

## Electronic Supplementary Information

### **Novel NiPt alloy nanoparticles decorated 2D layered g-C<sub>3</sub>N<sub>4</sub> Nanosheets: a highly efficient catalyst for hydrogen generation from hydrous hydrazine**

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## 1. Chemical and Materials

Hydrazine monohydrate ( $\text{H}_2\text{NNH}_2 \cdot \text{H}_2\text{O}$ , 85%), sodium borohydride ( $\text{NaBH}_4$ , >96%), sodium hydroxide ( $\text{NaOH}$ , >96%) were obtained from Sinopharm Chemical Reagent Co., Ltd. Melamine ( $\text{C}_3\text{H}_6\text{N}_6$ , 99%), lithium chloride ( $\text{LiCl}$ , >98%) were purchased from Aladdin Industrial Inc., Chloroplatinic acid hexahydrate ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ , AR), nickel chloride hexahydrate ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , AR) were supplied by Nanjing Chemical Reagent Co., Ltd., All above-mentioned reagent were used without further purification. All solutions were prepared using De-ionized water as solvent, which was obtained by reversed osmosis with the specific resistance of  $18.2 \text{ M}\Omega \cdot \text{cm}$ .

## 2. Synthesis

### 2.1. Synthesis of g- $\text{C}_3\text{N}_4$ NSs

g- $\text{C}_3\text{N}_4$  NSs were fabricated by molten-salt assisted thermal poly-condensation method and subsequently water exfoliation method.<sup>S1</sup> Specifically, 2 g melamine and 10 g lithium chloride were mixed in the mortar, grounded sufficiently and transferred into 150 mL alumina crucible. The reaction mixture was calcined at  $380 \text{ }^\circ\text{C}$  for 2 hours at ramp rate  $6.7 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$  and heated to  $550 \text{ }^\circ\text{C}$  for 4 hours at a same ramp rate. Afterwards the sample was cooled to room temperature at  $10 \text{ }^\circ\text{C} \cdot \text{minute}^{-1}$  and the g- $\text{C}_3\text{N}_4/\text{Li}^+\text{Cl}^-$  was obtained. 500 mg g- $\text{C}_3\text{N}_4/\text{Li}^+\text{Cl}^-$  was boiled under vigorously stirring and washed with deionized water. The dispersed suspension was centrifuged at 8000 rpm for 5 minutes to collect porous g- $\text{C}_3\text{N}_4$  NSs.<sup>S1</sup> For comparison, bulk-g- $\text{C}_3\text{N}_4$  was synthesized under exactly same condition without adding lithium chloride.

### 2.2. Synthesis of NiPt/g- $\text{C}_3\text{N}_4$ NSs catalysts

Typically, for preparation of  $\text{Ni}_{0.6}\text{Pt}_{0.4}/\text{g-}\text{C}_3\text{N}_4$  NSs, 5.0 mL of aqueous solution containing  $\text{NiCl}_2$  (0.24 mmol) and  $\text{H}_2\text{PtCl}_6$  (0.16 mmol) was added into the well dispersed g- $\text{C}_3\text{N}_4$  NSs

solution. After stirring for 24 h, a solution containing sodium borohydride ( $\text{NaBH}_4$ ) and sodium hydroxide ( $\text{NaOH}$ ) was added to the abovementioned mixture at  $0\text{ }^\circ\text{C}$  using an ice bath to maintain the temperature while stirring vigorously. The catalysts could be obtained by centrifugation, washing by ethanol and drying in the vacuum at  $100\text{ }^\circ\text{C}$  for 2 h.

For comparison, we further adjusted the molar ratio of Ni to Pt in the NiPt bimetallic alloy, and prepared a series of samples, including Ni/g- $\text{C}_3\text{N}_4$  NSs,  $\text{Ni}_{0.2}\text{Pt}_{0.8}$ /g- $\text{C}_3\text{N}_4$  NSs,  $\text{Ni}_{0.4}\text{Pt}_{0.6}$ /g- $\text{C}_3\text{N}_4$  NSs,  $\text{Ni}_{0.8}\text{Pt}_{0.2}$ /g- $\text{C}_3\text{N}_4$  NSs, and Pt/g- $\text{C}_3\text{N}_4$  NSs.

### **3. Characterization**

Powder X-ray diffraction (XRD) patterns were measured by a Bruker D8-Advance X-ray diffractometer using Cu  $K\alpha$  radiation source ( $\lambda = 0.154178\text{ nm}$ ) with a velocity of  $10^\circ\text{ min}^{-1}$ . The morphologies and sizes of the samples were observed by using a FEI Tecnai F20 at an acceleration voltage of 200 kV. Scanning electron microscopy (SEM) images were obtained using a Zeiss SIGMA microscope. X-ray photoelectron spectroscopy (XPS) measurement was performed with a Thermo Fischer ESCALAB 250Xi spectrophotometer. The composition of the collected gases were detected by using a Hiden QIC-20 quadruple mass spectrometer under Ar atmosphere. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was performed on Thermo iCAP6300 to measure the composition of the catalysts. The characterization of Brunauer–Emmett–Teller (BET) surface data, which was based on  $\text{N}_2$  adsorption/desorption isotherms at  $77\text{ K}$  and controlled by liquid nitrogen, was measured using a Micromeritics ASAP2020.

### **4. Catalytic dehydrogenation tests**

The catalytic dehydrogenation tests were performed in a two-necked round-bottom flask. The volume of the evolved gas was monitored by recording the displacement of water in the gas

burette (Fig.S1). The reaction was completed when there was no more gas generation. Specifically, 100 mg NiPt/g-C<sub>3</sub>N<sub>4</sub> NSs catalyst and 80 mg NaOH solid was added into a two-neck bottle containing 2 mL water with magnetic stirring, where one neck was connected to a gas burette to monitor the volume of the released gas, and the other one was used to introduce 2 mL water containing 0.1 mL N<sub>2</sub>H<sub>4</sub>•H<sub>2</sub>O (1.96 mmol) with a syringe. The gas released during the decomposition was passed through HCl solution (5.0 M) before being measured volumetrically. The hydrogen selectivity (X) can be calculated using eqn (1).

$$X = (3\lambda - 1) / 8 [\lambda = n(\text{H}_2 + \text{N}_2) / n(\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O})] \quad (1)$$

The TOF reported here is an apparent TOF value based on the number of (Ni+Pt) atoms in the catalysts, which is calculated from the equation as follows:

$$TOF = \frac{P_{atm} V_{H_2} / RT}{n_{Ni+Pt} t} \quad (2)$$

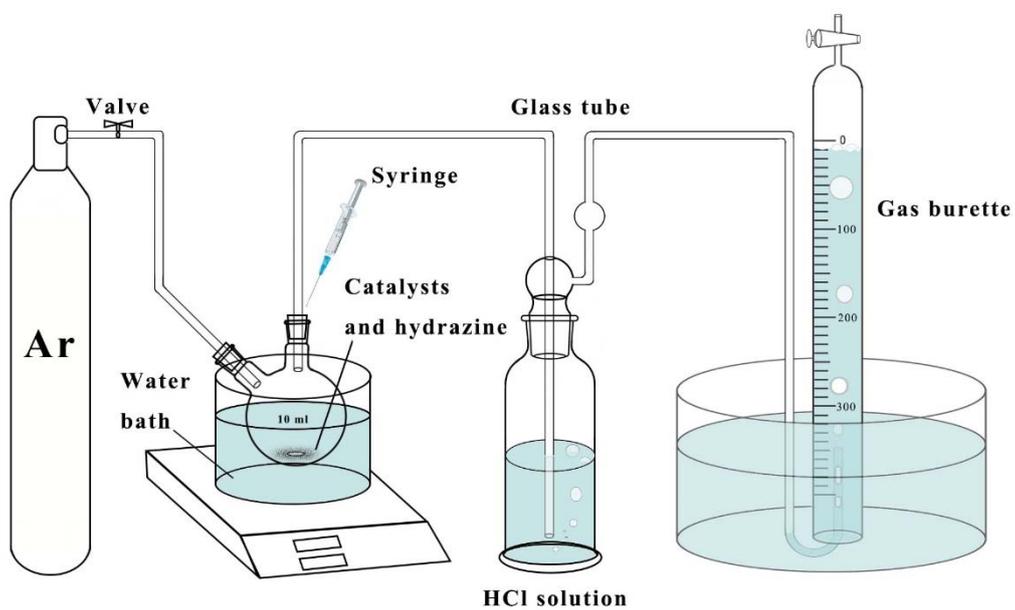
whereas, P<sub>atm</sub> is the atmospheric pressure (101325 Pa), V<sub>H<sub>2</sub></sub> is the volume of generated H<sub>2</sub> gas at the time of half-completion of reaction, R is the universal gas constant (8.3145 m<sup>3</sup> Pa mol<sup>-1</sup> K<sup>-1</sup>), T is the reaction temperature (303-333 K), n<sub>Ni+Pt</sub> is the total number of moles of (Ni+Pt) atoms in the catalyst and t is the time in hour for half-completion of reaction.

To investigate the effect of alkaline, the decomposition of hydrous hydrazine was conducted in present of different concentrations of NaOH, respectively.

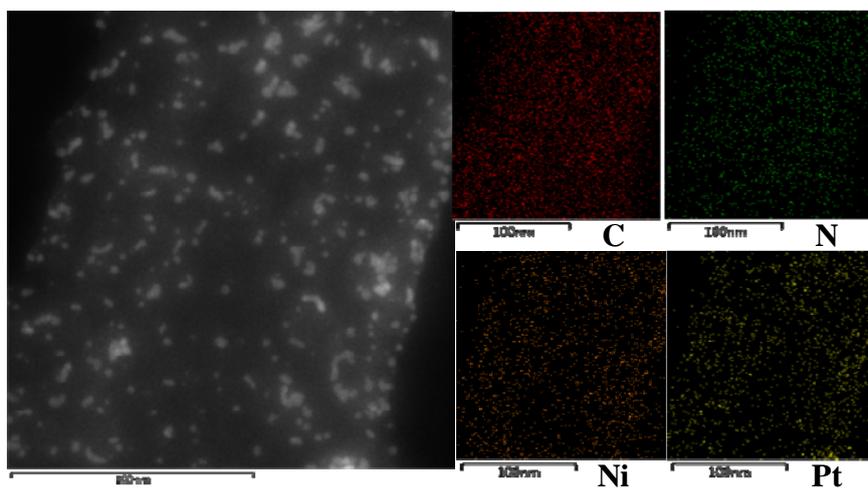
To obtain the activation energy (E<sub>a</sub>), the reaction temperatures for the catalytic decomposition were varied from 303 K to 333 K.

For the durability tests, catalytic reactions were repeated 5 times by adding another equivalent of hydrous hydrazine (1.96 mmol) into the mixture after the previous runs.

## 5. Figures



**Fig. S1** The detailed experimental setup for dehydrogenation reaction



**Fig. S2** The HAADF-STEM image for  $\text{Ni}_{0.6}\text{Pt}_{0.4}/\text{g-C}_3\text{N}_4$  NSs (left); The EDX elemental mapping of the  $\text{Ni}_{0.6}\text{Pt}_{0.4}/\text{g-C}_3\text{N}_4$  NSs (right).

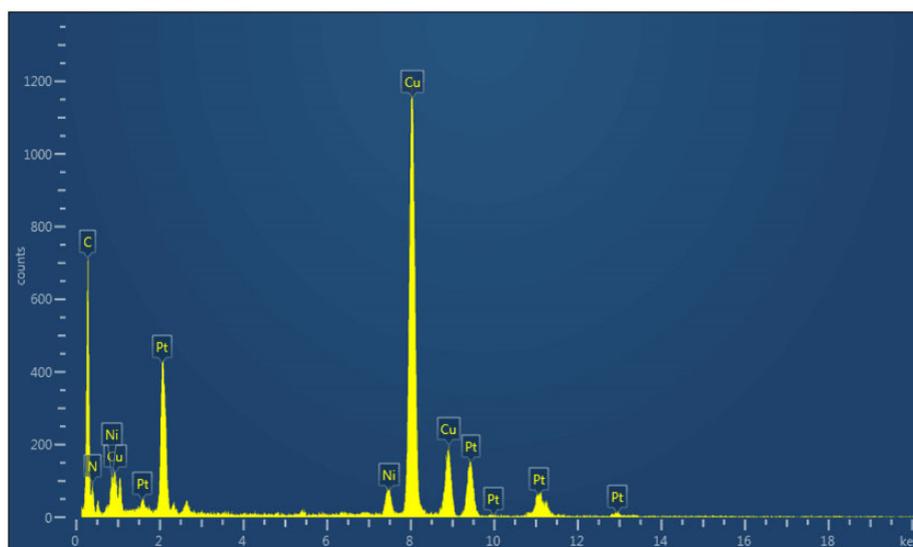


Fig. S3 EDX pattern of  $\text{Ni}_{0.6}\text{Pt}_{0.4}/\text{g-C}_3\text{N}_4$  NSs.

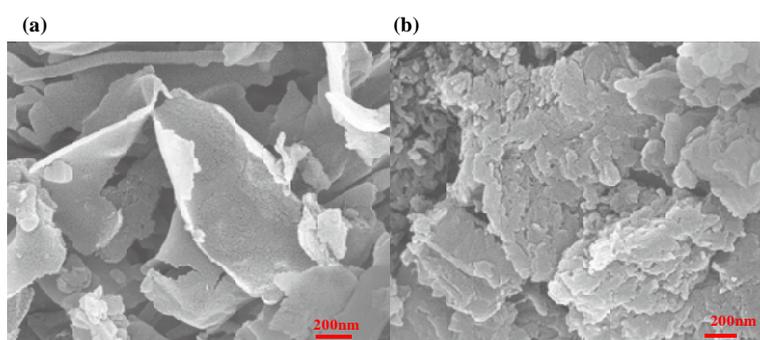
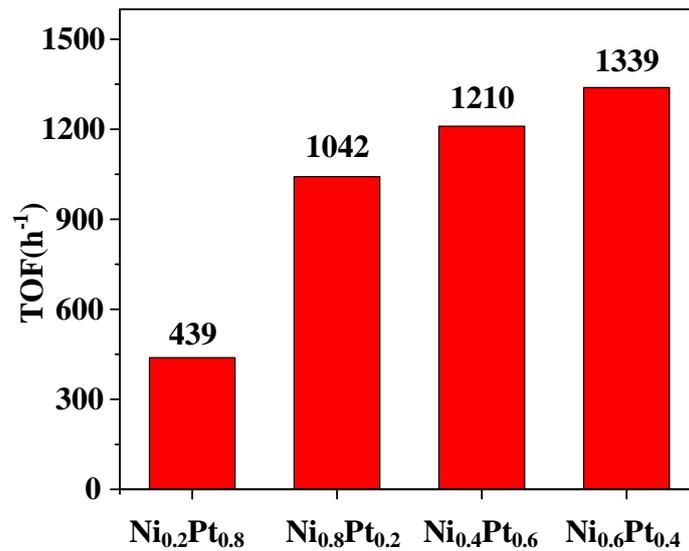
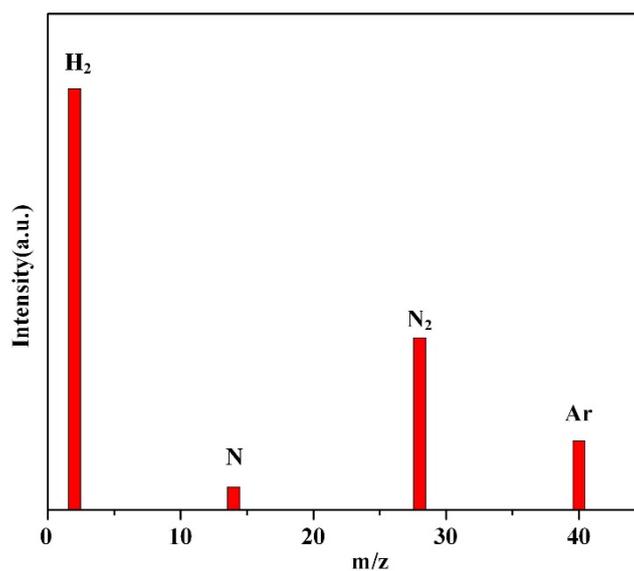


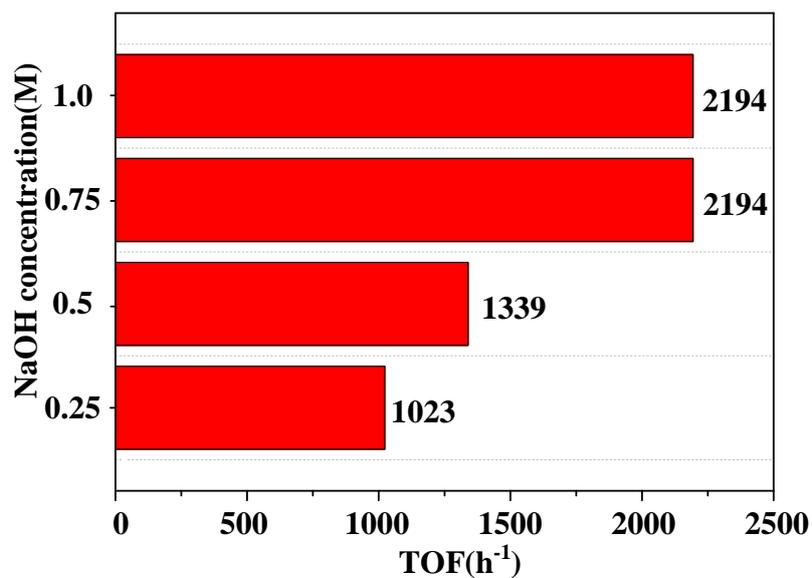
Fig. S4 SEM image of (a)  $\text{Ni}_{0.6}\text{Pt}_{0.4}/\text{g-C}_3\text{N}_4$  NSs and (b)  $\text{Ni}_{0.6}\text{Pt}_{0.4}/\text{g-C}_3\text{N}_4$ .



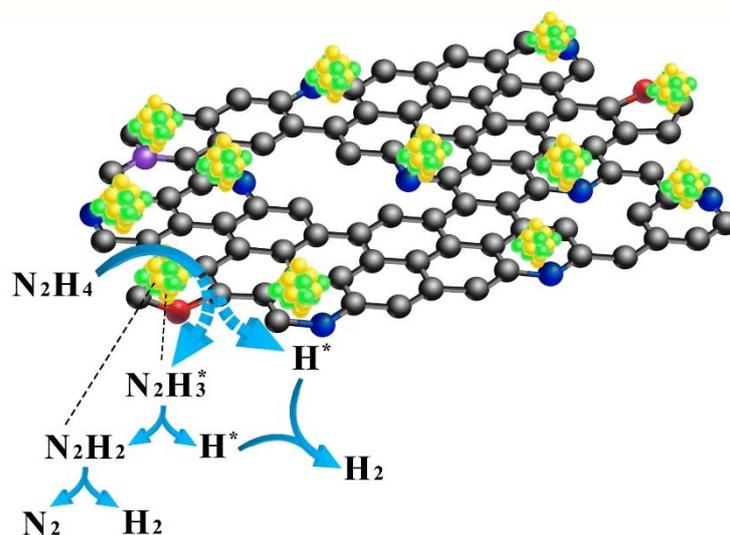
**Fig. S5** Corresponding TOF values for the dehydrogenation of hydrazine monohydrate over NiPt/g-C<sub>3</sub>N<sub>4</sub> NSs with different molar ratio of Ni-Pt alloy at 323 K ( $c_{\text{NaOH}}=0.5$  M,  $n_{\text{metal}}:n_{\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}}=0.05$ )



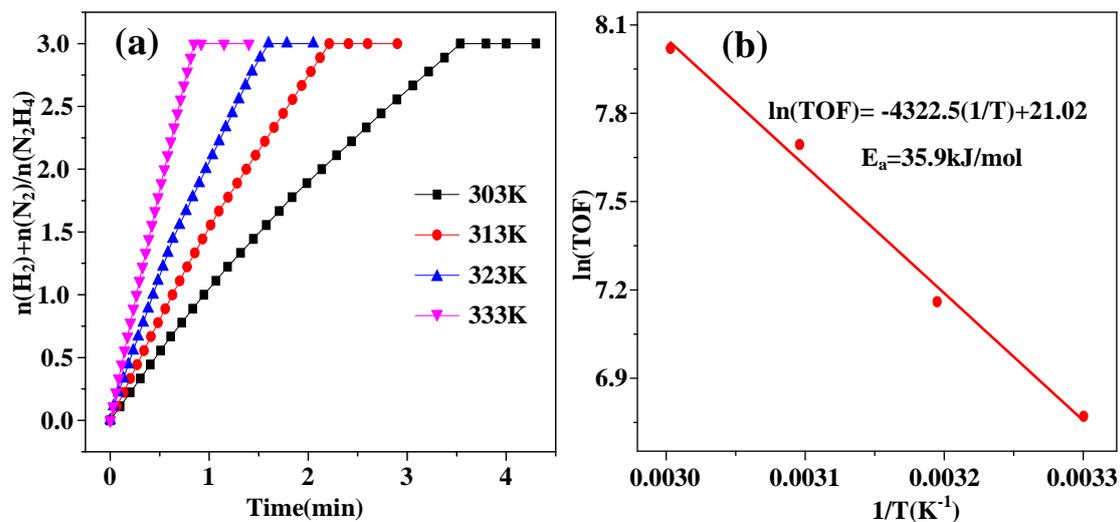
**Fig. S6** MS profile for the gases released from the decomposition of hydrazine hydrate in aqueous NaOH solution (0.75 M) over Ni<sub>0.6</sub>Pt<sub>0.4</sub>/g-C<sub>3</sub>N<sub>4</sub> NSs at 323 K under an argon atmosphere



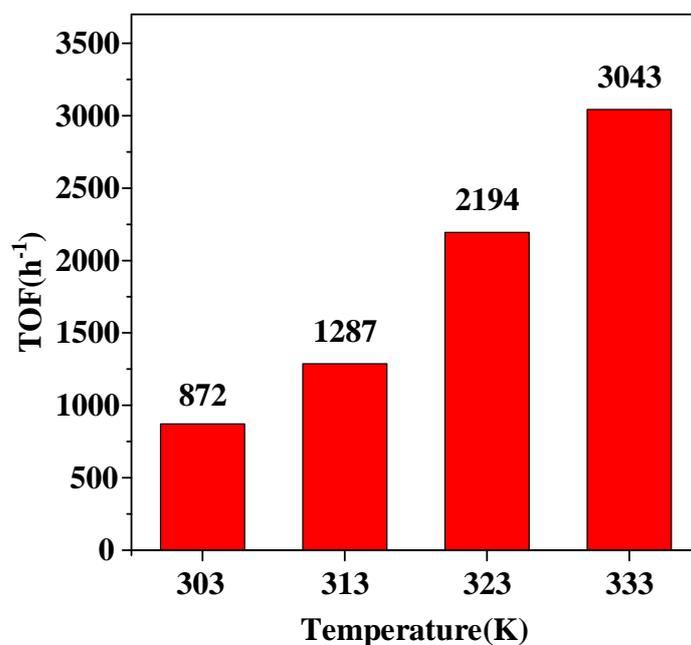
**Fig. S7** Corresponding TOF values for the dehydrogenation of hydrazine monohydrate over  $\text{Ni}_{0.6}\text{Pt}_{0.4}/\text{g-C}_3\text{N}_4$  NSs with different concentrations of NaOH at 323 K ( $n_{\text{metal}}:n_{\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}}=0.05$ )



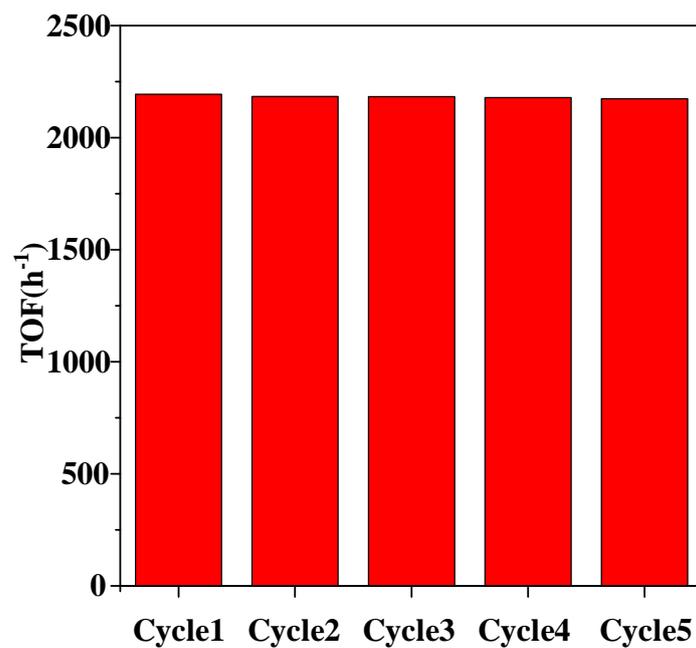
**Fig. S8** The possible mechanism for decomposition of hydrazine catalysed by  $\text{Ni}_{0.6}\text{Pt}_{0.4}/\text{g-C}_3\text{N}_4$  NSs



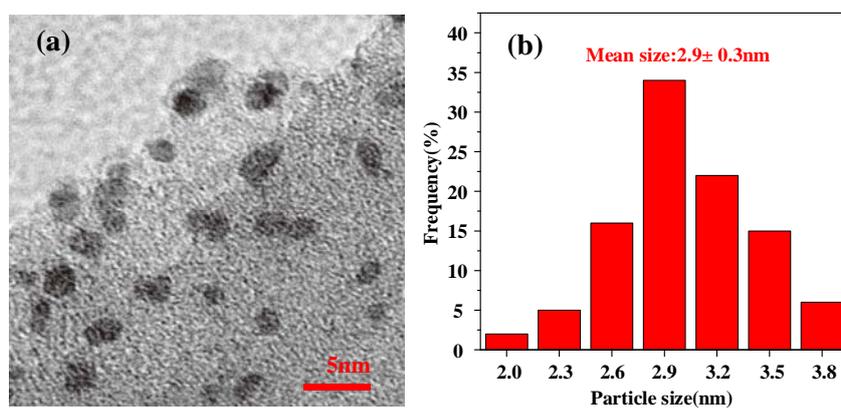
**Fig. S9** (a) Time course plots for hydrogen generation from the decomposition of hydrazine by Ni<sub>0.6</sub>Pt<sub>0.4</sub>/g-C<sub>3</sub>N<sub>4</sub> NSs at 303 K, 313 K, 323 K and 333K. (b) Plot of ln k *versus* 1/T during the hydrazine decomposition over Ni<sub>0.6</sub>Pt<sub>0.4</sub>/g-C<sub>3</sub>N<sub>4</sub> NSs at different temperatures.



**Fig. S10** Corresponding TOF values for the dehydrogenation of hydrazine monohydrate over Ni<sub>0.6</sub>Pt<sub>0.4</sub>/g-C<sub>3</sub>N<sub>4</sub> NSs at different temperatures ((c<sub>NaOH</sub> = 0.75 M, n<sub>metal</sub>:n<sub>N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O</sub> = 0.05)



**Fig. S11** Corresponding TOF values for the durability of hydrogen generation from hydrazine monohydrate over Ni<sub>0.6</sub>Pt<sub>0.4</sub>/g-C<sub>3</sub>N<sub>4</sub> NSs ((c<sub>NaOH</sub> = 0.75 M, n<sub>metal</sub>:n<sub>N<sub>2</sub>H<sub>4</sub>•H<sub>2</sub>O</sub> = 0.05)



**Fig. S12** (a) TEM images and (b) the corresponding size histogram of NiPt NPs in

Ni<sub>0.6</sub>Pt<sub>0.4</sub>/g-C<sub>3</sub>N<sub>4</sub> NSs after 5 cycles.

## 6. Tables

**Table S1.** BET surface areas and pore volumes for the prepared samples.

Sample	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )
Ni <sub>0.6</sub> Pt <sub>0.4</sub> /g-C <sub>3</sub> N <sub>4</sub> NSs	129.8	0.151
Ni <sub>0.6</sub> Pt <sub>0.4</sub> /g-C <sub>3</sub> N <sub>4</sub> NSs-recycled	121.6	0.147
Ni <sub>0.6</sub> Pt <sub>0.4</sub> /g-C <sub>3</sub> N <sub>4</sub>	10.9	0.031

**Table S2.** ICP-AES results of Ni-Pt 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 <sub>0.2</sub> Pt <sub>0.8</sub> /g-C <sub>3</sub> N <sub>4</sub> NSs	1.2	13.3	20:80	23:77	0.106
Ni <sub>0.4</sub> Pt <sub>0.6</sub> /g-C <sub>3</sub> N <sub>4</sub> NSs	2.2	11.7	40:60	38:62	0.112
Ni <sub>0.6</sub> Pt <sub>0.4</sub> /g-C <sub>3</sub> N <sub>4</sub> NSs	3.7	7.9	60:40	61:39	0.118
Ni <sub>0.6</sub> Pt <sub>0.4</sub> /g-C <sub>3</sub> N <sub>4</sub> NSs-recycled	3.6	8.4	60:40	59:41	0.119
Ni <sub>0.8</sub> Pt <sub>0.2</sub> /g-C <sub>3</sub> N <sub>4</sub> NSs	4.5	4.0	80:20	79:21	0.107
Ni <sub>0.6</sub> Pt <sub>0.4</sub> /g-C <sub>3</sub> N <sub>4</sub>	3.6	8.8	60:40	58:42	0.122

**Table S3.** Catalytic activity of Ni<sub>0.6</sub>Pt<sub>0.4</sub>/g-C<sub>3</sub>N<sub>4</sub> NSs toward dehydrogenation of hydrazine compared to other reported catalysts.

Catalyst	Solvent Medium	Temp (K)	Selectivity for H <sub>2</sub> (%)	TOF (h <sup>-1</sup> )	Ea(KJ mol <sup>-1</sup> )	Reference
Ni <sub>0.6</sub> Pt <sub>0.4</sub> /g-C <sub>3</sub> N <sub>4</sub> NSs	Aqueous NaOH	323	100	2194	35.9	Present work
Pt <sub>0.6</sub> Ni <sub>0.4</sub> /PDA-rGO	Aqueous NaOH	323	100	2056	33.9	S2
Pt <sub>0.5</sub> Ni <sub>0.5</sub> /NGNs-850	Aqueous NaOH	323	100	2116	32.28	S3
(Ni <sub>3</sub> Pt <sub>7</sub> ) <sub>0.5</sub> - (MnOx) <sub>0.5</sub> /NPC-900	Aqueous NaOH	323	100	706	50.15	S4
Ni <sub>3</sub> Pt <sub>7</sub> /rGO	Aqueous NaOH	323	100	416	49.36	S5
Ni <sub>84</sub> Pt <sub>16</sub> /graphene	Aqueous NaOH	323	100	415	40.4	S6
Ni <sub>88</sub> Pt <sub>12</sub> @MIL-101	Aqueous NaOH	323	100	350	50.5	S7
Ni <sub>80</sub> Pt <sub>20</sub> @ZIF-8	Aqueous NaOH	323	100	90	-	S8
Ni@Ni-Pt/La <sub>2</sub> O <sub>3</sub>	Aqueous NaOH	323	100	156	56.2	S9
Pt <sub>60</sub> Ni <sub>40</sub> -CNDs	Aqueous NaOH	323	100	170	43.9	S10
PtNi/C	Aqueous NaOH	323	100	210	55.3	S11
Ni <sub>0.9</sub> Pt <sub>0.1</sub> /Ce <sub>2</sub> O <sub>3</sub>	Aqueous NaOH	298	100	28.1	42.3	S12
RhNiP/rGO	Aqueous NaOH	323	100	471	40.4	S13
Ni <sub>0.6</sub> Fe <sub>0.4</sub> B	Aqueous NaOH	323	100	28.8	50.7	S14
Ni <sub>6</sub> Pt <sub>4</sub> -SF	Aqueous NaOH	298	100	150	-	S15
NiPt <sub>0.057</sub> /Al <sub>2</sub> O <sub>3</sub> -HT	Without additive	303	97	16.5	34	S16
Rh <sub>4.4</sub> Ni/graphene	Aqueous NaOH	298	100	28	-	S17
Ni <sub>3</sub> Fe/C	Without additive	293	100	528	48.1	S18
NiIr <sub>0.059</sub> /Al <sub>2</sub> O <sub>3</sub> -HT	Without additive	303	99	12.4	49.3	S19
Ni <sub>1.5</sub> Fe <sub>1.0</sub> /(MgO) <sub>3.5</sub>	Without additive	299	99	11	-	S20
Rh	Without additive	298	43.8	2.5	-	S21
Rh <sub>4</sub> Ni	Without additive	298	100	4.8	-	S22
Ni <sub>0.9</sub> 5Ir <sub>0.05</sub>	Without additive	298	100	2.2	-	S23

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