Supporting Information

Ultra-small β-Ni(OH)₂ Quantum Dots Catalyst with Abundant Edges for Efficient Urea Oxidation Reaction

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EXPERIMENTAL SECTION

Materials: Ni(NO₃)₂·6H₂O (purity, >99.99%), H₂C₂O₄ (Analytical Reagent), absolute alcohol (Analytical Reagent), and NaOH (purity, >99.99%) were obtained from Aladdin Reagent Company, China. N₂ (purity, >99.999%) was purchased from Tianjin Chemical Reagent Factory, China.

*Preparation of US-β-Ni(OH)*² *QDs:* 3 mmol Ni(NO₃)²·6H₂O was added into 50 mL alcohol to obtain solution A. 1.51 g H₂C₂O₄ was weighed and dissolved in 50 mL alcohol to obtain solution B. the solution A was slowly dropped into solution B with vigorous stirring for 2 hours at room temperature, and then left at room temperature for 12 h. After that, the obtained bright blue product was isolated by centrifugation, washed with ethanol three times, followed by drying at 40 °C for 24 hours to obtain NiC₂O₄ nanowires named NW-NiC₂O₄.

40 mg NW-NiC₂O₄ was dissolved in 20 mL ethanol with vigorous stirring at room temperature. Then 0.1 mM NaOH solution was added to the solution. After ultrasonic reaction for 2 hours, centrifugation was carried out. The obtained precipitate was transferred into 1 M NaOH + 1 M ethanol solution and kept static for 24 hours. Subsequently, it was centrifuged at room temperature and washed multiple times with ethanol. Then, it was dried at 40 °C for 24 hours to obtain ultra-small β -Ni(OH)₂ quantum dots (US- β -Ni(OH)₂ QDs).

*Preparation of β-Ni(OH)*² *nanosheets:* The β-Ni(OH)² nanosheets were prepared according to a literature method ^[1]. 5 mmol NiCl₂·6H₂O was dissolved in 200 mL water with vigorous stirring for 5 min followed by the adding of 0.6 mL of 28% ammonia solution. Then, the obtained solution was transferred into a 500 mL three neck flask and heated at 60 °C for 24 h. After cooling to room temperature, the light green product was collected by centrifugation, washed by ethanol several times, and then dried at 60 °C in air overnight for further characterization.

Physical Characterization: SEM measurements were performed using a Merlin Compact at an accelerating voltage of 20 kV (Carl Zeiss Company). SEM-EDS were carried out using a Teneo volume scope. TEM and HRTEM measurements were performed using a Tecnai G2 F30

transmission electron microscope with an accelerating voltage of 200 kV (FEI Company). Powder X-ray diffraction patterns were carried out using an Empyrean diffractometer (Panalytical company) assisted by monochromatic Cu-K α radiation ($\lambda = 1.54056$ Å) within the 2 θ range of 35°–70°. X-ray photoelectron spectroscopy (XPS) measurements were performed on a ThermoFisher ESCALAB 250Xi spectrometer. XPSPEAK software (Ulvac-phi Company) was used for the XPS data processing.

Electrochemical measurements: Electrochemical measurements of various catalysts were carried out using a CHI 660E workstation (Shanghai, China). A typical three-electrode system was used, with an Ag/AgCl as reference electrode, graphite rod as a counter electrode. Before the electrochemical test, the reference electrode was calibrated using Pt wire as the working electrode and counter electrode in high purity hydrogen saturated electrolyte solution, respectively. US-β-Ni(OH)₂ QDs was loaded on carbon fiber paper with a size of 1 cm × 1 cm, which acted as the working electrodes for the electrochemical tests, and the mass loading on the carbon fiber paper was about 0.5 mg·cm⁻². LSV curves were recorded at 5 mV·s⁻¹ in O₂-saturated 1.0 M KOH. The polarization curves were *iR*-corrected and the potentials were converted in reference to the reversible hydrogen electrode ($E_{RHE} = E_{(Ag/AgCl)} + E_{0(Ag/AgCl)} + 0.059 \cdot pH - iR$). Operando electrochemical impedance spectroscopy (EIS) was carried out at different potentials from a frequency range of 0.1 Hz to 1000 kHz.

Computational Detail: The US- β -Ni(OH)₂ QDs model with a 4 × 5 × 1 supercell and β -Ni(OH)₂ nanosheet with a 6 × 7 × 1 supercell was constructed to explore the dehydrogenation energy of Ni-OH and the adsorption energy of urea molecules. The density functional theory (DFT) was computed by Vienna ab initio Simulation Package (VASP). The projector augmented wave pseudopotential comprising the revised Perdew–Burke–Ernzerhof exchange-correlation functional was utilized to describe the interactions between core and electrons. An energy cutoff of 450 eV was used for the plane wave expansion of the electronic wave function. An 5 × 5 × 1 Monkhorst

Pack k-point setup were used for the slab geometry optimization of US- β -Ni(OH)₂ QDs and β -Ni(OH)₂ nanosheet, respectively. The force and energy convergence criteria were set to 0.02 eV Å⁻¹ and 10⁻⁵ eV, respectively.



Figure S1. SEM images of NW-NiC₂O₄ precursor



Figure S2. XRD patterns of the NW-NiC₂O₄ precursor and US- β -Ni(OH)₂ QDs samples



Figure S3. FTIR spectrum of the NW-NiC₂O₄ precursor and US- β -Ni(OH)₂ QDs samples



Figure S4. The images of the obtained US- β -Ni(OH)₂ QDs catalyst



Figure S5. The TEM-EDX spectrum of the obtained US-β-Ni(OH)₂ QDs catalyst



Figure S6. TEM and HRTEM images of the β -Ni(OH)₂ nanosheet



Figure S7. N₂ adsorption-desorption isotherm curves. (a) US-β-Ni(OH)₂ QDs. (b) β-Ni(OH)₂ nanosheet



Figure S8. The longer-time chronopotentiometry curves of US- β -Ni(OH)₂ QDs catalyst collected at the с

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Figure S9. CV curves measured in 1 M KOH solution at scan rates from 20 to 200 mV s⁻¹. (a) US- β -Ni(OH)₂ QDs. (b) β -Ni(OH)₂ nanosheets



Figure S10. LSV curves for UOR normalized by ECSA



Figure S11. The potential change of chronopotentiometry curves for the US-β-Ni(OH)₂ QDs after injecting CO₃²⁻

and NO₃⁻ solutions



Figure S12. The OH bond length of for the four distinct configurations of β -Ni(OH)₂

Catalyst	Current density (mA cm ⁻²)	Potential (V vs. RHE)	Substrate	References
US-β-Ni(OH) ₂ QDs	151	1.48	Carbon cloth	This work
Ni(OH)2 nanoflakes	142.4	1.62	Glassy carbon	Ref-2
Ni-MOF	~62.5	1.48	Glassy carbon	Ref-3
20% Pt/C	~4.5	1.48	Glassy carbon	Ref-3
β-Ni(OH) ₂	~80	1.48	Glassy carbon	Ref-4
β -Ni(OH) ₂ nanosheets	~35	1.48	Glassy carbon	Ref-5
V _{0.12} -doped Ni(OH) ₂	~120	1.48	Ni Foam	Ref-6
α-Ni(OH) ₂ -PNF-2	~125	1.48	Glassy carbon	Ref-7
Ni ₃ N-C	~50	1.48	Glassy carbon	Ref-8
Rh/C	~20	1.48	Self-standing	Ref-9
Ir/C	~30	1.48	Ni Foam	Ref-10
Ce-MOF-350	~5	1.48	Glassy carbon	Ref-11
Ni ₂ P	~50	1.48	Glassy carbon	Ref-12
V _{10%} -Ni ₅ P ₄	~150	1.48	Carbon cloth	Ref-13
Ni(OH) ₂ /NF	~75	1.48	Ni Foam	Ref-14
NF	~50	1.48	Ni Foam	Ref-15
NiFe(OH) _x /MnO ₂ /NF	~50	1.48	Ni Foam	Ref-16
Ce-Ni ₃ N@CC	>200	1.48	Carbon cloth	Ref-17
NiClO-D	~150	1.48	Glassy carbon	Ref-18
Co(OH)F/NF	>200	1.48	Ni foam	Ref-19
NiCoVO _x	~160	1.48	Carbon cloth	Ref-20

Table S1. UOR activity comparison between US- β -Ni(OH)₂ QDs and the reported UOR catalysts

NiMoO-H ₂	~100	1.48	Carbon cloth	Ref-21
Ni ₂ P nanoflake	~80	1.48	Carbon cloth	Ref-22
Ni-WOx	~250	1.48	Ni foam	Ref-23
CuNiP/NF	~100	1.48	Ni foam	Ref-24
Co(OH) ₂ -S	~110	1.48	Ni foam	Ref-25

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