

Electronic Supplementary Information

Synergistic effect of Rh-Ni catalysts on the highly-efficient dehydrogenation of aqueous hydrazine borane for chemical hydrogen storage

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Experimental

General. The HB was synthesized according to the reported literature.¹⁻² Other chemicals were commercial available and used without purification. Hydrazine monohydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, 99%), sodium borohydride (NaBH_4 , 99%) and hexadecyltrimethyl ammonium bromide (CTAB, 95%) were obtained from Aldrich. $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (95%) and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (99.9%) were purchased from Wako Pure Chemical Industries, Ltd. For accuracy and convenience, the RhCl_3 solution (1 mol/L) and NiCl_2 solution (1 mol/L) were prepared from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in advance, respectively.

Mass analysis of the generated gases was recorded on a Balzers Prisma QMS 200 mass spectrometer. Powder X-ray diffraction (XRD) studies were performed on a Rigaku RINT-2000 X-ray diffractometer ($\text{Cu K}\alpha$). Transmission electron microscope (TEM, FEI TECNAI G²) equipped with energy dispersed X-ray detector (EDS) were applied for the detailed microstructure information. The TEM samples were prepared by depositing few droplets of the nanoparticle suspension onto the amorphous carbon coated copper grids, which were dried under argon atmosphere. XPS analysis was carried out on a Shimadzu ESCA-3400 X-ray photoelectron spectrometer using an $\text{Mg K}\alpha$ source (10 kV, 10 mA). The Ar sputtering experiments were carried out under the conditions of background vacuum 3.2×10^{-6} Pa, sputtering acceleration voltage 2 kV.

Preparation of Rh-Ni nanocatalysts. The Rh_4Ni alloy nanocatalysts were prepared as a black suspension using a surfactant (hexadecyltrimethyl ammonium bromide, CTAB) aided co-reduction process, by quickly adding an aqueous solution of sodium borohydride (NaBH_4) to an aqueous solution of rhodium(III) chloride and nickel(II) chloride. In a typical synthetic procedure, a 1.0 mL aqueous

solution containing 44.0 μL $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (1.0 mol/L) and 11.0 μL $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (1.0 mol/L) was added to a 1.0 mL aqueous solution containing 0.050 g of CTAB drop by drop with continuous stirring. After the resulted solution sonicated for 5 min, a 2.0 mL aqueous solution of NaBH_4 (0.010 g) was rapidly added and the content of the flask was vigorously shaken for 2 min, resulting in the generation of Rh_4Ni nanocatalyst as a black suspension, which is used for the catalytic reaction.

The procedure for preparing other Rh-Ni nanocatalysts is similar to that for Rh_4Ni nanocatalyst. The volumes of RhCl_3 solution and NiCl_2 solution were respectively 48.5 μL and 0.0 μL for Rh, 48.0 μL and 3.0 μL for Rh_{16}Ni , 45.6 μL and 5.7 μL for Rh_8Ni , 37.8 μL and 18.9 μL for Rh_2Ni , 30.8 μL and 30.8 μL for RhNi , 22.6 μL and 45.2 μL for RhNi_2 , 14.7 μL and 58.8 μL for RhNi_4 , 8.7 μL and 69.6 μL for RhNi_8 , 4.8 μL and 76.8 μL for RhNi_{16} , 0.0 μL and 84.8 μL for Ni.

An important detail that needs to be mentioned is the preparation method of the Rh_4Ni nanocatalyst. We found that the activity of Rh_4Ni nanocatalyst was greatly affected by the reduction rate. As shown in Fig. S5, the hydrogen selectivity of the Rh_4Ni nanocatalyst prepared by adding sodium borohydride drop by drop is obviously lower than that of the Rh_4Ni nanocatalyst synthesized by adding sodium borohydride quickly, which can be attributed to the slightly different microstructures of the nanocatalysts produced by different procedures. The electrode potential of Rh^{3+}/Rh pair ($\varphi_{\text{Rh}^{3+}/\text{Rh}}$, +0.758 V) is much larger than $\varphi_{\text{Ni}^{2+}/\text{Ni}}$ (-0.257 V),³ which leads to the reduction of Rh^{3+} much easier than that of Ni^{2+} . Therefore, when the sodium borohydride was added to the mixed Rh^{3+} - Ni^{2+} solution drop by drop, Rh^{3+} will be reduced to Rh firstly, and thus it is difficult to form Rh-Ni alloy catalysts. To prepare the highly-active Rh_4Ni catalyst, the sodium borohydride should be added quickly and the reaction solution should be shaken intensely.

HB/ $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ dehydrogenation reaction. Catalytic reactions were carried out at 50 °C using a two-necked round bottom flask with one of the flask openings connected to a gas burette and the other for the introduction of HB / hydrazine monohydrate. Catalytic dehydrogenation reaction of aqueous HB / hydrazine for the release of hydrogen (along with nitrogen) was initiated by adding 0.5 mmol (0.024 g) of HB / by injecting 0.5 mmol (0.025 μL) of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ to the Rh-Ni catalytic system (prepared as

described above). The gas released during the reaction was passed through a trap containing 1.0 mol/L hydrochloric acid to ensure the absorption of ammonia, if produced, of which the volume was monitored using the gas burette.

Characterization of nanocatalysts. After the hydrazine decomposition reaction the suspension was centrifuged (15000 rpm, 10 min, 25 °C) to separate the solution and the nanocatalyst, which was washed twice with 5.0 mL of hot water, dried at 100 °C for 10 h and then used for XRD, TEM and XPS characterizations. For the XPS measurements, the dried Rh₄Ni sample was mounted on a carbon adhesive tape, which was adhered to an indium plate in advance. The indium plate was further attached to a stainless sample holder through a carbon adhesive tape, which was then put inside of the sample-preparation chamber through a manipulator.

References

- 1 J. Hannauer, O. Akdim, U. B. Demirci, C. Geantet, J. M. Herrmann, P. Miele and Q. Xu, *Energy Environ. Sci.*, 2011, **4**, 3355.
- 2 R. Moury, G. Moussa, U. B. Demirci, J. Hannauer, S. Bernard, E. Petit, A. van der Lee and P. Miele, *Phys. Chem. Chem. Phys.*, 2012, **14**, 1768.
- 3 (a) G. Milazzo, S. Garoli and V. K. Sharma, *Tables of Standard Electrode Potentials*, Wiley, Chichester, 1978; (b) A. J. Bard, R. Parsons and J. Jordan. *Standard Potentials in Aqueous Solutions*, Marcel Dekker, New York, 1985.

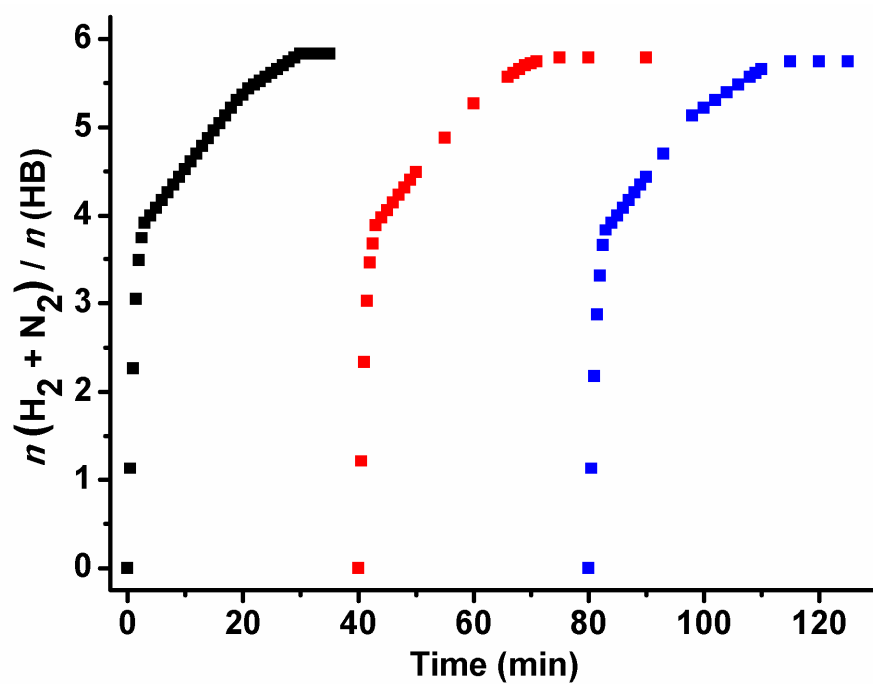


Fig. S1 Durability characterization of Rh₄Ni in three runs for dehydrogenation of aqueous HB.

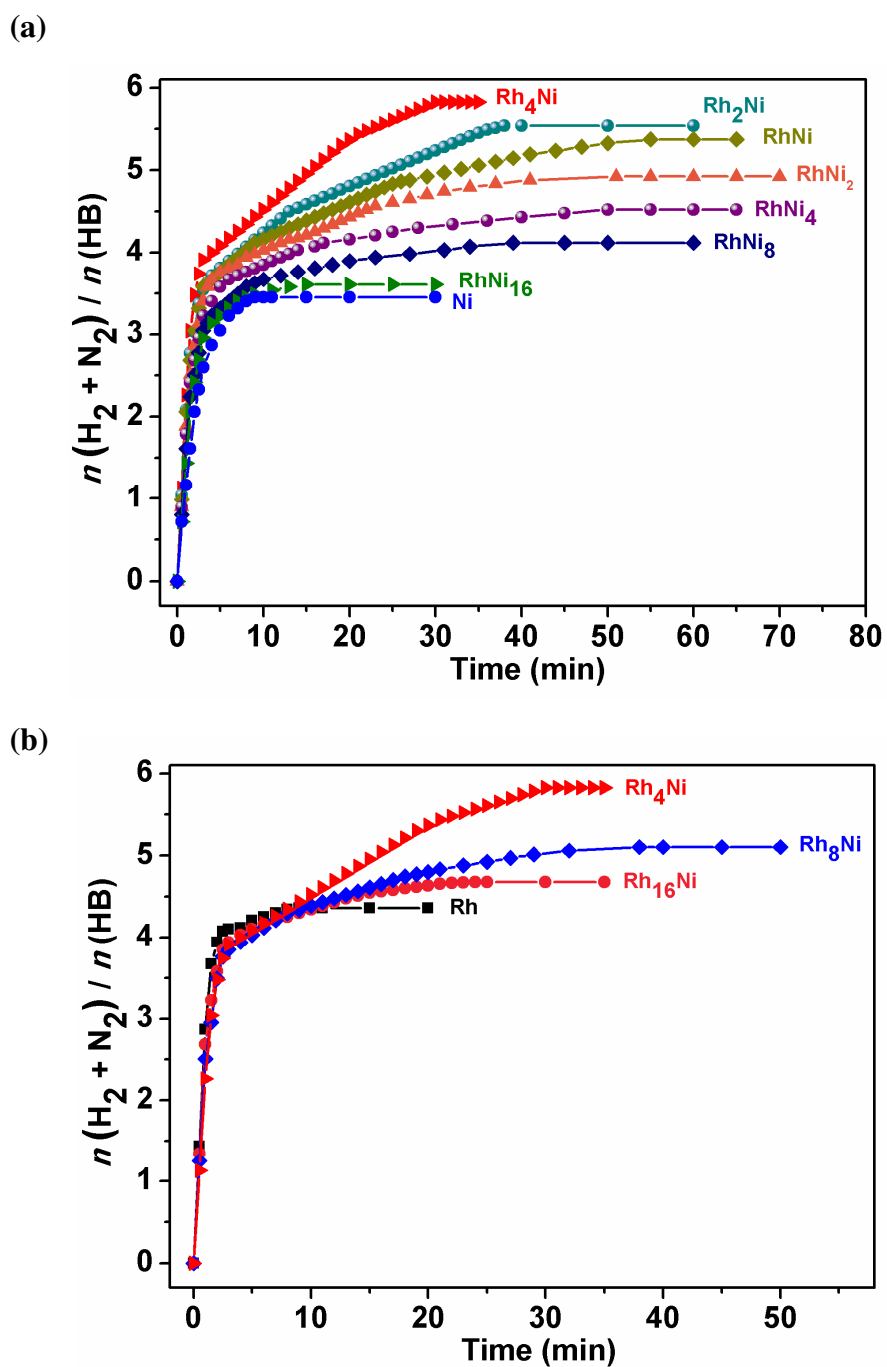


Fig. S2 Time course plots for dehydrogenation of aqueous HB catalyzed by Rh-Ni nanocatalysts at 50 °C (catalyst: 5 mg; HB: 0.5 mmol).

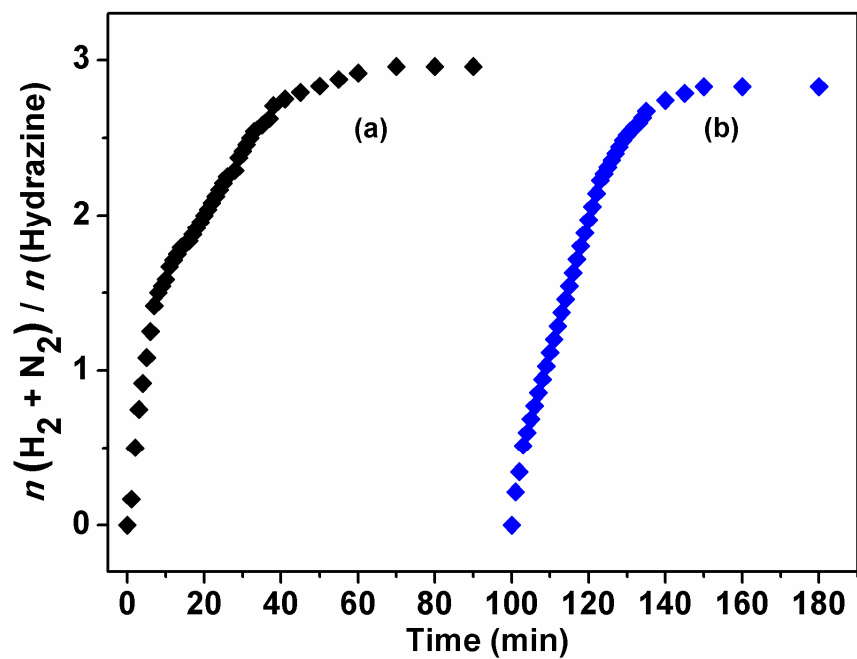


Fig. S3 (a) Time course plots for decomposition of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ catalyzed by Rh_4Ni nanocatalyst at $50\text{ }^\circ\text{C}$ (catalyst: 5 mg; $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$: 0.5 mmol). (b) Time course plots for decomposition of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (0.5 mmol), which was added to the solution where the dehydrogenation of HB just finished.

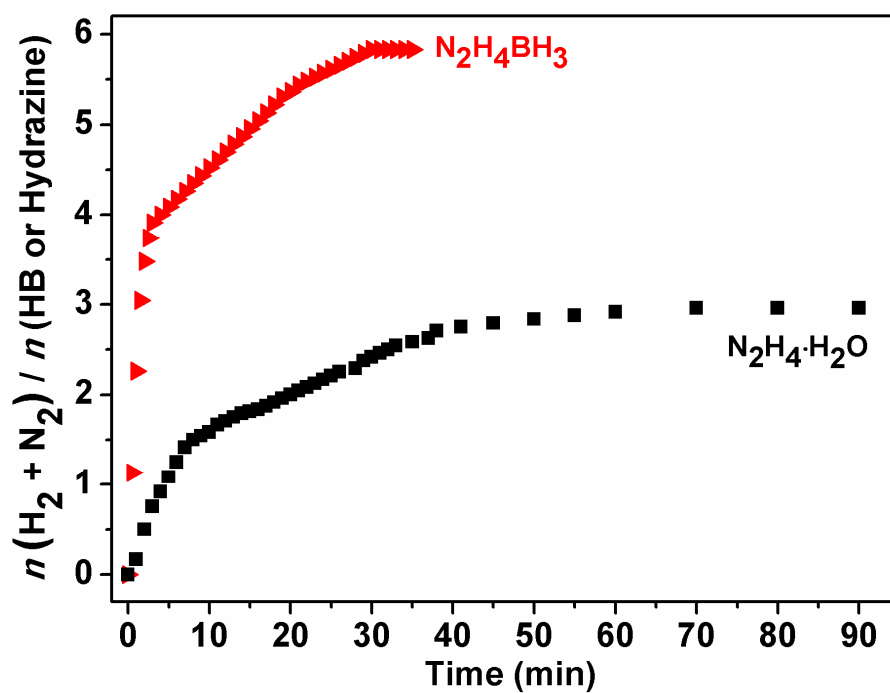


Fig. S4 Time course plots for dehydrogenation of aqueous HB and N₂H₄·H₂O catalyzed by Rh₄Ni nanocatalyst at 50 °C (catalyst: 5 mg; HB/N₂H₄·H₂O: 0.5 mmol).

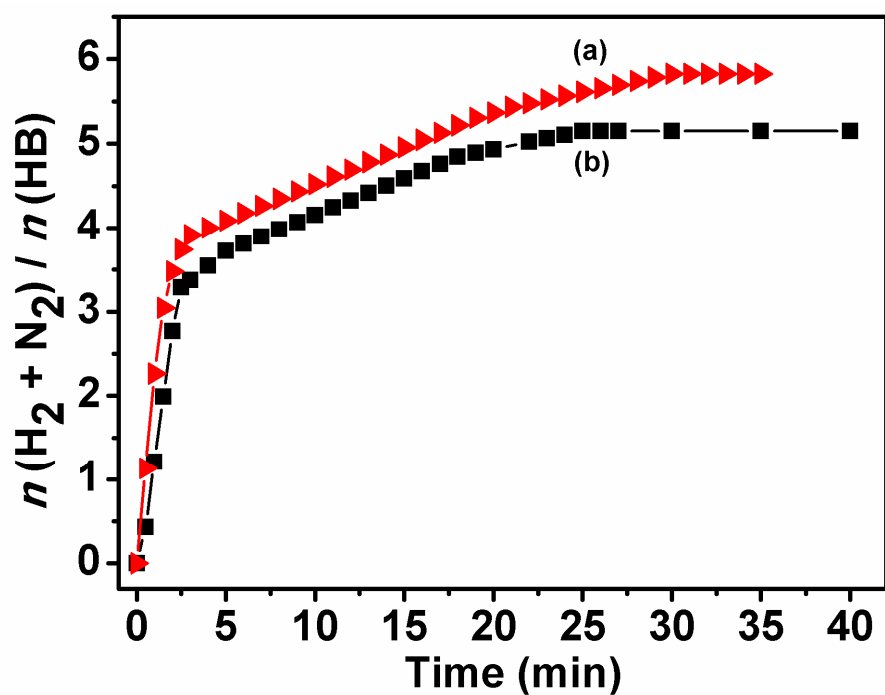


Fig. S5 Time course plots for dehydrogenation of aqueous HB catalyzed by Rh_4Ni nanocatalysts prepared by (a) quick and (b) slow reduction processes using sodium borohydride.

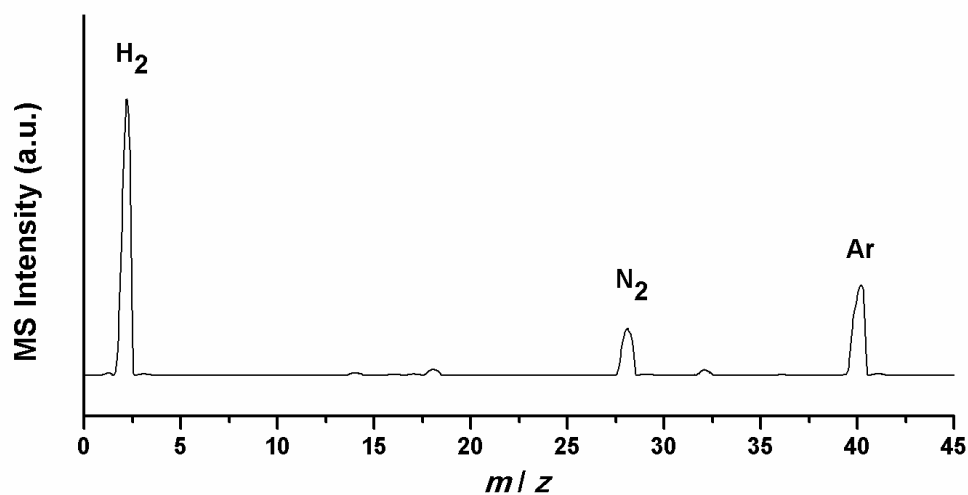


Fig. S6 Mass spectral profile of gases released from the dehydrogenation of aqueous HB using the Rh₄Ni nanocatalyst under an argon atmosphere at 50 °C.

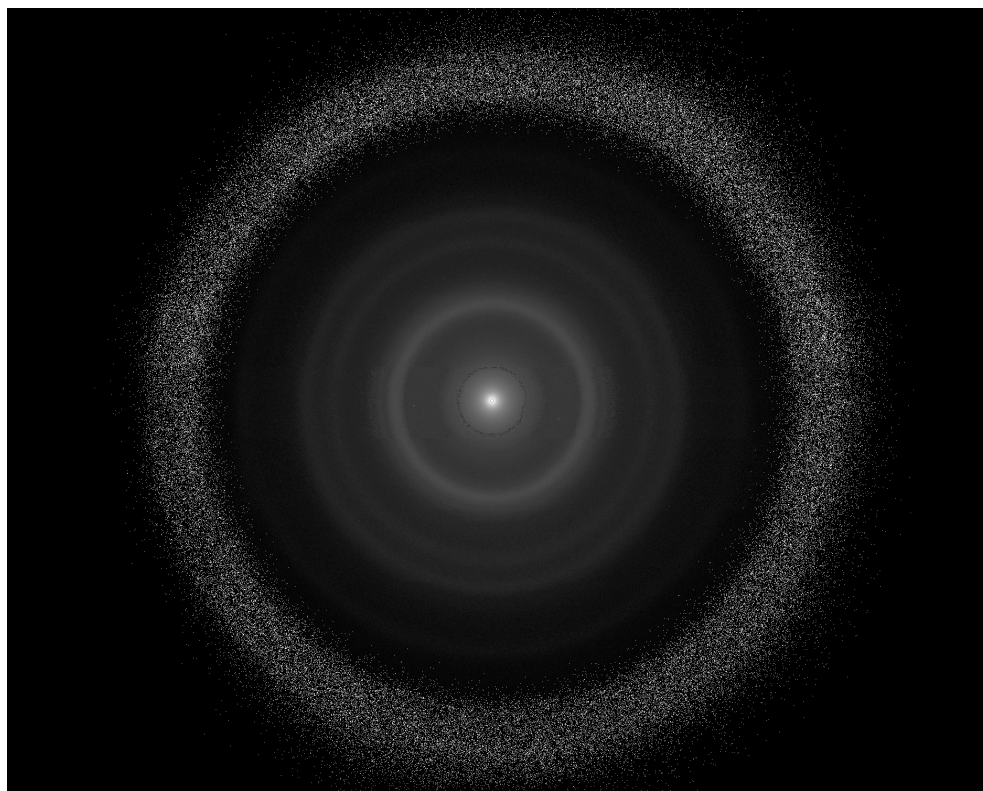


Fig. S7 SAED of the Rh₄Ni nanoparticle.

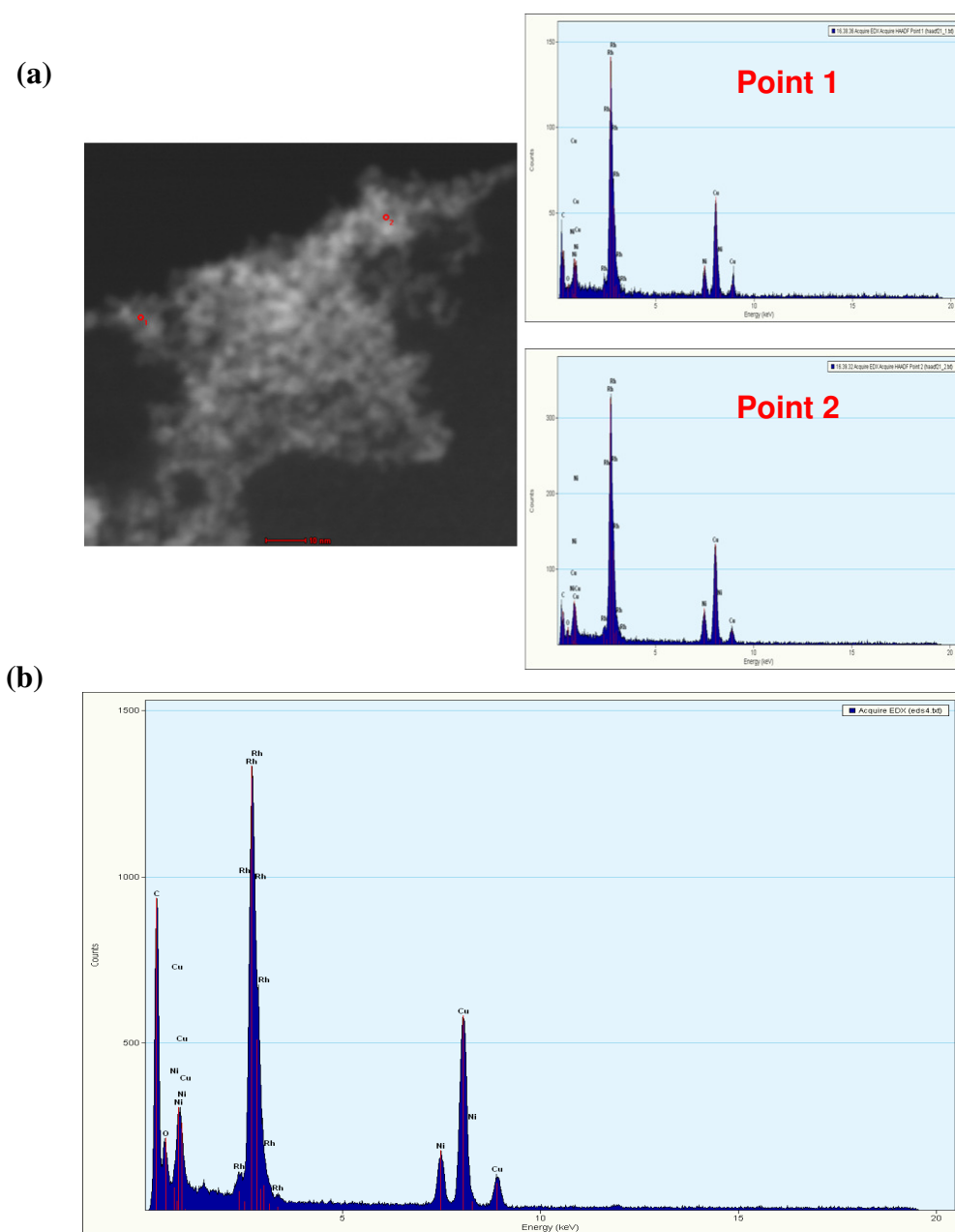


Fig. S8 (a) HAADF–STEM image of Rh₄Ni nanocatalyst with the corresponding EDS spectra. (b) EDS spectrum for the bulk area of Rh₄Ni nanocatalyst.

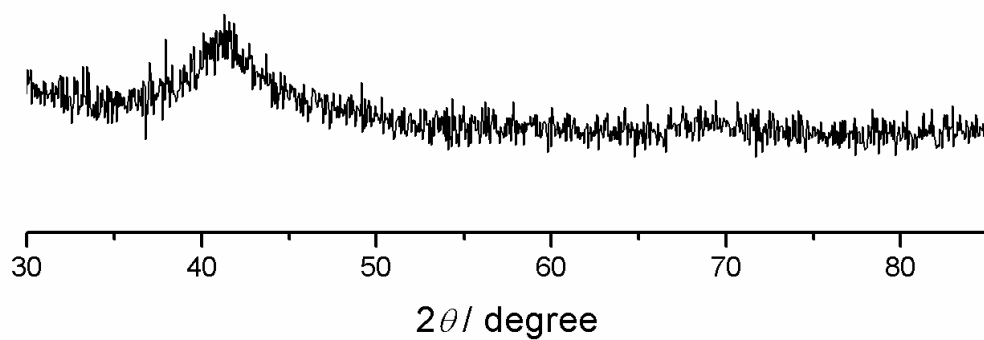


Fig. S9 The XRD pattern for Rh₄Ni catalyst.

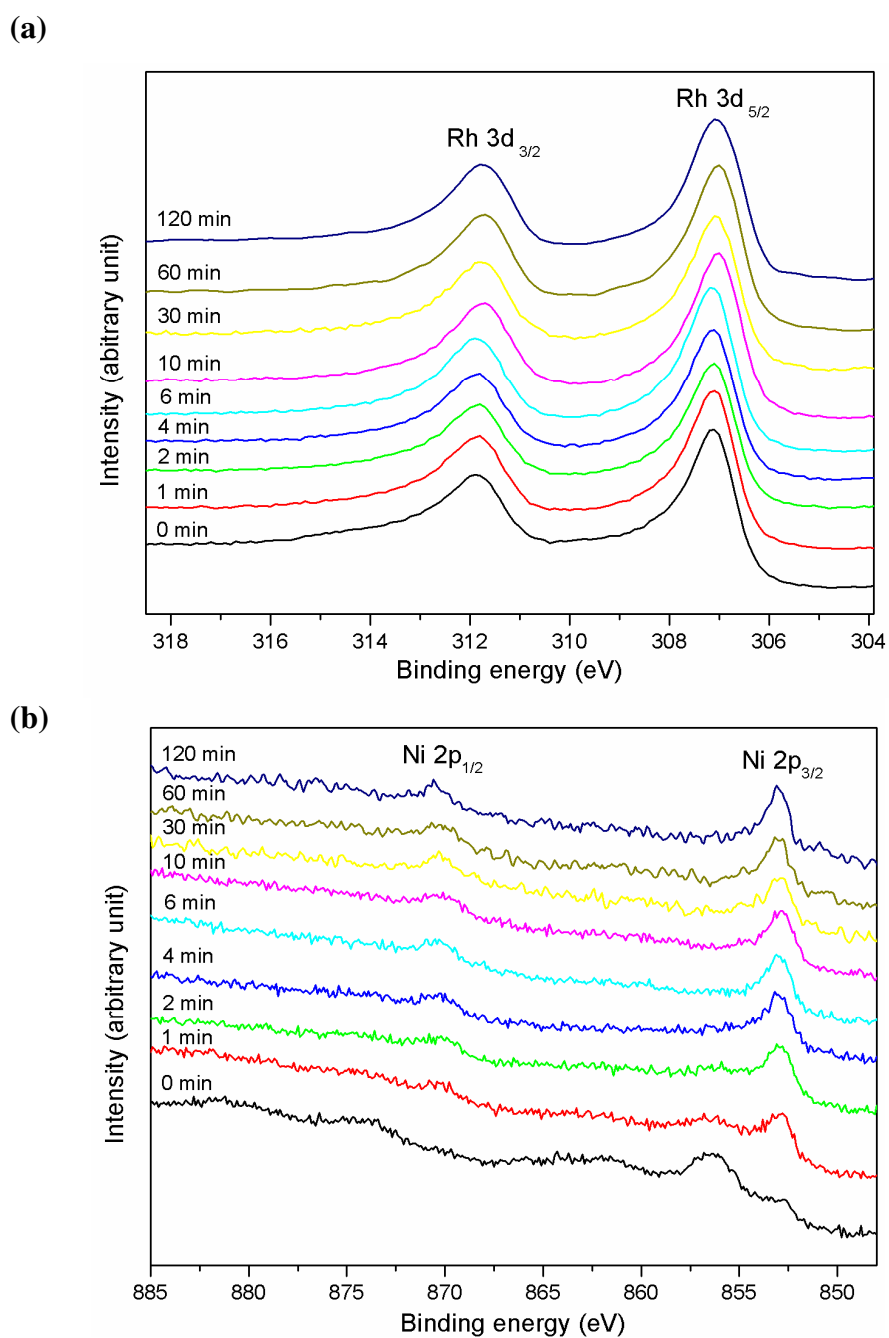


Fig. S10 The XPS profiles of (a) Rh and (b) Ni in the Rh_4Ni nanocatalyst before (0 min) and after (1~120 min) argon sputtering.