

Supporting Information

Nickel–platinum Nanoparticles Immobilized on Graphitic Carbon Nitride as Highly Efficient Catalyst for Hydrogen Release from Hydrous Hydrazine

Lixin Xu ^a, Na Liu^a, Bing Hong^a, Ping Cui ^a, Dang-guo Cheng ^b, Fengqiu Chen ^b, Yue An ^b,

Chao Wan ^{a,*}

^a *College of Chemistry and Chemical Engineering, Anhui University of Technology, 59 Hudong
Road, Ma'anshan 243002, China*

^b *College of Chemical and Biological Engineering, Zhejiang University, 38 Zheda Road,
Hangzhou 310027, China*

* Corresponding author. Tel.: +86 555 2311807; Fax: +86 555 2311822.

E-mail address: wanchao1219@hotmail.com (Chao Wan)

Experimental section

Materials

Melamine ($C_3H_6N_6$, 99%) was purchased from Aladdin Industrial Inc., Nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$, AR), chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, AR), hydrazine hydrate ($N_2H_4 \cdot H_2O$, $\geq 85\%$), sodium borohydride ($NaBH_4$, 96%) and sodium hydroxide (NaOH, AR), were all supplied by Sinopharm Chemical Reagent Co., Ltd. and used without further treatment. In our synthetic process, the reaction solvent is the deionized water.

Hydrogen release by catalytic decomposition of $N_2H_4 \cdot H_2O$

In a typical experiment, the as-prepared $NiPt/g-C_3N_4$ (100 mg) and 80 mg NaOH was placed into a two-necked round-bottom flask containing 4 mL water. One neck was used to introduce 0.1 mL $N_2H_4 \cdot H_2O$ (1.96 mmol) with a syringe, and the other was connected with a gas burette to measure the amount of gas. The temperature of the reaction solution was controlled at 323K by water bath. The dehydrogenation reaction initiated when hydrazine hydrate was injected into the two-necked flask under magnetic stirring. The release of gas was collected by passing through a bottle containing 200 mL 1.0 M HCl solution before being monitored. The gas produced by decomposition of hydrazine hydrate catalyzed with different catalysts were. The hydrogen selectivity (X) can be calculated using eqn (S1).

$$X = \frac{3\lambda - 1}{8} \left[\lambda = \frac{n(H_2 + N_2)}{n(N_2H_4 \cdot H_2O)} \right] \quad (S1)$$

The dehydrogenation reaction over $Ni_{37}Pt_{63}/g-C_3N_4$ were performed at various temperatures (298 K, 313 K, 333 K and 343 K) to calculate the activation energy (E_a) as above-mentioned procedure ($N_2H_4 \cdot H_2O = 0.1$ mL; catalyst = 0.100 g).

Stability test

The stability of catalysts were investigated repeatedly through dropping another 0.1 mL N₂H₄•H₂O into the reaction solution after completing the previous reaction.

Characterization

The composition of the catalysts was measured using inductively coupled plasma-atomic emission spectrometer (ICP-AES, Thermo iCAP6300). The surface area data were acquired by adsorption/desorption nitrogen isotherms after dehydration under vacuum at 423 K for 8 h by using Micromeritics ASAP2020. Powder X-ray diffraction (XRD) patterns were conducted using a Bruker D8-Advance X-ray diffractometer with a velocity of 4 °min⁻¹ using Cu K α radiation source (λ = 0.154178 nm). X-ray photoelectron spectrometry (XPS) was performed on an Escalab 250Xi X-ray photoelectron spectrometer using an Al K α source. Transmission Electron Microscopy (TEM) images were observed using a FEI Tecnai F20 working at 200 kV. MS of the gases produced from hydrazine were detected by using a Hiden QIC-20 quadruple mass spectrometer using Ar as carrying gas.

Calculation methods:

$$x_a = \frac{P_{atm}V_{H_2}/RT}{n_{FA}}$$

Where x_a is conversion, P_{atm} is the atmospheric pressure (101325 Pa), V_{H_2} is the generated volume of H₂, R is the universal gas constant (8.3145 m³ Pa mol⁻¹ K⁻¹), T is room temperature (298 K), and n_{FA} is the mole number of FA.

$$TOF_{initial} = \frac{P_{atm}V_{H_2}/RT}{n_{Ag+Pd}t} \quad (S2)$$

Where $TOF_{initial}$ is initial turnover frequency when x_a reaches 20%, n_{Ag+Pd} is the mole number of the Ag and Pd, and t is the reaction time when x_a reaches 20%.

(S1) J. K. Sun and Q. Xu, *ChemCatChem*, 2015, **7**, 526–531.

(S2) L. Yu, X. S. Zhang and L. Y. Yu, *Adv. Mater. Res.*, 2012, **130**, 396-398.

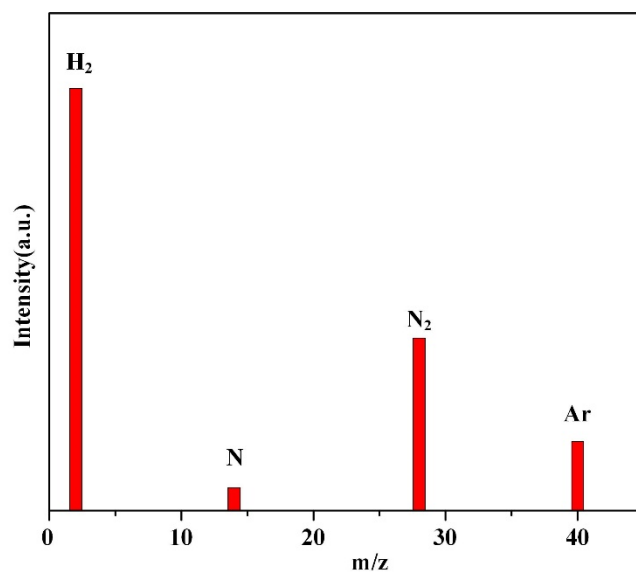


Fig. S1. MS profile for the gases released from the decomposition of hydrazine hydrate in aqueous NaOH solution (0.5 M) over Ni₃₇Pt₆₃/g-C₃N₄ at 323 K under an argon atmosphere

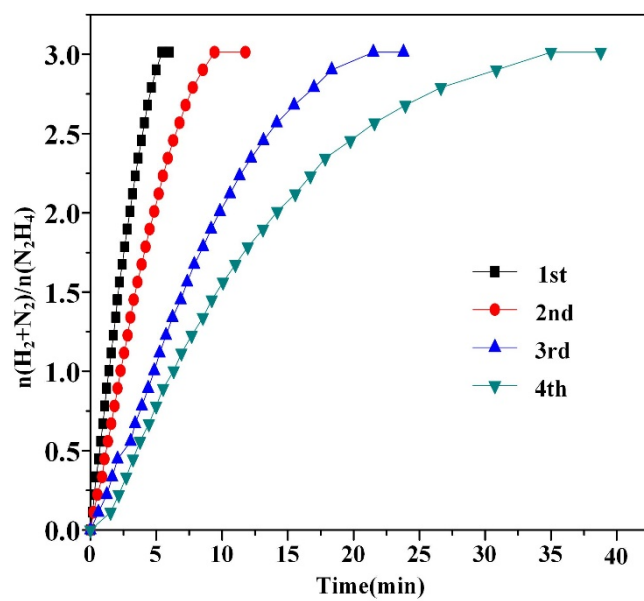


Fig. S2. Recyclability test $\text{Ni}_{37}\text{Pt}_{63}/\text{g-C}_3\text{N}_4$ catalyst for the decomposition of hydrous hydrazine at 323 K (catalyst= 100 mg, $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O} = 0.1$ mL).

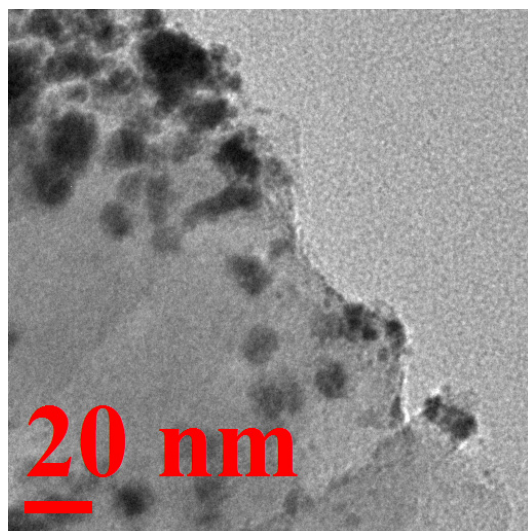


Fig. S3 TEM image of Ni₃₇Pt₆₃/g-C₃N₄ after four runs

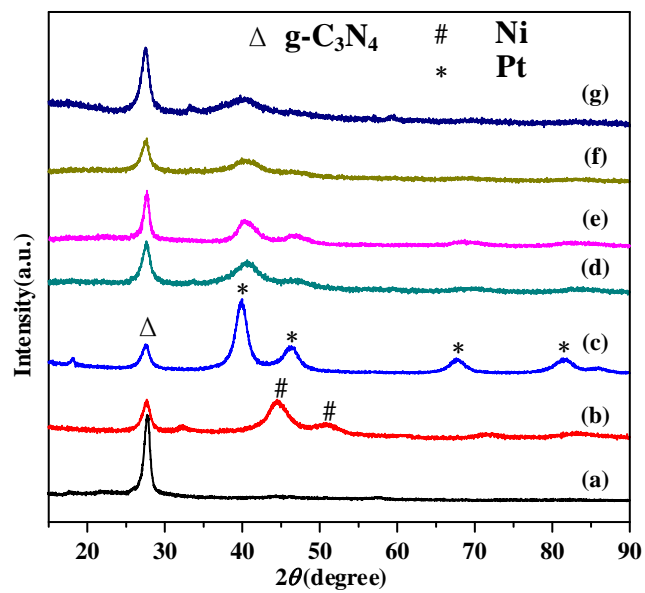


Fig. S4 XRD patterns of NiPt with different composition: (a) g-C₃N₄, (b) Ni/g-C₃N₄, (c) Pt/g-C₃N₄, (d) Ni₂₄Pt₇₆/g-C₃N₄, (e) Ni₃₇Pt₆₃/g-C₃N₄, (f) Ni₅₈Pt₄₂/g-C₃N₄, (g) Ni₈₂Pt₁₈/g-C₃N₄.

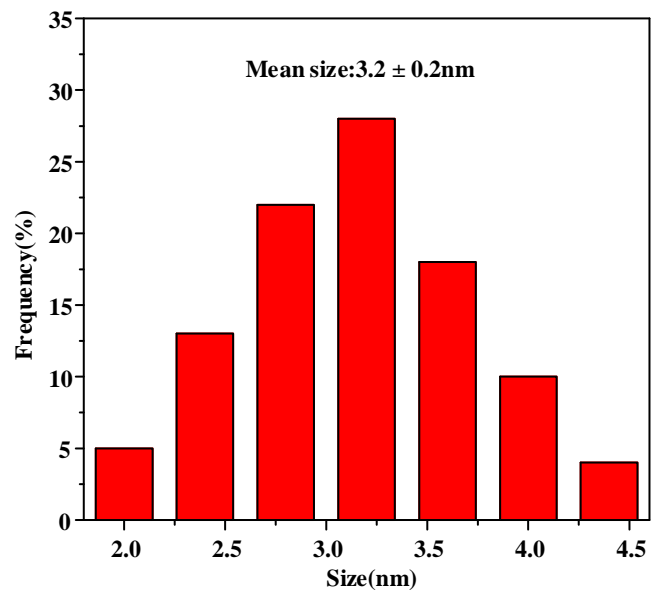


Fig. S5 Particle size distribution histograms of Ni₃₇Pt₆₃/g-C₃N₄.

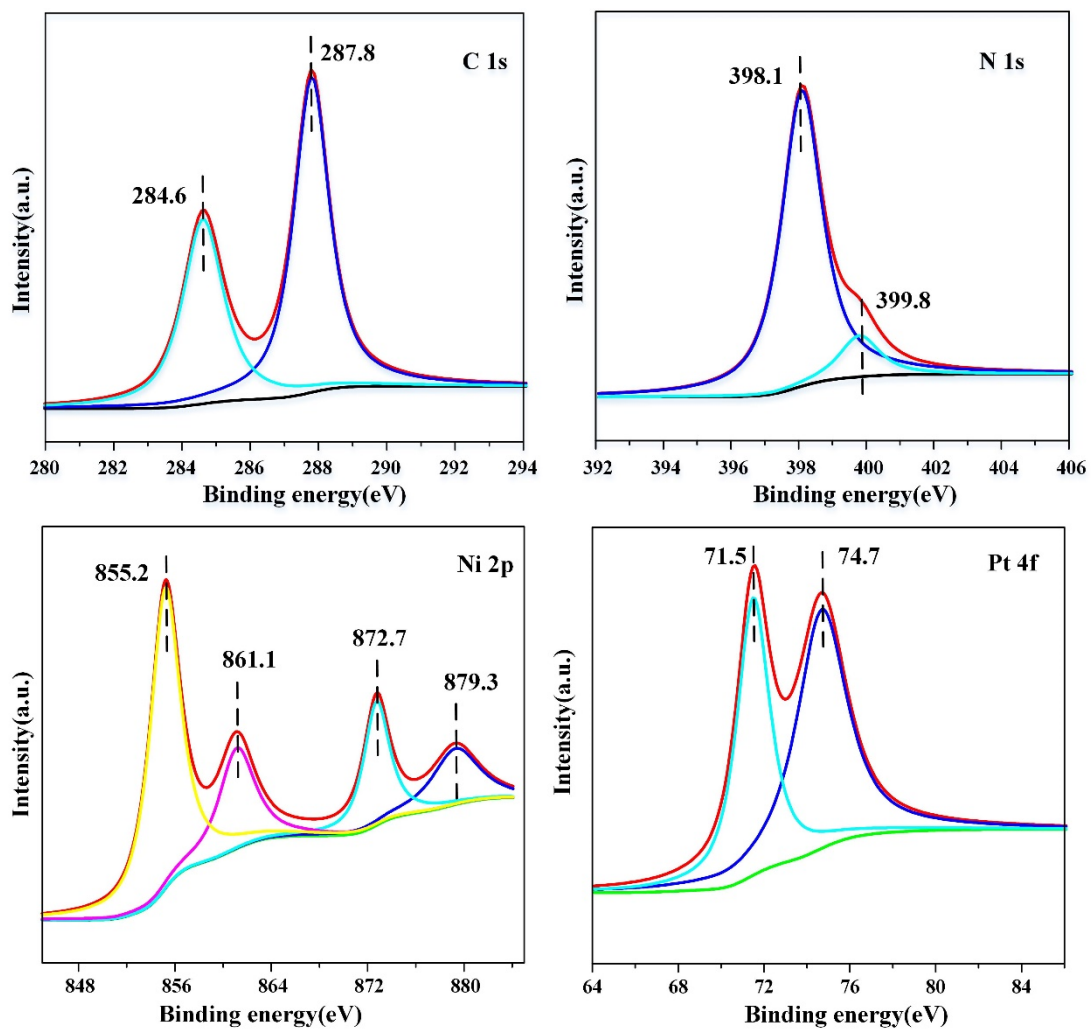


Fig. S6. XPS spectra for catalyst Ni₃₇Pt₆₃/g-C₃N₄ showing C 1s, N 1s, Ni 2p and Pt 4f.

Table S1. ICP-AES results of Ni-Pt/g-C₃N₄ catalysts

Catalyst	Ni (wt%)	Pt (wt%)	Ni-Pt initial composition (molar ratio)	Ni-Pt final composition (molar ratio)	Final Metals/Catalyst (mmol/100 mg)
Ni ₂₄ Pt ₇₆ /g-C ₃ N ₄	1.47	15.42	20:80	24:76	0.104
Ni ₃₇ Pt ₆₃ /g-C ₃ N ₄	2.52	14.26	40:60	37:63	0.116
Ni ₅₈ Pt ₄₂ /g-C ₃ N ₄	4.15	9.99	60:40	58:42	0.122
Ni ₈₂ Pt ₁₈ /g-C ₃ N ₄	5.44	3.97	80:20	82:18	0.113

Table. S2 Comparison of NiPt/g-C₃N₄ catalyzed decomposition of N₂H₄•H₂O

Catalyst	T/ K	Conversion/ %	TOF _{initial} / h ⁻¹	S _{BET} / m ² •g ⁻¹
Ni ₂₄ Pt ₇₆ /g-C ₃ N ₄	323	100	175	10.2
Ni ₃₇ Pt ₆₃ /g-C ₃ N ₄	323	100	570	10.6
Ni ₅₈ Pt ₄₂ /g-C ₃ N ₄	323	100	510	10.3
Ni ₈₂ Pt ₁₈ /g-C ₃ N ₄	323	88.9	462	9.8
Ni ₃₇ Pt ₆₃ /g-C ₃ N ₄	298	92.6	80	10.6
Ni ₃₇ Pt ₆₃ /g-C ₃ N ₄	313	100	276	10.6
Ni ₃₇ Pt ₆₃ /g-C ₃ N ₄	333	100	620	10.6
Ni ₃₇ Pt ₆₃ /g-C ₃ N ₄	343	100	845	10.6

TOF_{initial} is calculated when x_a reaches 20%.