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Supporting Information

A sensitive dual-signal electrochemiluminescence immunosensor based on $Ru(bpy)_3^{2+}$@HKUST-1 and $Ce_2Sn_2O_7$ for detecting heart failure biomarker NT-proBNP

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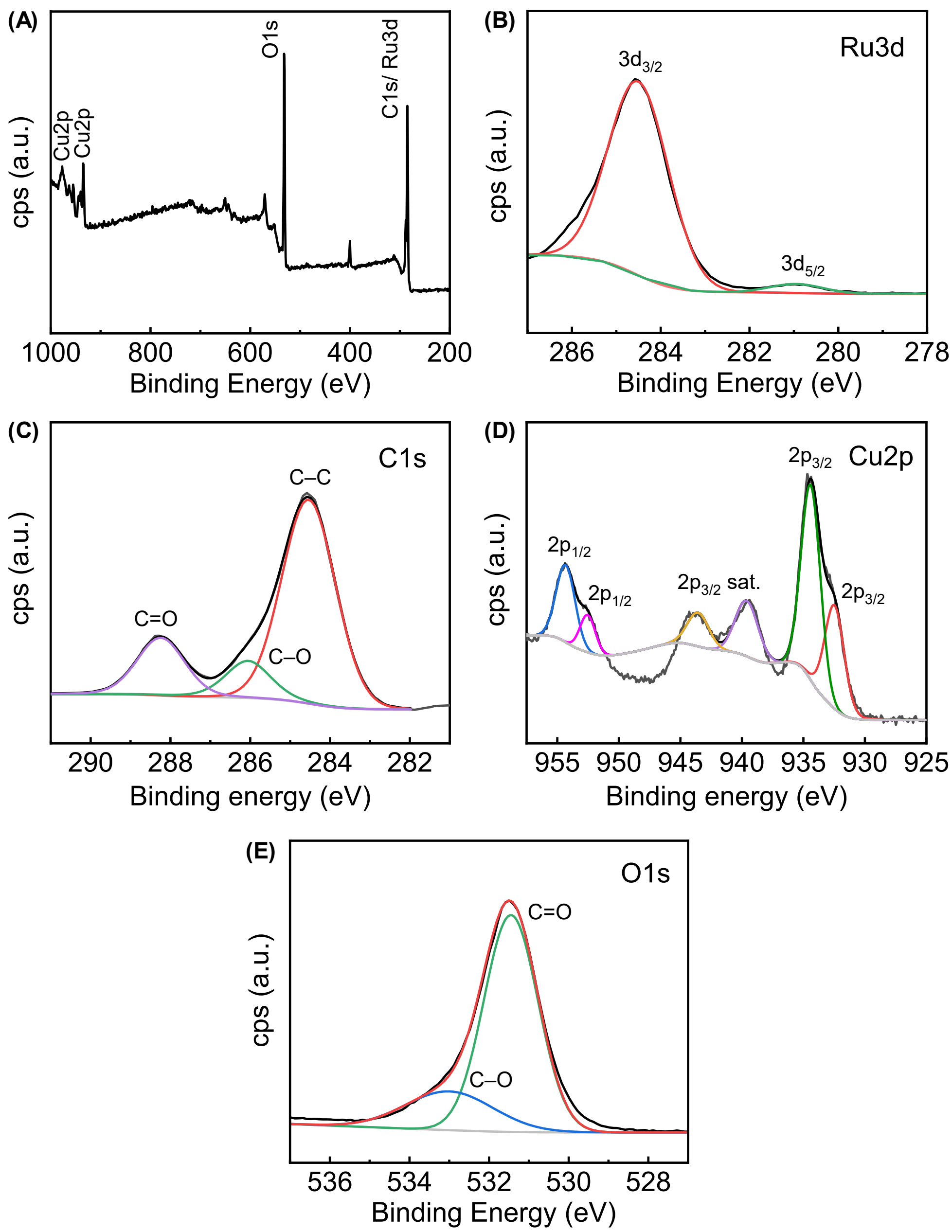

Fig. S1 (A) XPS spectra of the Ru(bpy)$_3^{2+}$@HKUST-1 composite and (B–E) the corresponding Ru3d, C1s, Cu2p and O1s core-level high-resolution spectra.

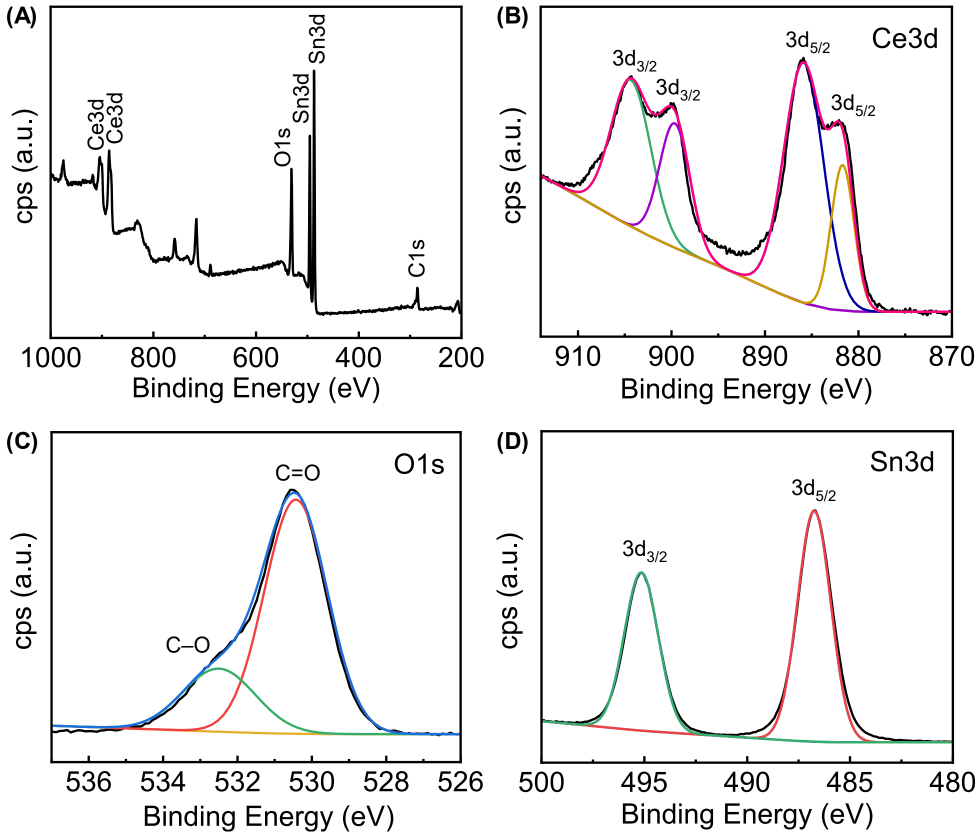

Fig. S2 (A) XPS spectra of the $Ce_2Sn_2O_7$ nanocubes and (B–D) the corresponding Ce3d, O1s and Sn3d core-level high-resolution spectra.

Table S1 The equivalent circuits fitting results of AC impedance spectra in Figure 3D.

Electrode*	R_s (Ω)	R_{ct} (Ω)	C_{dl} (μF)	Z_W (Ω)
a	113.2±1.1	130.4±3.6	3.4±0.6	260.5±26.9
b	111.9±1.2	127.9±5.5	24.4±4.8	263.5±24.2
c	108.0±1.3	150.4±22.4	2.7±0.8	664.4±68.7
d	103.5±0.9	272.9±5.0	2.3±0.3	201.6±33.0
e	112.6±1.1	401.1±39.0	2.3±0.4	1408±119.9
f	118.2±1.1	629.2±55.8	2.8±0.3	850.2±251.0

*(a) bare GCE, (b) $Ru(bpy)_3^{2+}$@HKUST-1/GCE, (c) Ab_1/$Ru(bpy)_3^{2+}$@HKUST-1/GCE, (d) BSA/Ab_1/$Ru(bpy)_3^{2+}$@HKUST-1/GCE, (e) NT-proBNP/BSA/Ab_1/$Ru(bpy)_3^{2+}$@HKUST-1/GCE, (f) $Ce_2Sn_2O_7$-Ab_2/NT-proBNP/BSA/Ab_1/$Ru(bpy)_3^{2+}$@HKUST-1/GCE.

Table S2 Comparison on the NT-proBNP detection techniques.

Methods	Linear range (ng mL^{-1})	Ref.
EC[a]	0.02–100	[1]
SERS[b]	1×10^{-6}–1	[2]
PEC[c]	1×10^{-4}–50	[3]
ECL[d]	5×10^{-4}–20	[4]
ECL	1×10^{-3}–50	[5]
ECL	5×10^{-4}–1×10^{4}	This work

[a]EC: electrochemistry. [b]SERS: surface-enhanced Raman spectroscopy. [c]PEC: photoelectrochemistry. [d]ECL: electrochemiluminescence.

Note S1 Calculations on LOD and LOQ

To calculate the limit of detection (LOD) and limit of quantification (LOQ), an ECL measurement of ten parallel blank solutions was implemented. The mean calibration signal intensity of the blank ($\triangle I_B$) is 4395 ($\triangle I_B$ = 4255, 4420, 4425, 4467, 4355, 4180, 4361, 4323, 4648, 4515, respectively) with a standard deviation (S_B) of 133.

Due to the negative linear relationship between calibration signal intensity ($\triangle I_{ECL}$) and logarithm of NT-proBNP concentration (Figure 5C), the largest detectable calibration signal intensity ($\triangle I_L$) and quantitative calibration signal intensity ($\triangle I_Q$) are calculated as follows [6]:

$\triangle I_L = \triangle I_B - 3S_B$

$\triangle I_Q = \triangle I_B - 10S_B$

Therefore, by substituting $\triangle I_L$ and $\triangle I_Q$ into the standard calibration curve ($\Delta I_{ECL} = -1468.04 \times \lg(C_{NT\text{-}proBNP}) + 88.03$), the LOD and LOQ of NT-proBNP are calculated to be 2.2 pg mL^{-1} and 9.4 pg mL^{-1}, respectively.

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