

Electronic Supplementary Information

Synthesis and characterization of Pd-Ni core-shell nanocatalysts for alkaline glucose electrooxidation

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(1) Pt-based and Pd-based bimetallic catalysts catalyze GORs

Table S1. GOR performances of carbon supported bimetallic catalysts (literature vs. this study).

Anode Catalyst	Onset potential (V vs. Hg/HgO)	Anodic peak for forward scan		Reference
		Peak potential (V vs. Hg/HgO)	Peak current (mA cm ⁻²)	
Pd-Au/C	-0.45	-0.15	2.5	[4]
Pt-Au/C	-0.59	-0.22	9.5	[7]
Pt-Pb/C	-0.56	-0.52	2.5	[9]
Pd-Rh/C	-0.55	0.05	3.5	[13]
Pd-Ni/C	-0.56	-0.03	34.2	This work

(2) SEM-EDS characterization of the Pd-Ni/C catalysts

In order to determine whether Ni elements exist in the Pd-Ni/C catalysts, the atomic characterization was performed by the SEM-EDS measurement, as shown in Fig. S1.

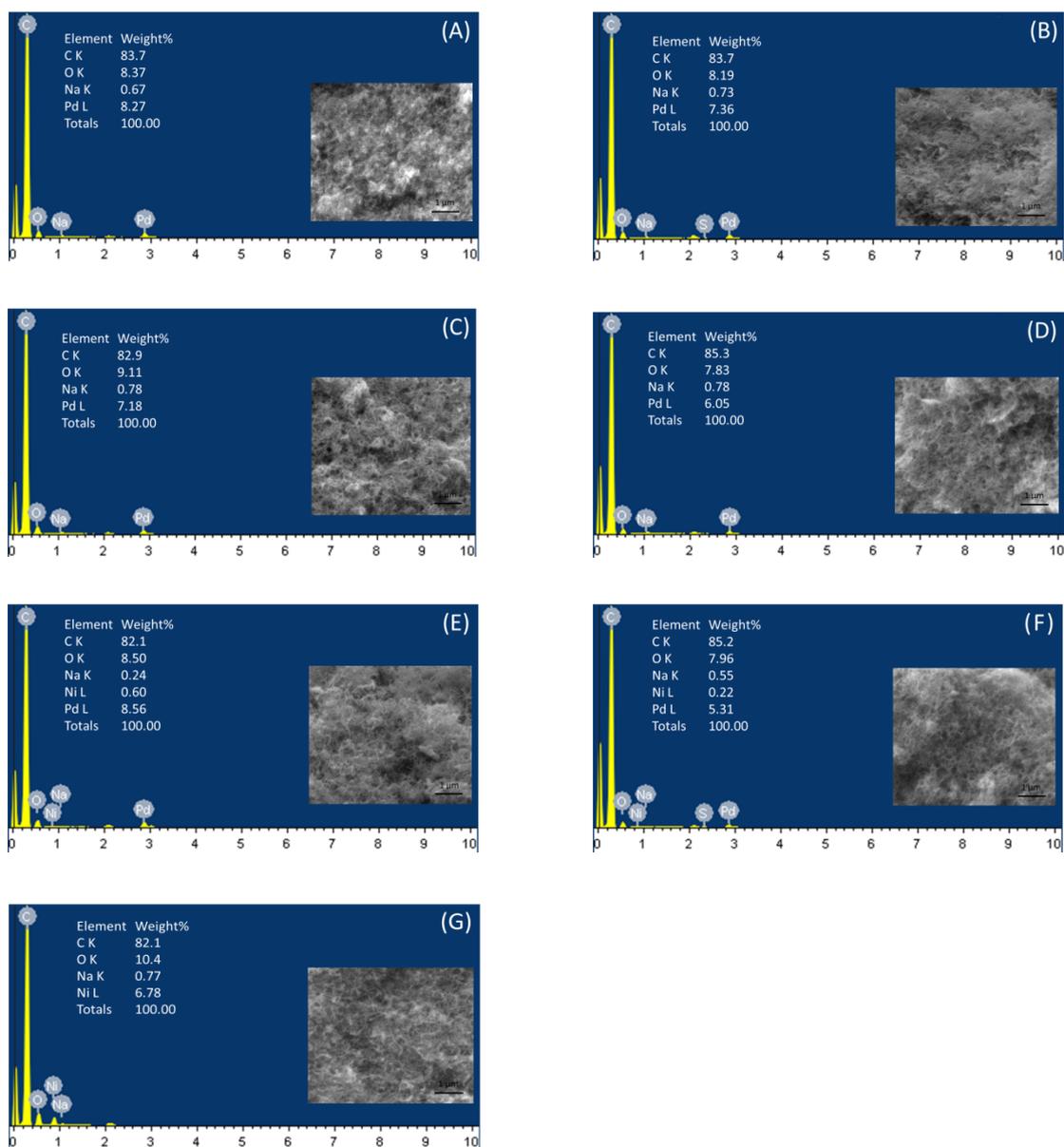
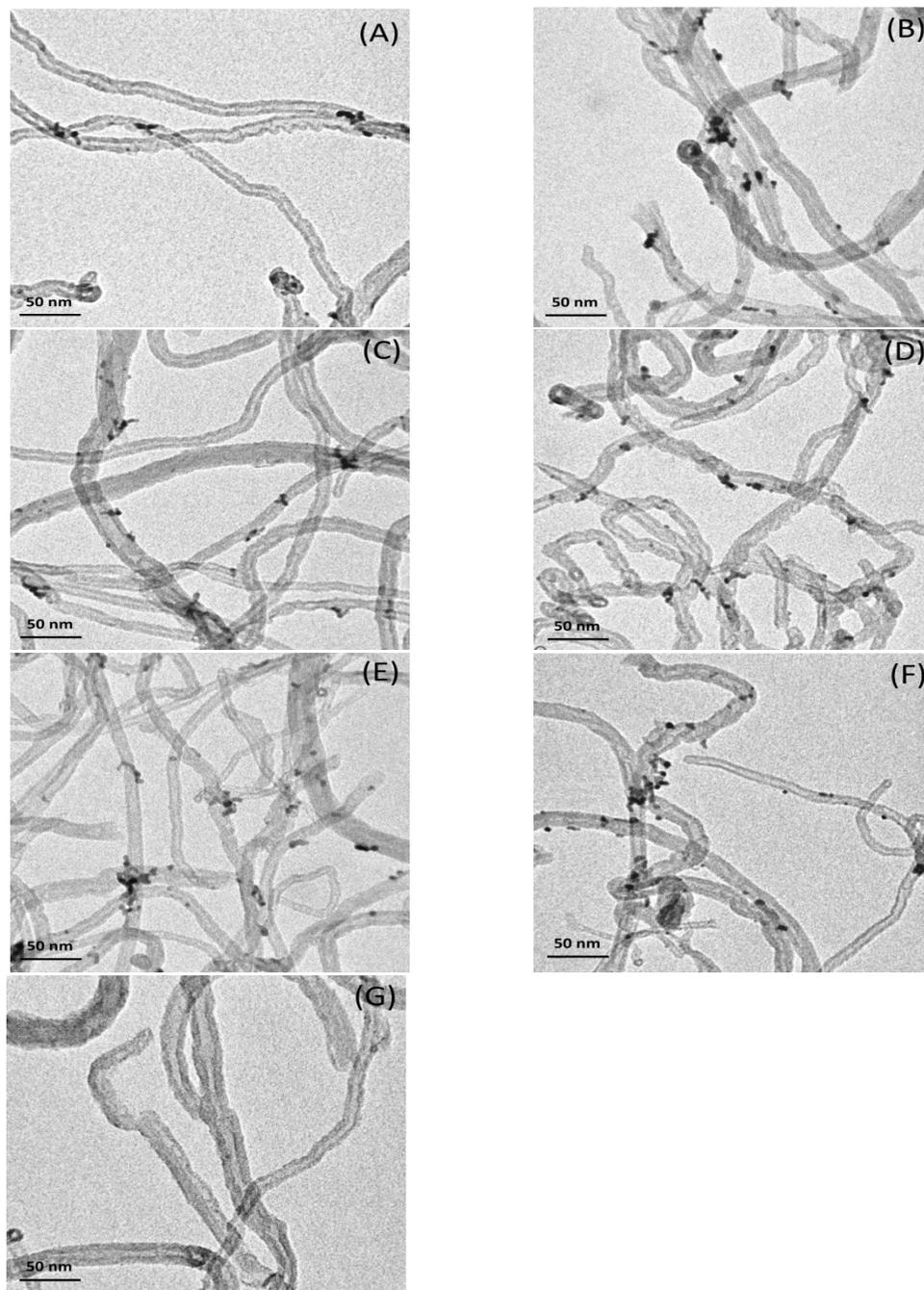


Figure S1. SEM-EDX micrographs of the Pd-Ni/C catalysts (A) Pd/C, (B) Pd-Ni/C (1:0.02), (C) Pd-Ni/C (1:0.03), (D) Pd-Ni/C (1:0.06), (E) Pd-Ni/C (1:0.14), (F) Pd-Ni/C (1:0.33) and (G) Ni/C.

(3) TEM characterization of the Pd-Ni/C catalysts

The size and distribution of the Pd_{shell}Ni_{core} nanoparticles were analyzed by TEM characterization, as shown in Fig. S2. The frequency of the metal particle size is estimated using a statistical analysis of about 50 particles which were randomly selected from the TEM data. It can be seen that the

average particle size of Pd/C is 4.7 nm and the Pd_{core}Ni_{shell} nanoparticles with an average diameter of 4.6, 4.2, 4.1, 5.4 and 6.6 nm for Pd-Ni/C (1:0.02), Pd-Ni/C (1:0.03), Pd-Ni/C (1:0.06), Pd-Ni/C (1:0.14) and Pd-Ni/C (1:0.33), respectively (Fig. S2A'-F').



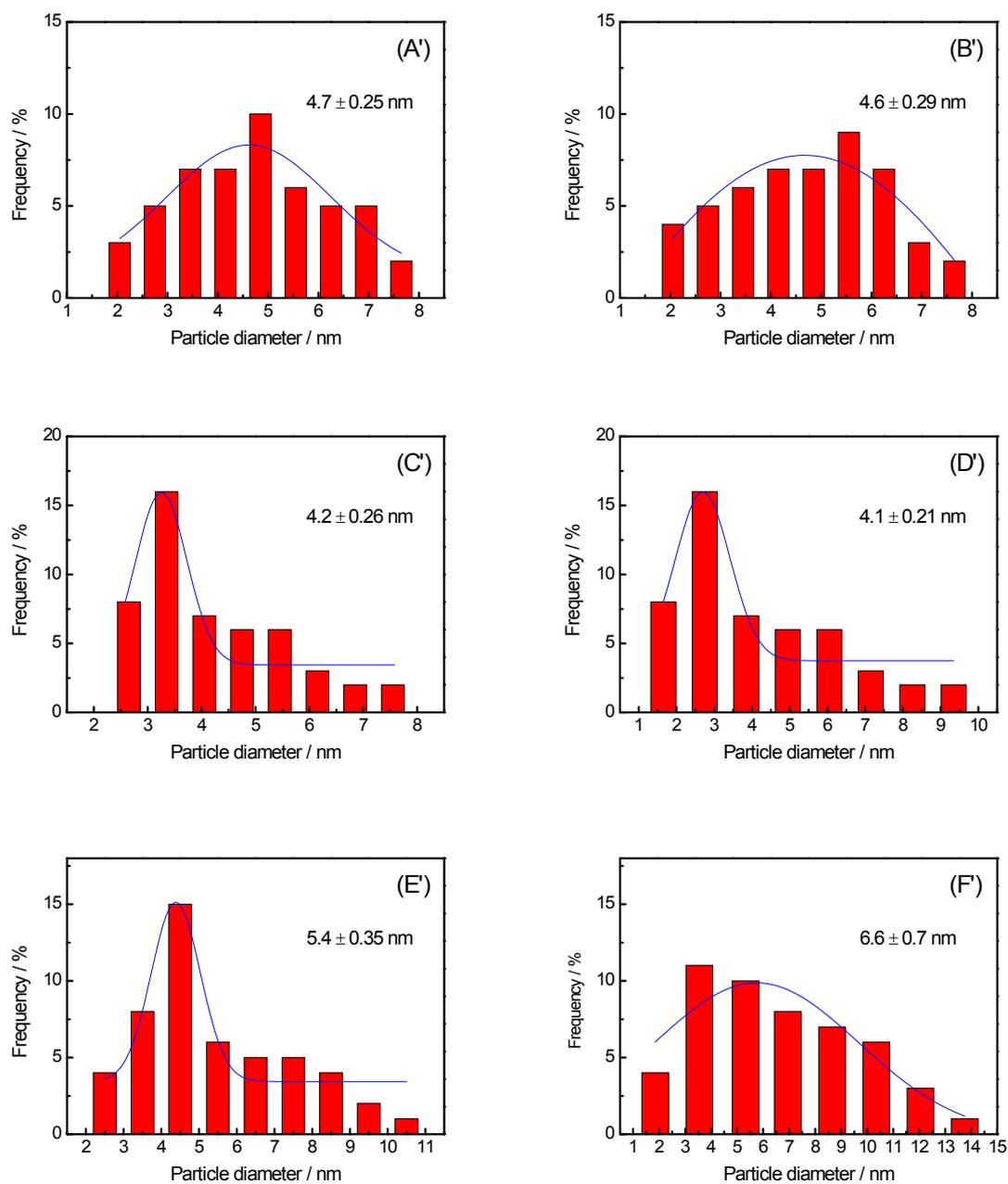


Figure S2. TEM images of the Pd-Ni/C catalysts (A) Pd/C, (B) Pd-Ni/C (1:0.02), (C) Pd-Ni/C (1:0.03), (D) Pd-Ni/C (1:0.06), (E) Pd-Ni/C (1:0.14), (F) Pd-Ni/C (1:0.33) and (G) Ni/C and their corresponding particle size distribution (A', B', C', D', E' and F').

(4) ECSA measurement of the Pd-Ni/C catalysts

The ECSA value (a measure of electrochemical active surface area) was determined by the voltammetric curves. During the forward scan of the Pd/C catalyst, the oxidation peak between -0.7 V and -0.5 V is ascribed to the absorption of hydrogen (Fig. S3A). In addition, the peak that occurs in the range between +0.0 V and +0.4 V is attributed to the formation of Pd-OH. In the backward scan, a sharp cathodic peak at -0.35 V indicates the reduction of Pd oxide. In Fig. S3B, the results show that the cathodic reduction peak current densities gradually increase to a maximum value as 12 mA cm⁻² on Pd-Ni/C (1:0.06) and then decline while the weight loadings of Ni increase. To estimate the palladium electrochemical active surface area (ECSA) CV profiles were recorded between -0.8 and 0.8 V vs. Hg/HgO with a scan rate of 50 mV s⁻¹. Cyclic voltammograms (CVs) were recorded in nitrogen saturated evaluated 0.5 mol L⁻¹ NaOH electrolyte through bubbling with nitrogen under nitrogen atmosphere at room temperature. The palladium ECSA was calculated using the mean integral coulombic charge (Q) of the reduction area between -0.4 V and 0.1 V and the reduction of palladium oxide monolayer is assumed as 405 μC cm⁻² according to the following equation (1):

$$\text{ECSA} \left[\frac{m^2}{g} \text{ of Pd} \right] = \frac{Q_H [\mu C] \times 10}{405 [\mu C \cdot cm^{-2}] \times Pd_{\text{loading}} [mg]} \quad (1)$$

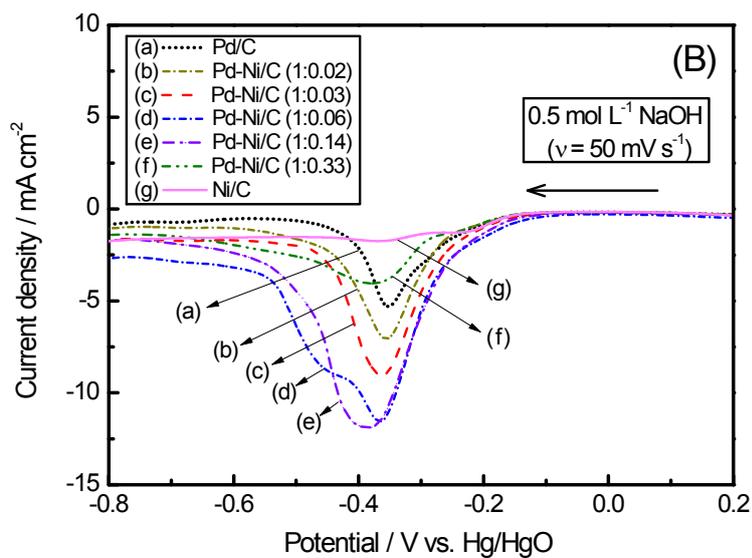
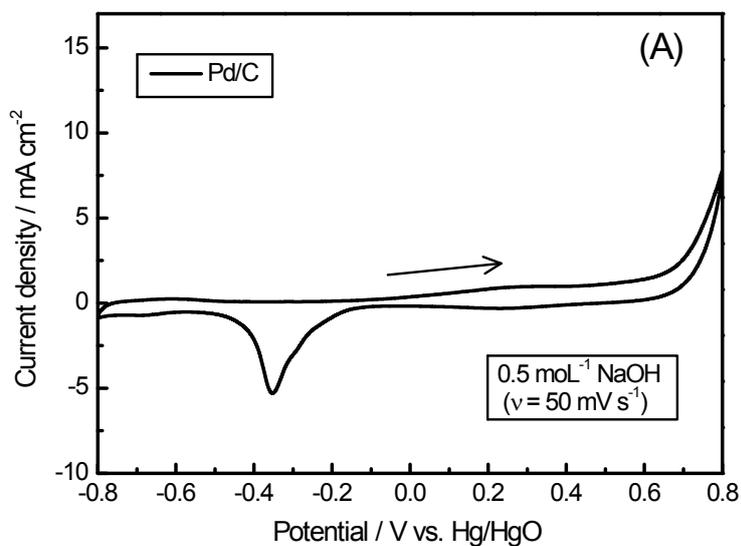


Figure S3. Cyclic voltammograms of (A) Pd/C and (B) the backward scan for the Pd-Ni/C catalysts: (a) Pd/C, (b) Pd-Ni/C (1:0.02), (c) Pd-Ni/C (1:0.03), (d) Pd-Ni/C (1:0.06), (e) Pd-Ni/C (1:0.14), (f) Pd-Ni/C (1:0.33) and (g) Ni/C in 0.5 mol L⁻¹ NaOH solution at a scan rate of 50 mV s⁻¹ at room temperature.

(5) Activation energy measurement of Pd-Ni/C (1:0.06) and Pd/C

The corresponding activation energy is determined using Arrhenius equation. Where I means the corresponding current density at a specific potential, R is the universal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the absolute temperature in K and E_a is the activation energy value. The result shows that the current densities of Pd/C and Pd-Ni/C (1:0.06) at an operating temperature of 318 K are 34.2 and 36.9 mA cm^{-2} , respectively, as shown in Fig. S4.

$$I = Ae^{-E_a/RT}$$

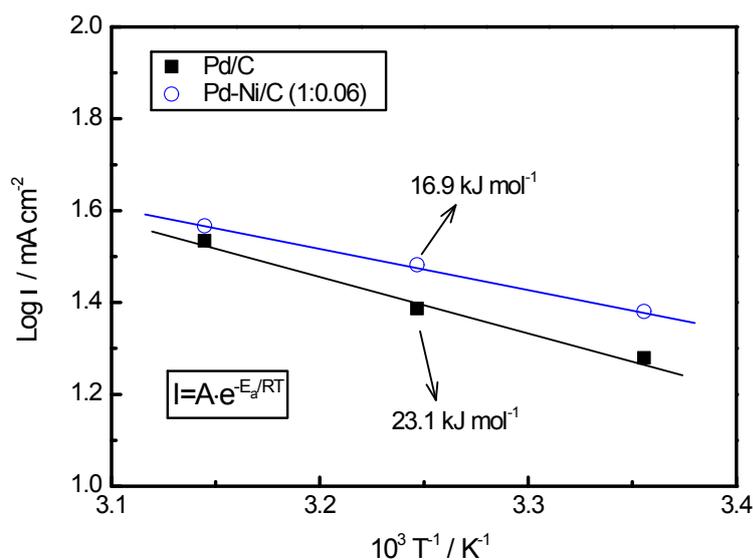


Figure S4. Arrhenius plots at different temperature ($T = 298, 308$ and 318 K) of the Pd/C and Pd-Ni/C (1:0.06) in 0.5 mol L^{-1} NaOH solution containing 0.5 mol L^{-1} glucose at a scan rate of 50 mV s^{-1} .

(6) Long-term durability measurement of Pd-Ni/C (1:0.06) and Pd/C

For 500 continuous GOR cycles, the Pd/C and Pd-Ni/C (1:0.06) were studied by CV (100 mV s^{-1}). The retained activities is calculated using the ratio of the GOR peak current density at cycle number n (I^n) to the one at the first cycle (I^0). The result shows a less activity loss of electrocatalytic activity for Pd-Ni/C (1:0.06) compared to Pd/C during the successive GOR duty cycles.

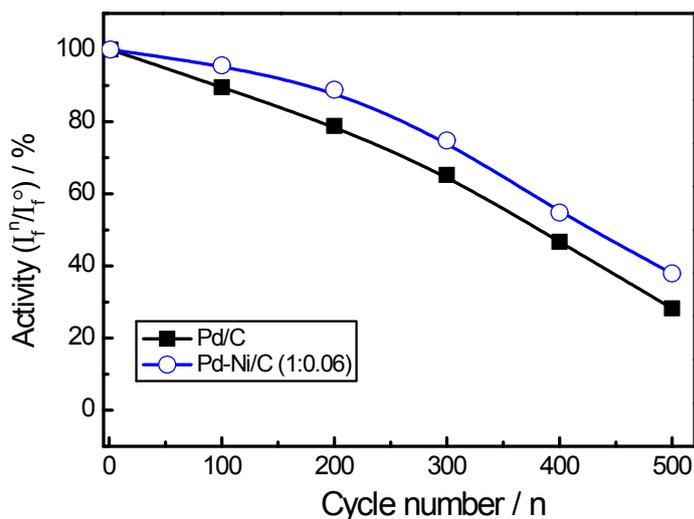


Figure S5. GOR cycling stability test for the Pd/C and Pd-Ni/C (1:0.06) in 0.5 mol L^{-1} NaOH solution containing 0.5 mol L^{-1} glucose at a CV scan rate of 100 mV s^{-1} at room temperature.