Supplementary Information (SI) for New Journal of Chemistry.

Supplementary Material

Immobilization of ultrafine bimetallic nanocatalysts on metal-organic framework derived N doped nanoporous carbon/manganese oxide carbon for efficient hydrous hydrazine decomposition

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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%), manganese chloride ($MnCl_2$, Sigma-Aldrich Co. LLC, 99%), rhodium trichloride ($RhCl_3$, Sigma-Aldrich Co. LLC, 99%), zirconium(IV) chloride ($ZrCl_4$, Sinopharm Chemical Reagent Co., Ltd, >98%), 2-aminoterephthalic acid ($C_8H_7NO_4$, Sinopharm Chemical Reagent Co., Ltd, >98%), sodium borohydride ($NaBH_4$, Sinopharm Chemical Reagent Co., Ltd, >96%), sulfuric acid (H_2SO_4, Sinopharm Chemical Reagent Co., Ltd, 95~98%), were used without further purification. Deionized water with a specific resistance of 18.2 MΩ·cm was obtained by reversed osmosis followed by ion exchange and filtration.

2、Characterization

Scanning electron microscopy (SEM) measurement was conducted on a JEOL JSM-7001F field-emission scanning electron microscope. The high-resolution transmission electron microscopy (HRTEM) measurement was carried out on an FEI Tecnai G2 F20 FE-TEM. The X-ray photoelectron spectroscopy (XPS) measurements were performed using a Kratos Axis Ultra instrument (Kratos Analytical Ltd.).

3、Synthesis of NH_2-UiO-66

Firstly, uniform octahedral-shaped NH_2-UiO-66 precursor was synthesized by a modified hydrothermal process. Typically, $ZrCl_4$ (0.466 mg, 0.2 mmol) and 2-amino terephthalic acid (0.332 mg, 0.2 mmol), acetic acid (1.37 mL), and DMF (10 mL) were mixed in a 20 mL Pyrex vial. This solution was treated by magnetic stirring until the solid was completely dissolved and then treated hydrothermally at 120 °C for 24 h.

4、Synthesis of MnO_x-$Ni_{0.4}Ru_{0.6}$/NC

The synthesis process of MnO_x-$Ni_{0.4}Rh_{0.6}$@NC is depicted in Fig. 1. After being calcined at 1173 K for 5 h under Ar flow and etched in H_2SO_4 solution for 3 days, the NH_2-UiO-66 precursor was transferred into NC, which was then used as the catalyst support. The NC was ultrasonically dispersed in water, followed by the addition of an aqueous solution of $RhCl_3$, $NiCl_2$ and $MnCl_2$. Finally, adding proper amount of $NaBH_4$ solution into the suspension resulted in the formation of ultrafine $Ni_{0.4}Rh_{0.6}$ NPs on MnO_x/NC, denoted as MnO_x-$Ni_{0.4}Rh_{0.6}$@NC.

Meanwhile, the MnO_x-NiRh@NC catalysts with different molar ratios of Ni to Rh were synthesized under the same procedure by adjusting the metallic precursor molar ratio. For comparison, the $Ni_{0.4}Rh_{0.6}$@NC, MnO_x@NC and $Ni_{0.4}Rh_{0.6}$ samples were also prepared by a similar process.

5、*Catalytic measurements*

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 an ambient atmosphere. The reaction started when 2 mmol 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/$N_2H_4 \cdot H_2O$ were theoretically fixed at 0.1 for all the catalytic reactions.

6、*Durability testing of the catalysts*

For testing the durability of MnO_x-NiRh@NC catalysts, 2 mmol of $N_2H_4 \cdot H_2O$ was subsequently added into the reaction flask after the completion of the first-run decomposition of $N_2H_4 \cdot H_2O$. Such test cycles of the catalyst for the decomposition of $N_2H_4 \cdot H_2O$ were carried out for 5 runs at 50 °C by adding $N_2H_4 \cdot H_2O$.

7、*Calculation of turnover frequency (TOF)*

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

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

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), it is the total mole number of Ni and Rh atoms in catalyst and *t* is the completion time of the reaction in an hour.

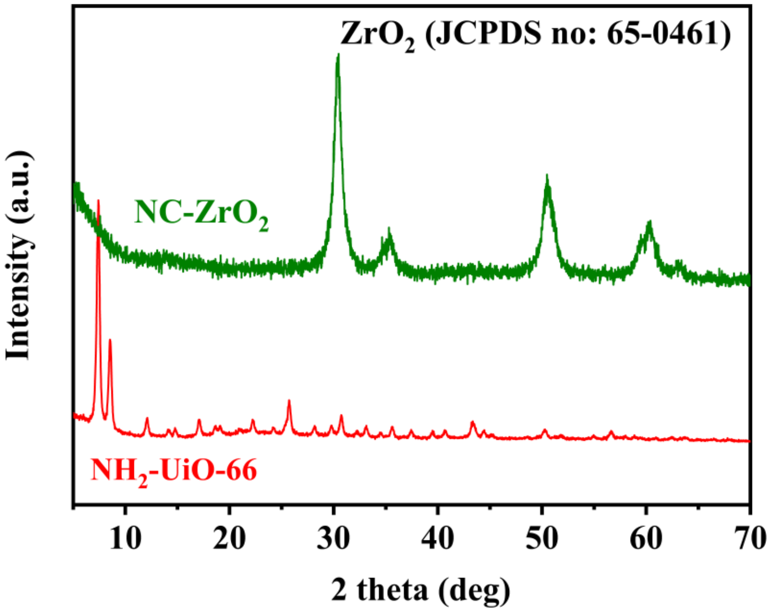

Figure S1. The XRD patterns of NH_2-UiO-66 and NC-ZrO_2.

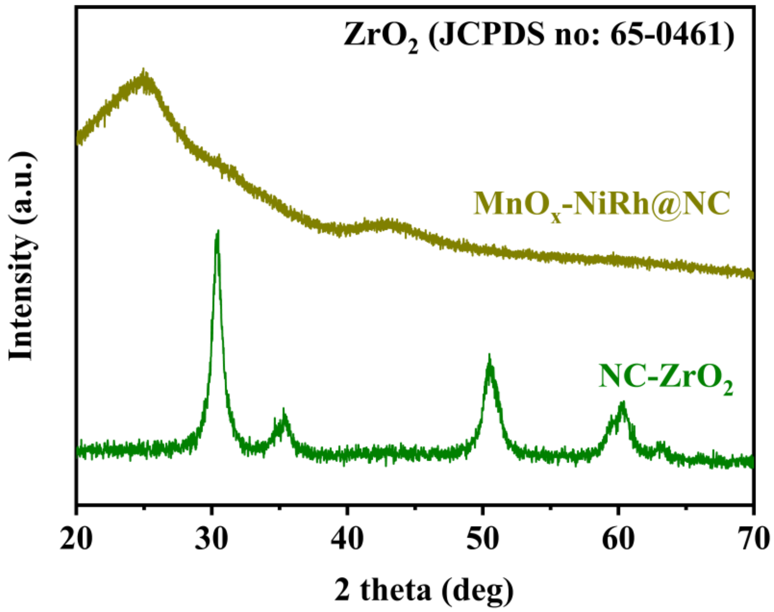

Figure S2. The XRD patterns of NC-ZrO_2 and MnO_x-$Ni_{0.4}Rh_{0.6}$@NC.

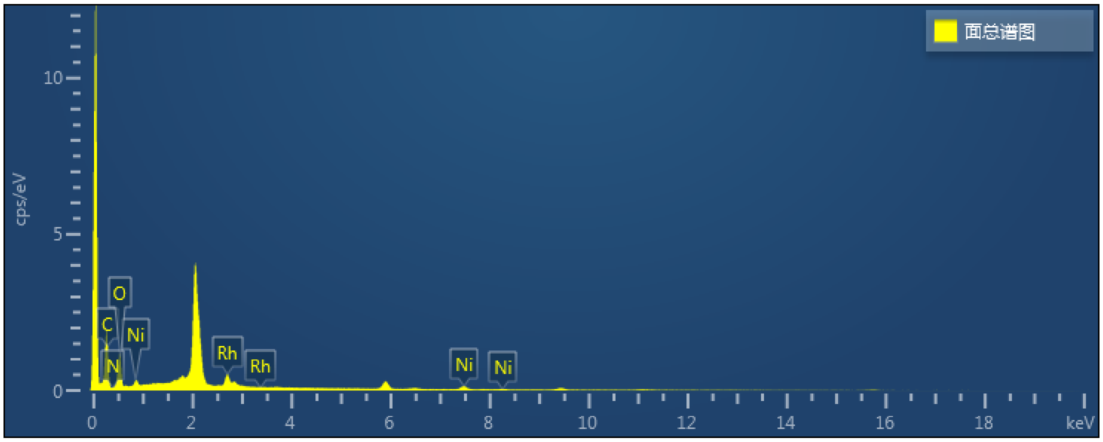

Figure S3. EDX spectrum of MnO_x-$Ni_{0.4}Rh_{0.6}$@NC.

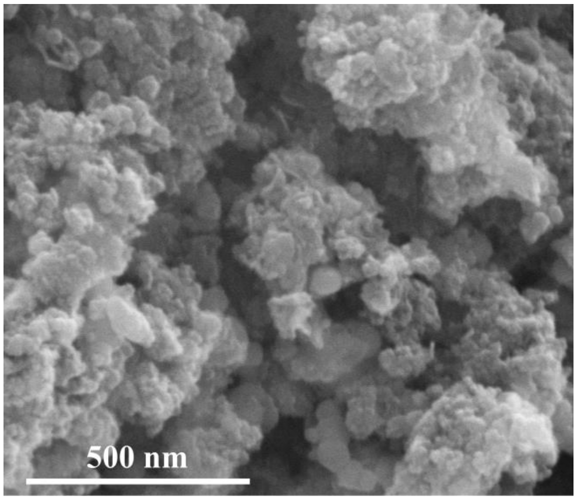

Figure S4. SEM image of MnO_x-$Ni_{0.4}Rh_{0.6}$@NC

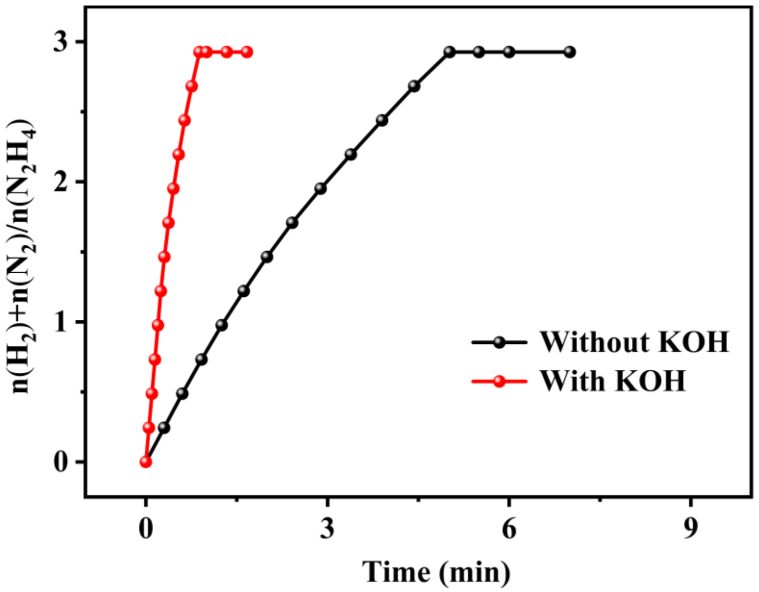

Figure S5. Gas (N_2+H_2) evolution from hydrous hydrazine dehydrogenation versus time over the MnO_x-$Ni_{0.4}Rh_{0.6}$/NC with and without KOH solution.

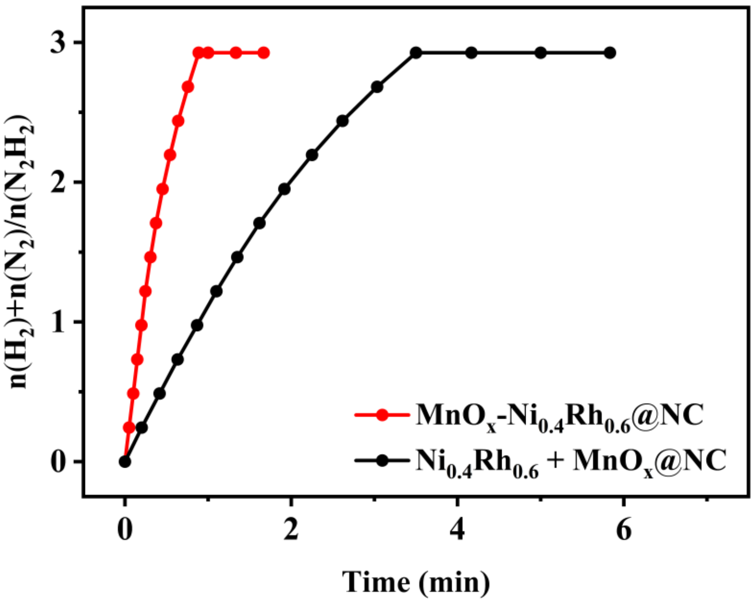

Figure S6. Gas (N_2+H_2) evolution from hydrous hydrazine dehydrogenation versus time over the MnO_x-$Ni_{0.4}Rh_{0.6}$/NC and the physical mixture of $Ni_{0.4}Rh_{0.6}$ and MnO_x@NC.

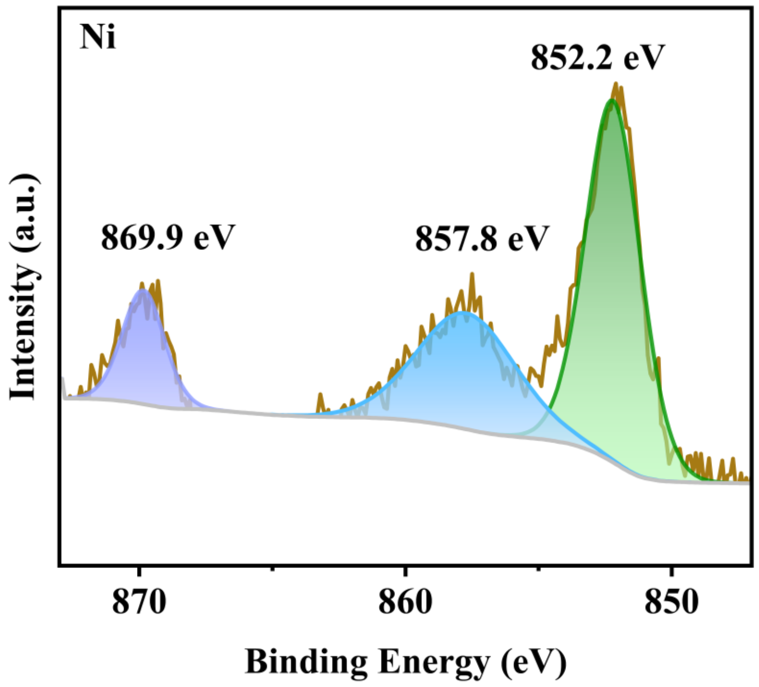

Figure S7. XPS spectra of MnO_x-$Ni_{0.4}Rh_{0.6}$@NC for Ni after the cyclic stability test

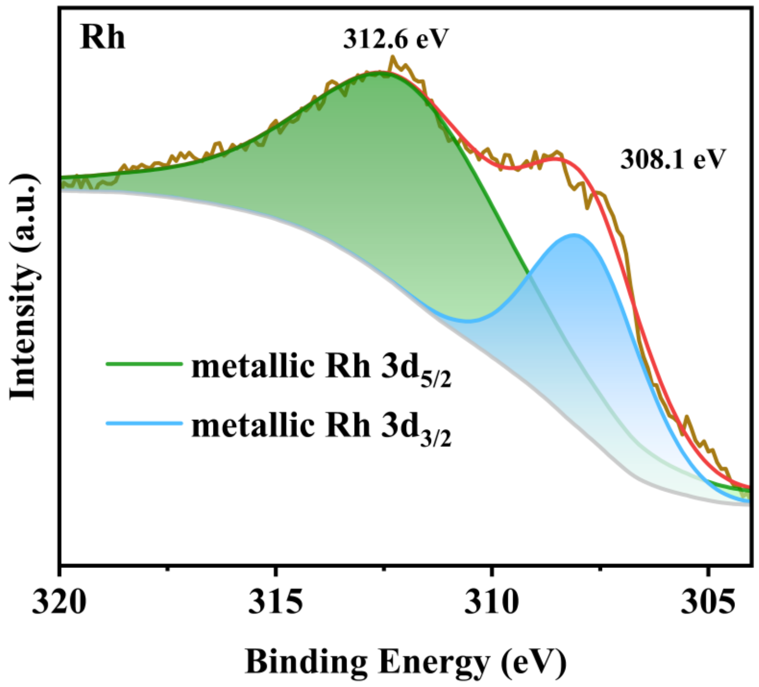

Figure S8. XPS spectra of MnO_x-$Ni_{0.4}Rh_{0.6}$@NC for Rh after the cyclic stability test

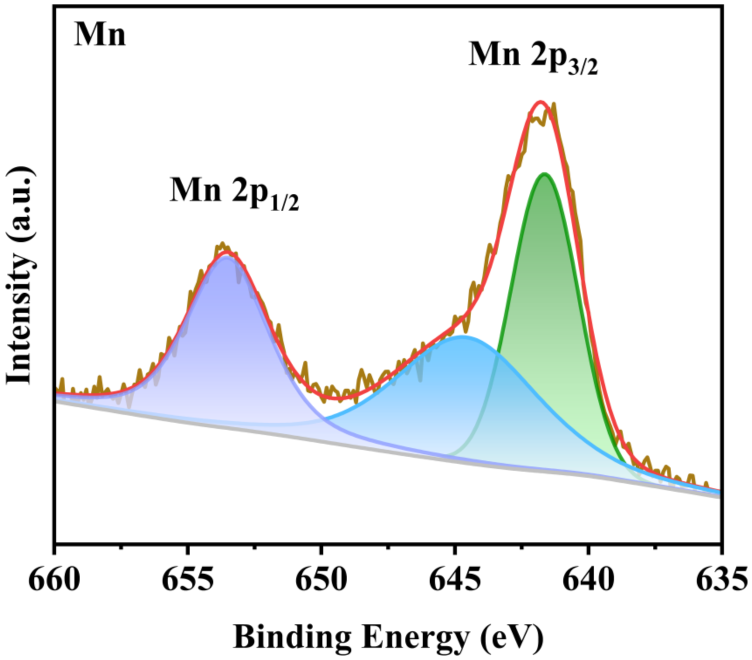

Figure S9. XPS spectra of MnO_x-$Ni_{0.4}Rh_{0.6}$@NC for Mn after the cyclic stability test