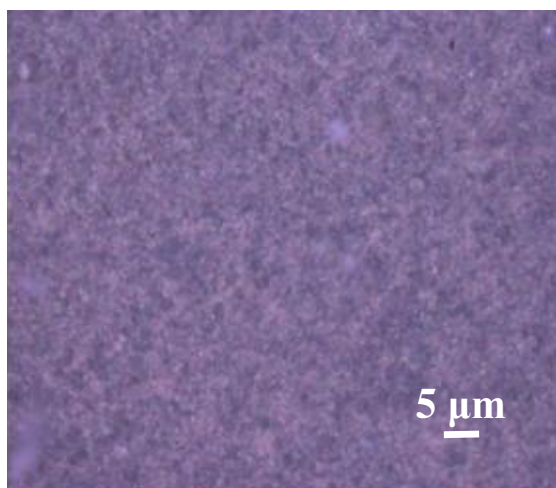
**Fig. S5** (a) Raman spectra of  $10^{-6}$  M R6G on the Ag/CdS NCs with the excitation laser line at 473 nm. (b) Raman image of R6G on the Ag/CdS NCs before excited at 473 nm (c) Raman image of R6G on the Ag/CdS NCs After excited at 473 nm



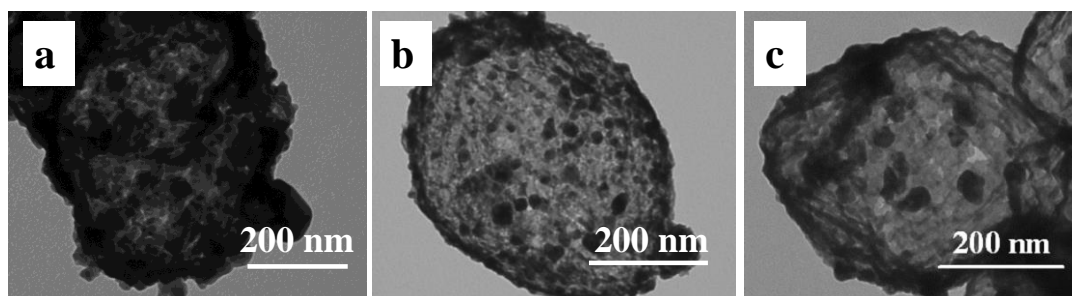
**Fig. S6** Raman spectrum of  $10^{-3}$  M R6G on Si substrate.



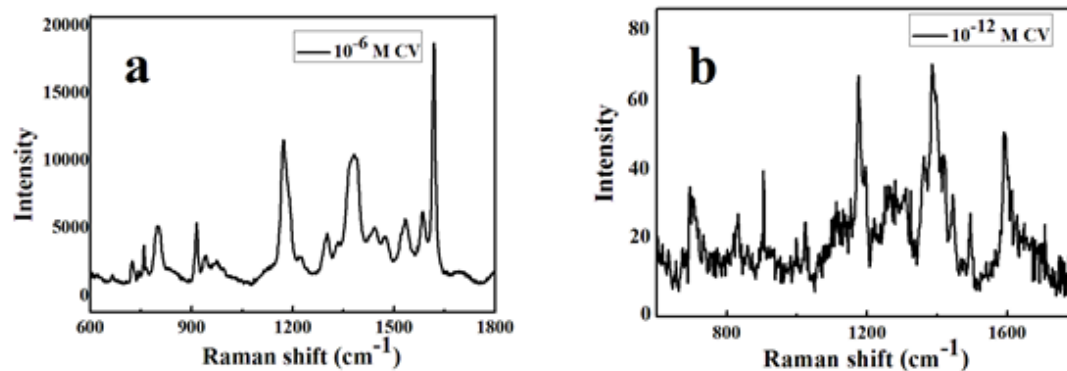
**Fig. S7** (a) XRD patterns of silver NPs. (b) TEM images of pure silver NPs prepared in present work.



**Fig. S8** Raman mapping image of the Ag/CdS NCs substrate.



**Fig. S9** TEM images of CdS/Ag NCs loaded with amount of silver at prepared Cd(Ac)<sub>2</sub> : AgNO<sub>3</sub> = 4:1, 6:1, 10:1, respectively.



**Fig S10** Raman spectrum of  $10^{-6}$  M and  $10^{-12}$  M CV on the Ag/CdS NCs substrate, respectively.

**Table S1** Enhancement factors (EFs) for some composite materials are reported in References

Material Probe	molecule	EF	LOD (mol/L)	Reference
Au–CdSe nanowires	CV	$10^4$	$10^{-5}$	1
Ag-NP-decorated ZnO nanoflower array	R6G	$10^7$	$10^{-10}$	2
Ag- ZnO thin film	R6G	$10^7$	$10^{-10}$	3
Ag-coated cellophane	CV	$10^5$	$10^{-9}$	4
AuNPs/WS <sub>2</sub> @AuNPs hybrids	R6G	$10^6$	$10^{-11}$	5
3D Ag butterfly wing scale arrays/graphene composites	CV	$10^6$	$10^{-8}$	6
<b>Ag/CdS NCs</b>	<b>R6G</b>	<b><math>10^7</math></b>	<b><math>10^{-12}</math></b>	<b>This work</b>

## References

1. G. Das, R. Chakraborty, A. Gopalakrishnan, D. Baranov, E. Di Fabrizio and R. Krahne, *J. Nanopart. Res.*, 2013, **15**, 1596.

2. Q. Tao, S. H. Li, C. Y. Ma, K. Liu, and Q. Y. Zhang, *Dalton Trans.*, 2015, **44**, 3447-3453.
3. N. D. Jayram, S. Sonia, S. Poongodi, P. S. Kumar, Y. Masuda, D. Mangalaraj, N. Ponpandian and C. Viswanathan, *Appl Surf Sci*, 2015, **355**, 969-977.
4. W. Wei and Q. Huang, *Spectrochim. Acta Part A*, 2018, **193**, 8-13.
5. Z. Lu, H. Si, Z. Li, J. Yu, Y. Liu, D. Feng, C. Zhang, W. Yang, B. Man and S. Jiang, *Opt Express*, 2018, **26**, 21626-21641.
6. M. Zhang, J. Meng, D. Wang, Q. Tang, T. Chen, S. Rong, J. Liu and Y. Wu, *J Mater Chem C*, 2018, **6**, 1933-1943.

**The details of Enhanced Factor Calculation are given as follows:**

$$EF = (I_{SERS}/I_{BULK}) \times (N_{BULK}/N_{SERS})$$

where  $I_{SERS}$  and  $I_{BULK}$  are the integrated intensities of R6G molecules adsorbed on Ag/CdS NCs and  $10^{-3}$  M of R6G bulk, respectively.  $N_{SERS}$  and  $N_{BULK}$  correspond to the number of R6G molecules adsorbed on the SERS substrate and in the bulk solution excited by the laser beam, respectively.

$N_{BULK}$  is calculated by the following formula:

$$N_{BULK} = \rho AhNA/M$$

where  $\rho$  correspond to the density of R6G molecules, A refer to the irradiation area under the laser beam (1  $\mu\text{m}$  in diameter), h is the focal depth of the laser (9.9  $\mu\text{m}$ ,  $h = (2\pi/633 \text{ nm}) \cdot (1 \mu\text{m})^2$ ).  $N_A$  is the Avogadro constant. M correspond to the molecule weight of R6G (479 g/mol)

$N_{SERS}$  is calculated by the following formula:

$$N_{SERS} = C_{SERS}VN_A/\pi r^2$$

where  $C_{SERS}$  correspond to the concentration of R6G molecules, V is the volume of one drop R6G molecules (20  $\mu\text{L}$ ), r is the diameter of the circle 20  $\mu\text{L}$  R6G solution spread and completely dried (4 mm).

### Details of LOD calculation are presented as follows:

A linear log plot of the corresponding Raman intensity at 1361  $\text{cm}^{-1}$  and R6G concentrations was established (see Fig.7c). The log-log plot of the Raman intensity  $I_{1361}$  and R6G concentrations  $C_{\text{R6G}}$  follows a linear relationship ( $R^2 = 0.99$ ),  $\log_{10}(I) = -0.234\log_{10}(C_{\text{R6G}}) + 4.759$ . And the error bars in the picture are standard deviations of 3 different positions for each sample. It is obviously observed that the linear equations and correlation coefficients indicate that there are high correlations between Raman intensities and concentrations of R6G. The limits of detection is calculated to  $10^{-13}$  M by the formula,<sup>1-2</sup>

$$\text{LOD} = \frac{3\sigma}{k}$$

Where  $\sigma$  means the standard deviation of several times detection for pure SERS substrate, and  $k$  represents the slope of the equation's linear fitting.

### Reference

1. J. Docherty, S. Mabbott, E. Smith, K. Faulds, C. Davidson, J. Reglinski and D. Graham, *Analyst*, 2016, **141**, 5857-5863.
2. K. H. Wang, M. Z. Huang, J. Chen, L.L Lin, L. L. Kong, X. Liu, *J. Raman Spectrosc.*, 2018, **49**, 493–498.