Supporting Information

Lanthanum-incorporated β-Ni(OH)$_2$ Nanoarrays for Robust Urea Electro-oxidation

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Experimental

Modification of the pristine carbon cloth (CC)

For the purpose of obtaining the porous surface, the pristine carbon cloths (1 × 4 cm^2) were immersed into the concentrated HNO_3 for 30 min and washed with ultrasonic for 20 min to eliminate oily impurities on the surface firstly. Then the clean carbon cloths were immersed into a 40 mL aqueous solution containing 0.25 M $Ni(NO_3)_2 \cdot 6H_2O$ and 0.5 M hexamine. The above solution was then poured into a 50 mL Teflon-lined stainless steel autoclave after stirring for 20 min, and heated at 120°C for 10 h. After cooling to the room temperature, the carbon cloths were cleaned with DI water and ethanol, then dried in the oven for a night. Followed by that, the carbon cloths were burned at 900°C in a tubular furnace in N_2 atmosphere for 1.5 h. Finally, the above carbon cloths were immersed into the concentrated HCl for 12 h, and rinsed with DI water and ethanol. After drying in the vacuum oven, the porous carbon cloths were obtained (named as CC).

Synthesis of La incorporated β-Ni(OH)$_2$ nanoarrays on CC (La: β-Ni(OH)$_2$/CC)

The catalysts with different molar ratios of La and Ni were synthesized in two steps: electrochemical deposition and followed by a hydrothemal process. Firstly, the electrodeposition process was carried out by setting up a three-electrode system, which was performed at -1.0 V (vs SCE) for 10 min in a 100 ml salt solution involving 0.571 mM $La(NO_3)_3 \cdot 6H_2O$ and 12 mM $Ni(NO_3)_2 \cdot 6H_2O$. CC (1 × 4 cm^2) was employed as working electrode while platinum plate and calomel electrode were used as counter electrode and reference electrode, respectively. After deposition, the sample was washed by DI water and ethanol and dried in the vacuum oven for a night to obtain the La-Ni/CC precursor (named as La-Ni/CC). Secondly, one piece of above La-Ni/CC precursor was placed into a 40 mL clear aqueous solution which was prepared in advance by dissolving 6 mmol dicyandiamide and stirring for 30 min.

Then the solution was poured into a 50 mL Teflon-lined stainless steel autoclave to heat at 100 °C for 8 h. After cooling to the room temperature naturally, the sample was removed from solution and cleaned by DI water and ethanol. After drying, the lanthanum-incorporated β-$Ni(OH)_2$ nanoarrays on carbon cloths (labeled as LN/CC 1:21) were prepared. Other molar ratios of La and Ni were synthesized by the same process but different concentrations of lanthanum ions in the solution during electrochemical deposition process.(0 mM $La(NO_3)_3 \cdot 6H_2O$ and 12 mM $Ni(NO_3)_2 \cdot 6H_2O$, 0.8 mM $La(NO_3)_3 \cdot 6H_2O$ and 12 mM $Ni(NO_3)_2 \cdot 6H_2O$, 0.667 mM $La(NO_3)_3 \cdot 6H_2O$ and 12 mM $Ni(NO_3)_2 \cdot 6H_2O$, 0.5 mM $La(NO_3)_3 \cdot 6H_2O$ and 12 mM $Ni(NO_3)_2 \cdot 6H_2O$, 0.444 mM $La(NO_3)_3 \cdot 6H_2O$ and 12 mM $Ni(NO_3)_2 \cdot 6H_2O$, denoted as β-$Ni(OH)_2$/CC, LN/CC 1:15, LN/CC 1:18, LN/CC 1:24 and LN/CC 1:27, respectively.)

Structural Characterization

The phase of catalysts was detected by X-ray powder diffraction (XRD) using a Philips X'Pert Pro Super diffractometer with Cu Kα radiation ($\lambda = 1.54178$ Å). Field-emission scanning electron microscope (FE-SEM, Hitachi SU8010A) was used to characterize the morphology of samples. High-resolution transmission electron microscopy (HRTEM, JEOLJEM2100F) was employed to study the detailed microstructure of catalysts. The compositional information of the samples was recorded on X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCLAB250Xi). X-ray spectroscopy (EDX) was used to investigate the element distribution. The molar ratios of La and Ni were investigated using the inductively coupled plasma optical emission spectroscope (ICP-OES, Perkin Elmer Optima 7300DV).

Electrocatalytic measurements

A three-electrode system was set up to test the electrocatalytic performance of catalysts. The potential we measured should be converted to a reversible hydrogen electrode (RHE) according to the equation of $E_{vs\ RHE} = E_{vs\ Hg/HgO} + E^{o}_{Hg/HgO} + 0.059pH$. In this work, all potentials are referred to RHE except as specifically indicated. The as-prepared catalysts were applied as the working electrode without binder while the Hg/HgO electrode and the platinum gauze ($2 \times 2\ cm^2$, 60 mesh) were employed as the reference electrode and the counter electrode, respectively. The UOR catalytic behaviour was tested in the mixed aqueous solution of 1 M KOH with 0.33 M urea with the scan rate of 2 mV s^{-1} on the electrochemical workstation (CHI660E). The pH value of the electrolyte is 13.6, which is the same with 1 M KOH solution. The electrochemical impedance spectroscopy (EIS) was performed at 1.53 V during the frequencies from 0.01 Hz to 100 kHz. The chronoamperometry measurement was conducted at 1.43 V for 20 h. The electrolyte didn’t replaced and was stirred throughout the chronoamperometric test.

Calculations

Density function theory (DFT) calculations were performed in the Vienna ab initio simulation package (VASP). A spin-polarized generalized gradient approximation (GGA) Perdew-Burke-Ernzerhof (PBE) functional, all-electron plane-wave basis sets with an energy cutoff of 400 eV, and a projector augmented wave (PAW) method were adopted. $Ni(OH)_2$ is simulated using a surface model of p (3 × 4) unit cell periodicity. A (3 × 3 × 1) Monkhorst-Pack mesh was used for the Brillouin-zone integrations to be sampled. 10 Å vacuum layer was added to avoid the interaction between adjacent layers. The conjugate gradient algorithm was used in the optimization. The convergence threshold was set $1*10^{-4}$ eV in total energy and 0.05 eV $Å^{-1}$ in force on each atom.

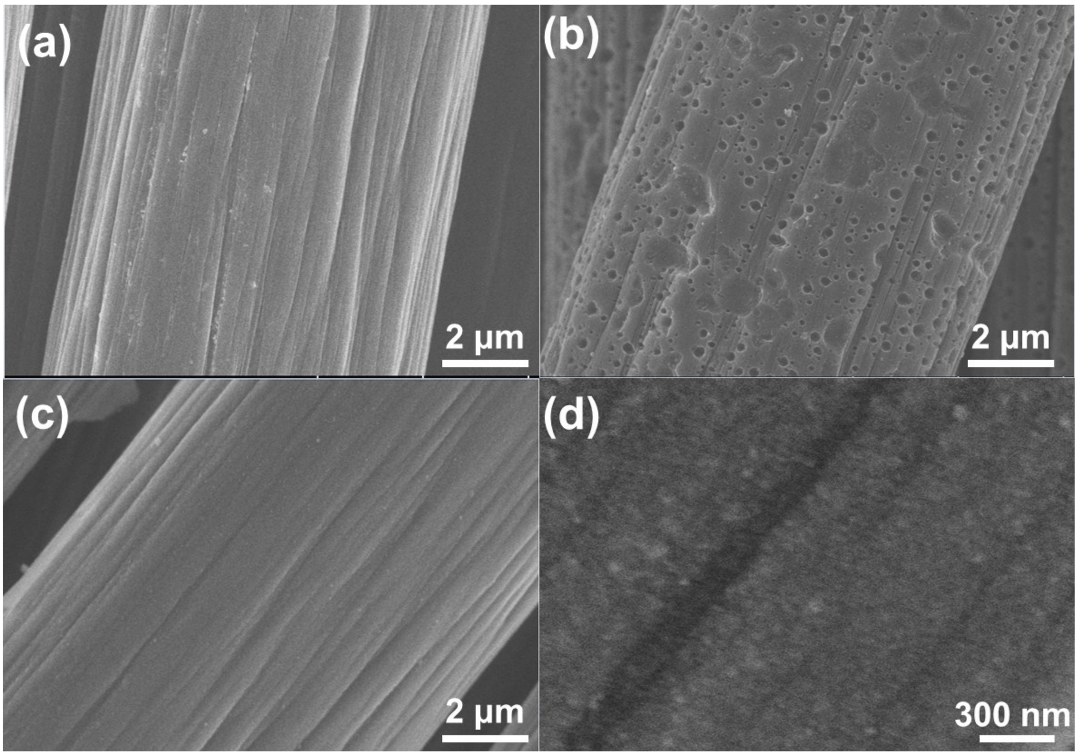

Fig.S1 SEM images of (a) pristine carbon cloths, (b) etched carbon cloths (CC), (c, d) La-Ni precursors on etched carbon cloths.

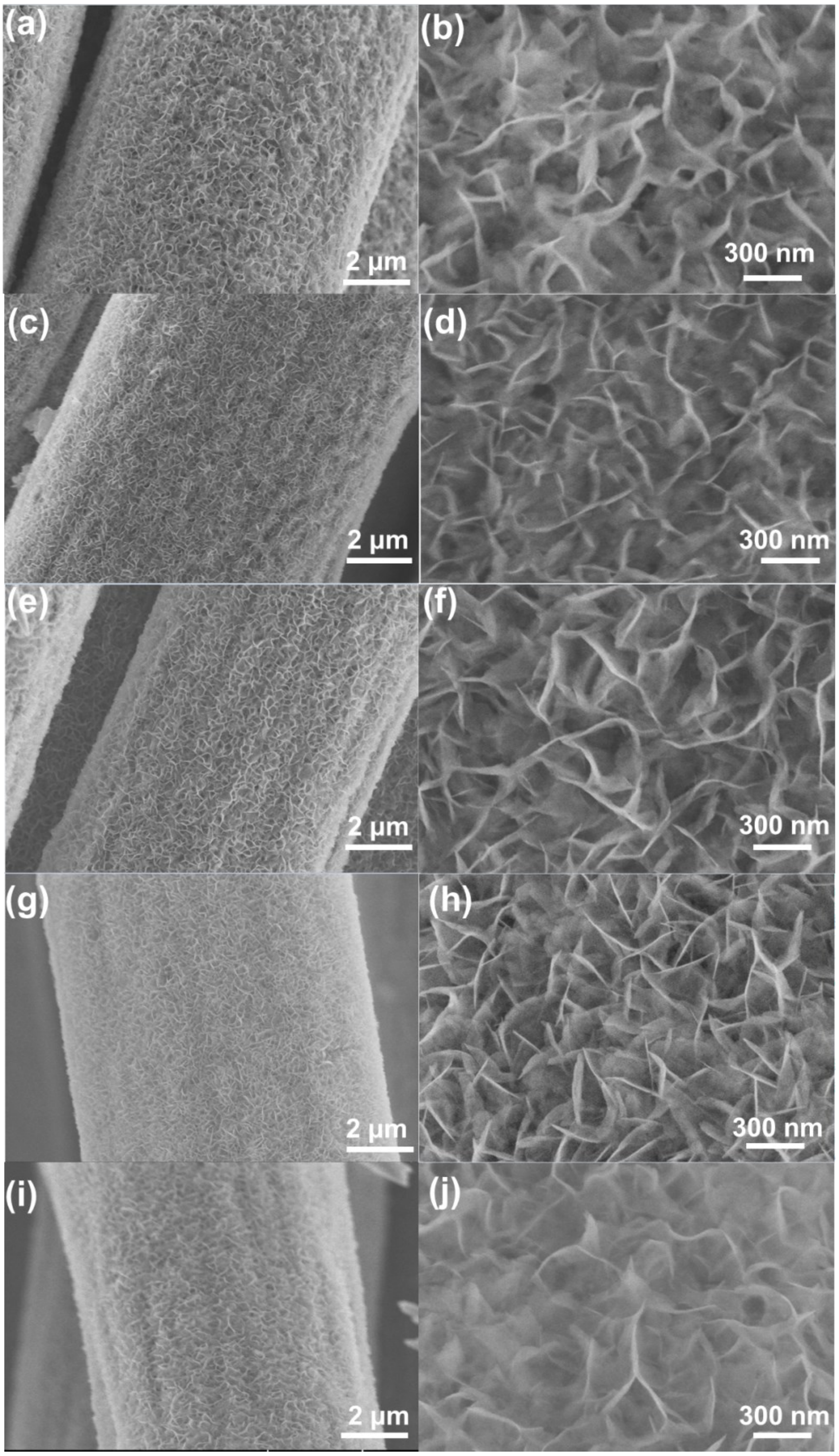

Fig.S2 SEM images of (a, b) β-Ni(OH)$_2$/CC, (c, d) LN/CC 1:27, (e, f) LN/CC 1:24, (g, h) LN/CC l:18 and (i, j) LN/CC 1:15.

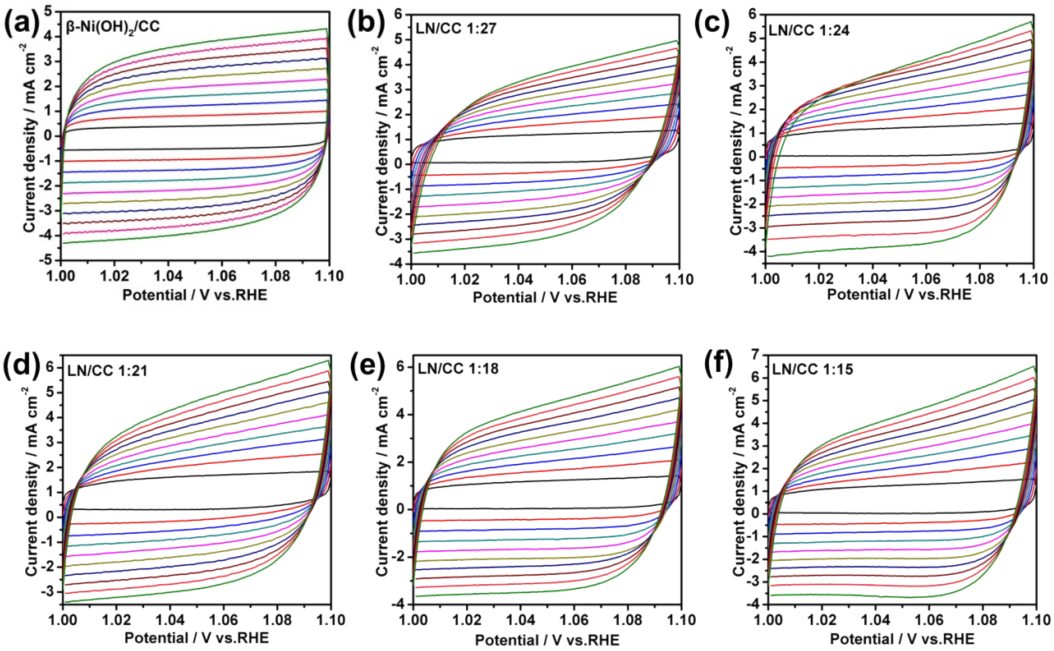

Fig.S3 CV curves of the samples at various scan rates from 10-100 mV s^{-1} in non-redox region.

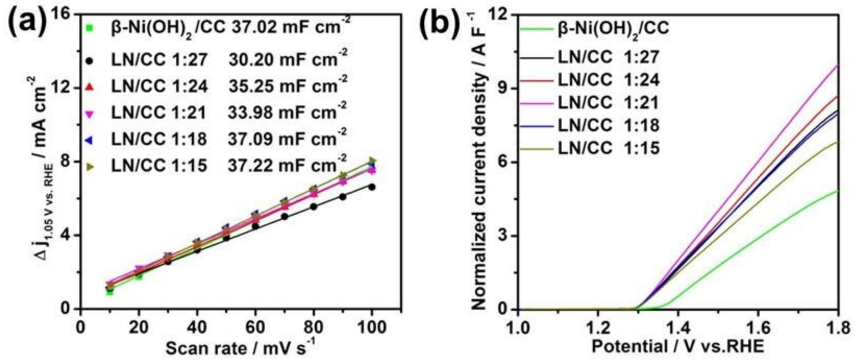

Fig.S4 (a) Current density variation at 1.05 V vs. RHE as a function of scan rates, (b) LSV curves normalized by C_{dl}.

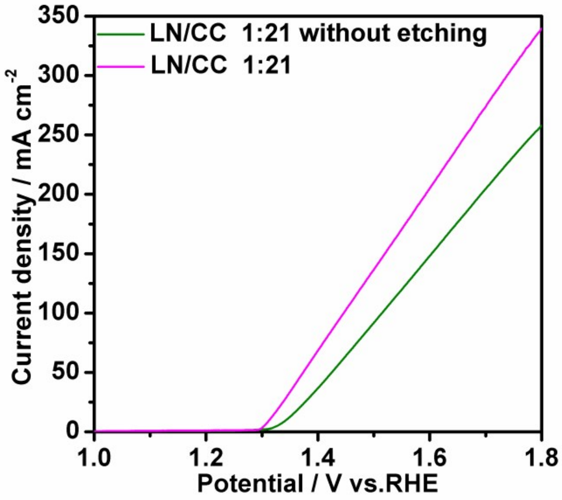

Fig.S5 LSV curves of LN/CC 1:21 grown on the carbon cloths with and without etching.

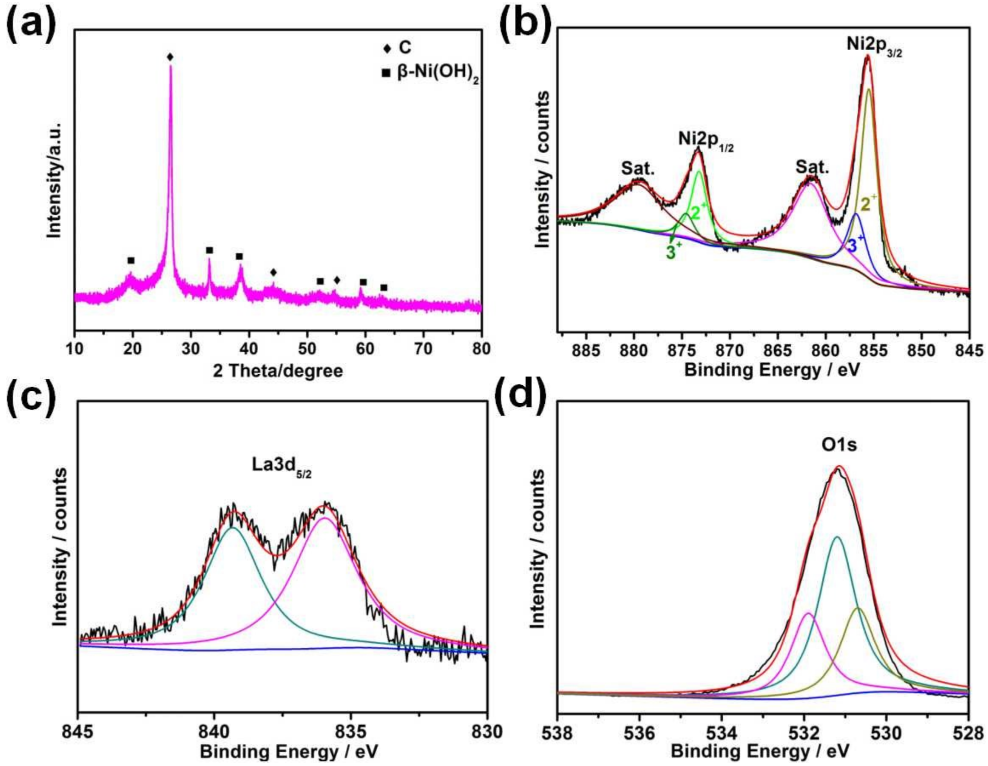

Fig.S6 XRD and high-solution XPS spectra of LN/CC 1:21 after chronoamperometric test: (a) XRD, (b) Ni, (c) La and (d) O.

Table S1. Molar ratios of Ni/La in the samples derived from the ICP analysis.

Sample	Molar ratio of Ni/La
β-Ni(OH)$_2$/CC	0
LN/CC 1:27	28.9
LN/CC 1:18	19.1
LN/CC 1:24	23.9
LN/CC 1:21	21.8
LN/CC 1:18	19.1
LN/CC 1:15	15.3

Table S2. The content of Ni in the etched carbon cloth derived from the ICP analysis.

Sample	Atomic% of Ni
CC	0

Table S3. Comparison of electrocatalytic performance for UOR

Sample	Required potential for 100 mA cm^{-2} [V vs. RHE]	C$_{dl}$[a] [mF cm^{-2}]	Tafel slope [mV per decade]	R$_s$[b] [Ω]	R$_{ct}$[c] [Ω]
β-Ni(OH)$_2$	1.58	37.02	70	5.32	5.57
LN/CC 1:27	1.49	30.20	33	4.85	1.85
LN/CC 1:24	1.46	35.25	30	4.54	1.71

LN/CC 1:21	1.44	33.98	26	4.44	1.36
LN/CC 1:18	1.46	37.09	28	4.78	1.73
LN/CC 1:15	1.48	37.22	35	4.69	1.67

[a] Electrochemical double-layer capacitance. [b] Series resistance. [c] Charge transfer resistance.

Table S4. Comparison of catalytic activity for UOR on different catalysts in 1.0 M KOH and a certain concentration of urea.

Catalyst	Concentration of Urea	Current density at 1.5 V (mA cm^{-2})	Required potential at 10 mA cm^{-2} (V vs. RHE)	Stability (time, potential)	Reference
Ni@NCNT	0.5 M	~45	1.38	~91.2% (10 h,1.39 V)	Ref.[1]
NF/NiMoO nanorods	0.5 M	~225	1.37	~90%(25 h,1.41 V)	Ref.[2]
$Ni_2P/Fe_2P/NF$	0.5 M	~145	1.36	NA	Ref.[3]
$Ni/Ni_{0.2}Mo_{0.8}N/MoO_3/NF$	0.5 M	NA	1.35	NA	Ref.[4]
Ni-Mo nanotube/NF	0.1 M	NA	1.36	NA	Ref.[5]
porous $Ni(OH)_2$ nanosheets	0.33 M	~50	~1.43	~91%(10 h,1.52 V)	Ref.[6]
β-NiS	0.33 M	~50	1.4	~67%	Ref.[7]

				(300 s, 1.42 V)	
Ni_2P/CFC	0.33 M	~35	1.34	~90%(10 h,1.45 V)	Ref.[8]
NiO/$NiCr_2O_4$	0.33 M	49.7	~1.36	~60%(1 h,1.5 V)	Ref.[9]
MOF-Ni@MOF-Fe-S	0.5 M	~125	1.35	NA	Ref.[10]
Ni-Co/Glassy carbon	0.33 M	NA	1.53	~90%(2 h,1.3 V)	Ref.[11]
$Ni(OH)_2$@NF	0.3 M	NA	1.35	NA	Ref.[12]
β-$Ni(OH)_2$/CC	0.33 M	68	1.38	74.29% (20 h,1.43 V)	This work
La: β-$Ni(OH)_2$/CC	0.33 M	137	1.31	94.71% (20 h,1.43 V)	This work

Note: "~" stands for the estimated value from the LSV curves.

Table S5. The Concentration of Ni and La in the electrolyte after chronoamperometric test derived from the ICP analysis.

element	Concentration (mg/L)
Ni	0.003
La	0

Reference

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