Supporting Information

Anchoring Ni$_3$S$_2$/Cr(OH)$_3$ hybrid nanospheres on Ti$_3$C$_2$@NF dual substrates by ion exchange for efficient urea electrolysis

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Experimental Section

1. Materials

Ni(NO$_3$)$_3$·6H$_2$O，Cr(NO$_3$)$_3$·9H$_2$O，Na$_2$S·9H$_2$O，Ti$_3$AlC$_2$(200 mesh)，LiF，HCl，KOH，urea and nickel foam(NF) were purchased from Shanghai Aladdin Biochemical Technology Co. Ltd.De-ionized water (resistance of 18.2 MΩ·cm^{-1} at 25 °C) was used for all experiments. Unless otherwise specified, all reagents are analytically pure without further processed.

2. Sample preparation

Synthesis of few-layered Ti$_3$C$_2$

Before selective etching of Ti$_3$AlC$_2$ MAX power, the size of Ti$_3$AlC$_2$ particles was screened to less than 40 μm by 400 mesh sieve. Firstly, 1.6 g LiF was added into 20 mL 12 M HCl under stirring for 5min. Then,1g

Ti_3AlC_2 powder was slowly added into the solution to prevent the mixed solution from boiling over. The mixed solution was stirred at room temperature for 36 h to obtain Ti_3C_2 MXene. Afterward, the sample was centrifuged several times with deionized water until the pH of the supernatant was neutral. Subsequently, the as-prepared Ti_3C_2 precipitate was dissolved in deionized water, sonicated in ice bath for 1h.Finally the dark green supernatant was obtained by centrifugation at 3000 rpm for 30min and named as few-layered Ti_3C_2. The Ti_3C_2 suspension was stored in a 4 °C refrigerator.

Synthesis of Ti_3C_2@NF

First of all, The NF (1 cm×2 cm) was cleaned with 3 M HCl, acetone, deionized water and ethanol by ultrasonic cleaning for 10 min to remove the surface oxide layer and improve its hydrophilicity, and dried under vacuum at 60 °C for 12 h. Then, The few layered Ti_3C_2 was adsorbed on NF by electrostatic adsorption method. Cleaned NF was soaked in the prepared Ti_3C_2 suspension for 2 h and taken out. Ti_3C_2@NF was obtained after vacuum drying for 12 h. The comparison chart is shown in Fig. S1.

Synthesis of Ni_3S_2/Cr(OH)$_3$-Ti_3C_2@NF electrode

Firstly, 0.8 mM $Ni(NO_3)_3 \cdot 6H_2O$ and 0.2 mM $Cr(NO_3)_3 \cdot 9H_2O$ were dissolved in 20 mL deionized water, and then Ti_3C_2@NF was put into the mixed solution and stirred for 1 h. Then 20 mL 0.025 M Na_2S solution was dropped into the above solution using a micro syringe. Ni_3S_2 is formed by

ion exchange, while $Cr(OH)_3$ is formed by double hydrolysis reaction in aqueous solution with continuous stirring during the reaction. Finally, the NF was taken out and dried at 60 °C for 12 h under vacuum to obtain $Ni_3S_2/Cr(OH)_3-Ti_3C_2$@NF electrode.

3. Materials characterization

The XRD patterns were obtained by using a Pgeneral XD-30 system with Cu kα radiation. The scanning electron microscopy(SEM) images were recorded by JEOL JSM-6700F SEM. The high-resolution TEM(HRTEM) was performed on a JEOL-2010 microscopy operated at 200kV. X-ray photoelectron spectroscopy(XPS) spectra was obtained on a Thermo Scientific ESCALAB 250Xi spectrometer with Al Kα radiation.

4. Electrochemical measurements

All electrochemical tests were measured at room temperature in a three-electrode system linked with the Ivium-N-Stat electrochemical workstation. The catalyst-loaded NF (1×1 cm^2) was used as the working electrode directly. Saturated calomel electrode(SCE)and graphite electrode were used as reference electrode and counter electrode, respectively. All potentials in this work were converted to a reversible hydrogen electrode (RHE) by the formula of : E(RHE)=E(Hg/HgO)+0.059×pH+0.098. All the catalytic performance were tested in the electrolyte of 1 M KOH with 0.5 M urea. The catalyst activity was assessed by scanning the LSV at a rate of 5mV s^{-1}. 95% iR-correction was performed to all the polarization curves.

The electrochemical impedance spectroscopy (EIS) were measured in the frequency range from 100 kHz to 0.1 Hz. In the non-Faradaic reaction zone, the cyclic voltammetry (CV) curves of the sample was recorded at different scan rate (20-100 mV s^{-1}), and the value of double layer capacitance (C_{dl}) was calculated from CV curves. The stability of samples were tested by i-t Chronoamperometry.
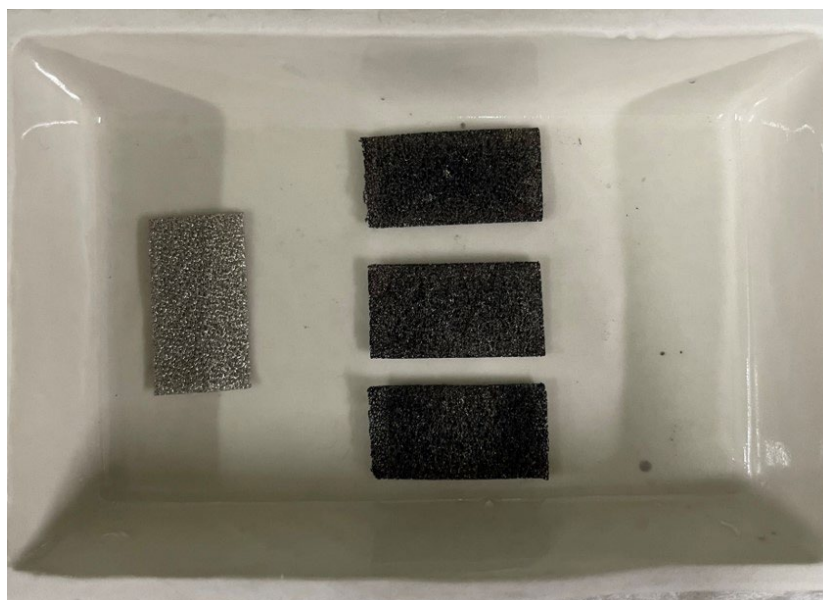
**Fig. S1 Comparison chart of NF and Ti$_3$C$_2$@NF**

Table S1 Comparison of adsorption time and the mass load of Ti$_3$C$_2$

	10 min	30 min	1 h	2 h	4 h	6h
NF before adsorption (g)	0.0634	0.0641	0.0621	0.0663	0.0652	0.0647
NF after adsorption (g)	0.0634	0.0643	0.0623	0.0667	0.0658	0.0653
Mass load（mg cm^{-2}）	0	0	0.1	0.2	0.4	0.4
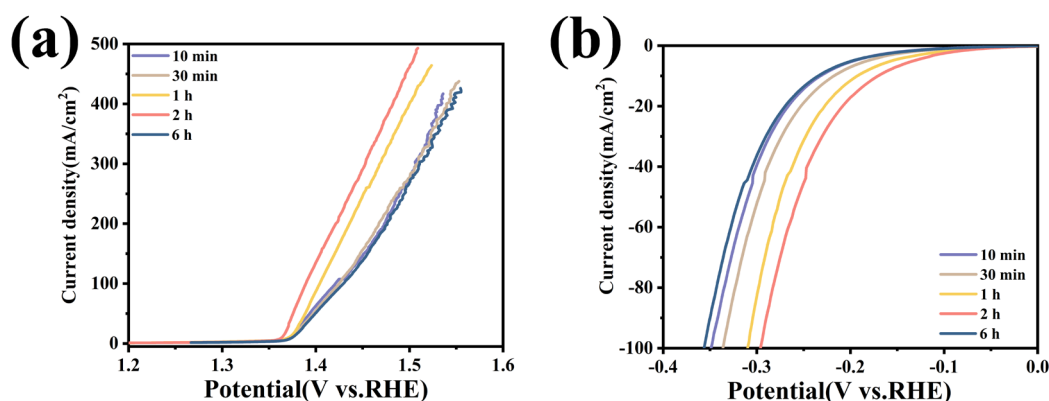
Fig. S2 (a) The LSV curves of UOR for different absorption time of Ti₃C₂. (b) HER curves.

The adsorption time and the suspension concentration may affect the mass load of Ti_3C_2. We explore the effect of adsorption time on the mass load of Ti_3C_2 and the catalytic activity of the electrode. The time is chosen as 10 min to 6 h. As shown in Table S1, the mass load of Ti_3C_2 increased gradually with adsorption time. After 4 h, the adsorption capacity remained basically unchanged. Under the same other preparation conditions, the linear sweep voltammetry (LSV) test of the catalyst obtained with different Ti_3C_2 adsorption time is shown in Fig. S2. It can be seen that the adsorption time of 2 h and the mass load of 0.2 mg cm⁻² shows optimal performance.
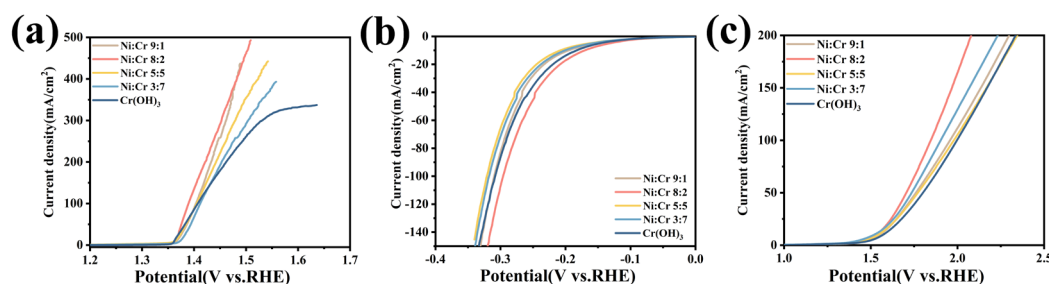
Fig. S3 (a) The LSV curves of UOR for different molar ratio of Ni, Cr. (b) HER curves. (c) Urea electrolysis.

The content effect of Ni_3S_2 and $Cr(OH)_3$ on the electrochemical performance of the electrode is investigated by changing feed ratio of Ni and Cr sources. As shown in Fig. S3 (a)~(c), the electrode exhibits optimal performance at feed ratio of Ni, Cr is 8:2 (0.8 mM $Ni(NO_3)_3 \cdot 6H_2O$ and 0.2 mM $Cr(NO_3)_3 \cdot 9H_2O$), and the electrocatalytic performance decreases with the decrease of Ni content, which corroborates the fact that Ni-based catalysts are mainly based on Ni elements as the active sites.
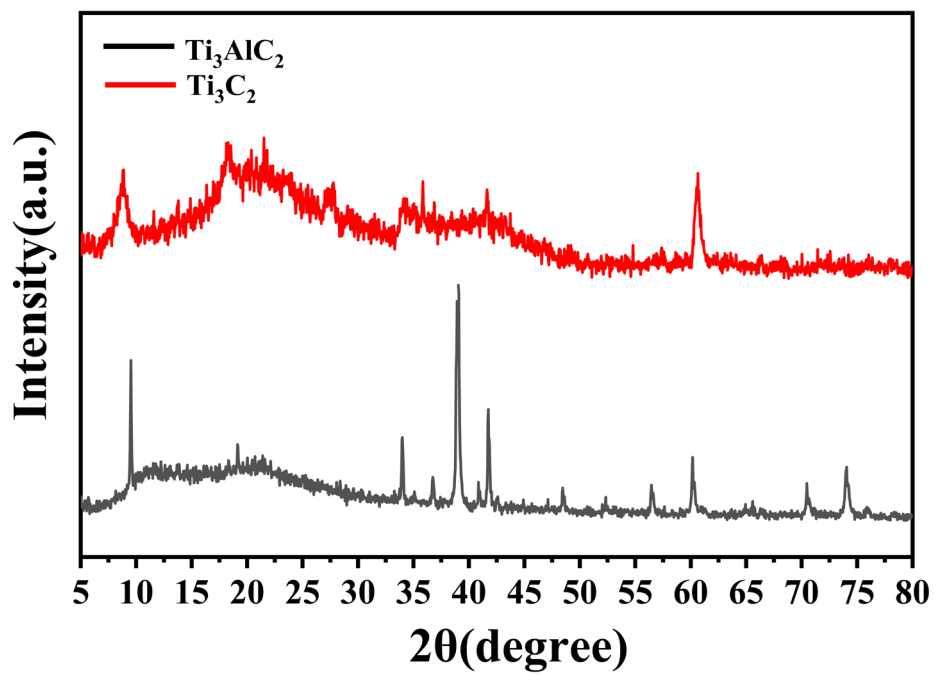
Fig. S4 XRD pattern of Ti$_3$AlC$_2$ and Ti$_3$C$_2$

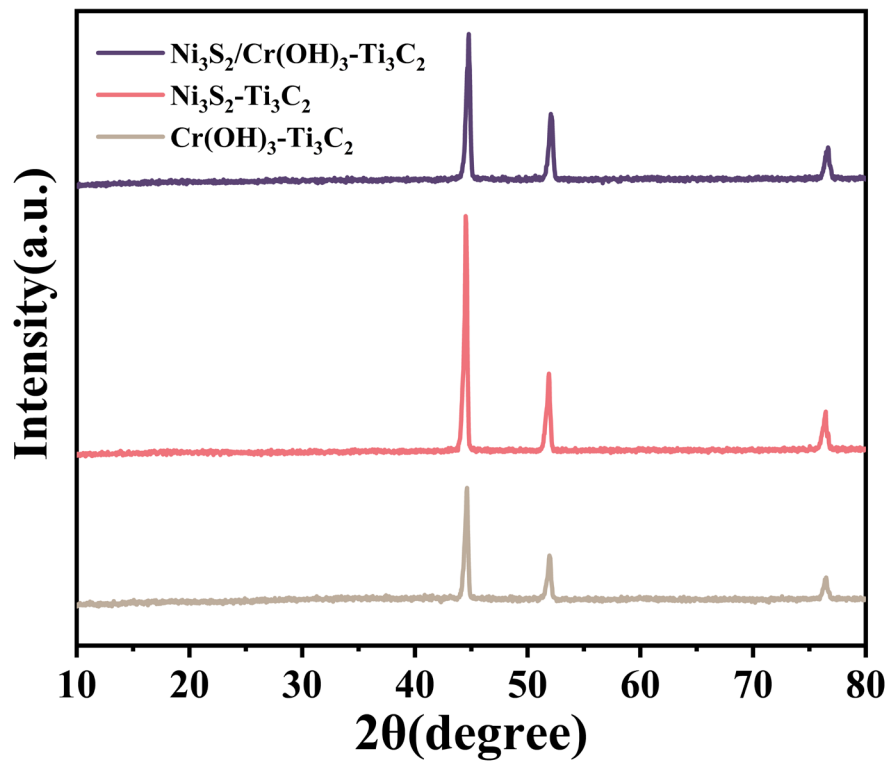**Fig. S5 XRD patterns of Ni₃S₂/Cr(OH)₃-Ti₃C₂, Ni₃S₂-Ti₃C₂ and Cr(OH)₃-Ti₃C₂.**
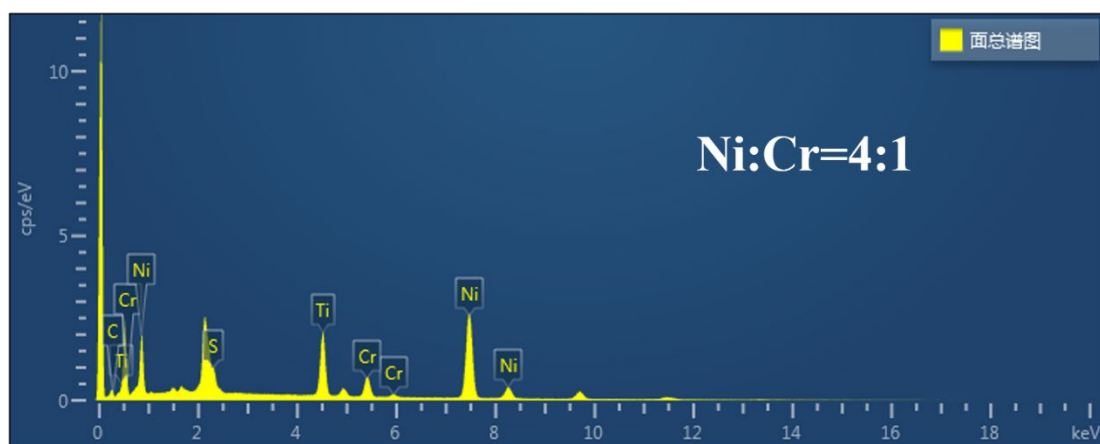
Fig. S6 EDS measurement of the prepared Ni₃S₂/Cr(OH)₃-Ti₃C₂ hybrid nanospheres.
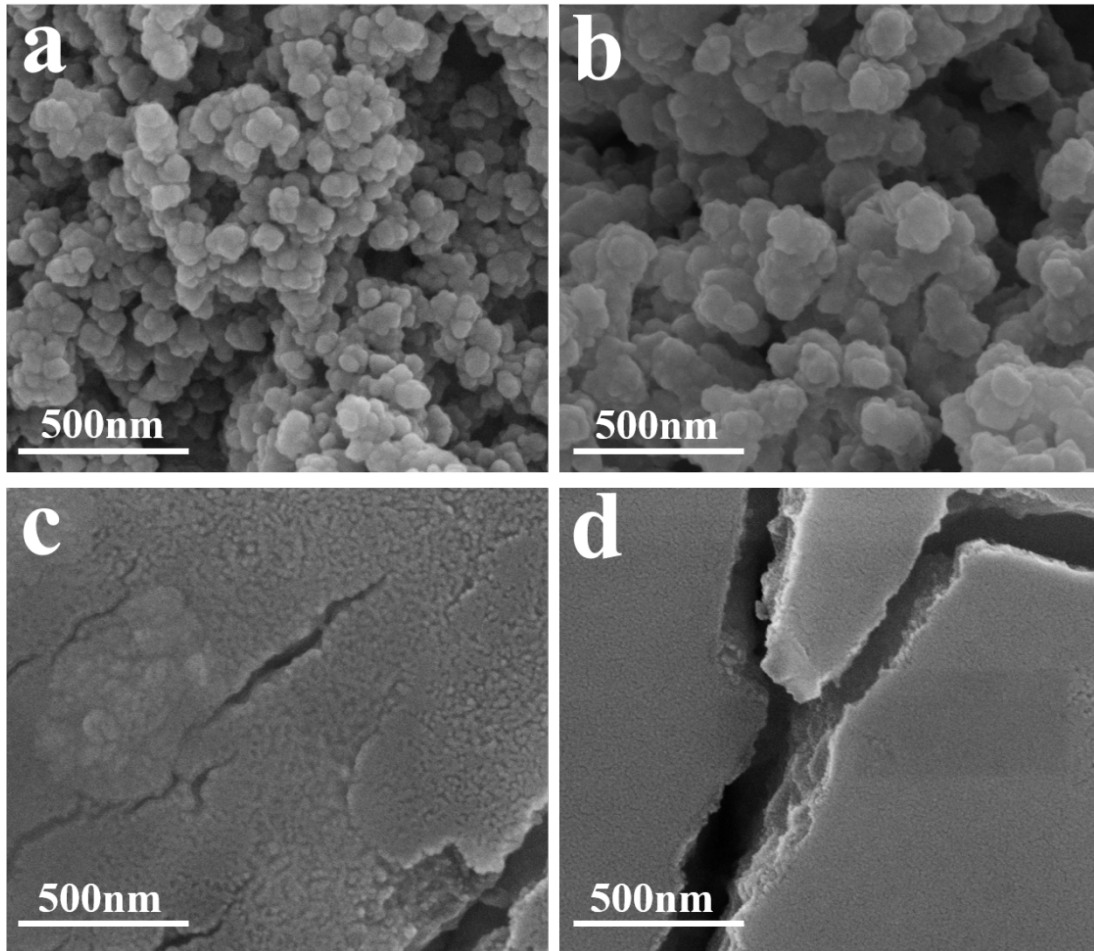
Fig. S7 SEM images of (a~b) $Ni_3S_2/Cr(OH)_3$-Ti_3C_2, (c~d) Ni_3S_2-Ti_3C_2.
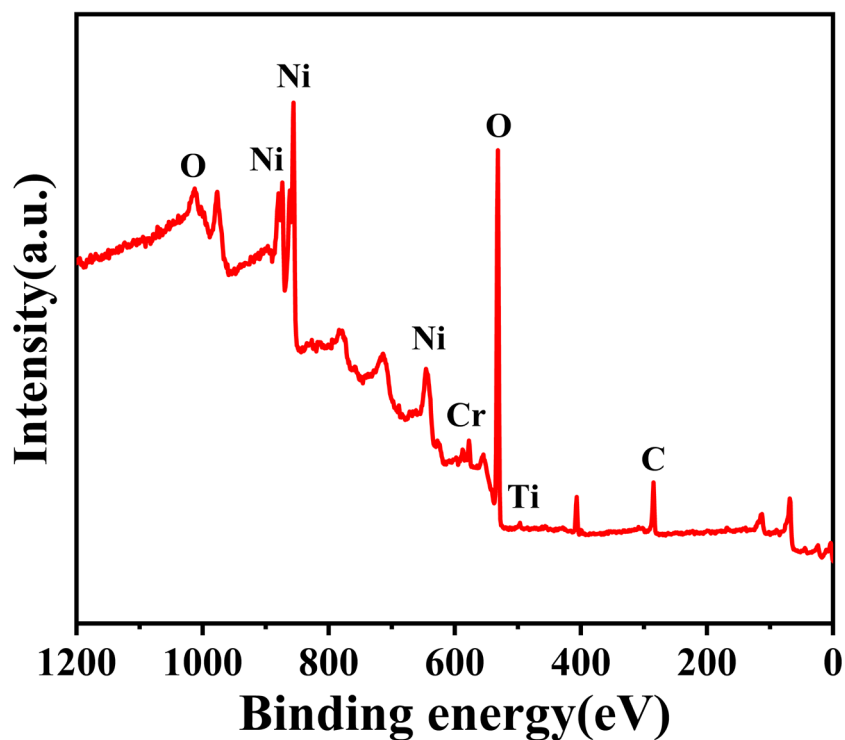
Fig. S8 XPS survey spectrum of Ni₃S₂/Cr(OH)₃-Ti₃C₂@NF.
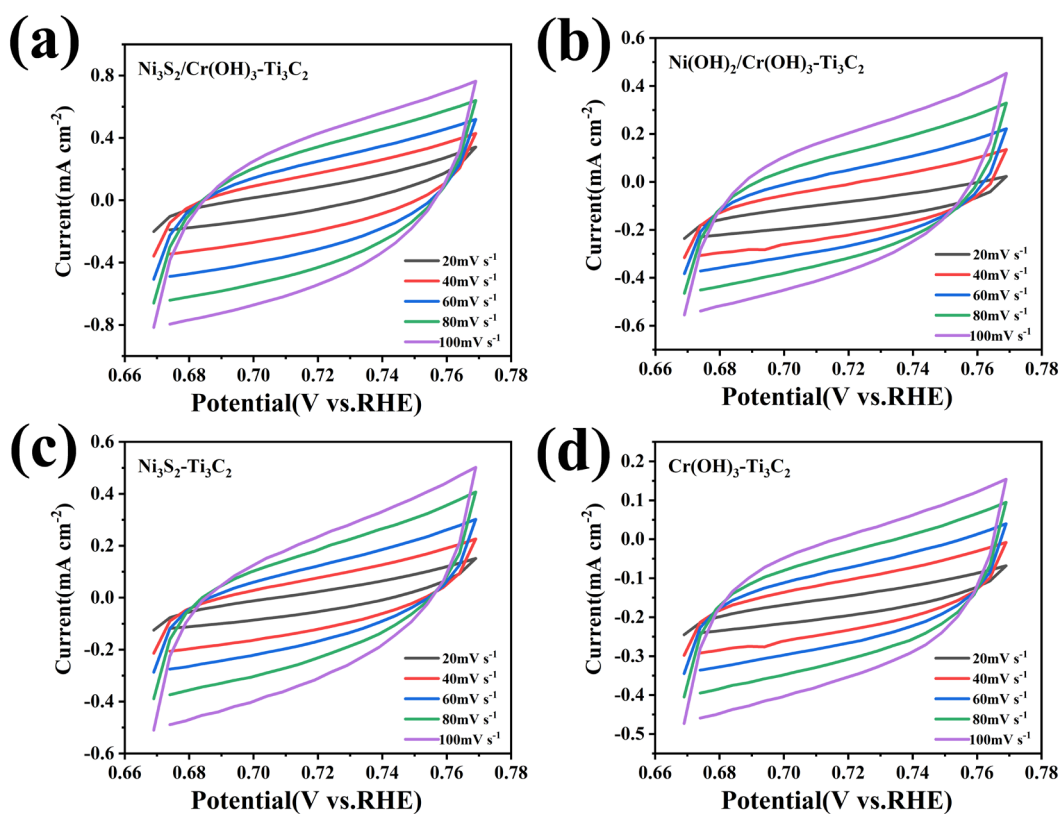
Fig. S9 CV curves of (a) Ni₃S₂/Cr(OH)₃-Ti₃C₂, (b) Ni(OH)₂/Cr(OH)₃-Ti₃C₂, (c) Ni₃S₂-Ti₃C₂, (d)Cr(OH)₃-Ti₃C₂.
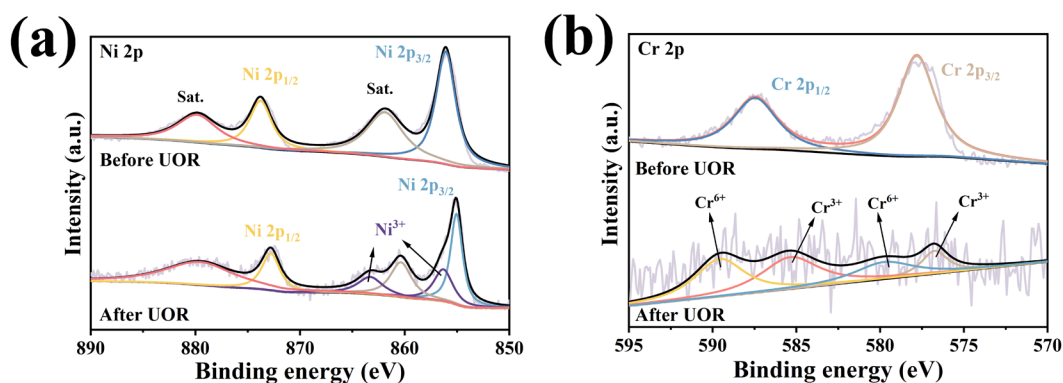
Fig. S10 XPS spectra in regions of (a) Ni 2p, (b) Cr 2p before and after long durability test.

Table S2 Comparison of different catalysts for urea electrolysis.

Catalysts	Urea concentration	Performance （mA cm^{-2}）	Corresponding V	References
$Ni_3S_2/Cr(OH)_3$-Ti_3C_2	0.5M	10 100	1.36 1.39	This work
$CoMn/CoMn_2O_4$	0.5M	10	1.32	Advanced Functional Materials, 2020, 30.
graphene–MnO_2	0.5M	10	1.33	Angew . Chem. Int. Ed. 2016, 55, 3804.
$NiMoO_4$	0.5 M	10	1.37	Energy Environ. Sci. 2018, 11, 1890.
$Ni(OH)_2$	0.33 M	10	1.38	Angew . Chem. Int. Ed. 2016, 55, 12465
$MnO_2/MnCo_2O_4$	0.5M	10	1.33	J. Mater . Chem. A 2017, 5, 7825.
Ni-Mo nanotube	0.1M	10	1.36	Nano Energy 2019, 60, 894.
$NiCo_2O_4$	0.33 M	250	1.62	Nanoscale 2014, 6, 1369.
Ni-MOF	0.33 M	10	1.36	Chem. Commun.　2017, 53, 10906.
CoS_2 NA/Ti//CoS_2 NA/Ti	0.33M	10	1.59	Electrochim. Acta 246 (2017) 776.
NiO-NiPi	0.5M	10 100	1.349 1.444	Chem. Eng. J. 2021, *425*, 130514-130524
N-NiFe/WRIF// N-NiFe/WRIF	0.33M	100	1.58	Chem. Eng. J. 2021, *414*, 128753-128762.
Ni_3S_2@$CoMoS_4$/NiFeOOH//	0.5M	100	1.66	Int. J.Hydrogen. Energ. 2021, *46*, 24078-24093.
CoFeCr LDH	0.3M	100	1.41	Appl. Catal B.Environ.2020, 272,118959
NiClO-D	0.3M	100	1.44	Angew. Chem. Int.Edit. 2019,58, 16820
Mo-Co-S-Se	0.5M	100	1.42	ACS Sustain. Chem.Eng. 2019, 7, 16577
NF-Ni_2P-Fe_2P	0.5M	100	1.46	J. Colloid Interface Sci.2019, 541, 279.
S-MnO_2	0.5M	100	1.46	Angew. Chem. Int.Ed., 2016, 55, 3804.

1% Fe:α-Ni(OH)$_2$	0.33M	100	~1.41	Chem. Eur. J. 2018,24, 18408.
NF/MiMoO-A	0.5M	100	1.42	Energy Environ. Sci.,2018, 11, 1890.