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# Highly efficient hydrogen generation from hydrous hydrazine using a reduced graphene oxide-supported NiPtP nanoparticle catalyst



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#### 1. Introduction

Hydrogen with huge applications for the future energy has drawn considerable attentions because of its clean and environmental nature [1–6]. Recently the developments in chemical hydrogen storage materials have been paid more attention to, such as hydrazine monohydrate (N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O), which is a liquid over a wide range of temperatures and has a H<sub>2</sub> storage capacity as high as 8.0 wt% [7–9]. Hydrogen stored in hydrazine monohydrate could be released via complete decomposition method (Eqn (1)) [10–12], making nitrogen as the only byproduct. However, from the perspective of hydrogen storage application, the undesired reaction pathway (eqn (2)) should be avoided.

$$H_2NNH_2(aq) \to N_2(g) + 2H_2(g)$$
 (1)

$$3H_2NNH_2(aq) \rightarrow N_2(g) + 4NH_3(g) \tag{2}$$

#### ABSTRACT

Ultrafine NiPtP nanoparticles (NPs) assembled on reduced graphene oxide (rGO) have been synthesized by a co-reduction route using sodium hypophosphite (NaH<sub>2</sub>PO<sub>2</sub>) as the source of the nonmetallic P. The well-dispersed ultrafine NiPtP NPs with a diameter about 2 nm can be readily obtained. It is found that these catalysts demonstrate high selectivity and excellent catalytic activity for the decomposition of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O at mild temperature. The enhanced catalytic performance can be attributed to synergistic effect of P-doping and strong high selectivity interaction with graphene support.

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Recently, it has been reported that bimetallic NPs based on nickel and Rh [5,13–15], Pt, Ir [7,16], or Fe [17,18] exhibited fast reaction kinetics and high hydrogen selectivity toward hydrogen generation from aqueous hydrazine solution. Among them, the NiPt bimetallic NPs exhibited extremely high catalytic activity [19–24]. To optimize catalytic property, effectively controlling the dispersion and size of the NiPt NPs is fundamental. Hence, applicable supports have been designed for controlling the agglomeration and size of metal NPs. Graphene, as a single-layer of sp<sup>2</sup> carbon lattices, is an effective support for growing and anchoring of NPs [25,26]. Although many studies have focused on NiPt NPs loading on graphene by co-reduction of nickel and platinum salts solution [19,22,23], doping bimetallic NPs with a non-metal element, such as B, P, and N, has rarely been reported. Zhang's group reported that boron-doping RhNiB NPs showed excellent catalytic activity and high stability towards selective and complete decomposition of hydrous hydrazine under ambient conditions [25]. In addition, the influence of phosphorus on the size and distribution of NPs has been also evaluated [27,28]. Therefore, developing metalloid-doped NPs might be an effective way toward rational design cost-effective and high performance catalysts for decomposition of hydrous hydrazine. Herein, we develop a one-step co-reduced route to construct NiPtP NPs on reduced graphene oxide (rGO) using sodium hypophosphite (NaH<sub>2</sub>PO<sub>2</sub>) as the source of the nonmetallic P, which affords high TOF value



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(224  $h^{-1}$  at 298 K and 742  $h^{-1}$  at 323 K) for hydrous hydrazine dehydrogenation.

#### 2. Experimental

#### 2.1. Materials

Hydrazine monohydrate (H<sub>2</sub>NNH<sub>2</sub>·H<sub>2</sub>O, Aladdin reagent Co., Ltd, >98%), nickel(II) chloride hexahydrate (NiCl<sub>2</sub>·6H<sub>2</sub>O, Sinopharm Chemical Reagent Co., Ltd, >98%), chloroplatinic acid hexahydrate (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, Sigma-Aldrich Co. LLC, 99%), sodium hypophosphite (NaH<sub>2</sub>PO<sub>2</sub>, Aladdin reagent Co., Ltd, 99%), sodium borohydride (NaBH<sub>4</sub>, Sinopharm Chemical Reagent Co., Ltd, >96%), isopropanol (C<sub>3</sub>H<sub>8</sub>O, Aladdin reagent Co., Ltd, 99%), potassium permanganate (KMnO<sub>4</sub>, Sinopharm Chemical Reagent Co., Ltd, ≥99.5%), graphite power (Sinopharm Chemical Reagent Co., Ltd,  $\geq$ 99.85%), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, Sinopharm Chemical Reagent Co., Ltd,  $\geq$ 30%), phosphoric acid (H<sub>3</sub>PO<sub>4</sub>, Sinopharm Chemical Reagent Co., Ltd, AR), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, Sinopharm Chemical Reagent Co., Ltd, 95–98%), sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>, Sinopharm Chemical Reagent Co., Ltd, >96%) were used without further purification. De-ionized water with the specific resistance of 18.2 M $\Omega$ ·cm was obtained by reversed osmosis followed by ionexchange and filtration.

#### 2.2. Experimental

#### 2.2.1. Graphene oxide (GO) preparation

GO was synthesized according to the reported procedure [29,30]. Firstly, a 9:1 mixture of concentrated  $H_2SO_4/H_3PO_4$  solution (180:20 mL) was added to the mixture of graphite power (1.5 g) and KMnO<sub>4</sub> (9 g) and then the solution was kept at 323 K with a water bath for 12 h. The solution was cooled to room temperature and poured into a flask containing ice (200 g) and  $H_2O_2$  (30%, 1.5 mL). The resultant solution was centrifuged to obtain the product. The product was washed by deionized water, 30% diluted hydrochloric acid and absolute ethyl alcohol for many times and dried under vacuum at 25 °C.

#### 2.2.2. Syntheses of NiPtP/rGO nanocatalysts

In a typical experiment, 20 mg GO was dissolved in 25 mL mixture of water and isopropyl alcohol (v:v = 4:1). Ultrasonication was required to get a uniform dispersion. Then, 7 mL nickel chloride solution (0.01 mol L<sup>-1</sup>) and 3 mL chloroplatinic acid solution (0.01 mol L<sup>-1</sup>) was added into the GO solution. The resulted mixture was stirred for 6 h. A 15 mL aqueous solution of sodium hypophosphite (0.02 mol L<sup>-1</sup>) was slowly dripped into the resulted mixture under vigorous stirring. The pH of the mixture was adjusted to 10 by adding 0.5 M Na<sub>2</sub>CO<sub>3</sub>, subsequently heated to 80 °C for 8 h, and then cooled in air. The NHPP/rGO nanocatalysts were collected by

centrifugation, washed with water and dried under vacuum at room temperature for 12 h.

Additionally, the NiPtP catalyst without GO was also prepared using the similar synthetic procedure.

#### 2.2.3. Syntheses of NiPt/rGO catalysts

NiPt/rGO catalysts were prepared by in-situ reduction of NiCl<sub>2</sub>·6H<sub>2</sub>O and H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O in water solution by used NaBH<sub>4</sub> as reducing agent. In a typical experiment, 20 mg GO were dissolved in 25 mL of water. Ultrasonication was required to get a uniform dispersion. Then, 7 mL nickel chloride solution (0.01 mol L<sup>-1</sup>) and 3 mL chloroplatinic acid solution (0.01 mol L<sup>-1</sup>) was added into the GO solution. A freshly prepared 10 mL NaBH<sub>4</sub> solution (8 wt %) was added into the above mixture under vigorous stirring at 25 °C. The resulted mixture was stirred for 20 min. The NiPt/rGO catalysts were obtained by washing with water and centrifugation.

#### 2.3. Catalyst characterization

Powder X-ray diffraction (XRD) measurements were performed on D-MAX 2500/PC Powder X-ray diffractometer using Cu K $\alpha$ ( $\lambda = 0.15405$  nm) radiation (40 kV, 40 mA). Transmission electron microscopy (TEM) images and high-resolution STEM measurements were obtained using Tecnai G2 F30 S-Twin instrument with a field emission gun operating at 200 kV. X-ray photoelectron spectroscopy (XPS) measurement was performed with ESCALAB 250Xi spectrophotometer. Mass spectrometry (MS) analysis of the generated gas was performed using an OmniStar GSD320 mass spectrometer, wherein Ar was chosen as the carrying gas. The metal contents of the catalyst were analyzed using inductively coupled plasma atomic emission spectroscopy (ICP–AES) on Leeman PRO-FILE SPEC.

#### 2.4. Catalytic performance

An aqueous suspension (4 ml) containing the as-prepared catalysts and NaOH was placed in a two-neck round-bottom flask (30 mL), which was placed in a water bath under ambient atmosphere. The reaction started when 0.1 mL of hydrazine monohydrate was injected into the mixture using a syringe. A gas burette filled with water was connected to the reaction flask to measure the volume of released gas. The gas released during the reaction was passed through a HCl solution (1.0 M) before it was measured volumetrically. The molar ratios of metal/ $N_2H_4$ · $H_2O$  were theoretically fixed at 0.005 for all the catalytic reactions.

#### 2.5. Durability testing of the catalysts

For testing the durability of NiPt/rGO catalysts, 0.1 mL of hydrazine monohydrate was subsequently added into the reaction flask after the completion of the first-run decomposition of



Fig. 1. Schematic representation of the preparation of the NiPtP/rGO catalyst.



**Fig. 2.** TEM images of the  $Ni_{0.7}Pt_{0.3}P/rGO$  (a) and HRTEM images of the  $Ni_{0.7}Pt_{0.3}P/rGO$  (b); high-angle annular dark-field STEM (HAADF-STEM) image of  $Ni_{0.7}Pt_{0.3}P/rGO$  (c); HAADF image (d) and corresponding element mapping of Pt (e), Ni (f) and P (g); TEM images of the  $Ni_{0.7}Pt_{0.3}/rGO$  by NaBH<sub>4</sub> reduction (h, i).

 $N_2H_4\cdot H_2O.$  Such test cycles of the catalyst for the decomposition of  $N_2H_4\cdot H_2O$  were carried out for 5 runs at 323 K by adding  $N_2H_4\cdot H_2O.$ 

#### 2.6. Calculation of turnover frequency (TOF)

The TOF reported here is an apparent TOF value based on the

number of Ni and Pt atoms in catalyst, which is calculated from the equation as follow:

$$\text{TOF} = 2P_0 V / (3RTn_{NiPt}t)$$

where  $P_0$  is the atmospheric pressure (101325 Pa), V is the final generated volume of  $H_2/N_2$  gas, R is the universal gas constant

(8.3145 m<sup>3</sup> Pa mol<sup>-1</sup> K<sup>-1</sup>), T is the room temperature (298 K),  $n_{NiPt}$  is the total mole number of Ni and Pt atoms in catalyst and *t* is the completion time of the reaction in hour.

#### 3. Results and discussion

#### 3.1. Physical characteristics of NiPtP/rGO and NiPt/rGO catalysts

The synthesis of NiPtP/rGO catalysts is illustrated in Fig. 1. In a typical synthesis, the NiPtP NPs supported graphene were prepared by slowly adding sodium hypophosphite solution into the precursor solution containing NiCl<sub>2</sub>, H<sub>2</sub>PtCl<sub>4</sub> and GO at room temperature. Subsequently, the aqueous solution of sodium hypophosphite was slowly dripped into the resulted mixture under vigorous stirring. The pH of the mixture was adjusted to 10 by adding 0.5 M Na<sub>2</sub>CO<sub>3</sub>, subsequently heated to 80 °C for 8 h and then cooled in air. The NiPtP/rGO composites were obtained after reaction at 90 °C for 8 h under magnetic stirring and centrifugal separation. The microstructure of NiPtP/rGO was characterized by transmission electron microscopy (TEM) (Fig. 2a) and highresolution TEM (HRTEM) (Fig. 2b). The TEM and high-angle annular dark-field scanning TEM (HAADF-STEM) (Fig. 2c) images of NiPtP/rGO show that discrete NiPtP NPs are homogeneously dispersed on rGO with an average size of 2 nm (Fig. S1). The particle size of the NiPtP NPs in this study is much smaller than that reported by Zhang et al. [31], who prepared dendritic NiPtP alloy without any supports. In addition, the particle size of the NiPtP NPs in this study is also much smaller than the NiPt/ rGO NPs synthesized by NaBH<sub>4</sub> reduction (Fig. 2h). In Fig. 2b, the *d*-spacing with NiPtP NPs is 0.215 nm slightly larger than 0.212 nm of NiPt NPs because of distorting lattice of NiPt alloy by P-doping [32,33]. The elemental mappings of Ni, Pt and P (Fig. 1e-g) corresponding to HAADF-STEM images reveal that Ni, Pt and P atoms were homogeneously dispersed throughout the NPs. From the results of inductively coupled plasma mass spectrometry (ICP-MS) in Table 1, the relative compositions of the NiPtP NPs yield the following compositions: 0.70 at% Ni, 0.295 at % Pt, and 0.19 at% P in the NiPtP/rGO. The powder XRD is used for analyzing the crystalline structures of the prepared NPs (Fig. 3). All the powder XRD patterns of NiPtP/rGO and NiPt/rGO catalysts exhibit a broad diffraction peak between 20° and 30°, corresponding to the reduced graphene oxide. As for the NiPt/rGO samples, the diffraction peak at  $41^{\circ}$  is attributed to the (111) plane of crystalline NiPt NPs. Unlike NiPt/rGO catalysts, the diffraction intensity of NiPtP/rGO catalysts has significantly reduced. The results indicate that the NiPtP NPs have small size. Besides, there is no characteristic diffraction peak of metal phosphides in XRD pattern of NiPtP/rGO catalysts, which demonstrates that the well-dispersed ultrafine NiPtP NPs are supported on rGO by one-step co-reduced route using NaH<sub>2</sub>PO<sub>2</sub> as a reductant.

Fig. 4 shows XPS spectra of NiPtP/rGO in the P 2p, Pt 4f, Ni 2p, and C 1s regions. The Pt 4f peak can be fitted to two pairs of

Table 1			
ICP-MS	results	of different	catalysts

Tabla 1

Ni Pt P initial ratio	Ni Pt P finial ratio
8:2:30	81:18:34
7:3:30	67:28:19
6:4:30	60:40:20
5:5:30	51:49:12
4:6:30	41:60:13
7:3	70:30
7:3:30	74:29:31
	Ni Pt P initial ratio 8:2:30 7:3:30 6:4:30 5:5:30 4:6:30 7:3 7:3:30



Fig. 3. XRD patterns of  $Ni_{0.7}Pt_{0.3}P/rGO$  before (a) and after stability test (b) and  $Ni_{0.7}Pt_{0.3}/rGO$  through the reduction of  $NaBH_4$  (c).

doublets with a spinorbit separation. The two peaks located at 74.2 eV and 70.8 eV could be assigned to elemental  $Pt^0 4f_{5/2}$  and  $Pt^0$  $4f_{7/2}$ , respectively. In addition, compared with NiPt/rGO, a definite negative shift in the binding energy of Pt 4f is found in NiPtP/rGO. The P 2p peaks at 131.5 and 132.3 eV are assigned to  $P^{\circ}$  and  $P^{V}$ , respectively (Fig. 4b). The peak at 131.5 eV is positively shifted 1.1 eV compared with that of pure phosphorus (130.4 eV). The positive shift of the P 2p peak of P indicates that there is a strong interaction between P, Ni, and Pt. These results further demonstrate the electron interactions occur among P, Ni, and Pt atoms in NiPtP NPs. Compared with NiPt/rGO, the Ni 2p binding energies of NiPtP/ rGO were negatively shifted (Fig. 4c, d). In Fig. S2, the 2p peaks of Ni<sup>0</sup> appear at 852.3 and 869.6 eV were observed. The formation of oxidized Ni observed at 857.4 and 874.5 eV most likely occurred during the sample preparation process for XPS measurements. Additionally, the peak at 284.5 eV is assigned to the binding energy of C 1s (Fig. S2).

## 3.2. Catalytic activities for decomposition of $N_2H_4{\cdot}H_2O$ by NiPtP/ rGO and NiPt/rGO

The catalytic performances of Ni<sub>x</sub>Pt<sub>1-x</sub>P/rGO ( $0 \le x \le 1$ ) for H<sub>2</sub> generation from N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O has been investigated at 323 K with a constant molar ratio of catalyst/N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O = 0.05 (Fig. 5a). It can be seen that the catalytic activity and selectivity for hydrogen were strongly dependent on the Ni/Pt molar ratio. Ni<sub>x</sub>Pt<sub>1-x</sub>P/rGO catalysts show high catalytic and high H<sub>2</sub> selectivity activity at x = 0.6 to 0.7. Among all the Ni<sub>x</sub>Pt<sub>1-x</sub>P/rGO catalysts investigated, Ni<sub>0.7</sub>Pt<sub>0.3</sub>P/rGO exhibits the highest catalytic activity with the TOF value of 742 h<sup>-1</sup>, which is higher than most of the reported values in Table 2. Mass spectrometry (MS) results further confirm the formation of H<sub>2</sub> and N<sub>2</sub> and the absence of NH<sub>3</sub> in the released gas (Fig. 6).

To study the effects of nonmetallic element P on catalytic performance,  $Ni_{0.7}Pt_{0.3}/rGO$  NPs have been synthesized for comparison. As shown in Fig 5b, their catalytic activity and hydrogen selectivity are both inferior to those of  $Ni_{0.7}Pt_{0.3}P/rGO$  NPs. The catalytic activity enhancement of these NiPtP/rGO NPs is likely caused by their ultrafine size and the doping of non-metallic phosphorus element with abundant valence electrons, which



Fig. 4. XPS spectra of Pt 4f (a), P 2p (b), Ni 2p (c), and is the magnified spectra of Ni 2p between 850 and 862 eV for the Ni<sub>0.7</sub>Pt<sub>0.3</sub>PrGO and Ni<sub>0.7</sub>Pt<sub>0.3</sub>/rGO (d).

has been proved to modulate the electronic structure of metal elements [33]. It was reported that the third-body effect and the d-band center shift effect account for improve the bimetallic catalysts' activity [45–48]. The doping of P can effectively modify the d-band electron density of Pt [49,50]. It is reasonable to understand that the doping of P leads to increase of the catalytic active surface areas of NiPtP by changing intermetallic electronic interaction. On the other hand, The Ni<sub>0.7</sub>Pt<sub>0.3</sub> particles on rGO have a poor size distribution with average from 3 to 4 nm (Fig. S1). The addition of P could reduce the aggregation of NiPt NPs, resulting in an ultrafine size and narrow size distribution.

For comparison, the catalytic activity of  $Ni_{0.7}Pt_{0.3}P$  catalysts without support is also tested (Fig. 5b and S3). The NiPtP aggregate to form large particles without graphene support in the TEM image. The catalytic activity and hydrogen selectivity are lower than those of NiPtP and NiPt NPs supported on graphene, highlighting the positive effect of utilization graphene as a two-dimensional support in facilitating the electron transfer and mass transport.

Besides the good dispersion of the ultrafine NPs and NiPt synergistic coupling with nonmetallic phosphorus, the presence of NaOH has a great effect on the catalytic activity of catalysts. The hydrogen generation from hydrazine solution with/without adding NaOH has been comparatively tested. As shown in Fig 5c, the dehydrogenation is incomplete and slow without NaOH, which is consistent with the previous results. It has been found that the catalytic activity increases with the amount of NaOH until the value reaches 4 mmol, and a further increase in the amount of NaOH shows little effect on the catalytic performance. The possible reason for the effects of the NaOH additive may be explained as below: the existence of OH<sup>-</sup> ions can decrease the concentration of undesirable N<sub>2</sub>H<sup>+</sup><sub>5</sub> (N<sub>2</sub>H<sup>+</sup><sub>5</sub> + OH<sup>-</sup>  $\rightleftharpoons$  N<sub>2</sub>H<sub>4</sub> + H<sub>2</sub>O) in aqueous solution and assist the rate-determining deprotonation step (N<sub>2</sub>H<sub>4</sub>  $\rightarrow$  N<sub>2</sub>H<sub>3</sub><sup>\*</sup> + H<sup>\*</sup>) in the decomposition process of N<sub>2</sub>H<sub>4</sub> to N<sub>2</sub> and H<sub>2</sub>. Additionally, in view of the chemical equilibrium, a strong alkaline environment will inhibit the generation of the basic byproduct NH<sub>3</sub>, which raises the H<sub>2</sub> selectivity.

In addition, the recycling stability of Ni<sub>0.7</sub>Pt<sub>0.3</sub>P/rGO NPs was tested at 323 K by adding aqueous hydrous hydrazine (1.96 mmol) to the catalyst after the reaction completion for the last run. It is evident from Fig. 5d, the H<sub>2</sub> selectivity and activity have almost no any decline after five runs. TEM measurements of the recovered catalysts show no obvious change in the particle size (Fig. S4.), indicating that the Ni<sub>0.7</sub>Pt<sub>0.3</sub>P/rGO catalyst has high stability and durability under the current dehydrogenation of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O.



**Fig. 5.** Volume of the generated gas  $(H_2 + N_2)$  versus time for the dehydrogenation of hydrous hydrazine with different Pt/Ni molar ratios (a) and time-course plots for the decomposition of hydrous hydrazine catalyzed by  $Ni_{0.7}Pt_{0.3}P/rGO$ ,  $Ni_{0.7}Pt_{0.3}/rGO$  and  $Ni_{0.7}Pt_{0.3}Pr_{0.3}P/rGO$  in different amounts of NaOH solution (c); durability test of  $Ni_{0.7}Pt_{0.3}P/rGO$  for dehydrogenation of hydrazine hydrazine hydrate in aqueous 0.5 M NaOH solution (d) ( $n_{metal}/n_{N2H4H2O} = 0.05$ , 323 K).

In order to obtain the activation energy ( $E_a$ ) of the N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O decomposition catalyzed by the Ni<sub>0.7</sub>Pt<sub>0.3</sub>P/rGO NPs, the reactions at different temperatures (298–333 K) were carried out and the results are shown in Fig. 7a. As expected, the gas generation rate over the Ni<sub>0.7</sub>Pt<sub>0.3</sub>P/rGO NPs catalyst greatly depends on the

reaction temperatures. The catalytic reactions are completed in 10.5, 5.5, 3.2, and 2.2 min at 298, 313, 323, and 333 K, respectively, which correspond to TOF values of 224, 427, 742, and 1050 h<sup>-1</sup>. The Arrhenius plot of ln TOF vs. 1/T for this catalyst is plotted in Fig. 7b, from which  $E_a$  was calculated as 50.7 kJ mol<sup>-1</sup>.

Table 2

Catalytic activities of different	catalysts for t	the dehydrogenation	of hydrous hydra	zine.
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Catalyst	Solvent/medium	Temp. (K)	Selectivity H <sub>2</sub> for (100%)	$TOF(h^{-1})$	Ea (kJ mol <sup>-1</sup> )	Ref.
Ni <sub>0.7</sub> Pt <sub>0.3</sub> P/rGO	Aqueous NaOH	323	100	742	50.7	This work
	Aqueous NaOH	298	100	224	50.7	This work
Pt <sub>0.6</sub> Ni <sub>0.4</sub> /PDA-rGO	Aqueous NaOH	323	100	2056	33.39	[23]
Ni <sub>3</sub> Fe/C	Without additive	293	100	528	48.1	[19]
Ni <sub>88</sub> Pt <sub>12</sub> /MIL-101	Aqueous NaOH	323	100	350	55.5	[10]
Rh <sub>55</sub> Ni <sub>45</sub> /Ce(OH)	Aqueous NaOH	323	100	395	38.8	[15]
Ni <sub>37</sub> Pt <sub>63</sub> /g-C <sub>3</sub> N <sub>4</sub>	Aqueous NaOH	323	100	570	36.6	[34]
(Ni <sub>3</sub> Pt <sub>7</sub> ) <sub>0.5</sub> -(MnO <sub>x</sub> ) <sub>0.5</sub> /NPC-900	Aqueous NaOH	323	100	706	50.15	[35]
cubic Rh <sub>2</sub> Ni	Aqueous NaOH	293	100	942	41.6	[36]
Ni <sub>6</sub> Pt <sub>4</sub> -SF	Aqueous NaOH	298	100	150		[37]
Ni <sub>3</sub> Pt <sub>7</sub> /graphene	Aqueous NaOH	298	100	68	49.4	[25]
Pt <sub>60</sub> Ni <sub>40</sub> -CNDs	Aqueous NaOH	323	100	170	43.9	[38]
Ni <sub>0.6</sub> Fe <sub>0.4</sub> Mo	Aqueous NaOH	323	100	28.8	50.7	[39]
Ni <sub>66</sub> Rh <sub>34</sub> @ZIF-8	Aqueous NaOH	323	100	140	58.1	[14]
Rh <sub>4.4</sub> Ni/graphene	Aqueous NaOH	298	100	28		[40]
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	[23]
NiIr <sub>0.059</sub> /Al <sub>2</sub> O <sub>3</sub> -HT	Without additive	303	99	12.4	49.3	[41]
NiPt <sub>0.057</sub> /Al <sub>2</sub> O <sub>3</sub> -HT	Without additive	303	97	16.5	34	[42]
Ni <sub>1.5</sub> Fe <sub>1.0</sub> /(MgO) <sub>3.5</sub>	Without additive	299	99	11		[43]
Rh <sub>4</sub> Ni	Without additive	298	100	4.8		[44]
Ni <sub>0.95</sub> Ir <sub>0.05</sub>	Without additive	298	100	2.2		[7]



Fig. 6. MS profile for the gases released from the decomposition reaction of hydrous hydrazine in aqueous NaOH solution (0.5 M) by Ni<sub>0.7</sub>Pt<sub>0.3</sub>P/rGO at 50 °C.



Fig. 7. Volume of the generated gas  $(H_2 + N_2)$  versus time for the dehydrogenation of hydrous hydrazine at different temperatures (a); arrhenius plot (ln(TOF) vs. 1/T (b).

#### 4. Conclusions

In summary, we have developed a co-reduction method to prepare P-doping NiPtP NPs on graphene by using NaH<sub>2</sub>PO<sub>2</sub> as a reducing agent. The well-dispersed ultrafine NiPtP NPs with a diameter about 2 nm can be readily obtained. It is found that these catalysts show high selectivity and excellent catalytic activity for the decomposition of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O at mild temperature. Such excellent catalytic performance can be attributed to synergistic effect of P-doping and strong interaction with graphene support. The present work provides an effective strategy to immobilize ultrafine Pdoping NPs on graphene as the catalysts of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O decomposition, which may be beneficial for the application of  $N_2H_4$ · $H_2O$  as a hopeful chemical hydrogen storage material.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at http:// dx.doi.org/10.1016/j.jallcom.2016.08.113.

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