

Supplementary Material (ESI) for Chemical Communications
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Electrochemiluminescence detection of oxygen vacancies in layered double hydroxides

Rui Zou, Ruyi Xie, Liren Wang*, Yanjun Lin, and Chao Lu*

Experimental Section

Chemicals and Materials. Melamine and sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) were purchased from J&K Scientific Ltd. (Beijing, China). Triethanolamine (TEA) was provided by Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). Tris(2,2'-bipyridyl)ruthenium(II) chloride hexahydrate ($\text{Ru}(\text{bpy})_3\text{Cl}_2$) was supplied from Alfa Aesar Chemicals Co., Ltd. (Shanghai, China). Other reagents were all obtained from Beijing Reagent Company (Beijing, China) and all of chemicals were analytical grade. In this work, Milli Q ultrapure water was used during this work (18.2 $\text{M}\Omega/\text{cm}$, Millipore, Barnstead, CA, U.S.A.)

Apparatus and Characterization. The ECL experiments were obtained using CHI 660E electrochemical workstation (Chenhua Instrument, Shanghai, China) coupled with a BPCL-2-KGC luminescence analyzer (Institute of Biophysics, Chinese Academy of Science, Beijing, China). A three-electrode electrochemical cell system was used, including the modified working electrode, Ag/AgCl reference electrodes, and Pt counter electrode. The voltammetric ECL emissions were obtained by cyclic voltammetry of 0 V \sim -1.5 V with a scan rate of 0.1 V/s. and the photomultiplier tube voltage was set at -900 V. Electrochemical impedance spectroscopy (EIS) was performed over the frequency range from 0.01 Hz to 100 kHz. Effective surface area was measured by CV method with the potential range from -0.2 V to +0.6 V, sweeping speed from 0.025 V/s to 0.250 V/s in 100 mM $\text{K}_3\text{Fe}(\text{CN})_6$. Mott-Schottky plot was carried out in 0.2

M Na₂SO₄ and the conversion between potential vs Ag/AgCl and vs. RHE is performed using the equation below:

$$E \text{ (vs. RHE)} = E \text{ (vs. Ag/AgCl)} + 0.197 + 0.0591 \text{ V} \times \text{pH}$$

The ECL spectrum was acquired in an F-7000 fluorescence spectrophotometer (Hitachi, Tokyo, Japan) coupling with CHI 660E without the exciting light. Binding energy and electronic structures were analyzed by X-ray photoelectron spectra (XPS) with an ESCALAB-MKII 250 (Thermo, Waltham, U.S.A.) using Al K α X-ray as excitation source. Element content measurement of all samples was operated by inductively coupled plasma optical emission spectrometry (ICP-OES, Thermo Fisher Scientific, U.S.A.). X-ray diffraction (XRD) was measured by a 2500VB2 (Rigaku Corporation, Japan) using the Cu K α (radiation $\lambda = 1.541844$ Å) at 40 kV and 50 mA with a 2θ range from 5° to 90° under a scanning rate of 5°/min. Scanning electron microscopy (SEM, HITACHI S-4700 microscopy) (Tokyo, Japan) and transmission electron microscopy (TEM) 2100 (Japan Electron Optics Laboratory Co., Ltd.) were employed to characterize the morphology of the obtained nanocomposite.

Synthesis of CN. CN was synthesized according to our previously reported method.^{11a} Briefly, 10.0 g melamine was placed into a tube furnace and calcined at 550 °C under air for 4 h (heating rates 3 °C/min). After cooled down, the bulk agglomerates were grinded into powders and further thermal treatment for another 2 h at 550 °C in N₂ atmosphere (heating rate 2 °C/min). The obtained powders were collected. 100 mg bulk CN samples were dispersed into 100 mL water and ultrasonic for 16 h. Then, the obtained suspension was centrifuged at 5000 rpm to remove the residual bulk powder.

Preparation of LDH Nanosheets. The MgAl-LDH was prepared by a one-step coprecipitation method which was reported by previous literature.^{11b} In a typical experiment, a 10.0 mL aqueous solution containing 75 mM Mg(NO₃)₂·6H₂O and 25 mM Al(NO₃)₃·6H₂O was added dropwise to a solution of 10.0 mL NaNO₃ (10.0 mM) containing 23 vol% formamide. Simultaneously, 0.25 M NaOH was added drop by drop into the flask to maintain the system at a pH value of

ca.10 under magnetic stirring at 80 °C. The reaction was completed within 10 min and then stirred for another 10 min. The precipitates were collected by centrifugation and washing with water for more than 3 times. Afterwards, the obtained products were immersed in 20.0 mL different concentration NaOH (0.1, 0.3, 0.5, 0.8, 1.0 M) for 2 h under magnetic stirring. The sample was centrifuged and rinsed three times by distilled water. The as-prepared oxygen vacancy-rich LDHs were dispersed in 20 mL water for following experiments. The concentration of oxygen vacancy-rich LDHs measured by drying sample was 3.16 mg/mL. The products were denoted as LDH-O_V-x (x corresponds to the concentration of oxygen vacancy measured by XPS, 29.8%, 30.4%, 32.6%, 34.9%, 35.6%, 40.3% respectively). Other samples were prepared by adding 20 mL NaBH₄ (0.8 M) solution to the LDH precipitates under magnetic stirring for 0.5 h, 1 h, and 2 h, respectively.^{7b} Acid etched LDH sample was obtained by reacting with 20 mL HNO₃ (0.001 M) for 2 h.²⁶

Fabrication of CN/LDH Nanocomposites. The CN/LDH nanocomposites were prepared *via* electrostatic self-assembly between positively charged LDHs and negatively charged CN. In brief, 2.0 mL LDHs stock solution and 500 μL CN solution added to 17.5 mL water and stirred for 1h. The probe (CN/LDH nanocomposites) was obtained for use.

Preparation of Nanocomposites Modified GCE. The glassy carbon electrode (3 mm in diameter) was polished successively by 0.3 and 0.05 μm alumina powders, rinsed thoroughly with water, and then sonicated in ethanol and ultrapure water. Subsequently, 5 μL of CN/LDH nanocomposite dispersion with 0.05% nafion-ethanol was dropped onto the pretreated surface of GCE electrode and dried in air at room temperature for further use.

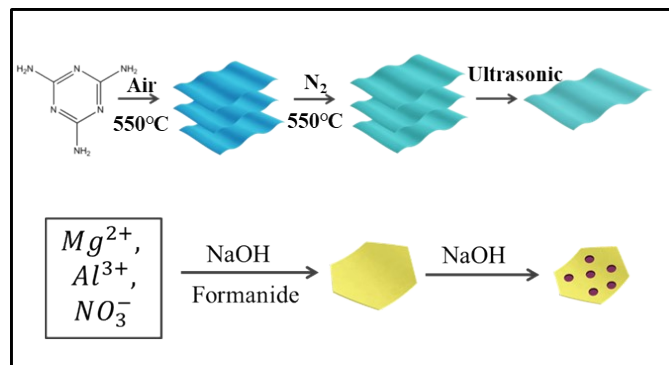


Figure S1. Schematic diagram of the preparation procedure of CN and MgAl-LDH with different contents of oxygen vacancy.

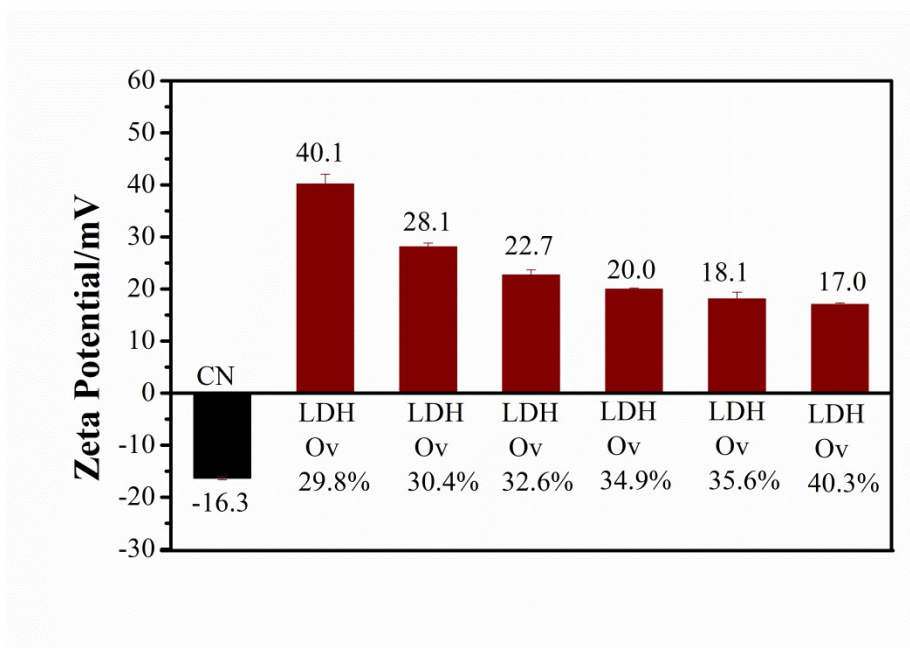


Figure S2. Zeta potential of CN and LDHs with different concentrations of oxygen vacancy.

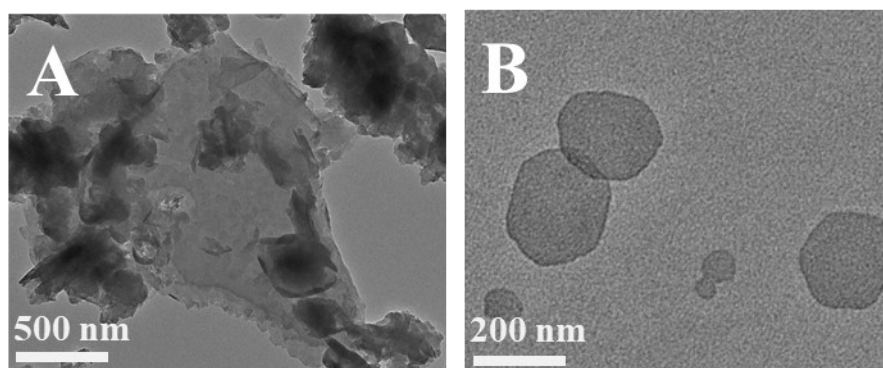


Figure S3. TEM images of (A) CN, (B) LDHs.

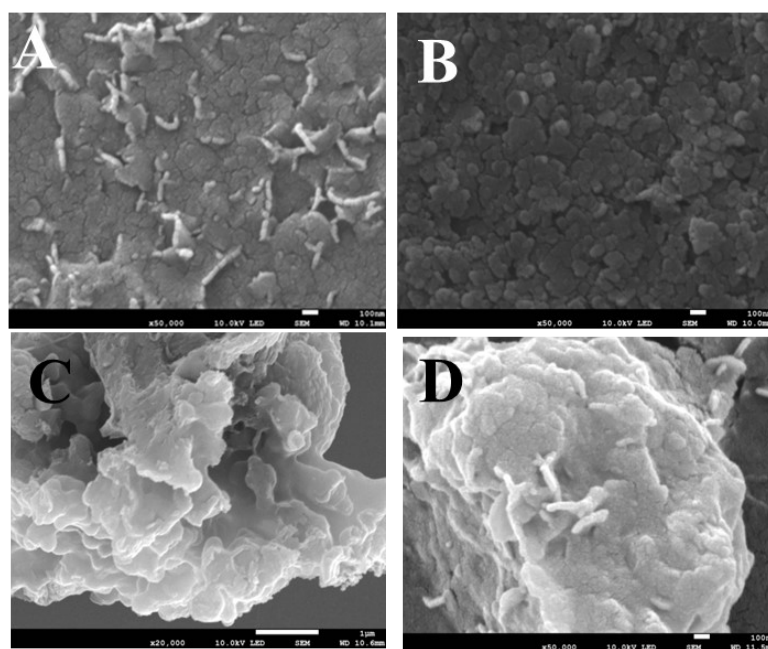


Figure S4. SEM images of (A) LDHs, (B) LDHs etched by 1M NaOH for 2h, (C) CN, and (D) CN/LDH nanocomposites.

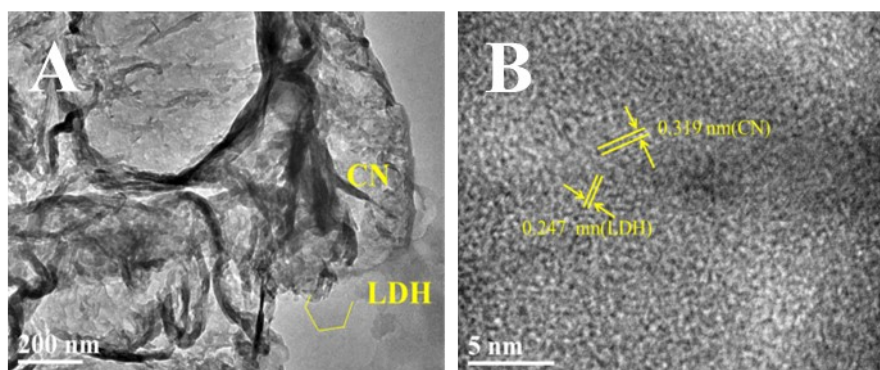


Figure S5. (A) TEM image of CN/LDH nanocomposites and (B) HRTEM image of CN/LDH nanocomposites

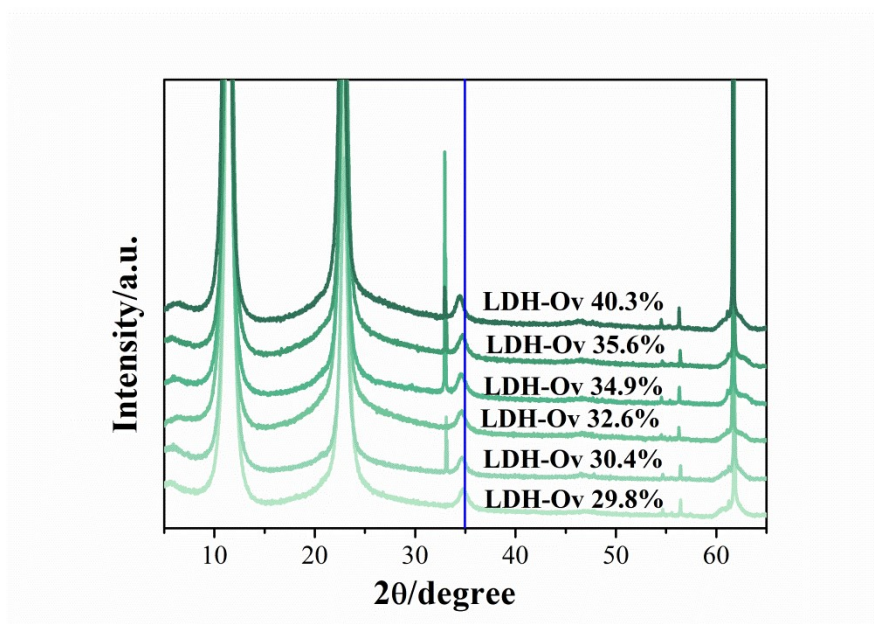


Figure S6. XRD patterns of the original MgAl-LDH and MgAl-LDH treated with different concentration of NaOH (0.1, 0.3, 0.5, 0.8, 1.0 M) for 2 h, respectively.

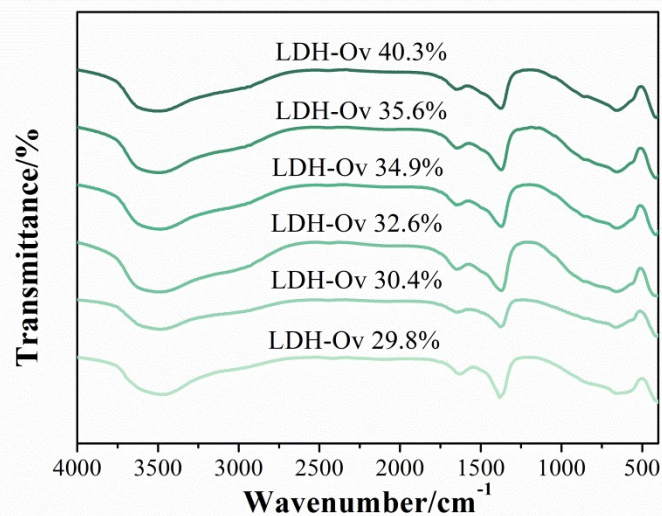


Figure S7. FT-IR spectra of the original MgAl-LDH and MgAl-LDH treated with different concentration of NaOH (0.1, 0.3, 0.5, 0.8, 1.0 M) for 2 h.

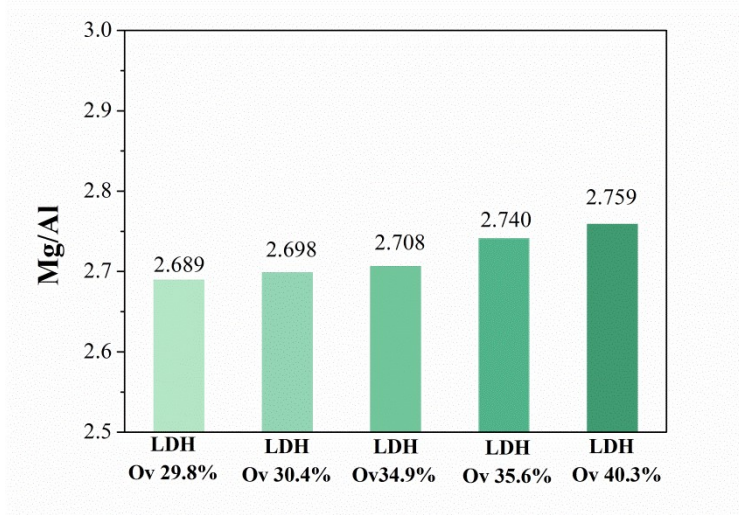


Figure S8. Mg/Al ration (measured by ICP) of the original MgAl-LDH and MgAl-LDH treated with different concentration of NaOH for 2 h.

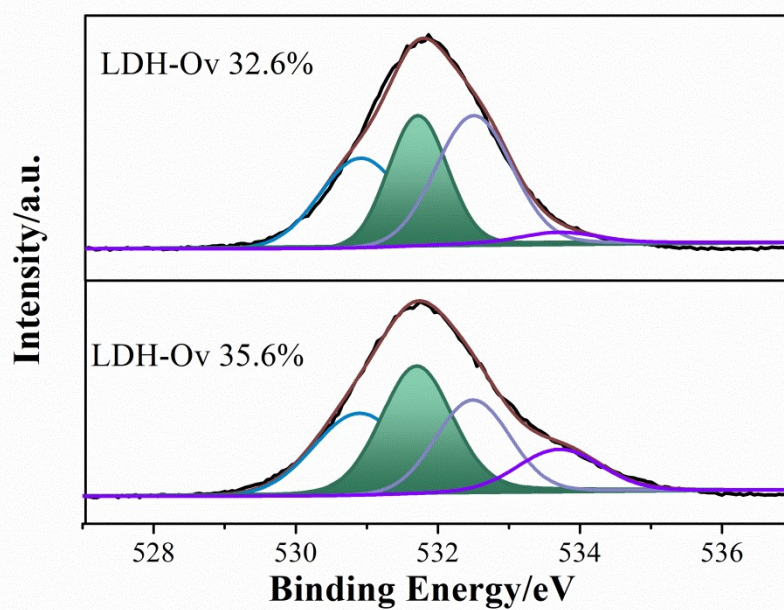


Figure S9. XPS of the original MgAl-LDH and MgAl-LDH treated with different concentration of NaOH (0.3, 0.8 M) for 2 h, respectively.

Table S1. Oxygen characteristic peak area and oxygen vacancy contents estimated by XPS of the original MgAl-LDH and MgAl-LDH treated with different concentration of NaOH.

C_{NaOH}	O_w area	O_v area	O_{OH} area	O_L area	Total area	O_v content
0	39038.85	41260.05	51215.03	6975.672	138489.6	0.298
0.1 M	52022.03	49384.25	56451.02	4386.359	162243.7	0.304
0.3 M	43787.1	47038.76	48008.23	5533.68	144367.8	0.326
0.5 M	32563.94	41905.38	40580.6	5030.022	120079.9	0.349
0.8 M	31518.04	45630.29	43528.65	7390.502	128067.5	0.356
1.0 M	38157.07	53001.38	36039.39	4284.22	131482.1	0.403

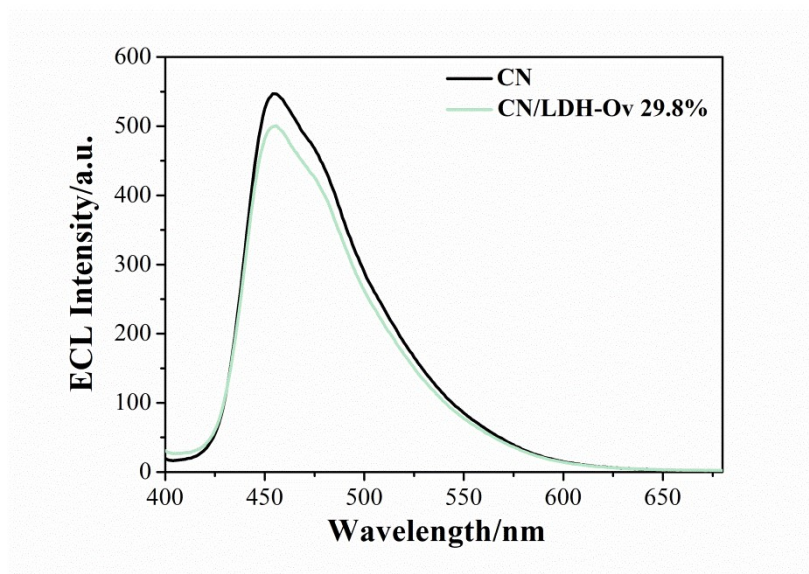


Figure S10. The fluorescence spectra of CN and CN/LDH nanocomposites.

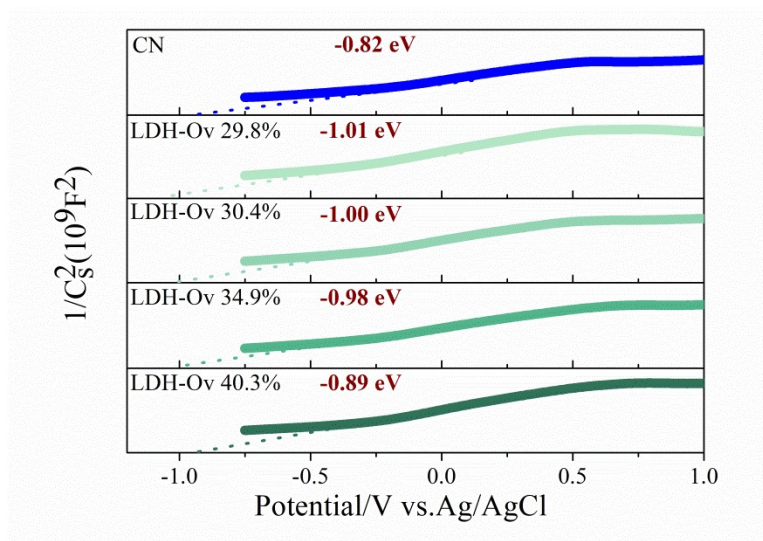


Figure S11. Mott–Schottky plots of CN, original LDHs and LDHs treated with different concentrations of NaOH (0, 0.1, 0.5, and 1.0 M).

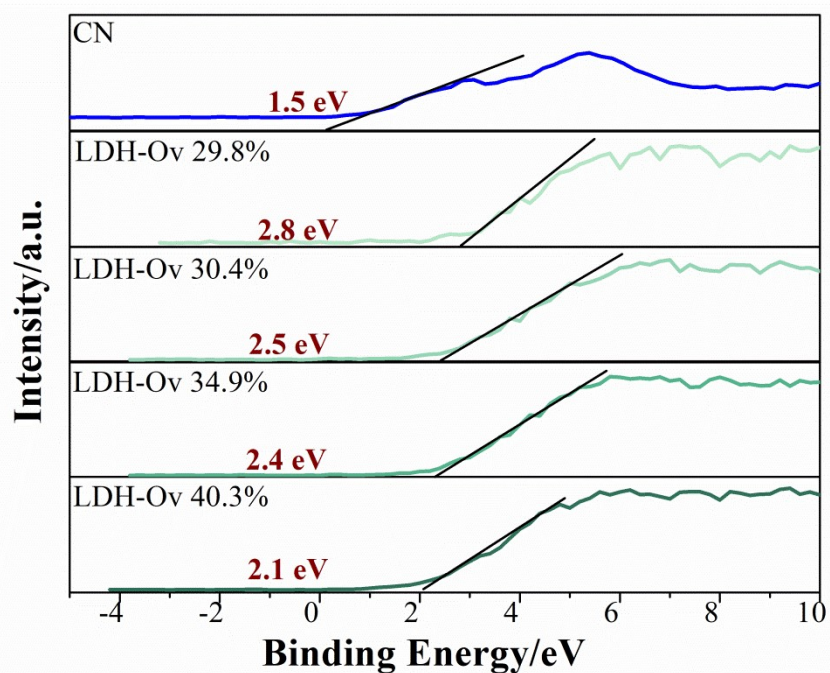


Figure S12. XPS valence band spectra of CN, original LDHs and LDHs treated with different concentrations of NaOH (0, 0.1, 0.5, and 1.0 M).

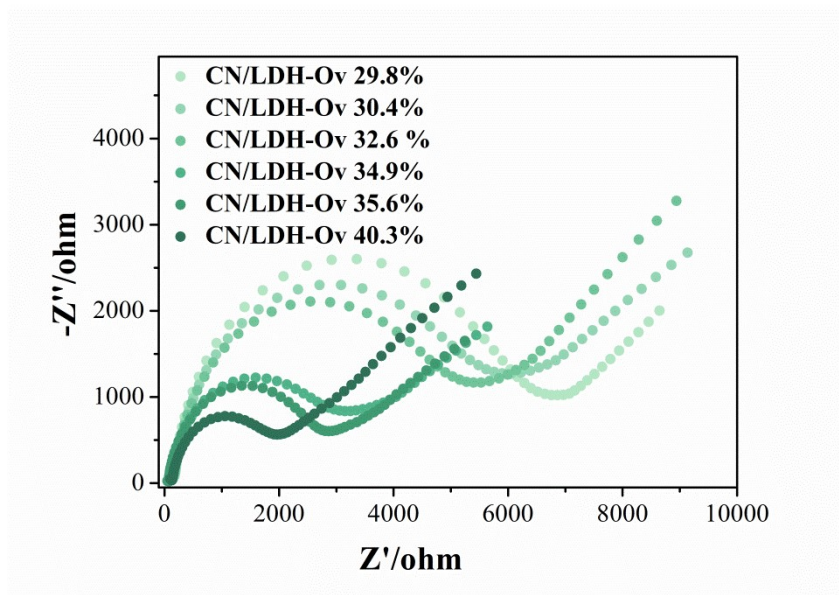


Figure S13. EIS curves of CN/LDH nanocomposites with different content of oxygen vacancy.

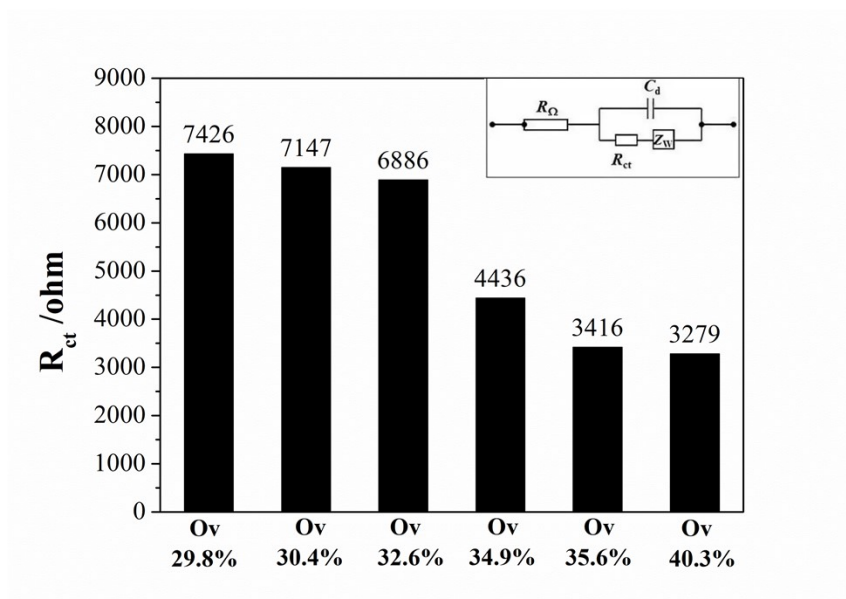


Figure S14. The charge transfer resistance (R_{ct}) value of CN/LDH nanocomposites modified electrode with different contents of oxygen vacancy estimated by the Nyquist plots. The Randles circuit (inset of Fig. S14) was chosen to fit the impedance data obtained in the revised manuscript. The resistance to charge transfer (R_{ct}) and the diffusion impedance (W) were both in parallel with the interfacial capacitance (C_{dl}). The diameter of the semicircle corresponds to the interfacial electrontransfer resistance (R_{ct})

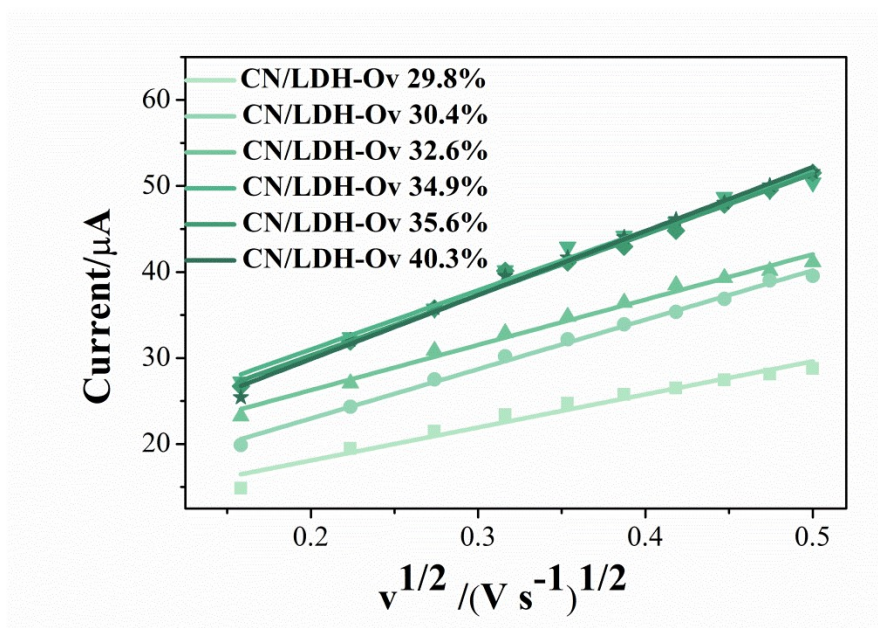


Figure S15. The effective electrode surface area test: calibration curves of the peak current against the square root of the scan rate for CN/LDH nanocomposites modified electrode with different concentration of oxygen vacancy. Electrolyte: 5.0 mM $[\text{Fe}(\text{CN})_6]^{4-/3-}$ at scan rates of 25–250 mV/s.

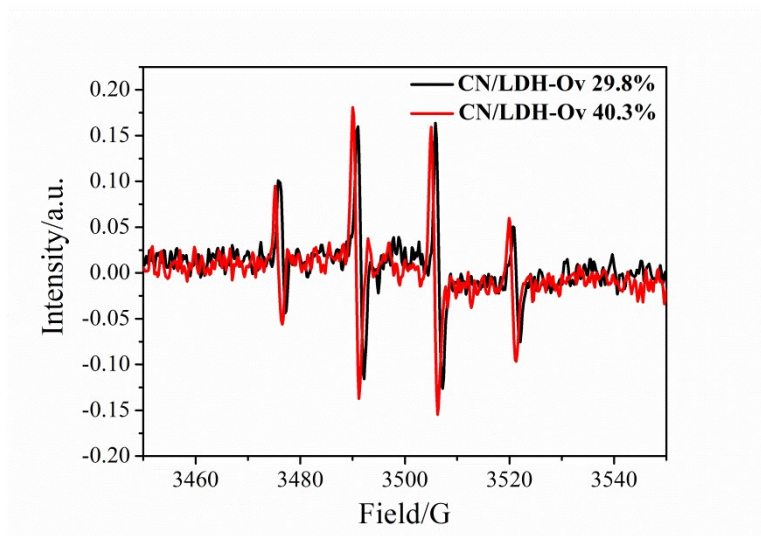


Figure S16. ESR spectra of 0.1 M PBS buffer (pH 7.5) containing, 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$ –100 mM DMPO recorded after application of a potential of -1.6 V on the CN/LDH-Ov 29.8% and CN/LDH-Ov 40.3% modified electrode for 150 s.

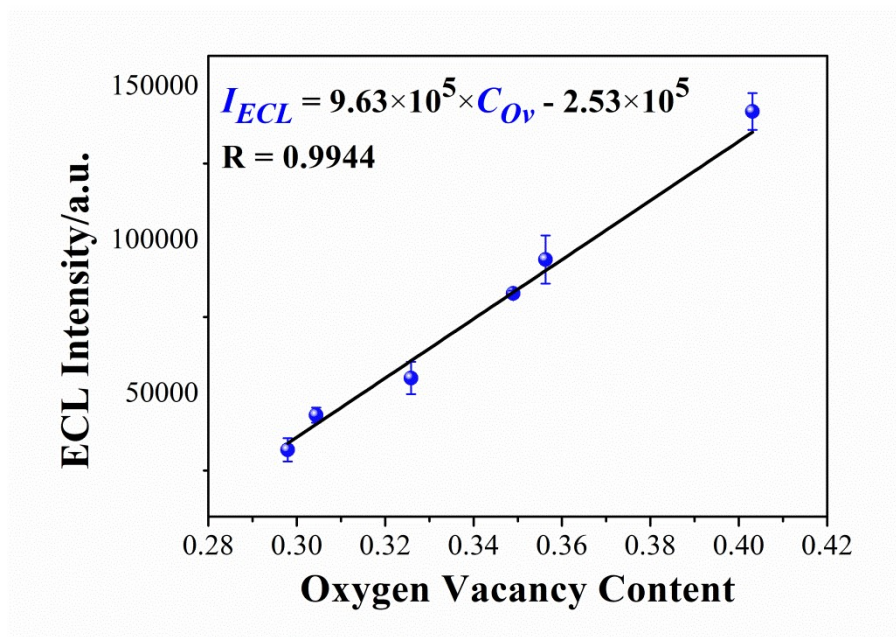


Figure S17. Calibration curves for oxygen vacancy detection.

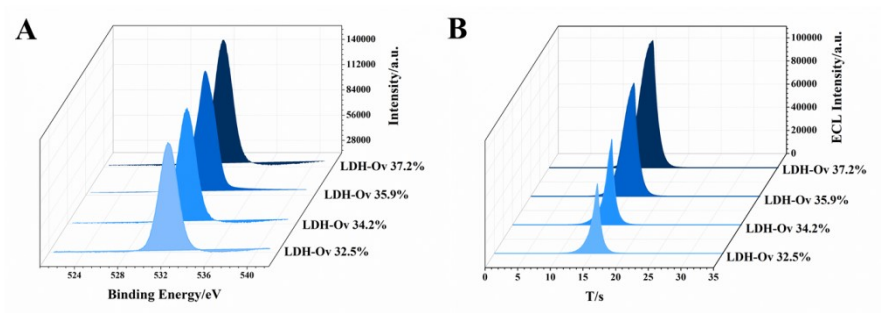


Figure S18. (A) XPS (O 1s) and (B) ECL intensity of the LDHs treated with NaBH_4 for 0.5 h (O_V 32.5%), 1 h (O_V 34.2%), 2 h (O_V 37.2%) and 0.001M HNO_3 (O_V 35.9%) for 2h.