

Electronic Supplementary Information

Patterned Catalyst Arrays of Pd/SnO₂ Core-Shell Nanowires for Electrooxidations of Biomass-Derived Alcohols

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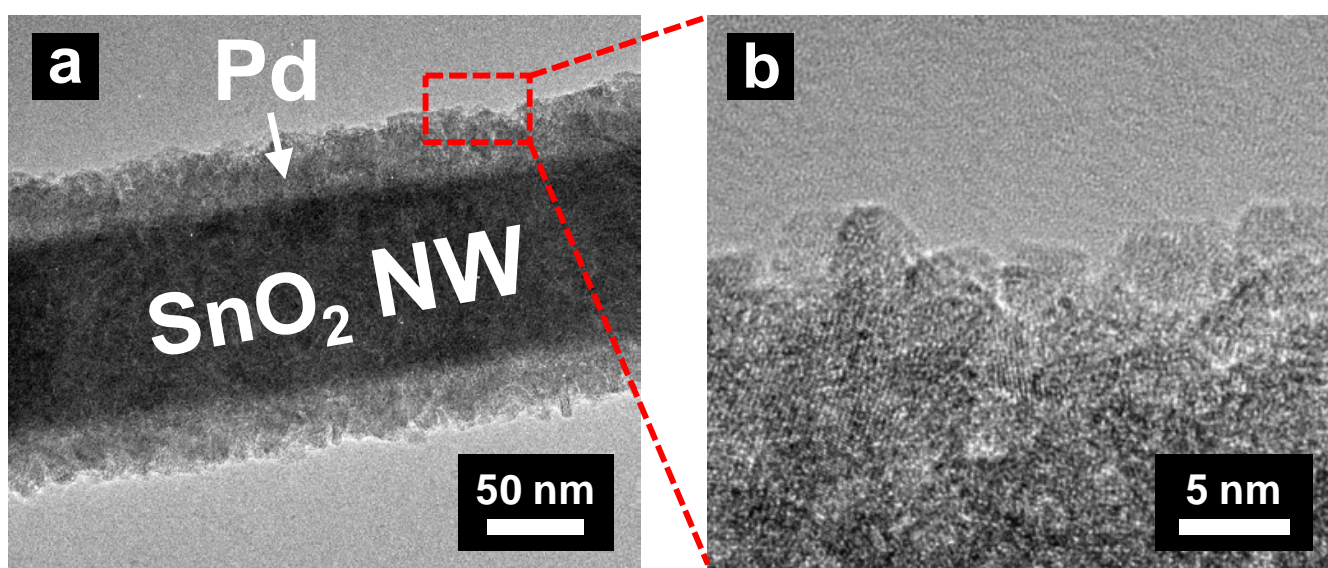


Figure S1. (a) TEM image for the individual core-shell Pd/SnO₂ NW. (b) High-resolution TEM image for the Pd catalyst layer that is formed over the SnO₂ NW support. These images indicate that the Pd electrocatalysts, which are composed with approximately 3 nm size particles, are strongly tangled around SnO₂ NW frameworks.

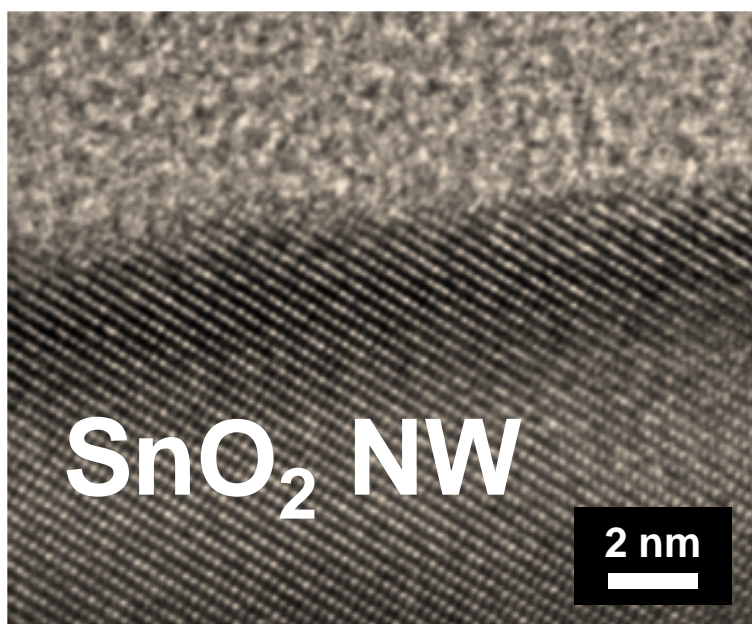


Figure S2. The representative high-resolution TEM image for the core SnO₂ NW, which consists of the outstanding crystalline structure. This indicates that these NW frameworks can promote the electron transport during the electrooxidation reactions.

Long-term cycle stability tests for the EASA profiles of five different catalyst samples (i.e., no pattern, pattern A, pattern B, pattern C, and pattern D) were carried out in a 1.0 M NaOH aqueous solution over a potential range of -0.85 V to 0.5 V (vs. Hg/HgO) at a scan rate of 50 mV/s (refer to the mass of the Pd catalysts in Table 1 of the manuscript). Figure S3 presents the long-term cyclic accelerate results with an increasing number of CV cycles. The long-term accelerate profiles were plotted based on the ratio of the EASA values obtained by the consecutive CV cycles to the maximum value ($EASA^1$) obtained by each of these Pd catalyst samples. The patterned electrodes maintain higher $EASA/EASA^1$ values than the non-patterned ones, and the pattern D, which has the largest flow channels among these four different patterned arrays, holds the most stable EASA until the 200th cycle.

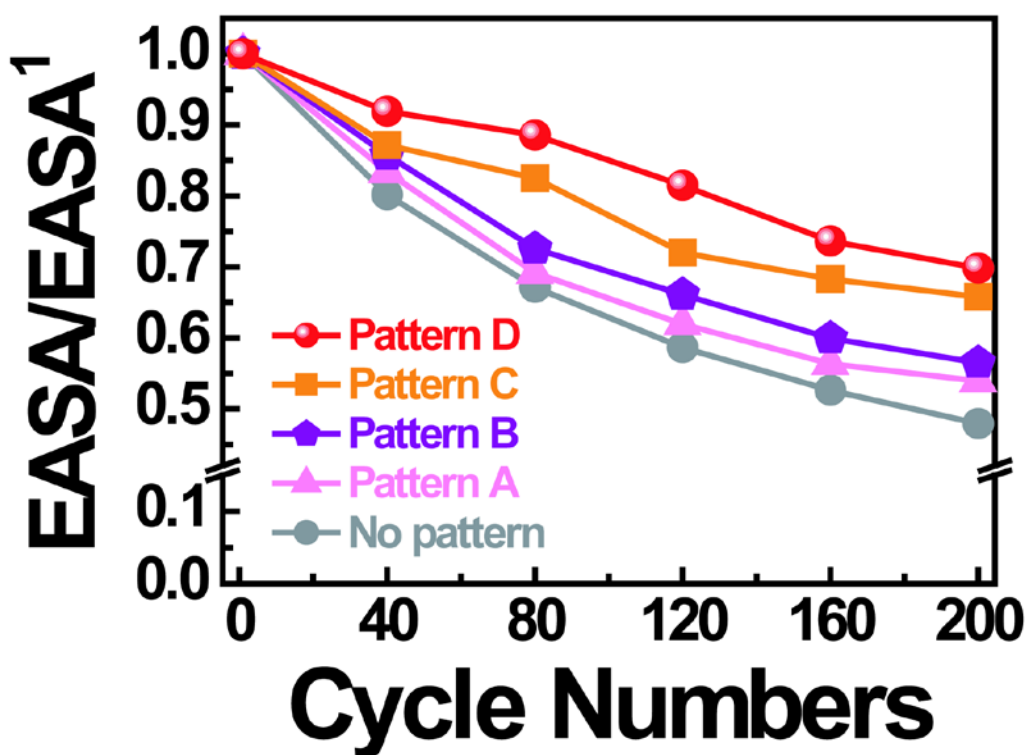


Figure S3. The long-term accelerate EASA tests for five different catalyst samples in 1.0 M NaOH aqueous solution over a potential range of -0.85 V to 0.5 V (vs. Hg/HgO) at a scan rate of 50 mV/s.

The same amount of the Pd catalysts (ca. 0.2 mg_{-Pd}) were loaded on these five different SnO₂ NW supports (i.e., no pattern, pattern A, pattern B, pattern C, and pattern D), and then the EASA properties were characterized in a 1.0 M NaOH aqueous solution. Figure S4 exhibits the results of cyclic voltammogram (CV) measurements over a potential range of -0.85 V to 0.5 V (vs. Hg/HgO). Here, the EASA values of all the samples were normalized by the mass of the Pd catalysts formed on SnO₂ NW supports. Similar to the EASA tendency reported in Figure 4a of the manuscript, the patterned Pd/SnO₂ NW platforms show more improved EASA values than the non-patterned ones. And, as the flow channels between the patterned electrodes are increased, the EASA values are also enhanced (refer to the EASA values in Table S1 below). Even if the same amount of the Pd catalysts was loaded over these SnO₂ NWs, the sample with more flow channels (i.e., pattern D) presented much larger EASA. These results indicate that the patterned electrodes with the increased flow channels effective in promoting the diffusion of the liquid electrolyte and reducing the embedded sites of the electrocatalysts, thereby leading to the improved electrode/electrolyte contact.

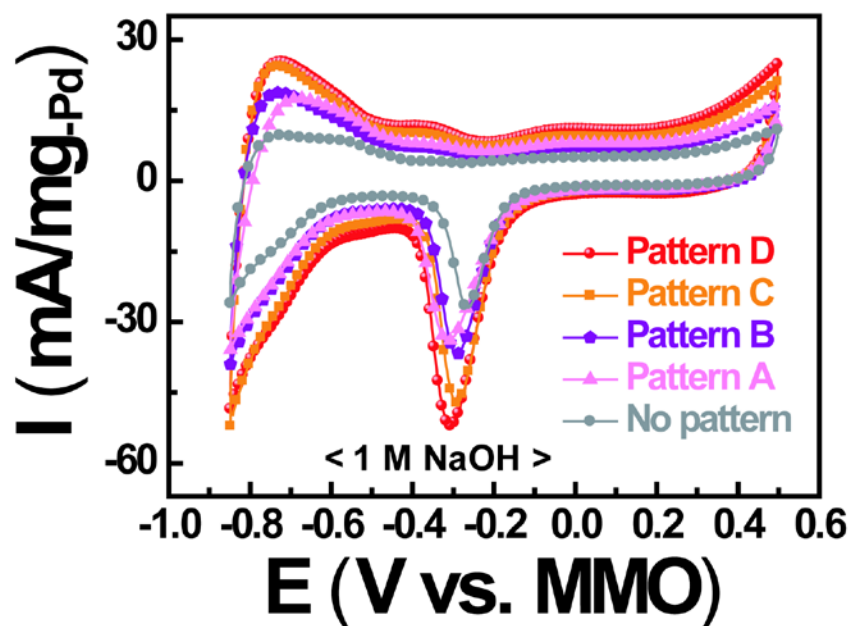


Figure S4. CV results for the five different Pd/SnO₂ NW electrodes in a 1.0 M NaOH aqueous solution over a potential range of -0.85 V to 0.5 V (vs. Hg/HgO) at a scan rate of 50 mV/s.

Table S1. Summary of the EASA properties of the five different Pd/SnO₂ NW platforms in Figure S4.

Pd	Pd mass^[a] (mg_{-Pd})	EASA^[b] (cm²/mg_{-Pd})
No pattern	0.20	94.69
Pattern A	0.20	146.22
Pattern B	0.23	183.84
Pattern C	0.20	263.47
Pattern D	0.22	330.96

^[a] Mass of the Pd catalysts without SnO₂ NWs (effective areas of current collectors: 1 cm²).

^[b] EASA evaluated by the reduction charge of the PdO monolayer (ca. 405 μC/cm²).

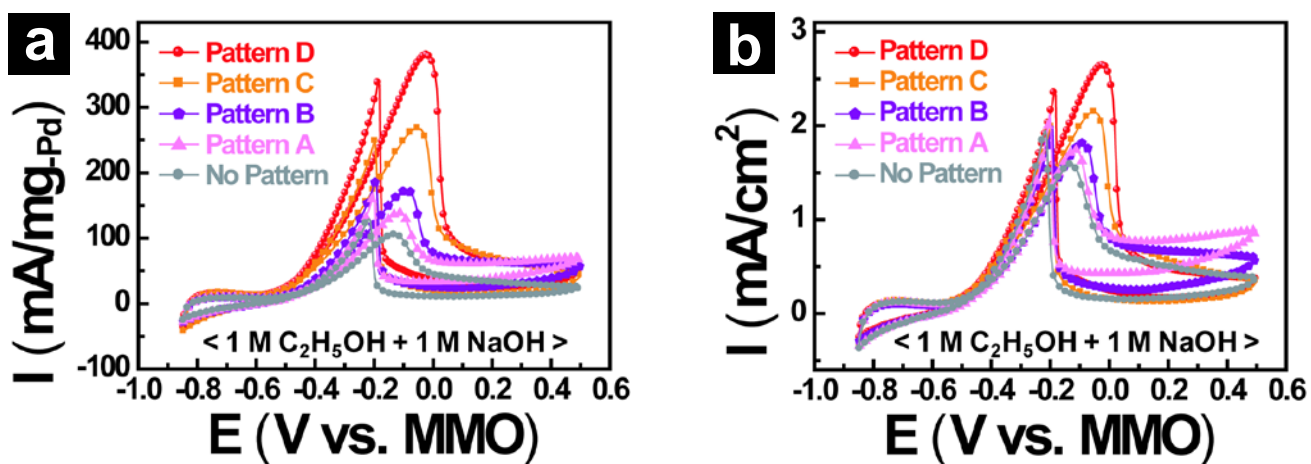


Figure S5. CV results for five different Pd/SnO₂ NW electrodes in a solution mixture of 1.0 M C₂H₅OH and 1.0 M NaOH over a potential range of -0.85 V to 0.5 V (vs. Hg/HgO) at a scan rate of 50 mV/s. The electrochemical activities for these electrode systems were normalized (a) by the mass of the Pd catalysts and (b) by the EASA of the Pd catalysts.

Table S2. Summary of the electrocatalytic performances of the modified catalyst patterns for ethanol oxidations in Figure 5.

Pd	Ethanol oxidation				
	Pd mass ^[a] (mg-Pd)	EASA ^[b] (cm ² /mg-Pd)	Onset potential (V vs. Hg/HgO)	Current density ^[c] (mA/mg-Pd)	Current density ^[d] (mA/cm ²)
Pattern D ₁	0.08	143.67	- 0.582	380.99	2.65
Pattern D ₂	0.07	154.58	- 0.587	411.09	2.66
Pattern D ₃	0.05	121.62	- 0.578	318.89	2.62

^[a] Mass of the Pd catalysts without SnO₂ NWs (effective areas of current collectors: 1 cm²).

^[b] EASA evaluated by the reduction charge of the PdO monolayer (ca. 405 μC/cm²).

^[c] Forward peak current density normalized by the mass of Pd catalysts.

^[d] Forward peak current density normalized by the EASA value of Pd catalysts.

Table S3. Summary of the molecular weight and viscosity for the alcohol molecules.

Alcohol	Molecular weight	Viscosity (at 293 K)
Methanol	32.04 g/mol	5.9 X 10⁻⁴ Pa·s
Ethanol	46.07 g/mol	1.2 X 10⁻³ Pa·s
Ethylene glycol	62.07 g/mol	1.6 X 10⁻² Pa·s
Glycerol	92.09 g/mol	1.4 Pa·s

Table S4. Summary of the electrocatalytic performances for diverse alcohol oxidation reactions in

Figure 6e.

Alcohol	Onset potential (V vs. Hg/HgO)		Current density (mA/mg _{Pd})	
	No pattern	Pattern D	No pattern	Pattern D
Methanol	- 0.431	- 0.493	128.8	401.4
Ethanol	- 0.482	- 0.582	105.6	380.9
Ethylene glycol	- 0.428	- 0.473	187.9	711.1
Glycerol	- 0.418	- 0.443	113.2	449.1

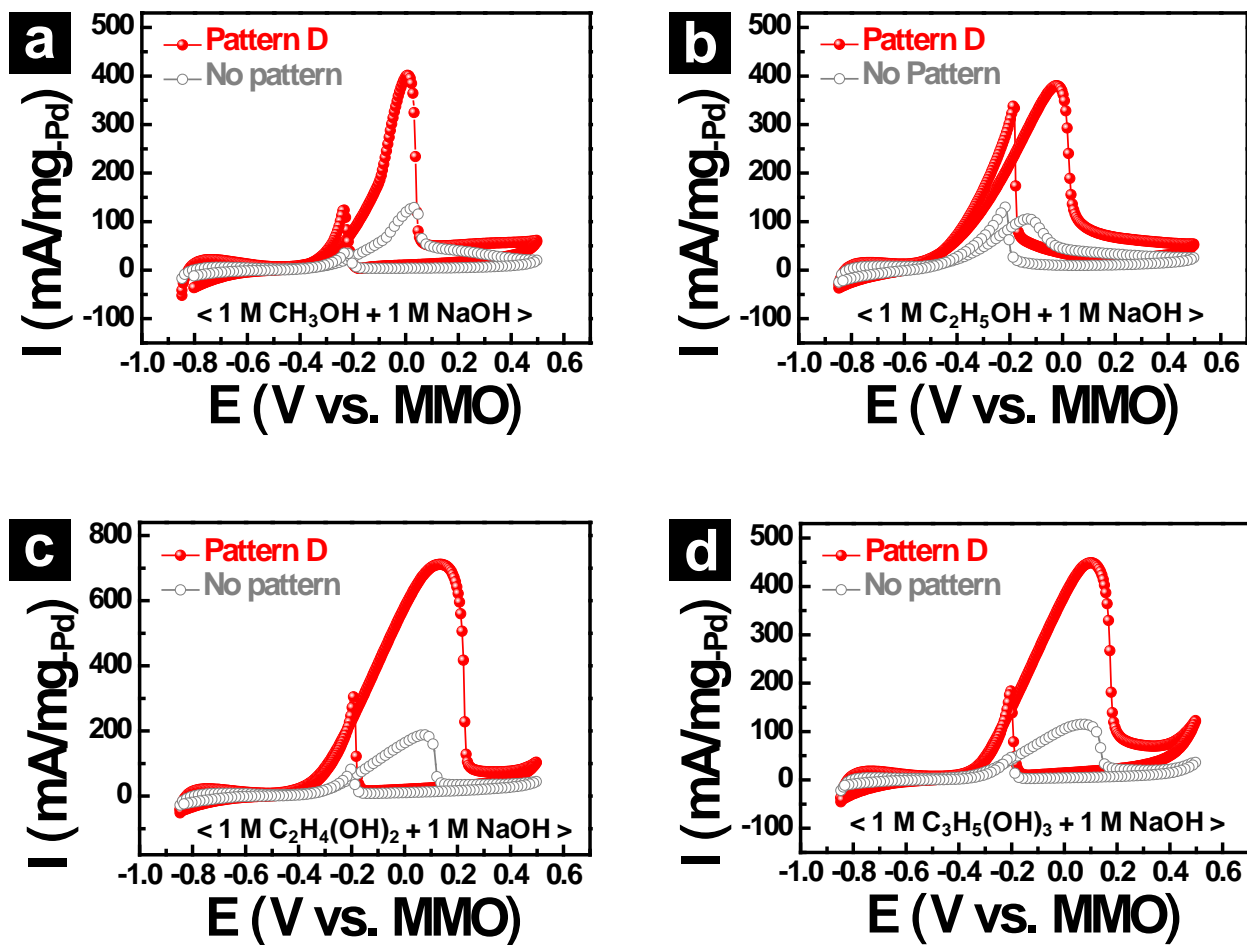


Figure S6. Comparable CV data of pattern D and no pattern samples for the electrooxidations of (a) methanol, (b) ethanol, (c) ethylene glycol, and (d) glycerol. These oxidation reactions were performed in a mixture of 1.0 M $\text{C}_x\text{H}_{2x+2}\text{O}_y$ (i.e., CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, $\text{C}_2\text{H}_4(\text{OH})_2$, and $\text{C}_3\text{H}_5(\text{OH})_3$) and 1.0 M NaOH over a potential range of -0.85 V to 0.5 V at a scan rate of 50 mV/s.

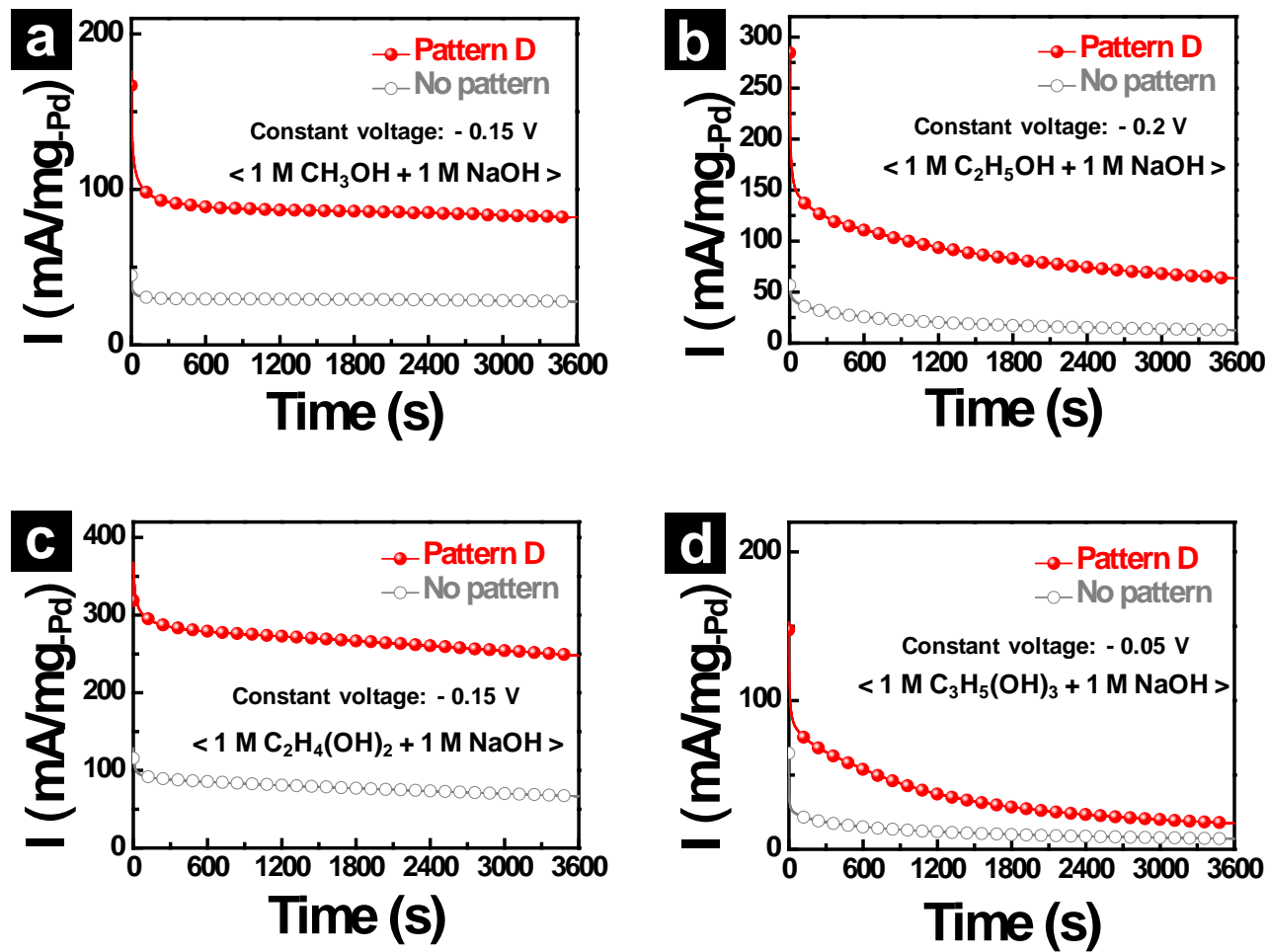


Figure S7. Comparable CA data of pattern D and no pattern samples for the electrooxidations of (a) methanol, (b) ethanol, (c) ethylene glycol, and (d) glycerol.