Supplementary Information

Bright and Stable Gold Nanocluster Assemblies by Silica/Zirconia Double-Shell Encapsulation

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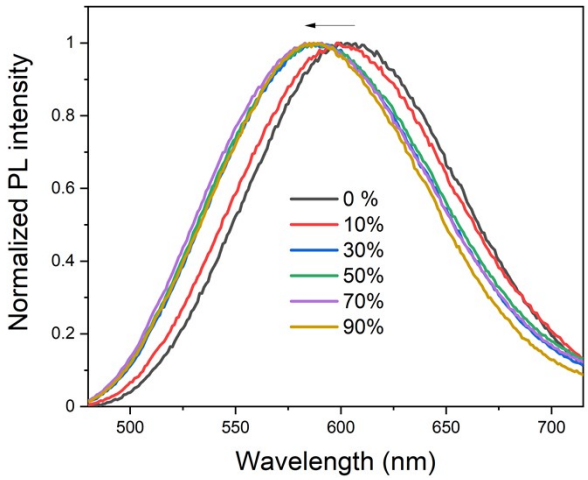

Figure S1. Normalized PL emission spectra of GNC water-ethanol mixture with the volume fraction of ethanol. The emission band keeps blue shifting when the volume fraction of ethanol increases.

Table S1. Absolute photoluminescence quantum yields (PLQYs) of GNCs, GNCA/SiO_2 NPs, and GNCA/SiO_2/ZrO_2 NPs.

Sample	PLQY (%)
GNCs in water	4.76
GNCA/SiO_2 NPs in ethanol	48.96
GNCA/SiO_2/ZrO_2 NPs in ethanol	54.79

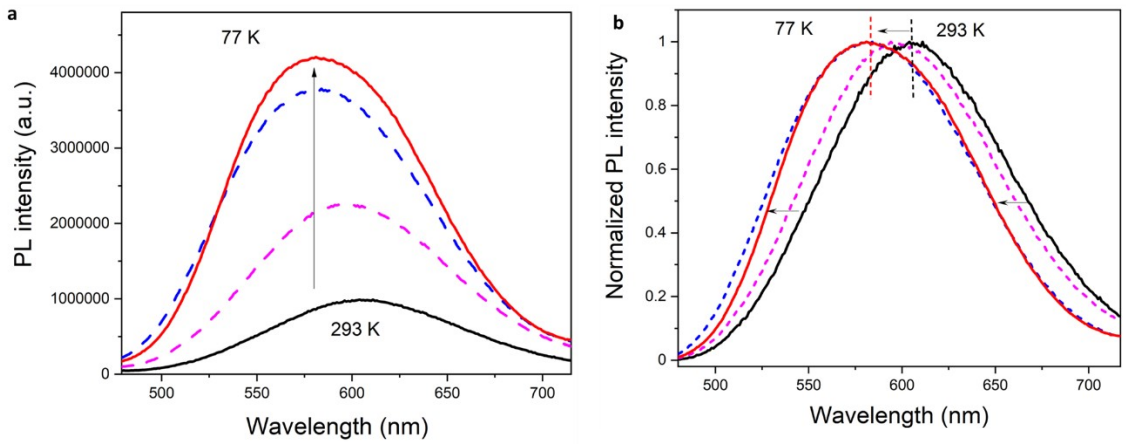

Figure S2. The absolute (a) and normalized (b) PL spectra of GNC aqueous solution at different temperatures. The emission band gradually blue-shifts from 603 nm to 589 nm with a great increase in the emission intensity when the temperature decreases.

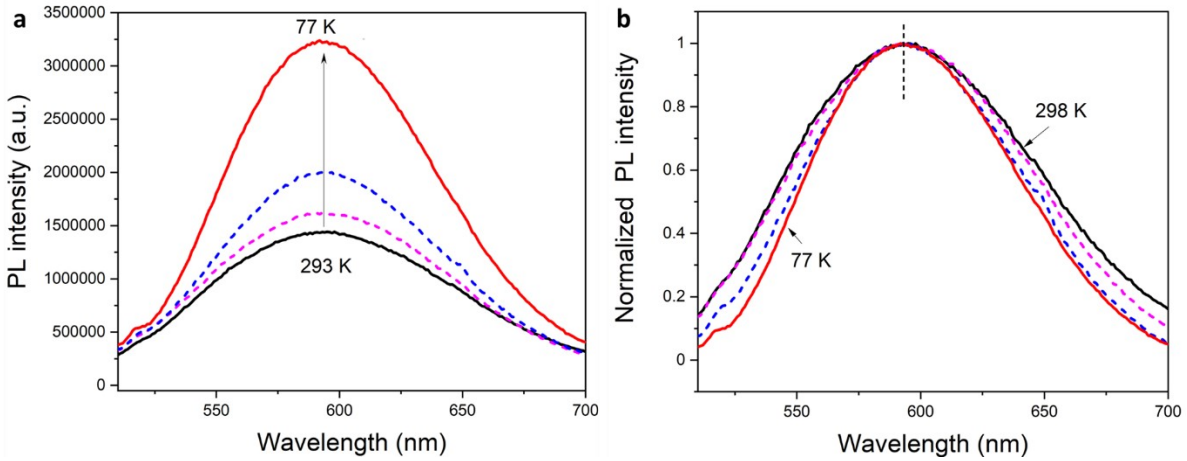

Figure S3. The absolute (a) and normalized (b) PL spectra of GNCA/SiO_2/ZrO_2 NPs at different temperatures. The emission intensity increases with the decreasing temperature. That is because all the thermal motions are further inhibited when the temperature drops, which enhances the emission.

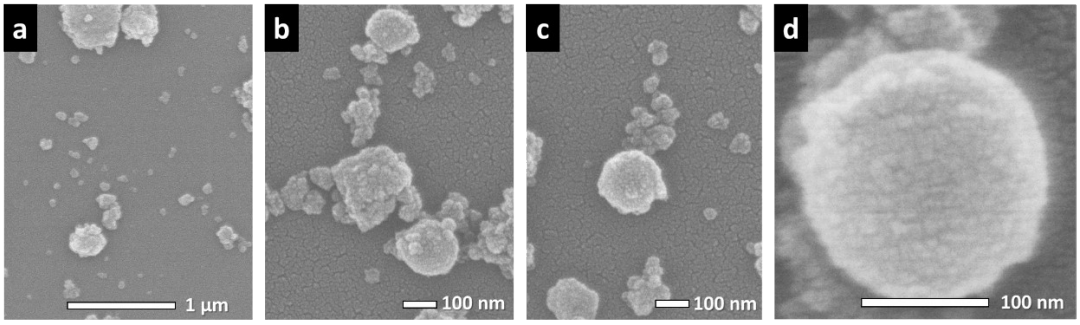

Figure S4. SEM images of GNCA/SiO_2/ZrO_2 NPs.

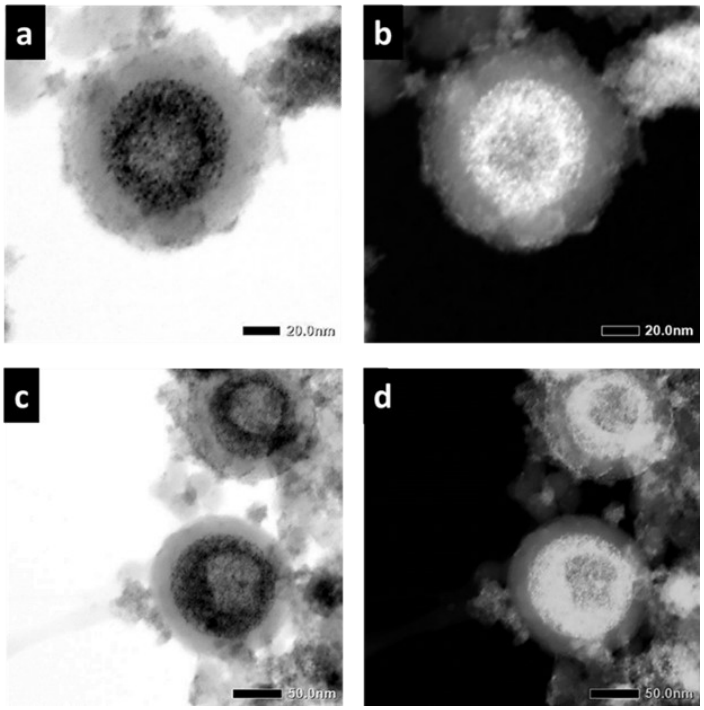

Figure S5. STEM images of GNCA/SiO_2/ZrO_2 NPs in both bright and dark field mode. Spherical assemblies of GNCs are well encapsulated in the shell.

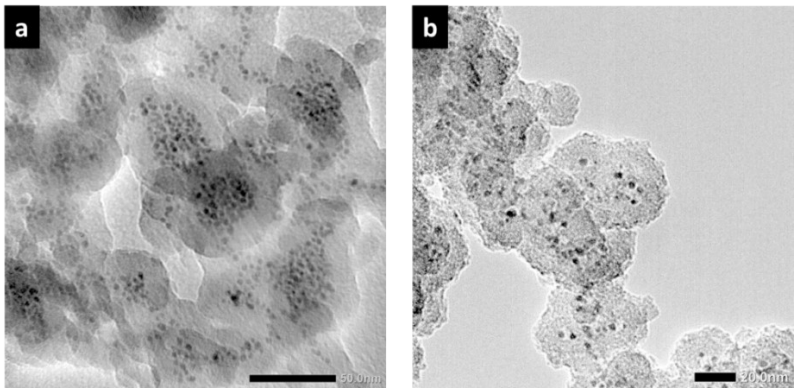

Figure S6. TEM images of GNCA/SiO_2 NPs that are synthesized with insufficient PVP (5 mg/mL).

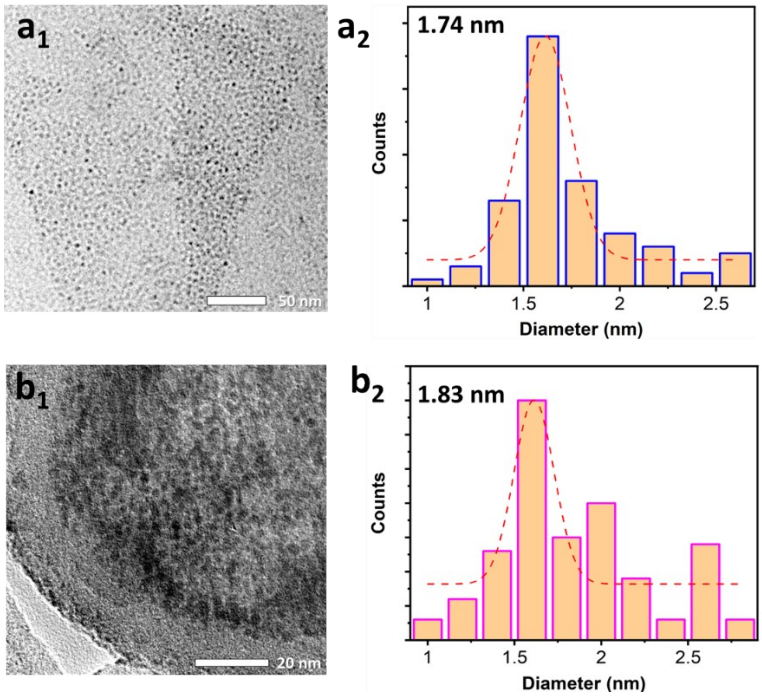

Figure S7. TEM images and size distributions of GNCs (a_1, a_2) and GNCA/SiO_2/ZrO_2 NPs (b_1, b_2). The average diameters of GNCs before and after encapsulation in the oxide matrix are measured to be ~1.7 nm, ~1.8 nm, respectively.

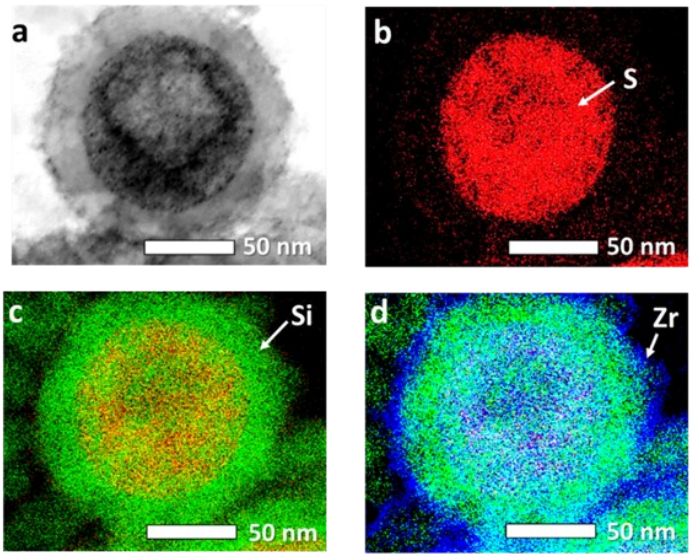

Figure S8. X-ray mapping results. (a) STEM image of a GNCA/SiO_2/ZrO_2 particle. (b) Distribution of S element of the GNCA/SiO_2/ZrO_2 particle. (c) Distribution overlap of S (Red) and Si (green) elements. (d) Distribution overlap of S (Red), Si (green) and Zr (blue) elements.

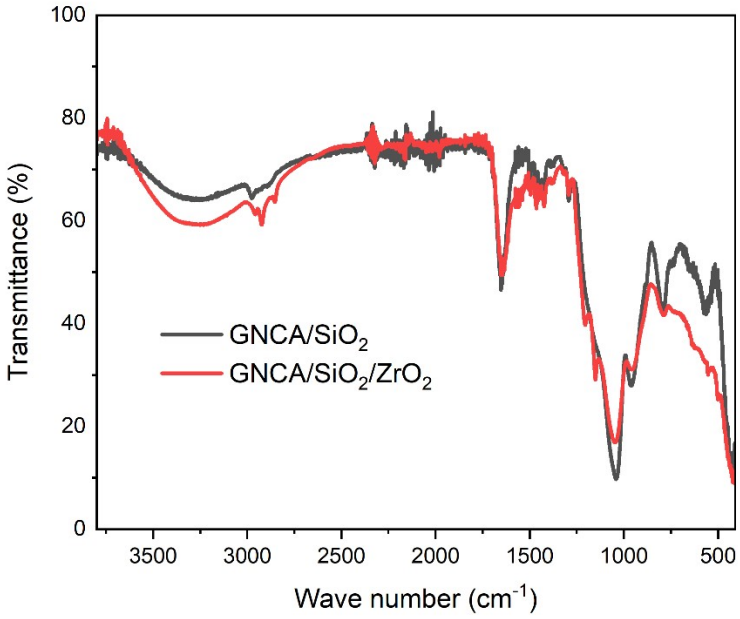

Figure S9. FTIR spectra of GNCA/SiO_2 NPs and GNCA/SiO_2/ZrO_2 NPs. The transmittance of GNCA/SiO_2/ZrO_2 NPs is greater than that of GNCA/SiO_2 NPs in the range of 400~800 cm^{-1}, due to the vibration of Zr-O bonds.

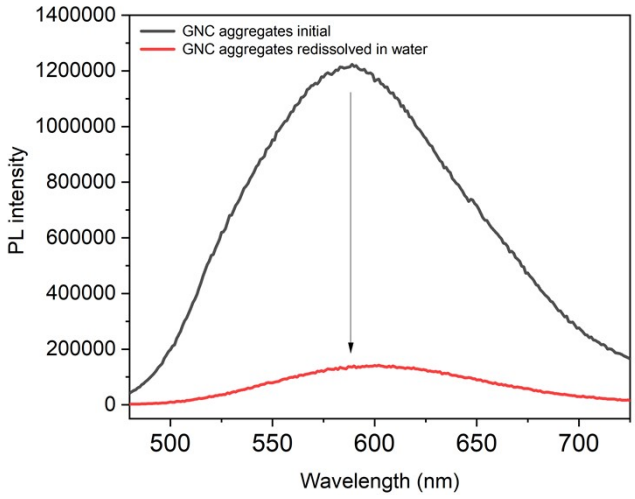

Figure S10. PL emission spectra of bare GNCAs before (black) and after (red) redispersion in water. A conspicuous intensity drop can be observed because bare GNCAs (without stabilization by PVP) are weakly bonded and the hydrophilic GNCs are extremely prone to separation and dispersion in water.

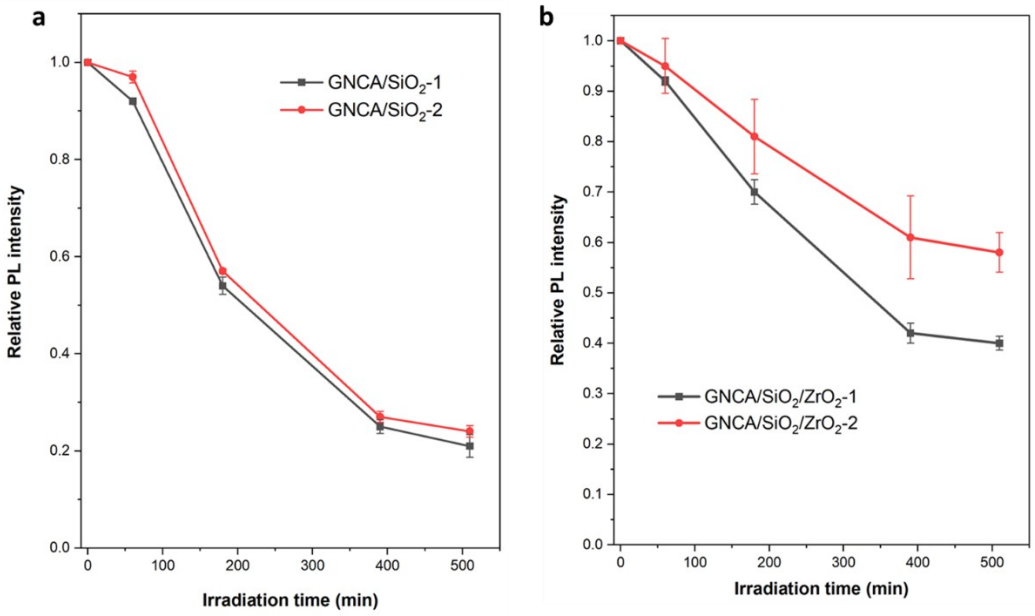

Figure S11. Relative PL intensity evolution of GNCA/SiO_2 NPs and GNCA/SiO_2/ZrO_2 NPs with different shell thicknesses under UV irradiation at 350 nm, 5.96 mw/cm^2. Amount of silica in GNCA/SiO_2-2 is as ~2 times as that in GNCA/SiO_2-1. Amount of zirconia in GNCA/SiO_2/ZrO_2-2 is as ~2 times as that in GNCA/SiO_2/ZrO_2-1 (amount of silica is the same). More details are shown in Table S2.

Table S2. Molar ratios of Au : Si : Zr in different GNCA/SiO_2 NPs and GNCA/SiO_2/ZrO_2 NPs, and their residual PL intensity with respect to the initial value under UV irradiation for 510 min.

Sample	n (Au) : n(Si) : n(Zr)	Residual relative PL intensity (%)
GNCA/SiO_2-1	1:2800:0	21
GNCA/SiO_2-2	1:5600:0	24
GNCA/SiO_2/ZrO_2-1	1:2800:650	40
GNCA/SiO_2/ZrO_2-2	1:2800:1300	58