

## **Electronic Supplementary Information**

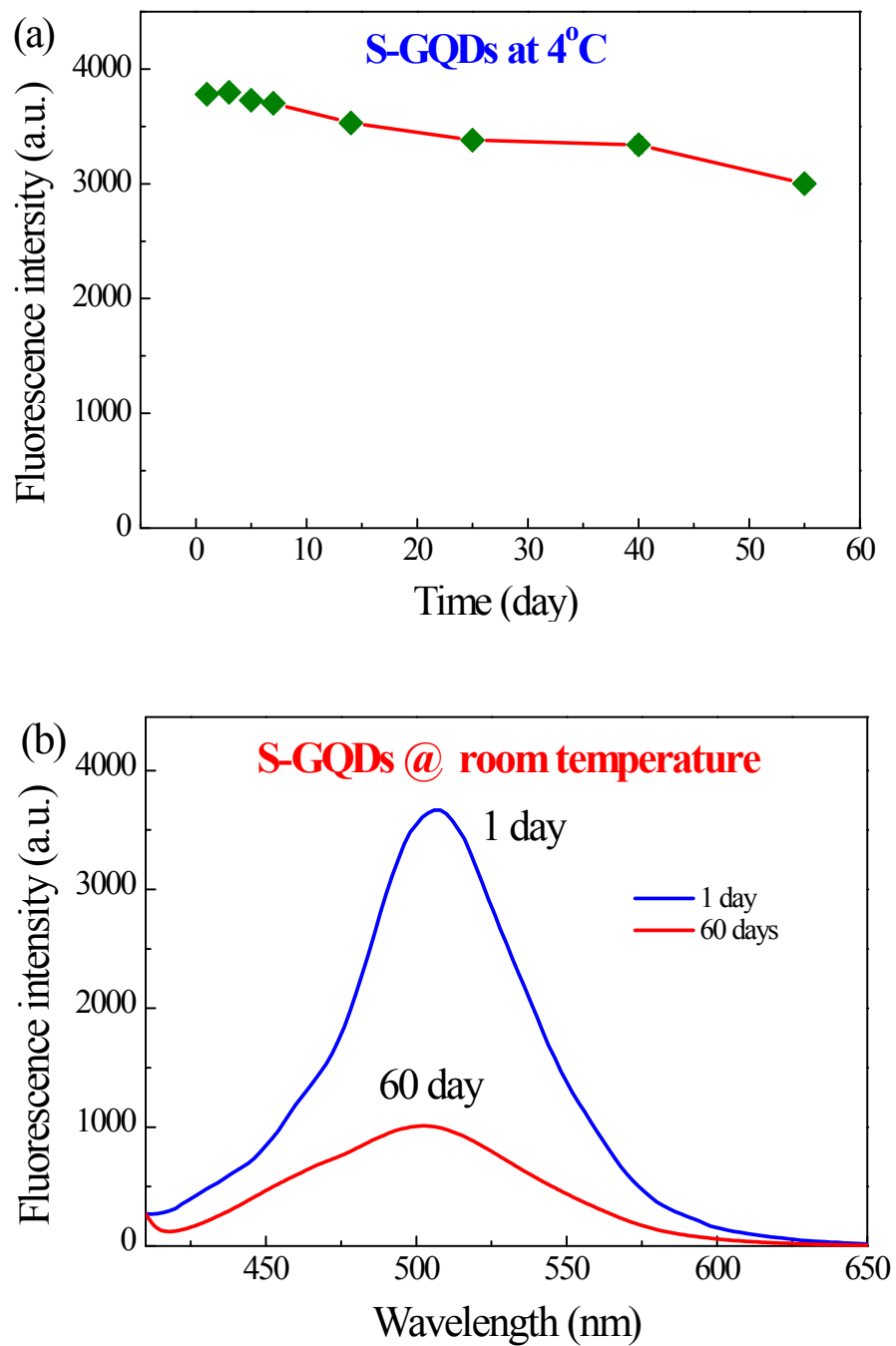
# **Sustainable Fabrication of Green Luminescent Sulfur-Doped Graphene Quantum Dots for Rapid Visual Detection of Hemoglobin**

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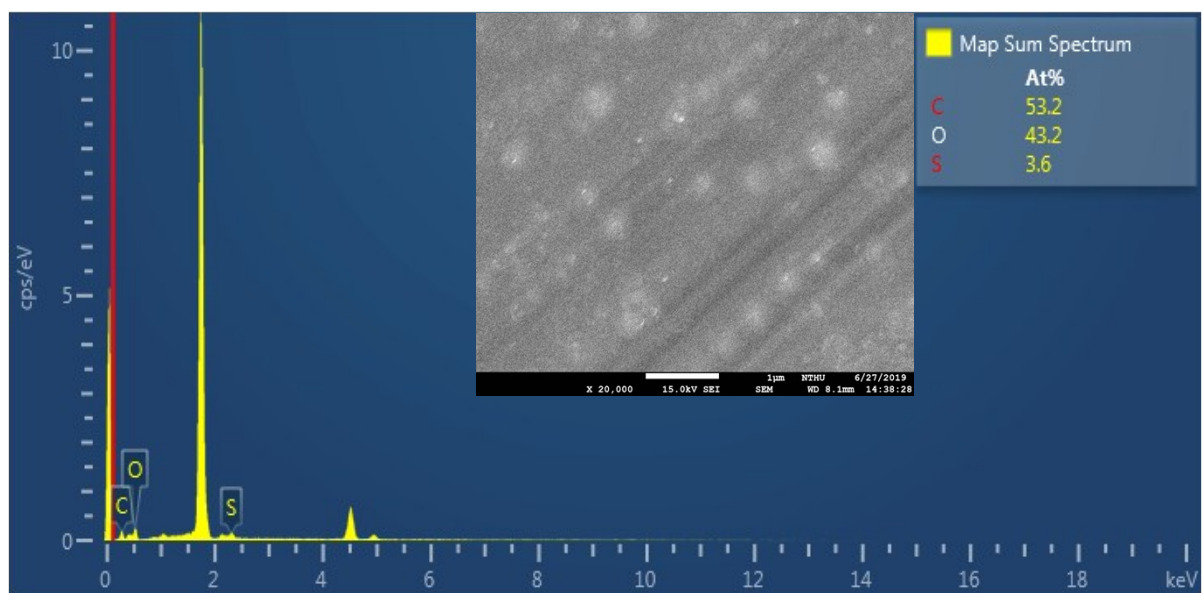
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**Fig. S1.** The stability of fluorescence intensity of as-prepared S-GQDs solutions in (a) 4 °C and (b) room temperature.

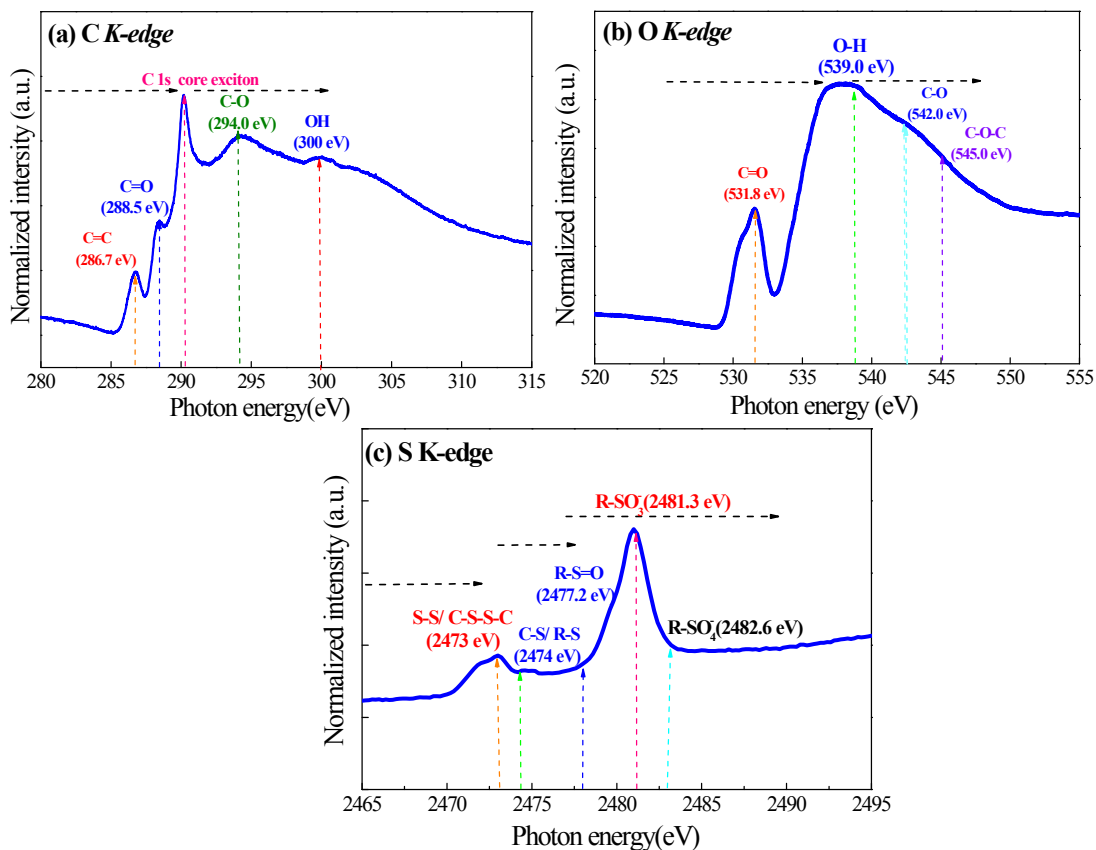


**Fig. S2.** Energy dispersive spectrum (EDS) of S-GQDs

## Results and Discussion on XAS and Raman spectra

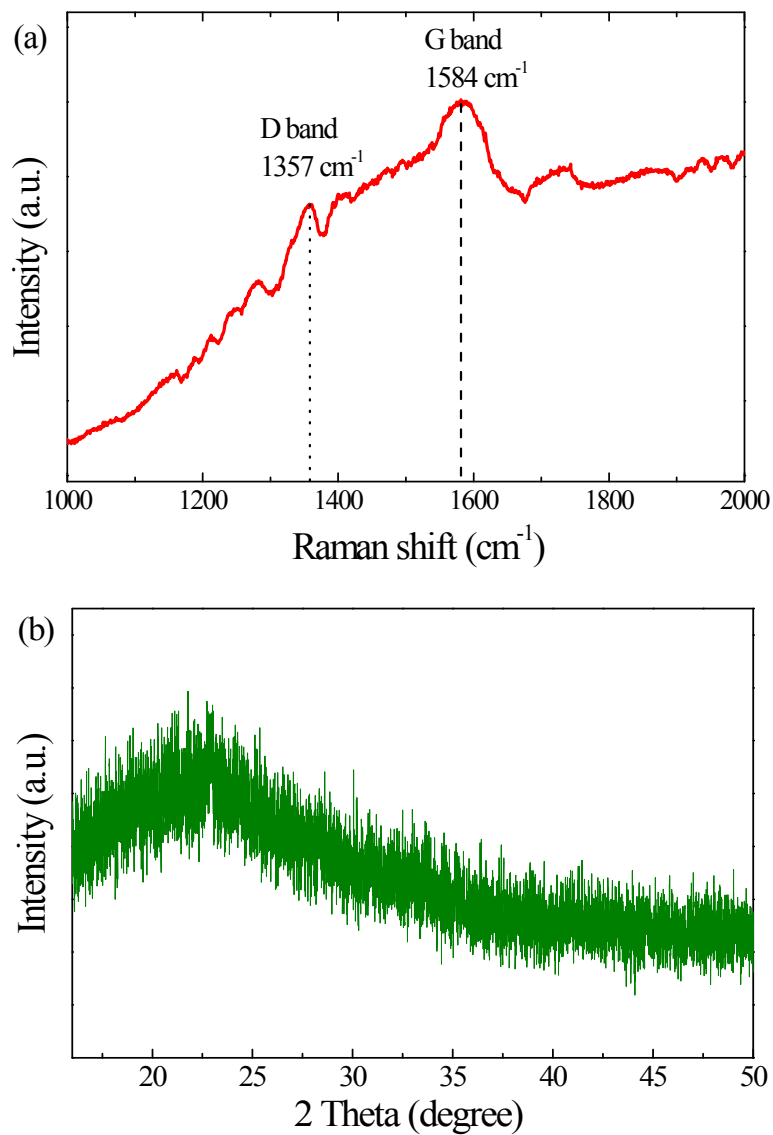
XANES was used to understand the local symmetry of elements in S-GQDs. As illustrated in Fig. S3a, the C K-edge spectra of S-GQDs shows a clearly sharp increase at 285.2 eV, which corresponds to the transition of C1s  $\rightarrow$   $\pi^*$ .<sup>1</sup> From the 286 to 290 eV region, the characteristic peaks of 286.7 and 288.5 eV are mainly attributed to the C1s  $\rightarrow$   $\pi^*$  transition of C=C and C=O bonds, respectively.<sup>2</sup> This indicates the fingerprint of sp<sup>2</sup>-hybridized carbon (graphitic) in GQD structures. The peak at 290.4 eV is the C 1s core exciton state due to the quantum confinement effect in S-GQDs. In addition, peaks at around 294.0 and 300 eV can be attributed to the  $\sigma^*$  excitation of C-O and OH functionalities, respectively.<sup>3</sup>

Similarly, the O K-edge spectrum was recorded in the 520 – 555 eV region (Fig. S3b). Two main absorption features located at 531.8 and 539–546 eV are clearly observed. The peak of around 531.8 eV is the O1s  $\rightarrow$   $\pi^*$  transition of C=O originated from the COOH group. Furthermore, the broad peaks in the region of 539 – 546 eV can be assigned to the O 1s  $\rightarrow$   $\sigma^*$  transitions of O-H (539.0 eV), C-O (542 eV), and C-O-C (545 eV) groups,<sup>4, 5</sup> which are consistent with the results of XPS and FTIR obtained in this study. Moreover, the S K-edge XANES spectra was measured in the energy range of 2465 – 2495 eV, which illustrates various oxidation states of sulfur from -2 to +6 on S-GQDs structure (Fig. S3c). The peak at 2473 eV represents the transition from S1s to the S-S  $\pi^*$  states of S<sub>8</sub> and C-S-S-C (S 1s  $\rightarrow$   $\pi^*$  transition), while the peak centered at 2473.7 eV is the S1s to the C-S  $\sigma^*$  excitation (S 1s  $\rightarrow$   $\sigma^*$ )<sup>6</sup>. On the other hand, the feature peaks at 2477.2, 2481.3, and 2482.6 eV are the transition from S 1s to the  $\sigma^*$  state of S-O in R-SO<sub>2</sub><sup>-</sup>, R-SO<sub>3</sub><sup>-</sup>, and R-SO<sub>4</sub><sup>-</sup> groups, respectively,<sup>7, 8</sup> clearly demonstrating the successful doping of S atoms to the GQD structures.



**Fig. S3** The (a) C K-edge, (b) O K-edge, and (c) S K-edge XANES spectra of S-GQDs.

The Raman spectrum was further used to confirm the carbon structures of S-GQDs (Fig. S4a). Two characteristic peaks appear at 1375 and 1583  $\text{cm}^{-1}$ , respectively, which signifies to the presence of  $\text{sp}^3$  defects (D bands) and the in-plane vibration of  $\text{sp}^2$  carbon (G band).<sup>9</sup> The ratio of  $I_D/I_G$  is calculated to be 0.88, depicting the crystalline and graphitic nature of S-GQDs.<sup>10</sup> Moreover, the XRD pattern illustrates a broad peak at  $23.33^\circ 2\theta$ , which corresponds to the (002) plane of graphene with several layers,<sup>11</sup> clearly indicating the formation of graphene-based nanostructures for sensing purposes, as in shown Fig. S4b.



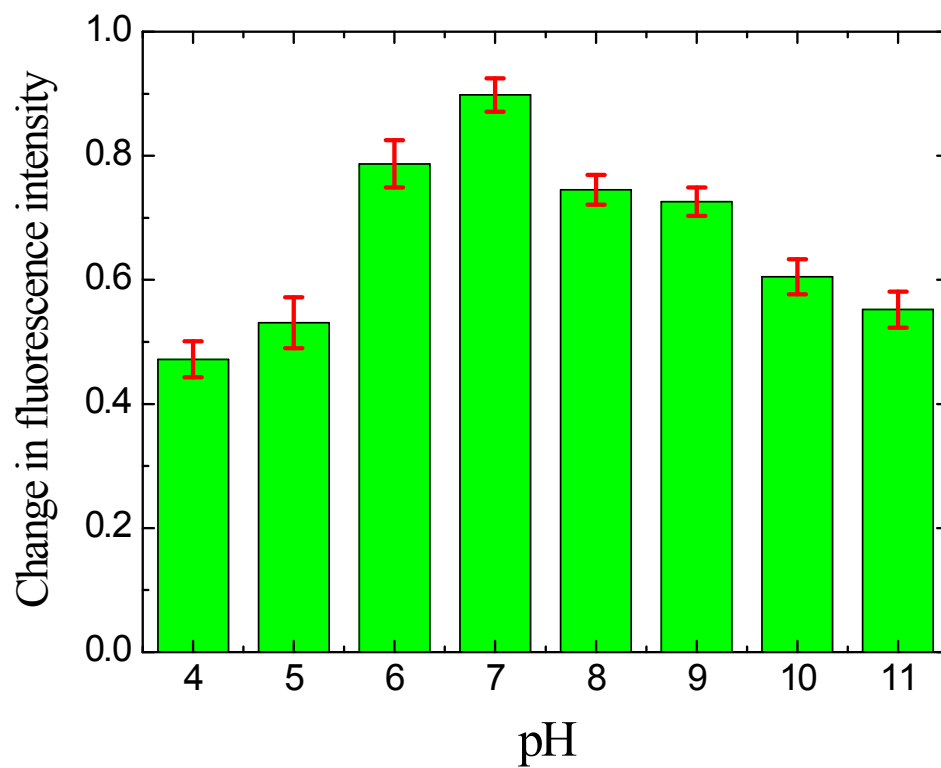
**Fig. S4** (a) The Raman spectrum and (b) XRD pattern of the S-GQDs.

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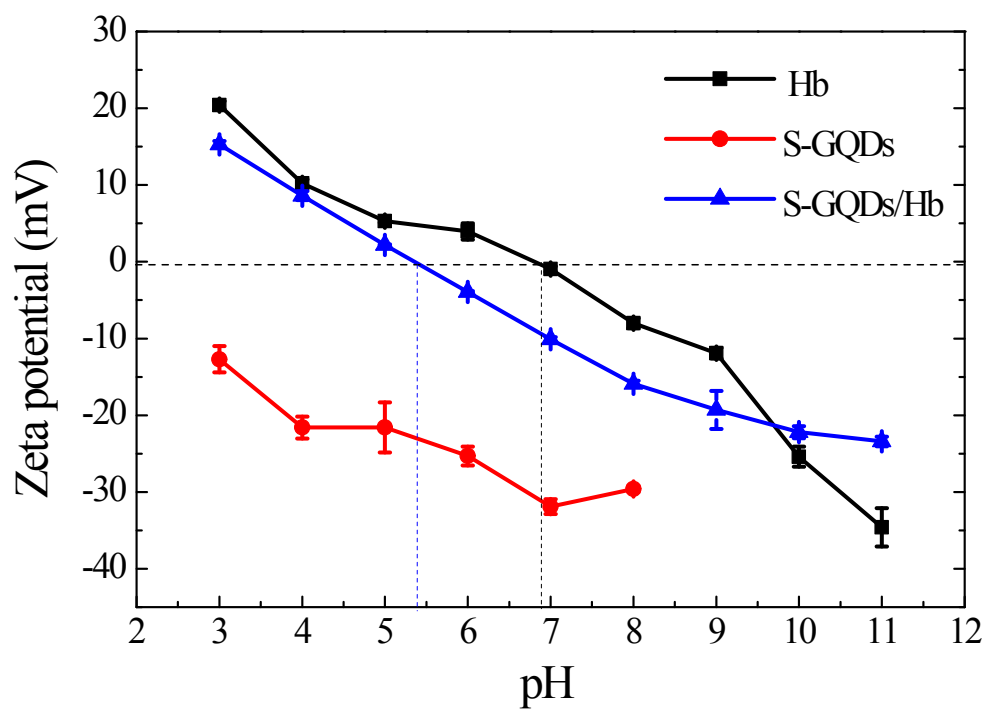
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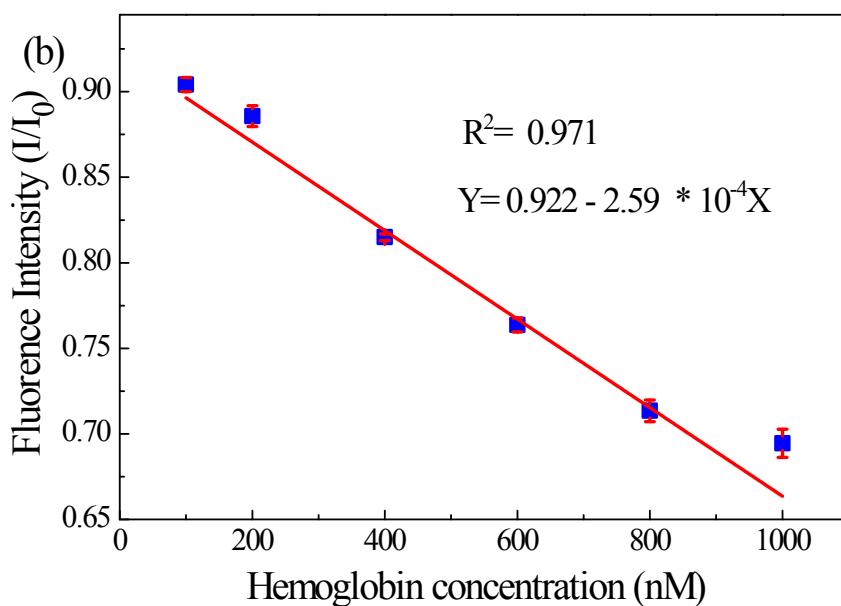
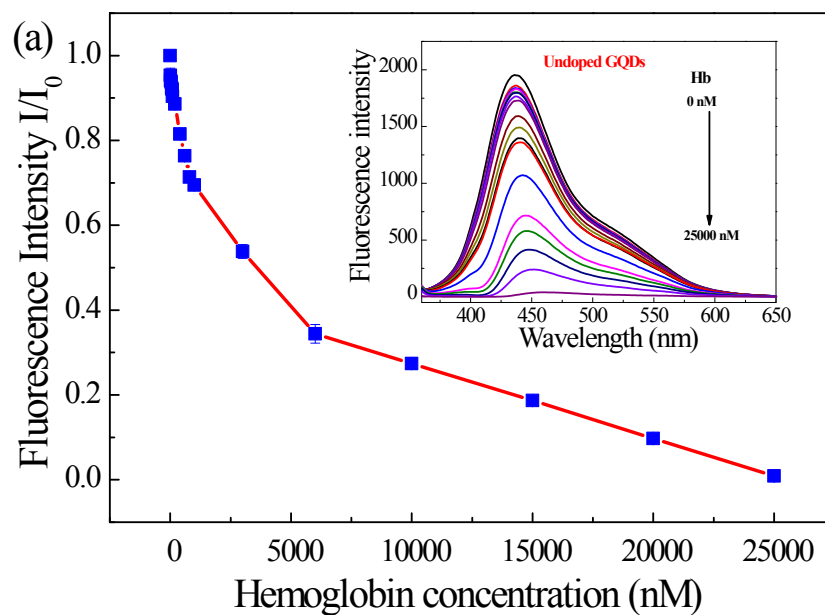


**Fig. S5.** The change in fluorescence intensity as a function of pH ranging from 4 to 11.





**Fig. S6.** The zeta-potential of Hb, S-GQDs, and S-GQDs/Hb complex as a functional of pH value ranging from 3 to 11.



**Fig. S7.** (a) The change in fluorescence intensity of undoped GQDs after addition of 0 – 25000 nM Hb, and (b) linear relationship between fluorescence intensity and Hb concentration ranging from 100 to 800 nM. The inset in Fig. S7a is the fluorescence spectra of undoped GQDs at various concentrations of Hb after the excitation of 360-nm UV wavelength.