

## Supporting Information

### Highly-effective palladium nanoclusters supported on *para*-sulfonated calix[8]arene functionalized carbon nanohorns for ethylene glycol and glycerol oxidation

Xin Ran<sup>a</sup>, Qing Qu<sup>a,\*</sup>, Chang Liu<sup>a</sup>, Shihong Zhang<sup>a</sup>, Xingcan Qian<sup>a</sup>, Qiang Wang<sup>c</sup>,  
Changliang Jiang<sup>c</sup>, Long Yang<sup>a,\*</sup>, Lei Li<sup>b,\*</sup>

<sup>a</sup> School of Chemical Science and Technology, Yunnan University, Kunming 650091, China.

<sup>b</sup> Laboratory for Conservation and Utilization of Bio-Resources, Yunnan University, Kunming, 650091, China.

<sup>c</sup> CNPC. South-east Asia Pipeline Co. Ltd, Beijing, 100000, China.

#### S1. Material characterization

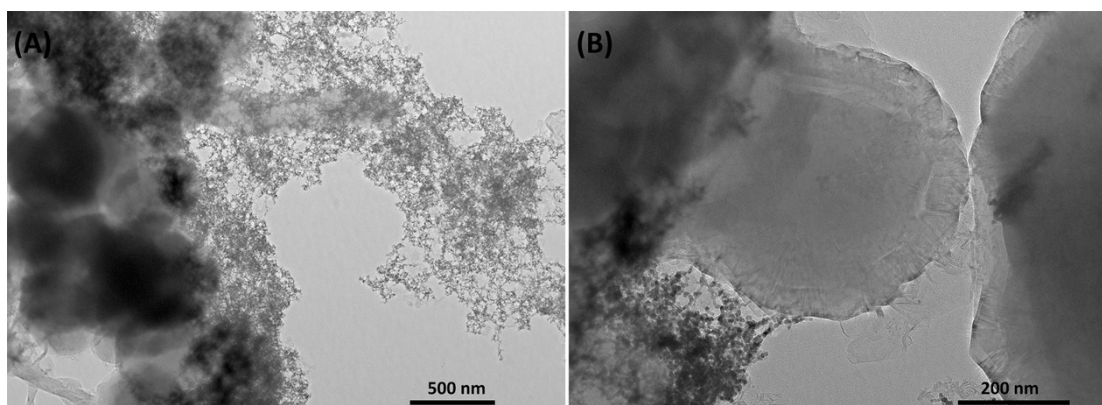
The morphologies of the prepared samples were characterized by a JEM 2100 transmission electron microscopy (TEM, JEOL, Japan) with an accelerating voltage of 200 kV. The samples for TEM characterization were prepared by depositing a drop of the diluted suspension on a copper grid coated by amorphous carbon. X-ray diffraction (XRD) patterns were recorded on a D8 ADVANCE (BRUKER, Germany) diffractometer using Cu-K $\alpha$  radiation with a Ni filter ( $\lambda = 0.154059$  nm at 30 kV and 15 mA). X-ray photoelectron spectroscopy (XPS) measurements were performed with Al K $\alpha$  X-ray radiation as the X-ray source for excitation, which were carried out on an

ESCALAB-MKII spectrometer (VG Co., United Kingdom). Fourier transform infrared (FTIR) study was performed over the wavenumber, range of 4000–400  $\text{cm}^{-1}$  by a Thermo Fisher SCIENTIFIC Nicolet IS10 (Massachusetts, USA) FTIR impact 410 spectrophotometer using KBr pellets. Thermogravimetric analysis (TGA) was carried out on a Q50 TGA (TA Instruments, New Castle, USA), at a heating rate of 5  $^{\circ}\text{C min}^{-1}$  from 35 to 800  $^{\circ}\text{C}$  in nitrogen. A Malvern Zetasizer Nano series was used for the zeta potential measurements.

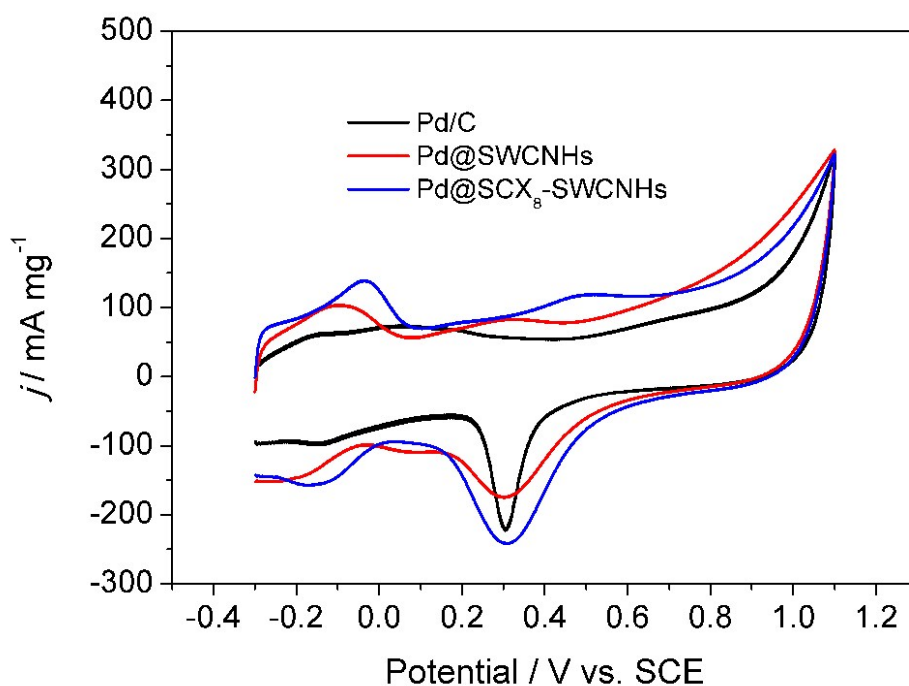
## **S2. Electrochemical measurements**

All the electrochemical measurements were carried out with a CHI 660E Electrochemical Workstation from Chenhua Instrument (Shanghai, China) and conducted using a three-electrode system, with the modified glassy carbon electrode (GCE, 3 mm in diameter) as working electrode, a platinum wire as the counter electrode, a saturated calomel electrode as the reference electrode. Before the modifications, GCE was polished carefully with 0.3 and 0.05  $\mu\text{m}$   $\text{Al}_2\text{O}_3$  powder to obtain a mirror-like surface, and then followed by sonication in ethanol and ultrapure water respectively. Then, the GCE was coated with the as-produced samples (5.0  $\mu\text{g}$ ) and dried at room temperature. Finally, 5.0  $\mu\text{l}$  of Nafion (0.1 wt%) was coated on the surface of the modified GCE and dried before electrochemical experiments. Alcohols electro-oxidation measurements were performed in a solution of 1.0 M KOH containing 1.0 M EG or glycerol at a scan rate of 50  $\text{mV}\cdot\text{s}^{-1}$ . The EG or glycerol solution was deoxygenated with  $\text{N}_2$  bubbling for 30 min before electrochemical

experiments. The electrochemically active surface area (ECSA) of each sample was estimated by cyclic voltammetry (CV) measurements carried out in 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions with a sweep rate of 50 mV·s<sup>-1</sup>. Mass current densities were normalized by the loaded Pd amount.



**Fig. S1** TEM images of Pd@SWCNHs (A and B) at different magnifications.



**Fig. S2** CV curves of Pd/C, Pd@SWCNHs, and Pd@SCX<sub>8</sub>-SWCNHs catalysts

modified GCE in a N<sub>2</sub> saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> at a scan rate of 50 mV s<sup>-1</sup>.