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Highly efficient dehydrogenation of hydrazine over graphene supported flower-like Ni-Pt nanoclusters at room temperature

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Experimental

Chemicals and materials

All chemicals were commercial and used without further purification. nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$, Sinopharm Chemical Reagent Co., Ltd., ≥99%), potassium chloroplatinate (K_2PtCl_6, Wuhan Greatwall Chemical Co., Ltd., 99%), hydrazine monohydrate ($H_4N_2 \cdot H_2O$, TCI Shanghai Co., Ltd., >98%), sodium borohydride ($NaBH_4$, Sinopharm Chemical Reagent Co., Ltd., 96%), potassium permanganate ($KMnO_4$, Shanghai Chemic Co., Ltd, ≥99.5%), hydrogen peroxide (H_2O_2, Sinopharm Chemical Reagent Co., Ltd, ≥30%), phosphoric acid (H_3PO_4, Sinopharm Chemical Reagent Co., Ltd, AR), sulfuric acid (H_2SO_4, Sinopharm Chemical Reagent Co., Ltd, 95~98%), graphite power (Sinopharm Chemical Reagent Co., Ltd, ≥99.85%) were used as received. We use ordinary distilled water as the reaction solvent.

Graphene Oxide (GO) preparation

GO was made by a modified Hummers method [S1-S2]. In an improved synthesis of graphene oxide, a 9:1 mixture of concentrated H_2SO_4/H_3PO_4 (360:40 mL) was added to a mixture of graphite flakes (3.0 g) and $KMnO_4$ (18.0 g). The reaction was then heated to 50 °C and stirred for 12 h. The reaction was cooled to room temperature and poured onto ice (~400 mL) with 30% H_2O_2 (3 mL). The addition of 2 mL of excess H_2O_2 was followed until observation of a permanent yellow color, which indicating the complete oxidation of graphite. 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 ^{o}C.

In situ synthesis of NiPt/graphene catalysts

In a typical experiment, 8 mg GO were dissolved in 5 mL of water kept in a two-necked round-bottom flask. Ultrasonication was required to get a uniform dispersion. 0.7 mL potassium chloroplatinate solution (0.1 mol L^{-1}) and 0.3 mL nickel chloride solution (0.1 mol L^{-1}) was added into the flask. The resulting mixture was then reduced by 4 ml of aqueous solution containing 75.8 mg $NaBH_4$ and 80 mg NaOH with vigorous stirring at 25 ^{o}C. One neck was connected to a gas burette to monitor the volume of the gas evolution, and the other for the introduction of hydrazine monohydrate (0.1 mL, 1.96 mmol). A water bath was used to control the temperature of the reaction solution at 50 ^{o}C. The gas released during the reaction was passed through a HCl solution (1.0 M) before it was measured volumetrically. The selectivity towards H_2 generation (X) can be calculated using eqn (3)

$$X = (3\lambda - 1) / 8 \quad [\lambda = n(H_2 + N_2) / n(H_2NNH_2)] \qquad (3)$$

In order optimize the reaction condition for catalytic dehydrogenation of hydrazine, the molar ratio of Ni/Pt varied from 1:9, 3:7, 5:5, 7:3, 9:1 in different reaction trials, when the molar ratio of metal to hydrazine was kept as a constant of 0.010.

The temperatures were varied from 25 to 60 ^oC, to obtain the activation energy (E_a). (metal/N_2H_4•H_2O = 0.005)

Sets of experiments were performed for comparison. Ni/graphene and Pt/graphene were performed in the same way as NiPt/graphene, and a physical mixture of 30% Ni/graphene and 70% Pt/graphene is used for testing the catalytic in hydrazine dehydrogenation. The mixture of Ni_3Pt_7 and graphene is following the analogous process.

Different support

Sets of experiments with different support (such as SiO_2, PVP and carbon black) were performed at room temperature (25±0.2 ^oC). All the experiments were performed in the same way as described in the section 2.3.

Characterization

The morphologies and sizes of the samples were observed by using a Titan G2 60-300 Probe Cs Corrector HRSTEM/Tecnai G20 U-Twin transmission electron microscope (TEM) equipped with an energy dispersive X-ray detector (EDX) at an acceleration voltage of 200 kV. Powder X-ray diffraction (XRD) patterns were measured by a Bruker D8-Advance/PANalytical X’Pert Pro X-ray diffractometer using Cu Ka radiation source (λ = 0.154178 nm) with a velocity of 1° min^{-1}. FTIR spectra were collected at room temperature using a Thermo FTIR-iS10 instrument with KBr discs in the 400-4000 cm^{-1} region. Raman spectra were carried out with a confocal Raman microscope (Renishaw, RM-1000) at 514.5 nm excitation wavelength. MS of the generated gases were collected by using a Ametek Dycor mass spectrometer under Ar atmosphere. X-ray photoelectron spectroscopy (XPS) measurement was performed with a Kratos XSAM 800 spectrophotometer.

References:

[S1]W. S. J. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.

[S2]D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Z. Sun, A. Slesarev, L. B. Alemany, W. Lu and J. M. Tour, *ACS Nano*, 2010, **4**, 4806.

[S3]K. Aranishi, A. K. Singh and Q. Xu, *ChemCatChem*, 2013, **5**, 2248.

[S4]S. K. Singh, A. K. Singh, K. Aranishi and Q. Xu, *J. Am. Chem. Soc.*, 2011, **133**, 19638.

[S5]N. Cao, J. Su, W. Luo and G. Z. Cheng, *Int. J. Hydrogen Energy*, 2014, **39**, 9726.

[S6]A. K. Singh and Q. Xu, *ChemCatChem*, 2013, **5**, 3000.

[S7]J. J. Zhang, Q. Kang, Z. Q. Yang, H. B. Dai, D. W. Zhuang and P. Wang, *J. Mater. Chem. A*, 2013, **1**, 11623.

[S8]S. K. Singh, Z. H. Lu and Q. Xu, *Eur. J. Inorg. Chem.*, 2011, 2232.

[S9]S. K. Singh, Y. Iizuka and Q. Xu, *Int. J. Hydrogen Energy*, 2011, **36**, 11794.

[S10] A. K. Singh, M. Yadav, K. Aranishi and Q. Xu, *Int. J. Hydrogen Energy*, 2012, **36**, 18915.

[S11] L. He, Y. Q. Huang, A. Q. Wang, X. D. Wang and T. Zhang, *AIChE J.*, 2013, **59**, 4297.

[S12] L. He, Y. Q. Huang, A. Q. Wang, Y. Liu, X. Y. Liu, X. W. Chen, J. J. Delgado, X. D. Wang and T. Zhang, *J. Catal.*, 2013, **298**, 1.

[S13] W. Gao, C. M. Li, H. Chen, M. Wu, S. He, M. Wei, D. G. Evansa and X. Duana, *Green Chem.*, 2014, **16**, 1560.

[S14] H. L. Wang, J. M. Yan, Z. L. Wang , S. –II O and Q. Jiang, *J. Mater. Chem. A*, 2013, **1**, 14957.

[S15] J. Wang, X. B. Zhang, Z. L. Wang, L. M. Wang and Y. Zhang, *Energy Environ. Sci.*, 2012, **5**, 6885.

[S16] S. K. Singh and Q. Xu, *J. Am. Chem. Soc.*, 2009, **131**, 18032.

[S17] S. K. Singh and Q. Xu, *Inorg. Chem.*, 2010, **49**, 6148.

[S18] S. K. Singh, X. B. Zhang and Q. Xu, *J. Am. Chem. Soc.*, 2009, **131**, 9894.

[S19] S. K. Singh and Q. Xu, *Chem. Commun.*, 2010, **46**, 6545.

Figure captions

Figure S1. (left) The HAADF-STEM image for Ni_3Pt_7/graphene. (right) The EDX elemental mapping of the Ni_3Pt_7/graphene.

Figure S2. Raman spectra of GO and Ni_3Pt_7/graphene.

Figure S3. FTIR spectra of GO and Ni_3Pt_7/graphene.

Figure S4. MS profile for the gases released from the decomposition reaction of hydrazine in aqueous NaOH solution (0.5 M) over Ni_3Pt_7/graphene (metal/N_2H_4•H_2O = 0.005) under an argon atmosphere at 25 °C.

Figure S5. (a) Time course plots for hydrogen generation by the decomposition of hydrazine by Ni_3Pt_7/graphene at 25°C, 40°C, 50°C and 60°C. (b) Plot of ln k versus 1/T during the hydrazine decomposition over Ni_3Pt_7/graphene at different temperatures. (metal/N_2H_4•H_2O = 0.005)

Figure S6. The XPS spectra of (a) Pt and (b) Ni in Ni_3Pt_7/graphene before (0 s) and after (514.8 s and 1017.5 s) argon sputtering

Figure S7. Durability test of Ni_3Pt_7/graphene and for decomposition of hydrazine in aqueous NaOH solution (0.5 M) at 25°C (metal/N_2H_4•H_2O = 0.005). Additional aliquots of hydrazine monohydrate were subsequently introduced into the reaction vessel after the completion of the last runs.

Figure S1

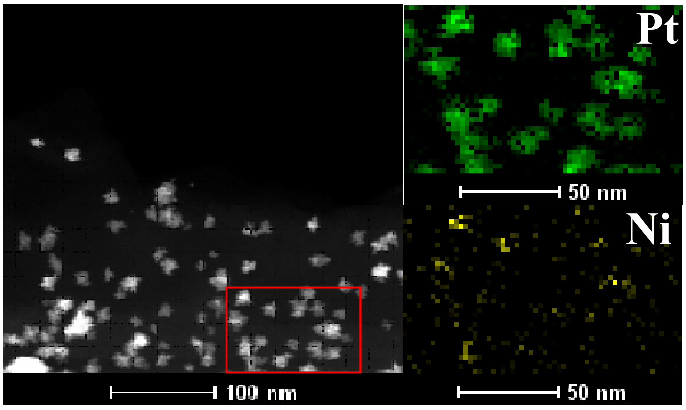


Figure S2

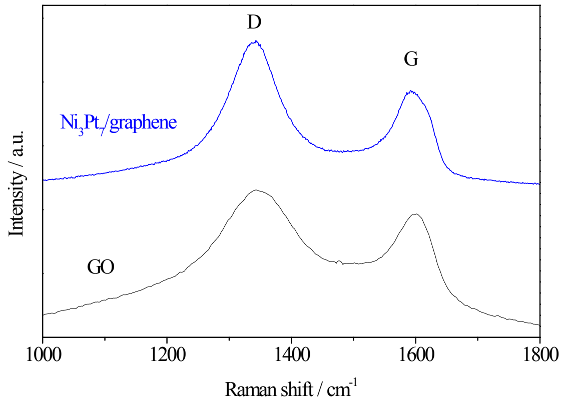
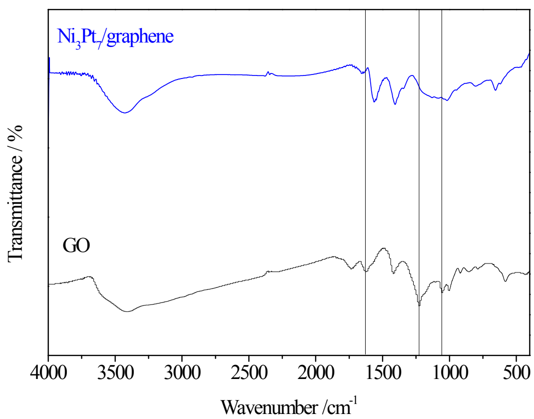


Figure S3



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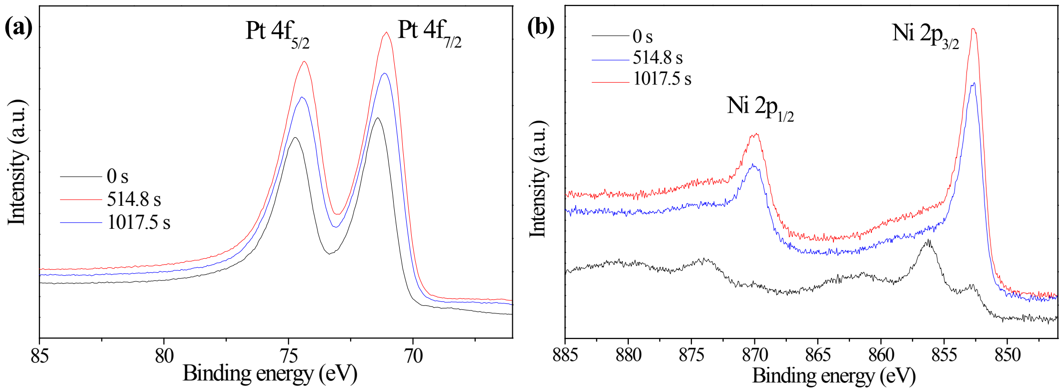


Figure S5

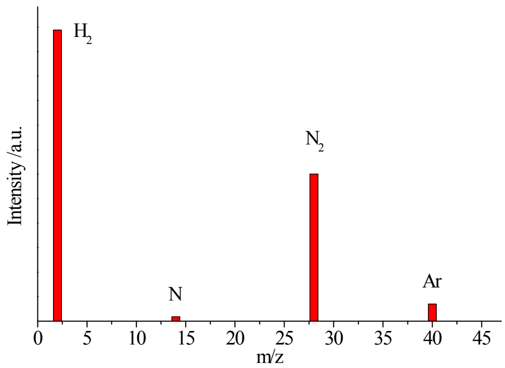
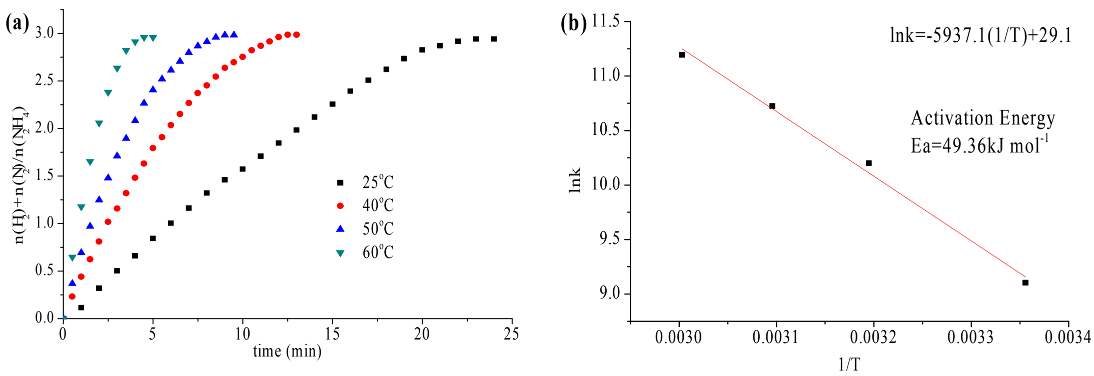


Figure S6



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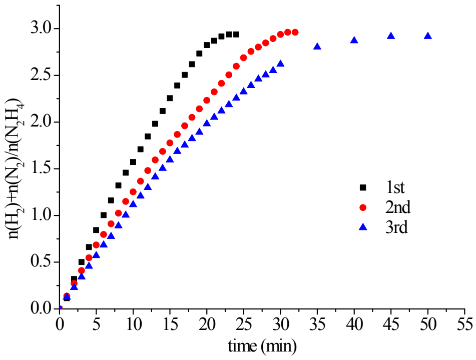

Table S1. Comparison of activities and Ea of different catalysts for hydrogen generation by $H_2NNH_2{\bullet}H_2O$ decomposition.

Catalyst	T (℃)	TOF(h^{-1})	Ea(kJ/mol)	Reference
G4-OH($Pt_{12}Ni_{48}$)	70	240	--	S3
NiFe	70	6.6	--	S4
Ni_3Pt_7/graphene	50	416	--	This study
$Ni_{88}Pt_{12}$@MIL-101	50	350	55.5	S5
$Ni_{80}Pt_{20}$@ZIF-8	50	90	--	S6
$Ni_{64.1}Mo_{11.5}B_{24.4}$-La$(OH)_3$	50	13.3	55.1	S7
$Ni_{0.99}Pt_{0.01}$	50	6	49.95	S8
$Ni_{0.6}Pd_{0.4}$	50	6	--	S9
$Rh_{10}Ni_{90}$	50	4.5	--	S10
Raney Ni-300	30	114	44.4	S11
$NiPt_{0.057}/Al_2O_3$	30	16.5	49.3	S12
Ni/Al_2O_3	30	2.2	34	S12
$Ni_{1.5}Fe_{1.0}$-alloy/$(MgO)_{3.5}$	26	1.9	--	S13
Ni_3Pt_7/graphene	25	68	49.36	This study
$Ni_{0.9}Pt_{0.1}/Ce_2O_3$	25	28.1	42.3	S14
Rh_4Ni/graphene	25	20	--	S15
Rh_4Ni	25	9.6	--	S16
$Ni_{0.93}Pt_{0.07}$	25	3	--	S17
Rh	25	2.8	--	S18
$Ni_{0.95}Ir_{0.05}$	25	1.6	--	S19