Electronic Supplementary Information

Pure Ni nanocrystallines anchored on rGO present ultrahigh electrocatalytic activity and stability in methanol oxidation

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S1.Experimental sections

Chemical Reagents and Materials

All chemicals used in this experiment were analytical grade and applied without further purification. Graphite powder was purchased from Tianjin Guangfu Fine Chemical Research Institute. GO (TEM image and XRD in Figure S1) was fabricated according to a modified Hummers method.^{1,2} Hydrazine hydrate was purchased from Aladdin Industrial Corporation (Shanghai, China). The commercial Pt/C catalyst (20 wt % Pt on Vulcan XC72R carbon) was purchased from Johnson Matthey. Double-distilled water (resistance >18 MΩ cm⁻¹) was used throughout all experiments.

Preparation of Ni nanoparticles modified reduced graphene oxide

Ni/rGO were fabricated by liquid phase laser ablation (LPLA) technique as shown in Scheme 1, the nickel target (99.99% in purity) was fixed in a vessel filled with 15 mL 0.01 M GO solution and ablated for 60 min by a Nd:YAG laser with wavelength of 1064 nm, pulse duration of 10 ns and per pulse laser energy of 60 mJ. After ablation to obtain brown flocculent precipitates (Figure S2b), hydrazine hydrate (0.2 ml) was then added to the above solution and kept at room temperature for 20 h. The resultant black solid (Figure S2c) was collected by centrifugation and washed with alcohol until the solution remained neutral.



Scheme 1. Schematic illustration of the formation of Ni/rGO

Materials characterization

A transmission electron microscopy (TEM) system (FEI Tecnai G2 F20) with a 200 kV acceleration voltage was used to obtain the structural information of the products and element distribution. X-ray diffraction (XRD) analysis of the collected powder products was performed by using a Philips X'Pert system with Cu-K α radiated (λ = 1.5419 Å). The surface chemical states were analysed by X-ray photoelectron spectroscopy (XPS, Thermo ESCACLB 250). The Ni content of the samples was measured by an inductively coupled plasma optical emission spectrometer (ICP-OES, Optima 7300 DV, America). Zeta potential were used to determine the surface charge of NiOx colloids with MALVERN instrument (Zetasizer3000HSa).

Electrochemical Measurements

Electrochemical measurements were performed on Zahner electrochemical workstation (Germany) using threeelectrode systems at room temperature. The reference and counter electrodes were Ag/AgCl (3M KCl) electrode and Pt foil respectively, and the working electrode was prepared through "drop-casting" method, namely, after polishing and washing the glass carbon electrode (GCE), 10 μL as-prepared Ni/rGO composites dispersion was pipetted onto the treated GCE. The concentrations of Ni were investigated by ICP measurement (Optima 7300 DV) and the total loading mass of the Ni was 0.75 μg. Detailed ICP measurements were performed as following: (1) Firstly, 2 mg Ni/rGO composites were dissolved in 1 mL water to form a colloidal solution; (2) 1 mL prepared Ni/rGO colloidal solution was extracted and added into 5 mL nitric acid (68 wt.%), then diluted with water to 25 mL; (3) The obtained solution was maintained at 100 °C for 24 h to ensure the samples sufficiently react with nitric acid; (4) Finally, 5 mL of the solution was extracted for ICP measurement. After drying the electrode in ambient environment for 12 h, 10 μL Nafion solution were following dropped onto these electrodes and dried for another 4 h. Cyclic voltammetry (CV) were conducted in 1 M KOH solution with different concentrations of CH_3OH at scan rates of 50 mV/s. Chronoamperometry (CA) and cycling stability were assessed in 1 M KOH with 1 M CH_3OH . The mass activity of Ni/rGO, which was defined as the peak current per amount of Ni loading, was adopted for evaluating their electrocatalytic performances. For comparison, the commercial Pt/C electrodes were prepared by the same method.





Figure S1. (a) TEM images and the corresponding SAED pattern of GO, (b) XRD patterns of GO and Graphite



Figure S2. (a) GO solution, (b) NiO_x -GO solution, (c) the prepared Ni/rGO.





Figure S3. Zeta potential of fresh NiO_x colloids by LAL in DI water.



Figure S5. Particle size distribution histogram of Ni nanocrystallines on graphene

Table S1 Electrocatalytic performance comparison between Ni/rGO composite and other recently reported Ni-

Catalysts	Mass activity (mA/mg)	Condition	Ref.
Ni/rGO	1600	1 M CH ₃ OH+1 M KOH	This work
commercial Pt/C	925	1 M CH ₃ OH+1 M KOH	This work
Ni-Co-P-O	1567	1 M CH ₃ OH + 0.5 M KOH	3
microsphere Ni-P-O	1490	1 M CH ₃ OH + 0.5 M KOH	4
CNT-Ni/SiC-700	1000	1 M CH ₃ OH +1 M KOH	5
Ni@CNT	966	$1 \text{ M CH}_3\text{OH} + 1 \text{ M KOH}$	6
CNFs-Ni	400	0.5 M CH ₃ OH +1 M KOH	7
Ni-P/RGO	117	0.5 M CH ₃ OH+1 M KOH	8
nanosphere-like NiCo ₂ O ₄	40.9	0.5 M CH ₃ OH + 1 M KOH	9

based catalysts at a scan rate of 50 mV/s.



Figure S6. (a) The relationship between the oxidation peak current and the square root of the scan rate for NiO/rGO, (b) The corresponding oxidation peak current of NiO/rGO at different concentration of methanol.



Figure S7. TEM images and HR-TEM images of NiO/rGO after 1000 cycling tests

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