Supporting Information

for

Germanium-doped carbon dots as a new type of sensitive and selective fluorescent probe for visualizing the dynamic invasions of mercury (II) ions into cancer cells†

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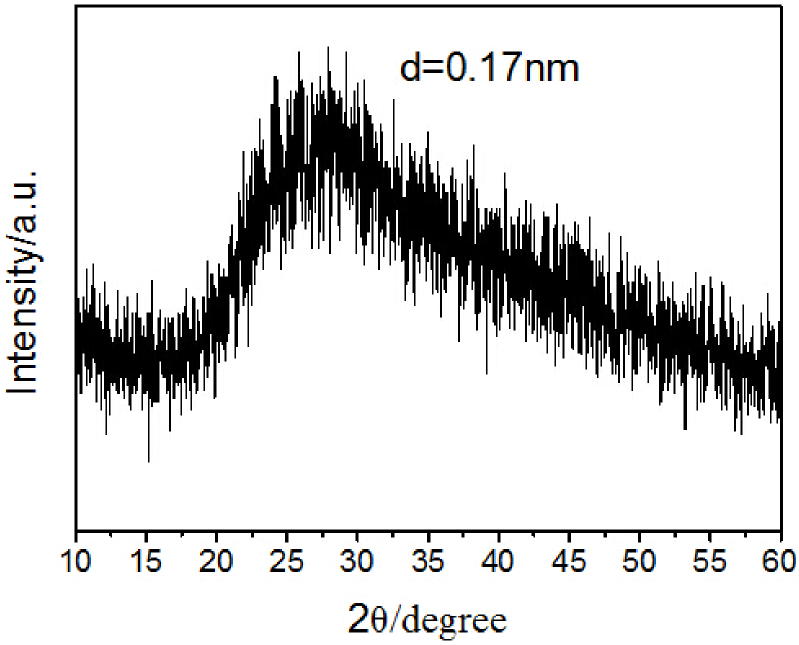

Fig.S1 The XRD of the product.

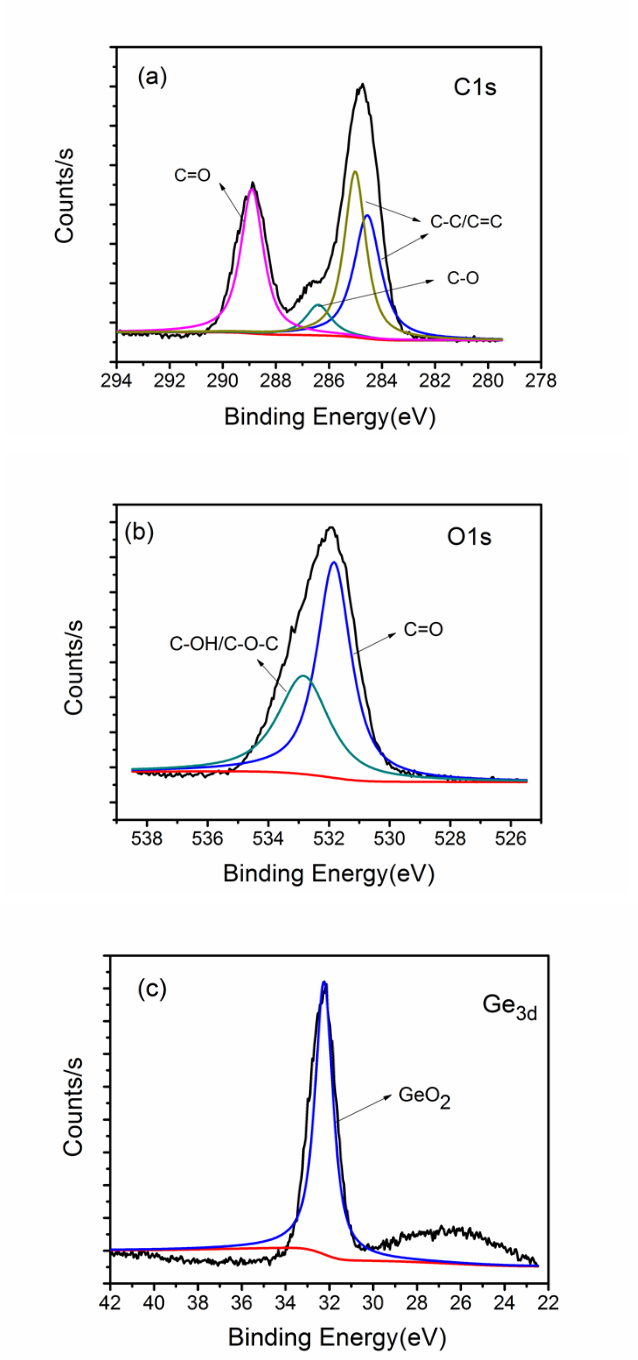

Fig.S2 The XPS spectra of (a) C1s, (b) O1s and (c) Ge3d in the product. The C1s spectrum shows four peaks at 284.6, 285.0, 286.4, and 288.9 eV, which are attributed to C-C/C=C, C-C/C=C, C-O and C=O, respectively (Fig. S2a, ESI†). The O 1s spectrum of the CDs displays two peaks at 531.8 eV and 532.8 eV, which can be assigned to C=O and C–OH/C–O–C groups, respectively (Fig. S2b, ESI†). It was found that a peak at 32.2 eV appeared (Fig. S2c, ESI†), which might be attributed to the Ge=O or Ge-O band[1].

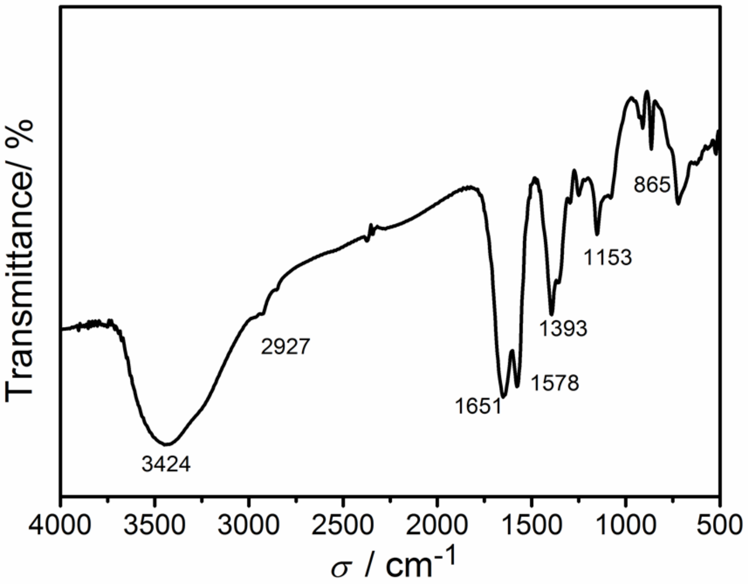

Fig.S3 The Fourier transformed infrared spectrum of the GeCDs.

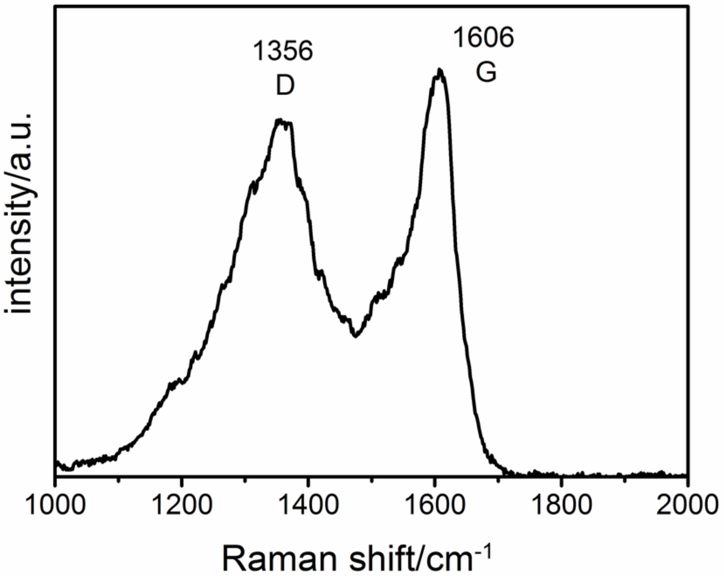

Fig.S4 The Raman spectrum of the GeCDs.

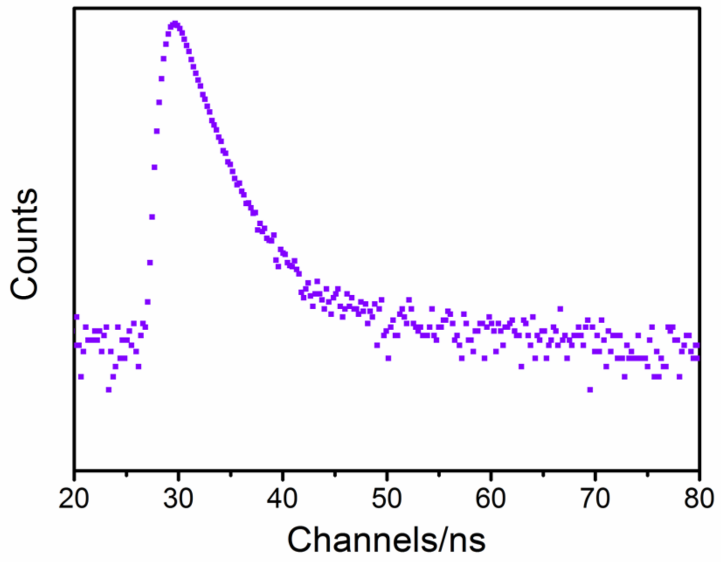

Fig.S5 Fluorescence decay of the CDs (370 nm excitation, delay time at 465 nm emission).

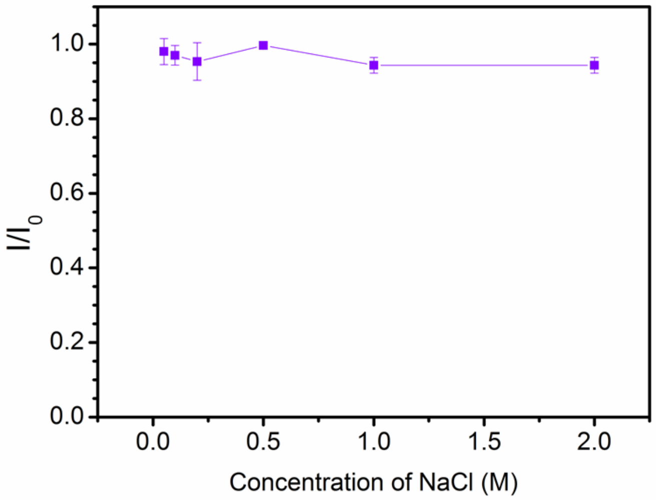

Fig.S6 The effect of the NaCl concentration (0, 0.05，0.1，0.2，0.5，1，2M) on CDs fluorescence.

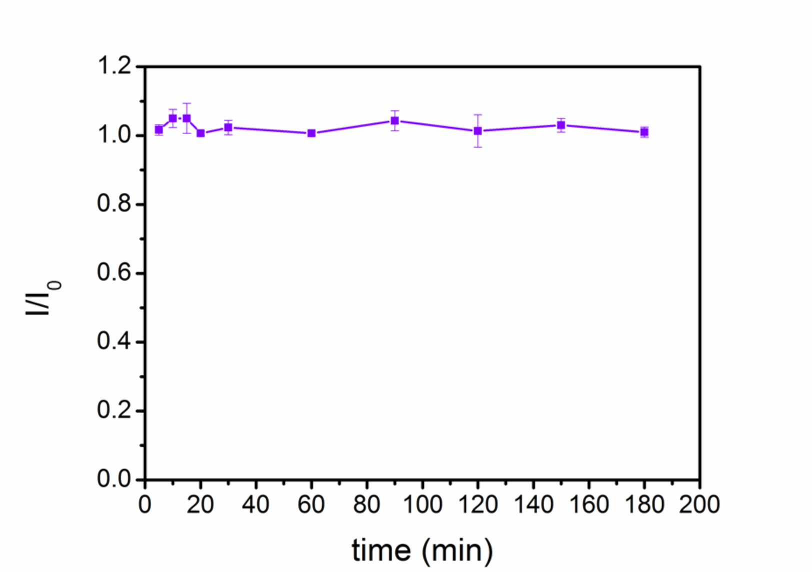

Fig.S7 The effect of UV light irradiation on CDs fluorescence (I_0 and I correspond to the fluorescence intensity of CDs at 465 nm in the absence and presence of irradiation, respectively).

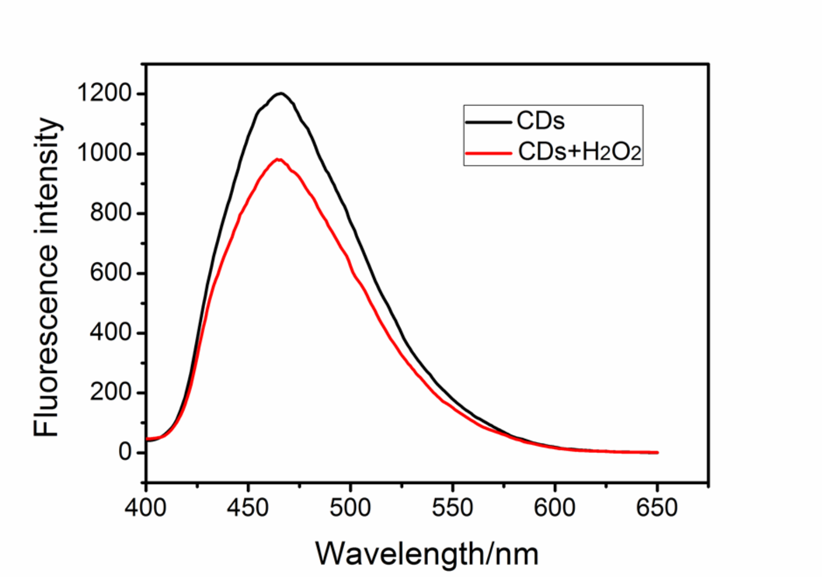

Fig.S8 The effect of the H_2O_2 on fluorescence intensity of CDs.

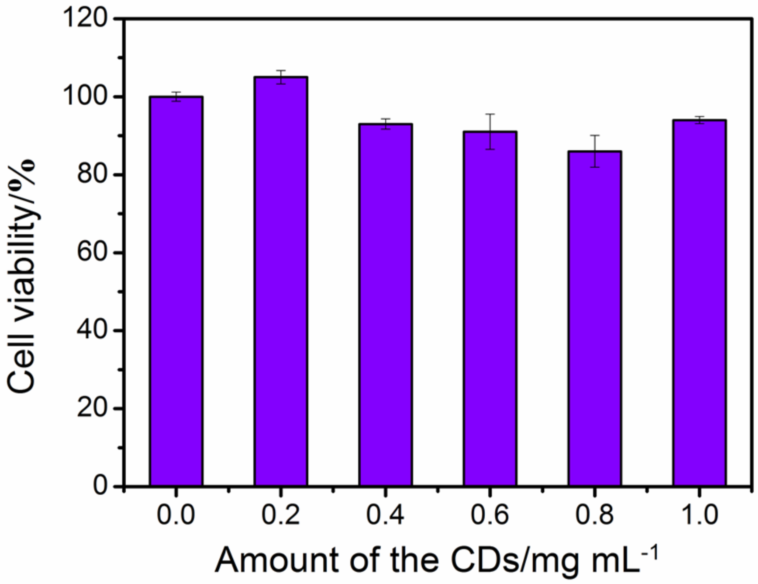

Fig.S9 Cell viability assays of the cells treated with different concentrations of the CDs.

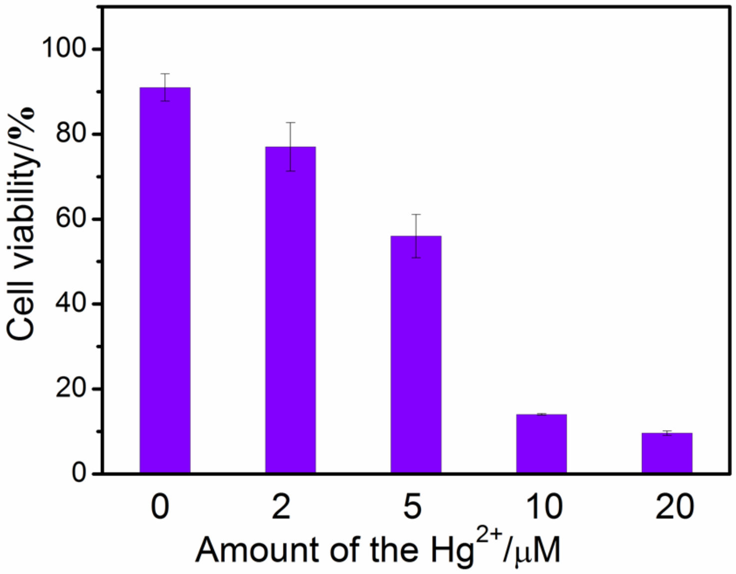

Fig.S10 Cell viability assays of the cells treated with different concentrations of the mercury (II) ions.

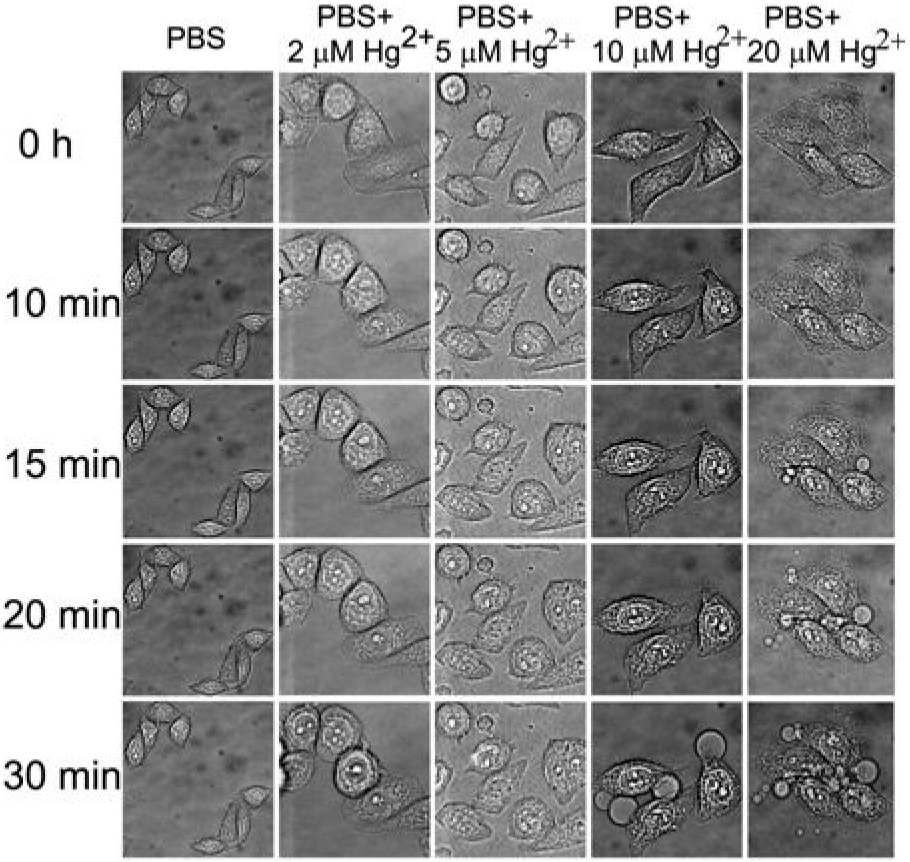

Fig.S11 Images of Hep-2 cells under the bright field. Bright field images of Hep-2 cells incubated with GeCDs for 12h. Then treated with PBS for 0, 10, 15, 20 and 30 min, PBS and 2 μM mercury ions for 0, 10, 15, 20 and 30min, PBS with 5 μM mercury ions for 0, 10, 15, 20 and 30 min, PBS with 10 μM mercury ions for 0, 10, 15, 20 and 30 min, and PBS with 20 μM mercury ions for 0, 10, 15, 20 and 30 min.

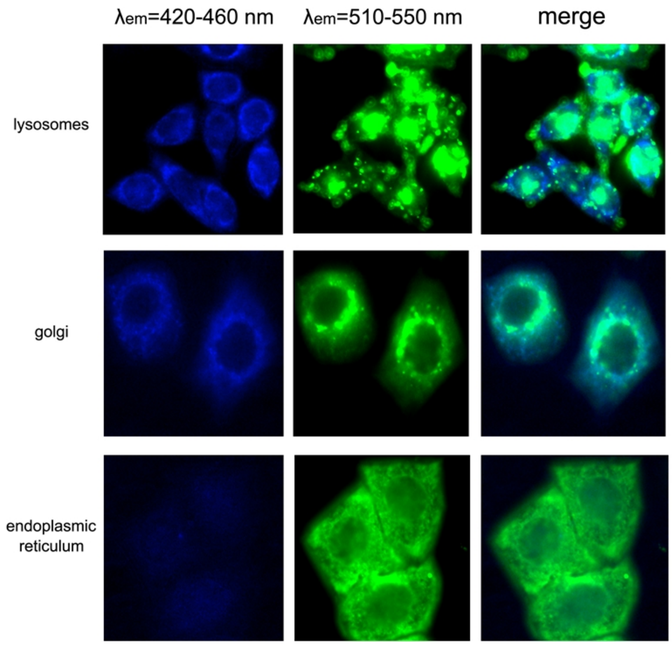

Fig.S12 The colocalization of the particles with lysosomes, golgi and endoplasmic reticulum.

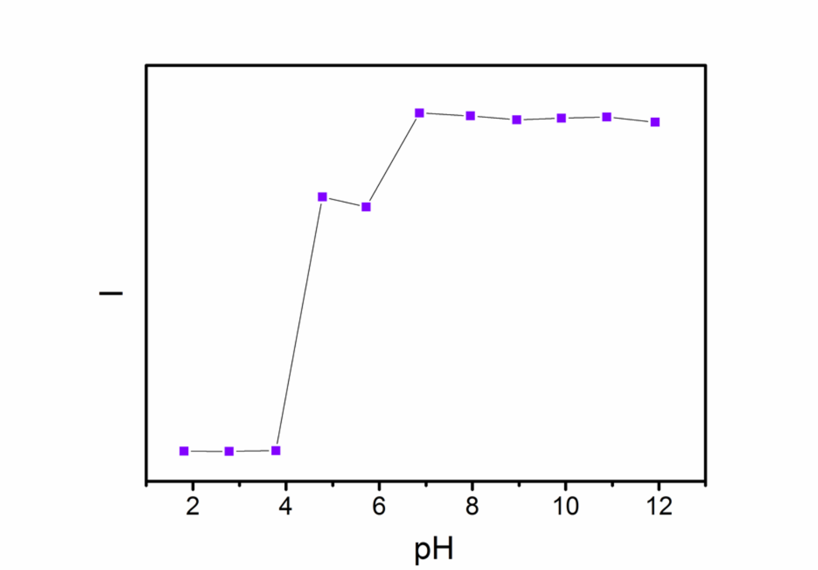

Fig.S13 The effect of the different pHs on CDs. When the pH was less than 4, the photoluminescence (PL) intensity was very low. With the increase of pH, the PL intensity of CDs was improved. When the pH was above 5, the PL intensity of CDs did not increase obviously. The results may be attributed to the protonation of the carboxyl groups in acidic solutions, which may lead to the aggregation of CDs, resulting in the fluorescence quenching[2]. Therefore, we selected pH 7.0 for the following experiments.

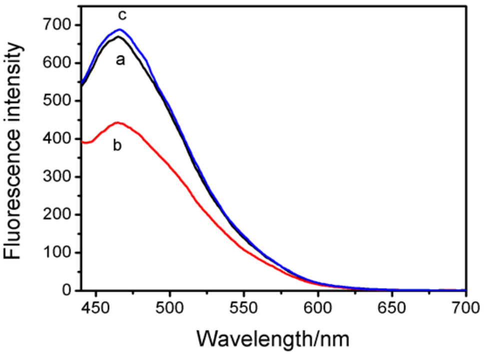

Fig.S14 FL spectra of solutions of CDs (curve a), CDs- Hg^{2+} mixture (curve b), and CDs- Hg^{2+} -cys mixture (curve c). It was noticeable that CDs solution shows a strong PL peak at 465 nm in the absence of Hg^{2+} (Fig. S14 , curve a, ESI†)，while the presence of Hg^{2+} leads to an obvious decrease of fluorescence in intensity, indicating that Hg^{2+} can effectively quench the fluorescence of CDs(Fig. S14 , curve b, ESI†). In addition，when adding Cys，a strong Hg^{2+} chelator，the PL almost restored to its original intensity(Fig. S14 , curve c, ESI†). The result indicates that Hg^{2+} is removed from the surface of CDs by forming the Hg-S bond with Cys.

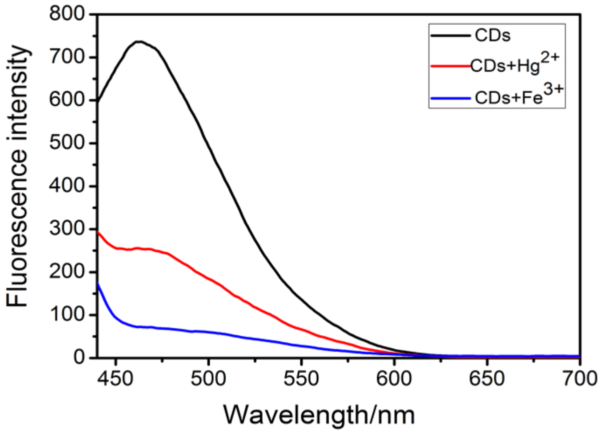

Fig.S15 FL spectra of solutions of CDs, CDs- Hg^{2+} mixture, and CDs- Fe^{3+} mixture (the CDs obtained from CA and succinic acid). The metal ions were detected by the material with the synthesis of CA and succinic acid in the same method mentioned above (The structure of Ge-132 is similar with the composition that two molecules of succinic acid off part the water). The result is that the fluorescence of the material can be quenched effectively by Fe^{3+} and Hg^{2+}, which indicates the germanium have an effect on the selectivity of the sensing system. It has been reported the log K_f of

$Hg(AcO)_2$ is the largest among those of metal ions(Ag^+,Cd^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+} and Pb^{2+}), so Hg^{2+} can interact more strongly with CDs than other metal ions[2], which might be another reason for the only Hg^{2+} can efficiently quench the fluorescence of the Ge-doped CQDs among the studied metal ions.

Table S1 Recovery rate of Hg^{2+} in honeysuckle dew samples.

Sample	Added Hg^{2+} (μM)	Found Hg^{2+} (μM)	RSD (n=3, %)	Recovery (%)
1	0.20	0.199	1.5	99.5
2	0.50	0.50	0.6	100.0
3	0.80	0.78	0.7	97.5
4	1.0	0.96	0.8	96.0
5	2.0	2.16	0.8	108.0

The concentrations of Ge influence the quantum yield (QY):

The specific procedure of CDs preparation, 0.2 g CA and 0.1 g Ge-132 were carbonized and the QY is 8.9%. 0.2g CA was separately reacted with 0.02 g or 0.05g Ge-132, the QY of the materials were 4.6% and 7.3%, respectively. And QY is 3.3%, if the materials prepared with only citric acid. That is to say, the doping of germanium element can modify the emission ability of CDs.

References

(1) Hollinger, G.; Kumurdjian, P.; Mackowski, J. M.; Pertosa, P.; Porte, L.; Duc, T. M. *J. Electron Spectrosc.* **1974**, *5*, 237-245.

(2) Guo, Y.; Wang, Z.; Shao, H.; Jiang, X. *Carbon* **2013**, *52*, 583-589.