Electronic Supplementary Information (ESI) available:

Synthesis of Pt-Ni-Graphene via *in situ* Reduction and its Enhanced Catalyst Activity for the Methanol Oxidation

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Experimental section:

Reagents: Graphite powder (99.998%, 200mesh), Platinum (II) pentanedionate ($[Pt(acac)_2]$, 99%), Nickel(II) acetylacetonate ($[Ni(acac)_2]$, 99%), Pt black (12755), and Nafion solution (5% w/w) werepurchased from Alfa Aecar. Analytical grade benzyl alcohol, benzoic acid, ascorbic acid, and PVP (MW = 30000, AR) were obtained from Beijing Chemical Reagents, P.R. China. All the chemicals were used as received.

Synthesis of graphene oxide (GO) sheets: GO was prepared by a modified Hummer's method. The graphite powder (3g) was added into concentrated H_2SO_4 (120 mL). Then KMnO₄ (15 g) was added gradually while stirring, and the temperature of the mixture was kept below 20 °C for 2 h using an ice bath. Successively, the mixture was stirred at 38°C for 2 h and diluted with deionized water (500 mL) to keep the temperature at 50 °C. Additional water (420 mL) and 30% H_2O_2 (20 mL) were added, producing a brilliant yellow mixture. The mixture was filtered and washed with a 10% HCl aqueous solution to remove metal ions, which was followed by a deionized water wash to remove the acid. The solid obtained on the filter was vacuum dried overnight at room temperature.

Preparation of the graphene-supported Pt and Pt-Ni Truncated Octahedral Nanocrystals: By adjusting the amount of the metal precursors, Pt-Ni/rGO nanocatalysts with Pt:Ni ratios of 1:0, 3:1, 3:2, 1:1 were prepared. The total metal (Pt+Ni) loading of the nanocatalysts was controlled to be approximately 30 wt%. In a typical synthesis of Pt and Pt-Ni octahedral nanocrystals, GO was firstly added into 5 mL of benzylalcohol to form 2mg/mL dispersion under ultrasonication. Then, Pt(acac)₂, (6.0 mg), poly(vinylpyrrolidone) (PVP, MW = 30000, (80.0 mg), Ni(acac)₂ (ranging from 0 mg to 6.0 mg) and ascorbic acid (50 μ L, 0.1 M) were dissolved in the above dispersion, followed by 10 min vigorous stirring. The resulting homogeneous solution was transferred into a 12mL Teflon-lined stainless-steel autoclave. The sealed vessel was then heated at 180 °C for a 6 h before it was cooled down to room temperature. The products were precipitated by acetone, separated via centrifugation, and further purified by an ethanol–acetone mixture. To review the effect of the addition VC, the control-experiments were carried out, which also followed the above procedure without VC or with other addition benzoic acid (50 μ L, 0.1 M). The Pt and Pt₃Ni Nanocrystals were synthesized followed the above procedure without the addition of GO.

Preparation of Pt-Ni/ active carbon: the weight loading of active carbon supported precursor catalyst was 30 wt%. The Pt₃Ni/active carbon catalyst was prepared by mixing Pt₃Ni nanoparticles

and active carbon in 20 mL of hexane and then sonicated for 2 hours (to ensure complete adherence of the nanoparticles onto the carbon support). After evaporation of hexane, the dispersion was heated for 12 hours at 70 $^{\circ}$ C.

Characterization: The crystalline structure and phase purity were determined using a Brukeer D8 Advanced X-ray powder diffractometer with CuKa radiation (λ = 1.540 Å). The composition of the product was measured by the inductively coupled plasma atomic emission spectroscopy (ICP-AES) and energy dispersive spectrometer (EDS). The catalysts' sizes and morphologies were analyzed on a Hitachi H-800 transmission electron microscope (TEM) and a FEI Tecnai G2 F20 S-Twin high-resolution transmission electron microscope (HRTEM). X-ray photoelectron spectroscopy (XPS) experiments were performed on a ULVAC PHI Quantera microprobe. The FT-IR spectra were collected on Perkin-Elmer Spectrum GX.

Electrochemical measurement: Electrochemical measurements were conducted in an electrochemical cell with a three-electrode configuration at room temperature. A Pt wire was used as the counter electrode, and a silver chloride electrode (Ag/AgCl) was used as the reference electrode. The working electrode was a glassy carbon disk with a diameter of 3.0 mm, polished with Al₂O₃ paste, and washed thoroughly with de-ionized water before 5 μ L of each catalyst was dropped on the glassy carbon electrode. After the electrode was dried, 5 μ L Nafion dilutes (0.05 wt%) was coated on the catalyst surface. Methanol electro-oxidation was conducted in 1 M methanol and 0.1 M HClO4 from -0.23 to 1 V (vs. Ag/AgCl) at a scan rate of 50 mV s⁻¹.The catalysts on the carbon support were separated by centrifugation and re-dispersed in de-ionized water to form a 1 mg/mL suspension. For comparison, the concentrations of Pt₃Ni/ active carbon and commercial Pt/C are equal to that of Pt-Ni/rGO.



Figure S1 The XRD patterns of different products



Figure S2 TheTEM images of $\mathsf{Pt}_3\mathsf{Ni}/\mathsf{rGO}$ NPs (a) without VC and (b) with other addition benzoic acid



Figure S3 The XPS patterns of (a) GO, (b) rGO



Figure S4 TheFR-IR patterns of different products

The reduction of the oxygen-containing groups in GO was also confirmed by FT-IR spectroscopy. As shown in Fig. S4, after reduction for rGO, Pt/rGO, and Pt₃Ni/rGO, the intensities of the FT-IR peaks corresponding to the oxygen functionalities, such as the C=O stretching vibration peak at1725 cm⁻¹, the vibration and deformation peaks of O–H groups at 3390 cm⁻¹ and 1380 cm⁻¹, respectively, the C–O(epoxy) stretching vibration peak at 1224 cm⁻¹, and the C–O (alkoxy) stretching peak at 1050 cm⁻¹ decreased dramatically, and some of them disappeared entirely.



Figure S5 The voltammetric responses of the oxidation of 1 M methanol at the different catalysts



Figure S6 The XPS patterns of Pt_3Ni/rGO of (a) Pt 4f and (c) Ni 2p, (b) the Pt $4f_{7/2}$ peak shift in different catalysts.



Figure S7 TEM images of Pt_3Ni/rGO NPs catalysts: (a) before and (b) after durability test; $Pt_3Ni/active$ carbon NPs catalysts: (c) before and (d) after durability test; commercial Pt/C: (e) before and (f) after durability test.

Nominal atomic	Actual atomic	2 $ heta$ for Pt (111) (°)	<i>d</i> -spacing (Å) ^b	Lattice	
ratio of Pt to Ni	ratio of Pt to Ni ^a			parameter (Å) $^{\circ}$	
Pure Pt	1:0	39.8	2.264	3.921	
3:1	0.74:0.26	40.1	2.245	3.890	
3:2	0.60:0.40	40.6	2.220	3.845	
1:1	0.48:0.52	41.2	2.189	3.791	

Table S1 A summary of the atomic ratios of Pt to Ni, the *d*-spacing values, and the lattice parameter a of the Pt-Ni-rGOnanocatalysts

a Estimated by the EDS measurements

b The value of *d*-spacing was calculated using Bragg's equation: $2d\sin\theta = n\lambda$.

c For the face centered-cubic crystal systemof the as-synthesized Pt-based alloys, the value of a

was calculated using the equation $d_{hkl} = \sqrt{h^2 + k^2 + l^2}$.

The atomicratios between Pt and Ni in individual particle of the preparednanocatalysts were very close to the nominal values as indicated by the data in Table S1, demonstrating that the molar ratios of Pt/Ni inindividual particle of the prepared nanocatalysts were almost thesame as the precursors involved in the reaction mixtures.

Table S2 Forward peak potential (Ef), forward peak current density (Jf), reverse peak potential (Eb), reverse peak current density (Jb), and Jf :Jb for methanol oxidation on different Pt-based catalysts recorded in $0.1 \text{ MHClO}_4 + 1 \text{ M MeOH}$

catalyst	E _f /V(vs.SCE)	J _f /mA∙cm ⁻²	E _b /V(vs.SCE)	J _b /mA•cm ⁻²	J _f :J _b
Pt/C	0.702	0.266	0.585	0.215	1.237
Pt/active carbon	0.712	0.650	0.582	0.643	1.012
Pt3Ni/active carbon	0.709	1.258	0.567	0.923	1.363
Pt/rGO	0.696	1.088	0.540	0.710	1.532
Pt₃Ni/rGO	0.690	2.065	0.546	1.321	1.564
Pt ₃ Ni ₂ /rGO	0.692	1.908	0.550	1.216	1.569
PtNi/rGO	0.694	1.594	0.555	0.862	1.850