

## Electronic Supporting Information

### Scalable synthesis of Pd nanoparticles loaded hierarchically porous graphene network through multiple synergistic interactions

Zheye Zhang, Yue Dong, Lu Wang and Shuai Wang\*

School of Chemistry & Chemical Engineering, Huazhong University of Science and Technology, Wuhan, 430074, P. R. China.

\*E-mail: chmsamuel@mail.hust.edu.cn

### Experimental Section

#### 1. Synthesis of graphene oxide (GO)

GO was synthesized from graphite powder based on modified Hummer's method.<sup>[1]</sup> In details, 1 g of graphite powder (100 mesh, from Alfa Aesar Reagent Co., Ltd, USA) was mixed with 0.5 g NaNO<sub>3</sub> and 23 mL H<sub>2</sub>SO<sub>4</sub> (98 %), the mixture was cooled to 0 °C. Then, 3 g KMnO<sub>4</sub> was added slowly to keep the temperature of the suspension lower than 5 °C and magnetic stirred for 2~3 h. Successively, the reaction system was transferred to 35 °C water bath and stirred for about 2 h, forming a thick paste. Then, 46 mL distilled water was added slowly to the solution, and the solution was stirred for 30 min at 95 °C. The mixture was further diluted with 140 mL distilled water, treated with 2 mL H<sub>2</sub>O<sub>2</sub> (30 %), washed with 50 mL HCl (1:10) and distilled water 2~3 times and then resuspended in distilled water. The concentration of prepared graphene oxide solution is about 5 mg mL<sup>-1</sup>.

#### 2. Synthesis of GF and GF/Ni composites

Ni foams (1 mm thick, pore size: 200~300 μm, from Changsha Lyrun New Material Co., Ltd, China) were used as 3D scaffold templates for the solution growth of GF. They were cut into pieces of 1 × 1 cm<sup>2</sup> and carefully washed by acetone, acetic acid and deionized water before use. Then the Ni foams were immersed into a 3 mg

mL<sup>-1</sup> GO suspension at 80 °C for 6 h. After they had cooled to room temperature, the GF/Ni were taken out and repeatedly rinsed with deionized water to remove physisorbed GO platelets. For comparison, GF was prepared by removing Ni from the GF/Ni through immersing GF/Ni in hydrochloric acid (6 mol L<sup>-1</sup>) at 80 °C for 6 h. Finally, the released GF were rinsed with deionized water to remove residual acid and metal ions.

### **3. Synthesis of Pd/GF and Pd/GF/Ni composites**

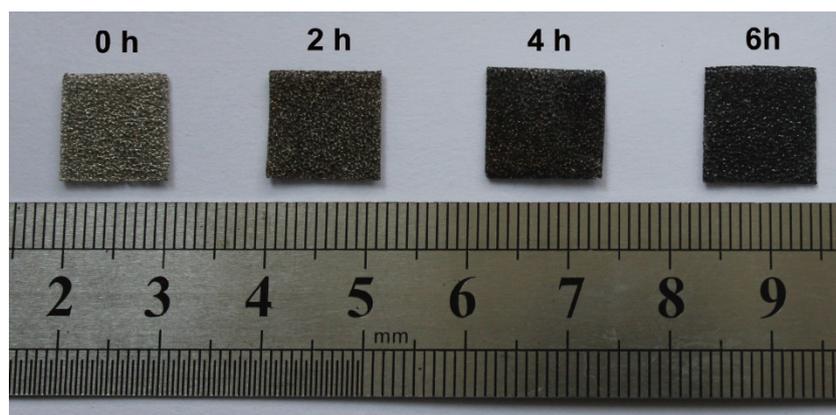
The prepared GF or GF/Ni was directly immersed into K<sub>2</sub>PdCl<sub>4</sub> aqueous solution (0.05~1 mM) for a desired period (5~30 min) in an ice bath and followed by rinsing with deionized water to remove the remaining reagents.

### **Materials characterization**

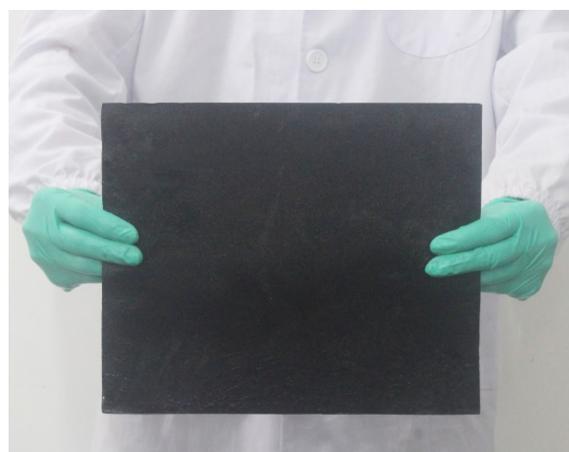
The specific surface area of the GF is determined by methylene blue absorption, which is widely used for graphitic materials.<sup>[2,3]</sup> GF with an area of 4 cm<sup>2</sup> are mechanically stirred in 10 ml methylene blue solution (4 × 10<sup>-4</sup> M) for 3 days to reach maximum absorption. The concentrations of methylene blue in the solution before and after the absorption by GF is determined by UV-Abs spectroscopy at 665 nm wavelength. Each absorbed methylene blue molecule corresponds to 1.35 nm<sup>2</sup> of surface area. The surface morphology and structure of the as prepared samples were characterized by field-emission scanning electron microscope (SEM, FEI, Nova NanoSEM 450), Transmission electron microscope (TEM, FEI, Tecnai G2 F20), high resolution TEM (HRTEM, 200 kV), and electron diffraction (ED) were also used to characterize the microstructures of the samples. X-ray powder diffraction (XRD) patterns were recorded using a diffractometer (X' Pert PRO, Panalytical B.V., Netherlands) equipped with a Cu K $\alpha$  radiation source ( $\lambda$  =1.5406 Å). X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos-Axis spectrometer with monochromatic Al K $\alpha$ (1486.71 eV) X-ray radiation (15 kV and 10 mA) and a hemispherical electron energy analyzer.

## **Electrochemical characterization**

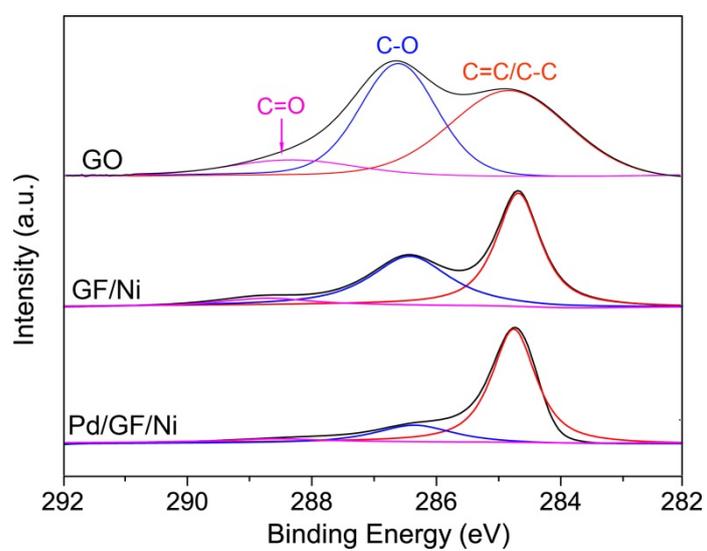
The electrochemical measurements of Pd/GF/Ni composites were conducted in a three-electrode cell by using a CHI 660E electrochemical workstation (CH Instruments Inc. US). The Pd/GF/Ni composites were directly served as working electrode, the counter and reference electrodes were Pt foil and saturated calomel electrode (SCE), respectively. For Pd/GF and commercial Pd/C electrocatalysts (Alfer Aesar, Pd 5 % on carbon) test, a glassy carbon electrode (GCE, 3 mm in diameter) served as working electrode, the thin film electrode was prepared as follows: 1 mg electrocatalyst was added into 1 mL of ethanol and 10  $\mu\text{L}$  of 5 wt% Nafion solution, and dispersed by ultrasonication for 30 min to form a uniform suspension. Next, 10  $\mu\text{L}$  of the dispersion was dropped onto a freshly polished GCE and was dried under ambient conditions. The activity evaluation of electrocatalysts for the ethanol oxidation reaction was carried out in a nitrogen-saturated 1 M KOH electrolyte containing 1 M ethanol. Cyclic voltammetry curves were recorded by applying a linear potential scan at a sweep rate of 50  $\text{mV s}^{-1}$ .



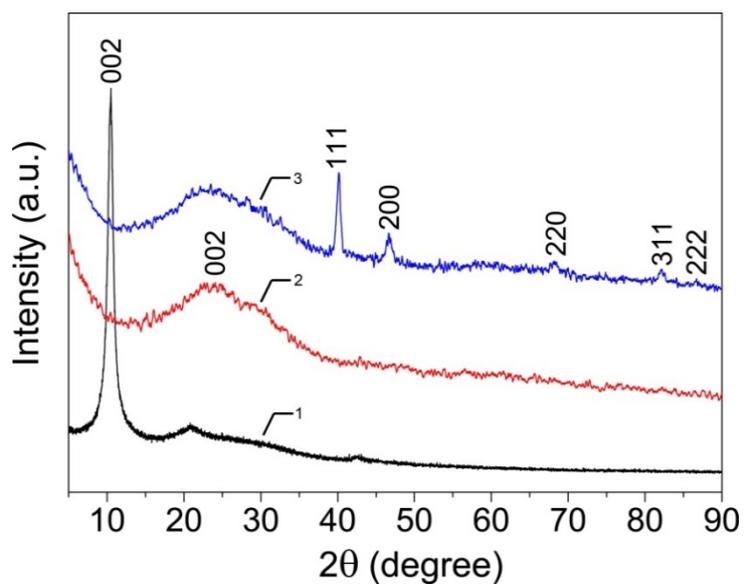
**Fig. S1** Photographs of the GF/Ni prepared by immersing Ni foam into GO solution for different time.



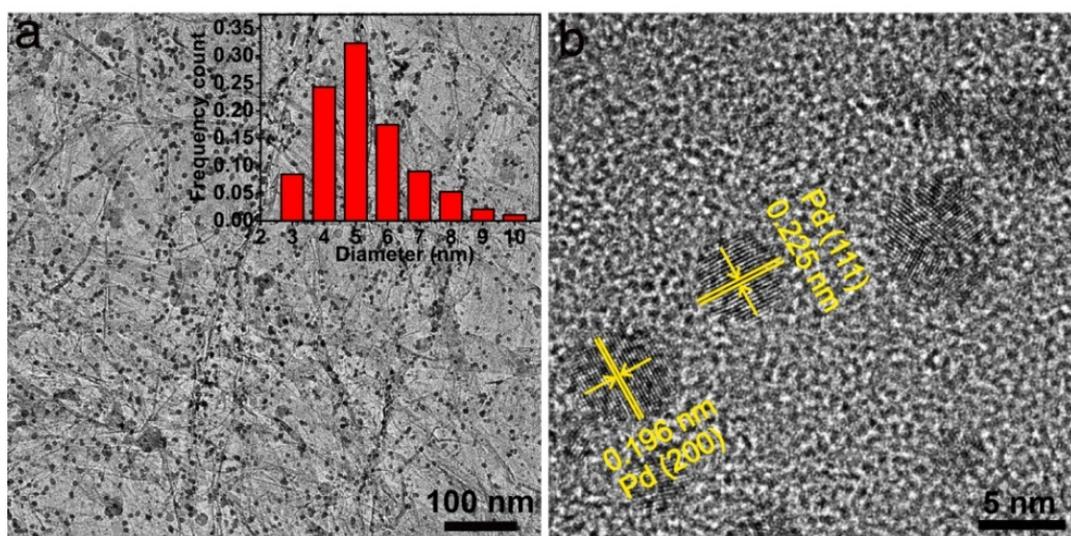
**Fig. S2** Photograph of GF/Ni with large size (30 × 25 cm).



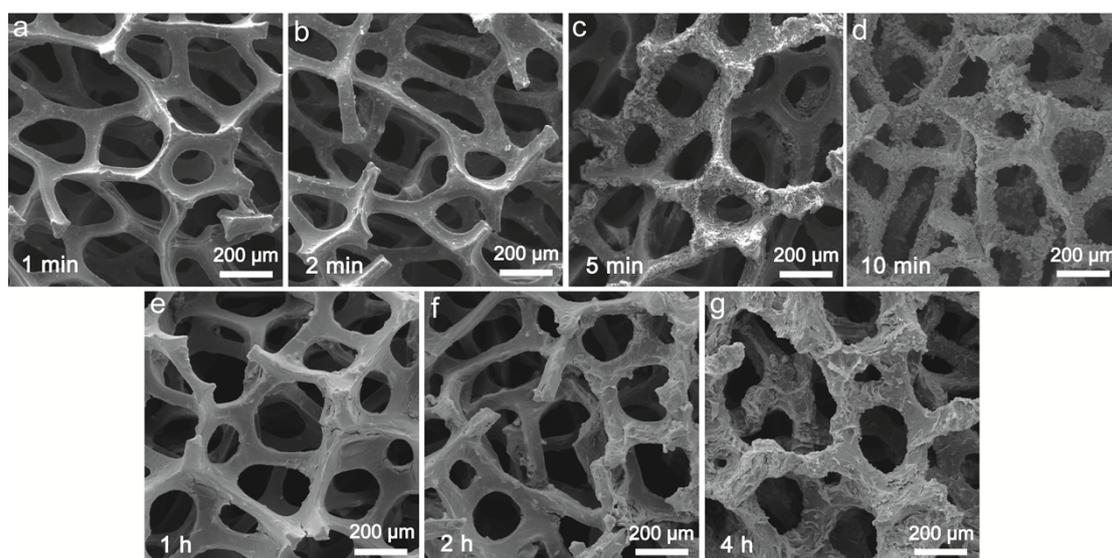
**Fig. S3** The deconvoluted C 1s spectrum of GO, GF/Ni and Pd/GF/Ni.



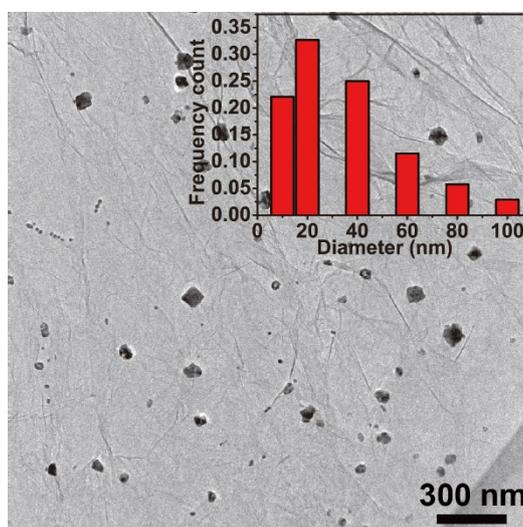
**Fig. S4** XRD patterns of (1) GO, (2) GF and (3) Pd/GF/Ni with etching Ni.



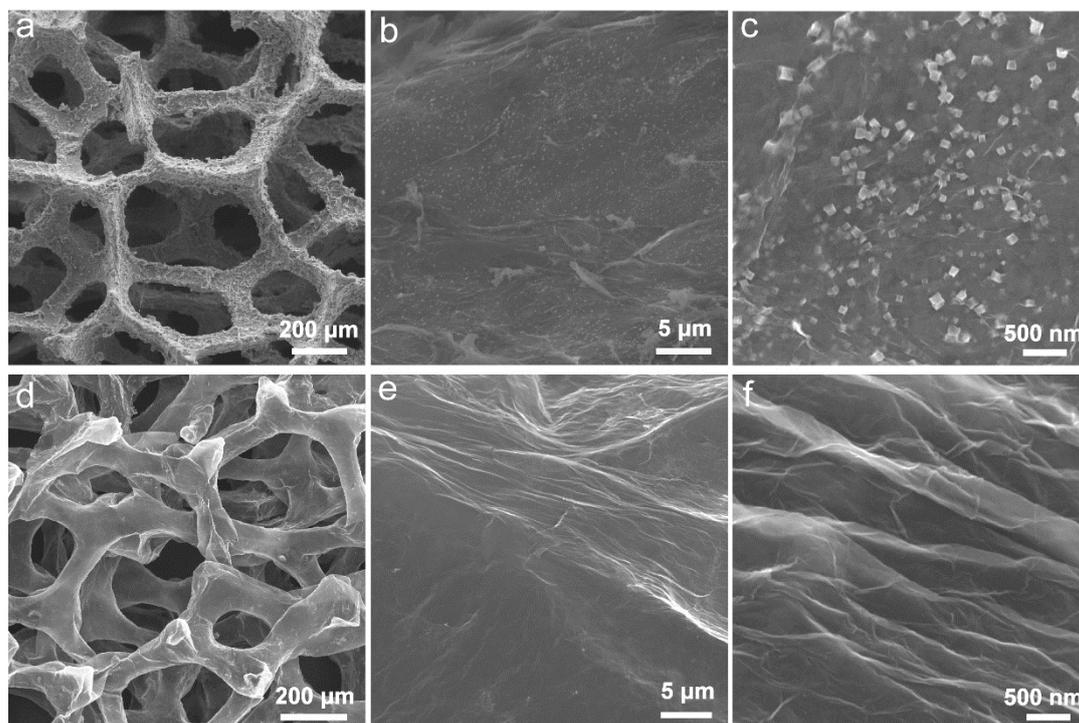
**Fig. S5** (a) TEM image of Pd/GF/Ni. (b) HRTEM image of Pd/GF/Ni. Insert is the corresponding particle size distribution histogram of Pd NPs.



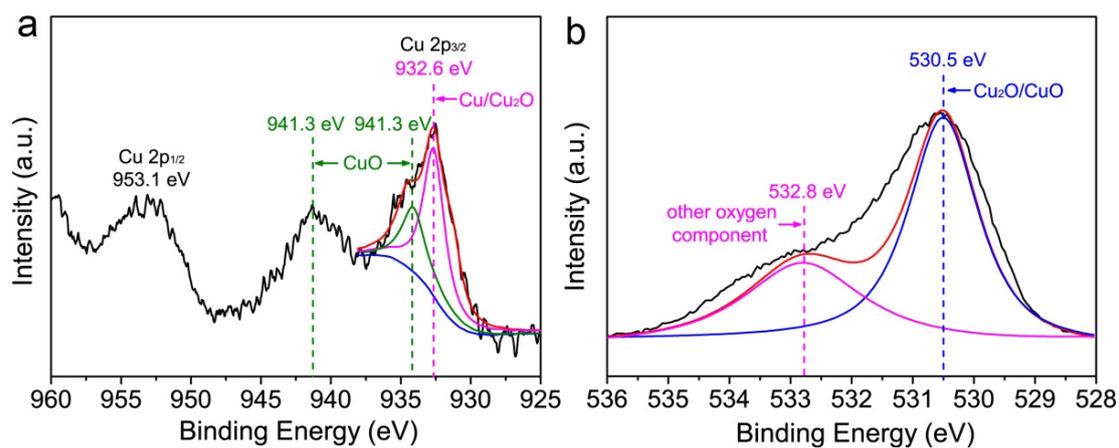
**Fig. S6** SEM images of Pd/GF/Ni (a-d) Time dependent effect of GF/Ni react with  $K_2PdCl_4$  solution. (e-g) Time dependent effect of Ni react with GO solution.



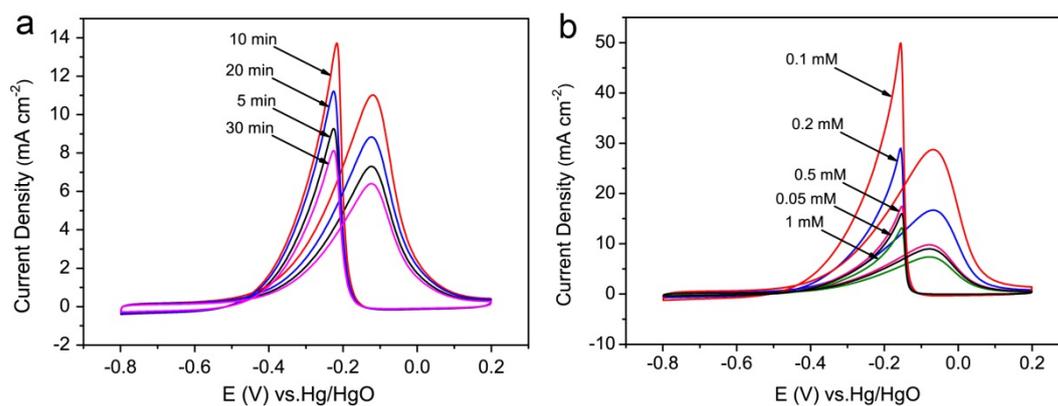
**Fig. S7** TEM image of Pd/GF. Insert is the corresponding particle size distribution histogram of Pd NPs.



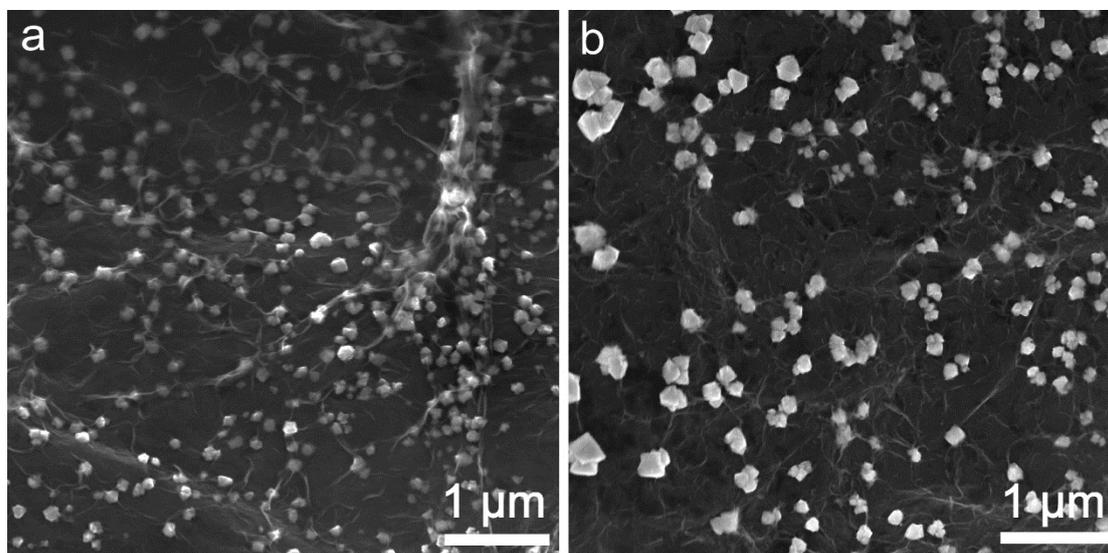
**Fig. S8** SEM images of the resultant products of immersing (a) GF/Ni and (b) GF in CuSO<sub>4</sub> solution.



**Fig. S9** XPS spectra of (a) Cu 2p and (b) O 1s on CuO<sub>x</sub> NPs

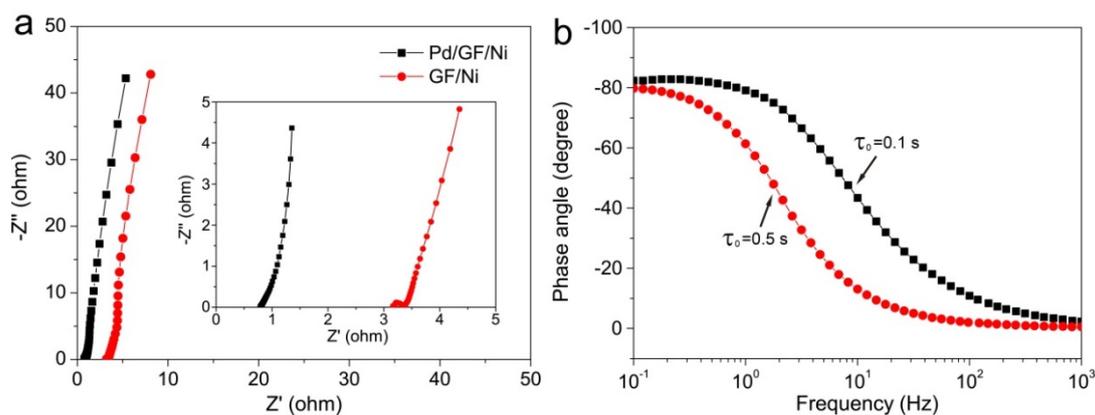


**Fig. S10** The CV curves of ethanol oxidation in a 1.0 M KOH with 0.5 M ethanol solution at a scan rate of  $50 \text{ mV s}^{-1}$  for Pd/GF/Ni: (a) react for different time in 0.1 mM  $\text{K}_2\text{PdCl}_4$  solution, (b) react for 10 min in different concentration of  $\text{K}_2\text{PdCl}_4$  solution.



**Fig. S11** SEM images of the Pd/GF/Ni: (a) react for 30 min in 0.1 mM  $\text{K}_2\text{PdCl}_4$  solution and (b) react for 10 min in 1 mM  $\text{K}_2\text{PdCl}_4$  solution.

To study the electrochemical performance of Pd/GF/Ni in real full cells, we have tested our catalyst in the electro-oxidation of ethanol in an alkaline medium under the optimized conditions, as shown in Fig. S10 and S11. Fig. S10 shows the CV curves of Pd/GF/Ni with different reaction time in 0.1 mM  $K_2PdCl_4$  solution and react for 10 min in different concentration of  $K_2PdCl_4$  solution. At first, the peak current density of CV curves increase with the immersion time and the concentration of  $K_2PdCl_4$  solution, indicating that more active Pd NPs deposited on GF/Ni contribute to the process of electrocatalysis. But then, the situation changes when the immersion time and concentration further increase from 10 to 30 min and 0.1 to 1 mM, respectively. This phenomenon can be ascribed to the Pd NPs will become large with the extension of reaction time, also the high concentration of  $K_2PdCl_4$  solution contributes to the growth and aggregation of Pd NPs (Fig. S11).



**Fig. S12** (a) Nyquist plots of GF/Ni and Pd/GF/Ni electrodes carried out in a frequency range from 10 mHz to 100 kHz. (b) Bode plots of phase angle versus frequency for GF/Ni and Pd/GF/Ni electrodes.

## Reference

- 1 W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.
- 2 M. F. El-Kady, V. Strong, S. Dubin and R. B. Kaner, *Science*, 2012, **335**, 1326.
- 3 X. Yang, C. Cheng, Y. Wang and L. Dan, *Science*, 2013, **341**, 534.