Electronic Supplementary Information

Facile synthesis of mesoporous spinel $NiCo_2O_4$ nanostructures as high efficient electrocatalysts for urea electro-oxidation

Rui Ding,[*a,b,c] Li Qi,[a] Minjun Jia[c] and Hongyu Wang[*a]

[a] *State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun 130022, China*

[b] *Graduate University of Chinese Academy of Sciences, Beijing 100039, China*

[c] *State Key Laboratory of Theoretical and Computational Chemistry, College of Chemistry, Jilin University, Changchun 130023, China*

[*] Email addresses: dingrui@ciac.ac.cn; hongyuwang@ciac.ac.cn;
Tel/Fax: +86 431 85262287;

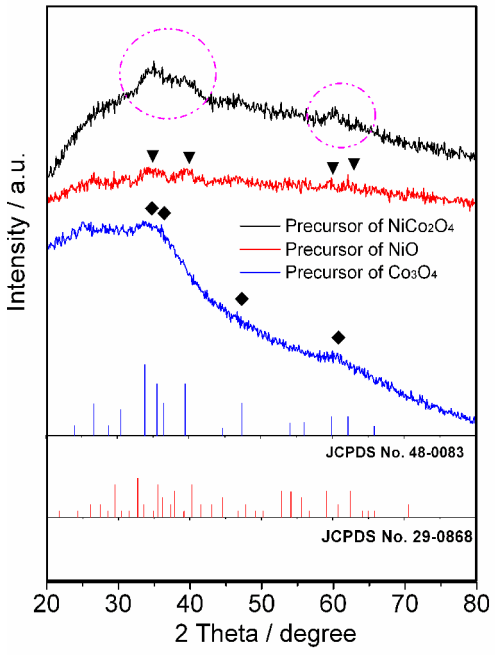

Fig. S1 XRD patterns of precursors of NCO, NO and CO.

As can be seen in Fig. S1, there are two distinguishable areas (marked as circles) in the precursor of NCO, which can be attributable to the overlap of the precursor of NiO ($Ni_2CO_3(OH)_2$•$2H_2O$, JCPDS No. 29-0868) and the precursor of Co_3O_4 ($Co(CO_3)_{0.5}(OH)$•$0.11H_2O$, JCPDS No. 48-0083) synthesized by the same method.

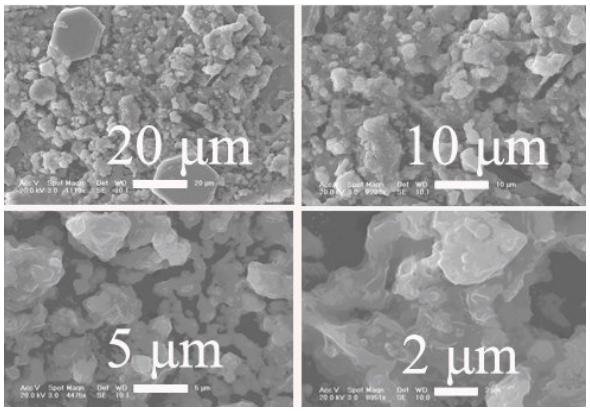

Fig. S2 SEM images of as-synthesized CO materials.

As can be seen in Fig. S2, the CO materials exhibit an obvious aggregated morphology, which is similar to that of NCO materials. However, The CO materials display a much larger particle size with the maximum value reaching as far as 20 μm in the observed scope. Moreover, the CO materials tend to be a smoother surface, suggesting their smaller surface area and porosity compared with those of NCO counterparts.

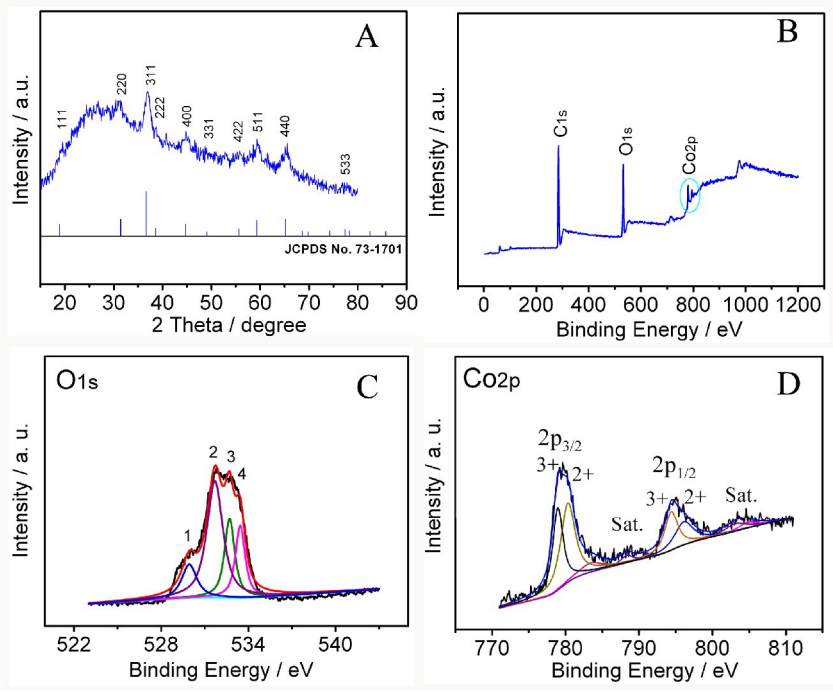

Fig. S3 XRD patterns (A) and XPS profiles (B–D) of CO.

The XRD patterns in Fig. S2A shows that the CO materials can be identified as standard Co_3O_4 phase (JCPDS No. 73-1701). XPS profiles in Fig. S2B–D demonstrate that the CO materials have a chemical composition of O and Co species and the Co element consist of two spin-orbit doublets characteristics of Co^{2+} and Co^{3+} and two shakeup satellites (identified as "Sat."), indicating the solid state redox couple of Co^{3+}/Co^{2+} exists in the CO structure.

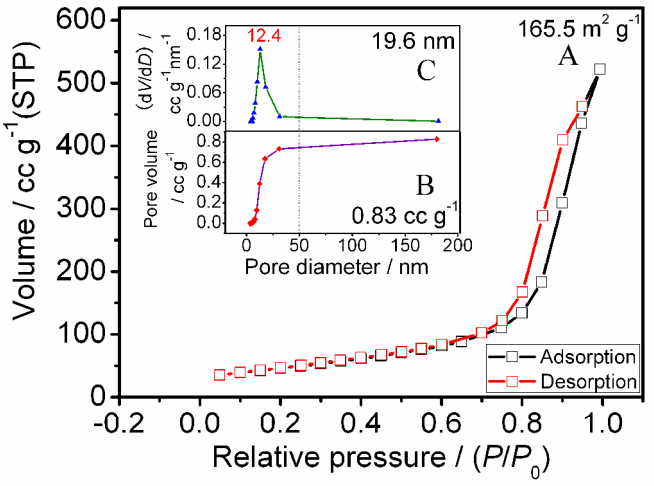

Fig. S4 N_2 adsorption/desorption istherms (A), pore volume plots (B) and PSD plots (C) of CO.

Fig. S3 shows that the CO materials exhibit the typical mesoporous characteristics, which is similar to that of NCO materials. The SSA, total pore volume, mesopore volume, and average pore diameter of CO materials are 165.5 m^2 g^{-1}, 0.83 cm^3 g^{-1}, 0.745 cm^3 g^{-1} and 19.6 nm respectively.

Table S1 XPS data of NCO materials.

Element	O1s				Co2p								Ni2p							
State	M-O	M-O_{1+x}	M-OH	H-OH	Co^{2+}				Co^{3+}				Ni^{2+}				Ni^{3+}			
No.	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
B.E.	528.9	530.4	531.8	533	780.7	789	795.9	805.2	779.2	785	794.2	802.1	854.2	860.8	871.5	876.8	856	863.5	872.8	880
I.R.	29.2	22.5	26.7	21.6	32.1	3.6	14.3	3.2	26	5.4	11.6	3.8	20.1	10.5	11.5	5.7	22	8.1	12.3	9.8
C			0.687				0..097				0.085				0.063				0.068	
A.R.			4.1[a]						1.39								1			

Note: [a] The calculated O ratio has been excluded the H-OH band; B.E. (binding energy, eV); I.R. (Intesity ratio); *C* (element content); A.R. (atomic ratio). Quantitative analysis of surface composition was carried out by integrating the peaks area (*I*) and by utilizing the atomic sensitivity factors (*S*) as shown in the following Equation:

$$C_x = \frac{I_x / S_x}{\sum I_x / S_x} \qquad (1)$$

Table S2 A comparison of nitrogen sorption data between NCO and CO.

Materials	**S_{BET} [a] ($m^2\ g^{-1}$)**	**V_T [b] ($cm^3\ g^{-1}$)**	**V_{meso} [c] ($cm^3\ g^{-1}$)**	**L_0 [d] (nm)**	**PSD [e] (nm)**
NCO	190.1	1.136	0.943	23.9	12.4
CO	165.5	0.828	0.745	19.6	12.4

Note: [a] BET surface area ($m^2\ g^{-1}$); [b] Total pore volume ($cm^3\ g^{-1}$); [c] Mesopore volume ($cm^3\ g^{-1}$); [d] Average pore diameter (nm); [e] Pore size distribution (nm).

Table S3 The fitting values of impedimetric parameters for NCO and CO electrodes in 1 M KOH electrolytes in absence (A) and presence (B) of 0.33 M urea.

Electrodes	Impedimetric parameters								
	L ($H\ cm^2mg^{-1}$)	R_e ($\Omega\ cm^2mg^{-1}$)	$Q1$, Y_0 ($\Omega^{-1}\ s^n\ cm^{-2}mg^{-1}$)	R_{ct} ($\Omega\ cm^2mg^{-1}$)	W, Y_0 ($\Omega^{-1}\ s^{0.5}\ cm^{-2}mg^{-1}$)	$Q2$, Y_0 ($\Omega^{-1}\ s^n\ cm^{-2}mg^{-1}$)	$n1$	$n2$	χ^2 (E-3)
NCO-A	6.0E-8	0.29	1.2E-3	0.35	0.64	0.79	0.90	1.0	0.52
NCO-B	3.0E-8	0.42	1.4E-3	0.71	0.83	0.17	0.86	0.75	0.45
CO-A	2.5E-8	0.38	8.2E-3	7.20	0.052	5.31	0.72	1.0	0.89
CO-B	6.8E-8	0.24	1.9E-3	2.24	0.047	0.13	0.85	0.81	0.62