

## Supporting Information

# **Regulating the Local Charge Distribution of Ni Active Sites for the Urea Oxidation Reaction**

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#### 1 1. Materials and Chemicals

2 Nickel (II) chloride hexahydrate (NiCl2•6H2O), sodium tungsten (VI) dihydrate 3 (NaWO<sub>4</sub>•2H<sub>2</sub>O), ethanol ( $\geq$  99.5%), sodium hydroxide (NaOH), urea (CO(NH<sub>2</sub>)<sub>2</sub>), Carbon nanoparticles (~100 nm), Ag nanoparticles (~100 nm) and Nafion solution (5 4 wt% in a mixture of lower aliphatic alcohols and water) were purchased from Sigma-5 6 Aldrich. All the chemicals were used without further purification. Ni foam (1.5 mm) was obtained from the Kunshan De Foam Metal Co. Ltd and cleaned through sonicating 7 8 consecutively in acetone, 3 M HCl, ethanol, and deionized water to remove impurities 9 and oxide layers prior to using as a substrate.

#### 10 2. Synthesis of Ni-WO<sub>x</sub> and NiO<sub>x</sub> catalyst

11 Ni-WO<sub>x</sub> catalysts were synthesized via a facile coprecipitation method. NiCl<sub>2</sub>•6H<sub>2</sub>O (2 mmol) and urea (2.5 mmol) was first dissolved in deionized water (15 mL) in a beaker 12 and kept stirring on a magnetic stirrer. The NaWO4•2H2O (2 mmol) was dissolved in 13 another beaker (15 mL), then gradually added it at a drop rate of 0.5 mL•min<sup>-1</sup> into the 14 NiCl<sub>2</sub>•6H<sub>2</sub>O solution and stirred for 2 minutes. The mixed solution precipitated for 15 16 overnight. The precursor was harvested by centrifugation at 8000 rpm for 3 minutes and thoroughly washed 5 times by deionized water to remove the impurity ions. After 17 18 that, the precursor was vacuum dried at room temperature. Then the precursor was annealed at 550 °C for 2 h under 5% H<sub>2</sub> + 95% Ar atmosphere. For comparison different 19 20 Ni:W molar ratios of pre-catalysts were fabricated by the same procedure.

NiO<sub>x</sub> pre-catalyst was synthesized using the same method as Ni-WO<sub>x</sub> procedure. The
difference is no NaWO<sub>4</sub>•2H<sub>2</sub>O added but the NaOH (4 mmol) dissolved in 15 mL
deionized water, and then slowly dropwise added in to the NiCl<sub>2</sub>•6H<sub>2</sub>O solution. The
following process is same as that of Ni-WO<sub>x</sub>.

#### 25 **3. Characterization**

Transmission electron microscopy (TEM) observations were performed with a Tecnai G2 20 TWIN TEM under an acceleration voltage of 200 kV. The TEM samples were prepared by dropping catalyst powder dispersed in ethanol onto carbon-coated copper TEM grids and were dried in vacuum for 6 h. X-ray photoelectron spectroscopy (XPS) was obtained using a VG ESCALAB 220I-XL device. All XPS spectra were corrected using C1s line at 284.8 eV.

#### 32 4. X-ray absorption fine spectroscopy (XAFS)

The W L<sub>3</sub>-edge and Ni K-edge XAFS data were collected on 1W1B beamline at Beijing 1 2 Synchrotron Radiation Facility (BSRF). The scanning energy range was set from 10.01 to 11.01 keV and 8.140 to 9.130 keV in fluorescence mode with a step-size of 0.5 eV 3 at the near edge for W L<sub>3</sub>-edge and Ni K-edge respectively. The in-situ XAFS were 4 conducted in a triangular electrochemical cell and the working electrodes were prepared 5 6 by loading catalyst samples onto thin carbon paper. We employed a chronoamperometry process at 1.6 V (vs. RHE) for the in-situ measurements. And no potential applied state 7 8 as control for the test. For the reference samples, we conducted ex-situ XAFS to obtain the Ni K-edge XAFS data of commercial Ni and NiO powers and L<sub>3</sub>-edge XAFS data 9 10 of commercial W and WO<sub>2</sub>. These power samples were prepared by uniformly placing 11 powders on 3 M tape.

#### 12 5. Extended X-ray absorption fine structure (EXAFS) analysis

IFEFFIT software were used to calibrate the energy scale, to normalize the intensity 13 and to correct the background signal. The spectra were normalized with respect to the 14 edge height after subtracting the pre-edge and post-edge backgrounds using Athena 15 16 software. To extract EXAFS oscillations, background was removed in k-space using a five-domain cubic spline. The corresponding k-space data,  $k^2 \chi(k)$ , was then Fourier 17 transformed. EXAFS curve fitting was carried out with Artemis and IFEFFIT software 18 19 using ab initio-calculated phases and amplitudes from the program FEFF 8.2. The EXAFS fitting results of coordination number (CN), bond distance (R (Å)), Amplitude 20 attenuation factor ( $S_0^2$ ) and Debye-Waller factor ( $\sigma^2$ ) are given at Table S5 and Table 21 S6. 22

#### 23 6. Electrochemical Measurements

Electrochemical measurements were conducted using a three-electrode configuration connected to an electrochemical workstation (MULTI Autolab M204). Hg/HgO (with 1M KOH as the filling solution) and platinum foil were used as reference and counter electrodes, respectively. All the electrochemical tests were conducted at room temperature.

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The catalytic electrode was prepared as follow. Typically, 15 mg of catalyst powders was dispersed in a 1 ml ethanol, and then 40  $\mu$ L of Nafion solution (5 wt% aqueous solution) was added. The suspension was immersed in an ultrasonic bath for 20 min to prepare a homogeneous ink. Then, working electrode was prepared by spraying all of the catalyst ink onto Ni foam (2 × 1.5 cm<sup>2</sup>). The actual loading was determined by mass 1 difference of the substrate before and after air-brushing (0.2 mg·cm<sup>-2</sup>). Then the Ni 2 foam loaded with catalysts was fixed at an area of  $0.4 \times 0.5$  cm<sup>2</sup> by coating water 3 resistant silicone glue.

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Each pre-catalyst electrode was firstly activated using cyclic voltammetry (CV) method 5 between -0.2 V ~ -0.7 V (vs. Hg/HgO) with a scan rate of 100 mV  $\cdot$ s<sup>-1</sup> for 30 cycles in 6 N<sub>2</sub>-saturated 1 M KOH aqueous solution. Then, CV measurements were performed 7 until the signals were stabilized in the electrolyte of 1 M KOH aqueous solution with 8 0.33 M urea, prior to recording linear sweep voltammetry at 10 mV·s<sup>-1</sup>. The 9 galvanostatic measurement were conducted at a constant current density of 100 mA·cm<sup>-</sup> 10 <sup>2</sup>. A flow of N<sub>2</sub> gas (99.99 % purity) into the electrolyte was maintained during the 11 12 electrochemical test.

#### 13 7. Electrochemical active surface area (ECSA) calculation

The ECSAs of catalysts were calculated based on their electrical double layer capacitor (C<sub>dl</sub>), which were obtained from CV plots in a narrow non-Faradaic potential window from -0.12 to -0.02 V (*vs.* Hg/HgO). The measured capacitive current densities at the average potential in the potential window were plotted as a function of scan rate and the slope of the linear fit was calculated as C<sub>dl</sub>. The specific capacitance was found to be 60  $\mu$ F·cm<sup>-2</sup>, and the ECSA of the catalyst is calculated from equation 2.<sup>[1]</sup>

$$ECSA = \frac{C_{dl}}{60\,\mu F \cdot cm^{-2}} cm_{ECSA}^2 \tag{1}$$

The intrinsic activity was revealed by normalizing the current to the ECSA to exclude the effect of surface area on catalytic performance. The ECSA values of the catalysts are listed at Table S4.

#### 24 8. Turnover frequencies (TOFs) calculation

25 The TOF value was calculated from equation:

26

$$TOF = \frac{J*A}{6*F*n} \tag{2}$$

*J* is current density obtained at 1.6 V (*vs.* RHE) and normalized by geometric area; A is the geometric area; *F* is the Faraday constant and n is the mole number of nickel atoms on the electrode, calculated *via* equation (3).

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31 This method is calculating based on all Ni atoms, from the following equation:

$$n = \frac{m * r * NA}{M_W} \tag{3}$$

- 1 where m is the loading mass of catalyst on Ni foam, in Ni-WO<sub>x</sub> and NiO<sub>x</sub> catalysts, NA
- 2 is Avogadro's constant and M<sub>w</sub> is the molecular weight of catalyst.

#### **3 9.** Theoretical methods

The structural relaxation and electronic structures were performed with the framework 4 of Density Functional Theory (DFT) using the Vienna Ab initio Simulation Package 5 (VASP)<sup>[2]</sup>. The exchange correlation interactions potential of electrons were described 6 by Perdew-Burke-Ernzerhof (PBE) functional within a generalized gradient 7 approximation (GGA)<sup>[3]</sup>. The monolayer of W doped Ni(OH)<sub>2</sub> was modelled with a 4×4 8 periodic slab. A Monkhorst-Pack 1x1x1 k-point grid was adopted to sample the 9 Brillouin zone. Throughout the calculations, a 400 eV energy cut-off was used for the 10 plane-waves expansion of the Kohn–Sham orbitals. A vacuum region of ~22 Å was 11 12 adopted to avoid periodic image interactions. All atoms in the system were allowed to relax in three dimensions. The geometry optimizations were stopped until the 13 Hellmann-Feynman force on each atom was less than 0.01 eV Å<sup>-1</sup>. Van der Waals 14 interactions were described with the empirical correction of the DFT-D3 method<sup>[4]</sup>. The 15 16 charge-transfer between the W doped and undoped catalysts was investigated based on charge difference analysis. 17

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#### 19 **10. Thermodynamic analysis**

According to the evaluation of the technoeconomic viability of CO<sub>2</sub> electroreduction<sup>[5]</sup>, a significant lowering of the overall cell potential is necessary to improve the economics of CO<sub>2</sub> electroreduction.

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24 Cathode:  $CO_2 + H_2 \rightarrow CO + H_2O$  ( $\Delta G^0_{reaction}$ ) = 20.10 kJ mol<sup>-1</sup> (4)

26 Anode: 
$$H_2 O \rightarrow H_2 + 0.5 O_2$$
  $(\Delta G^0_{reaction}) = 237.1 \text{ kJ mol}^{-1}$  (5)

27

25

28 Overall: 
$$CO_2 \to CO + 0.5 O_2$$
  $(\Delta G_{reaction}^0) = 257.2 \text{ kJ mol}^{-1}$  (6)

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A Gibbs free energy analysis of the conventional  $CO_2$  electroreduction reveals that the anodic OER is more energy-consuming compared with  $CO_2$  reduction at cathode. Utilizing the Hess's law to calculated the stander Gibbs free energy of the individual steps and whole reaction, as expressed in equations (4)-(6), we find that only 7.8% of the overall energy is used to drive  $CO_2$  reduction, which means OER causes a lot of energy waste. While the design of the alternative reaction UOR coupled to  $CO_2$  electroreduction can significantly lower the overall energy consumption. As shown in Table S7, the Gibbs free energy is 100.2 kJ·mol<sup>-1</sup> which is only 38.9% of the conventional CO<sub>2</sub> electroreduction coupled to OER (all the  $\Delta G_f^0$  values are listed in Table S8). Moreover, the theoretical cell potential  $E_{cell}^0$  of CO<sub>2</sub>R//UOR is 0.17 V, which is much lower than CO<sub>2</sub>R//OER (1.33 V).

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In addition, the alternative reactions of OER for the system are guided by three design 7 rules: 1) The process is energy intensive and no additional CO<sub>2</sub> emissions 2) The anode 8 feed is a cheap chemical or a waste 3) The anode reaction match the scale of CO<sub>2</sub>-based 9 commodity or intermediate chemicals. The electrooxidation of urea in which the anode 10 11 feed is a common waste in industrial and sanitary wastewater could further reduce the 12 cost of overall reduction. Also, the production CO and N2 are a demand at the scale of commodity. Furthermore, to satisfy all the design rules, the CO<sub>2</sub> generates at anode 13 reaction can be reduced through an ingenious design where CO<sub>2</sub> can penetrate a 14 breathable non-woven intermediate to the cathode to ensure no extra CO<sub>2</sub> emissions for 15 16 the whole reaction.

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#### 18 **11. CO<sub>2</sub>R//UOR electrolyzer**

19 Two-electrode electrolyzer was assembled to verify the promise of UOR, as an alternative anodic reaction to OER in CO2 electroreduction device. The cell used Ni-20 WO<sub>x</sub> as anode electrocatalyst for UOR and commercial Ag nanoparticles (Ag NPs) as 21 cathode for CO<sub>2</sub> electroreduction, whose voltages were recorded during the 22 23 galvanostatic measurement at a constant current density of 100 mA·cm<sup>-2</sup>. The size of the electrolyzer chambers was  $0.6 \times 0.6 \times 0.5$  cm<sup>3</sup>. The CO<sub>2</sub> rate was maintained at 40 24 sccm by a mass flow controller (Alicat Scientific Inc.). Aqueous 1M KOH solution with 25 and without 0.33 M urea were used as electrolyte for OER and UOR, respectively. The 26 flow rate of solution was controlled at 20 mL/min by two separate liquid pumps 27 (BT600-2J, Longer Precision Pump Co. Ltd). A non-woven fabrics was used to separate 28 the cathode and anode chambers. Electrolysis experiments were carried out with an 29 30 electrochemical workstation (MULTI Autolab M204). The Energy saving efficiency (n) 31 is calculated from the perspective of the energy of the full cell. The n value is calculated 32 from equation:

$$\eta = \frac{E_{cell,OER} - E_{cell,UOR}}{E_{cell,OER}} \times 100\%$$
(7)

2

1

#### 3 12. Products analysis

The gas products and liquid products were measured by chromatography (Agilent Technologies, 7890B) and NMR spectroscopy (Bruker AVANCE III HD 400 MHz), respectively. Nitrogen (Praxair, 99.999%) was used as the carrier gas of the chromatography.  $CH_4$  and  $C_2H_4$  concentration were quantified via a flame ionization detector (FID) directly and CO was converted to  $CH_4$  in a nickel catalyst kit and then quantified via an FID. Thermal conductivity detector (TCD) was used to quantify  $H_2$ concentration.

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The liquid products were analyzed offline using 1H nuclear magnetic resonance (NMR) analysis (AVANCE III HD 400 MHz). Quantified 0.54 mL electrolyte was mixed with 0.06 mL D<sub>2</sub>O and 0.006  $\mu$ L dimethyl sulfoxide (Sigma, 99.99%) as an internal standard. The one-dimensional 1H spectrum was measured with water suppression using a presaturation method. All the FEs were normalized to 100 when the liquid product FE was set as tested.

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Figure S1. SEM image and XRD pattern of NiO<sub>x</sub>.



**Figure S2.** Element compositions of the Ni-WO<sub>x</sub> HRTEM-EDS analysis. The atom ratio of Ni/W is 3.13.



**Figure S3.** XRD patterns of Ni-WO<sub>x</sub>, NiO<sub>x</sub>, carbon paper substrate and Ni (JCPDS no. 04-0850)



**Figure S4.** (a) Polarization curves and (b) Tafel plots of Ni-WO<sub>x</sub> with different ratio in 1M KOH with 0.33 M urea at scan rate of 10 mV $\cdot$ s<sup>-1</sup>.



Figure S5. Three independent UOR polarization curves of Ni-WO<sub>x</sub> and NiO<sub>x</sub> catalysts in 1M KOH electrolyte with 0.33M urea.



**Figure S6.** EIS plots of Ni-WO<sub>x</sub> and NiO<sub>x</sub> tested at onset potential (0.43 V vs. Hg/HgO). The inset gives the equivalent circuit. Rs: serious resistance; Rct: charge-transfer resistance; CPE: constant-phase element related to the double-layer capacitance.



**Figure S7.** CV curves recorded at different scan rates for (a) Ni-WO<sub>x</sub> and (b) NiO<sub>x</sub> catalysts in a potential window (-0.12 to -0.02 V *vs.* Hg/HgO) without faradaic processes. (c) Current density as a function of the scan rate to give the double-layer capacitance for Ni-WO<sub>x</sub> and NiO<sub>x</sub> catalysts.



Figure S8. The BET area of Ni-WO<sub>x</sub> and  $NiO_x$ .



Figure S9. Comparison of the current density normalized by ECSA (left axis) and mass activities (right axis) of Ni-WO<sub>x</sub> and NiO<sub>x</sub> catalysts at 1.6 V (vs. RHE).



**Figure S10.** The W L<sub>3</sub>-EXAFS fitting of the first-shell and the  $k^2$ -weighted XAFS  $\chi(k)$  of (a and c) Ni-WO<sub>x</sub>-no potential and (b and d) Ni-WO<sub>x</sub>-1.6V, respectively.



Figure S11. XPS O 1s spectra of Ni-WO<sub>x</sub>-no potential and Ni-WO<sub>x</sub>-1.6V.



**Figure S12.** Fourier transforms of  $k^2$ -weight EXAFS spectra of Ni-WO<sub>x</sub>-1.6 V and NiO<sub>x</sub>-1.6 V, respectively.



**Figure S13.** The Ni K-edge EXAFS fitting of the first-shell and the  $k^2$ -weighted XAFS  $\chi(k)$  of Ni-WO<sub>x</sub>-1.6V.



**Figure S14.** (a) Top and side view of the W-doped NiOOH, in which the top layer hydrogen atoms of Ni(OH)<sub>2</sub> are removed to mimic the realistic catalyst surface. (b) charge difference of the catalysts. The blue and pink contours show electron accumulation and depletion after W doping, respectively. The Ni, W, O, H atoms are represented with green, orange, red, and white balls, respectively. The isosurface values were  $\pm 0.01$  e Å<sup>-3</sup>.



**Figure S15.** (a) CO and H<sub>2</sub> Faradaic efficiency (b) Representative NMR spectrum for UOR//CO<sub>2</sub>R electrolyzer measured at current density of 100 mA $\cdot$ cm<sup>-2</sup> for 10000 s. (c) Urea (57-13-6) 1H NMR, in acetone, DMSO and tetramethylurea.

**Table S1.** ICP results of Ni-WOx sample.

ICP results	Ni 221.647	W 239.709	Ni:W ratios
Concentration	4.233 µg/ml	3.328 µg/ml	3.983
average			
Concentration per	4.229 µg/ml	3.325 µg/ml	3.984
Run1			
Concentration per	4.254 μg/ml	3.326 µg/ml	4.006
Run2			
Concentration per	4.215 μg/ml	3.334 µg/ml	3.960
Run3			

Catalyst	Potential @ 100 mA·cm <sup>-2</sup> (V vs. RHE)	Current density @ 1.6 V (vs. RHE) (mA·cm <sup>-2</sup> )	Stability	Electrolyte	Reference (ref.)
Ni-WO <sub>x</sub>	1.40±0.01	440±3	10h	0.33 M	This work
NiOx	1.48±0.02	182±6	-	0.33 M	This work
NF@p-Ni	1.55	135	3500s	0.33 M	[6]
Co1Mn1 LDH/NF	1.44	235	40h	0.33 M	[7]
Ni-MOF	1.43	292	-	0.33 M	[8]
NiO-Ni/NF	1.43	200	16h	0.33 M	[9]
Fe11.1%-Ni <sub>3</sub> S <sub>2</sub>	1.44	280	20h	0.33 M	[10]
NiMo@ZnO/NF	1.50	-	24h	0.33 M	[11]
NiFeCo LDH/NF	1.45	315		0.33M	[12]
Ni <sub>3</sub> S <sub>2</sub> @NF	1.43	-	10h	0.33M	[13]
1% Cu:α- Ni(OH) <sub>2</sub> /NF	1.41	356		0.33M	[14]

**Table S2.** Comparison of UOR performance for Ni-WOx and recent reportedelectrocatalysts. All electrochemical performances are collected on Ni foam.

<u> </u>		
Steps	Reactions	$\Delta G$
		$(kJ \cdot mol^{-1})$
1	$CO(NH_2)_2+M \rightarrow [M \bullet CO(NH_2)_2]_{ads}$	66.2
2	$[M \bullet CO(NH_2)_2]_{ads} + OH^- \rightarrow [M \bullet CO(NH_2 \bullet NH)]_{ads} + H_2O + 1e^-$	-28.9
3	$[M \bullet CO(NH_2 \bullet NH)]_{ads} + OH^{-} \rightarrow [M \bullet CONH_2 \bullet N]_{ads} + H_2O + 1e^{-}$	-185.1
4	$[M \bullet CONH_2 \bullet N]_{ads} + OH^{-} \rightarrow [M \bullet CONH \bullet N]_{ads} + H_2O + 1e^{-}$	75.4
5	$[M \bullet CONH \bullet N]_{ads} + OH^{-} \rightarrow [M \bullet CON_{2}]_{ads} + H_{2}O + 1e^{-}$	-178.2
6	$[M \bullet CON_2]_{ads} + OH^- \rightarrow [M \bullet CO \bullet OH]_{ads} + N_2 + 1e^-$	392.7
7	$[M \bullet CO \bullet OH]_{ads} + OH^{-} \rightarrow [M \bullet CO_{2}]_{ads} + H_{2}O + 1e^{-}$	-156.6
8	$[M \bullet CO_2]_{ads} \rightarrow M + CO_2$	1242.2
total	$CO(NH_2)_2+6OH^- \rightarrow N_2+5H_2O+CO_2+6e^-$	1227.7

**Table S3** Elementary steps of UOR and Gibbs free energy ( $\Delta G$ ) for all the intermediate steps (M=NiOOH).<sup>[15]</sup>

Sample	Geometric area (cm²)	Potential <sup>a</sup> (V vs. RHE)	ECSA (cm²)	BET (m <sup>2</sup> ·g <sup>-1</sup> )	Specific Activity <sup>b</sup> (mA·cm <sup>-2</sup> )	Mass activity <sup>b</sup> (A·g <sup>-1</sup> ) <sup>c</sup>	TOF <sup>c</sup> (s <sup>-1</sup> )	TOF <sup>d</sup> (s <sup>-1</sup> )
Ni-WO <sub>x</sub>	0.2	1.40	4.83	7.58	18.2	440	0.11	0.083
NiO <sub>x</sub>	0.2	1.48	2.77	3.27	13.1	182	0.023	0.023

Table S4. Parameters for each catalyst investigated on Ni foam electrode in 1 M KOH electrolyte with 0.33 M urea.

a: obtained at the current density of 100 mA · cm<sup>-2</sup> (based on projected geometric area).

b: obtained at the potential of 1.6 V (vs. RHE).

c: based on all Ni atoms, calculated *via* equation (2).

d: based on all Ni atoms and W atoms, calculated *via* equation (2).

Sample	Element	Path	CNs	$S_{2}^{0}$	$\sigma^2$	Eo	R
Ni-WO <sub>x</sub> -no	W	W-O	3.34	0.8	0.003529	12.56	2.00
potential		W-Ni	3.81	0.8	0.003529	10.82	2.52
Ni-WO <sub>x</sub> -	W	W-O	1.41	0.8	0.004271	13.75	1.87
1.6V		W-Ni	9.14	0.8	0.004271	15.28	2.52

Table S5. Parameters of EXAFS fitting of Ni-WO<sub>x</sub> W L<sub>3</sub>-edge.

Sample	Element	Path	CNs	S <sup>0</sup> <sub>2</sub>	$\sigma^2$	E <sub>0</sub>	R
Ni-WO <sub>x</sub>	Ni	Ni-Ni	8.01	0.8	0.00648	5.03	2.50
		Ni-W	1.59	0.8	0.00648	20.5	2.56
		Ni-O	0.57	0.8	0.00648	5.03	2.03

 Table S6. Parameters of EXAFS fitting for Ni-WOx Ni K-edge.

Table S7. Theoretical  $\Delta G_{reaction}^{0}$  and  $E_{cell}^{0}$  for electrooxidation of CO<sub>2</sub> to CO coupled to anodic O<sub>2</sub> evolution and urea electrooxidation.

Cathode reaction	Possible anode reactions	Possible overall reaction	Δ G <sup>0</sup> <sub>reaction</sub> (kJ·mol <sup>-1</sup> )	$E_{cell}^0$ (V)
$CO_2+H_2O+2e^-\rightarrow CO+2OH^-$	$2OH^{-} \rightarrow H_2O + 0.5O_2 + 2e^{-}$	$CO_2 \rightarrow CO + 0.5O_2$	257.2	1.33
$CO_2+H_2O+2e^-\rightarrow CO+2OH^-$	$CO(NH_2)_2 + 6OH^- \rightarrow N_2 + 5H_2O + CO_{2+}$ 6e <sup>-</sup>	$CO(NH_2)_2+2CO_2 \rightarrow N_2+2H_2O+$ 3CO	100.2	0.17

Molecular formula	Name	$\Delta G_f^0$ (kJ·mol <sup>-1</sup> )
H <sub>2</sub> O	Water	-237.1
$CO_2$	Carbon dioxide	-394.4
$CO(NH_2)_2$	Urea	-197.2
СО	Carbon monoixde	-137.2

**Table S8.** Gibb's free energy of formation  $\Delta G_f^0$  values.

All values are reported under standard conditions of 1 bar and 298K.

Cathode	Anode	Current density (mA·cm <sup>-2</sup> )	Cell potential (v)	Reference (ref.)
Ag/GDL	Ni-WO <sub>x</sub>	100	2.16	This work
Ag/GDL	Ni foam	100	2.53	[16]
CoPc-CN/CNT	CoOx/CNT	82	2.35	[17]
Ag/GDL	Ni foam	80-100	2.80	[18]
Ni <sub>1</sub> -N/CNT	IrO <sub>2</sub> /GDL	47	2.80	[19]
Au/C/APEM	IrO <sub>2</sub> /porous Ti sheet	100	2.25	[20]
Ag/MWCNT/GDL	IrO <sub>2</sub>	175	3.00	[21]
Ag/ GDL	Ni foam	100	~3.50	[22]

**Table S9.** Comparison of cell potential for co-electrolysis of  $CO_2$  and urea and recentreported electrocatalysts. All electrochemical performances are collected on Ni foam.

#### **References for the Supporting Information**

[1] Q. He, Y. Wan, H. Jiang, Z. Pan, C. Wu, M. Wang, X. Wu, B. Ye, P. M. Ajayan, L. Song, *ACS Energy Lett.* **2018**, *3*, 1373-1380.

[2] aG. Kresse, J. Furthmuller, *Phys. Rev. B* **1996**, *54*, 11169-11186; bG. Kresse, J. Furthmuller, *Comput. Mater. Sci.* **1996**, *6*, 15-50.

[3] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh,C. Fiolhais, *Phys. Rev. B* 1992, *46*, 6671-6687.

[4] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys. 2010, 132, 154104.

[5] S. Verma, B. Kim, H.-R. M. Jhong, S. Ma, P. J. A. Kenis, *Chemsuschem* **2016**, *9*, 1972-1979.

[6] M.-S. Wu, Y.-J. Sie, S.-B. Yang, *Electrochim. Acta* 2019, 304, 131-137.

[7] Z. Wang, Y. Hu, W. Liu, L. Xu, M. Guan, Y. Zhao, J. Bao, H. Li, *Chemistry* 2020, 26, 9382-9388.

[8] D. Zhu, C. Guo, J. Liu, L. Wang, Y. Du, S. Z. Qiao, *Chem. Commun.* **2017**, *53*, 10906-10909.

[9] Z. Yue, W. Zhu, Y. Li, Z. Wei, N. Hu, Y. Suo, J. Wang, *Inorg. Chem.* **2018**, *57*, 4693-4698.

[10] W. Zhu, Z. Yue, W. Zhang, N. Hu, Z. Luo, M. Ren, Z. Xu, Z. Wei, Y. Suo, J. Wang, *J. Mater. Chem. A* **2018**, *6*, 4346-4353.

[11] J. Cao, H. Li, R. Zhu, L. Ma, K. Zhou, Q. Wei, F. Luo, *J. Alloys Compd.* **2020**, *844*, 155382.

[12] P. Babar, A. Lokhande, V. Karade, B. Pawar, M. G. Gang, S. Pawar, J. H. Kim, ACS Sustainable Chem. Eng. 2019, 7, 10035-10043.

[13] M. Liu, Y. Jiao, S. Zhan, H. Wang, Catal. Today 2020, 355, 596-601.

[14] J. Xie, L. Gao, S. Cao, W. Liu, F. Lei, P. Hao, X. Xia, B. Tang, J. Mater. Chem. A 2019, 7, 13577-13584.

[15]D. A. Daramola, D. Singh, G. G. Botte, J. Phys. Chem. A 2010, 114, 11513-11521.

[16]X. V. Medvedeva, J. J. Medvedev, S. W. Tatarchuk, R. M. Choueiri, A. Klinkova, *Green Chem.* **2020**, *22*, 4456-4462.

[17]X. Lu, Y. Wu, X. Yuan, L. Huang, Z. Wu, J. Xuan, Y. Wang, H. Wang, *ACS Energy Lett.* **2018**, *3*, 2527-2532.

[18]C. M. Gabardo, A. Seifitokaldani, J. P. Edwards, C.-T. Dinh, T. Burdyny, M. G. Kibria, C. P. O'Brien, E. H. Sargent, D. Sinton, *Energy Environ. Sci.* **2018**, *11*, 2531-2539.

[19] S. Jin, Y. Ni, Z. Hao, K. Zhang, Y. Lu, Z. Yan, Y. Wei, Y. R. Lu, T. S. Chan, J. Chen, *Angew. Chem. Int. Ed.* **2020**, *59*, 21885-21889.

[20]Z. L. Yin, H. Q. Peng, X. Wei, H. Zhou, J. Gong, M. M. Huai, L. Xiao, G. W. Wang, J. T. Lu, L. Zhuang, *Energy Environ. Sci.* **2019**, *12*, 2455-2462.

[21]S. Ma, R. Luo, J. I. Gold, A. Z. Yu, B. Kim, P. J. A. Kenis, *J. Mater. Chem. A* **2016**, *4*, 8573-8578.

[22] D. A. Salvatore, D. M. Weekes, J. He, K. E. Dettelbach, Y. C. Li, T. E. Mallouk, C.P. Berlinguette, ACS Energy Lett. 2017, 3, 149-154.