Supporting Information

Label-free and Ultrasensitive Electrochemiluminescent Immunosensor Based on Novel Luminophores of $Ce_2Sn_2O_7$ Nanocubes

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Content

Chemicals and Materials. Human CEA antibody (anti-CEA) and Human CEA antigen were purchased from Shanghai Linc-Bio Science Co. Ltd. $HAuCl_4 \cdot 3H_2O$, Sodium borohydride ($NaBH_4$), $Ce(NO_3)_3 . 6H_2O$, $K_2SnO_3 . 3H_2O$, 3-aminopropyltriethoxysilane (APTES, 98%) and NaOH were obtained from Shanghai Aladdin Chemistry Co., Ltd, China. Potassium peroxydisulfate was acquired from Fuchen Chemical Reagent Co., Ltd. (Tianjin, China). Bovine serum albumin (BSA) was obtained from the Sigma-Aldrich (Beijing, China). The phosphate-buffered saline (PBS) with a number of pH value was prepared through mixing the stock solution of NaH_2PO_4 (0.1 M) and Na_2HPO_4 (0.1 M), PBS containing potassium peroxydisulfate as an electrolyte was used to perform the entire electrochemical measurements experiments. Double-distilled water was used during the whole of experiments. All of the chemicals were of analytical reagent grade and utilised without further treatment.

Instrumentation. The Transmission Electron Microscopy (TEM), High-Resolution TEM (HRTEM) and Energy Dispersive Spectroscopic (EDS) photos of $Ce_2Sn_2O_7$ and $Au@Ce_2Sn_2O_7$ were attained by an FEI Talos F200S G2 microscope (Thermo Scientific FEI, United States). X-ray power diffraction (XRD) pattern was accomplished with a D/MAX 2200 VPC powder diffractometer (Rigaku, Japan). The Raman spectroscopic spectra were recorded by a confocal Raman microspectrometer with an excitation wavelength of 533.0 nm (Renishaw inVia, UK). ECL tests for $Ce_2Sn_2O_7$ were attained with an EC&ECL multifunctional analyzer (MPI-E, Remex Electronic Instrument Co., Ltd., Xi'an, China) through using three conventional electrode systems: by using glassy carbon electrode (GCE, 3 mm in diameter) as a working electrode, Ag/AgCl as a reference electrode and platinum wire as an auxiliary electrode. ECL emission spectra of $Ce_2Sn_2O_7$–$K_2S_2O_8$ system and the related ECL photos on GC electrodes were recorded through an IsoPlane 160 spectrometer equipped with a ProEM HS EMCCD camera (Princeton Instruments) by a cooling temperature of -60 °C. The photoluminescence (PL) spectrum was recorded in the spectral range of 300–600 nm at RT (room temperature) using a Xe laser with a wavelength of 280 nm as the excitation source. Electrochemical impedance spectroscopy (EIS) tests were accomplished by Autolab AUT302N, Metrohm Autolab .BV (Netherlands) [1].

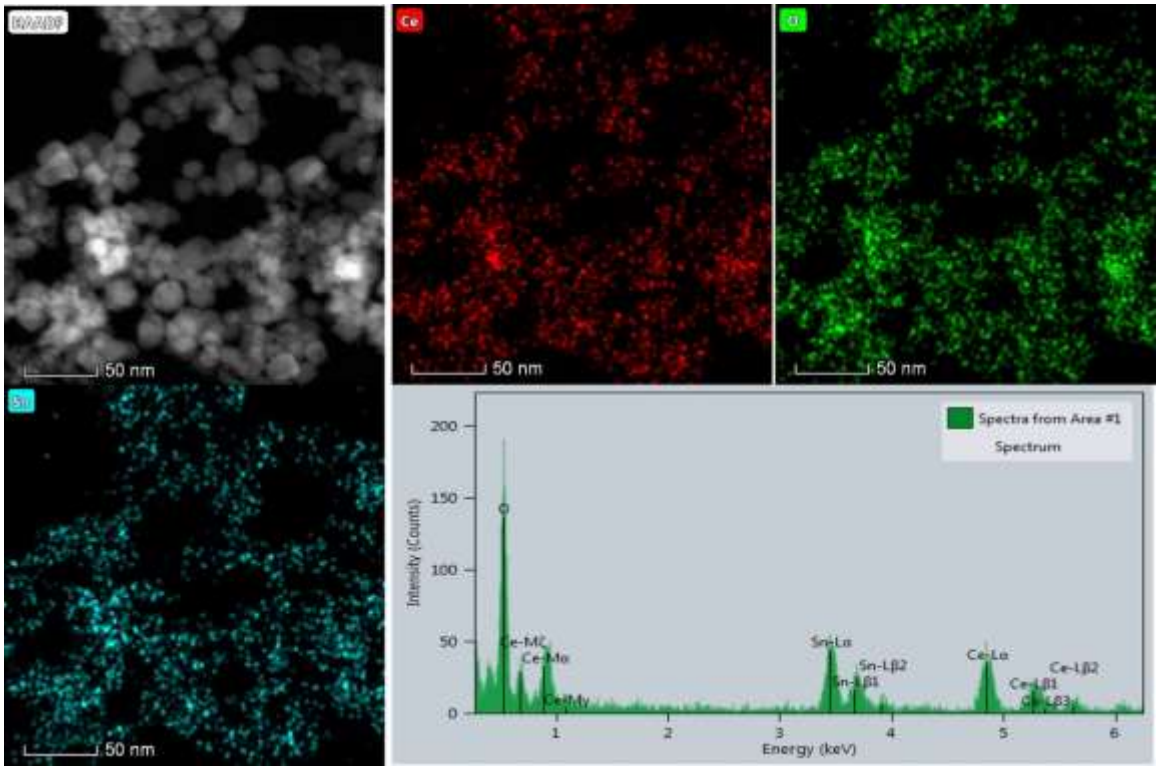

Figure S1. HAADF STEM image and corresponding mapping images and EDS of $Ce_2Sn_2O_7$.

Measurement for ECL Quantum Efficiency

The ECL quantum efficiency of $Ce_2Sn_2O_7$ nanocubes was measured according to Equation S1.[s1]

$$\emptyset_{ECL} = \emptyset^{\circ}_{ECL} \frac{IQ^{\circ}}{I^{\circ}Q} = 5\% \times \frac{11980(a.u.\ s) \times 0.1588\ (Coulombs)}{7950(a.u.\ s) \times 0.2626\ (Coulombs)} = 4.55\% \qquad \text{(S1)}$$

whereas $\emptyset_{ECL}$, $\emptyset^{\circ}_{ECL}$ are the ECL quantum efficiencies of $Ce_2Sn_2O_7$ (the target ECL luminophore) and $Ru(bpy)_3^{2+}$ (the standard ECL luminophore, $\emptyset^{\circ}_{ECL}$ = 5.0%), while I and I° are their integrated ECL intensities, where Q and Q° are the charges passed through $Ce_2Sn_2O_7$ and $Ru(bpy)_3^{2+}$, correspondingly. From the acquired result it can be concluded that the ECL efficiency of $Ce_2Sn_2O_7$ was strong with a value of 4.55%.

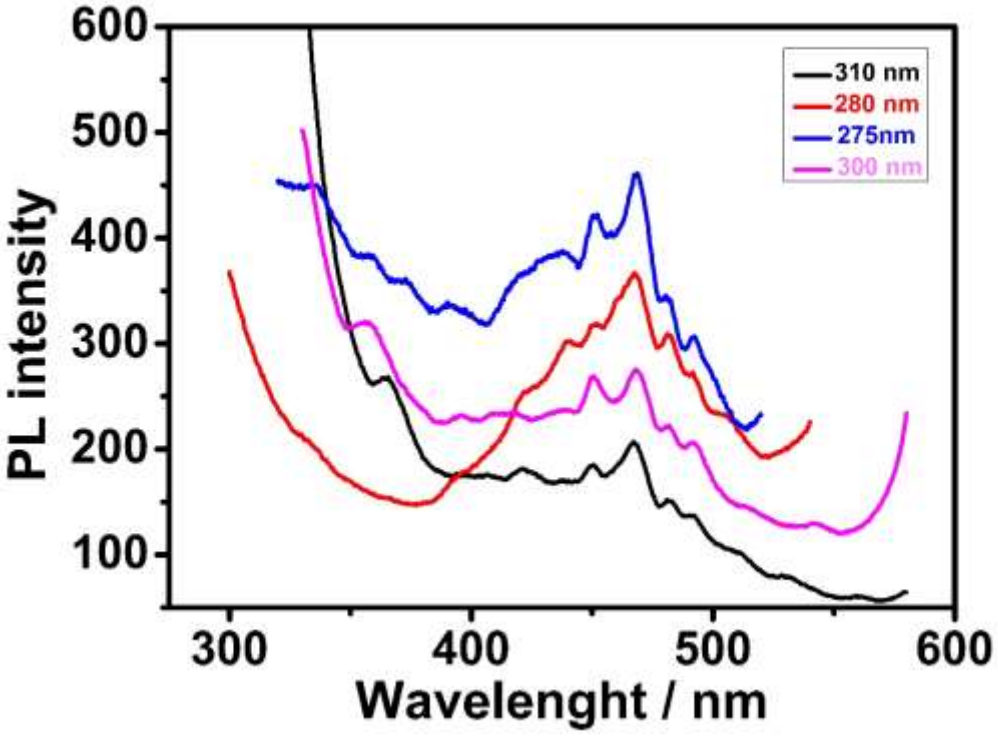

Figure S2. PL spectra of $Ce_2Sn_2O_7$ nanocubes under different excitation wavelengths.

Table S1. A comparison of the performances of proposed and referenced sensors for detection of CEA.

ECL materials of Sensors	Linear range	Detection limit	References
ZnS–CdS/MoS_2	0.05-20 ng/mL	31 pg/mL	S2
Au-g-C_3N_4 NHs	0.02−80 ng/mL	6.8 pg/mL	S3
GO/MWCNTs-COOH/Au@CeO_2	0.05-100 ng/mL	20 pg/mL	S4
AuNPs/PDDA/cit-rGO-$BaYF_5$	0.001-80 ng/mL	0.87 pg/mL	S5
Au@$Ce_2Sn_2O_7$	0.01-50 ng/mL	0.53 pg/mL	This work

Table S2. Results obtained for CEA detection in serum samples

Initial CEA concentration in sample (ng/mL)	Added CEA concentration (ng/mL)	Measured concentration after addition (ng/mL)	Average value (ng/mL)	RSD (%,n=5)	Recovery (%, n=5)
1.44	0.5	1.90, 2.01, 2.05, 1.97, 1.87	1.96	3.8	101.1
	1.5	2.94, 3.01, 2.91, 2.88, 2.99	2.95	1.8	100.3
	3.0	4.42, 4.36, 4.46, 4.39, 4.40	4.40	0.8	99.1

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