Controllable synthesis of mesoporous NiO/Ni nanorod as an excellent catalyst for urea electrooxidation

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This supplementary information file replaces that originally published on 09 April 2020, in which there were some errors in Fig. S4 due to incorrectly processed XRD data. The correct data are shown in Fig. S4 in this revised file. This does not affect the results or conclusions reported in the article.

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1. Materials and reagents

All chemicals, Ni(NO₃)₂·6H₂O, Na₂C₂O₄, Hexamethylenetetramine (C₆H₁₂N₄) , and ethanol (C₂H₅OH,), were purchased from Shanghai Sinopharm Chemical Reagent and used without further treatment or purification. All aqueous solutions were prepared with high-purity de-ionized water. (DI-water, resistance 18 M Ω cm⁻¹)

2. Preparation of rod-like assemblies NiC₂O₄·2H₂O

The rod-like assemblies NiC₂O₄·2H₂O were synthesized by an alcohol-assisted room temperature stirring route. Typically, a solution of Ni(NO₃)₂·6H₂O (0.515 mmol, 0.15 g) in 20 mL deionized water and 5 mL absolute ethyl alcohol was added to a solution of Na₂C₂O₄ (0.1mmol, 0.134 g), C₆H₁₂N₄ (0.1mmol, 0.14 g) in 20 mL deionized water and 5 mL absolute ethyl alcohol and mixed to obtain a stable solution, and then stirred vigorously at room temperature for 4 h. Finally, the obtained green samples were washed using deionized water and ethanol to remove the impurities, and dried in the air naturally. It is noteworthy that introducing the C₆H₁₂N₄ into the metal salt solution at room temperature, whereas after stirring, the C₆H₁₂N₄ decomposed into ammonia and carbonate anions. Subsequently, the OH⁻ may be formed by the interaction between ammonia and water, thus further dissociation of HMTA resulting in the increase in the OH⁻ concentration. C₆H₁₂N₄ is used as an auxiliary agent in the process of synthesis, which can not only adjust and control the growth size of the material, but is itself alkaline. the chemical reaction equations are as follows:

 $C_6H_{12}N_4 + 6H_2O \longrightarrow 4NH_3 + 6HCHO$

 $H_2O+ NH_3 \longrightarrow OH^- + NH^{4+}$

 $Ni^{2+} C_6 H_{12} N_4 \longrightarrow -(CH_2)_6 N_4 + Ni^{2+}$

3. Preparation of Porous NiO/Ni

The porous NiO/Ni was prepared via the as-obtained NiC₂O₄·2H₂O. The pyrolysis temperature was based on the thermogravimetric analysis (TGA) results and set at 340 °C. In a typical process, the precursor of NiC₂O₄·2H₂O was placed in a tube furnace, which was flushed by N₂ with a speed of 30 mL min⁻¹ to remove air before heating. Then, the furnace was heated to the target temperature of 340 °C (N-340) under N₂ flow at a rate of 1 °C min⁻¹ and holding 2 h. Finally, the product was taken out. For comparison, the annealing temperatures of the other two samples were controlled at 320 °C (N-320) and 360 °C (N-360) respectively.

4. Characterization

The products were tested by X-ray diffraction (XRD) on a Bruker D8 Advanced X-ray Diffractometer (Cu-K α radiation: λ =0.15406 nm) for the phase analysis. Scanning electron microscope (SEM, Zeiss_Supra55) was used for observing the morphology of the samples at an acceleration voltage of 5.0 kV. High-resolution transmission electron microscopy (HRTEM) images, selected area electron diffraction (SAED) images, and energy dispersive X-ray spectroscopy mapping were captured on a Tecnai G2 F30 transmission electron microscopy (XPS) was carried out on a Thermo Scientific ESCALAB 250 apparatus. In addition, Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) were tested on Autosorb IQ3. All electrochemical performances were carried out by a CHI 660E instrument.

5. Fabrication of working electrodes

The as-prepared NiO/Ni samples were suspended in a 1% Nafion solution (20 mg mL⁻¹). Before modification, the glassy carbon electrode (GCE, diameter with 3 mm) was polished with a 0.3 μ m Al₂O₃ slurry and later ultrasonically cleaned with ethanol and water. Then, 5 μ L of the above suspension was added onto the GCE surface (diameter = 3 mm) and dried at room temperature. The catalyst loading density was determined to be \approx 1.41 mg cm⁻². This modified electrode was then washed with deionized water three times to avoid the possible influence of the residual nafion for the following experiments. We evaluated the catalytic activity of rod-like assemblies modified GCE electrode toward reduction of 0.33M Urea in 1 M KOH with the protection of N₂.



Figure S1. FESEM and TEM images of the samples obtained at different conditions: (a_{1-3}) the precursor of NiC₂O₄·2H₂O, (b_{1-3}) N-320, (c_{1-3}) N-340, (d_{1-3}) N-360.



Figure S2. XRD patterns of the precursor of $NiC_2O_4 \cdot 2H_2O$.



Figure S3. TG curves in N₂ of the precursor of NiC₂O₄·2H₂O.



Figure S4. The XRD of the precursor calcined at 320 °C, 340 °C and 360 °C.



Figure S5. XPS survey spectra of the three samples.



Figure S6. The pore size distribution curves of the meso-NiO/Ni composites.



Figure S7. N_2 adsorption-desorption isotherms of the the meso-NiO/Ni composites.



Figure S8. LSV curves of the precursor in 1 M KOH with 0.33 M urea.



Figure S9. LSV curves of N-320 based on GCE in 1 M KOH solution with and without 0.33 M urea at the scan rate of 5 mV s⁻¹.



Figure S10. LSV curves of N-360 based on GCE in 1 M KOH solution with and without 0.33 M urea at the scan rate of 5 mV s⁻¹.



Figure S11. LSV curves based on GCE in 1 M KOH solution with 0.33 M urea at the scan rate of 5 mV s⁻¹ at current densities of 0.1 mA cm⁻².



Figure S12. The XRD of N-340 after the durability test.



Figure S13. Cyclic voltammograms of (a) N-320, (b) N-340 and (c) N-360 at scan rates from 5 to 100 mV s⁻¹ in 1 M KOH with 0.33 M urea. (d) Estimating the Cdl and relative electrochemically active surface areas in 1 M KOH with 0.33 M urea.



Figure S14. The EIS response of the three samples in 1 M KOH solution with 0.33 M urea.



Figure S15. The raw LSV curve (no iR compensation) and the real LSV curve (95% iR compensation) of the sample of N-340.



Figure S16. Stability response of N-320 (a) and N-360 (b) at a constant current density of 10 mA cm⁻².



Figure S17. SEM images of the three samples immersed in 1 M KOH solution with 0.33 M urea for (a_1-b_1) 0.5h; (a_2-b_2) 2h; (a_3-b_3) 4h.

Electrode materials	Electrolyte	Working	Substrate	Ref.
		Potential		
L-MnO ₂	1M KOH+0.5M Urea	1.37 V	Graphene/Ni foam	1
S-MnO ₂	1M KOH+0.5M Urea	1.33 V	Graphene/Ni foam	1
MnO ₂ /MnCo ₂ O ₄	1M KOH+0.5M Urea	1.33 V	Ni foam	2
Pt/C	1M KOH+0.5M Urea	1.68 V	Ni foam	1
Pt/C/IrO2	1M KOH+0.5M Urea	1.72 V	Ni foam	1
Co(OH)F	1M KOH+0.7M Urea	1.42 V	Ni foam	3
CuCo2O4	1MKOH+0.33M Urea	1.36 V	Ni foam	4
CoS2	1M KOH+0.3M Urea	1.59 V	Ti mesh	5
Fe-O-P	1M KOH+0.5M Urea	1.34 V	Ni foam	6
NiO/Ni	1MKOH+0.33M Urea	1.35 V	Glassy carbon	This work

Table S1. Comparison of the UOR catalytic performance of different materials.

Electrode	Electrolyte	Working	Substrate	Ref.
materials		Potential		
Ni-MOF (BTC)	1M KOH+1M Urea	1.5 V	carbon paper	7
Ni ₂ P	1M KOH+0.5M Urea	1.38 V	carbon cloth	8
Ni(OH) ₂	1M KOH+0.33M Urea	1.39 V	Glassy carbon	9
Ni(OH) ₂ NMs	1M KOH+0.33M Urea	1.35 V	Glassy carbon	10
C/Ni-Fe	1M KOH+0.33M Urea	1.39 V	Ni foam	11
NiCo ₂ S ₄	1M KOH+0.33M Urea	1.66 V	carbon cloth	12
Ni/C	1M KOH+0.33M Urea	1.60 V	Glassy carbon	13
Graphene/Ni(OH) ₂	1M KOH+0.33M Urea	1.52 V	Glassy carbon	14
LaNiO3	5M KOH+0.33M Urea	1.39 V	Glassy carbon	15
Ni ₆₀ Cr ₄₀ /C	1M KOH+0.33M Urea 1M	1.38 V	Glassy carbon	16
NiO/Ni	KOH+0.33M Urea	1.35 V	Glassy carbon	This work

Table S2. Comparison of the UOR catalytic performance of different Ni-basedmaterials.

Sample	Ni(0)/%	Ni(II)/%
N-320	10.63%	89.37%
N-340	15.26%	84.74%
N-360	19.27%	80.73%

Table S3. XPS peak results of percentages of Ni(0), Ni(II) species calculated from Ni2p.

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