Supporting Online Material for

Ultralong Pt-on-Pd Bimetallic Nanowires with Nanoporous Surface: Nanodendritic Structure for Enhanced Electrocatalytic Activity

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1. **Materials and Methods**

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1. *Materials and Methods*

(1) Materials: Poly-(N-vinyl-2-pyrrolidone) **(**PVP·K30, molecular weight: 30000-40000), H_2SO_4, ammonium hydroxide (NH_4•OH), acetone, hydrazine (50%), $PdCl_2$ and ethanol were purchased from the Shanghai Chemical Factory (Shanghai, China) and used as received without further purification. K_2PtCl_4 and ascorbic acid (AA) were purchased from Alfa Aesar. Na_2TeO_3 and Nafion (perfluorinated ion-exchange resin, 5 wt% solution in a mixture of lower aliphatic alcohols and water) were obtained from Aldrich. Water used throughout all experiments was purified with the Millipore system.

(2) Apparatus: A XL30 ESEM scanning electron microscope was used to determine the morphology and composition of products. TEM measurements were made on a HITACHI H-8100 EM with an accelerating voltage of 200 kV. HRTEM images were obtained with a JEM-2100F high-resolution transmission electron microscope operating at 200 kV. XPS measurement was performed on an ESCALAB-MKII spectrometer (VG Co., United Kingdom) with Al Kα X-ray radiation as the X-ray source for excitation. Nitrogen adsorption-desorption isotherms at the temperature of liquid nitrogen were measured by using a Micromeritics ASAP 2010 Analyser (USA) with nitrogen. Pore sizes were calculated by the BJH method. The composition of bimetallic nanowires (NWs) was determined by inductively coupled plasma-mass spectroscopy (ICP-MS, X Series 2, Thermo Scientific USA). CV experiments were performed with a CHI 832 electrochemical analyzer (CH Instruments, Chenhua Co., Shanghai, China). A conventional three-electrode cell was used, including an Ag/AgCl (saturated KCl) electrode as reference electrode, a platinum wire as counter electrode and modified GC as working electrode.

(3) Synthesis of Te nanowires (NWs): First, 2 g PVP was dissolved with 50 mL of double-distilled water under vigorous magnetic stirring to form a homogeneous solution at room temperature. Then, 0.2670 g of sodium tellurite (Na_2TeO_3) was added into the previous solution and dissolved, followed by the addition of hydrazine hydrate (5 mL, 50% w/w) and 4.5 mL of an ammonia solution (25% w/w). Then, the obtained solution was transferred into the container of Teflon-lined stainless steel autoclave, sealed and maintained at 180 ºC for 4 h. Finally, the product was centrifuged with acetone, washed with double-distilled water, and dissolved in 40 mL water.

(4) Synthesis of Pd NWs: 4 mL of Te NW solution were added into 25 mL water, followed by the addition of 4.5 mL of H_2PdCl_4 (56.4 mM) under stirring. The mixture was stored at room temperature for several minutes. Then, the solution was centrifuged and washed several times with double-distilled water and dissolved in 4 mL water.

(5) Synthesis of Pt-on-Pd bimetallic nanowires with dendritic morphology: 2 mL of Pd NWs, 1 mL of PVP aqueous solution (1 M) and 6 mL of AA aqueous solution (0.2 M) were added into 12 mL water. The mixture was heated to 90 ^{o}C in air under magnetic stirring. Meanwhile, 2 mL of K_2PtCl_4 aqueous solution (0.1 M) was then rapidly injected into the flask by pipette. The reaction mixture was heated at 90 ^{o}C in air for 2 h, and then cooled down to room temperature. The product was collected by centrifugation and washed several times with water for further electrochemical measurements.

(6) Electrocatalytic experiment: Prior to the surface coating, the GC electrode was polished carefully with 1.0, 0.3 and 0.05 µm alumina powder, respectively, and rinsed with deionized water, followed by sonicated in acetone and doubly distilled water successively. Then, the electrode was allowed to dry under nitrogen. For methanol oxidation reaction, 5 µL of Pt-on-Pd bimetallic NW (0.785 mg/mL with respect to Pt) or E-TEK Pt/C catalyst [20 wt.%, (1 mg/mL with respect to Pt)] was dropped on the surface of GC electrode and dried at infrared lamp. Then, 5 µL of Nafion (0.2 %) was placed on the surface of Pd-Pt bimetallic NWs or E-TEK modified GC electrode and dried before electrochemical experiments.

2. Figure S1-9 (Please see the following)

Figures

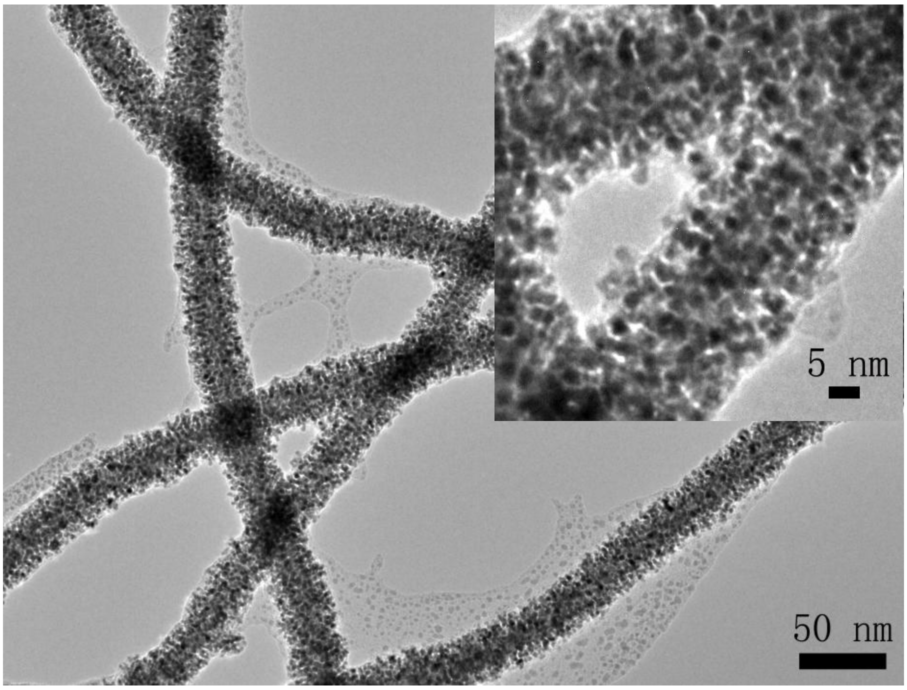

Figure S1 TEM image of Pt-on-Pd bimetallic nanowires. The inset shows the magnified image of bimetallic nanowires.

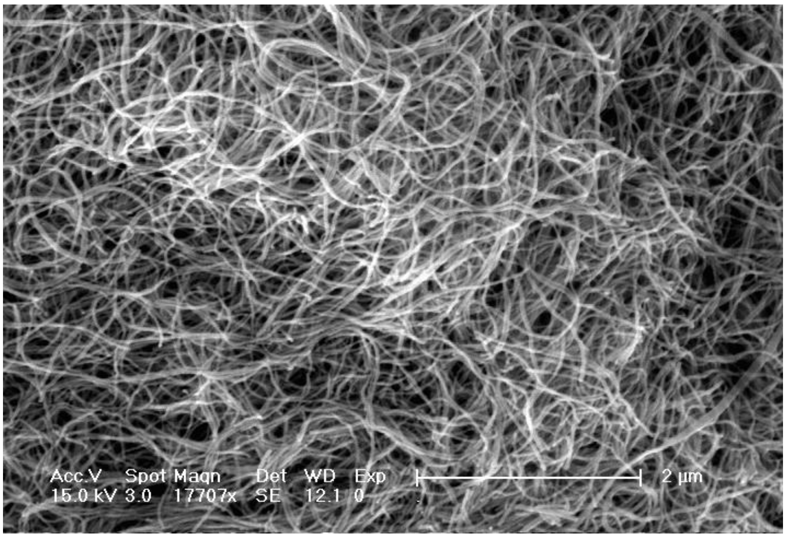

Figure S2 SEM image of Pt-on-Pd bimetallic nanowires.

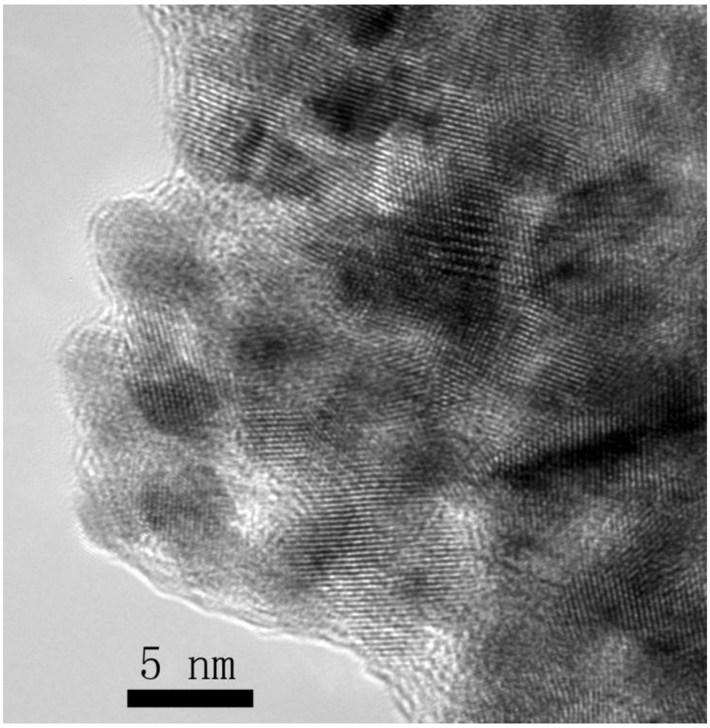

Figure S3 HRTEM image of Pt-on-Pd bimetallic nanowires.

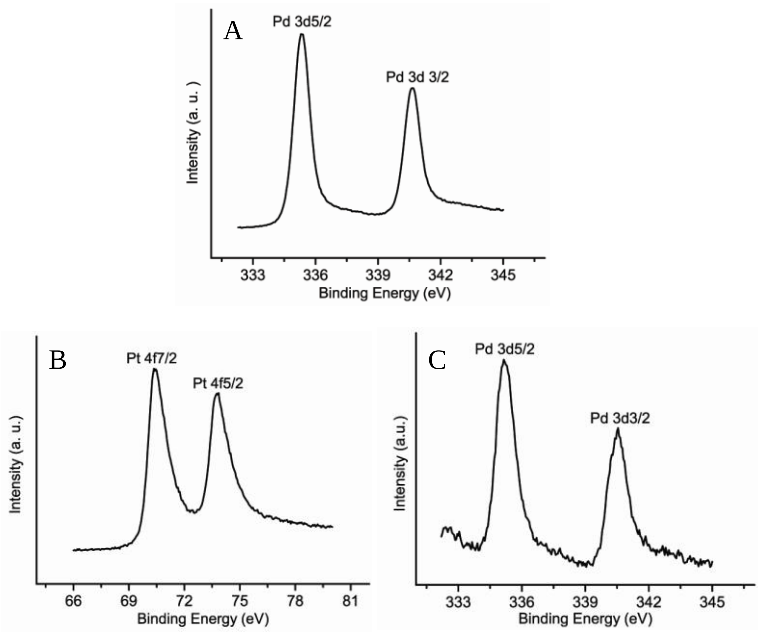

Figure S4 XPS spectroscopy of Pd nanowires (A) and Pt-on-Pd bimetallic nanowires (B, C).

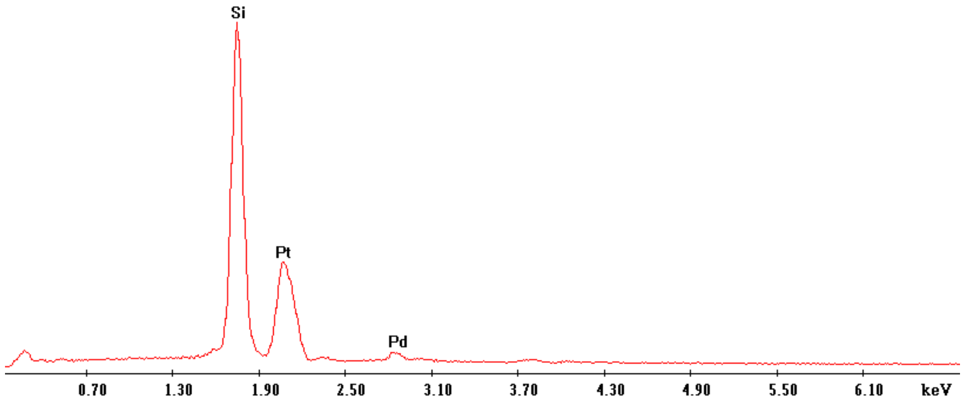

Figure S5 EDX image of Pt-on-Pd bimetallic nanowires.

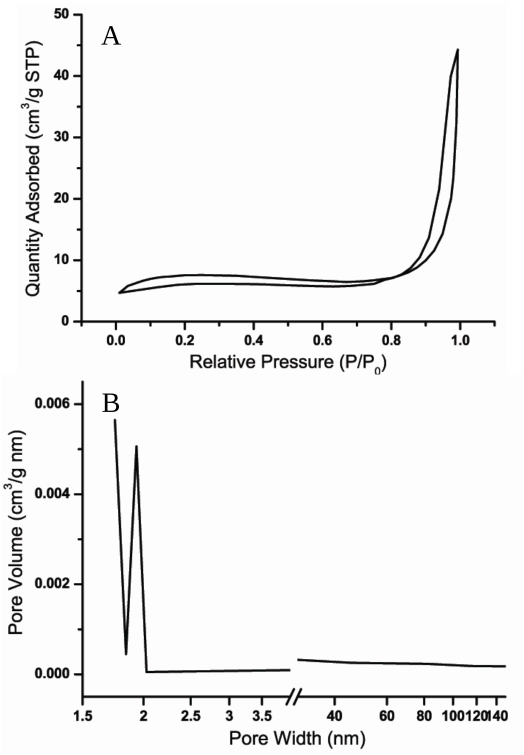

Figure S6 Nitrogen adsorption-desorption isotherm (A) of the Pt-on-Pd bimetallic nanowires, and its corresponding pore-size distribution curve (B) obtained from the adsorption data.

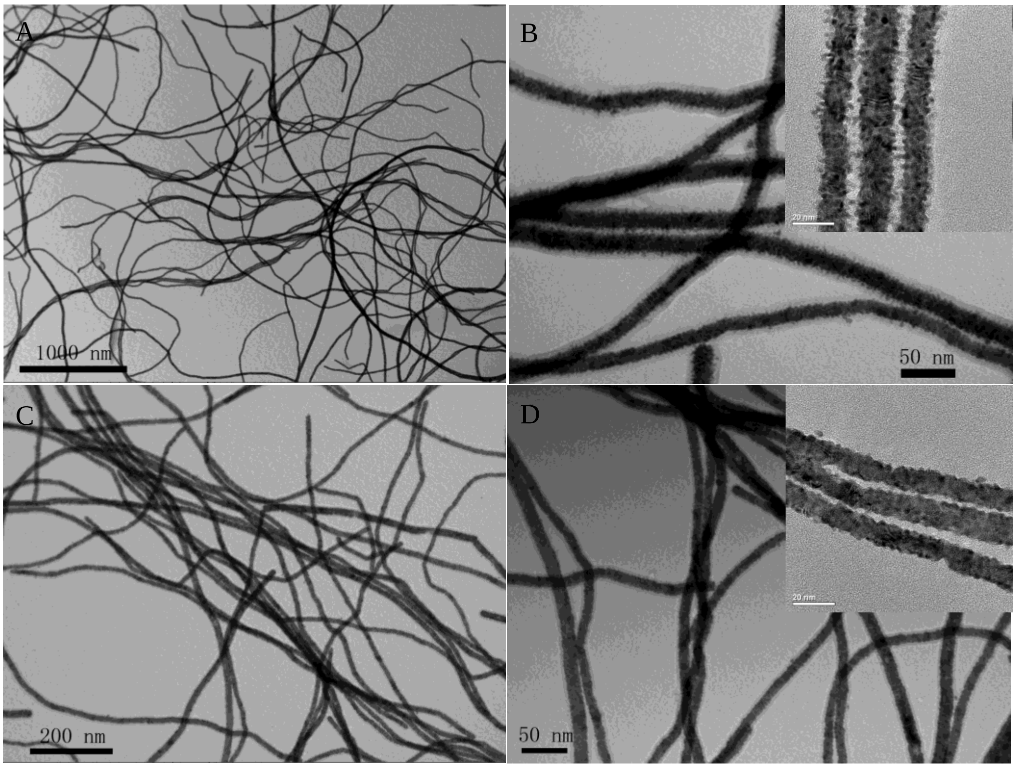

Figure S7 TEM images of Pt-on-Pd bimetallic nanowires at different magnifications (A, B). Reaction conditions: 2 mL of Pd nanowire aqueous solution, 0.5 mL of 1 M PVP aqueous solution, 3 mL of 0.2 M AA solution, 18 mL of water and 1 mL of 0.1 M K_2PtCl_4; TEM images of Pt-on-Pd bimetallic nanowires at different magnifications (C, D). Reaction conditions: 2 mL of Pd nanowire aqueous solution, 0.25 mL of 1 M PVP aqueous solution, 1.5 mL of 0.2 M AA solution, 20 mL of water and 0.5 mL of 0.1 M K_2PtCl_4.

Figure S8 Optical images of colloidal suspensions of Pt-on-Pd bimetallic nanowires in water (The concentration Pt reaches 20 mM).

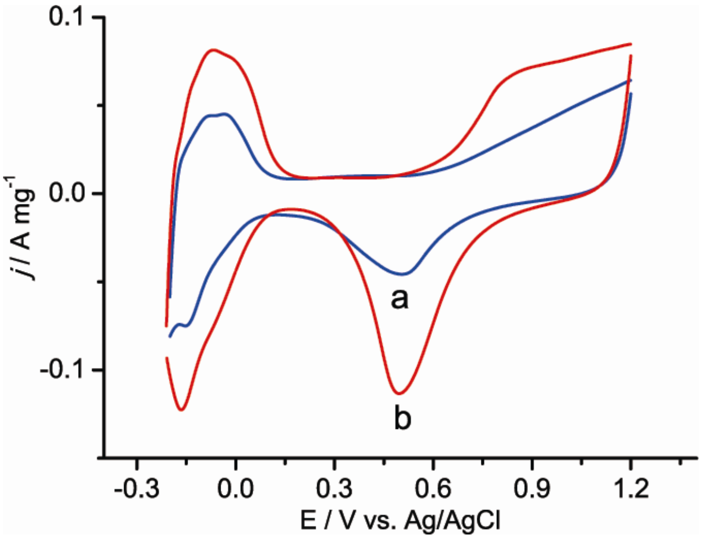

Figure S9 CVs of E-TEK catalyst (trace a) and Pt-on-Pd bimetallic nanowires (trace b) modified GC electrodes in a N_2-sparged 0.5 M H_2SO_4 solution at the scan rate of 50 mV/s. On the basis of the assumption that a monolayer of hydrogen corresponds to an adsorption charge of 210 mC cm^{-2},[1] the electrochemically active surface area of the Pt can be estimated.

Reference

1. (a) Gasteiger, H. A.; Kocha, S. S.; Sompalli, B.; Wagner, F. T. Applied Catalysis B: Environmental 2005, 56, 9. (b) Shao, M.-H.; Sasaki, K.; Adzic, R. R. J. Am. Chem. Soc. 2006, 128, 3526.