Electronic Supplementary Information

Water-soluble Gold Nanoclusters with pH-dependent Fluorescence and High Colloidal Stability over a Wide pH Range

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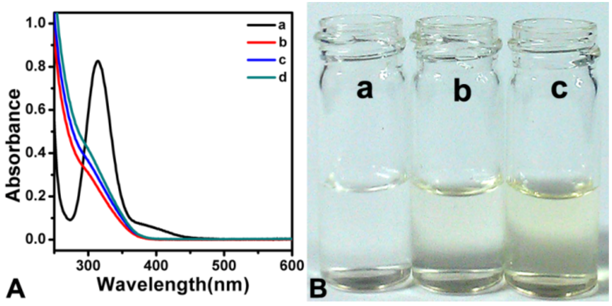

Fig. S1 (A) UV-vis absorption spectrum of $AuCl_4^-$ ions in initial $HAuCl_4$ solution (a, black curve), and in the GSH-$HAuCl_4$ mixture at different ratios: 1.0:1 (b, red curve), 1.2:1 (c, blue curve), and 1.4:1 (d, cyan curve). (B) Photographs of the GSH-$HAuCl_4$ mixture after 3 min at different molar ratios: 2.0:1 (a), 1.2:1 (b), and 1.0:1 (c). The concentration of GSH is 25 mM, 18.7 mM, and 16.7 mM, respectively. The concentration of $HAuCl_4$ used is 12.5 mM, 15.6 mM, and 16.7 mM, respectively.

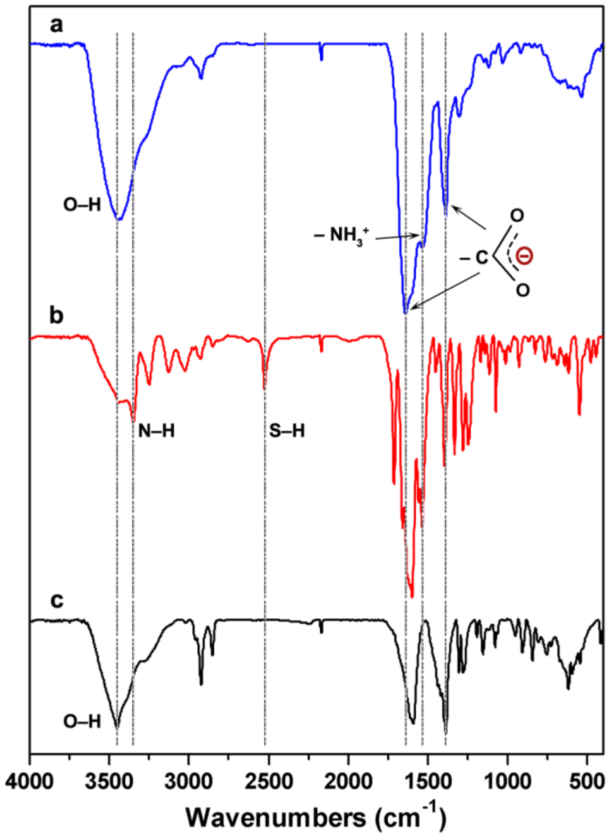

Fig. S2 Fourier transform infrared (FT-IR) spectra of GS/C−Au NCs (a, blue curve), GSH (b, red curve), and citrate (c, black curve).

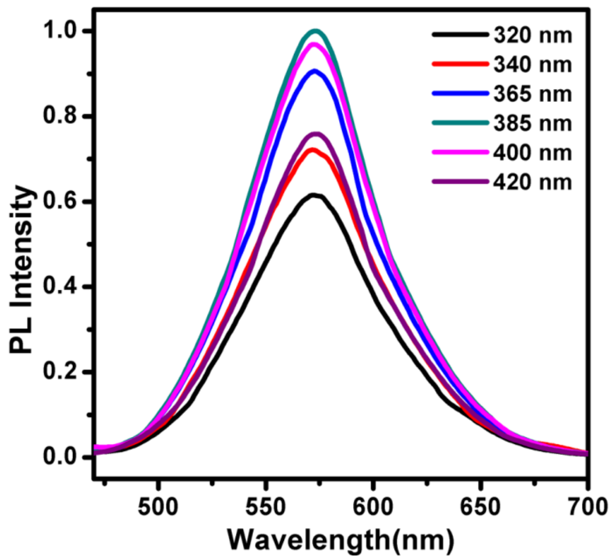

Fig. S3 Fluorescence emission spectra of as-prepared GS/C−Au NCs in Fig.3a at different excitation wavelengths: 320 nm (black curve), 340 nm (red curve), 365 nm (blue curve), 385 nm (cyan curve), 400 nm (magenta curve), and 420 nm (violet curve). The concentrations of GSH, citrate and $HAuCl_4$ used are 6.5 mM, 32.6 mM and 5.4 mM, respectively. The reaction temperature is 50 °C.

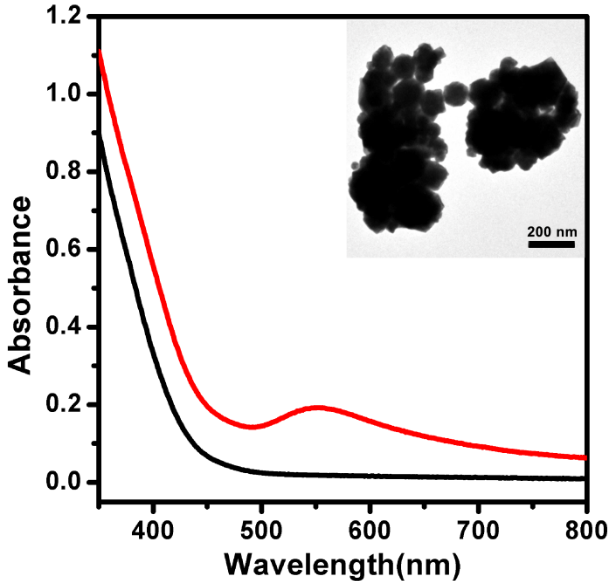

Fig. S4 UV-vis spectra of the GS/C−Au NCs obtained at different ratios of GSH to $HAuCl_4$: 1.2:1 (black curve) and 1.0:1 (red curve). The inset is the TEM image of the large aggregates of Au nanoparticles obtained at the ratio of GSH to $HAuCl_4$ as 1.0:1. The concentration of GSH is 6.5 mM (black curve), and 5.4 mM (red curve), respectively. The concentrations of $HAuCl_4$ and citrate used are 5.4 mM and 32.6 mM, respectively. The reaction temperature is 50 °C.

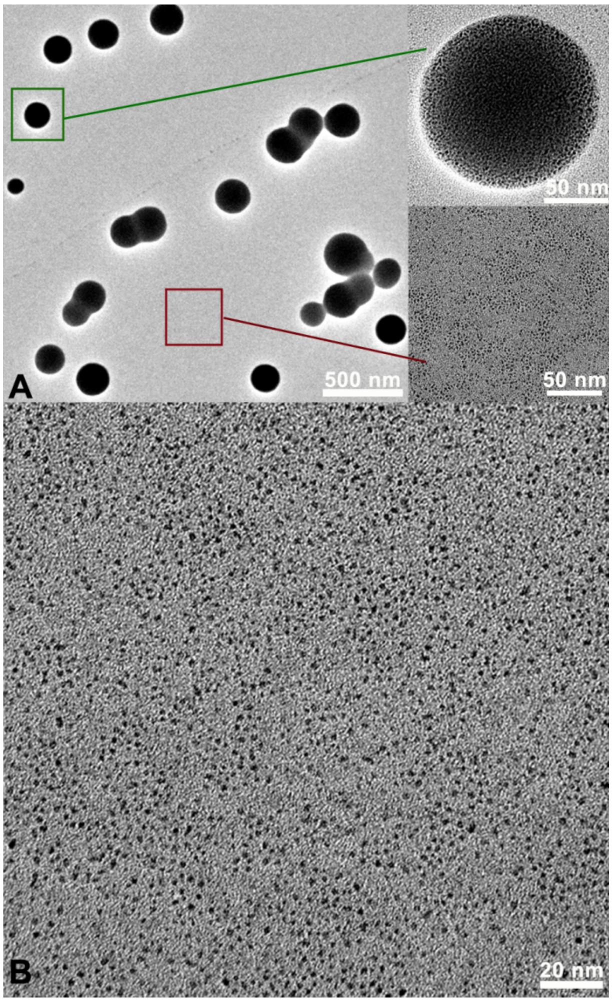

Fig. S5 The representative TEM images of the GS/C−Au NCs obtained at different concentrations of 1.5 ml citrate: 10.9 mM (A) and 43.5 mM (B). The final concentration of citrate is 10.9 mM and 43.5 mM, respectively. The concentrations of GSH and $HAuCl_4$ used are 6.5 mM and 5.4 mM, respectively. The reaction temperature is 50 °C.

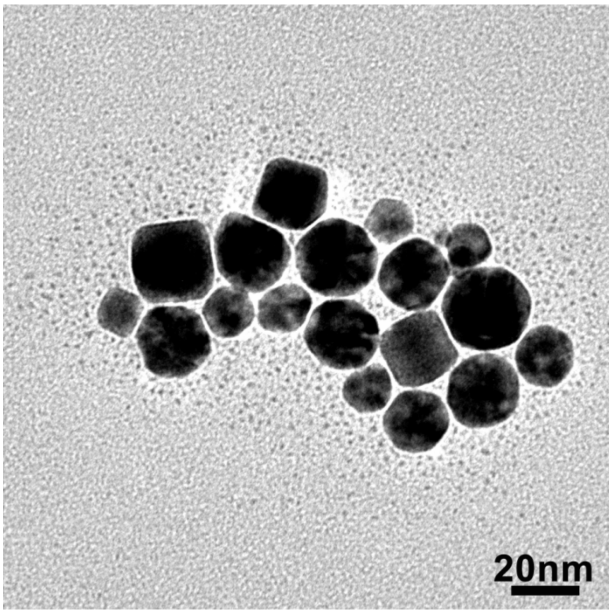

Fig. S6 TEM image of the large Au nanoparticles in the solution of Au NCs obtained at 60 °C. The concentrations of GSH, citrate and $HAuCl_4$ used are 6.5 mM, 32.6 mM and 5.4 mM, respectively.

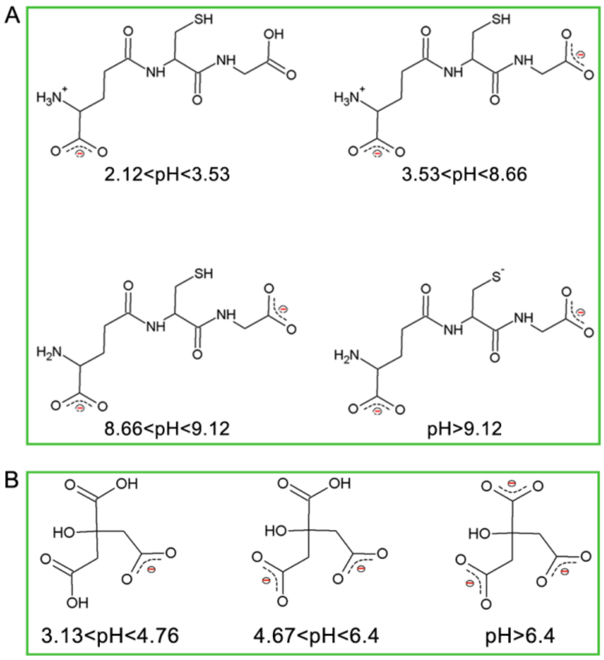

Fig. S7 The possible molecular structures of GSH (A) and citric acid (B) at different pH-ranges according to their pKa values. GSH: $pKa_1 = 2.12$, $pKa_2 = 3.53$, $pKa_3 = 8.66$, $pKa_4 = 9.12$; citric acid: $pKa_1 = 3.13$, $pKa_2 = 4.76$, $pKa_3 = 6.4$.

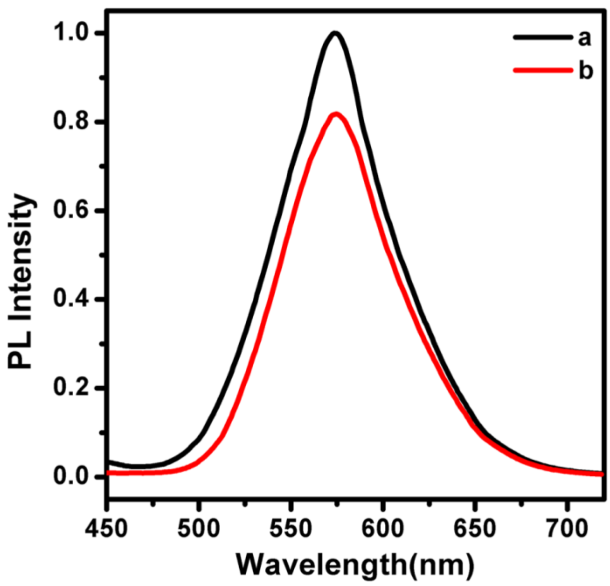

Fig. S8 Fluorescence emission spectra of GS/C−Au NCs solution before (a, black curve) and after storage at room temperature for 6 months (b, red curve). The concentrations of GSH, citrate and $HAuCl_4$ used are 6.5 mM, 32.6 mM and 5.4 mM, respectively. The reaction temperature is 50 °C.

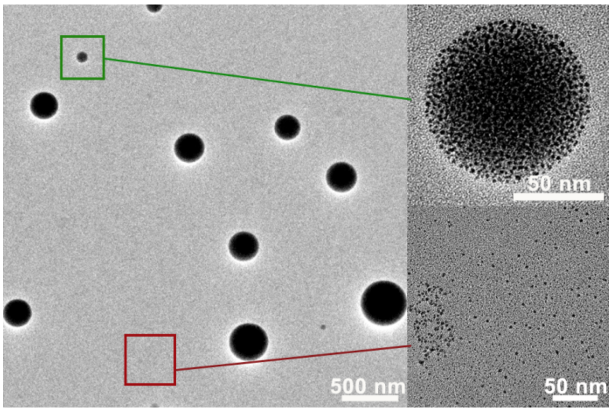

Fig. S9 The representative TEM image of GS/C−Au NCs in the solution with a pH of 4.1 by adding 180 μl of HCl solution (0.1 M) into the solution of as-prepared GS/C−Au NCs with an initial pH of about 5.6. The concentrations of GSH, citrate and $HAuCl_4$ used are 6.5 mM, 32.6 mM and 5.4 mM, respectively. The reaction temperature is 50 °C.

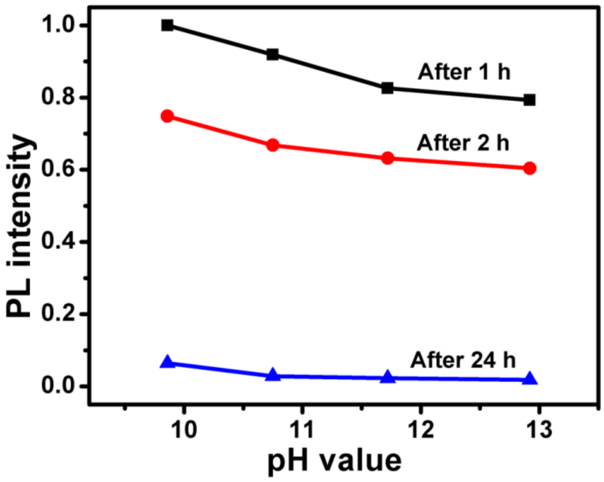

Fig. S10 The plot of the normalized fluorescence intensities of GS/C−Au NCs solutions versus the different pH values by addition of a certain volume of NaOH solution (0.1 M) into the initial solution with a pH of about 5.6. The pH from left to right is 9.8, 10.8, 11.7, and 12.9, respectively. The concentrations of GSH, citrate and $HAuCl_4$ used are 6.5 mM, 32.6 mM and 5.4 mM, respectively. The reaction temperature is 50 °C.

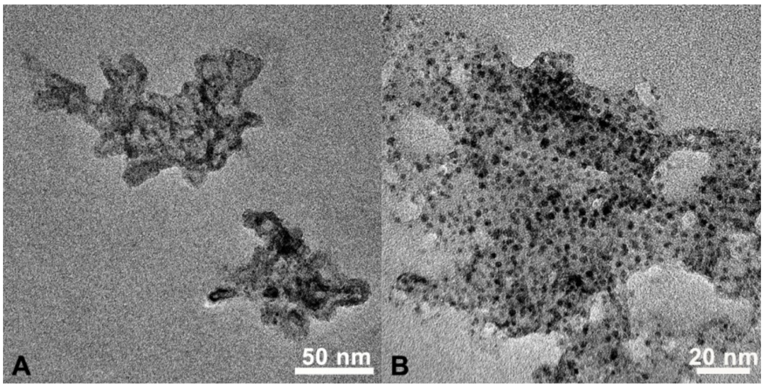

Fig. S11 The representative TEM images of GS/C−Au NCs in the solution with a pH of 11.7 taken under different magnifications: 60 K (A), and 100 K (B). The resulting solution was obtained by addition of NaOH (0.1 M) into the initial solution with a pH of about 5.6. The concentrations of GSH, citrate and $HAuCl_4$ used are 6.5 mM, 32.6 mM and 5.4 mM, respectively. The reaction temperature is 50 °C.

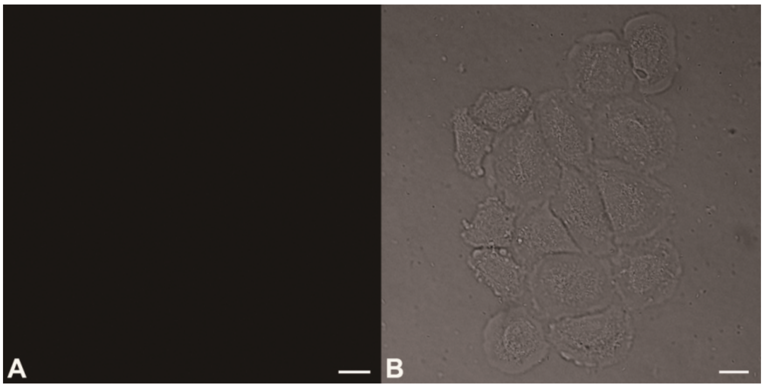

Fig. S12 Wide-field fluorescence image (A) of HeLa cells without the incumbation of GS/C−Au NCs, and differential interference contrast (DIC) image (B). λ_{ex} = 330-385 nm; λ_{em} > 410nm. Scale bar is 20 μm.

Scheme S1. Reactions Involved during the Reduction of Au(III) by GSH and Citrate.

(a) Redox reaction between GSH and Au(III) ions.

$$2\text{GSH} \rightarrow \text{GSSG} + 2\text{H}^{+} + 2\text{e}^{-}$$

$$\text{Au}\left(\text{III}\right) + 2\text{e}^{-} \rightarrow \text{Au}\left(\text{I}\right)$$

$$n\text{Au}\left(\text{I}\right) + n\text{GSH} \rightarrow \left(-\text{Au}\left(\text{I}\right) - \text{SG} -\right)_{n}$$

(b) Redox reaction between citrate and Au(III) ions.

$$\text{Au}\left(\text{III}\right) + \text{citrate} \rightarrow \text{Au}\left(\text{I}\right) + \text{SADC}$$

(c) Disproportionation of Au(I) ions.

$$3\text{Au}\left(\text{I}\right) \rightarrow 2\ \text{Au}\left(0\right) + \text{Au}\left(\text{III}\right)$$

Note: SADC is the abbreviation of sodium acetone dicarboxylate (the oxidation product of citrate).