Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Electrochemical control of emission enhancement in solid-state nitrogen-doped carbon quantum dots

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Synthesis information of nitrogen-doped carbon quantum dots (N-CQDs) and CQDs:

N-CQDs were synthesized via a hydrothermal method using branched polyethyleneimine (PEI) as carbon precursors. Specifically, 2.0 g PEI were dispersed in 10 mL deionized water, followed by the addition of 20.0 mg trisodium citrate. They were mixed ultrasonically and heated at 180 ℃ for 10 h in an autoclave. Then the suspension was obtained via centrifugation at 6800 rcf for 15 min and further dialyzed with 1000 Da dialysis tube for 24 h. The resulting dark brown solution was diluted to different concentrations with deionized water and stored at 4 ℃ for use.

Carbon quantum dots (1 mg/mL) with an average diameter of 5.4 nm were purchased from Nanjing Xianfeng Nanomaterials Technology Co., Ltd. According to the meager information provided by the supplier, the CQDs were synthesized from graphene oxide and dimethylformanmide by a hydrothermal method. The spectro-electrochemical (SEC) measurement conditions of CQDs films were the same as those of the doped sample N-CQDs films, except that the volume of the dripped sample became 1 mL because of the low concentration of CQDs.

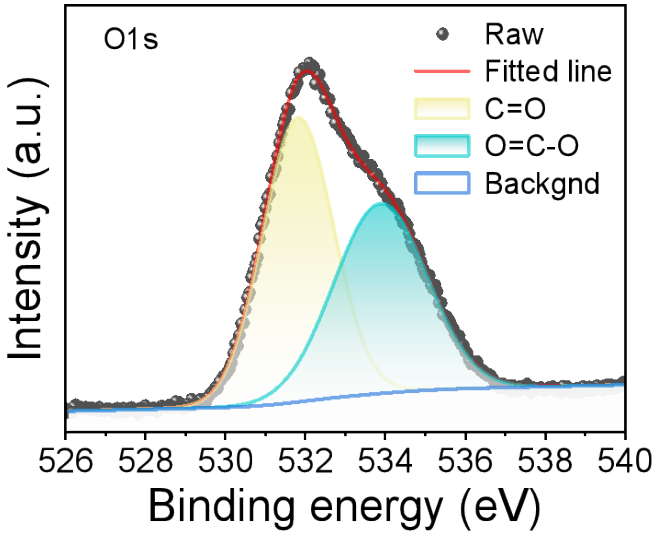

Figure S1. The high-resolution O1s spectrum of N-CQDs.

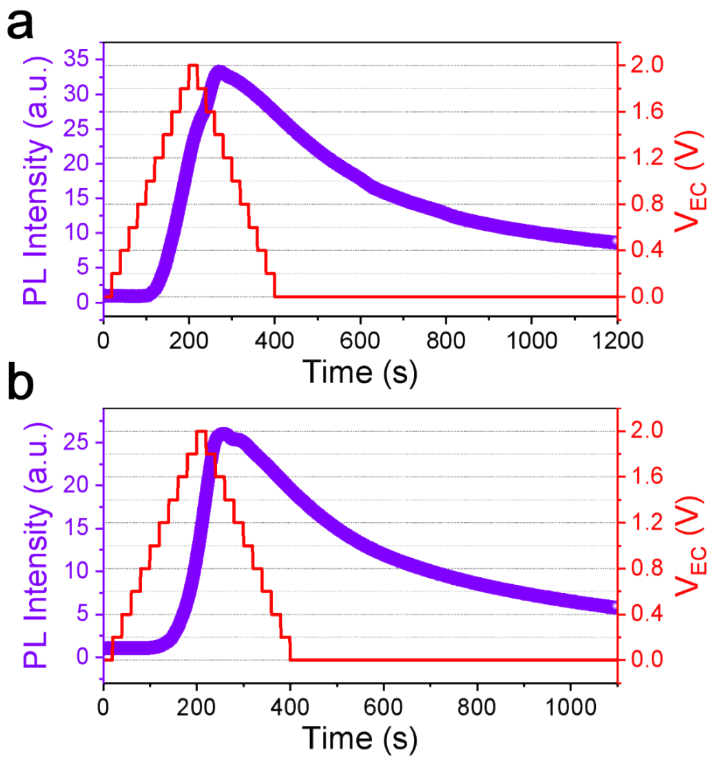

Figure S2. Spectrally integrated PL intensity (purple) of N-CQDs during the positive EC potential (red) scans (0 V→ +2.0 V→ 0 V, 200 mV steps each lasting 20s). All the PL spectra (under 3.06 eV excitation, 0.5 s acquisition time per frame) are recorded every 1 s and all intensities in (a) and (b) are normalized to their values at V_{EC} = 0 V.

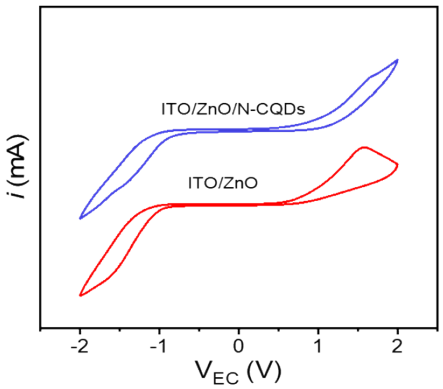

Figure S3. Cyclic voltammetry curves of N-CQDs and the corresponding blank measurement (ITO + ZnO). The scan rate is 100 mV/s (refers to Yan's work [1]), and the working electrode is ITO.

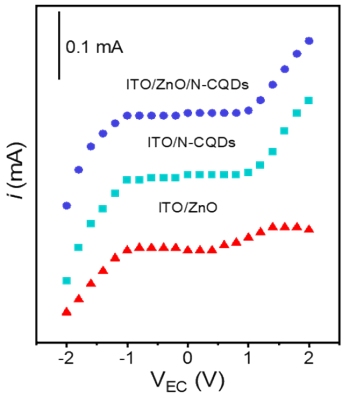

Figure S4. Current-voltage response (film structures: ITO/ZnO/N-CQDs, ITO/N-CQDs and ITO/ZnO) collected during a SEC scan using the setup described in Schematic 1 under both negative and positive potentials.

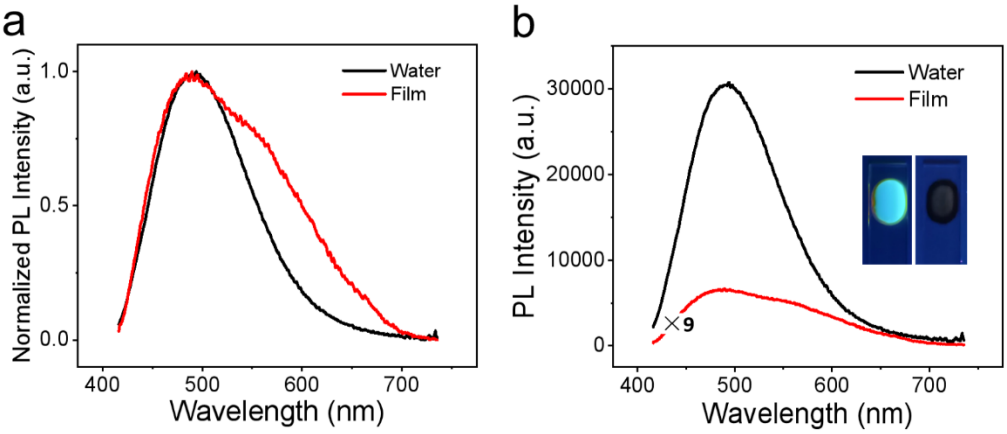

Figure S5. (a) Normalized PL spectra of N-CQDs in the liquid and solid states. (b) Original PL spectra of these samples. The insets in (b) are photographs of N-CQDs under a UV lamp before (left) and after (right) the solvent evaporation.

Table S1. Fitted Peak positions of Figure 2c-f expressed as a function of the energy.

Figure number	Peak position of EMA	Peak position of EMB
Figure 2c	2.651 eV (468 nm)	2.285 eV (543 nm)
Figure 2d	2.673 eV (464 nm)	2.446 eV (507 nm)
Figure 2e	2.657 eV (467 nm)	2.396 eV (518 nm)
Figure 2f	2.657 eV (467 nm)	2.332 eV (532 nm)

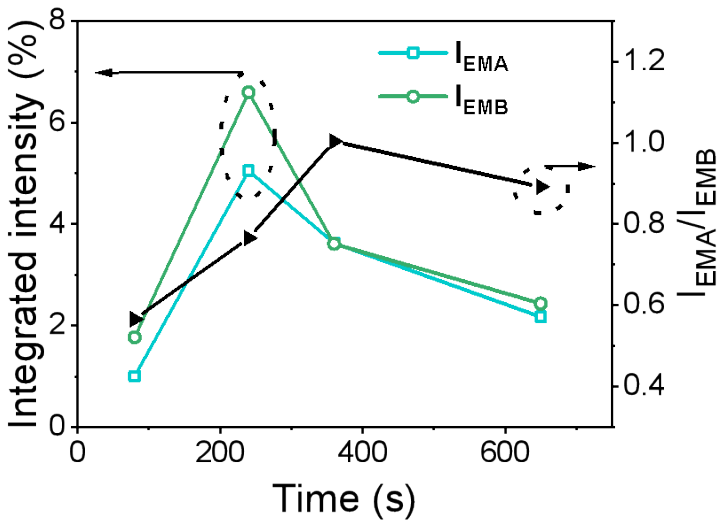

Figure S6. Integrated intensity (I_{EMA}, I_{EMB}) of EMA and EMB spectra of N-CQDs film sample as well as the corresponding intensity ratio I_{EMA}/I_{EMB} at four at four typical moments (V_{EC} = 0 V, +1.4 V, V_{EC} returned back to 0 V, and V_{EC} returned back to 0 V for 5 min). All intensities are normalized to the intensity of EMA at the initial moment.

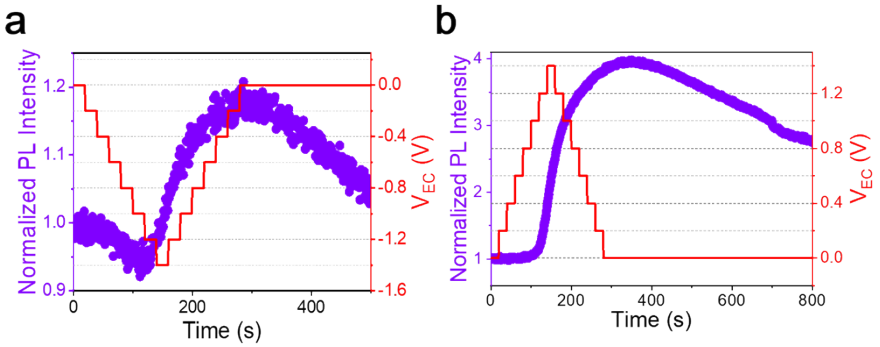

Figure S7. Spectrally integrated PL intensity (purple) of N-CQDs during the negative (a) and positive (b) EC potential (red) scans (0 V→ ±1.4 V→ 0 V, 200 mV steps each lasting 20s). All the PL spectra (under 3.06 eV excitation, 0.5 s acquisition time per frame) are recorded every 1 s and all intensities in (a) and (b) are normalized to their values at V_{EC} = 0 V. The N-CQDs were directly deposited onto the ITO coated surface without the ZnO nanoparticle layer.

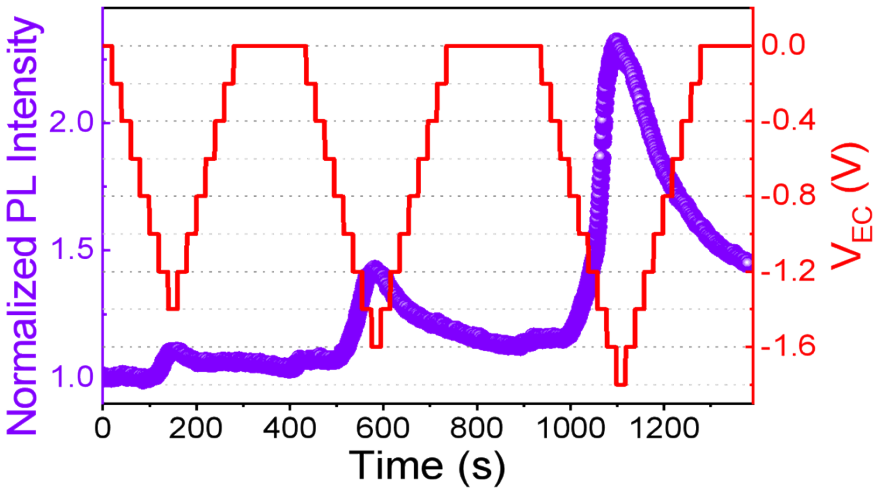

Figure S8. Spectrally integrated PL intensity of N-CQDs during continuous staircase voltammetry scans of the negative EC potentials (0 V→ -1.4 V→ 0 V→ -1.6 V→ 0 V→ -1.8 V→ 0 V, 200 mV steps each lasting 20s). All the PL spectra (under 3.06 eV excitation, 0.5 s acquisition time per frame) are recorded every 1 s and normalized to the initial value at V_{EC} = 0 V.

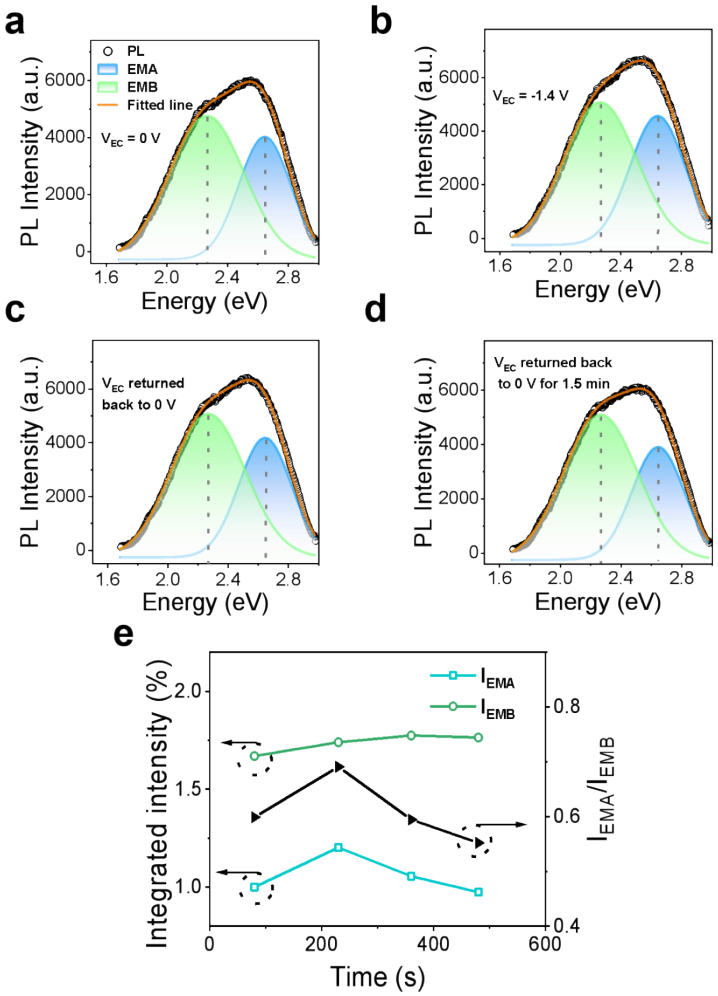

Figure S9. (a)-(d) Double-peak fitting results of PL spectra of N-CQDs film sample and (e) corresponding emission intensities (I_{EMA}, I_{EMB}) of EMA and EMB spectra as well as the intensity ratios I_{EMA}/I_{EMB} at four typical moments: V_{EC} = 0 V, V_{EC} = -1.4 V, V_{EC} returned back to 0 V and V_{EC} returned back to 0 V for 1.5 min, respectively. All intensities in (e) are normalized to the intensity of EMA at the initial moment.

Table S2. Fitted Peak positions of Figure S9a-d expressed as a function of the energy.

Figure number	Peak position of EMA	Peak position of EMB
Figure 9a	2.649 eV (468 nm)	2.267 eV (547 nm)
Figure 9b	2.647 eV (468 nm)	2.266 eV (547 nm)
Figure 9c	2.649 eV (468 nm)	2.271 eV (546 nm)
Figure 9d	2.648 eV (468 nm)	2.269 eV (546 nm)

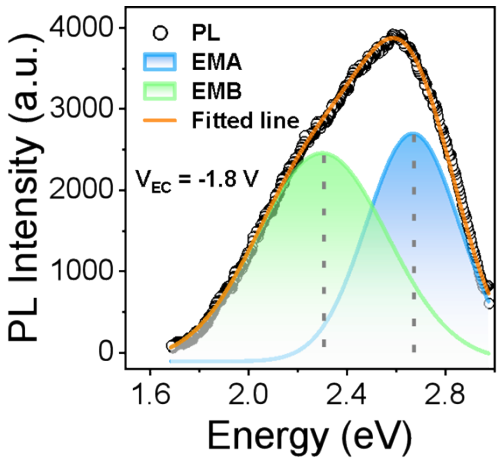

Figure S10. Double-peak fitting results of PL spectrum of N-CQDs film at V_{EC} = -1.8 V.

Table S3. Fitted Peak positions of Figure S10 expressed as a function of the energy.

Peak position of EMA	Peak position of EMB
2.671 eV (464 nm)	2.302 eV (538 nm)

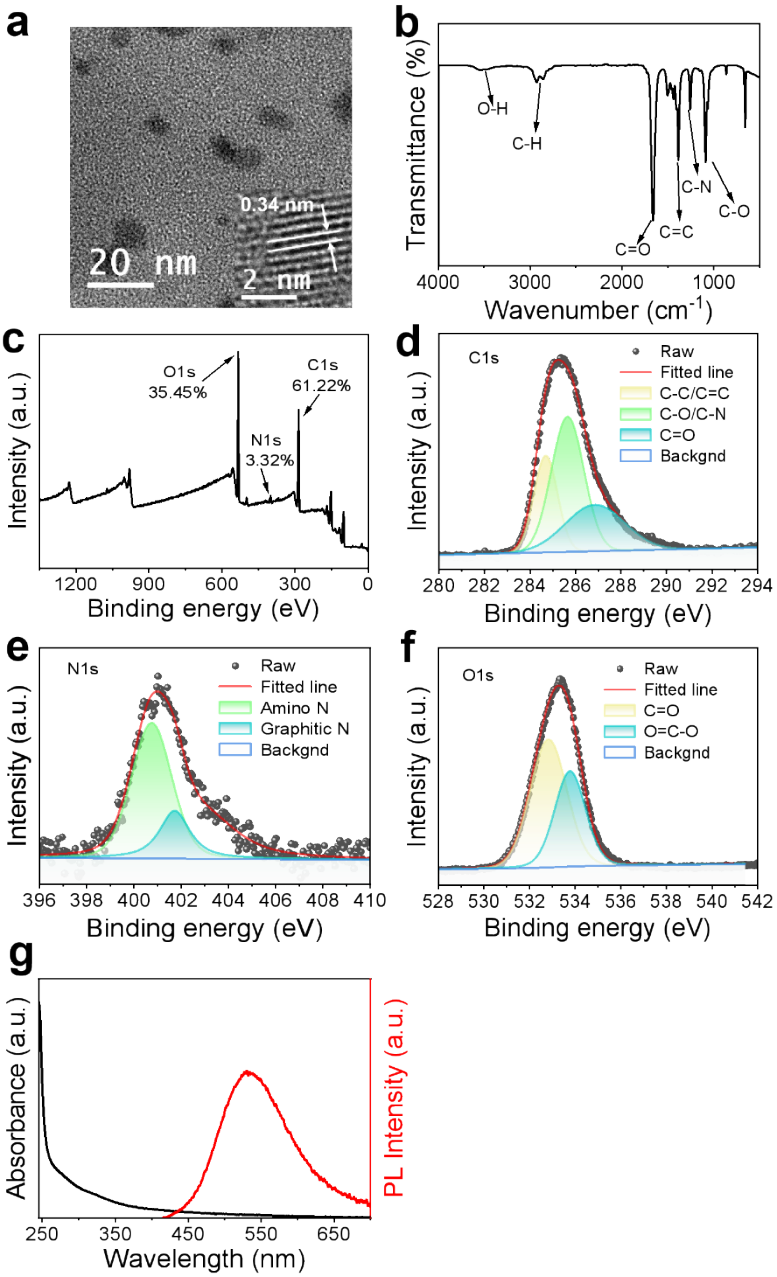

Figure S11. (a) TEM image of CQDs. The inset shows the HR-TEM image of CQDs, and the white solid lines and arrows indicate the lattice spacing. (b) FTIR spectrum of the CQDs. XPS survey scan (c) as well as high-resolution scans of C1s (d), N1s (e) and O1s (f) photoelectron of CQDs. (g) Absorption and PL spectra of CQDs dispersed in aqueous solution.

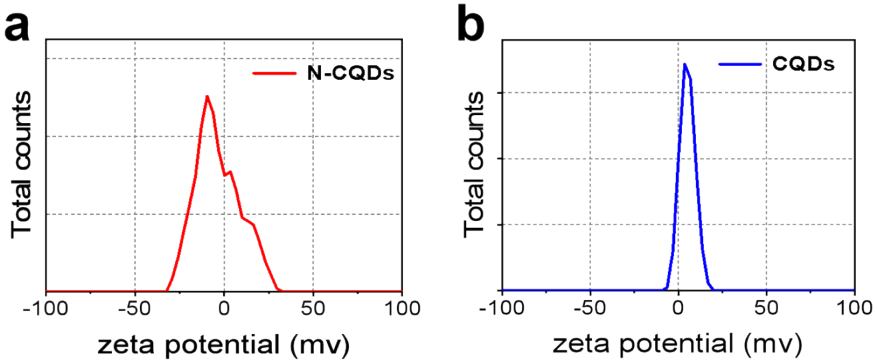

Figure S12. The zeta potential values for (a) N-CQDs and (b) CQDs dissolved in aqueous solution.

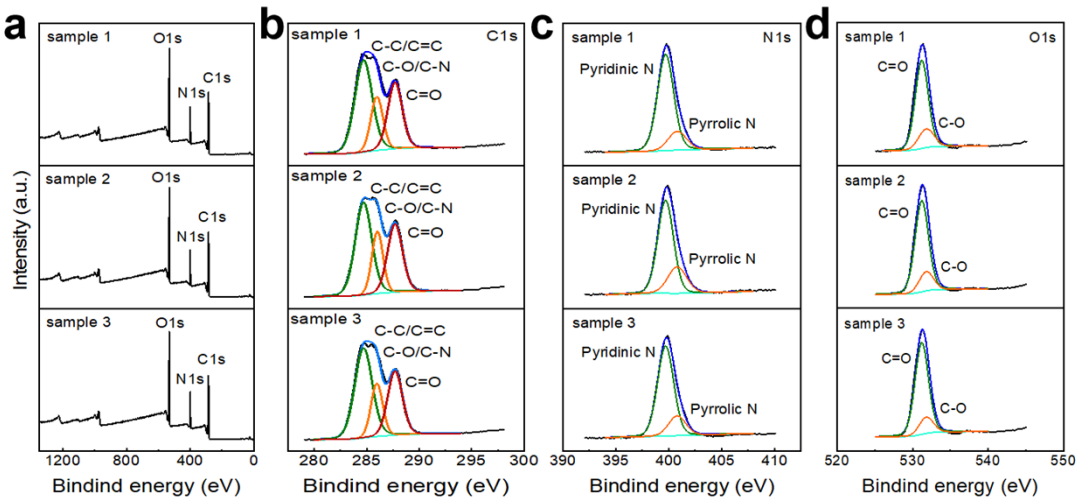

Figure S13. XPS survey scan as well as high-resolution scans of C1s, N1s and O1s for three N-CQDs film samples. Before the XPS measurement, sample 1 and sample 2 experienced positive (0 V→+2.0 V→ 0 V) and negative (0 V→-2.0 V→ 0 V) EC potential scans, respectively. Sample 3 was used as a reference sample without any SEC experiments.

Table S4. C, N, O element contents of the three samples (in Figure S13) determined by XPS results.

	Atomic %		
	C	N	O
sample 1	59.89	14.55	25.56
sample 2	59.63	14.65	25.72
sample 3	60.07	14.36	25.58

Reference

[1] L.P. Yan, Y.Z. Yang, C.Q. Ma, X.G. Liu, H. Wang, B.S. Xu, Synthesis of carbon quantum dots by chemical vapor deposition approach for use in polymer solar cell as the electrode buffer layer, Carbon. 109 (2016) 598-607.