Electronic Supplementary Material

Double protein directed synthesis of chemically etched sulfur doped quantum dots for signal "on-off-on" sensing of glutathione mediated by copper ion

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Instrumentation

Excitation and emission spectra were measured on Shimadzu RF-5301 PC fluorometer with slit width of 3 nm and 1 cm quartz cuvette. Transmission Electron Microscope (TEM) was used to investigate the morphology of SQ-dots (JEOL JEM-100CX II-unit). FT-IR measurements were carried out on Nicolet™ iS™10 spectrometer. Elemental analysis (EDX) was used to show the elemental composition of SQ-dots using NEX QC+ QuantEZ. The X-ray diffraction spectrometer (XRD) PW 1710 was used to investigate the peak diffraction. Raman spectra were taken on Micro-Raman spectrometer (U.K.). Dynamic light scattering measurements (DLS) were carried out using Zetasizer Red badge instrument of ZEN 3600 Nano ZS model (Malvern, UK). X-ray photoelectron spectrometer (XPS, ESCA Ulvac-PHI 1600, PHI Quantum 2000 XPS system, Physical Electronics, USA) was used to reveal the surface functional groups of SQ-dots.

Calculation of quantum yield (QY)

The QY of the fluorescent SQ-dots was determined by a relative slope method. Quinine sulfate (QY=54% in 0.1 M H_2SO_4) was selected as a standard for the prepared SQ-dots. The aqueous solution of SQ-dots and quinine sulfate ware diluted to keep the absorption intensity below 0.1 at the best excitation wavelength of 360. The QY of the prepared SQ-dots was calculated according to the following equation:

$$\varphi_x = \varphi_{st} (K_x/K_{st}) (\eta_x/\eta_{st})^2$$

Where φ is the quantum yield, K is the slope of the fitted line, and η is the refractive index of the solvent. The subscript "x" refers to the testing sample, and "st" refers to the standards. The value of the refractive index is 1.33 for water.

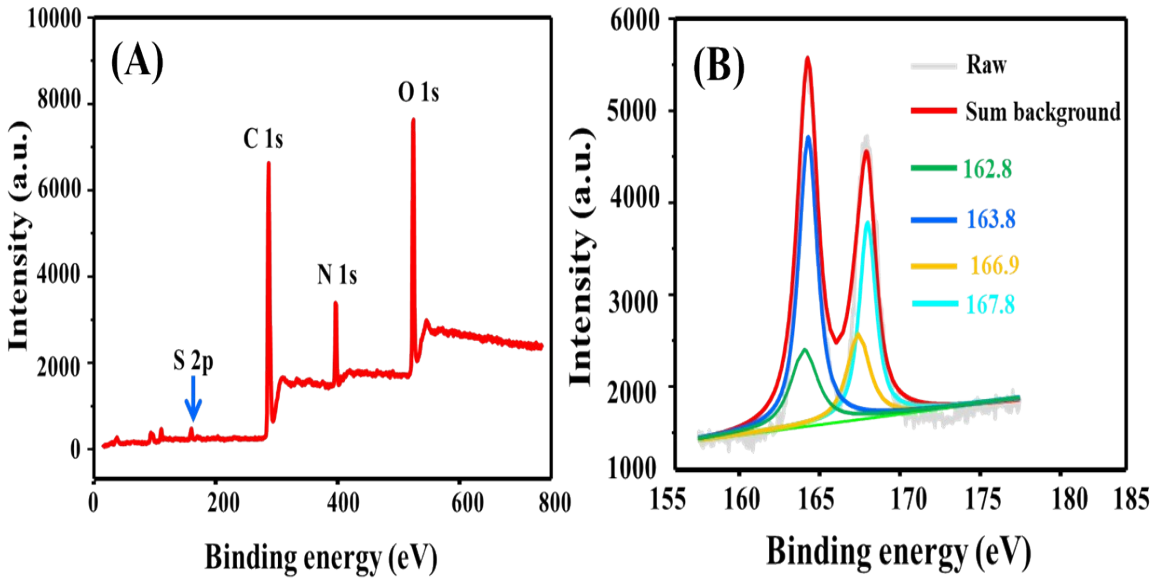

Fig.S1 The XPS survey (A) and HR-XPS of S 2p of SQ-dots.

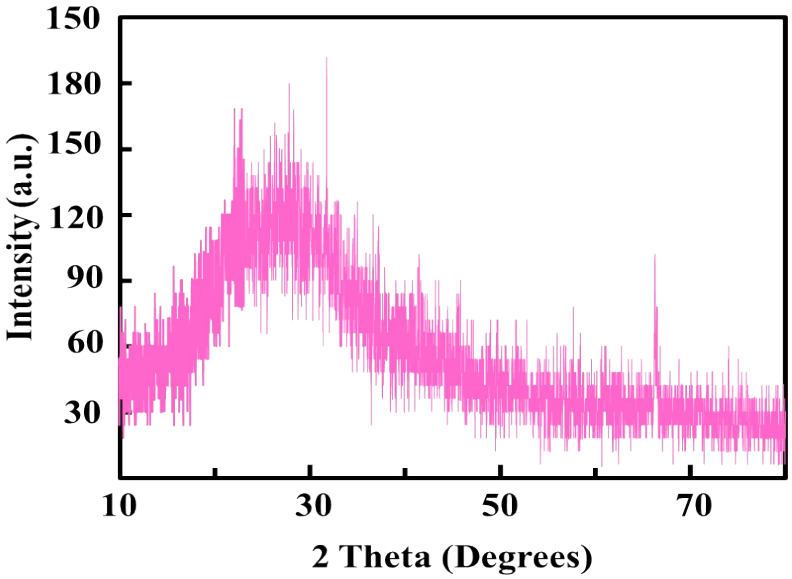

Fig.S2 The XRD of SQ-dots.

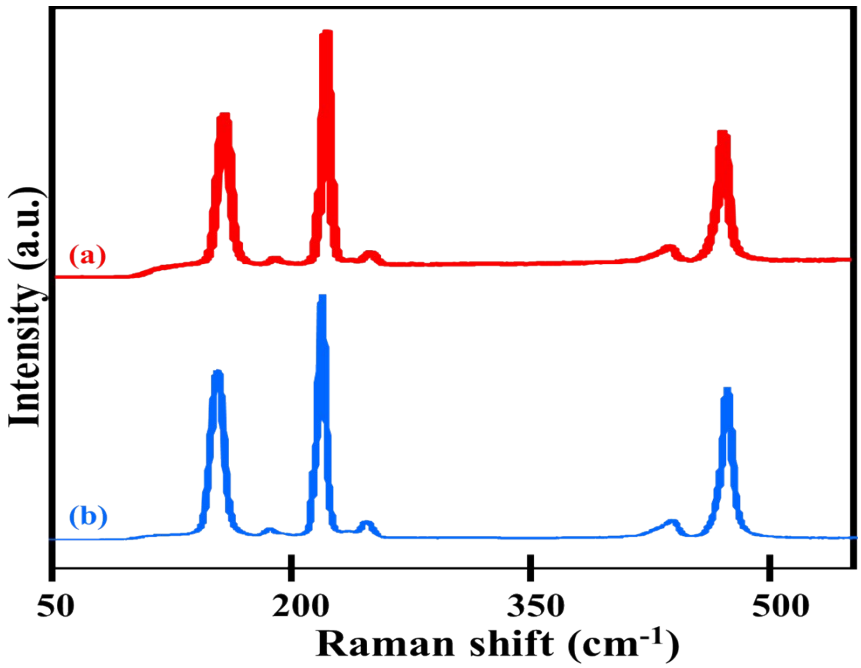

Fig.S3 Raman spectra of (a) elemental sulfur and (b) SQ-dots.

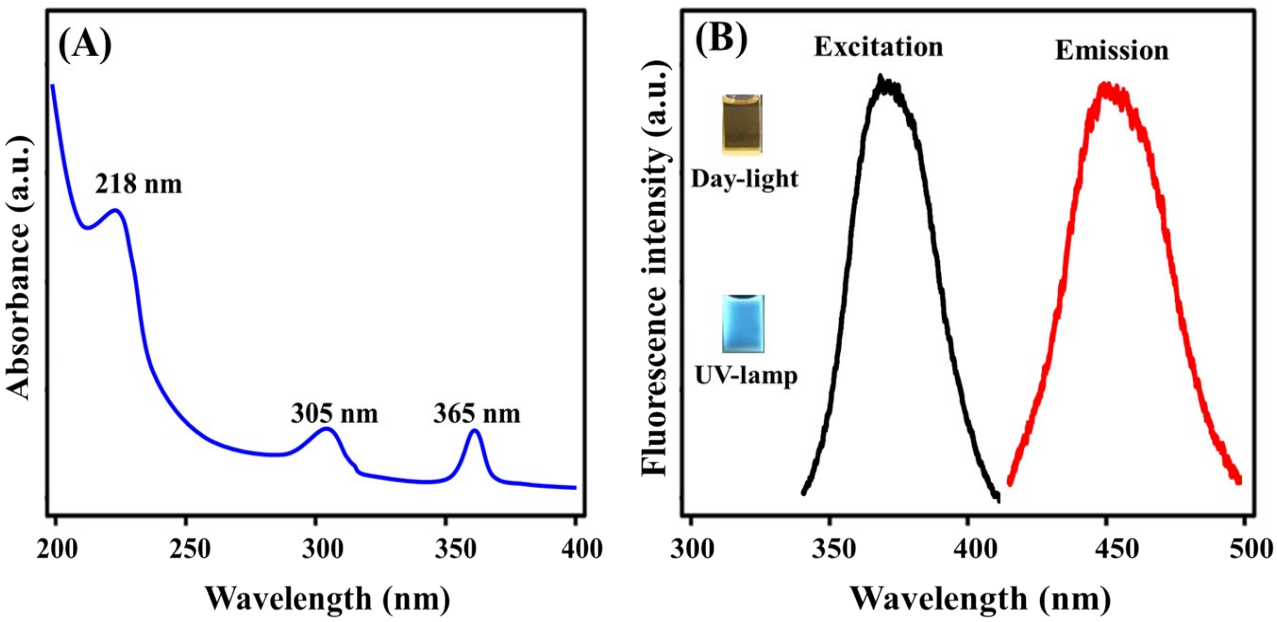

Fig.S4 (A) UV/VIS absorption spectra and (B) fluorescence spectra of the as-prepared SQ-dots.

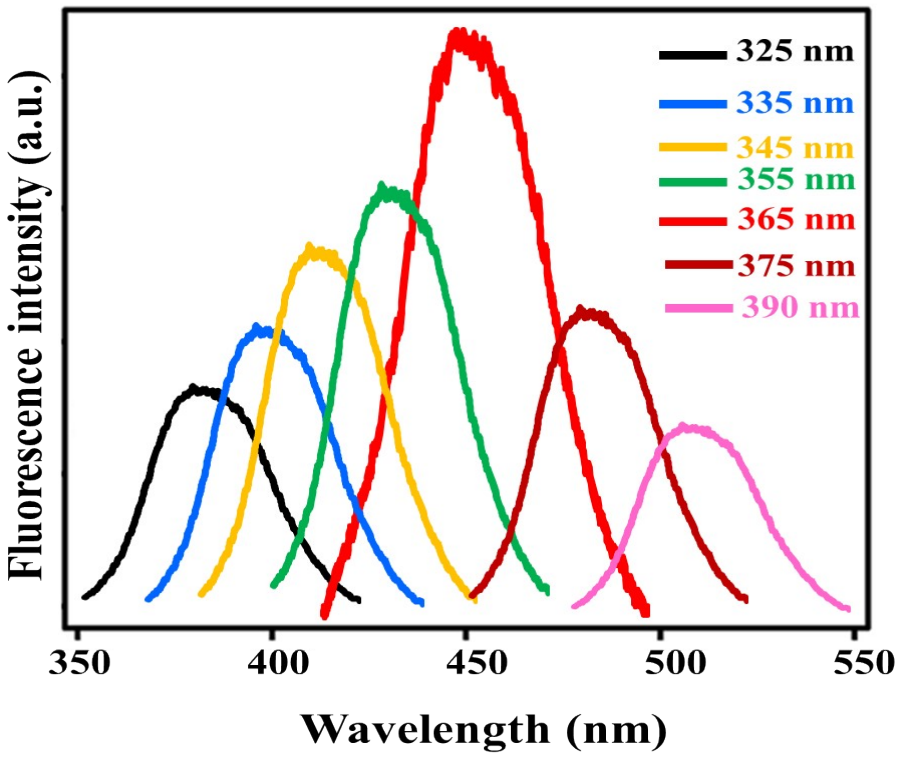

Fig.S5 Dependency of the emission wavelengths on the excitation wavelengths.

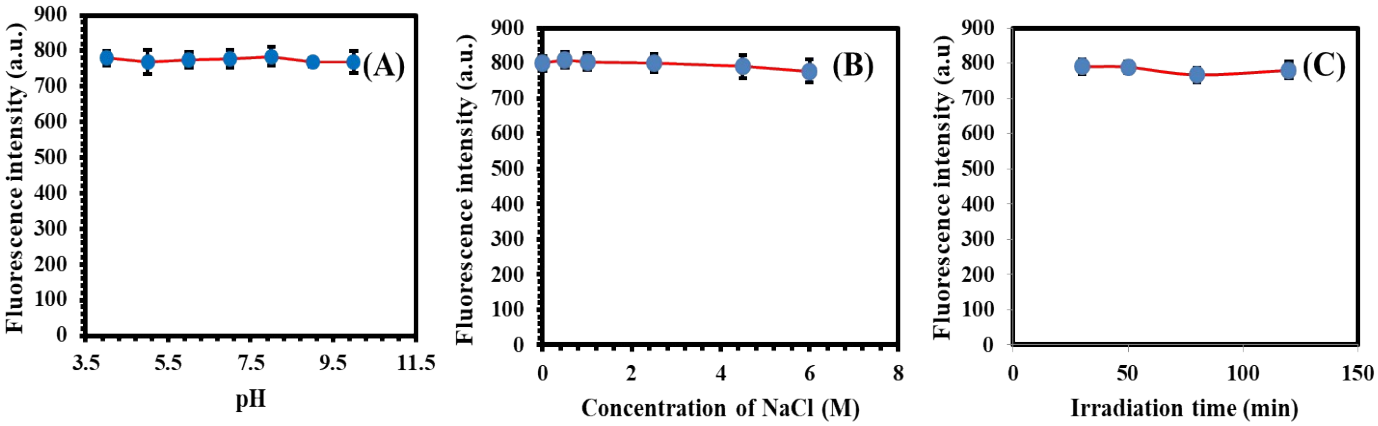

Fig.S6 Influence of different pH values, ionic strengths, and irradiation times on the stability of SQ-dots.

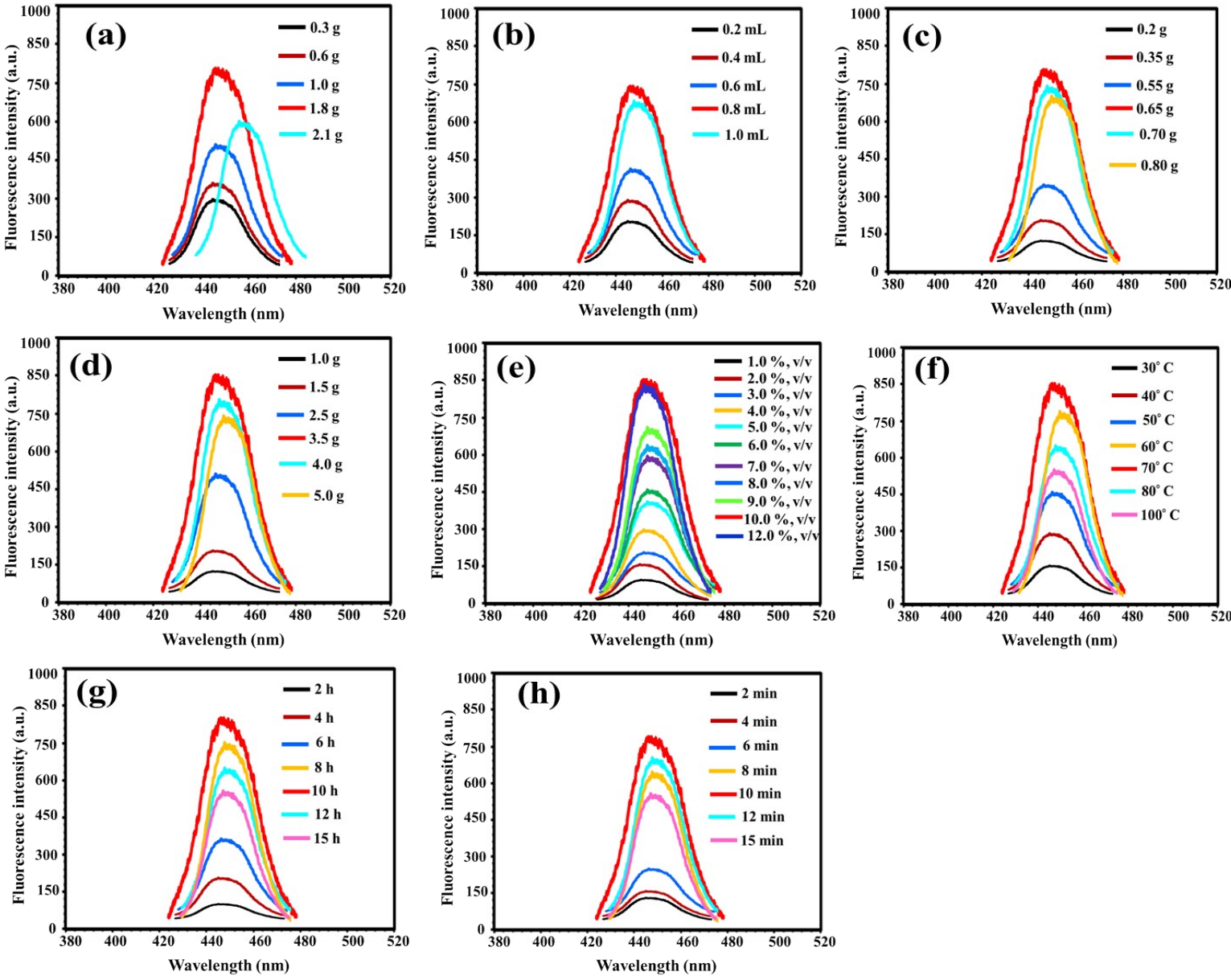

Fig.S7 The influence of amount of elemental sulfur, volume of egg white, amounts of bovine serum albumin (BSA), amount of sodium hydroxide (NaOH), reaction temperature, synthesis time, concentration of H_2O_2, and itching time on the fluorescence intensity of SQ-dots.

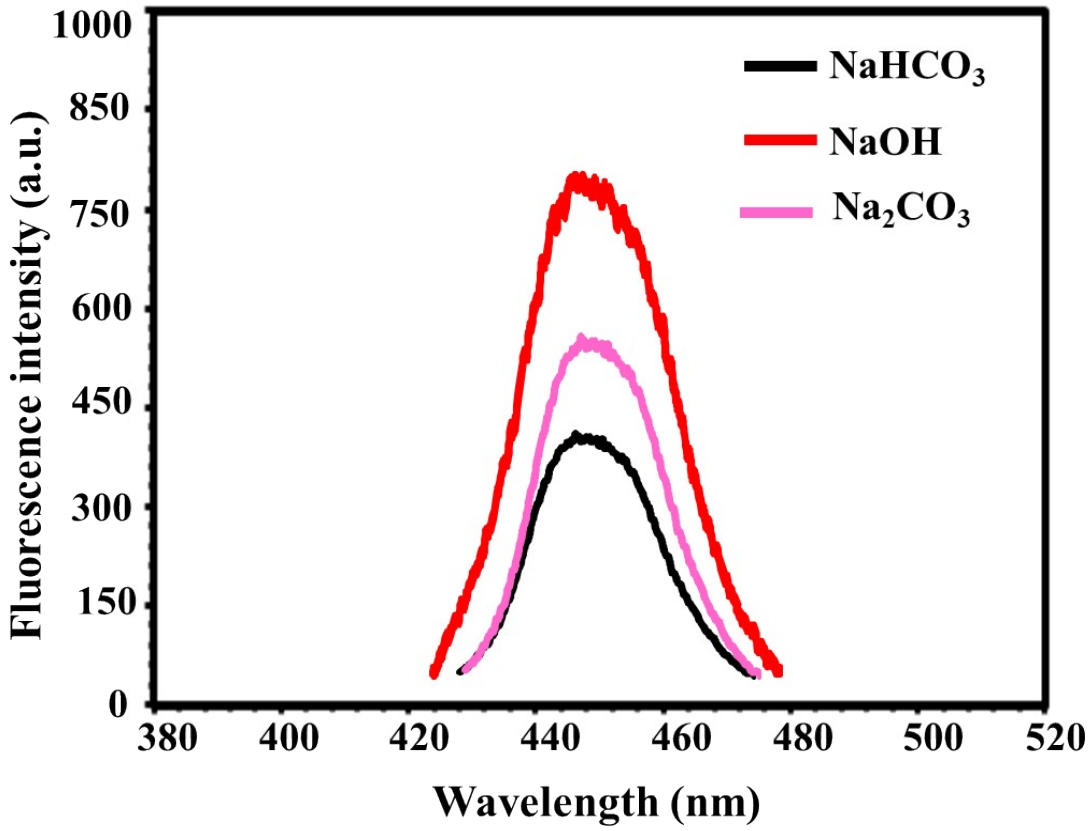

Fig.S8 The influence of different alkalis (3.5 g for each) on the fluorescence intensity of SQ-dots.

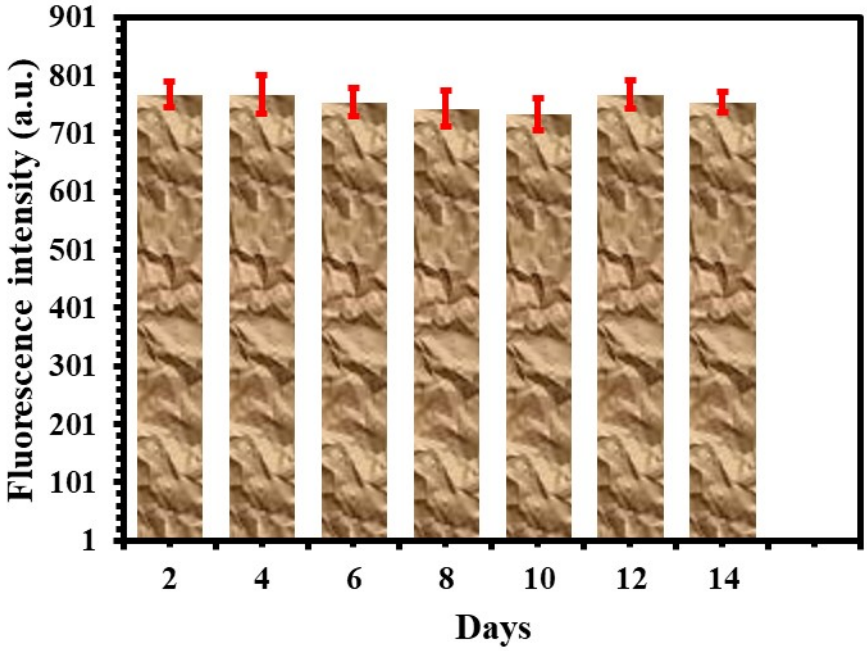

Fig.S9 The fluorescence intensity of SQ-dots incubated at 4°C for 14 days.

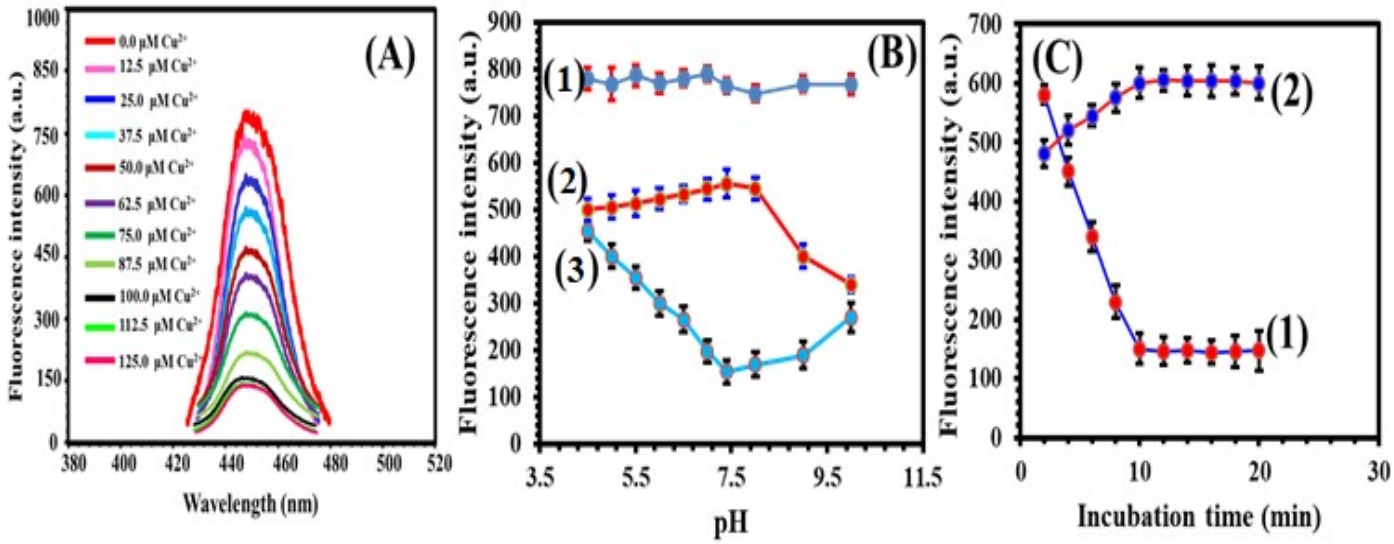

Fig.S10 Construction of GSH sensing nanoswitch based on SQ-dots/Cu^{2+} probe. (A) Fluorescence spectra of the prepared SQ-dots that was incubated with Cu^{2+} of different concentrations. (B) The effect of different pH values: (1) SQ-dots; (2) SQ-dots+Cu^{2+}; (3) SQ-dots/Cu^{2+}+GSH. (C) The effect of incubation time on the fluorescence intensity of: (1) SQ-dots+Cu^{2+} and (2) SQ-dots/Cu^{2+}+GSH.

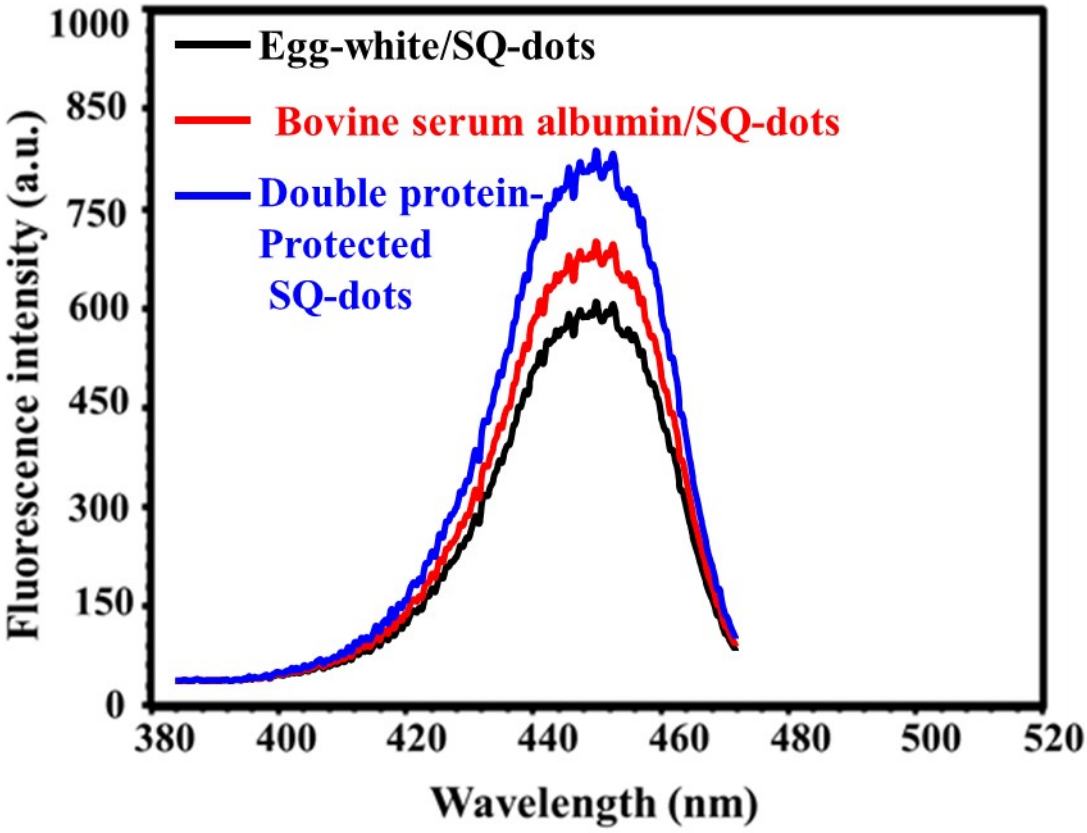

Fig.S11 Fluorescence spectra of egg-white/SQ-dots, bovine serum albumin/SQ-dots, and egg-white/bovine serum albumin protected SQ-dots (double-protein-protected SQ-dots).

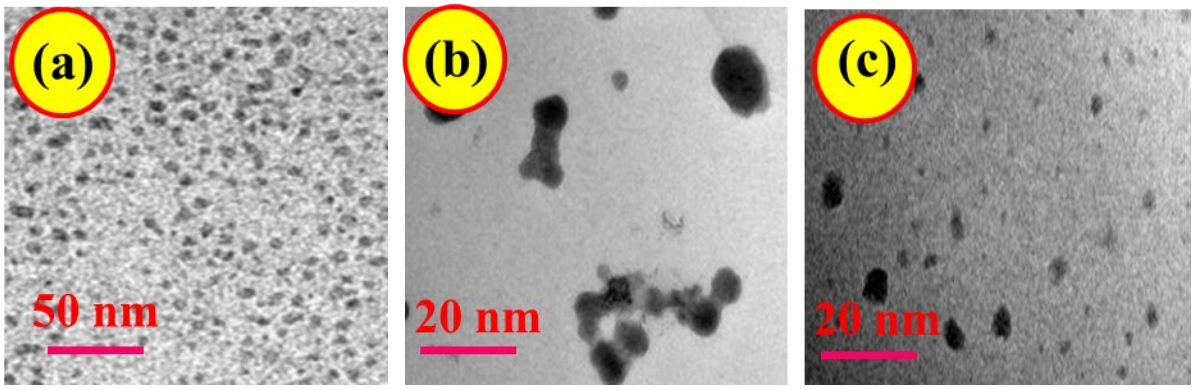

Fig.S12 TEM images of (a) SQ-dots; (b) SQ-dots+Cu^{2+}; (c) SQ-dots/Cu^{2+}+GSH.

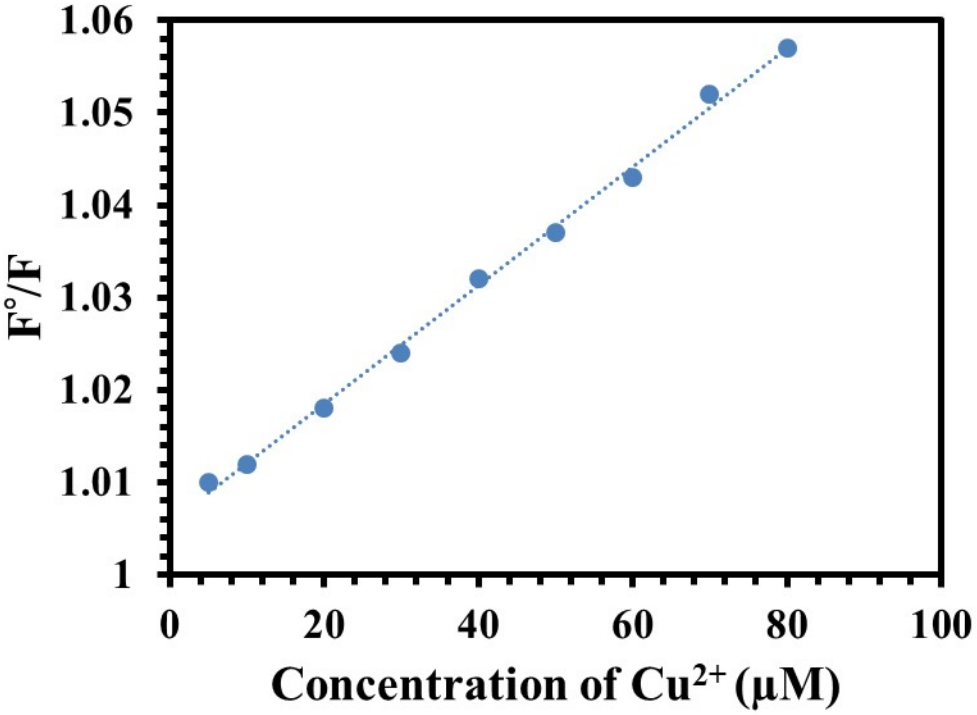

Fig.S13 Stern-Volmer plot between F°/F vs. concentration of Cu^{2+}.

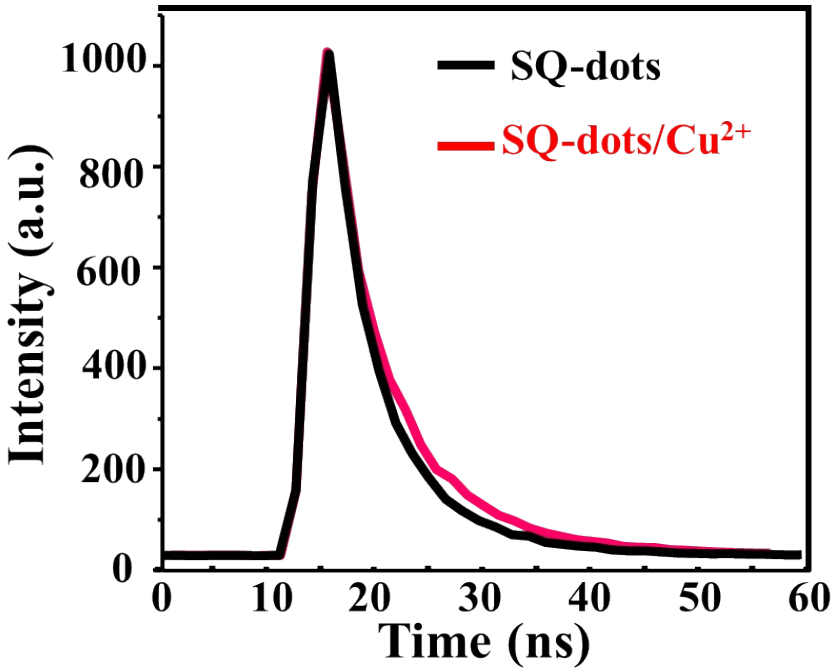

Fig.S14 Time-resolved fluorescence decay curves of the as-fabricated SQ-dots and Cu^{2+}-treated SQ-dots mixture.

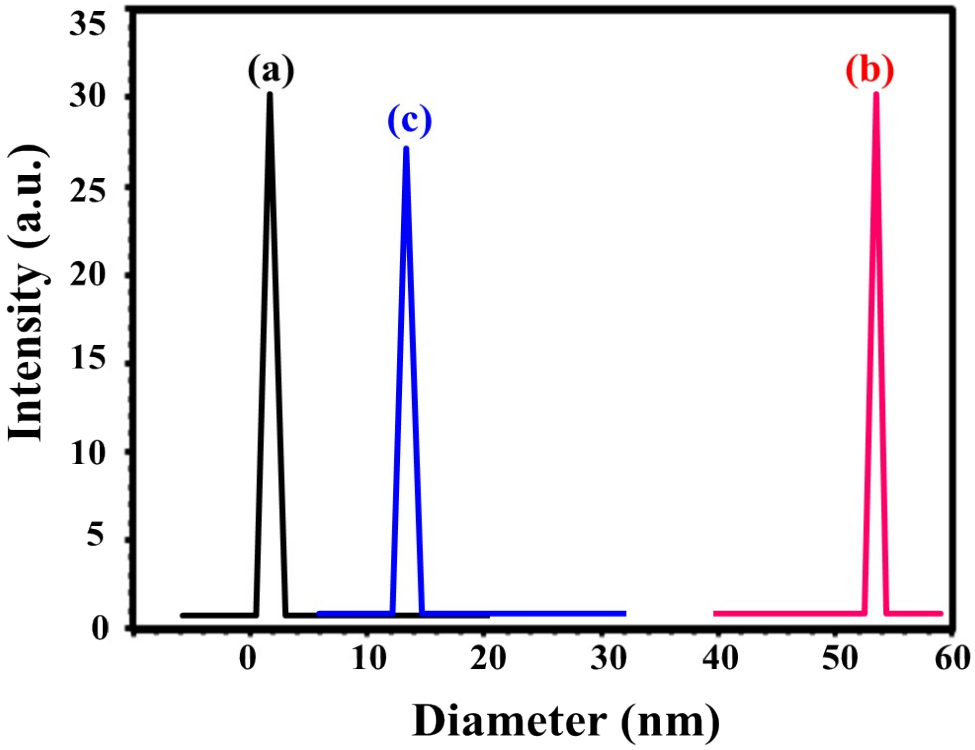

Fig.S15 Hydrodynamic size distribution of: (a) SQ-dots; (b) SQ-dots+Cu^{2+}; (c) SQ-dots/Cu^{2+}+GSH.

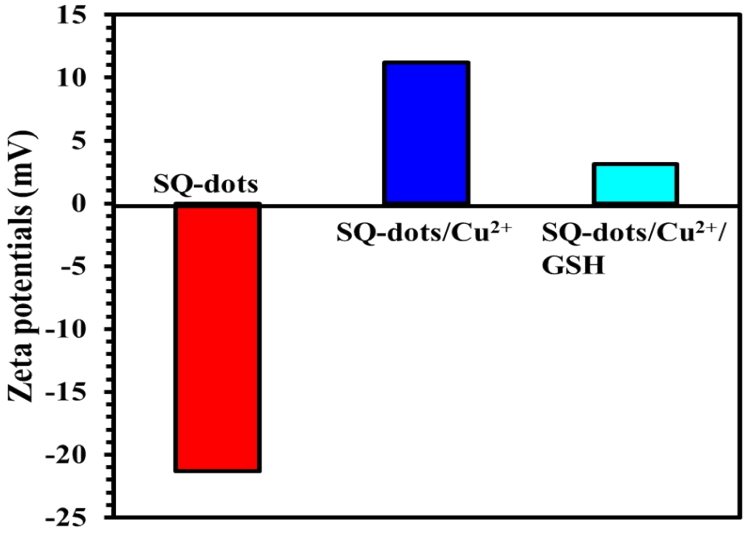

Fig.S16 Zeta potentials of SQ-dots, the mixture of SQ-dots and Cu^{2+}, and the mixture of SQ-dots and Cu^{2+} in the presence of GSH.

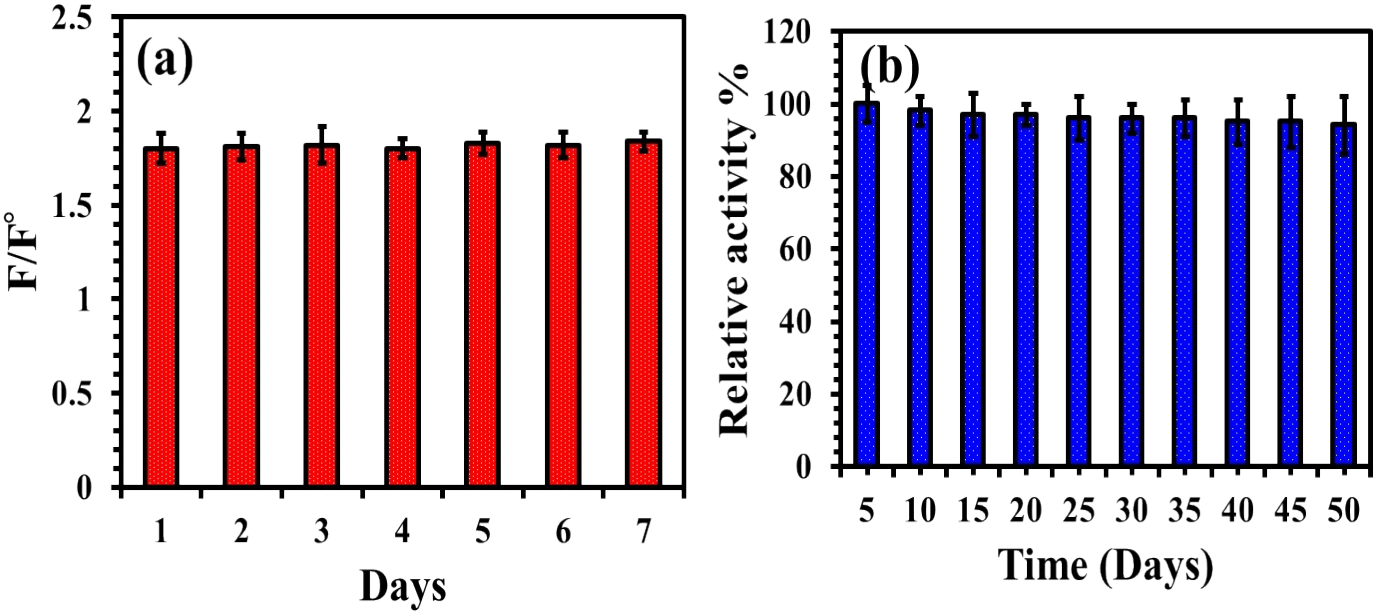

Fig.S17 (a) Reproducibility of the as-fabricated SQ-dots towards 50 μM GSH for seven days. (b) Relative activity % of the as-fabricated SQ-dots.