Supplementary Materials for:

A reversible fluorescent pH-sensing system based on the one-pot synthesis of nature silk fibroin-capped copper nanoclusters

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Figure S1. Optimization of reaction conditions of the fluorescent SF@CuNCs. (A) The fluorescence intensity of the SF@CuNCs under different volume ratio (1:1, 1:2, 1:3 and 1:4). The proportion of Cu(NO$_3$)$_2$·3H$_2$O and SF were fixed at 1:3, respectively. The reaction temperature was 55°C and 6h. (B) The fluorescence intensity of the SF@CuNCs under the different concentrations of NaOH (0, 2.99, 6.21, 12.35, 24.39, 36.14 and 47.62 mM). The concentration of NaOH was fixed at 6.21 mM, and the reaction temperature and time were 55°C and 6h, respectively. (C) The fluorescence intensity of the SF@CuNCs under different reaction temperatures (25, 37, 55, 75 and 90°C). The proportion of Cu(NO$_3$)$_2$·3H$_2$O and SF were fixed at 1:3, respectively. The reaction time was 6h. (D) The fluorescence intensity of the SF@CuNCs under different reaction times (2, 4, 6, 8 and 10h). The proportion of Cu(NO$_3$)$_2$·3H$_2$O and SF were fixed at 1:3, respectively. The reaction temperature was 55 °C.
**Figure S2.** The UV-vis absorption spectrum of SF (black line) and SF@CuNCs (red line) in aqueous solution. All the parameters are the same in both cases.

**Figure S3.** The reproducibility of the SF@CuNCs synthesis.
Figure S4. Fluorescence spectrum of SF@CuNCs at different time indicating the high stability of CuNCs.
Figure S5. (a) Fluorescence spectra of SF@CuNCs in HEPES-NaOH buffers of different pH values: 6.80, 7.05, 7.25, 7.64, 7.98, 8.18 (inset: The calibration curve of the pH values in the range of 6.80-8.18 versus the fluorescence intensity of the SF@CuNCs in HEPES-NaOH buffers); (b) Fluorescence spectra of SF@CuNCs in Tris-HCl buffers of different pH values: 6.95, 7.24, 7.56, 7.99, 8.68, 9.00 (inset: The calibration curve of the pH values in the range of 6.95-9.00 versus the fluorescence intensity of the SF@CuNCs in Tris-HCl buffers); (c) Fluorescence spectra of SF@CuNCs in PBS buffers of different pH values: 3.08, 4.11, 4.98, 6.02, 7.13, 8.00, 9.07, 10.04, 11.01, 12.00; (d) The calibration curve of the pH values in the range of 6.02-10.04 versus the fluorescence intensity of the SF@CuNCs in PBS buffers. The squared correlation coefficient ($R^2$) is 0.9931.
Figure S6. Effect of ionic strength on the fluorescence intensity of SF@CuNCs by exposing the SF@CuNCs to 0.04-0.22 M NaCl in BR buffer with the pH of 7.00. The excitation wavelength was 326 nm and the fluorescence intensity was monitored at 420 nm.