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Supplementary Information

Anchoring ultrafine RhNi nanoparticles on titanium carbides/manganese oxide as an efficient catalyst for hydrogen generation from hydrous hydrazine

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1. Materials

Hydrazine monohydrate ($H_2NNH_2 \cdot H_2O$, Aladdin reagent Co., Ltd, >98%), nickel(II) chloride hexahydrate ($NiCl_2 \cdot 6H_2O$, Sinopharm Chemical Reagent Co., Ltd, >98%), rhodium trichloride ($RhCl_3$, Sigma-Aldrich Co. LLC, 99%), manganese chloride ($MnCl_2$, Sigma-Aldrich Co. LLC, 99%), sodium borohydride ($NaBH_4$, Sinopharm Chemical Reagent Co., Ltd, >96%), potassium permanganate ($KMnO_4$, Sinopharm Chemical Reagent Co., Ltd, ⩾99.5%), graphite power (Sinopharm Chemical Reagent Co., Ltd, ⩾99.85%), hydrogen peroxide (H_2O_2, Sinopharm Chemical Reagent Co., Ltd, ⩾30%), phosphoric acid (H_3PO_4, Sinopharm Chemical Reagent Co., Ltd, AR), sulfuric acid (H_2SO_4, Sinopharm Chemical Reagent Co., Ltd, 95~98%), sodium carbonate (Na_2CO_3, Sinopharm Chemical Reagent Co., Ltd, >96%), vulcanxc-72 carbon (Cabot corporation, ≥97 %), multi-walled carbon nanotube (Shandong Dazhan nano materials Co., Ltd, 97%) were used without further purification. 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 Mxene:

The support Mxene was initially prepared at room temperature using Ti_3AlC_2 as raw material and concentrated hydrofluoric acid as the etching agent. Specifically, concentrated hydrofluoric acid (40%, 100 mL) was slowly added to a beaker containing

Ti_3AlC_2 (5 g). The solution was stirred for 24 h to remove the Al layer in Ti_3AlC_2. The black precipitate was then separated from the as-prepared suspension by centrifugation and washed several times with distilled water and absolute ethanol. Finally, the product was dried under vacuum at 60 ^oC for 12 h.

3. Catalytic measurement:

An aqueous suspension (4 ml) containing the as-prepared catalysts was placed in a two-neck round-bottom flask (30 mL), which was placed in a water bath under ambient atmosphere. The reaction started when 0.15 mL of hydrazine monohydrate was injected into the mixture using a syringe. A gas burette filled with water was connected to the reaction flask to measure the volume of released gas. The gas released during the reaction was measured volumetrically. The molar ratios of metal/$N_2H_4•H_2O$ were theoretically fixed at 0.03 for all the catalytic reactions.

4. Durability testing of the catalysts:

For testing the durability of RhNi/Mxene catalysts, 0.15 mL of $N_2H_4•H_2O$ was subsequently added into the reaction flask after the completion of the first-run decomposition of $N_2H_4•H_2O$. Such test cycles of the catalyst for the decomposition of $N_2H_4•H_2O$ were carried out for 6 runs at 50 °C by adding $N_2H_4•H_2O$.

5. Calculation of turnover frequency (TOF)

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

$$TOF= 2P_0V / (3RTn_{NiRh}t)$$

Where P_0 is the atmospheric pressure (101325 Pa), V is the final generated volume of H_2/N_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_{NiRh} is the total mole number of Ni and Rh atoms in catalyst and t is the completion time of the reaction in hour.

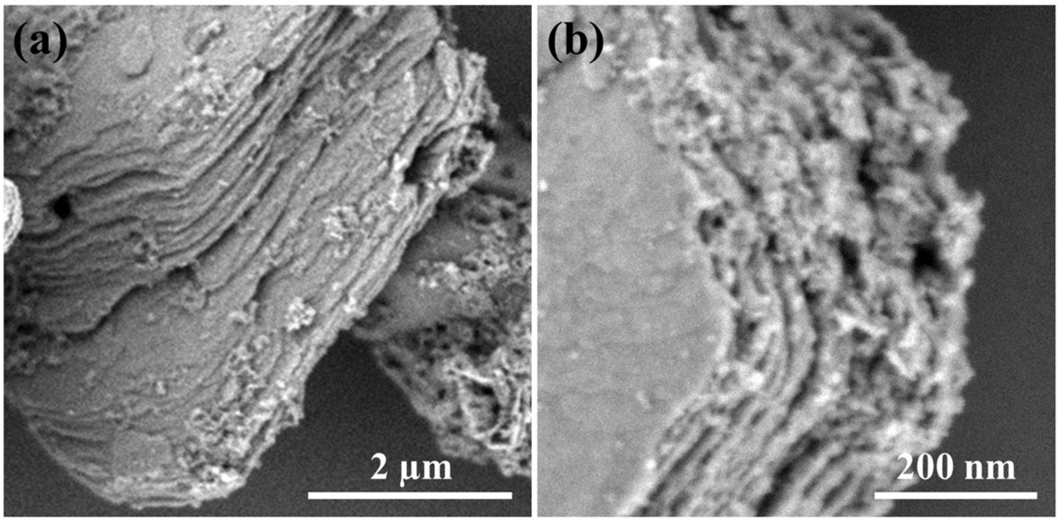

Figure S1. SEM images of pristine MXene.

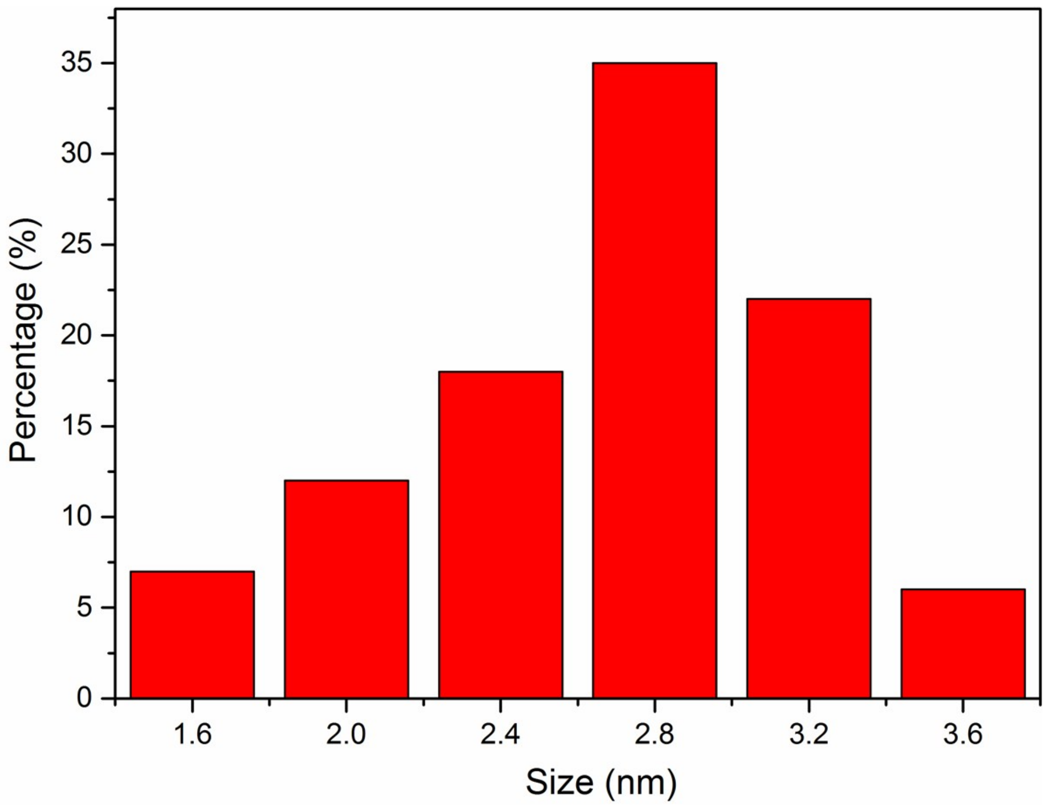

Figure S2. Particle size distribution histogram of the synthesized $Rh_{0.7}Ni_{0.3}/MnO_x$-MXene.

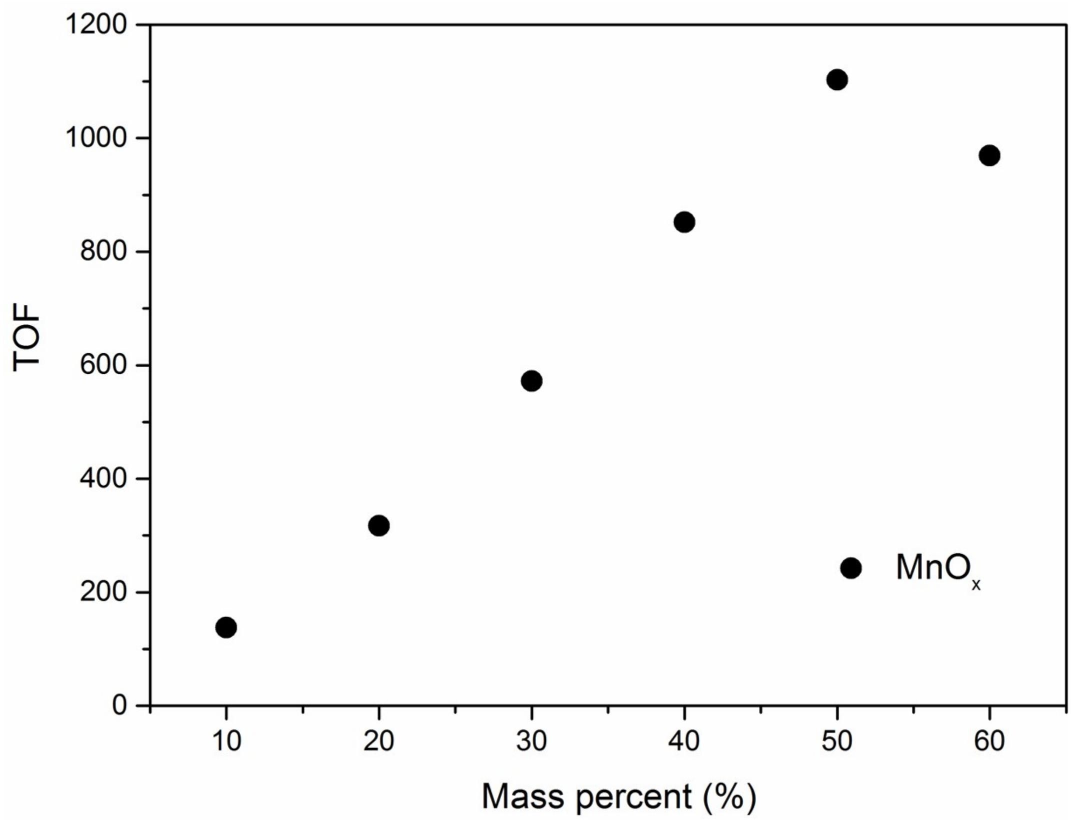

Figure S3. The corresponding TOF values of $N_2H_4 \cdot H_2O$ decomposition catalyzed by $Rh_{0.7}Ni_{0.3}/MnO_x$-MXene with different MnO_x amount at 50 ℃.

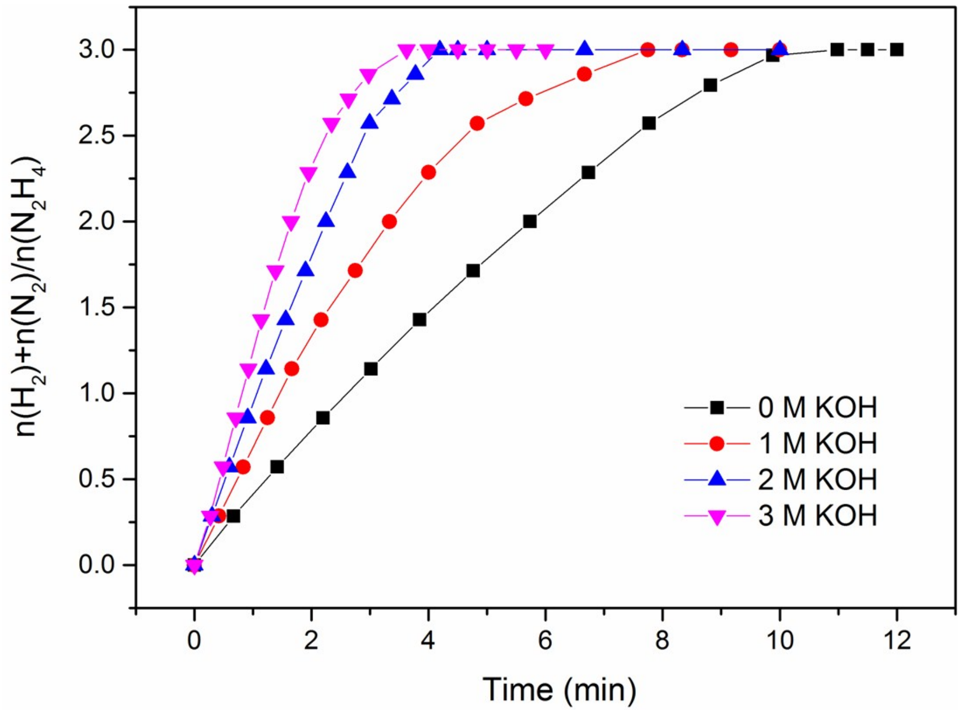

Figure S4. Time course plots for N_2+H_2 production from $N_2H_4 \cdot H_2O$ decomposition over $Rh_{0.7}Ni_{0.3}$/MnOx-MXene with different NaOH amounts. The molar ratio of metal/$N_2H_4 \cdot H_2O$ = 0.03.

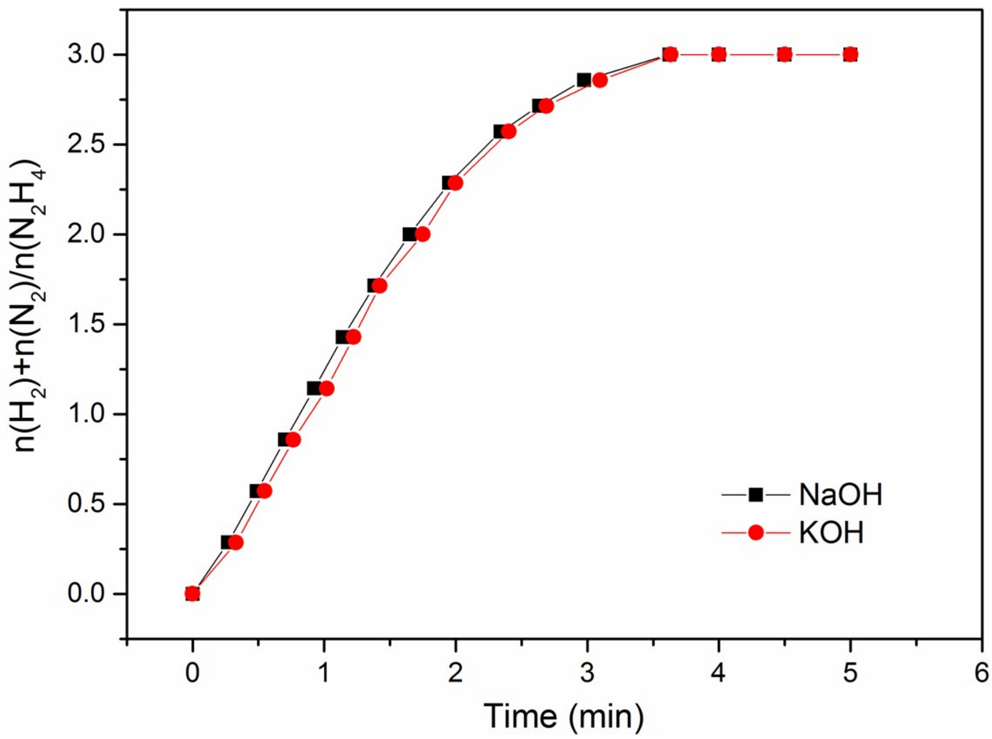

Figure S5. Time course plots for N_2+H_2 production from $N_2H_4 \cdot H_2O$ decomposition over $Rh_{0.7}Ni_{0.3}$/MnOx-MXene with NaOH or KOH. The molar ratio of metal/$N_2H_4 \cdot H_2O$ = 0.03.

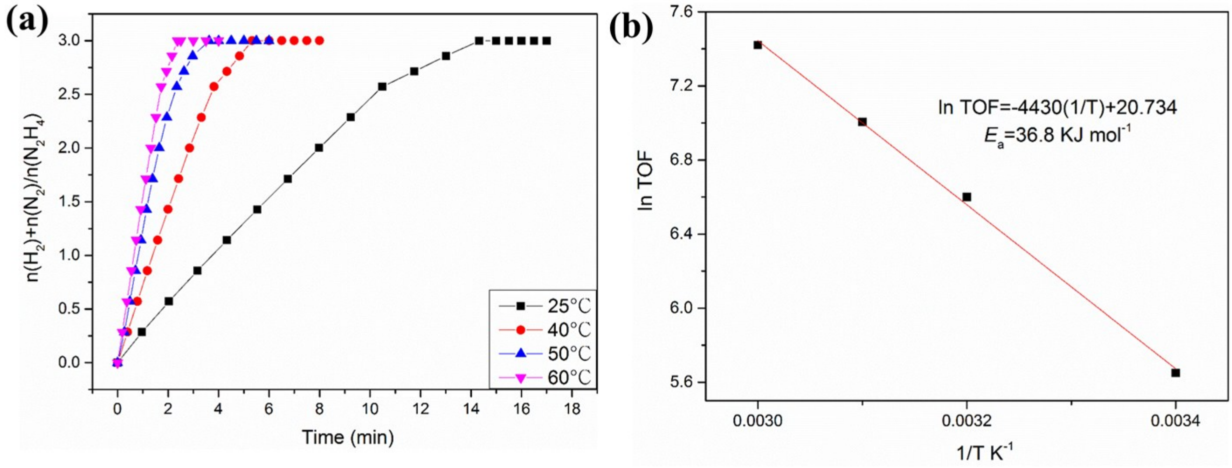

Figure S6. Time course plots for N_2+H_2 production from $N_2H_4 \cdot H_2O$ decomposition over $Rh_{0.7}Ni_{0.3}/MnO_x$-MXene at different reaction temperatures (a); arrhenius plot (ln(TOF) vs. 1/T (b). The molar ratio of metal/$N_2H_4 \cdot H_2O$ = 0.03.