Electronic Supplementary Material (ESI) for Catalysis Science & Technology. This journal is © The Royal Society of Chemistry 2017

Supplementary Materials

Pt_xNi_{10-x}O Nanoparticles Supported on N-doped Graphene Oxides with A Synergetic Effect for Highly Efficient Hydrolysis of Ammonia Borane

Binhua Zhao,^{a,1} Kun Feng, ^{a,1} Yun Wang, ^a Xiaoxin Lv, ^a Hechuang Zheng, ^a Yanyun Ma, ^{a,*} Wensheng Yan, ^b Xuhui Sun, ^{a,*} and Jun Zhong ^{a,*}

^a Institute of Functional Nano and Soft Materials Laboratory (FUNSOM), Jiangsu Key Laboratory for

Carbon-Based Functional Materials & Devices, Soochow University, Suzhou 215123, China

^b National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei,

Anhui 230029, China

¹ The two authors have equal contribution to this work.

* Address correspondence to mayanyun@suda.edu.cn (Y. Ma); xhsun@suda.edu.cn (X. Sun);

jzhong@suda.edu.cn (J. Zhong)



Fig. S1. Illustration of the preparation processes for the Pt₃Ni₇O-NGO sample.



Fig. S2. SEM images of (a) pure NGO and (b) Pt₃Ni₇O-NGO.



Fig. S3. XRD patterns of NGO and $Pt_xNi_{10-x}O$ -NGO samples. The two broad diffraction peaks are attributed to NGO substrate. No obvious XRD peak can be observed for the $Pt_xNi_{10-x}O$ NPs.



Fig. S4. The particle size distribution of Pt₃Ni₇O-NGO with an average size of 2.1 nm.



Fig. S5. Dark field TEM image and the high-resolution elemental mappings of Pt₃Ni₇O-NGO.



Fig. S6. XPS spectra of Pt₃Ni₇O-NGO, Pt₃Ni₇-GO and Ni-NGO: (a) the survey spectra, (b) the high-resolution spectra at B 1s edge.



Fig. S7. (a) Stoichiometric hydrogen evolution in aqueous solution at a fixed amount of AB with various Pt₃Ni₇O-NGO/AB molar ratios at 298 K; (c) Relationship between hydrogen-generating rate and AB concentration at a fixed amount of Pt₃Ni₇O-NGO in aqueous solution at 298 K; (b) and (d): Logarithmic plots of rate versus [Pt₃Ni₇O-NGO] and [AB], respectively. (e) Hydrogen-generating rate as a function of temperature in the

hydrolysis of AB catalyzed by Pt_3Ni_7O -NGO. Inset: Arrhenius plot of ln(TOF) versus 1/T. The activation energy is calculated to be 52.85 kJ/mol.



Fig. S8. TEM image (a), particle size distribution (b) and XRD pattern of Pt_3Ni_7 -GO. The XRD patterns of NGO, Pt_3Ni_7O -NGO and the standard Pt are shown for comparison.



Fig. S9. (a) N_2 adsorption-desorption isotherms of NGO and GO at 77 K. (b) The corresponding pore size distributions of NGO and GO.



Fig. S10. (a) and (b): TEM images of the as-prepared Pt₃Ni₇O-NGO and Pt₃Ni₇O-NGO after 9 cycles (labeled as Pt₃Ni₇O-NGO 10th), respectively. (c) XRD patterns of NGO, Pt₃Ni₇O-NGO, Pt₃Ni₇O-NGO and Pt₃Ni₇O-NGO 10th.



Fig. S11. XPS spectra of Pt_3Ni_7O -NGO at (a) N 1s, (b) Ni 2p, and (c) Pt 4f edges, respectively.



Fig. S12. Soft X-ray XAS spectra of Ni-NGO, Pt₃Ni₇O-NGO and Pt₇Ni₃O-NGO at Ni *L*-edge.

Samples	Pt-loading (wt%)	Ni-loading (wt%)	The atomic ratio of Pt and Ni	TOF (H ₂) mol/(Cat-M)mol·min	TOF (H ₂) mol/(Cat-Pt)mol·min
Pt ₃ Ni ₇ O-NGO	4.92	7.21	2:10	120.7	709.6
Pt ₅ Ni ₅ O-NGO	9.14	4.49	6.1:10	67.1	176.9
Pt ₇ Ni ₃ O-NGO	10.12	6.41	4.7:10	42.5	132.0
Pt ₃ Ni ₇ -GO	1.16	1.39	2.5:10	68.2	339.2
Ni-NGO	-	17.82	-	1.3	-
Pt-NGO	13.50	-	-	104.2	104.2
NGO	-	-	-	0	0

Table S1. Pt and Ni contents (measured by ICP-OES) and the TOF values of various $Pt_xNi_{10-x}O$ -NGO, Pt_3Ni_7 -GO, Ni-NGO, Pt-NGO and NGO samples.

Catalyst	TOF (H2) mol/(Cat-Pt)mol·min	Т (°С)	Ref.
PtNi/NiO	1240.3	25	1
Pt ₃ Ni ₇ O-NGO	709.6	25	This work
Pt ₄ Ni ₁ @PVP NPs	638	25	2
Pt/CNTs-O-HT	468	25	3
Pt@MIL-101	414	25	4
PEI-GO/Pt _{0.17} Co _{0.83}	377.83	25	5
Pt-TiO ₂	311	25	6
G4-OH(Pt ₁₂ Ni ₄₈)	239.7	70	7
Pt/γ-Al ₂ O ₃	222.22	25	8
Pt/C	111	25	9
PtO ₂	20.8	25	9
Pt black	13.9	25	9

Table S2. Comparison of the TOF value of Pt-based catalysts for the hydrolysis of amine boranes in this work and those reported in the literatures.

References listed in Table S2:

- Y. Ge, W. Ye, Z. H. Shah, X. Lin, R. Lu and S. Zhang, ACS Appl. Mater. Interfaces, 2017, 9, 3749-3756.
- S. Wang, D. Zhang, Y. Ma, H. Zhang, J. Gao, Y. Nie and X. Sun, ACS Appl. Mater. Interfaces, 2014, 6, 12429-12435.
- W. Chen, J. Ji, X. Duan, G. Qian, P. Li, X. Zhou, D. Chen and W. Yuan, *Chem. Commun.*, 2014, 50, 2142-2144.
- 4. A. Aijaz, A. Karkamkar, Y. Choi, N. Tsumori, E. Rönnebro, T. Autrey, H. Shioyama and Q. Xu, J. Am. Chem. Soc., 2012, **134**, 13926-13929.
- 5. M. Li, J. Hu, Z. Chen and H. Lu, *RSC Advances*, 2014, 4, 41152-41158.
- 6. M. Khalily, H. Eren, S. Akbayrak, H. Akbayrak, N. Biyikli, S. özkar and M. Guler,

Angew. Chem. Int. Ed., 2016, 55, 12257-12261.

- 7. K. Aranishi, A. Singh and Q. Xu, ChemCatChem, 2013, 5, 2248-2252.
- 8. M. Chandra and Q. Xu, J. Power Sources, 2007, 168, 135-142.
- 9. Q. Xu and M. Chandra, J. Alloy Compd., 2007, 446-447, 729-732.

Cycles	TOF (H ₂) mol/(Cat-Pt)mol·min	Catalytic Efficiency
1 st	709.6	100%
2 nd	681.2	96.0%
3rd	627.8	88.5%
4 th	627.8	88.5%
5 th	584.7	82.4%
6 th	584.7	82.4%
7 th	544.9	76.8%
8 th	544.9	76.8%
9 th	544.9	76.8%
10 th	544.9	76.8%

Table S3. TOF values and the catalytic efficiencies of Pt₃Ni₇O-NGO in different cycles during the stability test.