Supplementary data

Na Wu[a], Xiaoyu Chi[b], Yujuan Zhang[b], and Tuoping Hu[b]*

a. Department of Chemical and Materials Engineering, Lyuliang University, Lyuliang 033001, PR China

b. Department of Chemistry, School of Chemistry and Chemical Engineering, North University of China, Taiyuan 030051, PR China

1. Experimentals section

1.1 Pretreatment of CC

CC was soaked in concentrated nitric acid for 3 days at ambient temperature, and rinsed several times alternately by deionized (DI) water and anhydrous C_2H_5OH, and then dried under vacuum for 24 h at 60°C.

1.2 Preparation of working electrode

3 mg of finely ground NiO-CrO@N-C samples were dispersed in a mixed solution of 20 μL DI water and 10 μL anhydrous C_2H_5OH for 10 min under ultrasound to prepare a slurry, which of 30 μL was evenly covered on the CC (0.5 × 0.5 cm^2) and dried for later use.

1.3 Optimization experiments

To obtain superior UOR catalyst, the effects of the molar ratio of $Ni(NO_3)_2/C_2H_5NO_2$ and $Ni(NO_3)_2/Cr(NO_3)_3$, and reaction temperature on the UOR performance of as-prepared samples were investigated. Without adding $Cr(NO_3)_3$, the optimal molar ratio of $Ni(NO_3)_2/C_2H_5NO_2$ (1:1-5:1) was studied by LSV tests at a scan rate of 10 mV s^{-1}. As shown in Fig. S1a, the onset potential is lowest in 1.0 M KOH electrolyte, when the molar ratio of $Ni(NO_3)_2/C_2H_5NO_2$ is 3:1. After 0.33 M urea was added into the above electrolyte, the j value of the sample prepared by with a 3:1 molar ratio of $Ni(NO_3)_2/C_2H_5NO_2$ was the highest (Fig. S1b). Therefore, the optimal molar ratio of $Ni(NO_3)_2/C_2H_5NO_2$ is 3:1.

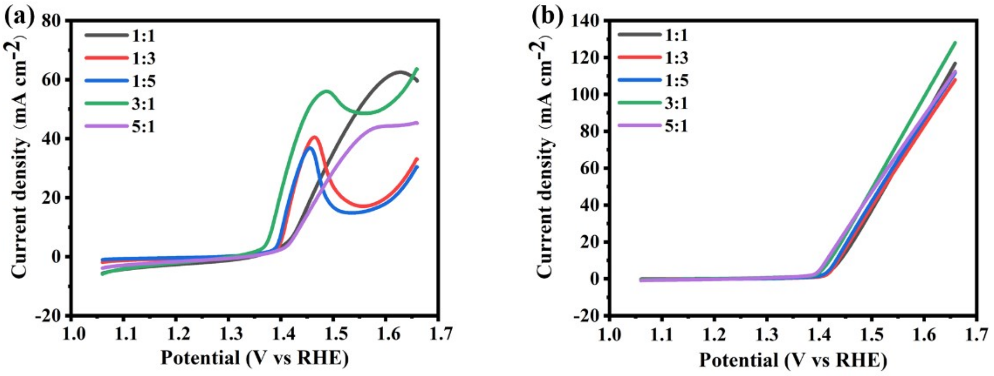

Fig. S1. LSV plots of samples prepared by different molar ratios of $Ni(NO_3)_2/C_2H_5NO_2$ (a) in 1 M KOH electrolyte; (b) in 1 M KOH + 0.33 M urea electrolyte.

To further improve the performance of UOR, when the molar ratio of $Ni(NO_3)_2/C_2H_5NO_2$ is 3:1, CV was used to investigate the UOR performance of the as-synthesized samples at different $Cr(NO_3)_3$ concentrations. In 1 M KOH electrolyte, the sample prepared by 1.0 mM $Cr(NO_3)_3$ has the largest CV enclosed area (Fig. S2a), and the j value was the highest after urea was added into the 1.0 M KOH electrolyte (Fig. S2b).

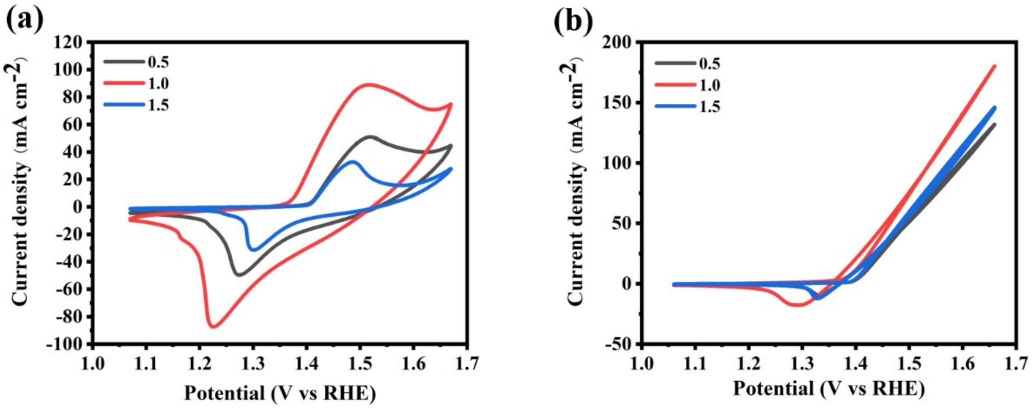

Fig. S2. CV plots of samples prepared with different concentrations of $C_2H_5NO_2$ in 1 M KOH electrolyte (a) and 1 M KOH + 0.33 M urea electrolyte (b).

To study the influence of the reaction temperature on the performance of UOR, LSV tests were carried out in 1.0 M KOH electrolyte. The sol-gel self-propagating combustion method takes advantage of the huge thermal energy released by the chemical reaction to suddenly increase the temperature of the adjacent material for triggering new chemical reaction, which quickly spreads to the entire reactant in the form of a combustion wave. Whereas, the high temperature step would consume energy and lead to the agglomeration of particles [1]. After the catalyst agglomeration, the exposed area of the active ingredient decreases correspondingly, the sample made at 220℃ showed the decrease of catalytic activity and the increase of overpotential. As illustrated in Fig. S3a, the samples prepared at 200℃ has the lowest onset potential. At the same time, the j value of the sample was the highest in mixed electrolyte of 1 M KOH and 0.33M urea (Fig. S3b).

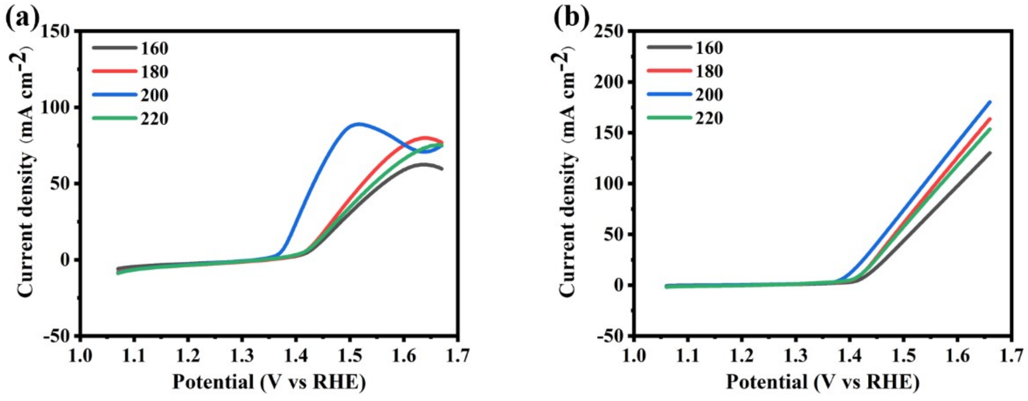

Fig. S3. LSV plots of samples prepared with different reaction temperatures in 1 M KOH electrolyte (a) and 1 M KOH + 0.33 M urea electrolyte (b).

Samples NiO-CrO@N-C and NiO@N-C for subsequent physical characterization were prepared under optimal conditions.

1.4 Optimization of electrolyte concentration

To study the influence of KOH (0.1-1.5 M) and urea (0.1-1.0 M) concentrations on the performance of UOR, LSV tests were carried out. As illustrated in Fig. S4a, the j value enhances gradually with the increase of the KOH content when the urea concentration is constant. The j value decreases when the KOH concentration exceeds 1.0 M, which is due to adsorption competition between urea molecules and OH- ions. The amounts of OH^- ions on the catalyst surface increase, which reduces the chance of urea molecules contacting active sites and the j value decreases. As a result, the concentration of KOH was chosen to be 1.0 M.

The j value begins to decrease when the urea concentration exceeds 0.33 M at constant concentration of KOH, which is because the rate of UOR is controlled by diffusion under the condition of low urea concentration, UOR is dynamically controlled when the urea concentration is high, as illustrated in Fig. S4b. Similarly, with the increase of urea concentration, the adsorption competition between urea and OH^- ions on the catalyst surface becomes more obvious, and the adsorption amount of OH^- ions decreases, thus reducing the oxidation rate of urea. In summary, the electrolyte of KOH (1.0 M) + urea (0.33 M) was used in the following experiments. The performance comparison of NiO-CrO@N-C sample with those of the previous literatures for UOR was listed in Table S1.

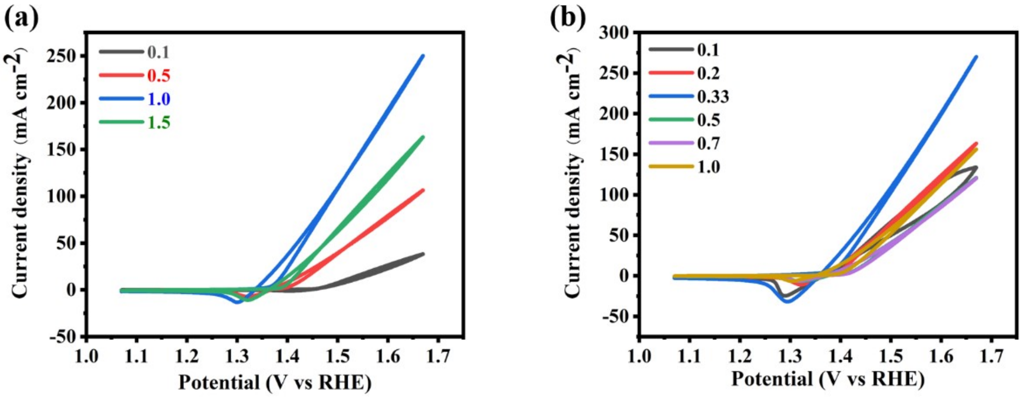

Fig. S4. (a) LSV curves of NiO-CrO@N-C in different concentrations of KOH and 0.33 M urea electrolyte; (b) CV curves of NiO-CrO@N-C in electrolytes with 1 M KOH and different concentrations of urea at a scan rate of 10 mV s^{-1}.

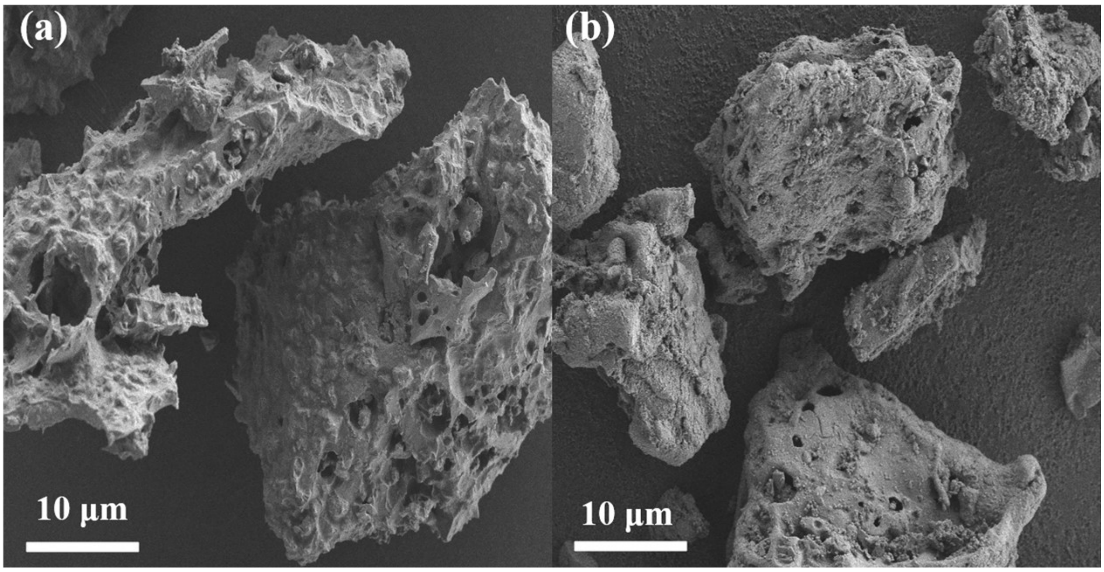

Fig. S5. SEM images of NiO-CrO@N-C before (a) and after (b) long-term stability tests.

Table S1. Comparisons of the NiO-CrO@N-C catalyst with those of the literatures for UOR

Electrocatalyst	Method	Electrolyte	Onset potential vs. RHE	Scan rate (mV s^{-1})	Ref. (year)
Ni-NiO/Gr	freeze-drying /annealing approach	1 M KOH+0.33 M urea	1.34 V	10	[2] (2021)
Ni/NiO-N-C-500	hydrothermal and pyrolysis	1 M KOH+0.33 M urea	1.38 V	10	[3] (2021)
Cu/Fe-MOFs	binder-free thin film of ultrathin sheets of bimetallic	1 M KOH+0.33 M urea	1.37 V	10	[4] (2022)
NC-PB@CNT	an ion-exchange strategy	1 M KOH+0.33 M urea	1.37 V	50	[5] (2021)
NiO-CrO@N-C	sol-gel self-propagating combustion reaction	1 M KOH+0.33 M urea	1.37 V	10	This work

Notes and references

[1] D. Bai, H. Feng, N. Chen, L. Tan, J. Qiu, J. Magn. Magn. Mater. (2017), 152-157.

[2] S. Wang, P. Xu, J. Tian, Z. Liu, L. Feng, Electrochim. Acta, 2021, 370, 137755.

[3] N. Wu, R.H Guo, X. Zhang, N. Gao, X.Y. Chi, D.L. Cao, T.P. Hu, J. Alloys Compd., 2021, 870, 159408.

[4] Supriya A. Patil, Nabeen K. Shrestha, Akbar I. Inamdar, Chinna Bathula, Jongwan Jung, Sajjad Hussain, Ghazanfar Nazir, Mosab Kaseem, Hyunsik Im, Hyungsang Kim, Nanomaterials, 2022, 12, 1916.

[5] Supriya A. Patil, Sangeun Cho, Yongcheol Jo, Nabeen K. Shrestha, Hyungsang Kim, Hyunsik Im, Chem. Eng. J. 2021, 426, 130773.