Supporting information

Enhanced Catalytic Activity and Stability of Pt Nanoparticles by

Surface Coating of Nanosized Graphene Oxide for Hydrogen

Production from Hydrolysis of Ammonia-Borane

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1. Chemicals

Polyoxyethylene (20) cetyl ether (Brij®58, Acros Organics), ammonium hydroxide (NH₃·H₂O, 25%–28%, Tianjin Damao Chemical Reagent Co. Inc., China), tetraethyl orthosilicate (TEOS, Sinopharm Chemical Reagent Co., Ltd.), cyclohexane (Sinopharm Chemical Reagent Co., Ltd.), isopropanol (IPA, Sinopharm Chemical Reagent Co., Ltd.), hexachloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O, Sinopharm Chemical Reagent Co., Ltd.), trisodium citrate dihydrate (C₆H₃Na₃O₇·2H₂O, Na₃Cit, Tianjin Fuchen Chemical Reagent Co. Inc., China), potassium permanganate (KMnO₄, Tianjin Guangfu Fine Chemical Reagent Institute), graphite (Tianjin Bodi Chemical Co., Ltd.), concentrated phosphoric acid (Tianjin Fuyu Fine Chemical Co., Ltd.), concentrated sulfuric acid (H₂SO₄, 98%, Tianjin Chemical Reagent Factory), hydrochloric acid (HCl, Tianjin Chemical Reagent Factory), sodium borohydride (NaBH₄, Sinopharm Chemical Reagent Co., Ltd.), (3-aminopropyl) triethoxysilane (APTES, Shanghai Aladdin Biochemical Polytron Technologies Inc.).

2. Synthesis of catalysts

2.1 Synthesis of NGO. Nanosized graphene oxide (NGO) was prepared by a two-step oxzidation process.¹ Firstly, large-sized graphene oxide (LGO, micrometer scale) was synthesized by a modified Hummers method.²⁻³ Typically, 6.0 g of KMnO₄ powders, 1.0 g of graphite and 13 mL of concentrated phosphoric acid were added in a 250 mL three-neck round-bottom flask at 50 °C. Then 120 mL of concentrated sulfuric acid was very slowly added into the above mixture with continuous stirring overnight. The resulted sticky mixture was slowly added into 300 mL ice-water under stirring, followed by slow addition of 10 mL of H₂O₂ solution (30 wt%). The mixture was centrifuged at 9000 rpm for 10 min then washed with dilute hydrochloric acid and water for 3

times, respectively. The products were collected after drying for 10 h under air. For the synthesis of NGO, 50 mg of LGO and 50 mL of concentrated H_2SO_4 (98%) were added into a 100 mL threeneck round-bottom flask. Then, 150 mg of KMnO₄ was slowly added to the above solution with vigorous stirring at 45 °C. The mixture was stirred for another 2.5 h and then slowly poured into 95 mL of ice-water under stirring. After that, 5 mL of H_2O_2 solution (30 wt%) was added to the above solution and stirred for another 1 h. Finally, the solution was ultrasonicated for 0.5 h to obtain the exfoliated NGO. The solution was stored for further using.

2.2 Synthesis of SiO₂(a)Pt. Firstly, amino-functionalized silica nanoparticles (SiO₂-NH₂) were synthesized by a reverse microemulsion method.⁴⁻⁵ Typically, 3.37 g of Brij®58 (3 mmol) and 15 mL of cyclohexane were added into a 50 mL single-neck round-bottom flask under the stirring rate of 500 rpm at 50 °C to form transparent solution. 1 mL of ammonium hydroxide was added dropwise to the above solution and stirred for 0.5 h, then 2.0 g of TEOS was added. After 5 h hydrolysis of TEOS, 0.5 mL of APTES was added and stirred for another 2 h. Then, 15 mL of IPA was added to demulsify the microemulsion, the mixture was collected and centrifuged at 6000 rpm for 10 min and washed by 30 mL of IPA for another 2 times. The resulting products were dried at 100 °C for 5 h. For the synthesis of silica supported Pt nanoparticles (SiO₂@Pt, Pt loading of 2 wt%), 0.30 g of SiO₂-NH₂ was dispersed in 25 mL of H₂O and ultrasonicated for 0.5 h, then transferred to a 100 mL single-neck round-bottom flask under the stirring rate of 550 rpm at 4 °C. Subsequently, 25 mL of H_2PtCl_6 aqueous solution (1.23 mM) was added dropwise into the above mixture. After 5 minutes of stirring, 0.62 mL of Na₃Cit aqueous solution (0.17 M) and 1 mL of freshly prepared NaBH₄ aqueous solution (0.062 M) were injected directly into the system.⁶ After 10 min of reduction, the mixture was separated via centrifugation at 6000 rpm for 10 min and

washed with water for two times, the products were redispersed in 20 mL of water for the following experiments.

2.3 Synthesis of SiO₂@Pt@NGO. For the synthesis of SiO₂@Pt@NGO with NGO loading of 1 wt%, 9 mL of NGO solution were added dropwise into the 20 mL of redispersed SiO₂@Pt suspension with continuous stirring at room temperature overnight. The mixtures were separated *via* centrifugation at 8000 rpm for 5 min and washed with water for several times to totally remove the H₂SO₄. The products were dried at 100 °C for 5 h under air.

2.4 Synthesis of Pt/LGO. For the activity comparison, we also prepared LGO supported Pt nanoparticles (Pt/LGO). Typically, 12 mg of LGO were dispersed with 20 mL of water in a single-neck round-bottom flask to form a homogeneous solution. Then 25 mL of H_2PtCl_6 aqueous solution (1.23 mM) were added dropwise into the above mixture with continuous stirring at 4 °C. 0.62 mL of Na₃Cit aqueous solution (0.17 M) and 1 mL of freshly prepared NaBH₄ aqueous solution (0.062 M) were injected directly into the above solution. After 10 min of reaction, the mixture was separated *via* centrifugation at 9000 rpm for 10 min and washed with water for two times.

3. Catalytic activity measurement

3.1 Catalytic hydrolysis of AB. The procedure of this reaction was performed as reported.⁷ Typically, 40 mg of catalyst and 5 mL of water were mixed in a double-neck round-bottom flask with stirring in a water bath at 30 °C. There was an inverted cylinder full with water connected with the flask to measure the volume of gas generated from it. The reaction started as soon as the aqueous solution of AB (5 mL, 0.75 mmol) were injected into the system. The time interval of

every 5 mL of displacement was recorded. The reaction was completed when there was no more gas generated.

3.2 Durability test. The procedure of durability test was similar to the above. Generally, 40 mg of SiO₂@Pt@NGO and 5 mL of water were added in a double-neck round-bottom flask stirring at 30 °C. The reaction started when aqueous solution of AB (5 mL, 0.75 mmol) were injected into the system. The time interval of every 5 mL of displacement was recorded. The first cycle was completed when the gas generation stopped. The catalyst was separated by centrifugation and washed with water for next cycle.

3.3 Calculation method. The turnover frequency (TOF) value was measured based on the total number of Pt atoms added into the reaction system which shows as follow⁸:

$$TOF = \frac{V_{H_2}}{22.4V_s C_{P_t} t}$$

 V_{H_2} represented the total volume of hydrogen generated, V_s was the total volume of solution (10 mL in this report), C_{Pt} was the concentration of Pt in the reaction mixture, and t was the total reaction time. The unit of TOF used in this study was mol_{H2} mol_{Pt}⁻¹ min⁻¹.

3. Characterizations

TEM images were captured by a Tecnai G² 20 S-Twin transmission electron microscopy (TEM) at an accelerating voltage of 200 kV. Scanning transmission electron microscopy (STEM) and energy-dispersive X-ray spectroscopic (EDS) data were recorded with a JEM-2100F instrument operating at 200 kV. Atomic Force Microscope (AFM) images were captured by a Bruker Dimension ICON instrument. The XRD patterns were recorded on a Rigaku DMAX IIIVC X-ray

diffractometer with Cu Ka (0.1542 nm) radiation scanning from 5 ° to 90 ° (2θ) at the rate of 6 °/min. X-ray photoelectron spectroscopy (XPS) was acquired by ThermoFisher ESCALABTM 250 Xi with an Al K α X-ray source operating at 150 W (15 kV). The binding energies were calibrated using the C 1s peak at 284.6 eV, and the software XPS PEAK 4.1 was used for curve fitting. Raman spectra were measured on a confocal laser micro-Raman spectrometer (Thermo DXR Microscope, USA).



Figure S1. TEM images of SiO₂@Pt with Pt loading of (A) 1 wt%, (B) 2 wt%, (C) 5 wt%, and (D) 10 wt%.

	Sample	Content of Pt (mg/L)	Pt content in SiO ₂ @Pt (%)		Loading percentage (%)	
			Practical	Theoretical		
1	SiO ₂ @Pt	15.40	0.77	1	77	
2	SiO ₂ @Pt	39.44	1.97	2	98.5	
3	SiO ₂ @Pt	103.9	5.20	5	104	
4	SiO ₂ @Pt	190.6	9.53	10	95.3	

Table S1. Content of Pt in SiO₂@Pt@NGO with different loadings based on ICP-AES analysis^a.

^{*a*}For the ICP analysis, 10 mg of product was dissolved with 1 mL of HF and 1 mL of aqua regia, and then transferred to a 5 mL volumetric flask. Practical Pt content = content of Pt based on ICP-AES × volume of solution (0.005 L) × 100% / (amount of SiO₂@Pt (0.01 g)). Theoretical Pt content = amount of Pt⁴⁺ precursor added / (total amount of SiO₂@Pt). Loading percentage of Pt = practical Pt content in SiO₂@Pt / (theoretical Pt content in SiO₂@Pt).



Figure S2. XRD patterns of SiO₂@Pt with different loadings of Pt.



Figure S3. Time curves for hydrogen generation from hydrolysis of AB catalyzed by SiO₂@Pt with different Pt loadings ($n_{Pt}/n_{AB} = 0.0055$, $n_{AB} = 0.75$ mmol, $V_s = 5$ mL).



Figure S4. (A-B) TEM images of NGO; (C) AFM image of NGO; (D-E) size and thickness of NGO.



Figure S5. HRTEM images of SiO₂@Pt@NGO

Table S2.	Catalytic	activities	comparison	with recently	reported	Pt-based	catalysts	for hyd	rolysis
of ammon	nia borane.								

Catalyst	Temp	Metal/AB molar	TOF	Ref
	(°C)	ratio	(min ⁻¹)	
Pt/C	25	0.018	111	9
Pt/SiO ₂ (2 wt%)	rt	0.018	33	9
Pt@SiO ₂	25	0.00245	158.6	10
Pt-CeO ₂ /rGO	25	0.0079	93.8	11
Pt@MIL-101	rt	0.0029	414	12
Pt/CNT	30	0.0047	567	13
Pt25@TiO ₂	25	0.0016	311	14
Pt/γ - Al_2O_3	25	0.018	222	15
Pt-CeO ₂	25	0.018	182	16
(Zn ₆)Pt/RGO	25	0.01	284	17
SiO ₂ @Pt@NGO	30	0.0055	324.6	This work



Figure S6. Raman spectra of GO and SiO₂@Pt@NGO.



Figure S7. TEM images of large scale graphene oxide supported Pt nanopartilces (Pt/LGO).



Figure S8. (A-B) TEM images of SiO₂@Pt@NGO and SiO₂@Pt@LGO respectively; (C) time curves for hydrogen generation catalyzed by these two samples.



Figure S9. XPS spectra of element N in SiO₂-Pt@NGO with different NGO loading of 0 wt%,





Figure S10. XRD patterns of SiO₂-Pt@NGO with different NGO loading of 0 wt%, 0.5 wt%,

1.0 wt%, and 2.0 wt%.



Figure S11. TEM images of SiO₂@Pt@NGO before catalyzing hydrolysis of AB (A), SiO₂@Pt with same Pt loading (B), SiO₂@Pt@NGO with 1 wt% NGO (C), SiO₂@Pt@NGO with 2 wt% NGO (D) after six runs for catalytic reaction.

4. References

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