Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Cerium versus zirconium UiO66 metal organic frameworks in coupling with CdS for H_2 evolution under visible light

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Experimental procedures for sample synthesis

Ce-U66 and CdS/Ce-U66. Ce-U66 was prepared according to previous report.[1] Terephthalic acid (286 mg, 1.72 mmol) was dissolved in 9.6 mL of DMF, and then mixed with $Ce(NH_4)_2(NO_2)_6$ (3.2 mL, 0.535 M). The mixture was stirred at 100 °C for 15 min. After that, the precipitate was collected by centrifugation, washed three times with DMF and ethanol, respectively, and dried under a vacuum oven (60 °C, 12 h) CdS/Ce-U66 was prepared with the same procedure used for the synthesis of CdS/Ce-U66(NH_2).

Zr-U66 and CdS/Zr-U66. Zr-U66 was synthesized according to previous report.[2] $ZrCl_4$ (233 mg) and terephthalic acid (166 mg) were dispersed in DMF (50 mL), followed by addition of 150 µL acetic acid. After heating at 120 °C for 24 h, the solid was collected, washed with DMF and ethanol several times, respectively, and dried under a vacuum oven at 60 °C overnight. Then 40% CdS/Zr-UiO-66 was synthesized with the same procedure used for the synthesis of CdS/Ce-U66(NH_2).

Zr-U66(NH_2) and CdS/Zr-U66(NH_2). Zr-U66-NH_2 was synthesized according to previous report.[2] $ZrCl_4$ (233 mg) and 2-aminoterephthalic acid (181 mg) were dispersed in DMF (50 mL), followed by addition of 150 µL H_2O. After heating at 120 °C for 24 h, the solid was collected, washed with DMF and ethanol several times, respectively, and dried under a vacuum oven at 60 °C overnight. Then 40% CdS/Zr-UiO-66-NH_2 was synthesized with the same procedure used for the synthesis of CdS/Ce-U66(NH_2).

0.5% Pt/CdS and 0.5% Pt/Ce-U66(NH_2). A mixture of 3.2 µL H_2PtCl_6 solution (8 wt%), 50 mL sacrifice aqueous solution (0.35 M Na_2S, and 0.25 M Na_2SO_3), and 25 mg CdS or Ce-U66(NH_2) was purged with N_2 for 30 min, and then irradiated for 2 h with four 3 W LED lamps (420 nm). After that, the solid was collected by centrifugation, washed with water, and dried in a vacuum oven at 60 °C overnight.

References

1 M. Lammert, M. T. Wharmby, S. Smolders, B. Bueken, A. Lieb, K. A. Lomachenko, D. D. Vos and N. Stock, *Chem. Commun.*, 2015, **51**, 12578–12581.
2 C. Gomes Silva, I. Luz, F. X. Llabrés i Xamena, A. Corma and H. García, *Chem. Eur. J.*, 2010, **16** 11133–11138.

Table S1. Recipe for synthesis of CdS/Ce-U66(NH$_2$) samples

Reagents	30% CdS	40% CdS	50% CdS	60% CdS	CdS
Ce-U66(NH$_2$) (mg)	70	60	50	40	0
$Cd(CH_3COO)_2 \cdot 2H_2O$ (mg)	55.3	73.8	92.2	110.6	184.4
$Na_2S \cdot 9H_2O$ (mg)	49.8	66.4	83.0	99.6	166

Table S2. Band gap energies estimated through different methods[a]

Samples	E_{sp} (eV)	E_{diff} (eV)	$E_{g,\ direct}$ (eV)	$E_{g,\ indirect}$ (eV)
Zr-U66	3.92	3.85	4.00	3.82
Ce-U66	3.05	2.95	3.18	2.98
Zr-U66(NH$_2$)	2.80	2.85	2.82	2.65
Ce-U66-66(NH$_2$)	1.92	–	2.86	1.60
CdS	2.25	2.25	2.38	2.08

[a] E_{sp} is the spectral edge, while E_{diff}, $E_{g,\ direct}$, and $E_{g,\ indirect}$ are the differentiated, direct and indirect band gap energies, respectively. Please see the details in Fig. S3. Because E_{diff} is independent of the transition type, its value is used as the working band gap energy. However, the E_{diff} for Ce-U66(NH$_2$) was not clearly defined. Then the E_{sp} is used as the working band gap energy for Ce-U66(NH$_2$).

Table S3. XPS analysis for Ce^{3+} and Ce^{4+} species in different samples[a]

Species	U66(Ce)-NH$_2$			40% CdS/U66(Ce)-NH$_2$			[b]40% CdS/U66(Ce)-NH$_2$		
	BE (eV)	*A*	*Y* (%)	BE (eV)	*A*	*Y* (%)	BE (eV)	*A*	*Y* (%)
Ce^{3+}	881.2	5322	45.4	881.3	3963	45.1	881.3	5907	40.5
	885.6	66820		885.7	31254		885.6	46795	
	899.4	21364		899.4	14230		899.4	18903	
	904.0	112709		904.0	41811		904.0	53462	
Ce^{4+}	883.0	58591	54.6	883.0	38520	54.9	882.8	44138	59.5
	887.5	52388		887.6	22316		887.6	35676	
	898.4	4322		898.5	2041		898.5	7336	
	901.5	23936		901.5	10051		901.3	22936	
	907.4	49349		907.5	20006		907.4	37996	
	917.1	59796		917.1	18022		917.0	35627	

[a] BE, binding energy; *A*, peak area; *Y*, relative content. [b] After 8 h photoreaction.

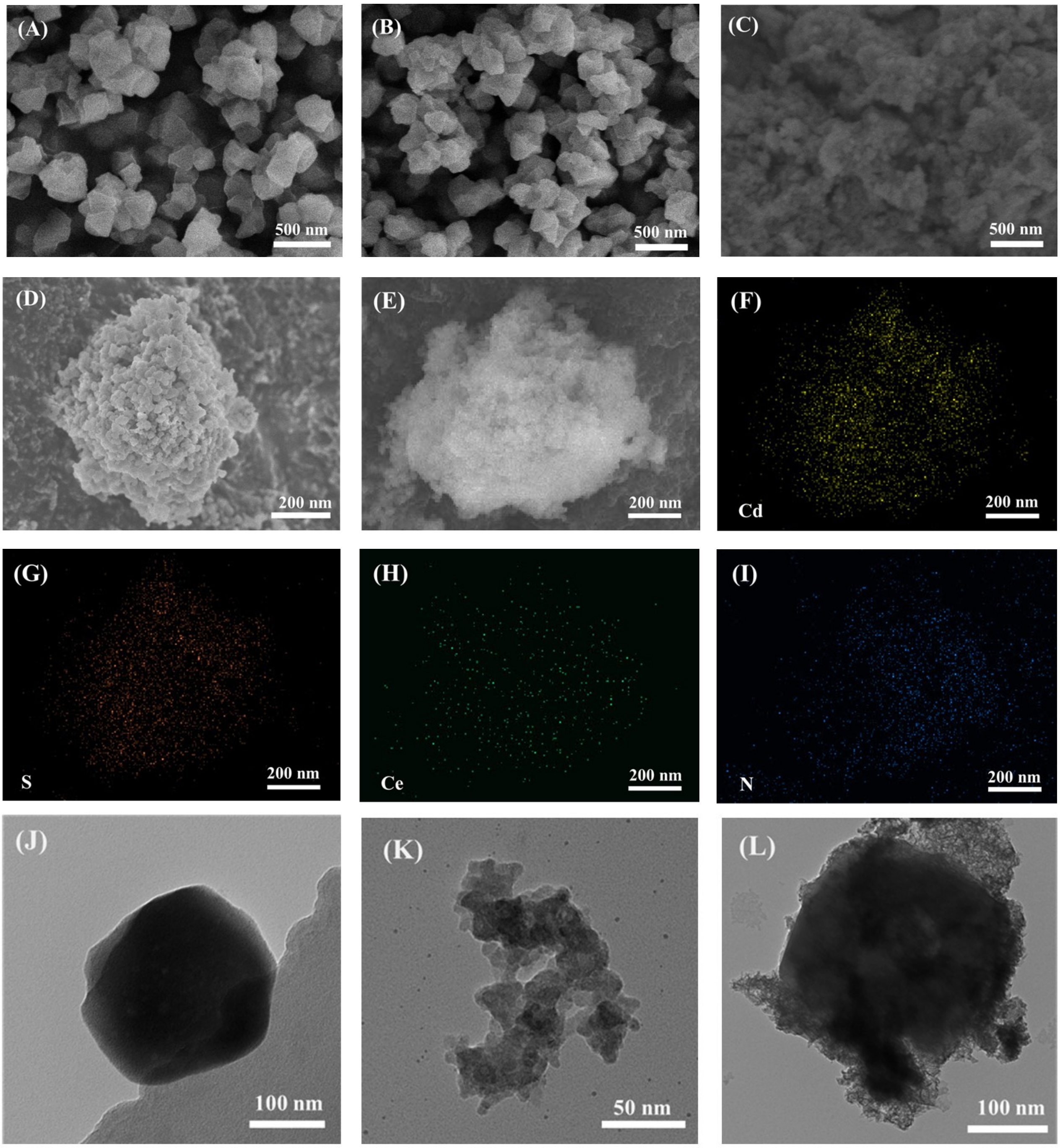

Fig. S1 SEM images (top two panels) for (A) Ce-U66, (B) Ce-U66(NH_2), (C) CdS, (D) 40% CdS/ Ce-U66(NH_2), and (E-I) Elemental mapping for 40% CdS/Ce-U66(NH_2). TEM images (bottom panel) for (J) Ce-U66(NH_2), (K) CdS, and (L) 40% CdS/Ce-U66(NH_2).

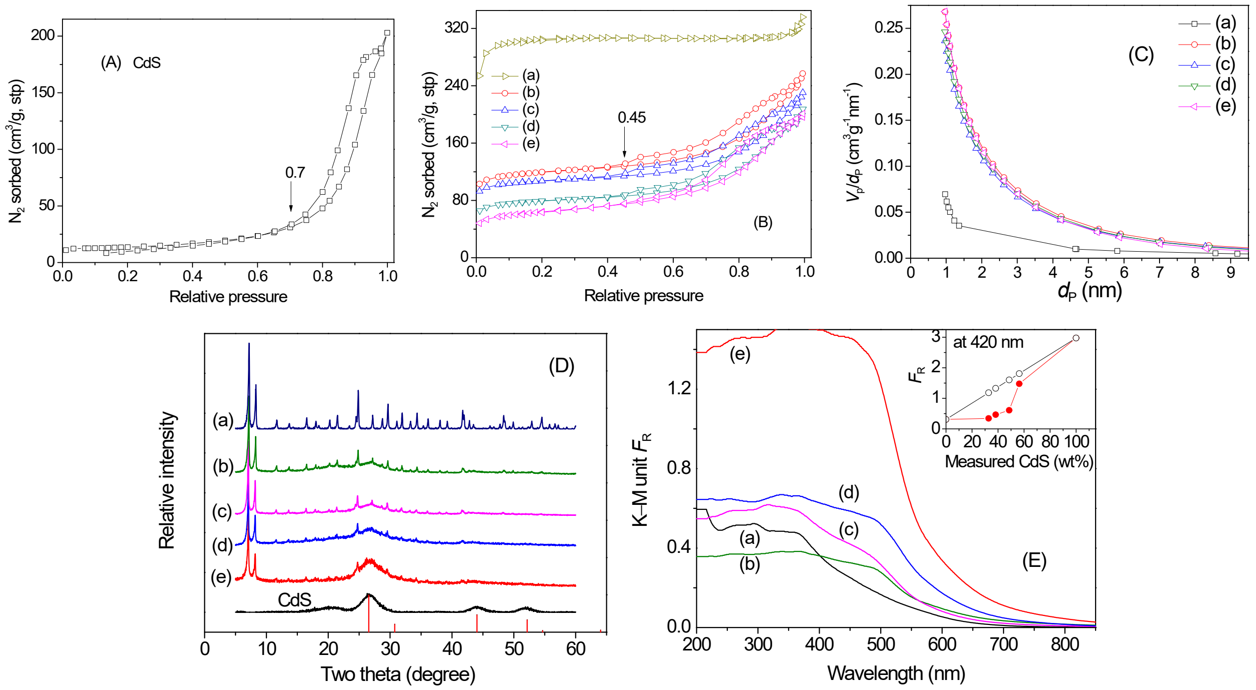

Fig. S2 (A, B) Adsorption and desorption isotherms N$_2$, (C) BJH pore size distribution, (D) XRD patterns, and (E) absorption spectra for *x*CdS/Ce-U66(NH$_2$), where *x* was (a) 0, (b) 30, (c) 40, (d) 50, and (e) 60 wt%. The column bars represent the patterns for cubic CdS (PDF 80-0019).

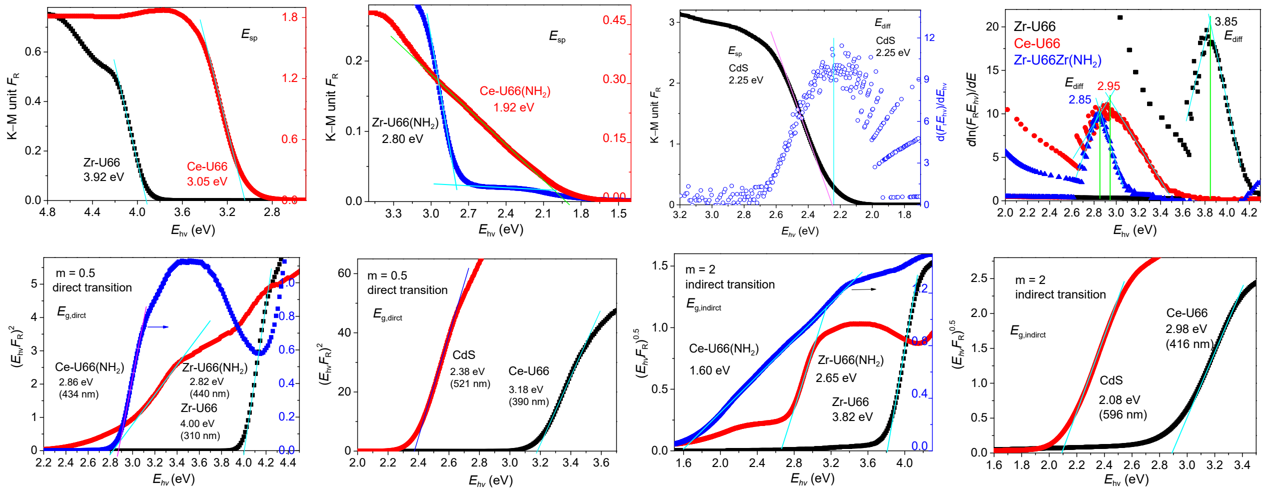

Fig. S3 Spectral edge (E_{sp}), differentiated band gap energy (E_{diff}), direct transition band gap energy ($E_{g,\ direct}$), and indirect transition band gap energy ($E_{g,\ indirect}$). The calculation is based on the equation of $\alpha E_{hv} = a(E_{hv} - E_g)^m$, where α is absorption coefficient, E_{hv} is light energy, *a* is constant, E_g is band gap energy (*m* = 0.5, direct; *m* = 2, indirect). From the equation, we have $d(\alpha E_{hv})/dE_{hv} = m/(E_{hv} - E_g)$. Then $d(\alpha E_{hv})/dE_{hv}$ is infinite at $E_{hv} = E_g$, which is E_{diff}, and is independent of *m*. These values are compiled in Table S2.

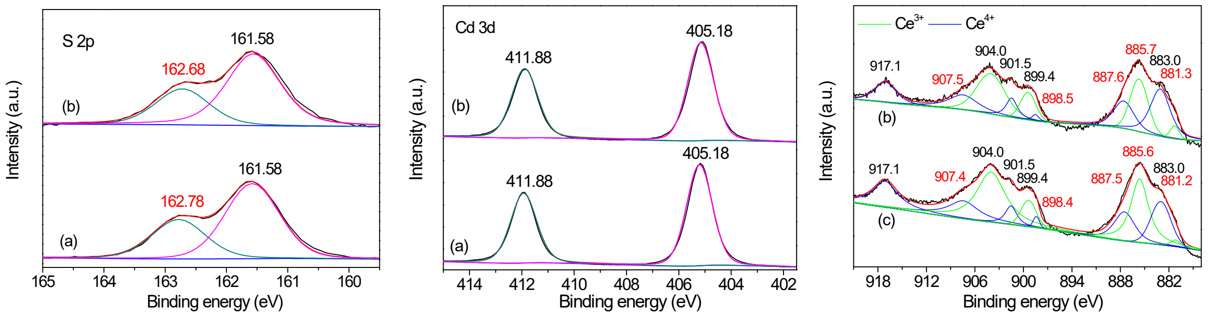

Fig. S4 XPS spectra for (a) CdS, (b) 40% CdS/Ce-U66(NH_2), and (c) Ce-U66(NH_2).

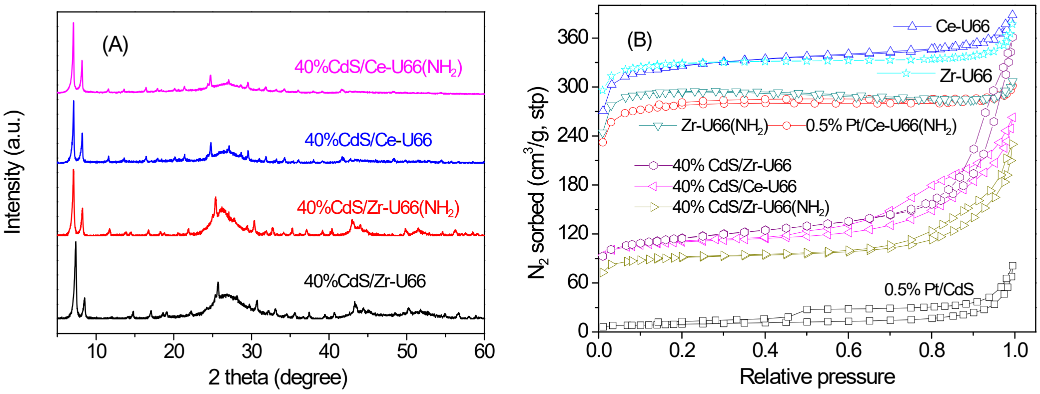

Fig. S5 (A) XRD patterns and (B) N_2 adsorption/desorption isotherms for diffent samples.

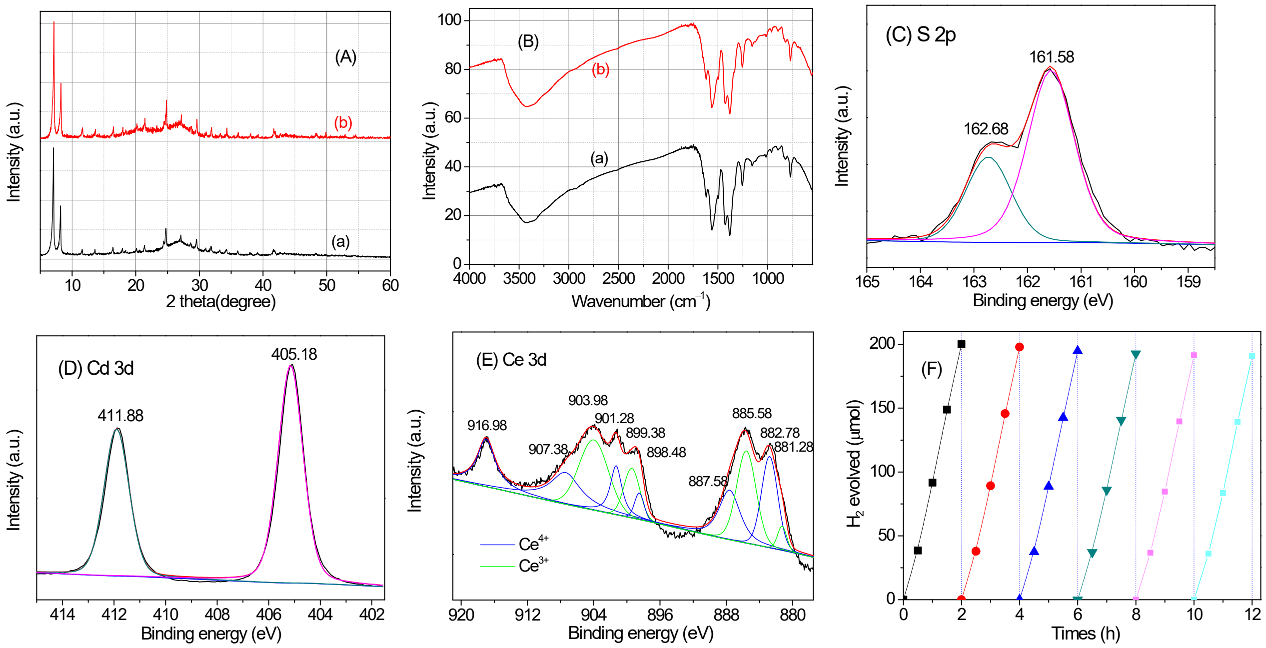

Fig. S6 (A) XRD patterns, (B) FT-IR spectra, and (C–E) XPS spectra for 40%CdS/Ce-U66(NH_2), (a) before and after H_2 production for 8 h. (F) Six-repeat production of H_2 on 40%CdS/Ce-U66(NH_2). After one run, the suspension was purged with N_2 for 30 min, and then irradiated, without addition of any new components.

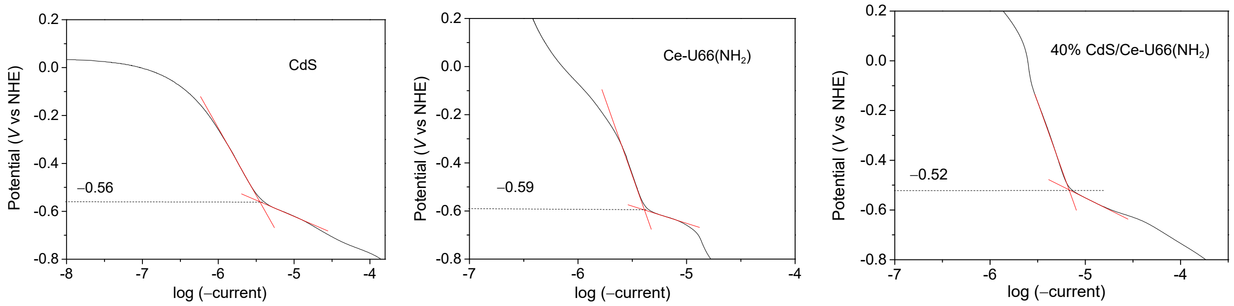

Fig. S7 Curve fitting for proton reduction (top panels) and water oxidation (bottom panels).

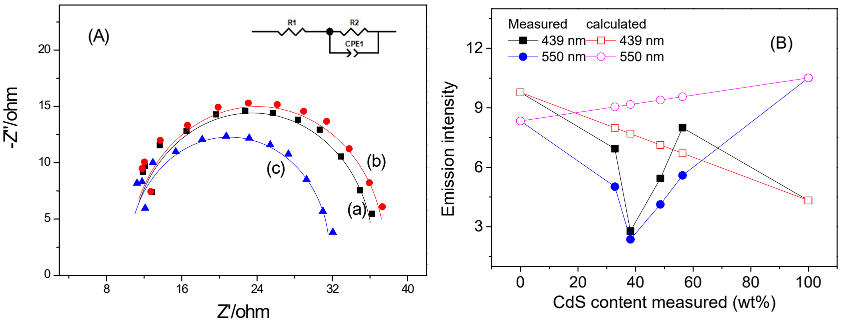

Fig. S8 (A) Nyquist plots at 0.2 V vs. NHE for (a) CdS, (b) Ce-U66(NH_2), (c) 40% CdS/Ce-U66(NH_2), measured in 0.5 M $NaClO_4$ under N_2. The solid curves match an equivalent circuit model (insert), where R_1 is series resistance, R_2 is charge transfer resistance, and CPE_1 is bulk capacitance. (B) Measured and calculated emission intensity for CdS/Ce-U66(NH_2), where the CdS content was measured by ICP.

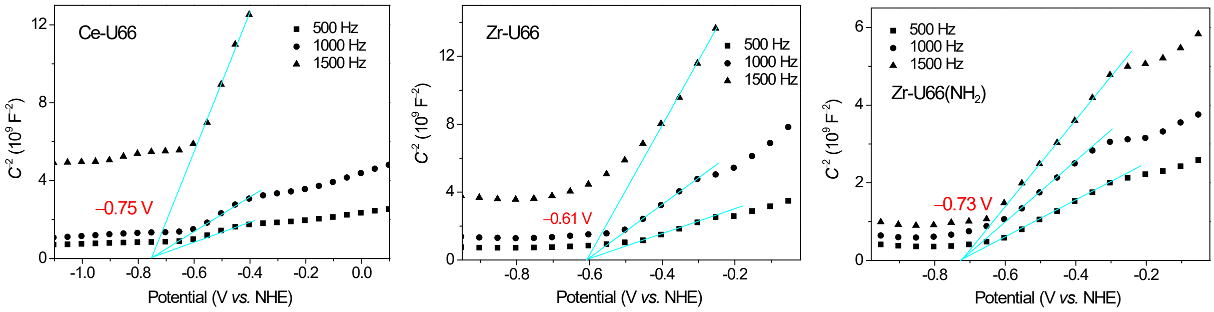

Fig. S9 Mott–Schottky plots for the samples as indicated by the legends. Experiment was conducted at different frequencies in a bubbling N_2 of 0.5 M $NaClO_4$.