Electronic Supplementary Information

Rhodium-Nickel Nanoparticles Grown on Graphene as Highly Efficient Catalyst for Complete Decomposition of Hydrous Hydrazine at Room Temperature for Chemical Hydrogen Storage

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1. Chemicals and materials

Hydrazine monohydrate ($H_2NNH_2 \cdot H_2O$, Tokyo Chemical Industry Co., Ltd, 98%), rhodium (III) chloride ($RhCl_3 \cdot xH_2O$, Aladdin Reagent, Rh: 38.5-42.5%), nickel (II) chloride ($NiCl_2 \cdot 6H_2O$, Beijing Chemical Works, ≥98%), sodium borohydride ($NaBH_4$, Beijing Chemical Works, ≥98%), sodium hydroxide (NaOH, Beijing Chemical Works, 97%), potassium hydroxide (KOH, Beijing Chemical Works, 97%), ethanol (CH_3CH_2OH, Beijing Chemical Works, >99.7%)，sulfuric acid (H_2SO_4, Beijing Chemical Works, 98%), hydrochloric acid (HCl, Beijing Chemical Works, 36%~37%), potassium peroxodisulfate ($K_2S_2O_8$, Aldrich, ≥99%), phosphorus pentoxide (P_2O_5, Aldrich, ≥99.99%), potassium permanganate ($KMnO_4$, Sinopharm Chemical Reagent Co., Ltd, ≥99%), hydrogenperoxide (H_2O_2, Beijing Chemical Works, 30%), XC-72R carbon (Cabot Corp.), paradimethylaminobenzaldehyde ($C_9H_{11}NO$, PDAB, Sinopharm Chemical Reagent Co., Ltd, 99%), graphite powder (Alfa, 325 mesh) and nylon filter membranes (Aldrich, pore size 0.2 μm) were used as received. De-ionized water with the specific resistance of 18.2 MΩ·cm was obtained by reversed osmosis followed by ion-exchange and filtration.

2. Graphite Oxide (GO) preparation

GO was made by a modified Hummers method.[1,2] Briefly, graphite powder (3 g, 325 mesh) was put into an 80 °C solution of concentrated H_2SO_4 (12 mL), $K_2S_2O_8$ (2.5 g), and P_2O_5 (2.5 g). After keeping at 80 °C for 4.5 h using a hotplate, the mixture was cooled to room temperature and diluted with 0.5 L of de-ionized water and left overnight. Then, the mixture was filtered and washed with de-ionized water using a 0.2 micron Nylon Millipore filter to remove the residual acid. The product was dried under ambient condition overnight. Next, the pretreated graphite powder was put into cold (0 °C) concentrated H_2SO_4 (120 mL) in a 250-mL round-bottom flask equipped with a magnetic stir bar. 15 g $KMnO_4$ was added gradually under stirring while the temperature of the mixture was kept below 20 °C. The solution was then stirred at 35 °C for 2 h. Afterwards, 250 mL of de-ionized water was added and the suspension was stirred for another 2 h. Subsequently, additional 0.7 L of de-ionized water was added. Shortly after that, 20 mL of 30% H_2O_2 was added to the mixture to destroy the excess of permanganate. The suspension was then repeatedly centrifuged and washed first with 5% HCl solution and then with water. Exfoliation of

graphite oxide to GO was achieved by ultrasonication of the dispersion for 30 min.

3. Catalyst preparation

Graphene-supported RhNi catalyst was synthesized by a co-reduction route. Briefly, an aqueous solution of $RhCl_3 \cdot xH_2O$ (37.98 mM, 5.26 mL) was add into a beaker containing a 2.74 mL solution of $NiCl_2 \cdot 6H_2O$ (0.011 g) and GO solution (1g, containing 15‰ GO) under sonication condition. Then a 2 mL aqueous solution of $NaBH_4$ (50 mg) and NaOH (5 M) was added into the above obtained solution as reducing agent with vigorous stirring. The mixture was kept stirring for 24 h before the catalytic reaction. The RhNi and RhNi/XC-72R catalyst was prepared using the same procedure except that the GO and NaOH are not used or XC-72R is used instead of GO, respectively.

4. Instrumentation

Powder X-ray diffraction (XRD) measurements were performed on a Rigaku-Dmax 2500 diffractometer with Cu Kα radiation ($\lambda = 0.15405$ nm). Scanning electron microscopy (SEM) was performed on a field emission Hitachi S-4800 instrument, operating at an accelerating voltage of 10 kV. Samples for SEM were prepared by dispersing the as-prepared product in ethanol by sonicating for about 30 min, and then depositing the sample onto an ITO glass, attached to a SEM brass stub. Transmission electron microscope (TEM) was performed using a FEI Tecnai G2 S-Twin instrument with a field emission gun operating at 200 kV. Samples for all of these TEM experiments were prepared by dispersing the samples in ethanol, sonicating for 30 min to ensure adequate dispersion of the nanostructures, and evaporating one drop of the solution onto a 300 mesh Cu grid, coated with a lacey carbon film. Mass analysis of the generated gases was performed using a Balzers Prisma QMS 200 mass spectrometer, wherein argon gas is chosen as carrying gas. Ultraviolet visible (UV-Vis) spectra were collected on a UV5800 modal spectrophotometer. The chromogenic agent was prepared by mixing PDAB (0.5 g), ethanol (25 mL) and hydrochloric acid (1 M, 2.5 mL) together. And then a 5 mL cuvette was fulfilled with hydrous hydrazine (0.2 M, 0.05 mL) before or after reaction, the chromogenic agent (0.1 mL) prepared above and de-ionized water (2.85 mL). The mixture was kept for 30 min before tests. Raman spectra were collected with a Renishaw 1000 model confocal microscopy Raman spectrometer with a CCD detector and a holographic notch filter at ambient conditions. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurements were performed on a TJA (Thermo Jarrell Ash) Atomscan Advantage instrument. The dry samples were dissolved in boiling aqua fortis using microwave digestion system
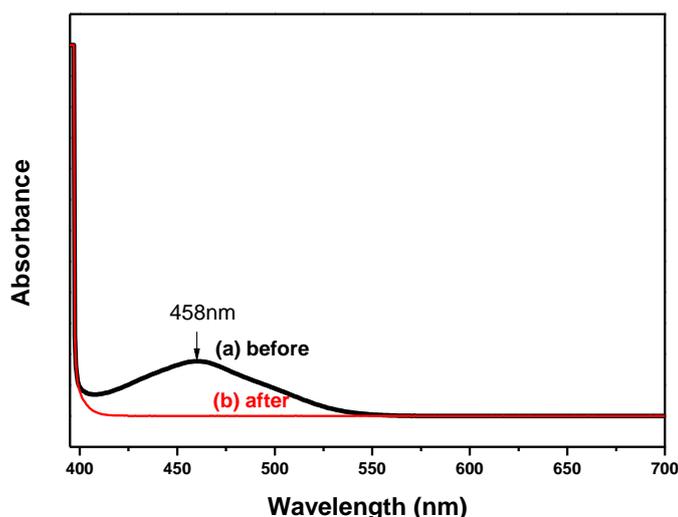
5. Hydrous hydrazine decomposition reaction

Catalytic reactions were carried out at room temperature 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 hydrazine monohydrate. Catalytic decomposition reaction of hydrous hydrazine for the release of hydrogen (along with nitrogen) was initiated

by stirring the mixture of 2 mmol of hydrazine monohydrate introduced via a pressure-equalization funnel and the aqueous suspension of the catalyst prepared as described above. The molar ratio of Rh in the catalysts to hydrazine was kept unchanged ($Rh/N_2H_4 = 1/10$). The gas released during the reaction was passed through a trap containing 1.0 M sulfuric acid to ensure the absorption of ammonia, if produced, of which the volume was monitored using the gas burette. For preparing the samples for mass spectral analysis of the released gases the acid trap was not used.

6. Catalyst characterization

The catalyst was collected by a consecutive centrifugation (15000 rpm for 5 min) and washing cycle for at least three times with water and/or ethanol. The collected product was dried at 353 K for 10 h for XRD, ICP-AES and Raman tests.


Fig. S1. UV-Vis spectra of hydrous hydrazine (a) before and (b) after the completion of hydrazine decomposition reaction over the RhNi nanocatalysts supported on graphene. The liquid samples were obtained by centrifuging the reaction suspensions to separate the solutions and the RhNi/graphene nanocatalysts.

The results shows a characteristic adsorption peak at 458 nm, which is attributed to the yellow resultant of PDAB and hydrazine in acid solution. After catalytic reaction, the absence of this characteristic adsorption peak indicates no existence of hydrazine in the solution, i.e., complete conversion of hydrazine.
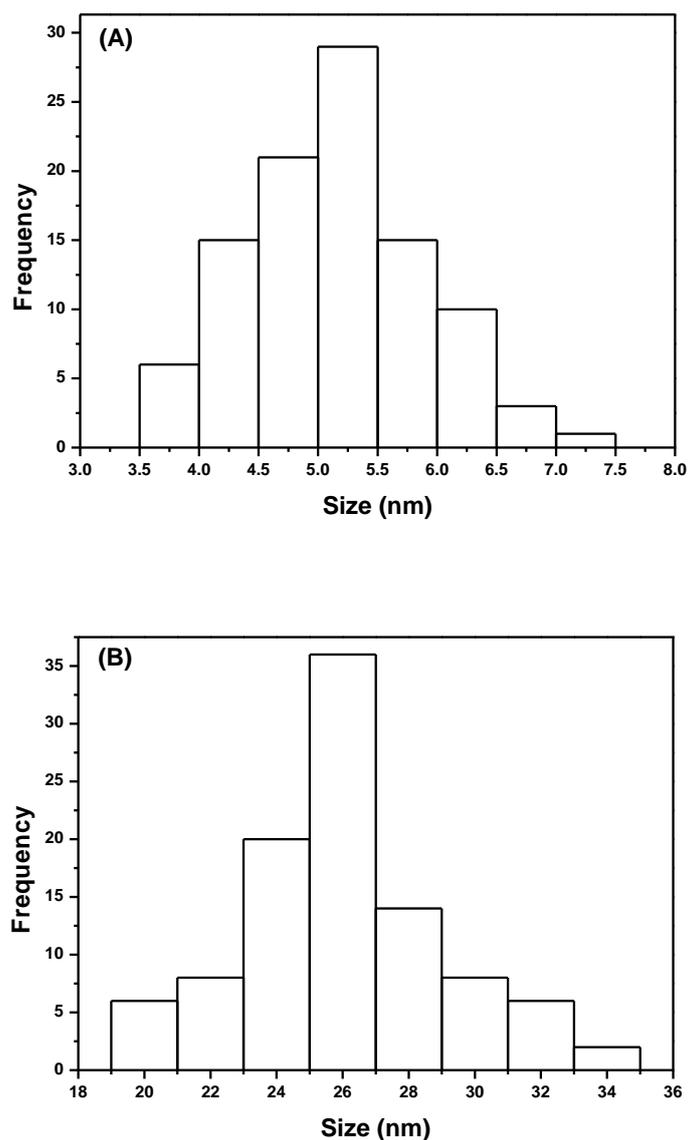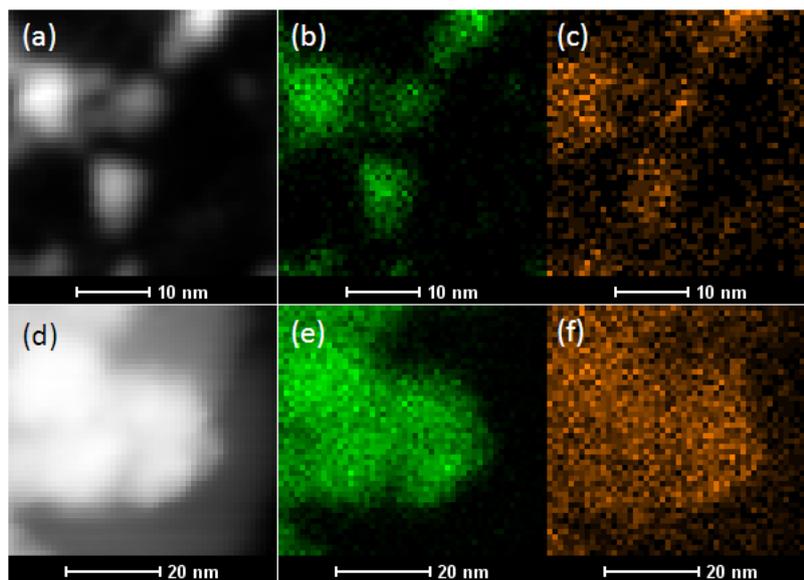
Fig. S2. Size distribution histograms for RhNi NPs prepared (A) with and (B) without GO sheets according to Fig. 3b and 3d.

The mean particle size for (A) and (B) is calculated to be ca. 5 nm and 26 nm, respectively, indicating that GO is benefit to disperse RhNi NPs and restrain its agglomeration during the synthetic process.
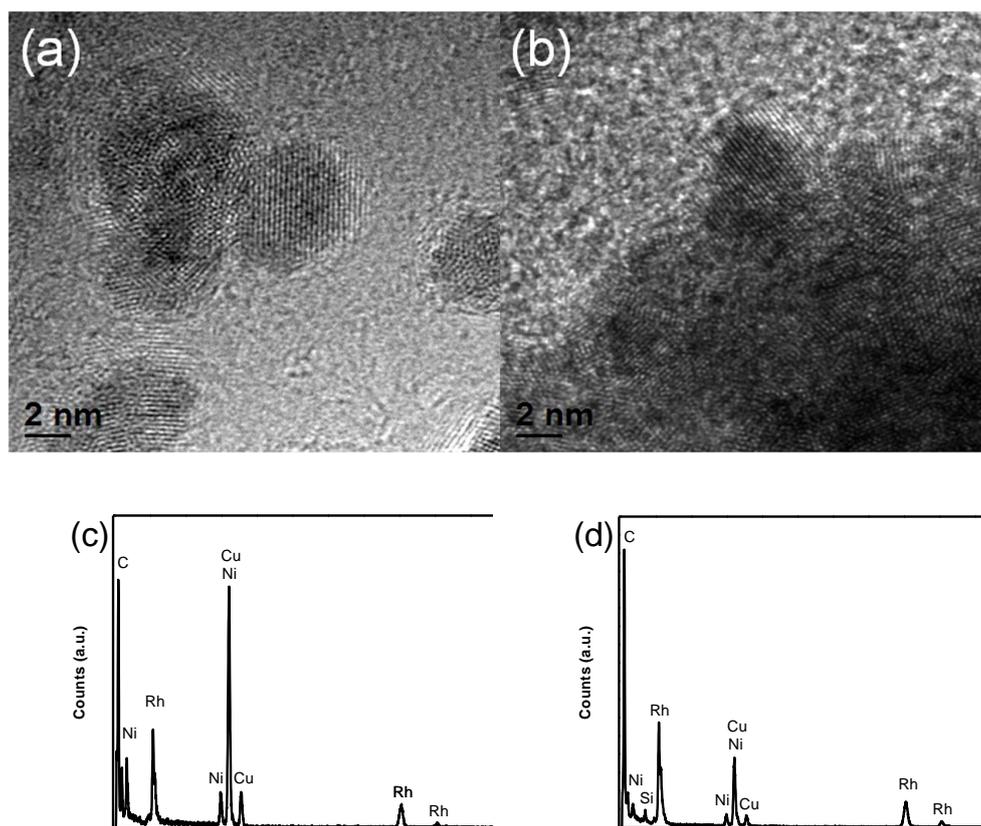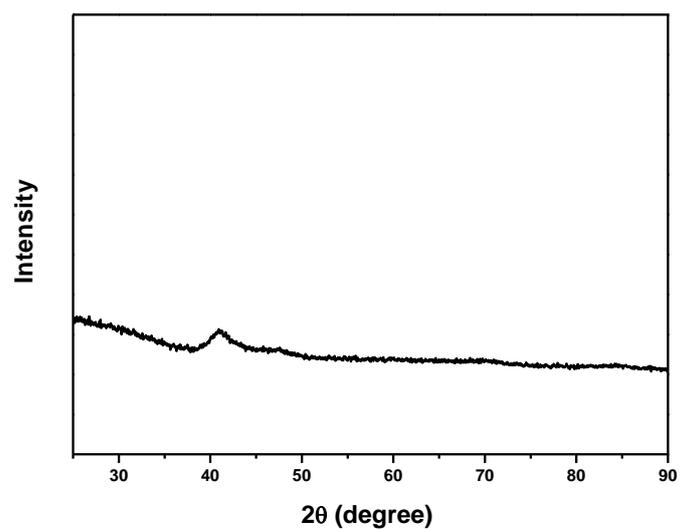
**Fig. S3.** HRTEM images (a, b) and EDS (c, d) of RhNi NPs prepared (a, c) with and (b, d) without GO sheets.

Fig. S4. Elemental mapping profiles of Rh (b, e) and Ni (c, f) for RhNi NPs prepared (a-c) with and (d-f) without GO sheets.
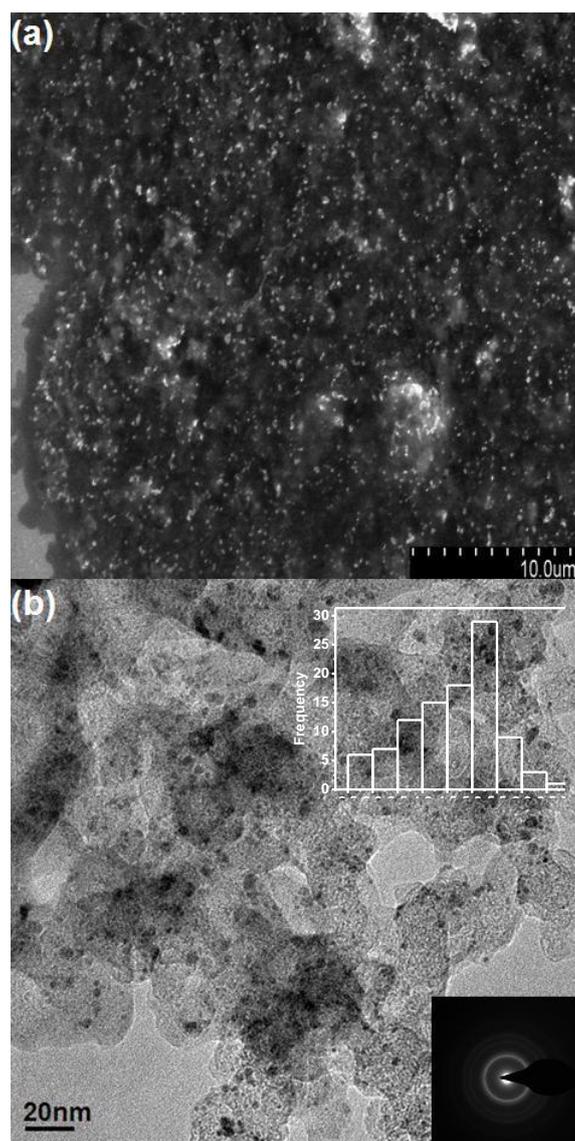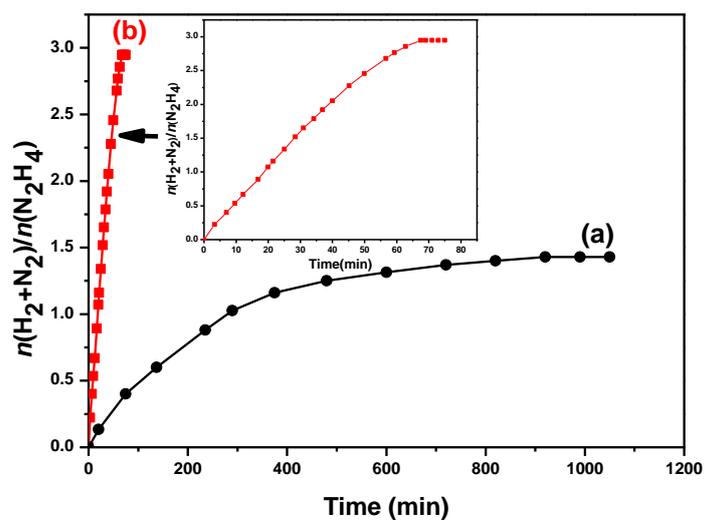
Fig. S5. SEM (a) and TEM (b) images of RhNi NPs supported on Vulcan XC-72R carbon. Inset in (b): the corresponding size distribution histogram and SAED pattern.

**Fig. S6.** XRD profiles of RhNi NPs supported on Vulcan XC-72R carbon.
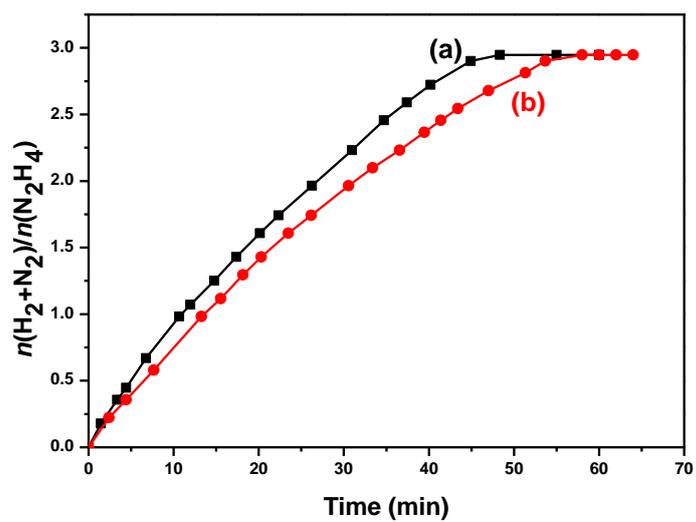
Fig. S7. Time profiles for decomposition of hydrous hydrazine catalyzed by RhNi NPs supported on (a) graphene or (b) Vulcan XC-72R carbon.
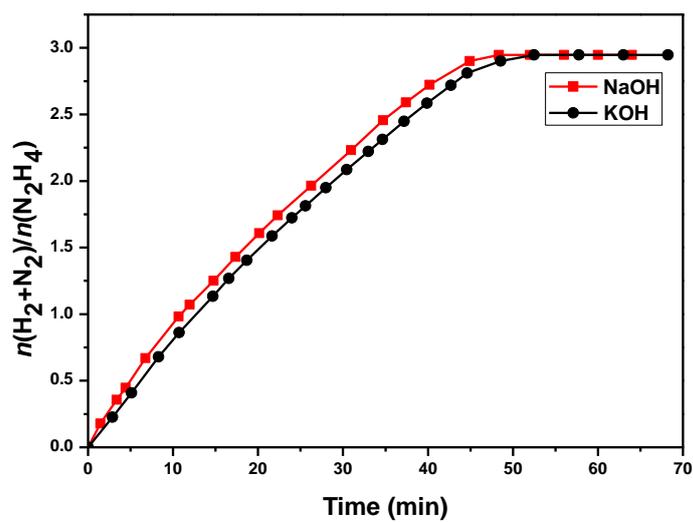
Fig. S8. Time profiles for decomposition of hydrous hydrazine catalyzed by RhNi NPs prepared with GO sheets and then wash NaOH away (a) and re-add equivalent amount of NaOH (b) in the catalytic process.
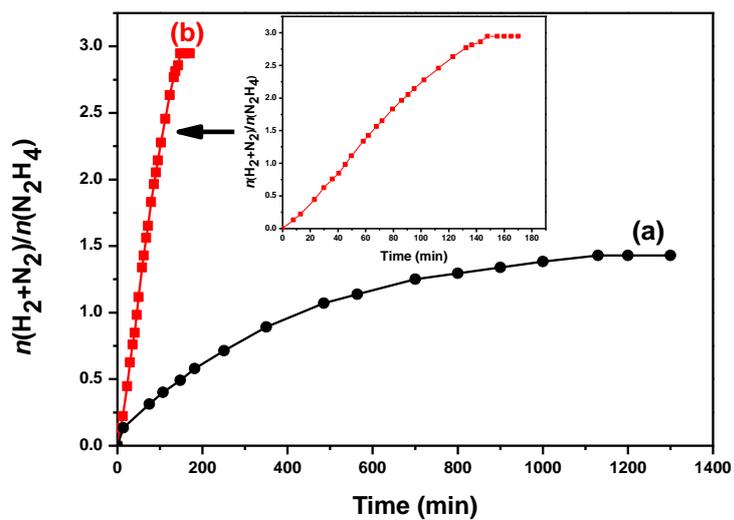
Fig. S9. Time profiles for decomposition of hydrous hydrazine catalyzed by RhNi NPs (no NaOH in the synthesis process) without adding (a) or adding (b) NaOH in the catalytic process.
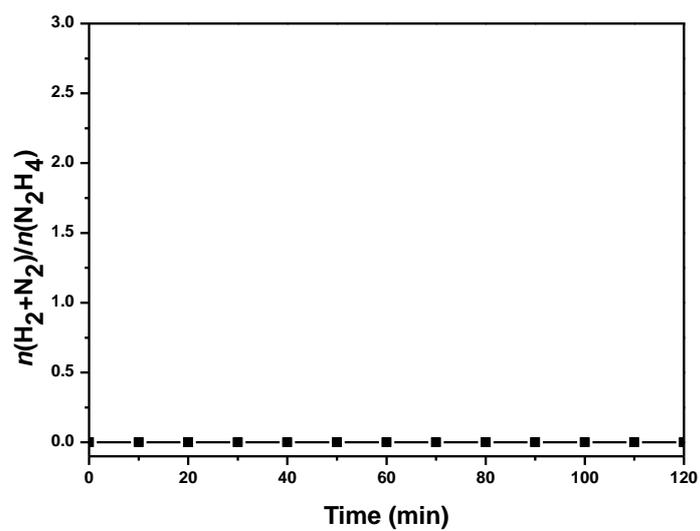
Fig. S10. Time-independent stability of hydrous hydrazine in the presence of GO and NaOH.

Fig. S11. Time profiles for decomposition of hydrous hydrazine catalyzed by RhNi NPs prepared with GO sheets stabilized in aqueous NaOH or KOH solution.
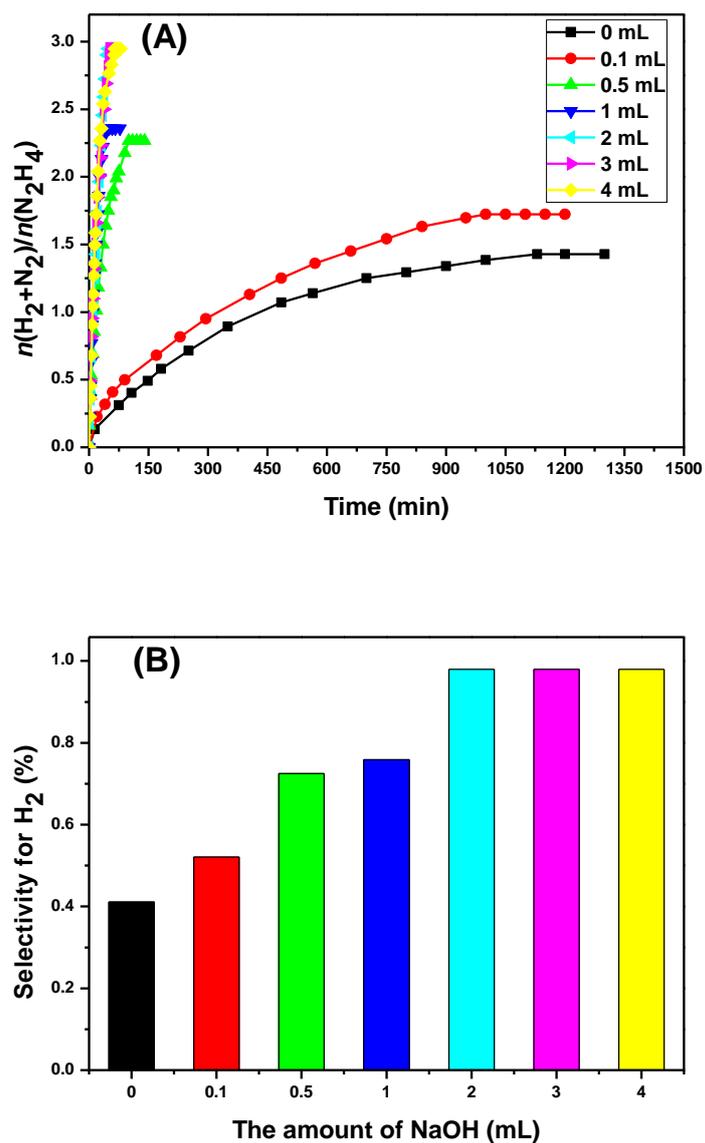
Fig. S12. (A) Decomposition of hydrous hydrazine catalyzed by RhNi NPs prepared with GO sheets stabilized with different amount of NaOH (5 M) solution and (B) the according selectivity for H_2.
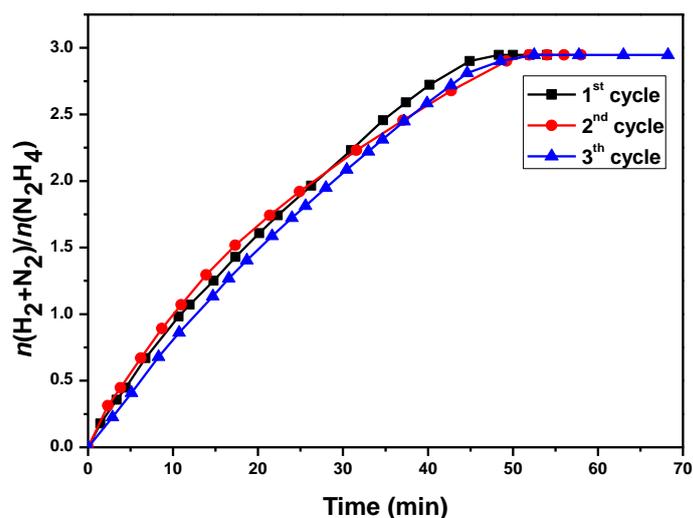
Fig. S13. Lifetime test of the RhNi nanocatalysts prepared with GO sheets toward the decomposition of hydrous hydrazine. Additional aliquot of hydrazine monohydrate was subsequently introduced into the reaction vessel after the completion of the previous run.

Reference

(1) W. Hummers, R. Offeman, *J. Am. Chem. Soc.,* 1958, **80**, 1339.

(2) N. I. Kovtyukhova, P. J. Ollivier, B. R. Martin, T. E. Mallouk, S. A. Chizhik, E.

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