Facile electrolysis-solvothermal synthesis of NiO_x/graphene for enhanced ethanol oxidation to acetate

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Experimental section

Chemicals and materials

Nickel wire was bought from Runde Metal Material Company (China). Graphite powder (80 mesh) was bought from Qingdao Graphite Company. Tetrabutylammonium tetrafluoroborate (TBABF4, 98%) and propylene carbonate (PC, 99.9%) were purchased from Aladdin.

Preparation of NiO_x/G

The NiOx/G was prepared by a two electrode electrolysis-solvothermal method. 40 mg graphite was put in a plastic tube with Pt plate inserted and used as cathode. Polished Ni wire was served as anode. The two electrodes were immersed in PC solvent containing 0.6 M TBA BF4. The working voltage was set at 30 V for 2 h, 4 h and 6 h respectively. Subsequently, the exfoliated graphene was collected from the cathode and mixed with the electrolyte solvent. This mixed solution was finally transferred to an 80 mL Teflon-lined container. Under Ar atmosphere, the resultant suspension was stirred (500 rpm) and treated at 160 °C for 12 h. Finally, the solution was filtered. As-obtained product was washed with PC solution twice and ethanol twice, and dried at 60 °C for 8 h. the same method was applied for the synthesis of NiO_x, except that exfoliated graphene was excluded from the electrolyte solvent.

Characterization

X-ray diffraction (XRD) analysis was used to analysis the crystalline of as-prepared samples on an X-ray diffractometer (Ultima IV-185) with Cu Ka radiation. X-ray photoelectron spectroscopy (XPS) was operated to detect the chemical compositions of the materials on Thermo Fisher SCIENTIFIC using Al Ka X-ray source. Transmission electron microscopy (TEM, FEI Tecnai F20) and scanning electron microscopy (SEM, JSM-7001F) were used to study the morphologies of the samples.

Electrochemical tests

Electrochemical studies of NiO_x/G were carried out in 1 M KOH solution with 1 M ethanol by a CHI Instruments 760 E electrochemical workstation using a standard three-electrode setup. A graphite rod, a catalyst-coated glassy carbon electrode (GCE, 3mm), and Hg/HgO (dipped in 1M KOH) were used as the counter, working, and reference electrodes, respectively. The catalyst ink was prepared by dispersing 5.0 mg of catalyst into 0.75 ml of anhydrous ethanol and 0.25 ml of ultrapure water with 0.03 ml of Nafion solution (5 wt%), then treated with ultra-sonication for 30 min. 5 μl such ink was dip coated on glassy carbon electrode and dried for several hours. The electrocatalytic activity for EOR was investigated by cyclic voltammograms (CVs) with a scan rate of 50 mV/s. All electrochemical measurement was performed at room temperature. All potentials were converted to reversible hydrogen electrode (RHE) according to the following equation:

$$E(RHE) = E(Hg/HgO)+0.0591*pH+0.098$$

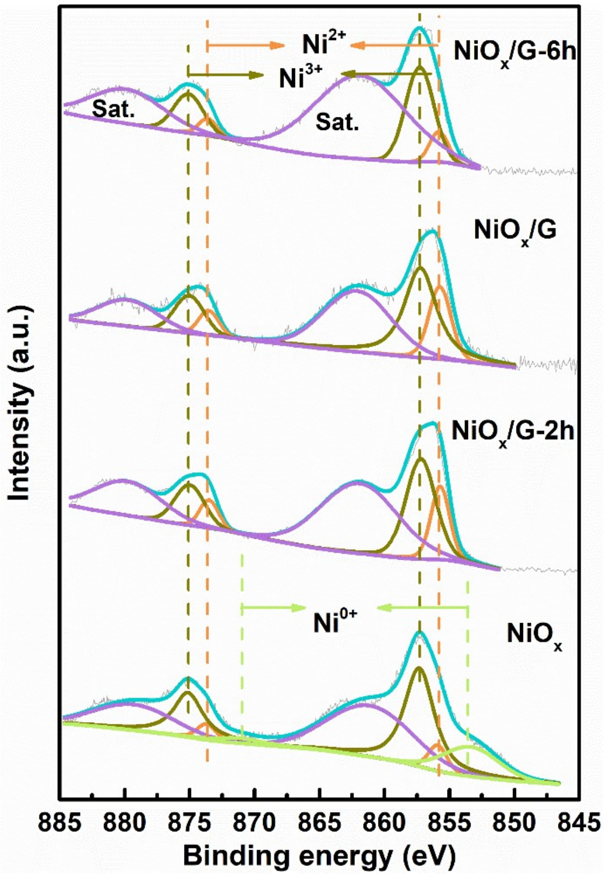


Fig. S1 XPS Ni 2p spectra for NiOx, NiO_x/G, NiO_x/G-2h and NiO_x/G-6h.

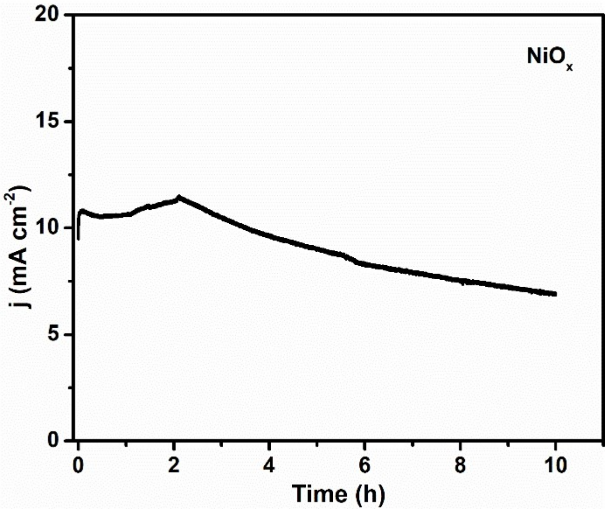


Fig. S2 chronoamperometry curve of NiO_x

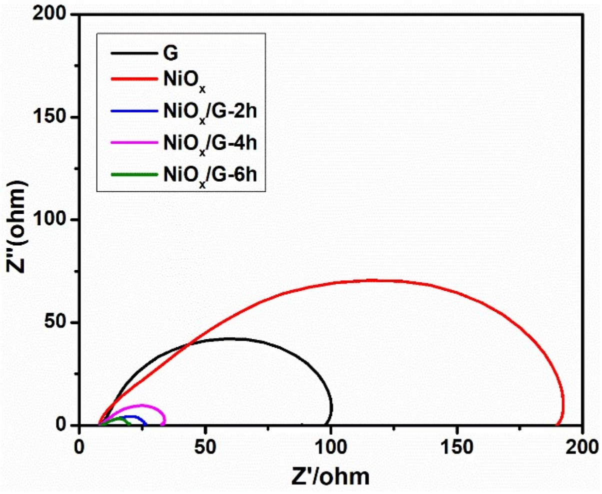


Fig.S3 EIS spectra for NiO_x/G electrolyzed for different time, NiO_x and G.

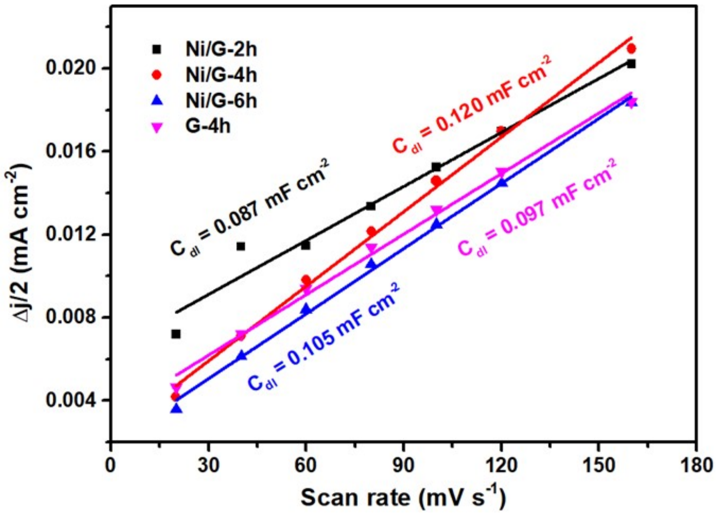
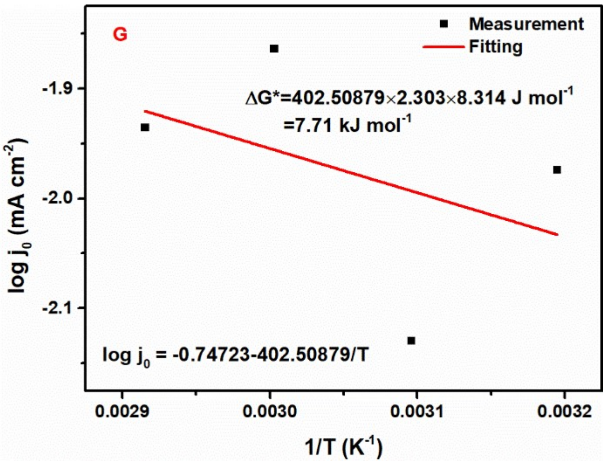


Fig. S4 C_{dl} values of catalysts derived from CV curves in non-faradaic region



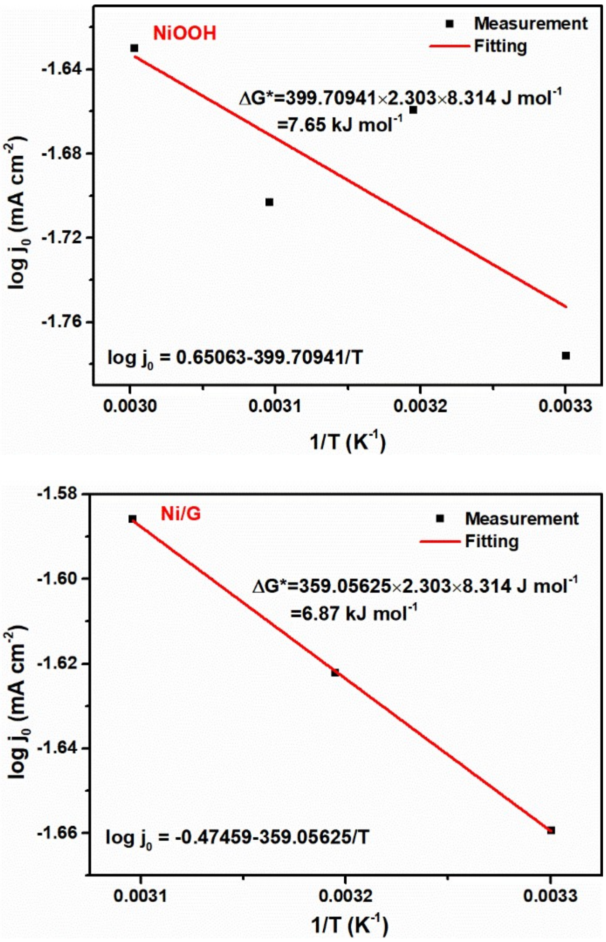


Fig. S5 Arrhenius curves of catalysts derived from LSV curves at various temperatures.

Table S1. Calculated Ni^{3+} ratio for all catalysts based on XPS spectra.

catalysts	NiO_x	NiO_x/G-2h	NiO_x/G	NiO_x/G-6h
$Ni^{3+}/(Ni^{2+}+Ni^{3+})$	0.87	0.68	0.70	0.81

Table S2 Summary of the ethanol oxidation activities on Ni-based catalysts

Catalyst	Onset potential (V vs.RHE)	Peak current density (mA cm^{-2})	Electrolyte	References
NiOx/G	1.34	296.5	1M Ethanol 1M KOH	This work
NiO@C/CC		119.1	1M Ethanol 1M KOH	[1]

Ni3S2 NW	1.31	Around 225	1M Ethanol 1M KOH	[2]
Ni/aHC	1.47	17.64	1M Ethanol 1M NaOH	[3]
Cu,Ni,Fe2O3/ GCE	0.3 V vs.Hg/HgO	101	1 M Ethanol 0.5 M NaOH	[4]
Ni/RGO	1.39	12	3M Ethanol 1M KOH	[5]
Cu-doped NiOOH		227	1M Ethanol 1M KOH	[6]
β-$Ni(OH)_2$	1.29	13 (300 on NF)	0.5M Ethanol 1M KOH	[7]
Ni0.75Co0.25 Se2	About 1.3	About 90	1M Ethanol 1M KOH	[8]
$Ni(OH)_2$ NS	1.4	163	1M Ethanol 1M KOH	[9]
$Ni_{0.9}Co_{0.1}$	1.42	142	1M Ethanol 3M KOH	[10]

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