Electronic Supporting Information

Near-infrared Electrochemiluminescence from Toxic-less $CuInS_2$ Nanocrystals

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Content

(a) Chemicals and reagents

All chemicals were of analytical grade and used as received. Copper (I) iodide (CuI, 99.5%), 1-dodecanethiol (DDT, 98%), 1-octadecene (ODE, 90%), oleic acid (OA), tripropylamine (TPrA, 99%), were purchased from Aladdin Industrial Co., Ltd. (Shanghai, China). Acetonitrile (MeCN), chloroform, and acetone were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Tetra-n-butylammonium hexafluorophosphate ($TBAPF_6$) were purchased from Sigma-Aldrich (Milwaukee, WI, USA). Indium (III) acetate ($In(OAc)_3$, 99.99%) was purchased from Acros Organics. The N_2-saturated supporting electrolyte solution was prepared by bubbling the solution with high-purity nitrogen for 5 min, and then the electrochemical and ECL measurements were performed under nitrogen atmosphere via blowing N_2 over the surface of supporting electrolyte solution. The O_2-saturated supporting electrolyte solution was prepared by bubbling the solution with high-purity oxygen for 5 min, and then the electrochemical and ECL measurements were performed under oxygen atmosphere via blowing O_2 over the surface of supporting electrolyte solution.

(b) Apparatus

The common optical, electrochemical and ECL characterizations were performed out with the apparatuses and methods reported previously.[1, 2] Photoluminescence (PL) spectra were recorded with F-320 spectrofluorimeter (Tianjin GangdongSci & Tech Development Co., Ltd., China). Ultraviolet-visible (UV-vis) absorption spectra were conducted with a TU-1901 UV−vis spectrophotometer (Beijing Purkinje General Instrument Co., Ltd., China). The fluorescence lifetime and PL quantum yields (QY) was determined with FSL 920 fluorescence spectrometer (Edinburgh Instrument. U.K.). X-ray photoelectron spectroscopy (XPS) was taken from ESCALAB 250 XPS using monochromatic Al Kα radiation (Thermo Fisher Scientific Co., U.S.A.). High-resolution transmission electron microscopy (HRTEM) pattern was recorded on TecnaiG2 F30 transmission electron microscope (Thermo Fisher Scientific Co., U.S.A) with an acceleration voltage of 300 kV. Scanning electron micrographs (SEM) patterns were acquired using a JEOL JSM-6700F field emission scanning electron microscope (Japan Electron Optics Laboratory Co., Ltd., Japan). Electron paramagnetic resonance (EPR) spectra were recorded at room temperature using a Bruker E500 spectrometer

(Bruker, Germany). Electrochemistry and ECL were performed on an MPI-EII ECL analyzer (Xi'An Remex Analytical Instrument Co., Ltd., China) using a three-electrode system, including a GCE (5 mm in diameter) work electrode, a Pt coil counter electrode, and Ag/Ag^+ as the reference electrode. Nonaqueous Ag/Ag+ reference electrodes were fabricated from silver wires that were dipped into a 10 mM silver nitrate solution in 0.1 M $TBAPF_6$/MeCN. ECL spectra and image were obtained with a homemade ECL spectrum acquiring device,[3, 4] including an Acton SP2300i monochromator (Acton, 300 mm, the 150 G/mm ruled grating with 500 nm blaze wavelength was blazed at 500 nm), a PyLoN 400BR-eXcelon digital CCD (Princeton Instruments, USA), a VersaSTAT 3 analyzer (Princeton Applied Research, USA), a specially designed light path and a controlling device, which could synchronously trigger and operate the CCD and VersaSTAT 3 analyzer for timely recording the ECL spectrum. Scanning electron micrographs (SEM) patterns were acquired using a SUPRA 55 field emission scanning electron microscope (Carl Zeiss AG, Germany). Differential pulse voltammetry (DPV) was recorded with a CHI 822 electrochemical analyzer (Shanghai, China).

(c) PL Life time parameters of CIS NCs

Table S1. PL Life time parameters for as-prepared CIS NCs

Sample	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	τ_{av} (ns)	χ^2
$CuInS_2$	156.6	37.8	420.3	62.2	371.6	1.135

The PL decay curves of as-prepared CIS NCs could be well-fitted by a biexponential decay model by the equation $I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$. The τ_1 and τ_2 were the decay time of the PL emission while A_1 and A_2 were the relative weights of the decay components at t= 0

(d) XPS spectra of CIS NCs

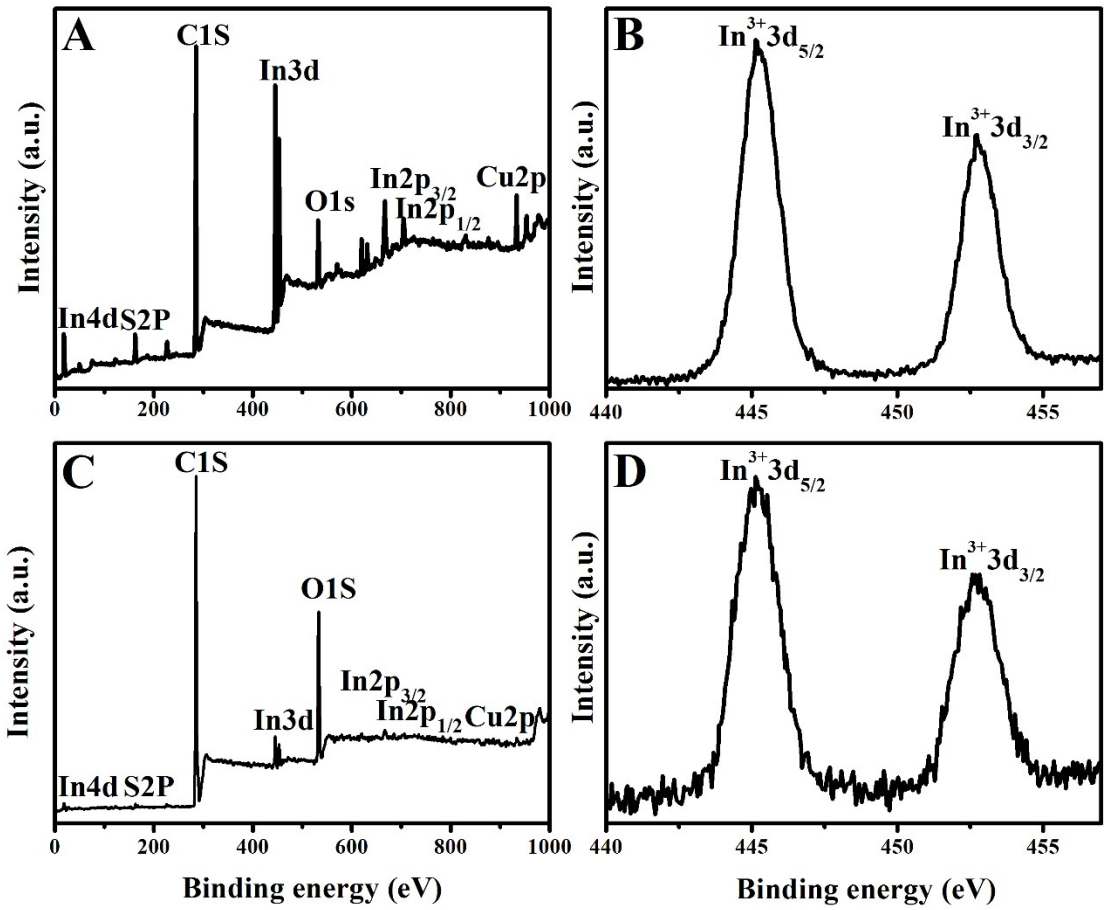

Fig. S1 XPS patterns of (A, B) normal CIS NCs and electrochemically oxidized (C, D) CIS NCs in the (A, C) survey spectra region and (B, D) In3d binding energy region, respectively.

(e) SEM pattern of CIS NCs|GCE

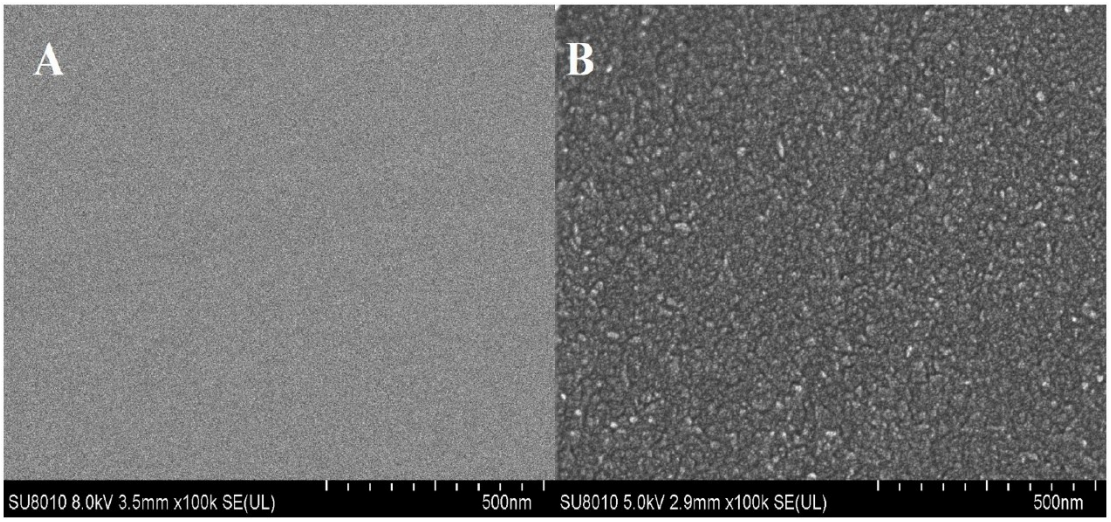

Fig. S2 SEM patterns of (A) bare GCE and (B) CIS NCs|GCE.

SEM pattern of CIS NCs|GCE proved that CIS NCs were evenly distributed on the GCE surface. The nanocrystal film of CIS NCs|GCE was composed of plenty tiny CISD NCs with size around 5 nm.

(f) Cathodic electrochemical behaviors of bare GCE in control

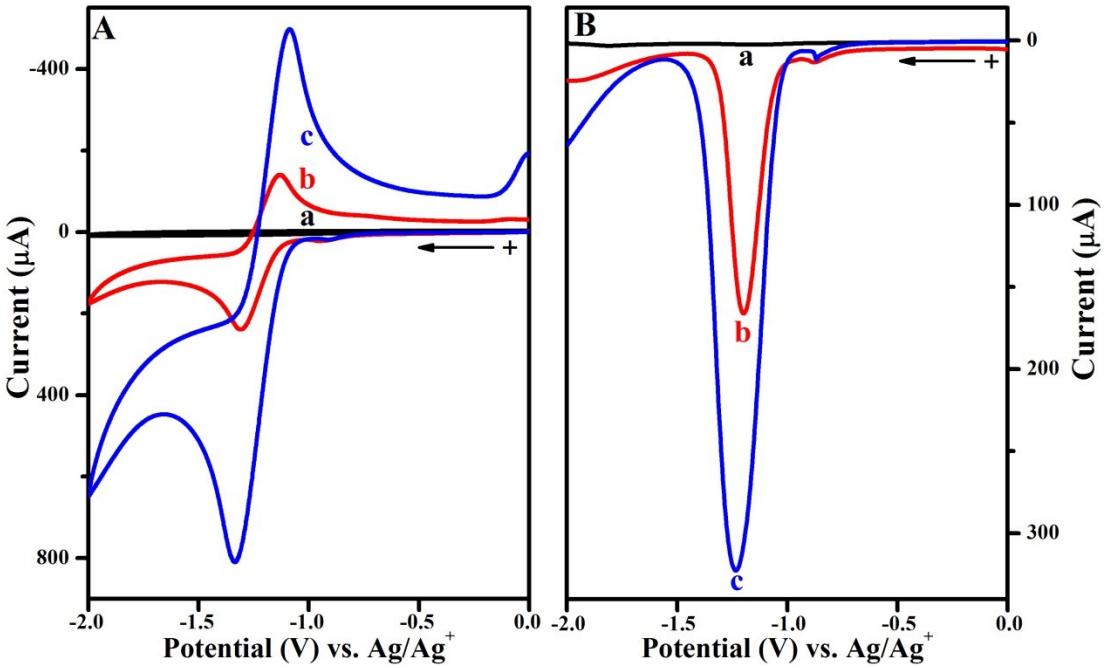

Fig. S3 Cathodic (A) CV and (B) DPV behaviors of bare GCE in (a, black line) N_2-saturated, (b, red line) air-saturated, and (c, blue line) O_2-saturated 0.1 M $TBAPF_6$/MeCN at 100 mV/s. The arrow shows the direction of potential scan. The cross indicates the starting potential.

(g) Effects of dissolved oxygen on ECL behaviors of CIS NCs|GCE

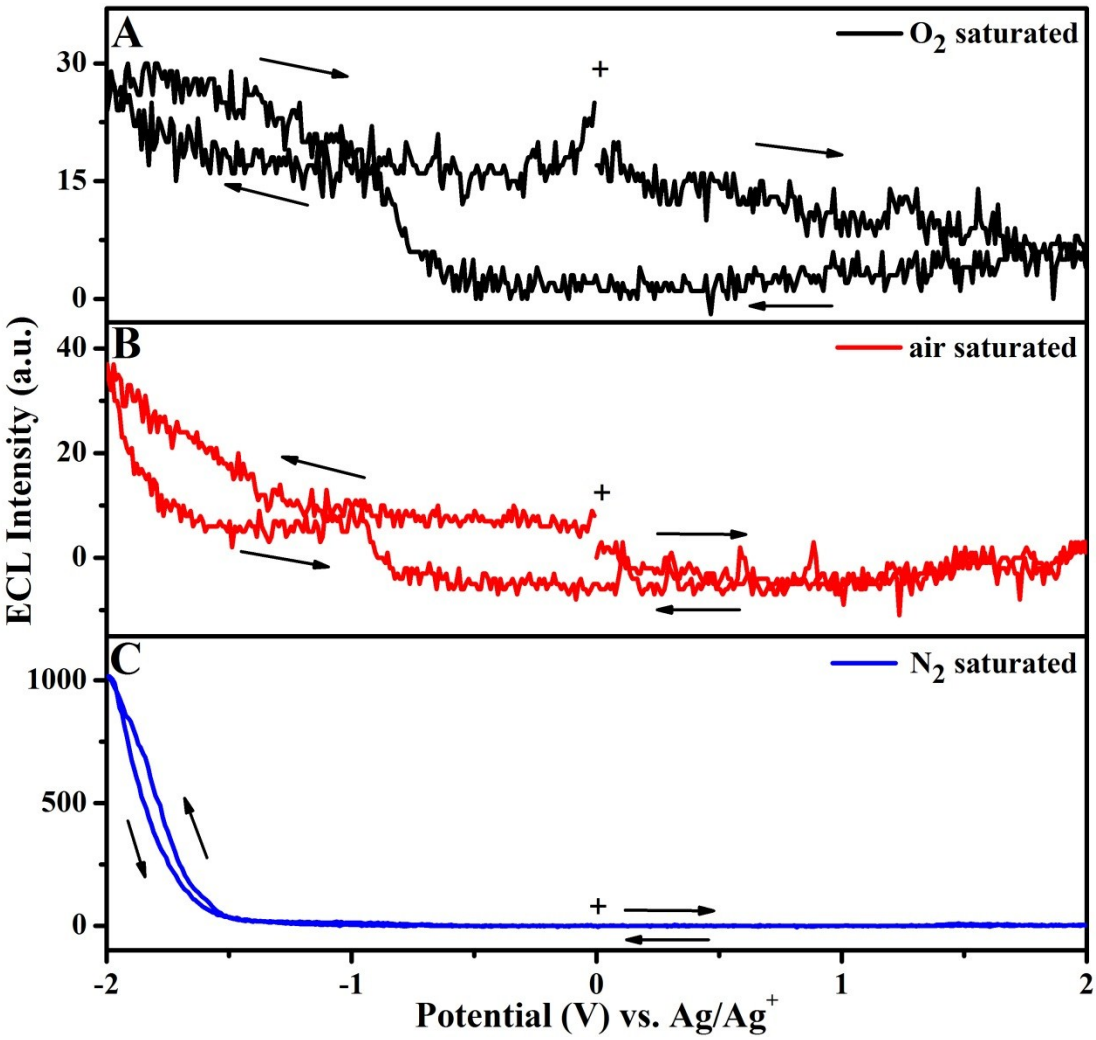

Fig. S4 Potential-resolved ECL of CIS NCs|GCE in (A, black) O_2-saturated, (B, red) air-saturated and (C, blue) N_2-saturated 0.1 M $TBAPF_6$/MeCN with positive started potential scan from 0 V and scan rate of 100 mV/s.

(h) ECL behavior of GCE and CIS NCs|GCE in air-saturated MeCN

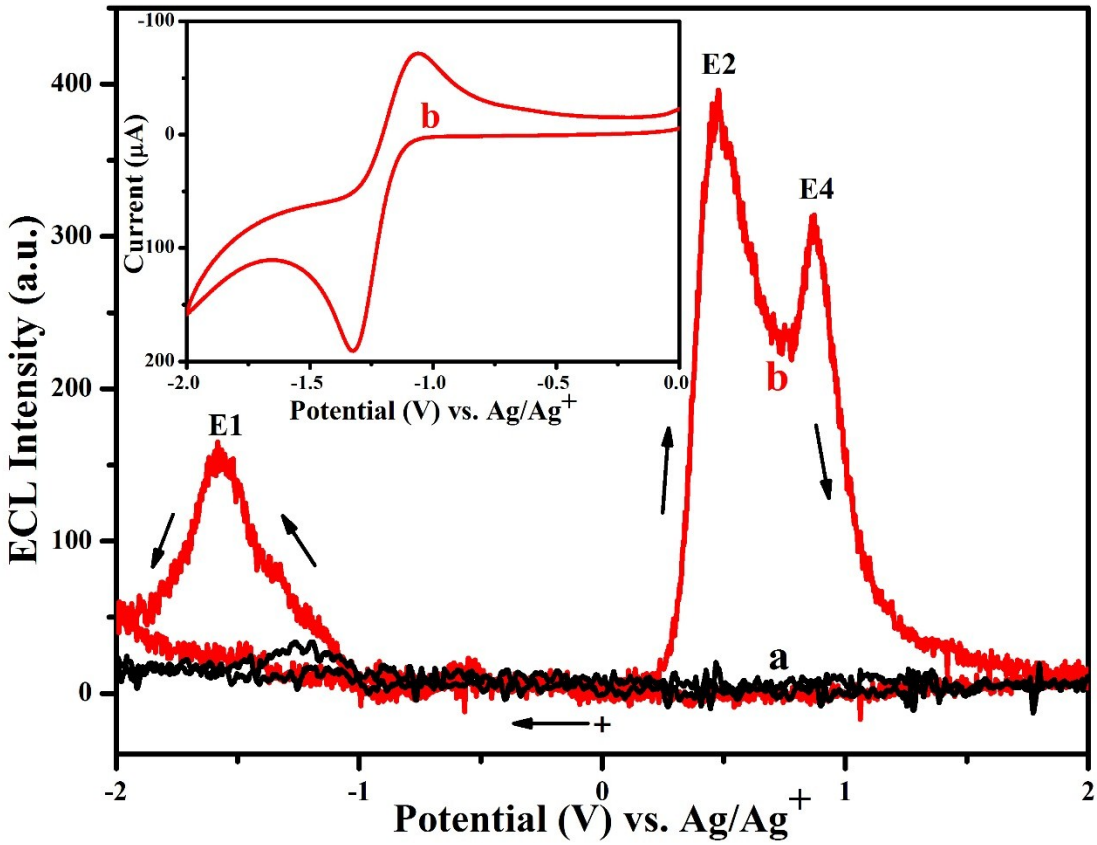

Fig. S5 Potential-resolved ECL of (a, black line) bare GCE and (b, red line) CIS NCs|GCE in air-saturated 0.1 M $TBAPF_6$/MeCN with negative started potential scan from 0 V and scan rate of 100 mV/s. Inset: cathodic CV behavior of CIS NCs|GCE in air-saturated 0.1 M $TBAPF_6$/MeCN at 100 mV/s.

(i) ECL behavior of GCE and CIS NCs|GCE in O_2-saturated MeCN

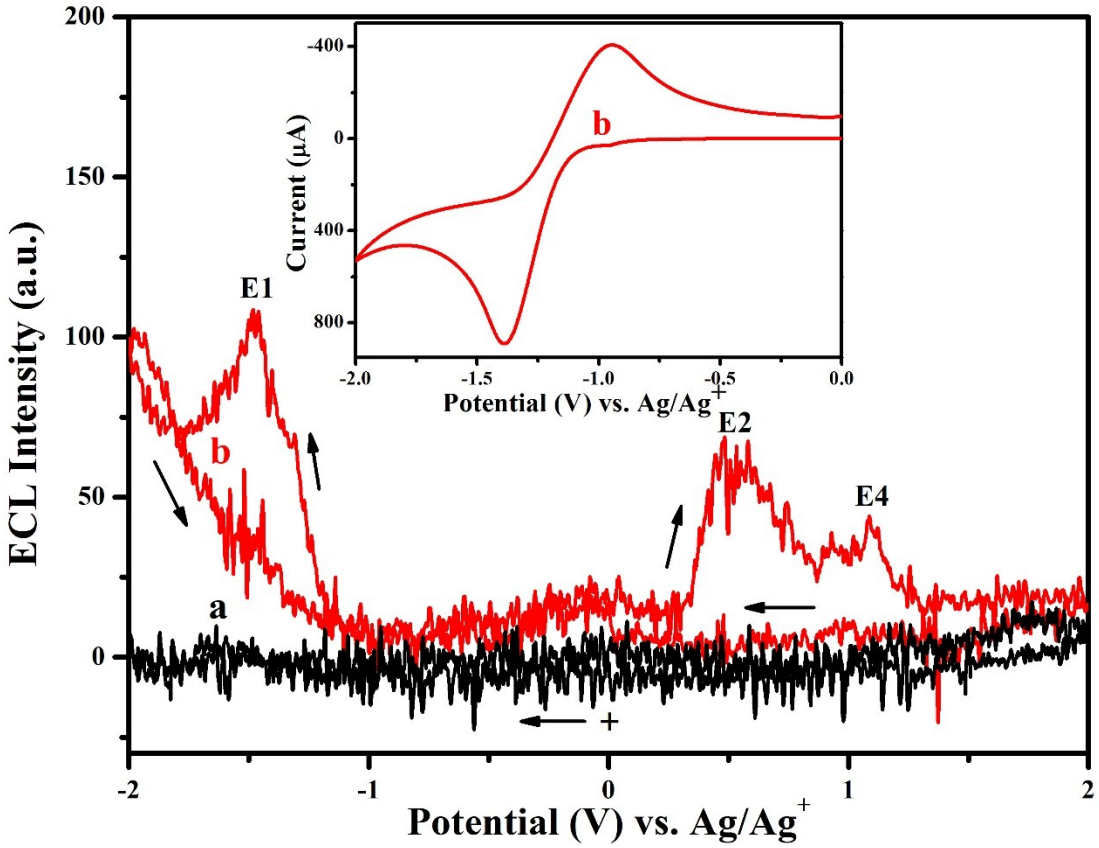

Fig. S6 Potential-resolved ECL of (a, black line) bare GCE and (b, red line) CIS NCs|GCE in O_2-saturated 0.1 M $TBAPF_6$/MeCN with negative started potential scan from 0 V and scan rate of 100 mV/s. Inset: cathodic CV behavior of CIS NCs|GCE in O_2-saturated 0.1 M $TBAPF_6$/MeCN at 100 mV/s.

(j) Reference

1. X. Tan, B. Zhang and G. Zou, *J. Am. Chem. Soc.*, 2017, **139** 8772-8776.

2. Y. Huang, M. Fang, G. Zou, B. Zhang and H. Wang, *Nanoscale*, 2016, **8**, 18734-18739.

3. X. Zhang, B. Zhang, W. Miao and G. Zou, *Anal. Chem.*, 2016, **88**, 5482-5488.

4. X. Zhang, X. Tan, B. Zhang, W. Miao and G. Zou, *Anal. Chem.*, 2016, **88**, 6947-6953.