Supplementary Information

Two-dimensional titanium carbide supported ultrafine non-noble bimetallic nanocatalysts for remarkable hydrolytic evolution from ammonia borane

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1 Materials

All chemical reagents were purchased from commercial suppliers and no further purification was required before use. $NaBH_4$ (>96%) was purchased from Sinopharm Chemical Reagent Co., Ltd. Ti_3AlC_2 (98%) was purchased from Sinopharm Chemical Reagent Co.Ltd. $Cu(NO_3)_2{\cdot}3H_2O$ (99%) was purchased from Sinopharm Chemical Reagent Co.Ltd. $Ni(NO_3)_2{\cdot}6H_2O$ (98%) was purchased from Sinopharm Chemical Reagent Co.Ltd. De-ionized water with the specific resistance of 18.2 MΩ·cm was obtained by reversed osmosis followed by ion-exchange and filtration.

2 Synthesis of $Ti_3C_2T_x$

Multilayered $Ti_3C_2T_x$ was prepared by etching its MAX phase (Ti_3AlC_2) in a mixture of HCl and LiF. Firstly, add 0.8 g of LiF powder to 7.5 mL of 9.0 M HCl and 2.5 mL of DI water, and stirred for 15 min until the powder was dissolved completely. Then, 0.5 g of Ti_3AlC_2 was added to the solution and stirred continuously in a water bath environment maintained at 35℃ for 24 h. The reaction solution was washed several times with deionized water until the pH up to 6, and the power was obtained by drying the sediment in a vacuum oven for 24 h.

3 Synthesis of $Cu_{0.9}Ni_{0.1}$@$Ti_3C_2T_x$

Firstly,15 mg $Ti_3C_2T_x$ was dissolved in 6.5 mL deionized water and then dispersed by ultrasonic treatment for 30 min. Next, $Cu(NO_3)_2{\cdot}3H_2O$ (0.144mmol) and $Ni(NO_3)_2{\cdot}6H_2O$ (0.016 mmol) was added to the dispersed solution and the solution was stirred for 30 minutes. Immediately afterwards, 50 mg of $NaBH_4$ in 0.9 mL of aqueous solution was added to the mixture and stir vigorously for 5 minutes until the bubbles disappear. Clean the mixture with DI water and centrifuge three times. After the process, the mass underwent a 6 h drying period in a vacuum environment at room temperature, resulting in the creation of the necessary $Cu_{0.9}Ni_{0.1}/Ti_3C_2T_x$.

4 Catalytic measurement

The $Cu_{0.9}Ni_{0.1}/Ti_3C_2T_x$ pre-catalyst was dispersed in 1 mL of deionized water using the ultrasonic method for 1 minute; after dispersing the solution, it was then transferred to a two-necked round bottom flask, which was immersed in a water bath set at a specific temperature (30-60 °C) under ambient atmospheric conditions. The reaction began after adding 1mL water solution containing 0.2 mmol AB. The reaction vessel was connected to wet type gas flowmeter, observing the volume and rate of drainage determined the catalyst performance. The experimental data were repeated more than three times to ensure the authenticity of the results.

5 Durability testing of the catalysts

For testing the durability of $Cu_{0.9}Ni_{0.1}/Ti_3C_2T_x$ catalysts, 0.2 mmol of AB aqueous solution was subsequently added into the reaction flask after the completion of the first-run hydrolysis of AB. Such test cycles of the catalyst for the AB hydrolysis were carried out for 5 runs at 50 °C by adding AB aqueous solution.

6 Calculation of turnover frequency (TOF)

The TOF reported here is an apparent TOF value based on the number of Cu and Ni atoms in catalyst, which is calculated from the equation as follow:

$$\mathrm{TOF} = 2P_0V / (3RTn_{CuNi}t)$$

Where P_0 is the atmospheric pressure (101325 Pa), V is the final generated volume of H_2 gas, R is the universal gas constant (8.3145 m^3 Pa mol^{-1} K^{-1}), T is the room temperature (298 K), n_{CuNi} is the total mole number of Cu and Ni atoms in catalyst and t is the completion time of the reaction in hour.

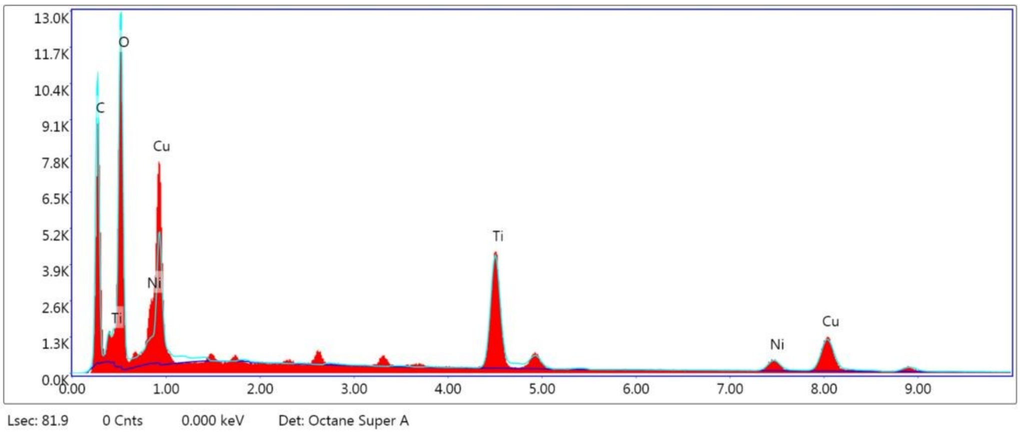

Fig. S1 EDAX Spectrum of $Cu_{0.9}Ni_{0.1}/Ti_3C_2T_x$

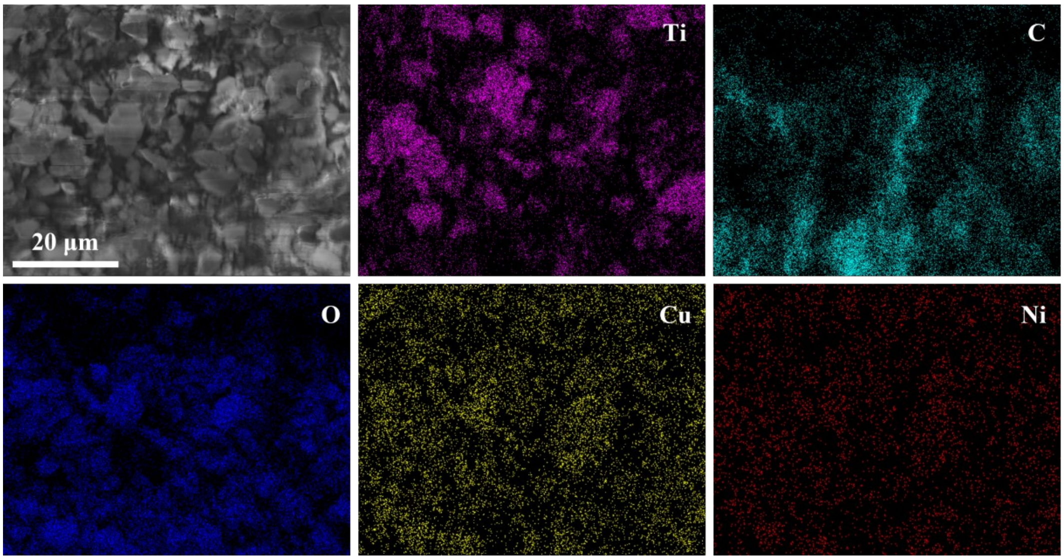

Fig. S2 The mapping of $Cu_{0.9}Ni_{0.1}/Ti_3C_2T_x$

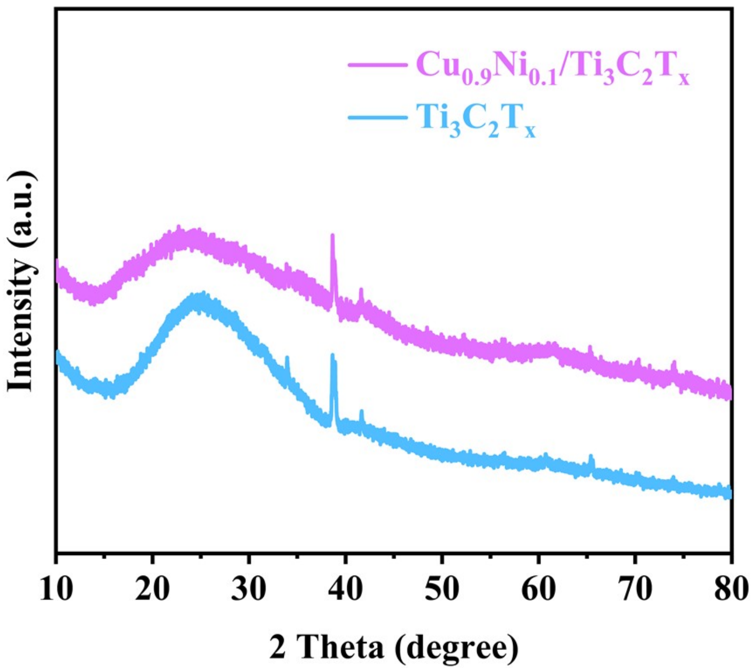

Fig. S3 XRD pattern o $Cu_{0.9}Ni_{0.1}/Ti_3C_2T_x$ and $Ti_3C_2T_x$

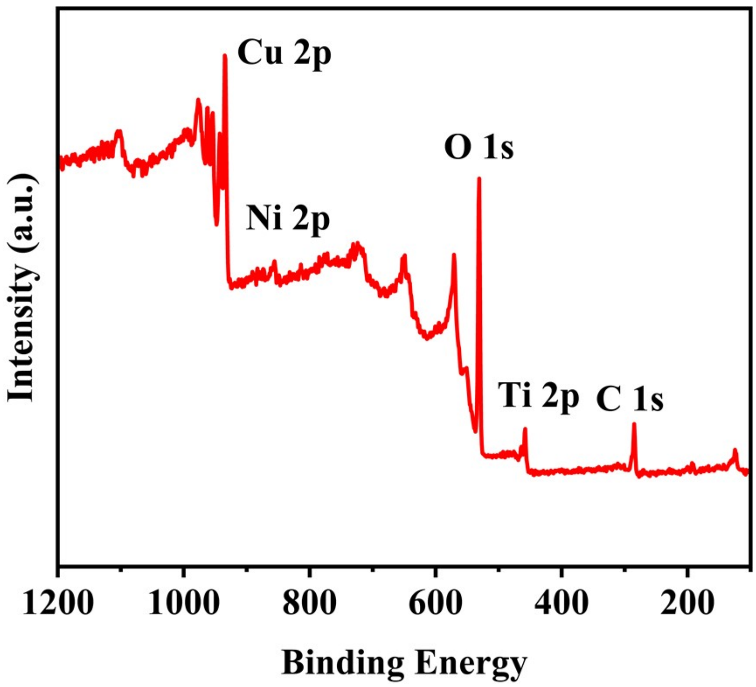

Fig. S4 Survey spectrum of $Cu_{0.9}Ni_{0.1}/Ti_3C_2T_x$

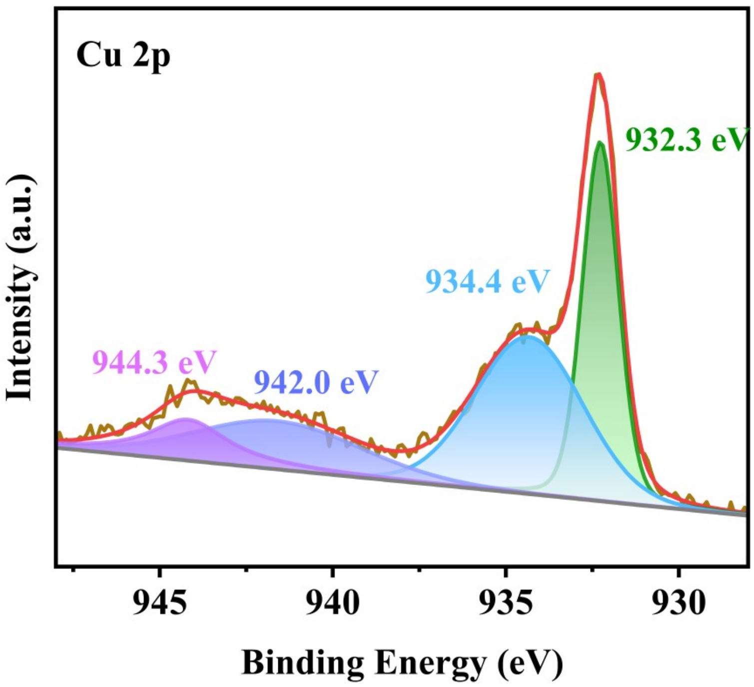

Fig. S5 Cu 2p XPS spectrum of $Cu_{0.9}Ni_{0.1}$

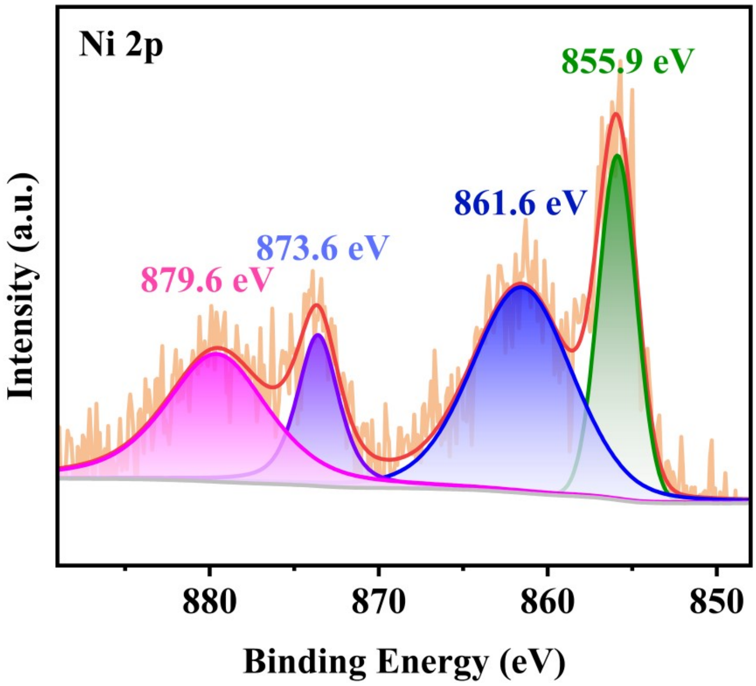

Fig. S6 Ni 2p XPS spectrum of $Cu_{0.9}Ni_{0.1}$

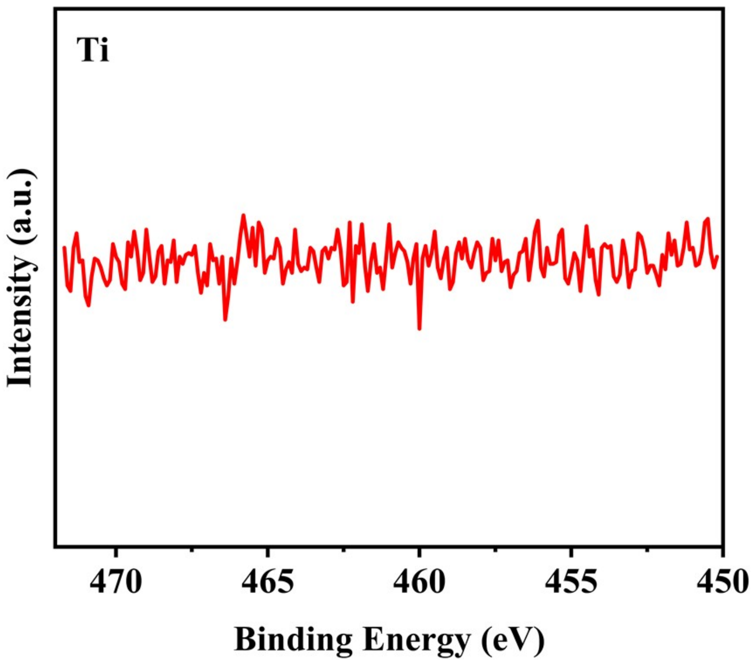

Fig. S7 Ti 2p XPS spectrum of $Cu_{0.9}Ni_{0.1}$.

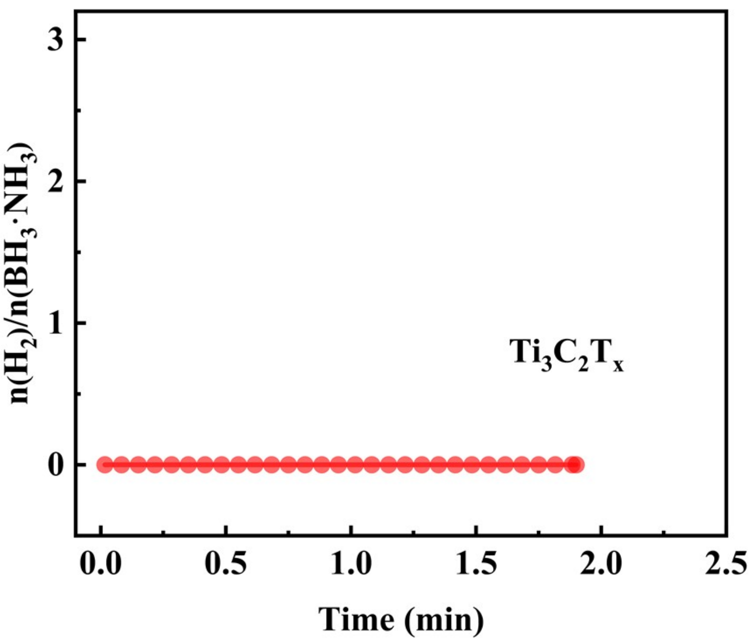

Fig. S8 The catalytic performance of $Ti_3C_2T_x$.

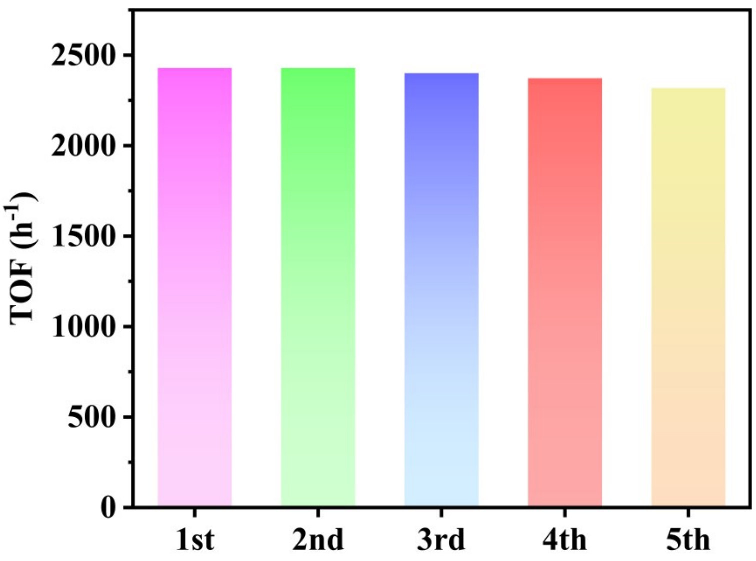

Fig. S9 TOF value of $Cu_{0.9}Co_{0.1}/Ti_3C_2T_x$ for five consecutive catalytic cycles

Table S1 Catalytic performance of non-noble catalysts reported for AB hydrolysis

Catalyst	TOF (h^{-1})	Temperature (K)	kJ mol^{-1}	Reference
$Cu_{0.9}Ni_{0.1}/Ti_3C_2T_x$	665	298	41.61	This work
	907	303		
	2429	323		
$Cu_{0.7}Ni_{0.3}/g\text{-}C_3N_4$	124.8	303	23.58	*Int. J. Hydrog. Energy*, 2023, **48**, 18245-18256
$Cu_{0.5}Ni_{0.5}$/h-BN	361.8	303	23.02	*Int. J. Hydrog. Energy*, 2022, **47**, 33741-33753
Co-CoP-NC/NF	600	303	30.6	*Appl. Catal. B-Environ.*, 2023, **325**, 122317
p (AMPS)-Cu	43.2	303	48.8	*Int. J. Hydrog. Energy*, 2011, **36**, 8209-8216
P (4-VP)-Co	168	303	34.98	*Fuel Process. Technol.*, 2014, **126**, 324-331
$Cu_{0.3}@Fe_{0.1}Co_{0.6}$ NPs	630	298	38.75	*Int. J. Hydrog. Energy*, 2014, **39**, 436-441
Co^0/CeO_2	450	298	43	*New J. Chem.*, 2017, **41**, 6546-6552
CoCu-NC-5	487.2	298	34.25	*Int. J. Hydrog. Energy*, 2023, **48**, 26162-26172
Co/$CoFeO_x$-25	735	298	48.51	*J. Alloy. Compd.*, 2022, **913**, 165215
$Co_{0.9}Ni_{0.1}$/graphene NPs	984	298	13.49	*Int. J. Hydrog. Energy*, 2014, **39**, 3371-3380
$Co_{0.52}Cu_{0.48}$	204	298	50.2	*Int. J. Hydrog. Energy*, 2017, **42**, 30691-30703
Pd/graphene aerogel	582	298	30.82	*J. Hydrog. Energy*, 2016, **41**, 15225-15235
$Ni_{91}P_9$/rGO	798	298	34.7	*Int. J. Hydrog. Energy*, 2017, **42**, 14181-14187
Fe-Ni-B/$Cu(OH)_2$-Cu	336	298	46.3	*Int. J. Hydrog. Energy*, 2024, **81**, 1156-1162
Cu/RGO	216.6	298	38.2	*RSC Adv.*, 2014, **4**, 13749-13752