Electronic Supplementary Information

Anisotropic growth of gold anchors onto CdSe semiconductor quantum platelets for self-assembled architectures with well-connected electronic circuits for the electrochemical detection of enrofloxacin

Yue Cao,[a] Shengyan Wang,[a] Huan Li,[a] Yan-Yan Gao,[a] Mei Li,[b] Hua Wang,[c] Wenlei Zhu[b] and Yang Zhou*[a]*

[a] *Key Laboratory for Organic Electronics & Information Displays and Institute of Advanced Materials, Nanjing University of Posts & Telecommunications (NJUPT), Nanjing 210023, PR China*

[b] *School of Environment, State Key Laboratory of Pollution Control and Resource Reuse, the Frontiers Science Center for Critical Earth Material Cycling, Nanjing University, Nanjing 210023, PR China*

[c] *Huzhou Key Laboratory of Medical and Environmental Application Technologies, School of Life Sciences, Huzhou University, Zhejiang 313000, PR China*

Corresponds: wenleizhu@nju.edu.cn (W.Z.); iamyangzhou@njupt.edu.cn (Y.Z.)

Contents

Reagents and materials

Sodium myristate (98%), methanol (99.5%), cadmium nitrate tetrahydrate ($Cd(NO_3)_2 \cdot 4H_2O$, 99.99%), cadmium acetate dihydrate ($Cd(OAc)_2 \cdot 2H_2O$, 98.0%), oleic acid (OA, 90%), *n*-hexane (99%), 1-octadecene (ODE, 90%), ethanol (95%), enrofloxacin standard (99%), dodecylamine (98%), Se powder (99.9%), gold (III) chloride ($AuCl_3$, 99%), 1,6-hexanedithiol (99.5%), potassium chloride (KCl, 99.5%), potassium ferrocyanide ($K_4Fe(CN)_6$, 99%), and potassium ferricyanide ($K_3Fe(CN)_6$, 99.5%) were purchased from Aladdin Reagent Co., Ltd. (China). Sodium chloride (NaCl, 99.5%), potassium chloride (KCl, 99%), disodium hydrogen phosphate (Na_2HPO_4, 99%), and sodium dihydngen phosphate (NaH_2PO_4, 99%) were supplied by Macklin Biochemical Co., Ltd. (China). Pure water prepared by Millipore Elix 5 Pure Water System from Purelab Classic Corp (USA) was used for all aqueous solution.

Apparatus

X-ray powder diffraction (XRD) measurements were performed on a Shimadzu XRD-6000 X-ray powder diffractometer (Shimadzu Co., Japan). Fourier transform infrared (FT-IR) spectra were measured by a Nicolet 6700 spectrophotometer (Nicolet Co., USA). Transmission electron microscopy images were obtained by a JEOL-2010 electron microscope (JEOL, Ltd., Japan). Photoluminescence (PL) emission and UV-visible absorption spectra were measured with an FL-7000 spectrophotometer (Hitachi, Japan) and a Lambda 1050+ UV-Vis-NIR spectrophotometer (PerkinElmer, USA), respectively. Electrochemical impedance spectroscopy (EIS) was measured by an Autolab electrochemical workstation (Metrohm, Switzerland). X-ray photoelectron spectroscopy were analyzed by an ESCALAB250Xi spectrometer (Thermo Fisher Scientific Co., USA). PL lifetime was detected by an FLS980 PL spectrometer (Edinburgh, England).

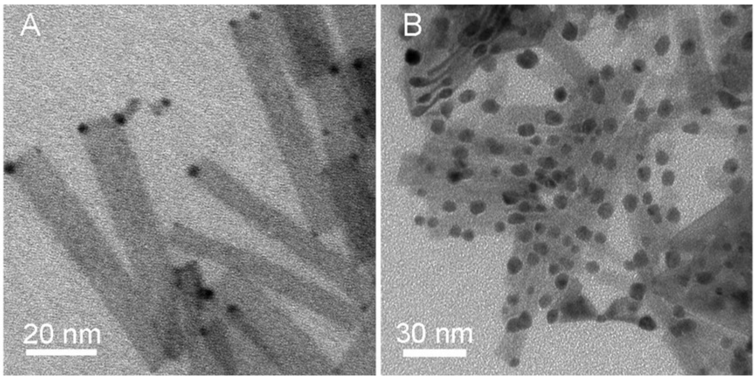

Fig. S1 TEM images of the CdSe NPLs treated with the $AuCl_3$-dodecylamine precursor solution containing (A) a tenth and (B) ten times of the normal amount of dodecylamine.

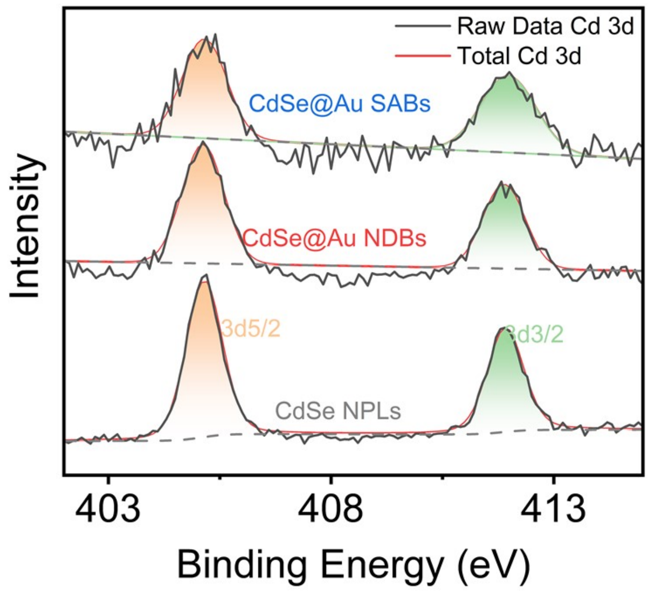

Fig. S2 High-resolution XPS spectra of Cd 3d in CdSe NPLs (bottom), CdSe@Au NDBs (middle), and CdSe@Au SABs (top).

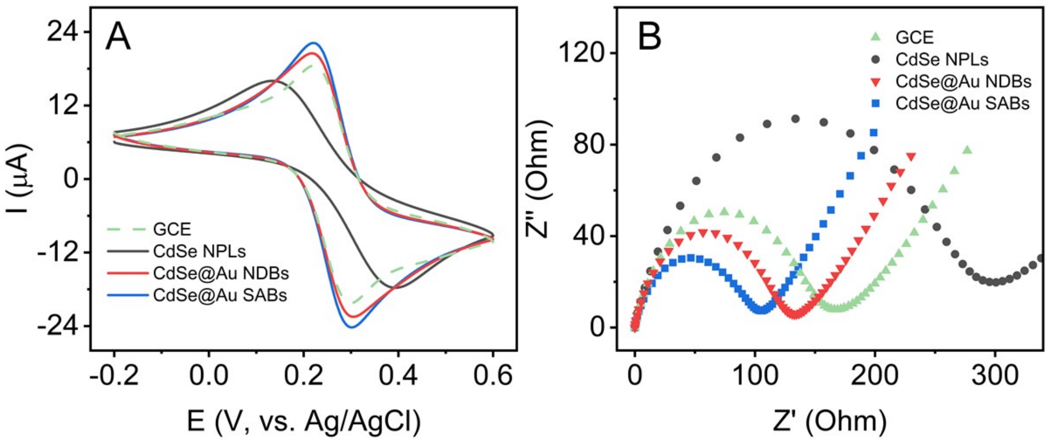

Fig. S3 (A) CV and (B) EIS characterizations of bare GCE (green), CdSe NPLs (black), CdSe@Au NDBs (red), and CdSe@Au SABs (blue).

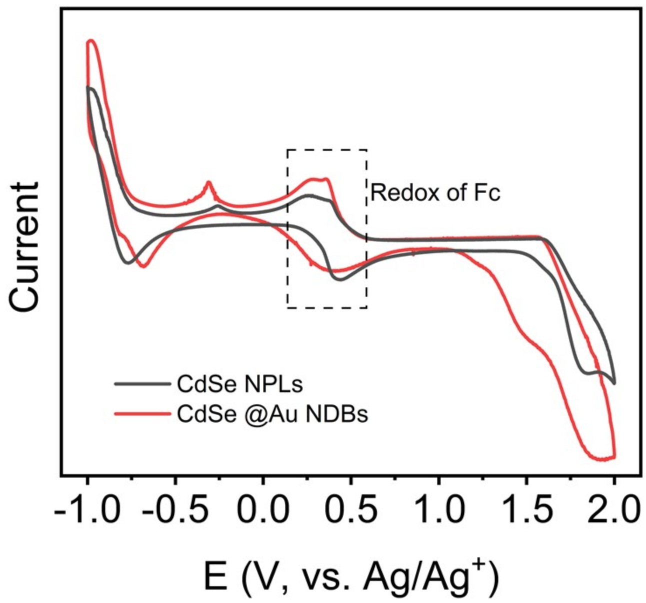

Fig. S4 CV curves of CdSe NPLs (black) and CdSe@Au NDBs (red) in anhydrous acetonitrile with 0.1 M of Bu_4NPF_6 as the supporting electrolyte and 0.05 M of ferrocene (Fc) as the internal standard, the modified GCE as the working electrode, platinum wire as the counter electrode, and Ag/Ag^+ as the reference electrode under a nitrogen atmosphere.

Table S1 Electrochemical properties of investigated CdSe NPLs and CdSe@Au NDBs.

Sample	E_{ox} (V)[a]	E_{red} (V)[a]	E_{ox}^{Fc} (V)[a]	E_{HOMO} (eV)[b]	Eg_{Ele} (eV)[c]	E_{LUMO} (eV)[d]	Eg_{Opt} (eV)[e]
CdSe NPLs	1.84	-0.26	0.43	-6.21	2.10	-4.11	~2.16
CdSe@Au NDBs	1.48	-0.31	0.40	-5.88	1.79	-4.09	~1.77

[a] CVs were carried out in anhydrous acetonitrile with 0.1 M Bu_4NPF_6 as the supporting electrolyte and 0.05 M Fc as the internal standard;

[b] $E_{HOMO}=-(E_{ox}+4.8(\text{vs. } Ag/Ag^{+})-E_{ox}^{Fc})$;

[c] $Eg_{Ele}=E_{ox}-E_{red}$;

[d] $E_{LUMO}=E_{HOMO}+Eg_{Ele}$;

[e] $Eg_{Opt}=1240/\lambda_{abs,edge}$.

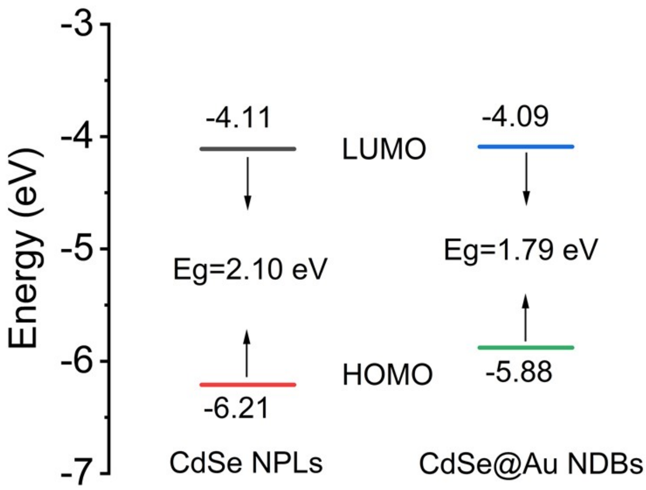

Fig. S5 Calculated HOMO-LUMO energy levels of CdSe NPLs and CdSe@Au NDBs based on the electrochemical data in Table S1.

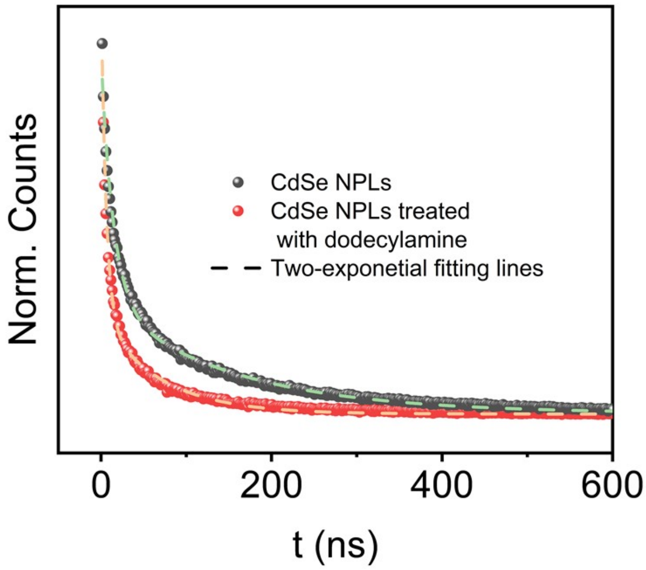

Fig. S6 Normalized PL decay plots and the corresponding two-exponential fitting lines of CdSe NPLs (black) and CdSe NPLs treated with dodecylamine (red).

Table S2 The double-exponential fitting parameters for the PL decay curves of CdSe NPLs and CdSe NPLs treated with dodecylamine in Fig. S6.

Sample	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	$\tau_{ave.}$ (ns)	χ^2
CdSe NPLs	14.361	68.8	152.221	31.2	128.47	0.995
CdSe@Au NDBs	5.977	77.3	68.977	22.7	54.60	0.993

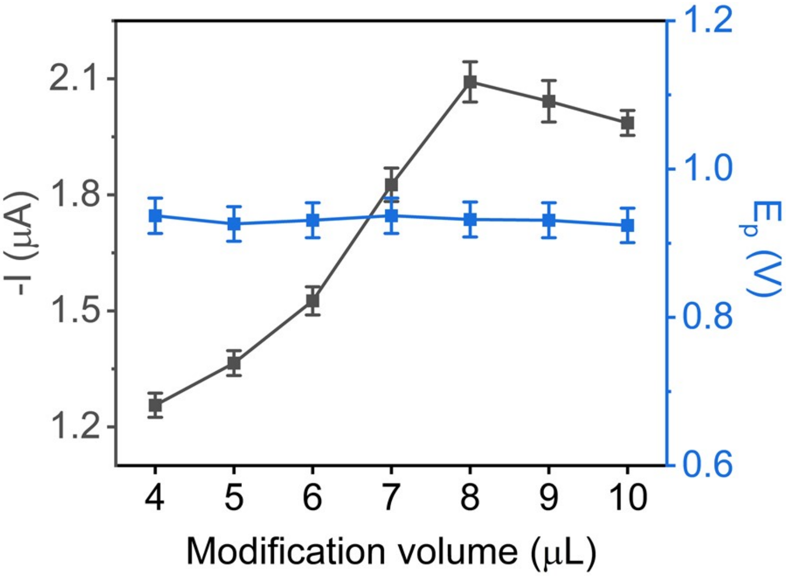

Fig. S7 The optimization of modification volume of CdSe@Au SABs in terms of peak current response (black) and peak potential (blue).

Table S3 Comparison of the as-proposed electrochemical sensors with other reported ones.

Method	Linear range μM	LOD μM	Reference
Fluorescence	0.278-139.1	0.164	1
Fluorescence	0-26.00	0.08	2
Fluorescence	2.78-139.1	0.111	3
Field-effect transistors	0.3-30	0.010	4
SERS	0.0278-2780	0.0161	5
Electrochemistry	0.001-115	0.021	6
Electrochemistry	10-100	20	7
Electrochemistry	0.1-10000	0.095	8
Electrochemistry	0.05-120	0.041	9
Electrochemistry	1-30	1.64	10
Electrochemistry	0.0696-2.78	0.0159	11
This work	0.01-250	0.0026	/

References

1. S. Feng, Y. Lin, J. Xu and X. Lu, *Sensor. Actuat. B Chem.*, 2023, **394**, 134342.
2. X.-W. Wang, L. Fu and G.-H. Cui, *J. Mol. Struct.*, 2023, **1289**, 135881.
3. J. Xu, Q. Qi, L. Sun, X. Guo, H. Zhang and X. Zhao, *J. Alloy. Compd.*, 2022, **908**, 164519.
4. Y. Cao, H. Qu, B. Dong, Y. Mao and L. Zheng, *J. Electroanal. Chem.*, 2023, **935**, 117325.
5. L. Xu, J. Ma, G. Wei, C. Gu and T. Jiang, *Sensor. Actuat. B Chem.*, 2022, **370**, 132431.
6. N. Karuppusamy, V. Mariyappan, S. M. Chen and R. Ramachandran, *Nanoscale*, 2022, **14**, 1250-1263.
7. A. Gallegos-Tabanico, J. Jimenez-Canale, S. G. Hernandez-Leon, A. J. Burgara-Estrella, J. C. Encinas-Encinas and J. A. Sarabia-Sainz, *Chemosensors*, 2022, **10**, 448.
8. Y. Liu, J. Zhang and D. Li, *Chirality*, 2019, **31**, 174-184.
9. S. Lu, S. Wang, P. Wu, D. Wang, J. Yi, L. Li, P. Ding and H. Pan, *Adv. Powder Technol.*, 2021, **32**, 2106-2115.
10. C. Canales, E. Peralta and M. Antilen, *J. Electroanal. Chem.*, 2019, **832**, 329-335.
11. F. Dönmez, Y. Yardım and Z. Şentürk, *Diam. Relat. Mater.*, 2018, **84**, 95-102.