Supporting Information

Electrochemically-assisted Flexible Lanthanide Upconversion Luminescent Sensing of Heavy Metal Contamination with High Sensitivity and Selectivity

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Table of Contents:

1.	Characterizations and photoluminescent properties of UCNPs	S-3
2.	Characterizations of CFC-UCNP probe	S-8
3.	The UV/VIS absorption of metal ions	S- 10
4.	Solution-based assay with ligand free core@shell UCNPs	S- 11
5.	Stern-Volmer (SV) analysis of Cu ²⁺ ion sensing with CFC-UCNP probe	S-12
6.	E-chem performance and voltage effects on CFC-UCNP probe	S-14
7.	Mechanism studies of Cu ²⁺ ion sensing under E-chem assistance	S- 17
8.	Selectivity test of CFC-UCNP probe for UCL sensing at 0 V	S-20



1. Characterizations and photoluminescent properties of UCNPs

Figure S1. The transmission electron microscopy (TEM) images and the size distribution of (a, b) the core@shell upconversion nanopartricles (UCNPs) and (c, d) the core UCNPs. The TEM images proved the mono-dispersed core UCNPs had a morphology change from spherical to hexagonal shape after the shell growth, with a size increase from 34.88 nm to 43.8 nm.



Figure S2. X-ray diffraction (XRD) patterns of the core and core@shell UCNPs in comparison to the standard pattern of hexagonal phase NaGdF₄ crystals (JCPDS#27-0699). The well-matched XRD patterns to the standard card suggested the as-prepared UCNPs were hexagonal phase NaGdF₄ crystals.



Figure S3. Fourier-transform infrared spectroscopy (FTIR) spectra of oleate (OA)-capped and ligand free core@shell UCNPs.



Figure S4. (a) The upconversion luminescent (UCL) spectra of core UCNPs and core@shell UCNPs with oleate (OA) surface. (b) The photographs of 1 mg/ mL (left) core UCNPs and (right) core@shell UCNPs in cyclohexane under 980 nm excitation. (c) The energy migration-mediated upconversion (EMU) mechanism for the UCL of core@shell UCNPs.



2. Characterizations of CFC-UCNP probe

Figure S5. (a) The fabrication process of the CFC-UCNP probe. After 6 h electrostatic adsorption process of ligand free core@shell UCNPs to the acid-treated CFC, the characteristic purple UCL could be observed by naked eye in the photograph under 980 nm laser irradiation. (b) The UCL spectra of the ligand free core@shell UCNPs before/ after being used for the adsorption process.



Figure S6. The SEM images of (a, c) CFC and (b, d) CFC-UCNP probe and the EDX spectrum of (e) CFC and (f) CFC-UCNP probe.

3. The UV/VIS absorption of metal ions



Figure S7. (a) UV-VIS spectra of $CuSO_4$ (aq.) in D.I. water compared to NaCl (aq.) media with various [Cl⁻]:[CuSO₄] ratios. The inset is a representative photograph of CuSO₄ (aq.) (left) in D.I. water and (right) in concentrated NaCl (aq.). (b) UV-VIS spectra of various cations in NaCl (aq.).

A color change from blue to green can be observed at higher [Cl⁻] due to the formation of Cu (I) chloride complexes.¹ The spectral overlap of various metal cations with the UCL at 615 nm from Eu³⁺ ions, indicating that resonance energy transfer can possibly occur for UCL deactivation.





Figure S8. UCL spectra and the corresponding quenching efficiency at 615 nm of ligand free core@shell UCNPs for Cu^{2+} ion sensing (a, b) in D.I. water and (c, d) in 1 M NaCl (aq.) under 980 nm excitation. The quenching efficiency was calculated by the difference between UCL in the absence and presence of Cu^{2+} ions, followed by division of UCL in the absence of Cu^{2+} ions.



5. Stern-Volmer (SV) analysis of Cu²⁺ ion sensing with CFC-UCNP probe

Figure S9. The representative plots of the UCL sensing (a) at 0 V and (b) at 0.3 V based on the SV relationship. The representative plots obtained (c) at 0 V and (d) at 0.3 V based on the modified SV relationship. I_0 and I refer to the UCL intensity of the CFC-UCNP probe at 615 nm before and after adding Cu²⁺ ions, correspondingly.

For a dynamic quenching process, a linear relationship between the luminescence of phosphors and the quencher concentration can be characterized from the SV relationship:^{2, 3}

$$\frac{I_o - I}{I} = K_{SV}[Q] \tag{1}$$

On the other hand, a negative deviation from the SV linearity indicates the occurrence of mixed dynamic and static quenching mechanisms. In addition, it is attributed to the heterogeneity of the hybrid system, in which the quenching process can be described by the following modified SV relationship:³

$$\frac{I_o}{I_o - I} = \frac{1}{f_a} + \frac{1}{f_a K_{sv}[Q]}$$
(2)

where I_o and I are the emission intensity before and after adding Cu²⁺ ions respectively, f_a is the factor of quenchable sites, K_{SV} is the Stern-Volmer constant and [Q] is the quencher concentration. The negative deviations from linear fittings obtained by the SV equation imply that both dynamic and static quenching likely contributed to the UCL quenching (Figure S9a-b). This can be explained by the heterogeneity in composite-based sensor, whose optical signals from inner and surface core@shell UCNPs on the porous cloth are deactivated by the analyte ions at various quenching constants.³ The Cu²⁺ ion sensing at 0 V could be characterized by this modified relationship (Figure S9c) in contrast to the assays at 0.3 V, as revealed by the negative deviation from a linear plot in Figure S9d. It suggests the heterogeneity is reduced or additional quenching mechanisms involved under the Echem effect. 6. E-chem performance and voltage effects on CFC-UCNP probe



Figure S10. CV curves of the acid-treated CFC probe and CFC-UCNP probe. The nearly identical CV curves implies that the core@shell UCNPs are E-chem inert within the potential window selected for Cu^{2+} ion sensing.



Figure S11. Linear relationship between current density and $[Cu^{2+}]$ obtained from the CV measurement of the CFC-UCNP probe at 0.2 V reduction potential. The inset is the enlarged plot for 0 - 2 ppm Cu^{2+} ions. The limit of detection was estimated to be about 132 ppb.



Figure S12. (a) The UCL intensity at 615 nm of the CFC-UCNP probe relative to that at 0 V under different applied anodic voltages. (b) Photoluminescence decay curves of the CFC-UCNP probe in the absence of Cu^{2+} ions under monitoring the characteristic UCL at 615 nm at 0 V (circle) and 0.3 V (triangle). All the decay curves were fitted by single exponential decay. The relative UCL intensity monitored at 615 nm for 20 min (c) at 0 V and (d) at 0.3 V, respectively.

7. Mechanism studies of Cu²⁺ ion sensing under E-chem assistance



Figure S13. The relative UCL intensity at 615 nm of the CFC-UCNP probe with 20 and 50 ppm Cu^{2+} ions at 0.3 V.



Figure S14. Photoluminescence decay curves of the CFC-UCNP probe for sensing (af) 0, 10, 20, 50, 100 and 200 ppm Cu^{2+} ions at 0.3 V by monitoring UCL at 615 nm upon 980 nm excitation. All the lifetimes were estimated by single exponential decay fitting.



Figure S15. Photoluminescence decay curves of the CFC-UCNP probe for sensing (af) 0, 10, 20, 50, 100 and 200 ppm Cu^{2+} ions at 0 V by monitoring UCL at 615 nm upon 980 nm excitation. All the lifetimes were estimated by single exponential decay fitting.

8. Selectivity test of CFC-UCNP probe for UCL sensing at 0 V



Figure S16. The quenching efficiency of UCL at 615 nm of the CFC-UCNP probe at 0 V for sensing various non-specific cations. ($[Cu^{2+}] = 315 \ \mu\text{M}$, $[Ba^{2+}] = 5.1 \ \mu\text{M}$, $[Ni^{2+}] = 1.2 \ \mu\text{M}$, $[Pb^{2+}] = 48.3 \ n\text{M}$, $[Cr^{3+}] = 1 \ \mu\text{M}$, $[Co^{2+}] = 25 \ \mu\text{M}$ and $[Ca^{2+}/Mn^{2+}/Zn^{2+}/Fe^{3+}] = 500 \ \mu\text{M}$)

References

- 1. W. Shao, G. Pattanaik and G. Zangari, J. Electrochem. Soc., 2007, 154, D201.
- 2. S. M. Saleh, R. Ali and O. S. Wolfbeis, *Chem. Eur. J.*, 2011, 17, 14611-14617.
- 3. B. C. Barja and P. F. Aramendia, *Photochem. Photobiol. Sci.*, 2008, 7, 1391-1399.