

Supporting Information

Monodispersed PtNi Nanoparticles Deposited on Diamine-alkalized Graphene for Highly Efficient Dehydrogenation of Hydrous Hydrazine at Room Temperature

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1. Chemicals

All chemicals were commercial and used without further purification. Graphite (C, Sigma-Aldrich, >99.8%), sulfuric acid (H₂SO₄, Kishida Chem. Co., 98%), phosphoric Acid (H₃PO₄, Tokyo Chemical Industry Co., 89%), hydrogen peroxide (H₂O₂, Kishida Chem. Co., 30%), potassium permanganate (KMnO₄, Kishida Chem. Co., 99.3%), potassium tetrachloroplatinate (K₂PtCl₄, Wako Pure Chemical Industries, Ltd., >98%), nickel chloride hexahydrate (NiCl₂·6H₂O, Wako Pure Chemical Industries, Ltd., 99%), sodium borohydride (NaBH₄, Aldrich, 99%), sodium hydroxide (NaOH, Chameleon Reagent, >98%), hydrochloric acid (HCl, Tokyo Chemical Industry Co., >35%), hydrazine monohydrate (H₂NNH₂·H₂O, Sigma-Aldrich, 98%), 1,4-phenylenediamine (C₆H₈N₂, Tokyo Chemical Industry Co., 98%), acetone (C₃H₆O, Kishida Chem. Co., >99.5%) and ethanol (C₂H₅OH, Kishida Chem. Co., >99.8%) were used as received.

2. Instrumentation

Powder X-ray diffraction patterns were collected for synthesized catalysts on a Rigaku Ultima IV X-ray diffractometer with Ni filtered Cu-K α radiation ($\lambda = 0.15406$ nm) (40 kV, 40 mA). X-ray photoelectron spectroscopic (XPS) measurements were conducted on a Shimadzu ESCA-3400 X-ray photoelectron spectrometer using an Mg K α source (10 kV, 10 mA). The argon sputtering experiments were carried out under the conditions of background vacuum of 3.2×10^{-6} Pa and sputtering acceleration voltage of 2 kV and sputtering current of 10 mA. The charging potential of the catalyst samples was corrected by setting the binding energy of the adventitious carbon (C 1s) at 284.6 eV. The TEM and HAADF-STEM images and EDX spectra were recorded on Transmission electron microscope (TEM, TECNAI G² F20) with operating voltage at 200 kV equipped with energy-dispersive X-ray detector (EDX). Scanning electron microscopic (SEM) analyses were carried with a Hitachi S5000 field emission scanning electron microscope. FTIR spectra were measured by using a Bruker spectrometer IFS 66v/s. Mass analysis of the prepared gas was performed using a Balzers Prisma QMS 200 mass spectrometer.

3. Syntheses of catalysts

3.1 Synthesis of graphene oxide (GO): GO was synthesized according to the reported procedure.¹ Firstly, a concentrated H₂SO₄/H₃PO₄ solution (180:20 mL) was added to the mixture of graphite flakes (1.5 g) and KMnO₄ (9 g) and then the solution was kept at 323 K with a water bath for 12 hours. The solution was cooled to room temperature and poured into a flask containing ice (200 g) and H₂O₂ (30%, 1.5 mL). The solid material was separated by centrifugation and washed with water (100 mL), HCl (100 mL), and ethanol (100 mL) (for 2 times). Finally, the obtained solid was dried in vacuum oven at room temperature for 12 h.

3.2 Syntheses of PtNi nanoparticle/diamine-alkalized graphene catalysts (PtNi/PDA-rGO, PDA = 1,4-phenylenediamine): GO (50 mg) was dispersed in water (50 mL) under sonication for 2.5 h. PDA (0.27 g) was dissolved in acetone (4 mL) and then added dropwise into the GO solution. The mixture was stirred for 48 h, resulting in the formation of a black precipitation (PDA-GO) (Fig. S1). The precipitation was separated by centrifugation and washed with water. Subsequently, the prepared PDA-GO was dispersed in water (25 mL), to which an aqueous solution of K₂PtCl₄ (0.06 mmol) and NiCl₂·6H₂O (0.04 mmol) was added, followed by an immediate addition of NaBH₄ (30 mg) dissolved in an aqueous NaOH solution (1 mL, 5 M) with vigorous shaking, resulting in the formation of PtNi NPs on PDA-rGO. Finally, the PtNi/PDA-rGO catalyst was collected by centrifugation, washed with water and dried under vacuum at room temperature for 12 h, giving the PtNi/PDA-rGO catalyst. For comparison, the catalysts with different molar ratios of Pt²⁺/Ni²⁺ were prepared by the same procedure using K₂PtCl₄ and NiCl₂·6H₂O as follows: 0.1 mmol (K₂PtCl₄) for Pt/PDA-rGO; 0.09 mmol (K₂PtCl₄) and 0.01 mmol (NiCl₂) for Pt_{0.9}Ni_{0.1}/PDA-rGO; 0.08 mmol (K₂PtCl₄) and 0.02 mmol (NiCl₂) for Pt_{0.8}Ni_{0.2}/PDA-rGO; 0.07 mmol (K₂PtCl₄) and 0.03 mmol

(NiCl₂) for Pt_{0.7}Ni_{0.3}/PDA-rGO; 0.05 mmol (K₂PtCl₄) and 0.05 mmol (NiCl₂) for Pt_{0.5}Ni_{0.5}/PDA-rGO; 0.04 mmol (K₂PtCl₄) and 0.06 mmol (NiCl₂) for Pt_{0.4}Ni_{0.6}/PDA-rGO; 0.03 mmol (K₂PtCl₄) and 0.07 mmol (NiCl₂) for Pt_{0.3}Ni_{0.7}/PDA-rGO; and 0.1 mmol (NiCl₂) for Ni/PDA-rGO.

Additionally, the Pt_{0.6}Ni_{0.4}/rGO catalyst was also prepared using the similar synthetic procedure with GO instead of diamine-alkalized GO.

To avoid the oxidation of PtNi NPs, the catalysts were kept in an Ar-filled glove box immediately after dried under vacuum.

4. Catalytic activity characterization

4.1 Procedure for the dehydrogenation of hydrous hydrazine: In general, a mixture of as-synthesized catalyst and aqueous NaOH solution was placed in a two-necked round-bottom flask (30 mL), which was placed in a water bath at a preset temperature (298-323 K). A gas burette filled with water was connected to the reaction flask to measure the volume of released gas (temperature kept constant at 298 K during measurements). The reaction started when hydrous hydrazine (0.1 mL) was injected into the mixture using a syringe. The volume of the evolved gas was monitored by recording the displacement of water in the gas burette. The reaction was completed when there was no more gas generation. The molar ratios of (Pt+Ni)/hydrazine were theoretically fixed at 0.05 for all the catalytic reactions.

4.2 Durability testing of the catalysts: For testing the durability of PtNi NPs/PDA-rGO, hydrous hydrazine (0.1 mL) was subsequently added into the reaction flask after the completion of the first-run decomposition of hydrous hydrazine. Such test cycles of the catalyst for the dehydrogenation of hydrous hydrazine were carried out for 5 runs at 303 K by adding aliquots of hydrous hydrazine.

4.3 Stability of the catalysts: After the reaction, the Pt_{0.6}Ni_{0.4}/PDA-rGO catalyst was separated from the reaction solution by centrifugation and dried under vacuum at room temperature for TEM analyze.

4.4 Calculation method for specific surface area of metal nanoparticles: Assuming all the PtNi NPs to be spherical, the specific surface area of PtNi NPs was calculated on the basis of the average particle diameter by using the equation: $S = 6/(d_p \times \rho)$, where S is specific surface area, d_p is the average particle diameter measured by TEM and ρ is the density, which was calculated by using the values of 21.35 g cm⁻³ for Pt and 8.91 g cm⁻³ for Ni and considering the molar ratio of Pt to Ni in the catalyst.

Table S1. Catalytic activities of different catalysts for the dehydrogenation of hydrous hydrazine

Catalyst	Solvent/medium	Temp. (K)	Selectivity for H ₂ (100 %)	TOF (h ⁻¹)	E _a (kJ mol ⁻¹)	Ref.
Pt_{0.6}Ni_{0.4}/PDA-rGO	Aqueous NaOH	323	100	2056	33.39	This work
	Aqueous NaOH	303	100	903		This work
Ni ₈₈ Pt ₁₂ /MIL-101	Aqueous NaOH	323	100	350	55.5	2
Ni ₆₆ Rh ₃₄ @ZIF-8	Aqueous NaOH	323	100	140	58.1	3
Ni _{0.6} Fe _{0.4} B	Aqueous NaOH	323	100	28.8	50.7	4
NiMoB-La(OH) ₃	Aqueous NaOH	323	100	13.3	55.1	5
Pt ₆₀ Ni ₄₀ -CNDs	Aqueous NaOH	323	100	170	43.9	6
Co _{0.65} Pt _{0.3} (CeOx) _{0.05}	Aqueous NaOH	298	72.1	194.8		7
Ni ₆ Pt ₄ -SF	Aqueous NaOH	298	100	150		8
Ni ₃ Pt ₇ /graphene	Aqueous NaOH	298	100	68	49.4	9
Ni _{0.9} Pt _{0.1} /Ce ₂ O ₃	Aqueous NaOH	298	100	28.1	42.3	10
Rh _{4.4} Ni/graphene	Aqueous NaOH	298	100	28		11
Fe-B/multiwalled carbon nanotubes	Without additive	293	97	4032	46.7	12
Co-B-N-H	Without additive	293	100	4434	39.9	13
Ni ₃ Fe/C	Without additive	293	100	528	48.1	14
NiFe/Cu	Without additive	343	100	35	44	15
NiIr _{0.059} /Al ₂ O ₃ -HT	Without additive	303	99	12.4	49.3	16
NiPt _{0.057} /Al ₂ O ₃ -HT	Without additive	303	97	16.5	34	17
Ni _{1.5} Fe _{1.0} /(MgO) _{3.5}	Without additive	299	99	11		18
Rh	Without additive	298	43.8	2.5		19
Rh ₄ Ni	Without additive	298	100	4.8		20
Ni _{0.95} Ir _{0.05}	Without additive	298	100	2.2		21

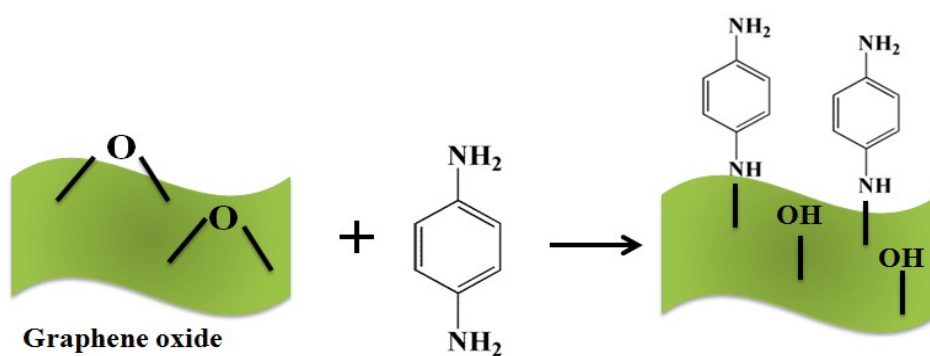


Fig. S1 Schematic illustration for the synthesis of PDA-GO.



Fig. S2 Photographic images of (left) $\text{Pt}_{0.6}\text{Ni}_{0.4}/\text{PDA-rGO}$ (50 mg) and (right) $\text{Pt}_{0.6}\text{Ni}_{0.4}/\text{rGO}$ (50 mg).

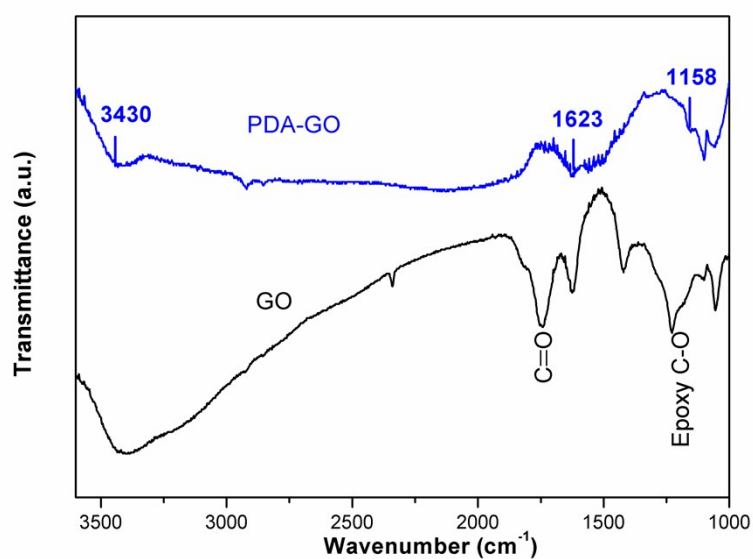


Fig. S3 IR spectra of GO and PDA-GO.

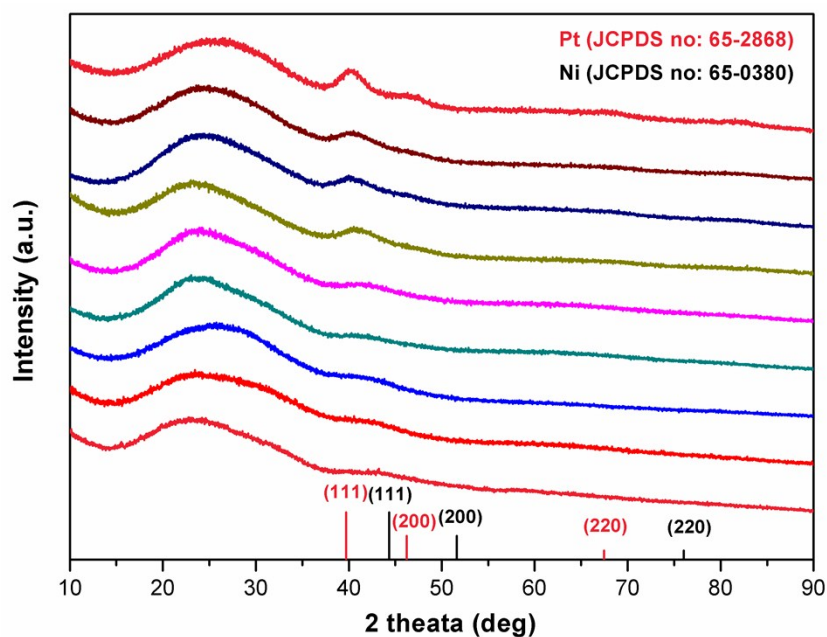


Fig. S4 PXRD patterns of $\text{Pt}_x\text{Ni}_{1-x}/\text{PDA-rGO}$ ($0 \leq x \leq 1.0$): (a) $\text{Ni}/\text{PDA-rGO}$, (b) $\text{Pt}_{0.3}\text{Ni}_{0.7}/\text{PDA-rGO}$, (c) $\text{Pt}_{0.4}\text{Ni}_{0.6}/\text{PDA-rGO}$, (d) $\text{Pt}_{0.5}\text{Ni}_{0.5}/\text{PDA-rGO}$, (e) $\text{Pt}_{0.6}\text{Ni}_{0.4}/\text{PDA-rGO}$, (f) $\text{Pt}_{0.7}\text{Ni}_{0.3}/\text{PDA-rGO}$, (g) $\text{Pt}_{0.8}\text{Ni}_{0.2}/\text{PDA-rGO}$, (h) $\text{Pt}_{0.9}\text{Ni}_{0.1}/\text{PDA-rGO}$ and (i) $\text{Pt}/\text{PDA-rGO}$.

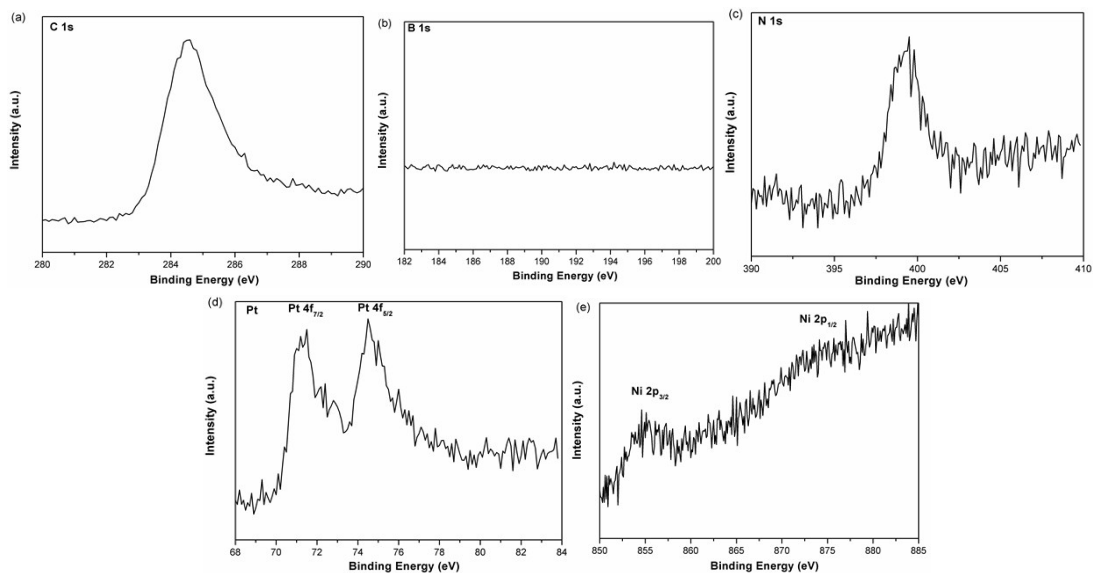


Fig. S5 XPS spectra of C 1s, B 1s, N 1s, Pt 4f and Ni 2p for $\text{Pt}_{0.6}\text{Ni}_{0.4}/\text{PDA-rGO}$.

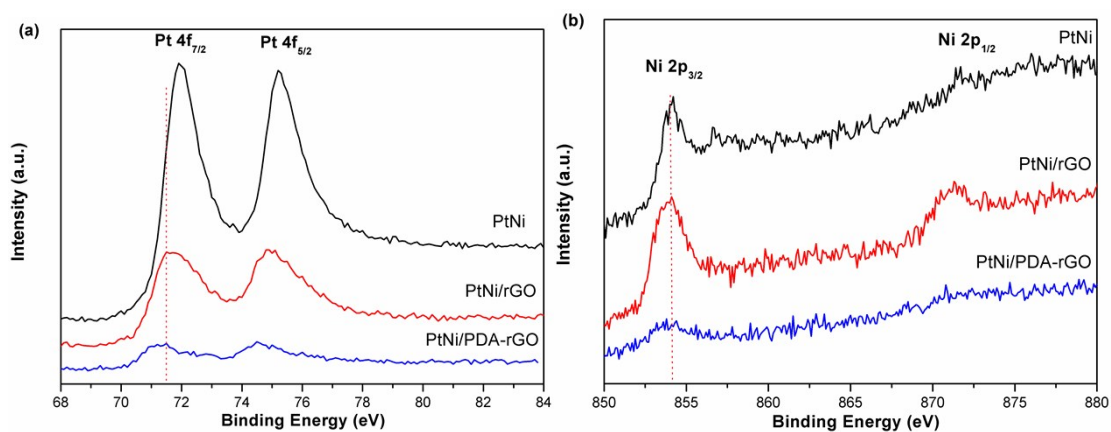


Fig. S6 XPS spectra of Pt 4f and Ni 2p for Pt_{0.6}Ni_{0.4}, Pt_{0.6}Ni_{0.4}/rGO and Pt_{0.6}Ni_{0.4}/PDA-rGO.

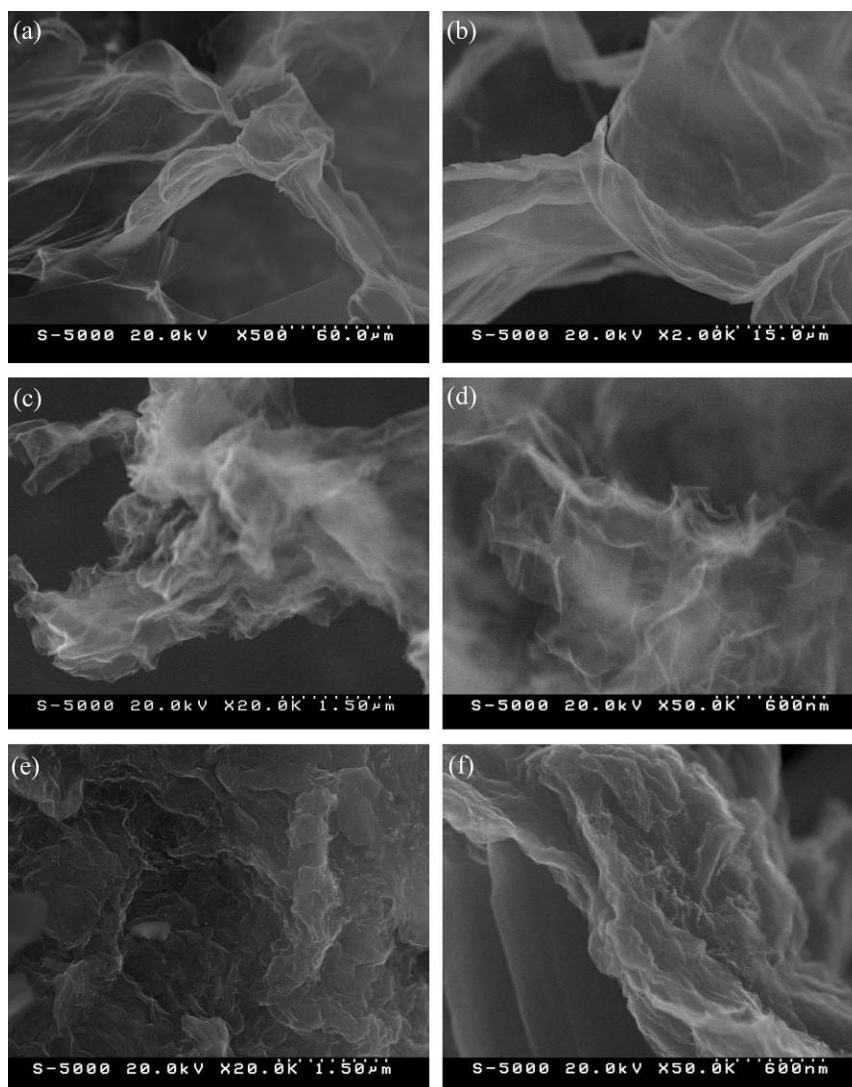


Fig. S7 SEM images of (a, b) GO, (c, d) PDA-GO and (e, f) Pt_{0.6}Ni_{0.4}/PDA-rGO.

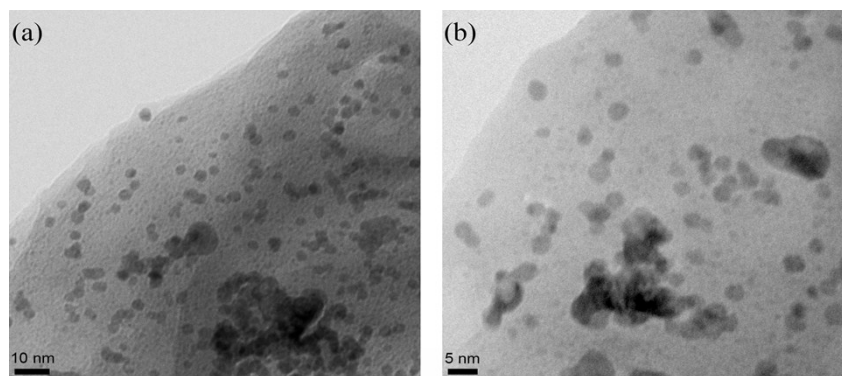


Fig. S8 TEM images of $\text{Pt}_{0.6}\text{Ni}_{0.4}/\text{rGO}$.

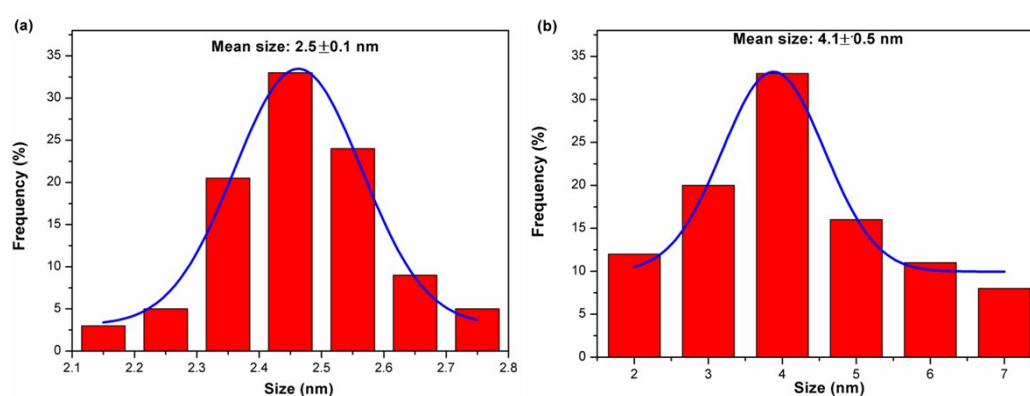


Fig. S9 Particle size distribution histograms of (a) $\text{Pt}_{0.6}\text{Ni}_{0.4}/\text{PDA-rGO}$ and (b) $\text{Pt}_{0.6}\text{Ni}_{0.4}/\text{rGO}$.

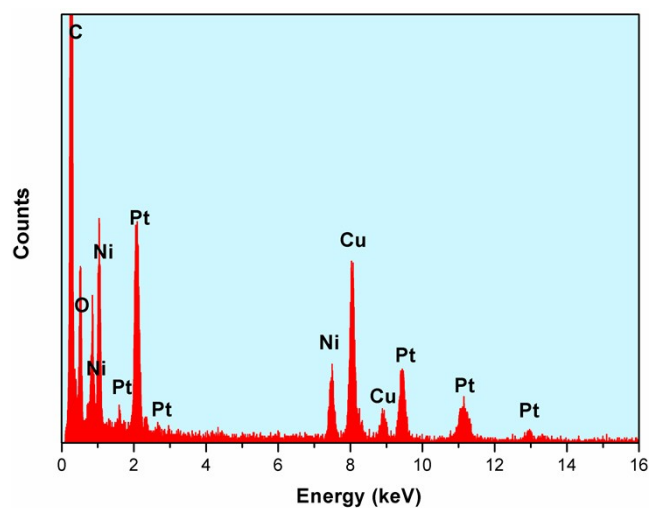


Fig. S10 EDX pattern of $\text{Pt}_{0.6}\text{Ni}_{0.4}/\text{PDA-rGO}$.

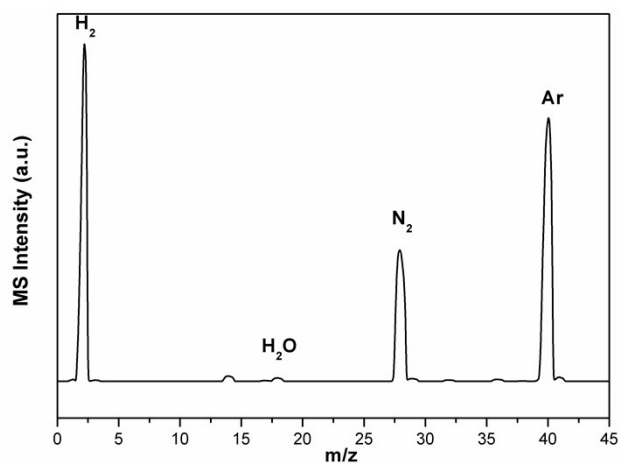


Fig. S11 Mass spectrum of the released gas from the dehydrogenation of hydrous hydrazine over $Pt_{0.6}Ni_{0.4}/PDA-rGO$ under an argon atmosphere at room temperature, showing the absence of NH_3 in the released gas.

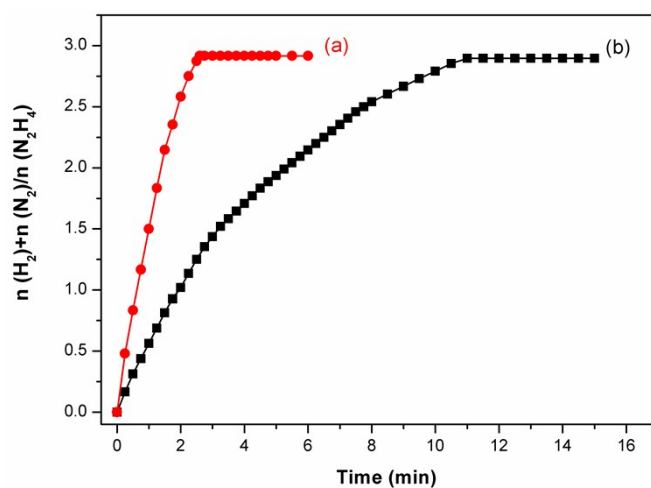


Fig. S12 Volume of the generated gas ($H_2 + N_2$) versus time for the dehydrogenation of hydrous hydrazine over (a) $Pt_{0.6}Ni_{0.4}/PDA-rGO$ and (b) $Pt_{0.6}Ni_{0.4}/rGO$ ($n_{metal}/n_{N_2H_4 \cdot H_2O} = 0.05$, 303 K).

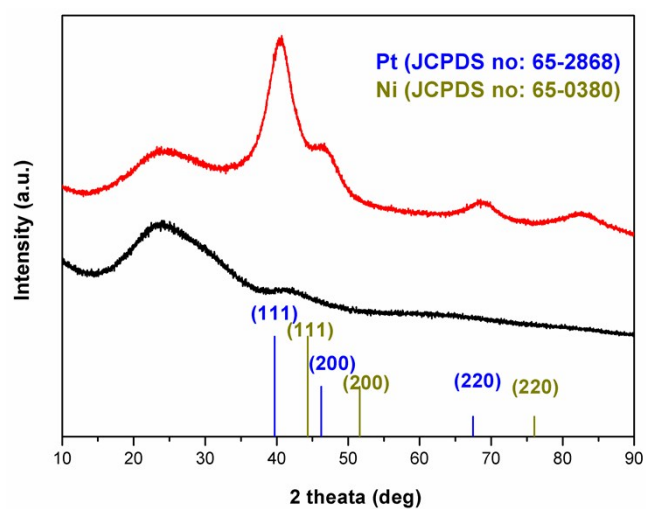


Fig. S13 PXRD patterns of $\text{Pt}_{0.6}\text{Ni}_{0.4}/\text{PDA-rGO}$ and $\text{Pt}_{0.6}\text{Ni}_{0.4}/\text{rGO}$.

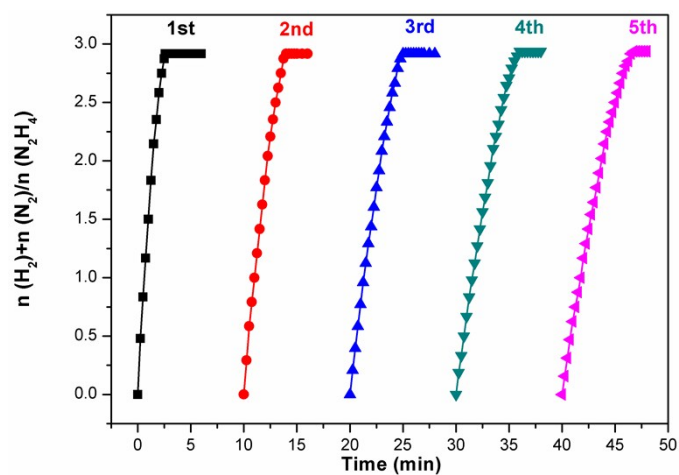


Fig. S14 Durability test for the dehydrogenation of hydrous hydrazine over $\text{Pt}_{0.6}\text{Ni}_{0.4}/\text{PDA-rGO}$ ($n_{\text{metal}}/n_{\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}} = 0.05$, 303 K).

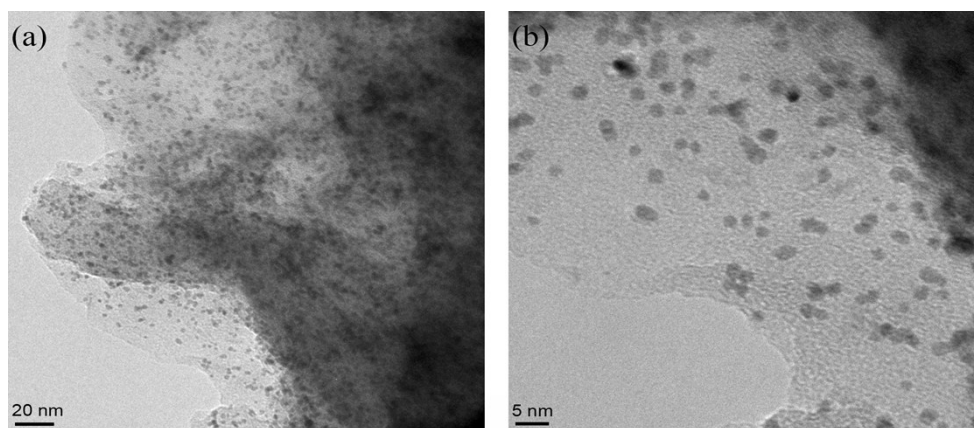


Fig. S15 TEM images of $\text{Pt}_{0.6}\text{Ni}_{0.4}/\text{PDA-rGO}$ after catalysis.

5. References

- 1 D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. S. Sun, A. Slesarev, L. B. Alemany, W. Lu and J. M. Tour, *ACS nano*, 2010, **4**, 4806.
- 2 N. Cao, J. Su, W. Luo and G. Z. Cheng, *Int. J. Hydrogen Energy*, 2014, **39**, 9726.
- 3 B. Q. Xia, N. Cao, H. M. Dai, J. Su, X. J. Wu, W. Luo and G. Z. Cheng, *ChemCatChem*, 2014, **6**, 2549.
- 4 H. L. Wang, J. M. Yan, S. J. Li, X. W. Zhang and Q. Jiang, *J. Mater. Chem. A*, 2015, **3**, 121.
- 5 J. J. Zhang, Q. Kang, Z. Q. Yang, H. B. Dai, D. W. Zhuang and P. Wang, *J. Mater. Chem. A*, 2013, **1**, 11632.
- 6 J. K. Sun and Q. Xu, *ChemCatChem*, 2015, **7**, 526.
- 7 O. Song, J. M. Yan, H. L. Wang, Z. L. Wang and Q. Jiang, *Int. J. Hydrogen Energy*, 2014, **39**, 3755.
- 8 A. K. Singh and Q. Xu, *Int. J. Hydrogen Energy*, 2014, **39**, 9128.
- 9 N. Cao, L. Yang, C. Du, J. Su, W. Luo and G. Z. Cheng, *J. Mater. Chem. A*, 2014, **2**, 14344.
- 10 H. L. Wang, J. M. Yan, W. L. Wang, S. O and Q. Jiang, *J. Mater. Chem. A*, 2013, **1**, 14957.
- 11 J. Wang, X. B. Zhang, Z. L. Wang and Y. Zhang, *Energy Environ. Sci.*, 2012, **5**, 6885.
- 12 D. G. Tong, W. Chu, P. Wu, G. F. Gu and L. Zhang, *J. Mater. Chem. A*, 2013, **1**, 358.
- 13 F. Yang, Y. Z. Li, W. Chu, C. Li and D. G. Tong, *Catal. Sci. Technol.*, 2014, **4**, 3168.
- 14 D. G. Tong, D. M. Tang, W. Chu, G. F. Gu and P. Wu, *J. Mater. Chem. A*, 2013, **1**, 6425.
- 15 K. V. Manukyan, A. Cross, S. Rouvimov, J. Miller, A. S. Mukasyan and E. E. Wolf, *Appl. Catal., A*, 2014, **476**, 47.
- 16 L. He, Y. Q. Huang, X. Y. Liu, L. Lin, A. Q. Wang, X. D. Wang, X. D. Wang, C. Y. Mou and T. Zhang, *Appl. Catal., B*, 2014, **147**, 779.
- 17 L. He, Y. Q. Huang, A. Q. Wang, X. D. Wang, A. Q. Wang, Y. Liu, X. W. Chen, J. J. Delgado, X. D. Wang and T. Zhang, *J. Catal.*, 2013, **298**, 1.
- 18 W. Gao, C. M. Li, H. Chen, M. Wu, S. He, M. Wei, D. Evans and X. Duan, *Green Chem.*, 2014, **16**, 1560.
- 19 S. K. Singh, X. B. Zhang and Q. Xu, *J. Am. Chem. Soc.*, 2009, **131**, 9894.
- 20 S. K. Singh and Q. Xu, *J. Am. Chem. Soc.*, 2009, **131**, 18032.
- 21 S. K. Singh and Q. Xu, *Chem. Commun.*, 2010, **46**, 6545.