

Supporting Information

Single-Step Electrophoretic Deposition of Non-Noble Metal Catalyst Layer with Low Onset Voltage for Ethanol Electro-oxidation

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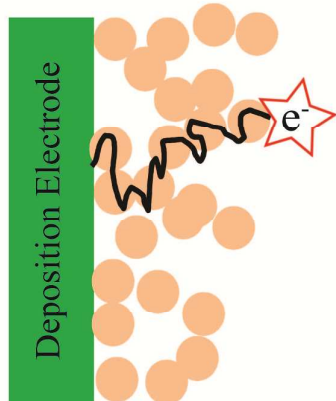
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a) Drop casting



b) Electrophoretic deposition

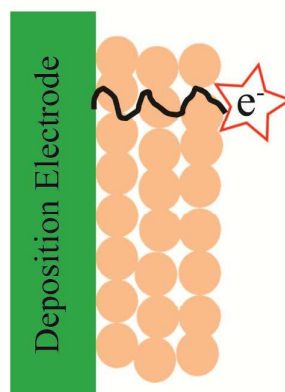


Figure S1 Schematic illustrations of the coating structures deposited by (a) drop casting and (b) electrophoretic technique.

To understand the behavior of nanographitic flakes and NiO nanoparticles during the EPD process, the measured zeta potential and mobility of the different suspensions displayed in **Table S1**. The suspension of the EPD process (Suspension 1) exhibits a positive mobility of $1.14 \times 10^{-9} \text{ m}^2/\text{Vs}$, but the values of the mobility and zeta potential of the suspension having only NGr and MNH (Suspension 2) are two times higher than those of Suspension 1. The positive sign of the mobilities of Suspensions 1 and 2 is due to the attachment of Mg^{2+} ions to NGr. As for the suspensions which do not have nanographitic flakes, the solution with colloidal NiO nanoparticles and MNH (Suspension 3) shows a slightly positive mobility, which becomes negative when NiO concentration further increases (Suspension 4). It can be seen from **Table S1** that an increase in the NiO nanoparticles concentration leads to negatively charged colloids. It means that NiO nanoparticles show a negative behavior in isopropyl alcohol. Reason for small positively charged NiO nanoparticles in Suspension 3 is the attachment of Mg^{2+} ions to NiO nanoparticles. In the EPD solution, the concentration of Mg^{2+} ions is similar to the concentration of that in Suspension 3 but a part of Mg^{2+} ions are attached to the surface of graphene. Therefore, it is most likely that NiO nanoparticles in the EPD solution become slightly negative.

The EPD experiments were carried out on Suspensions 3 and 4 to study the behavior of NiO nanoparticles in isopropyl alcohol. In these experiments, copper plates were applied as the cathode electrode (negative pole) and as the anode (positive pole) electrode. The EPD procedure was the same as the one used for the fabrication of the sample NGr-NiO/ITO. The Raman spectra and XPS spectra analysis of the EPD cathode (the same electrode used for fabrication of the catalyst layers) are presented in **Figure S2**. These results demonstrate that NiO nanoparticles have not been deposited on the

cathode during the EPD.

The value of the mobility of NiO nanoparticles in Suspension 3 and 4 is slightly positive and negative, respectively. Consequently, in these suspensions NiO nanoparticles cannot be deposited on the EPD cathode. Furthermore, the negative mobility of NiO nanoparticles measured in the case of Suspension 4 may be explained by the possible dehydrogenation of isopropyl alcohol on NiO nanoparticles [1, 2]. The influence of MNH on the surface of NiO nanoparticles is the same as in the case of nanographitic flakes (MNH positively charges the surfaces of NiO nanoparticles and nanographitic flakes) but the role of MNH is not dominant in the case of Suspensions 3 and 4. In other words, during the EPD process, NiO nanoparticles attach to the surface of nanographitic flakes during the ultrasonic dispersion in Suspension 1 (containing 5 mg of NGr, 5 mg of NiO and 10 mg of MNH in 20 mL of IPA) and only then NiO nanoparticle-attached nanographitic flakes are deposited on the cathode (ITO).

Table S1 Zeta potential and mobility of the different solutions used in this study.

Suspension	NGr (mg)	NiO (mg)	MNH (mg)	IPA (mL)	Mobility (m^2/Vs)	Zeta potential (mV)
1 (suspension used for the EPD)	5	5	10	20	1.14×10^{-9}	16.9
2	5	-	10	20	2.13×10^{-9}	31.7
3	-	5	10	20	2.78×10^{-11}	0.4
4	-	10	10	20	-3.26×10^{-10}	-4.9

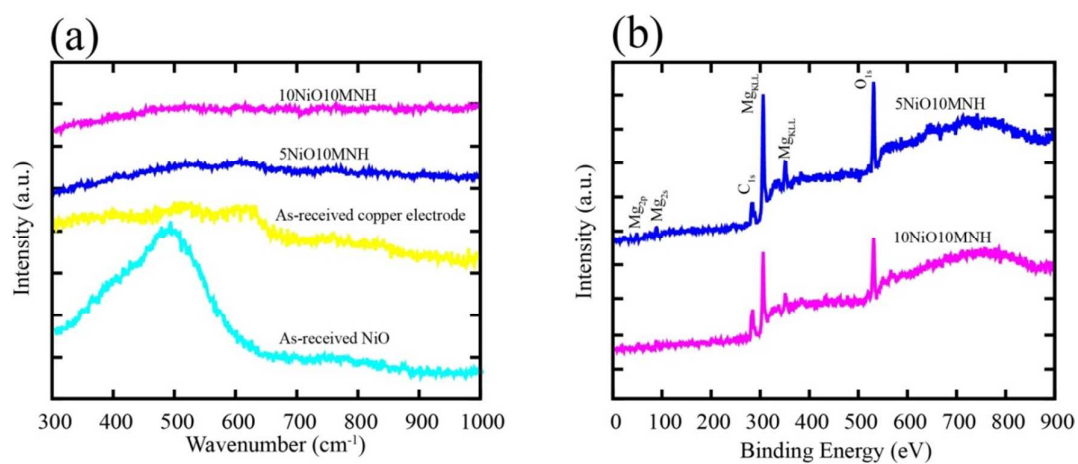


Figure S2 (a) Raman spectra and (b) XPS spectra analysis of the EPD cathodes obtained with Suspensions 3 and 4.

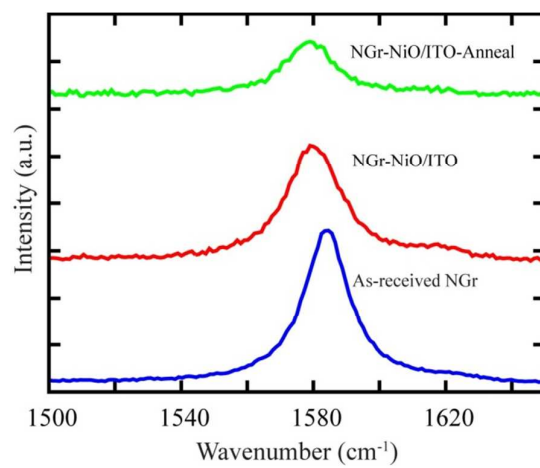


Figure S3 Enlarged spectral region around the Raman G-band of the NGr-NiO/ITO, NGr-NiO/ITO-Anneal and pure nanographitic flakes.

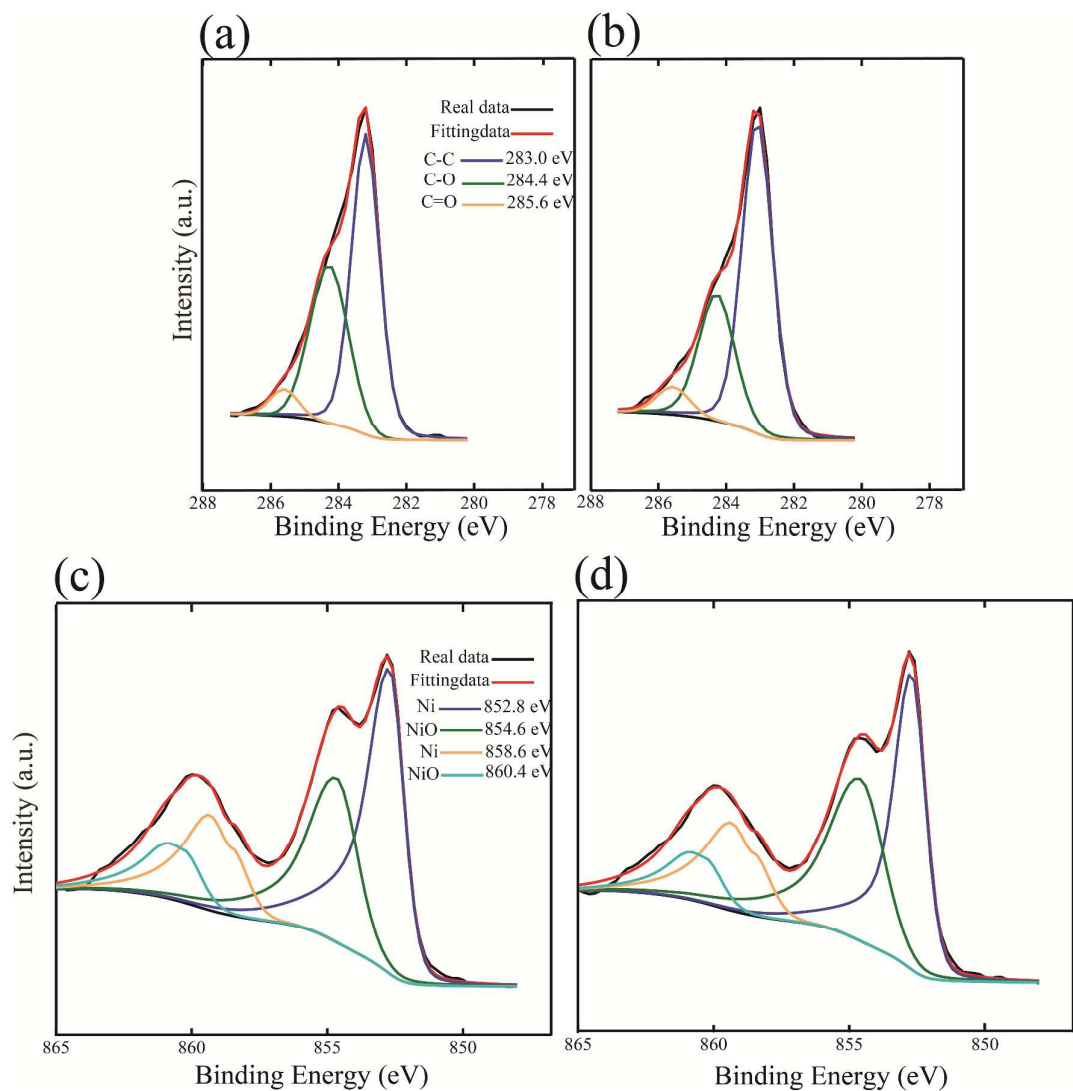


Figure S4 Deconvolution of XPS peaks in the C_{1s} spectra for (a) NGr-NiO/ITO and (b) NGr-NiO/ITO-Anneal, and in the $Ni_{2p_{3/2}}$ spectra for (c) the as-received NiO nanoparticles and (d) the as-received NiO nanoparticles after the annealing treatment.

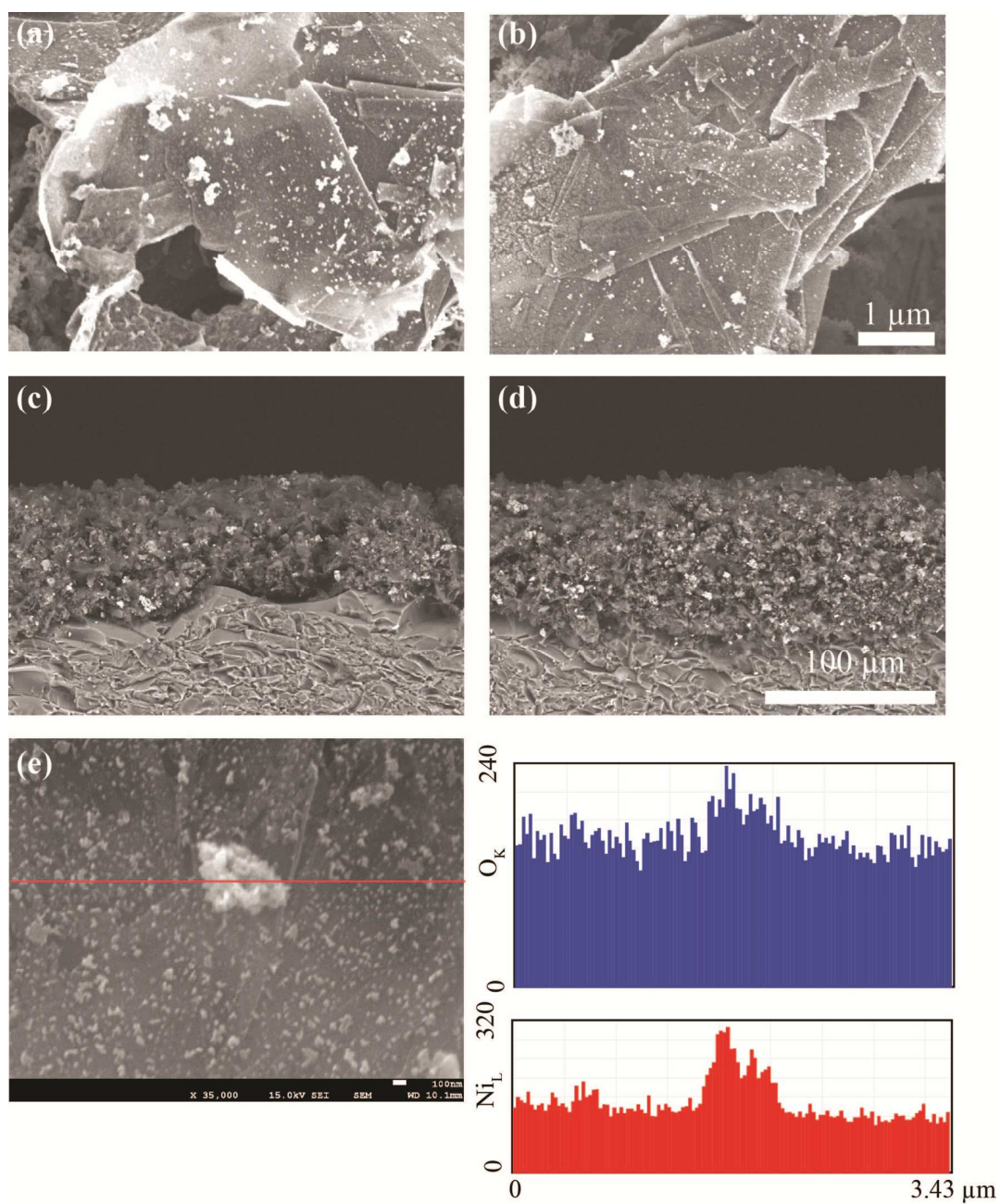


Figure S5 Top-view SEM images of (a) the non-annealed and (b) the annealed samples. The cross-section images of (c) NGr-NiO/ITO and (d) NGr-NiO/ITO-Anneal. (e) EDS elemental line mappings for NGr-NiO/ITO.

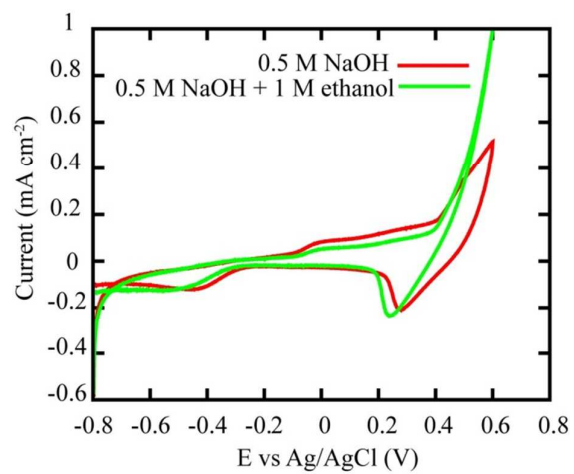


Figure S6 CV graphs of NGr-NiO/ITO annealed at 300°C in 0.5 M NaOH with and without 1.0 M ethanol.

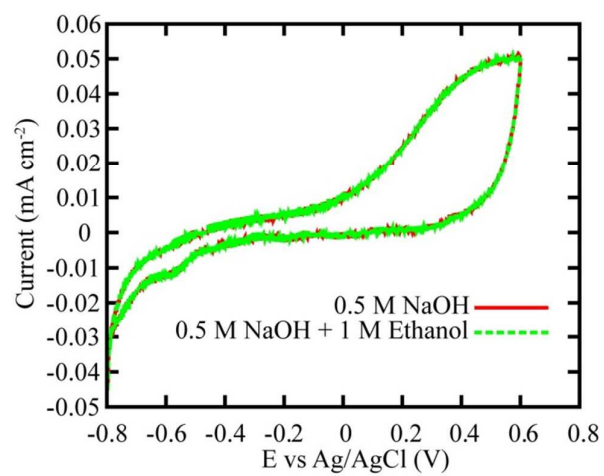


Figure S7 CV graphs of the samples made by the same EPD process but without NiO nanoparticles.

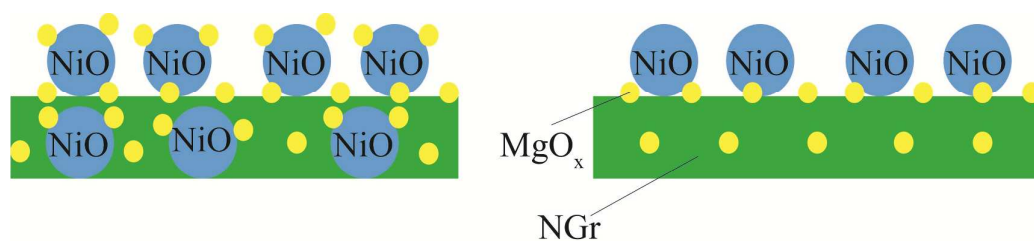


Figure S8 Schematic diagrams of the catalyst layers fabricated by (left) the one-step EPD technique (NGr-NiO/ITO) and (right) the EPD followed by the ALD process for NiO. Both samples show similar behavior in their CV curves (same onset voltage of -0.2 V (vs. Ag/AgCl)).

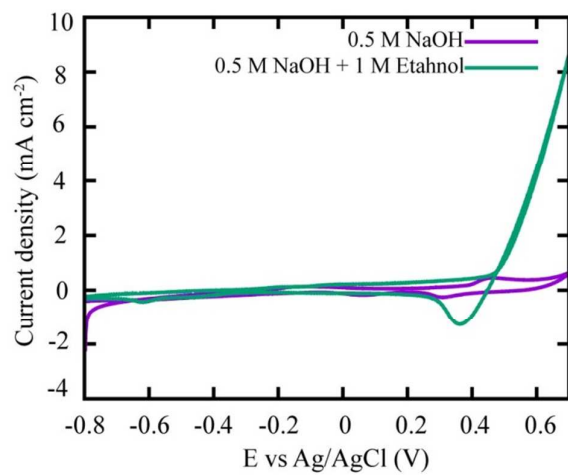


Figure S9 CV Curves of NGr-NiO/ITO-Anneal shown in a wider potential range.

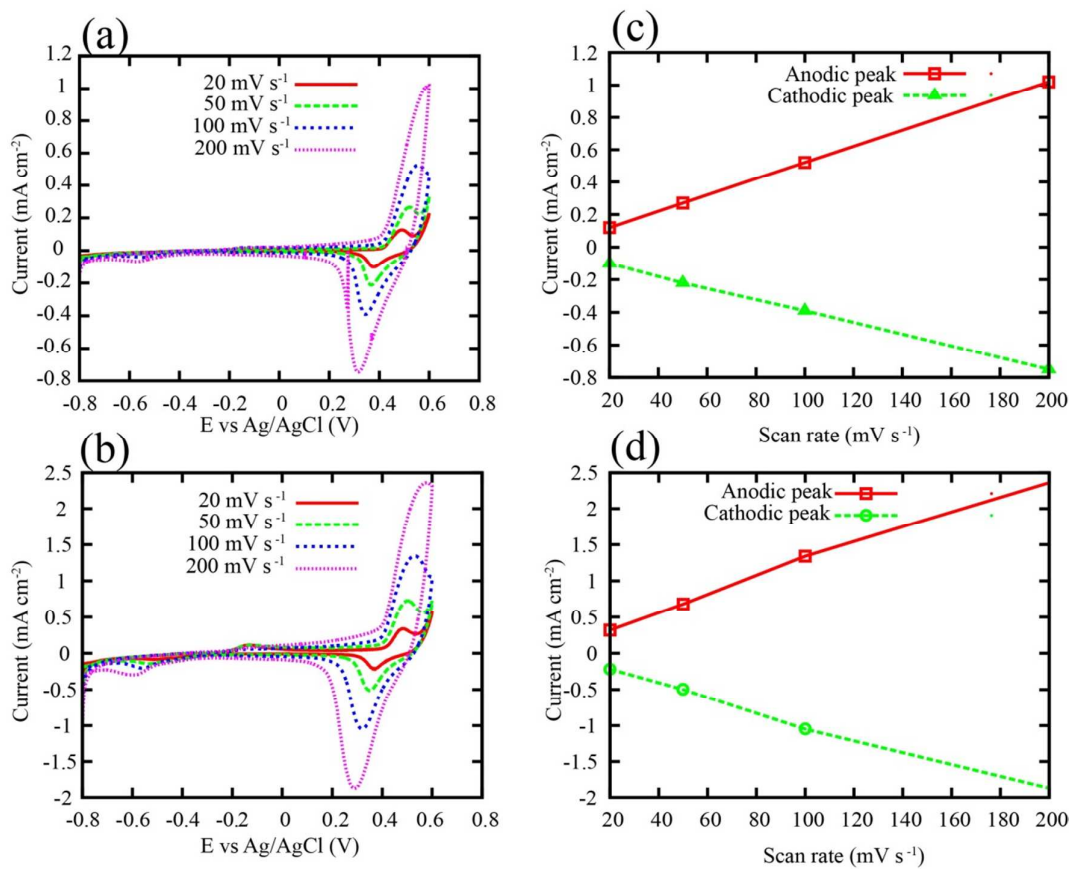


Figure S10 Cyclic voltammograms for (a) NGr-NiO/ITO and (b) NGr-NiO/ITO-Anneal samples in the presence of an aqueous solution with 0.5 M NaOH at different scan rates; plots of the forward peak current vs. scan rate for (c) NGr-NiO/ITO and (d) NGr-NiO/ITO-Anneal.

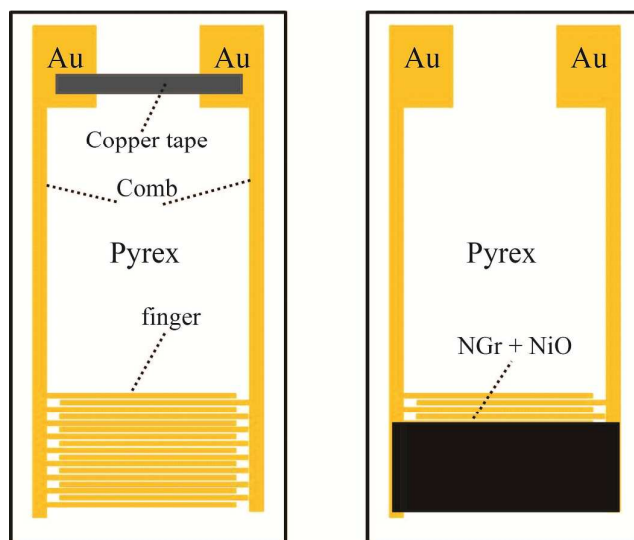


Figure S11 Illustration scheme of the interdigitated electrode (IDE) before the EPD process (left) and after the EPD process (right).

The resistances of NGr-NiO/IDE and NGr-NiO/IDE-Anneal for different temperatures are calculated from the slope of the linear fitting of the I-V curves in the voltage range between -2 and 2 V.

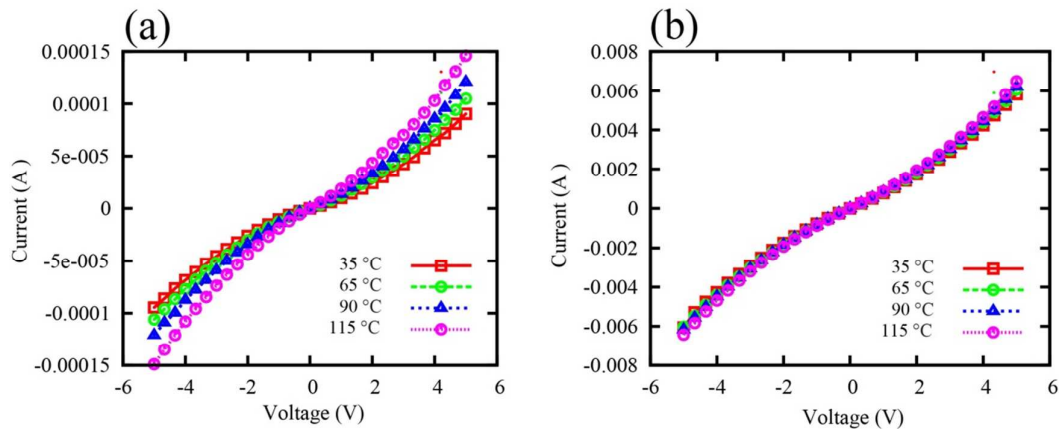


Figure S12 I-V experiments of (a) NGr-NiO/IDE, and (b) NGr-NiO/IDE-Anneal measured at various temperatures.

Figure S11 demonstrates the Nyquist plots of non-annealed and annealed samples in the frequency range of 100 kHz–300 mHz taken at voltages of 0.25 and 0.55 V (vs. Ag/AgCl). The measured Nyquist plots consist of two semicircles in the high and the intermediate-frequency regions. The semicircle at high frequencies corresponds to the parallel combination of the charge transfer resistance R_{int} and the interface capacitance C_{int} , which are due to the injection of electrons from the fabricated catalyst layers to the ITO. The R_{ct} and C_{dl} , which arise from the electron transfer from the solution to the fabricated catalyst layers, represent ethanol electro-oxidation. The R_{ct} of NGr-NiO/ITO-Anneal is lower than that of NGr-NiO/ITO at 0.55 V due to the increased charge carrier density and the extended conjugated network of NGr, while the R_{ct} of NGr-NiO/ITO is much lower than that of NGr-NiO/ITO-Anneal at 0.25 V owing to the hopping charge transport.

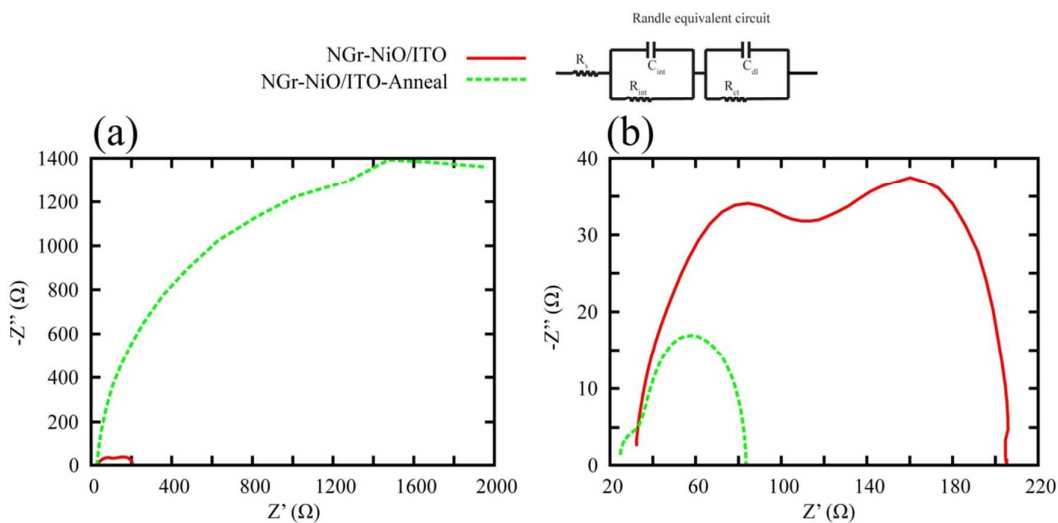


Figure S13 Nyquist plots for NGr-NiO/ITO and NGr-NiO/ITO-Anneal samples obtained at (a) 0.25 and (b) 0.55 V (vs. Ag/AgCl) in 0.5 M NaOH with 1 M ethanol.

References

- (1) Kulkarni, D.; Wachs, I. E. Isopropanol Oxidation by Pure Metal Oxide Catalysts: Number of Active Surface Sites and Turnover Frequencies *Appl. Catal. A* **2002**, 237, 121-137.
- (2) Hussein, G. A. M.; Gatesy, B. C. Surface and Catalytic Properties of Yttrium Oxide: Evidence from Infrared Spectroscopy *J. Catal.* **1998**, 176, 395-404.