Supplementary Information (SI) for ChemComm.

Surface chemistry-controlled growth of NiBDC on carbon nanotubes governs urea oxidation activity

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Experimental Procedures

Materials: Cobalt nitrate hexahydrate ($NiCl_2 \cdot 6H_2O$, > 98%), potassium hydroxide (KOH, > 95%) and Nafion solution (5 wt%, 99.9%) were all purchased from Sigma-Aldrich; 1,4-dicarboxybenzene acid (BDC, > 99%), urea (> 99.9%), hydroxylated carbon nanotubes, amino-functionalized carbon nanotubes and multi-walled carbon nanotubes were purchased from Macklin Biochemical Co., Ltd; Nickel foam (NF) was purchased from Kunshan Shengshijing new new material Co., Ltd; Ethanol absolute (≥99.7%) and N, N-dimethylformamide (DMF, > 99.5%) were bought from Sinopharm Chemical Reagent Co., Ltd. The water used was deionized (DI) water. All the chemicals were used as obtained without further purification.

Synthesis of NiBDC/CNT-OH: 20 mg of hydroxylated carbon nanotubes, 11.8 mg of $NiCl_2 \cdot 6H_2O$, and 8.3 mg of BDC were dissolved in a mixed solvent of water, ethanol, and N, N-dimethylformamide (DMF) (volume ratio = 1:1:16 mL), and stirred for 30 min to form a homogeneous solution. The obtained solution was transferred into a Teflon-lined autoclave and then heated at 120 °C for 12 h in an oven, followed by naturally cooled down to room temperature. After being repeatedly washed with DMF, ethanol, and deionized (DI) water and dried in an oven at 60 °C, a final product of NiBDC grown on CNT-OH was obtained.

Synthesis of NiBDC/CNT-NH_2: 20 mg of amino-functionalized carbon nanotubes, 11.8 mg of $NiCl_2 \cdot 6H_2O$, and 8.3 mg of BDC were dissolved in a mixed solvent of water, ethanol, and N, N-dimethylformamide (DMF) (volume ratio = 1:1:16 mL), and stirred for 30 min to form a homogeneous solution. The obtained solution was transferred into a Teflon-lined autoclave and then heated at 120 °C for 12 h in an oven, followed by naturally cooled down to room temperature. After being repeatedly washed with DMF, ethanol, and deionized (DI) water and dried in an oven at 60 °C, a final product of NiBDC grown on CNT-NH_2 was obtained.

Synthesis of NiBDC/CNT: 20 mg of multi-walled carbon nanotubes, 11.8 mg of $NiCl_2 \cdot 6H_2O$, and 8.3 mg of BDC were dissolved in a mixed solvent of water, ethanol, and N, N-dimethylformamide (DMF) (volume ratio = 1:1:16 mL), and stirred for 30 min to form a homogeneous solution. The obtained solution was transferred into a Teflon-lined autoclave and then heated at 120 °C for 12 h in an oven, followed by naturally cooled down to room temperature. After being repeatedly washed with DMF, ethanol, and deionized (DI) water and dried in an oven at 60 °C, a final product of NiBDC grown on MWCNT was obtained.

Synthesis of Ni/CNT-NH_2: 20 mg of amino-functionalized carbon nanotubes, and 11.8 mg of $NiCl_2 \cdot 6H_2O$ were dissolved in a mixed solvent of water, ethanol, and N, N-dimethylformamide (DMF) (volume ratio = 1:1:16 mL), and stirred for 30 min to form a homogeneous solution. The obtained solution was transferred into a Teflon-lined autoclave and then heated at 120 °C for 12 h in an oven, followed by naturally cooled down to room temperature. After being repeatedly washed with DMF, ethanol, and deionized (DI) water and dried in an oven at 60 °C, a final product of Ni/CNT-NH_2 was obtained.

Characterizations: The morphologies of the as-prepared catalysts were examined by FESEM (Gemini Sigma 360) and HRTEM (Jeol-2100P). The crystal structures of the as-prepared catalysts were measured by XRD (MiniFle×600). Raman spectra of the as-prepared catalysts were measured with a Horiba/LabRAM Odyssey at 532 nm. The functional groups was determined by INVENIO-S Fourier Transform-Infrared Spectroscopy (FT-IR). The test specimens were prepared by the KBr-disk method. The chemical environments of the as-prepared catalysts were measured by XPS (ESCALAB Xi+) with Al Kα radiation. All XPS spectra were calculated after correction with C 1 s peak at 284.8 eV. X-ray absorption fine structure (XAFS)spectroscopy was carried out using the Rapid-XAFS IM (Anhui Absorption Spectroscopy Analysis Instrument Co., Ltd.) by transmission mode at 25 kV and 40 mA.

Electrochemical measurements: An electrochemical analyzer (CHI 760E) was used to perform all electrochemical experiments in a standard three-electrode configuration.A Hg/HgO electrode filled with 1 M KOH and a graphite rod were used as a reference and counter electrode, respectively. The potential was converted to reversible hydrogen electrode (RHE) via a Nernst equation ($ERHE = E_{Hg/HgO} + 0.059 \times pH + 0.098$). The scan rate of linear sweep voltammetry (LSV) was set to 5.0 mV s^{-1}, with potentials ranging from 1.2 to 1.5 V vs. RHE in 1.0 M KOH + 0.33 M urea to investigate the UOR activities of the as-prepared catalysts. All polarization curves were calibrated with the iR correction. CV cycles (CVs) with the scan rates from 20 to 100 mV s^{-1} were applied to analyze ECSA. The catalyst ink was formulated by dispersing 3 mg of sample in a mixture of 20 μL Nafion solution and 480 μL isopropanol, followed by vigorous stirring for 30 min to achieve homogeneity. Subsequently, 16 μL of the resulting ink was drop-cast onto a L-shaped electrode surface. After ambient drying, this yielded a uniform catalyst loading of 500 μg cm^{-2}.

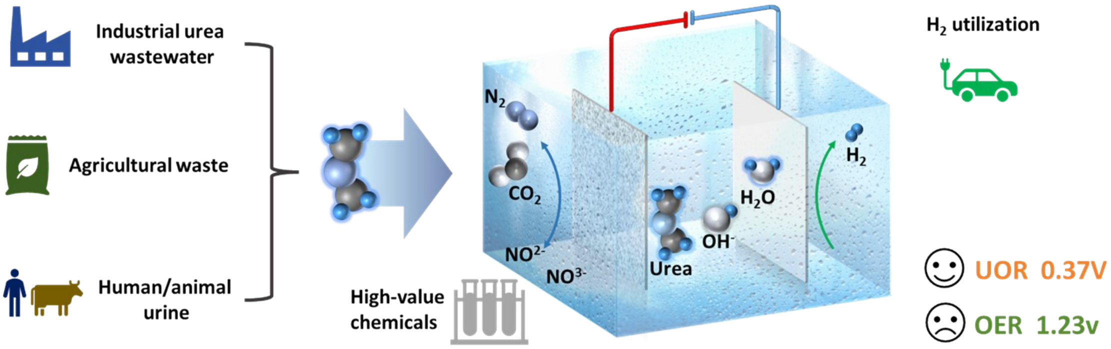

Fig. S1. Scenario of the UOR towards clean water and energy production.

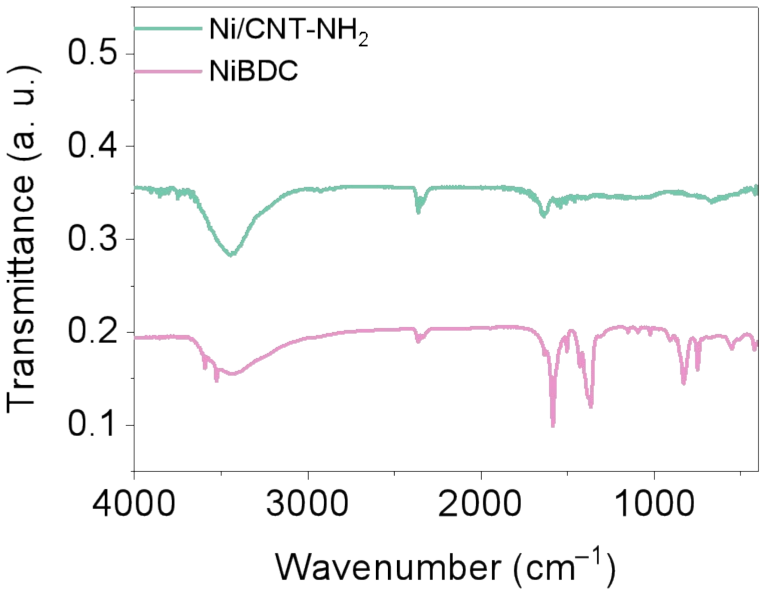

Fig. S2. The FT-IR, (b) PXRD, (c) Raman spectra of the NiBDC/CNT-OH, NiBDC/CNT-NH$_2$ and NiBDC/CNT.

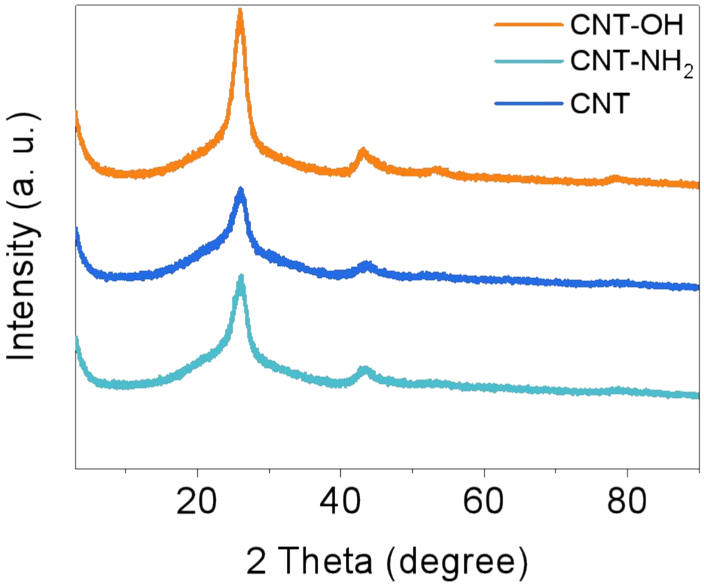

Fig. S3. PXRD of the CNT-OH, CNT-NH$_2$ and CNT.

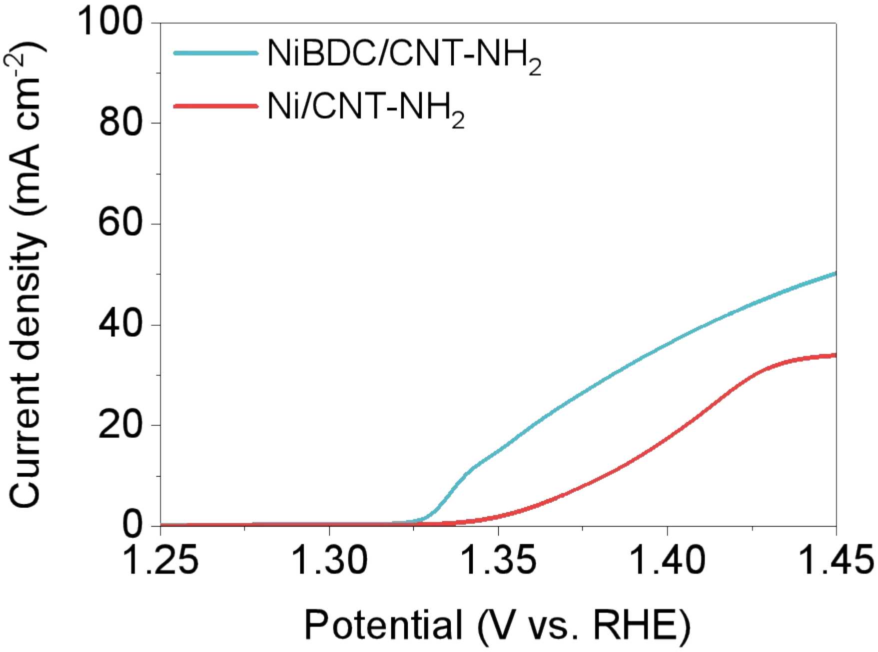

Fig. S4. Polarization curves of NiBDC/CNT-NH$_2$ and Ni/CNT-NH$_2$ in 1 M KOH + 0.33 M urea

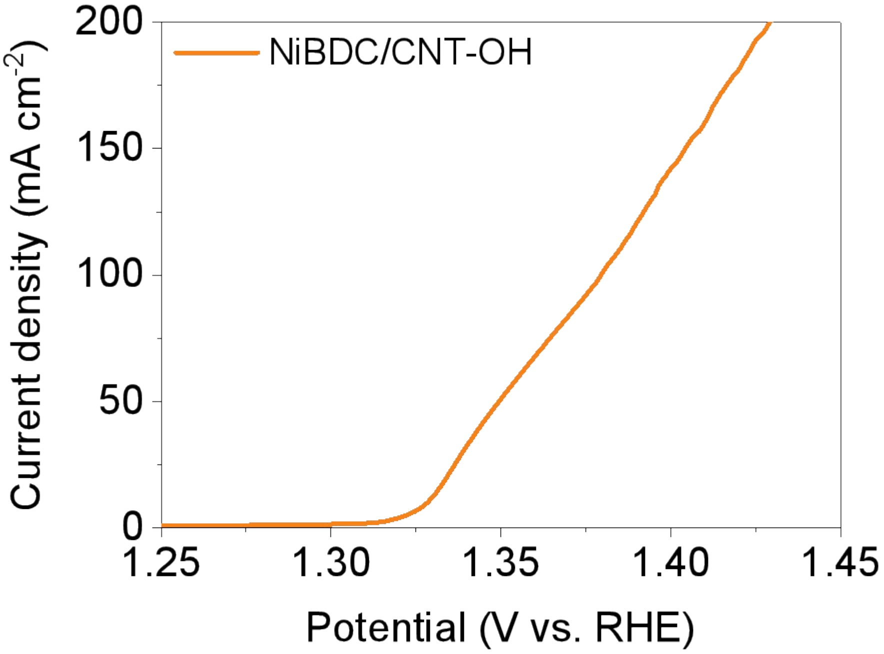

Fig. S5. Polarization curves of NiBDC/CNT-OH in 1 M KOH + 0.33 M urea

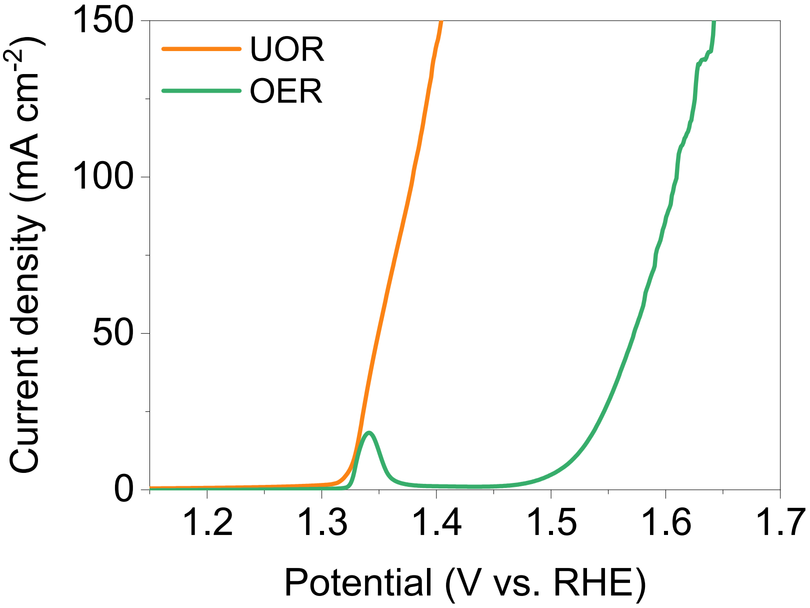

Fig. S6. Polarization curves of NiBDC/CNT-OH in 1 M KOH + 0.33 M urea and 1 M KOH.

Supplementary Table 1. Comparison of the overpotential of the NiBDC/CNT-OH catalyst with the recently reported powder catalyst at 10 mA cm^{-2} current.

Sample	Electrolyte	J (mA cm^{-2})	Overpotential (V vs.RHE))	Ref.
NiBDC/CNT-OH	1 M KOH + 0.33 M urea	10	0.958	This work
Ni-SO_X	1 M KOH + 0.33 M urea	10	0.968	1
Cu- NiFe LDH	1 M KOH + 0.33 M urea	10	0.980	2
CoNi@NCNTs-LDH/CC	1 M KOH + 0.33 M urea	10	0.989	3
$Ni_2P_4O_{12}$/NiTe	1 M KOH + 0.33 M urea	10	0.989	4
Fe-Ni_3S_2@$NiSe_2$	1 M KOH + 0.33 M urea	10	0.99	5
$Ni_2Fe(CN)_6$	1 M KOH + 0.33 M urea	10	0.976	6
Ni $(OH)_2$(O_{vac}-V-Ni $(OH)_2$)	1 M KOH + 0.33 M urea	10	1.014	7
NF/NiMoO-Ar	1 M KOH + 0.33 M urea	10	1.008	8
$Ni(OH)_2$-Ni_3S_2/NF	1 M KOH + 0.33 M urea	10	0.98	9
TAPP[Fe]-OFPc[Ni]-COF	1 M KOH + 0.33 M urea	10	1.000	10
P-Mo-Ni_3S_2@NF	1 M KOH + 0.50 M urea	10	0.984	11
NiFe LDH/WO_{3-x}	1 M KOH + 0.33 M urea	10	1.034	12

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