Electronic Supporting Information

Dual-emitting zein-protected gold nanoclusters for ratiometric fluorescent detection of Hg^{2+} /Ag^{+} ions in both aqueous solution and self-assembled protein film

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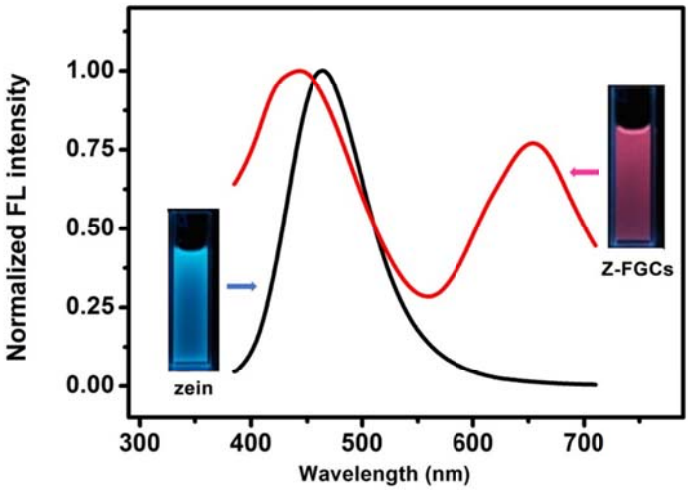

Fig. S1. Fluorescence emission spectra of zein (black) and Z-FGCs (red) under 365 nm excitation.

Inset: Photographs of zein and Z-FGCs under 365 nm UV lamp.

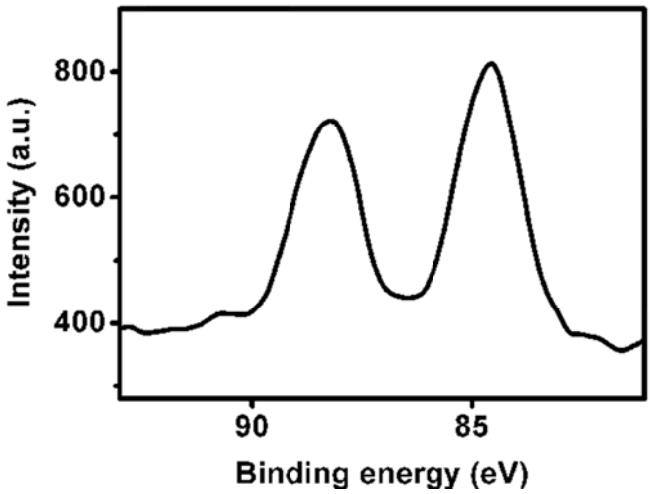

Fig. S2. Au 4f XPS spectrum of the Z-FGCs.

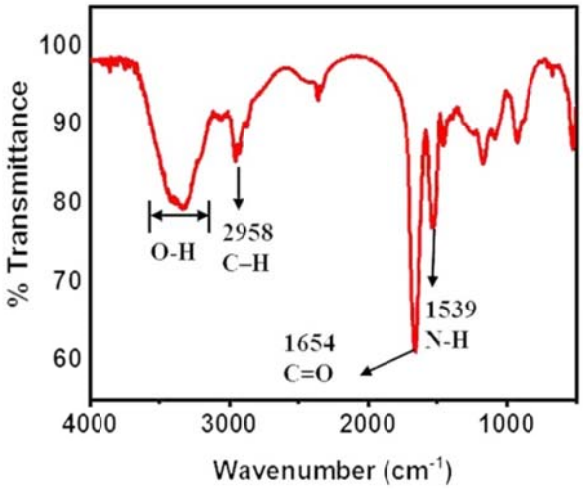

Fig. S3. FTIR spectrum of the Z-FGCs. The FTIR study of Z-FGCs exhibited the typical stretching vibration bands of C-H, C=O, N-H and O-H in protein, indicating the encapsulation of FGCs by zein. The bands at 1539 and 1654 cm^{-1} can be attributed to the N-H and C=O stretching vibration, respectively. The band at 2958 cm^{-1} can be assigned to C-H vibration. In addition, it appeared a broad band at 3100–3700 cm^{-1}, which should be corresponded to the O-H stretches.

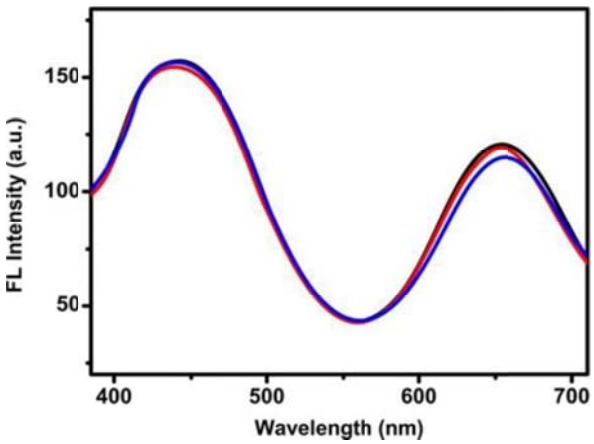

Fig. S4. Fluorescence emission spectra of the redispersed solution of Z-FGCs precipitate (black) and Z-FGCs powder acquired through freeze-drying for 12 h (red) or drying at 70 °C for 5 h (blue). No significant difference was observed in the fluorescence of the redispersed solution of the Z-FGCs precipitate/powder obtained through different ways.

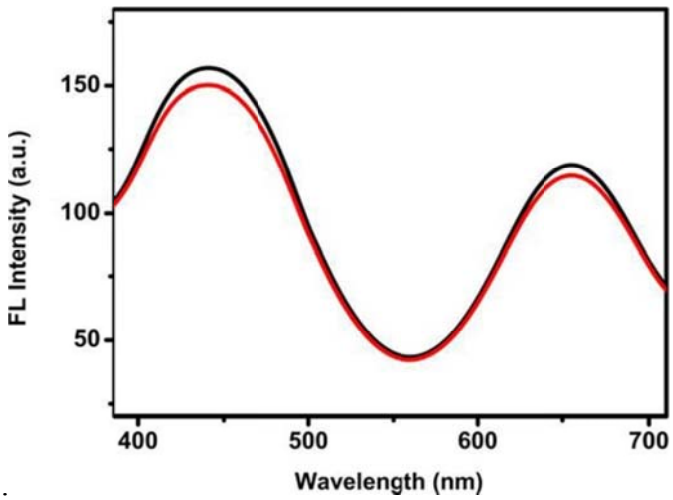

Fig. S5. Fluorescence emission spectra of the redispersed solution of Z-FGCs powder before (black) and after (red) the storage at 4 °C for 6 months. No significant loss in fluorescence intensity was observed, indicating that the Z-FGCs powder can be stored at 4 °C for at least 6 months.

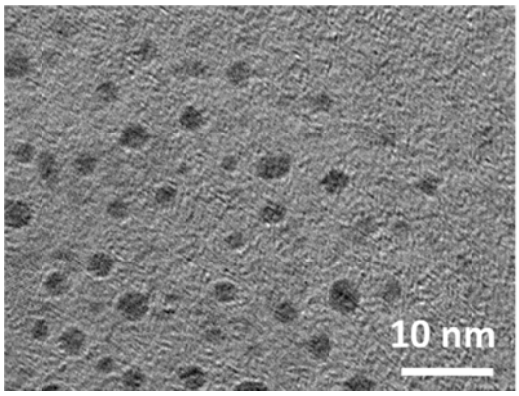

Fig. S6. TEM image of Z-FGCs after the addition of 50 μM Ag^{+}.

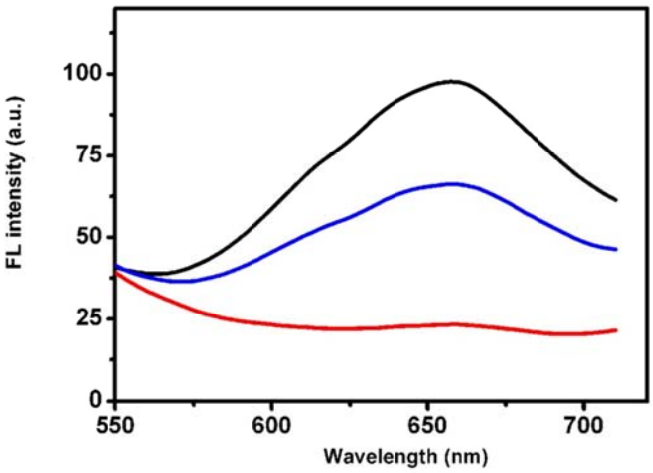

Fig. S7. Fluorescence emission spectra of Z-FGCs (black), Z-FGCs+ 50 μM Hg^{2+} ions (red) and Z-FGCs + 50 μM Hg^{2+} ions + 1.0 mM $NaBH_4$ (blue).

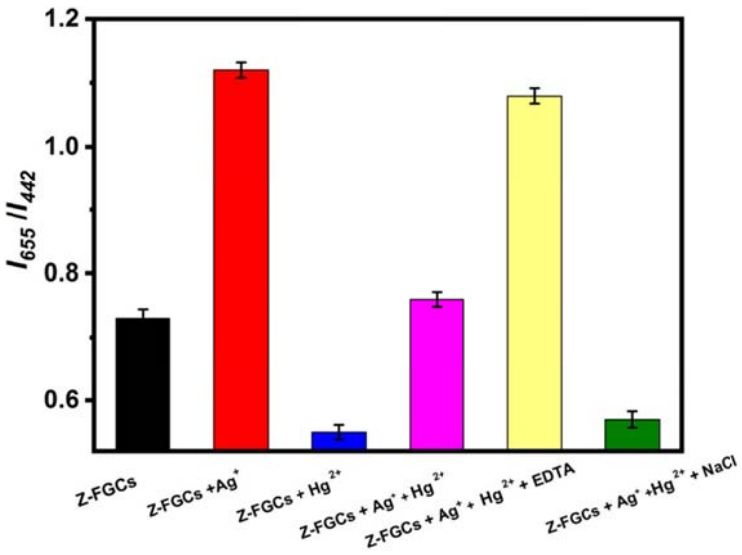

Fig. S8. The change in I_{655}/I_{442} of Z-FGCs before (black) and after the addition of Ag^{+} (15 μM, red), Hg^{2+} (15 μM, blue), Ag^{+} (15 μM) +Hg^{2+} (15 μM, magenta), Ag^{+} (15 μM) +Hg^{2+} (15 μM) + EDTA (1 mM, yellow) and Ag^{+} (15 μM) +Hg^{2+} (15 μM) + NaCl (10 mM, green).

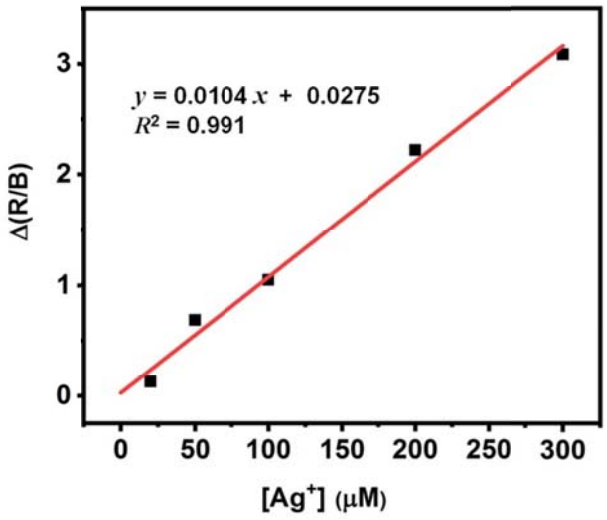

Fig. S9. Change in the Δ(R/B) of Z-FGCs-based film sensor for detection of Ag^+ ions. Photographs of Z-FGCs film before and after the addition of different concentration of Ag^+ were acquired by using Nikon D80 digital camera. The photographs were then processed by using a free RGB analysis software (Color cop) for recording the intensity ratio of red to blue (R/B) channel (in RGB chroma). The Δ(R/B) was calculated by using intensity ratio of (R/B) of Z-FGCs film after the addition of different concentration of Ag^+ minus that of (R/B) of Z-FGCs film alone. The detection limit was estimated to be ~6 μM by the IUPAC method.

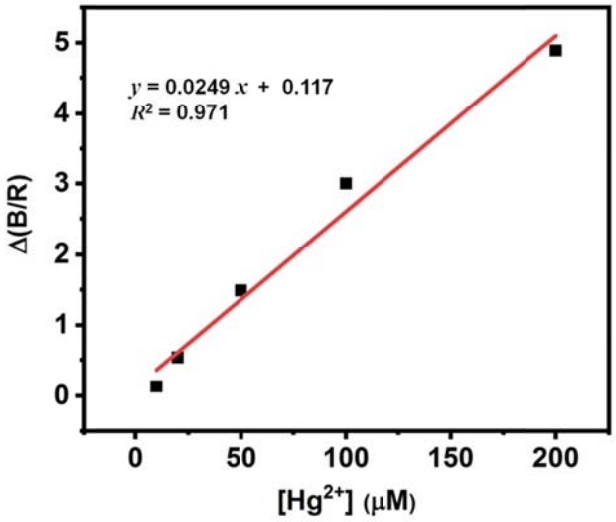

Fig. S10. Change in the Δ(B/R) of Z-FGCs-based film sensor for detection of Ag^{+} ions. The Δ(B/R) was calculated by using intensity ratio of (B/R) of Z-FGCs film after the addition of different concentration of Hg^{2+} minus that of (B/R) of Z-FGCs film alone. The detection limit was estimated to be ~3 μM by the IUPAC method.

Table S1. List of FGCs-based method for detection of Ag^{+} and the relevant parameters of probe synthesis and purification

Probe	method	Time for probe synthesis	Purification	Linear range	LOD	refs
glutathione - FGCs	turn-on	24 h	dialysis for 24 h	0.5 nM–20 μM	0.2 nM	13
BSA- FGCs	turn-on	12 h	dialysis	0−40.0 μM	-	14
cytidine- FGCs	turn-on	1 h	-	0.01 – 6 mM	10 nM	40
11-mercaptoundecanoic acid–FGCs	turn-off	2 h	adding NaCl	25 nM – 3 mM	9 nM	41
BSA- FGCs	turn-on	6 h	dialysis for 24 h	0–20.0 mM	0.46 mM	42
zein- FGCs	ratiometric	10 min	mixing with acidic buffer for several minutes	1-15 μM	200 nM	this work

Table S2. List of FGCs-based method for detection of Hg^{2+} and the relevant parameters of probe synthesis and purification

Probe	method	Time for probe synthesis	Purification	Linear range	LOD	refs
aprotinin- FGCs	turn-off	12 h	dialysis for 24 h	0 - 330 μM	19.43 μM	7
esterase- FGCs	turn-off	18 h	dialysis for 24 h	1−30 nM	0.88 nM	8
BSA- FGCs	turn-off	12 h	dialysis for 24 h	1–20 nM	0.5 nM	12
keratin- FGCs	turn-off	12 h	size exclusion column	2.44–2500 nM	2.31 nM	16
egg-white–FNCs	turn-off	5 min	-	5–100.0 nM	0.89 nM	17
Tb^{3+}/BSA–FGCs conjugates	ratiometric	12 h	dialysis for 10 h	0.005 - 7 μM	1 nM	18
N-acetyl-l-cysteine - FGCs	turn-off	24 h	dialysis for 72 h	2.0–3200 nM	0.2 nM	43
zein- FGCs	ratiometric	10 min	mixing with acidic buffer for several minutes	0.1-15 μM	25 nM	this work

Table S3. Detection of Ag^{+} by Z-FGCs probe in tap water

Samples	Ag^{+} added (μm)	Ag^{+} found (μm)[a]	Recover (%)
Tap water	-	N.D.[b]	-
	2	2.21±0.06	107.5
	4	4.25±0.11	106.2
	6	6.28±0.14	104.7
	8	8.60±0.20	106.3

[a] Average of six replicate measurements ± standard deviation.

[b] N.D. : not detected.

Table S4. Detection of Hg^{2+} by Z-FGCs probe in tap water

Samples	Hg^{2+} added (μm)	Hg^{2+} found (μm)[a]	Recover (%)
Tap water	-	N.D.[b]	-
	4	4.30±0.12	106.7
	6	6.35±0.14	105.8
	8	8.58±0.17	107.2
	10	10.60±0.22	106.0

[a] Average of six replicate measurements ± standard deviation.

[b] N.D. :not detected.