Supplementary Material (ESI) for Energy & Environmental Science

Supporting Online Material for

Pt/Pd Bimetallic Nanotube with Petal-like Surface: Thin Pd Nanoshell for Enhanced Catalytic Activity and Stability towards Ethanol Electrooxidation

Shaojun Guo, Shaojun Dong* and Erkang Wang*

State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin,130022, China, and Graduate School of the Chinese Academy of Sciences, Beijing, 100039, China.

*To whom correspondence should be addressed. E-mail: dongsj@ciac.jl.cn; ekwang@ciac.jl.cn

Experimental Section

Materials: Poly-(N-vinyl-2-pyrrolidone) (PVP·K30, molecular weight: 30000-40000), H_2SO_4, ammonium hydroxide (NH_4•OH), acetone, hydrazine (50%), H_2PtCl_6 and ethanol were purchased from Shanghai Chemical Factory (Shanghai, China) and used as received without further purification. Na_2PdCl_4, ascorbic acid (AA) and E-TEK Pd/C catalyst 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.

Apparatus: Transmission electron microscopy (TEM) and high-resolution (HRTEM) measurements were made on 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. X-ray diffraction (XRD) analysis was carried out on a D/Max 2500 V/PC X-ray diffractometer using Cu (40 kV, 30 mA) radiation. The composition of Pt/Pd bimetallic nanotubes with petal-like surface (PBNPSs) 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.

Synthesis of petal-like Pt nanotubes: The Te NWs were synthesized according to the reported reference.[18] Then, 0.05 mmol of Te NWs was added into 30 mL ethylene glycol and followed by the addition of 5.2 mL 1% H_2PtCl_6 aqueous solution. After being stirred at 50 ºC for more than 12 h, the Pt nanotubes with petal-like surface were obtained.

Synthesis of Pt/Pd bimetallic nanotubes with petal-like surface: 8.8 mL of the above solution was added into 16 mL of water, followed by the addition of 200 μL of Na_2PdCl_4 (93.75 mM), 80 μL of PVP aqueous solution (1 M). After being stirred for one min, 300 μL of ascorbic acid (AA) aqueous solution (0.4 M) was additionally added into the above mixture at 50 ºC and kept this temperature for 10 min. The product was collected by centrifugation, washed several times with water and dissolved in 4 mL of water for further electrochemical measurements.

Electrocatalytic experiment: Prior to the surface coating, the glassy carbon (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 ethanol and formic acid oxidation reactions, 5 μL of PBNPSs or PNPS or Pd/C E-TEK catalyst aqueous solution 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 the above materials modified GC electrode and dried before electrochemical experiments.

Figures

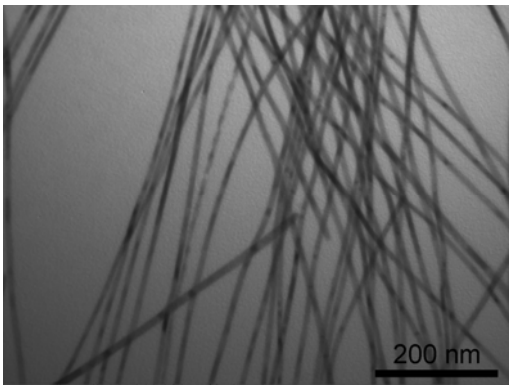

Figure S1 TEM image of the as-prepared Te nanowires (NWs).

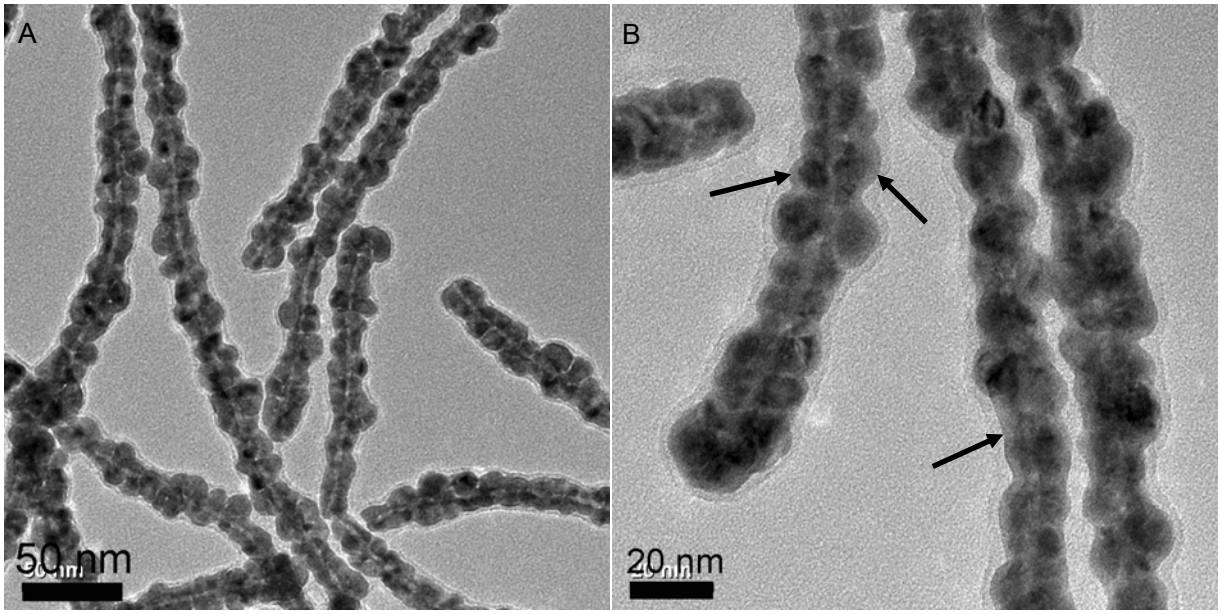

Figure S2 TEM images of the as-prepared Pt/Pd bimetallic nanotubes with petal-like surface.

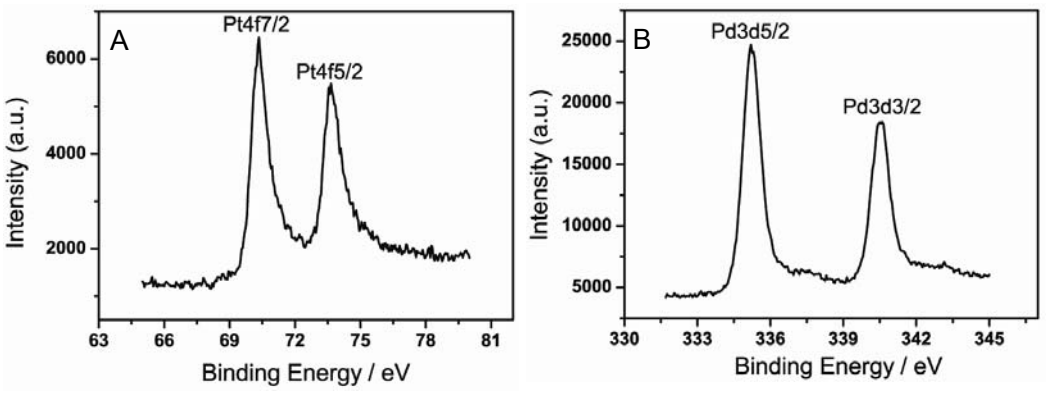

Figure S3 XPS pattern of the as-prepared Pt/Pd bimetallic nanotubes with petal-like surface. A: Pt4f; B: Pd3d.

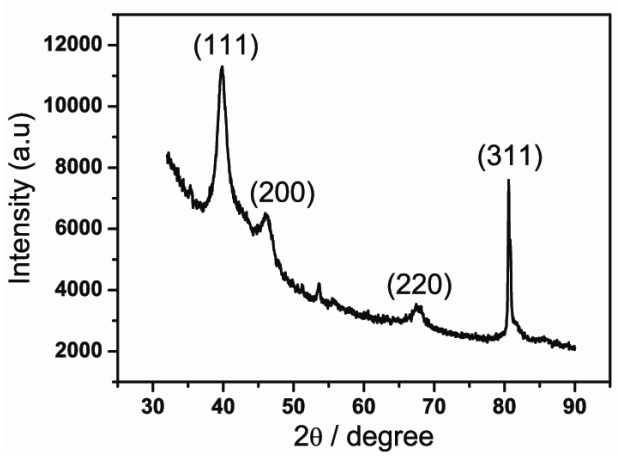

Figure S4 XRD pattern of the as-prepared Pt/Pd bimetallic nanotubes with petal-like surface.

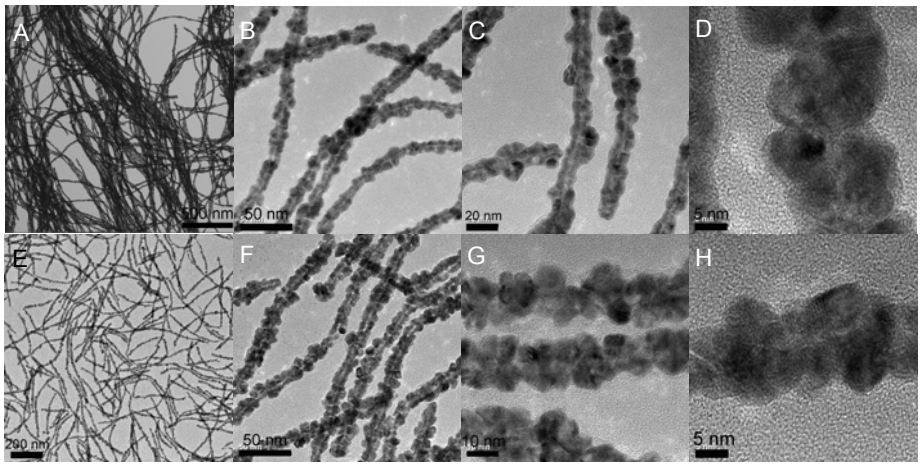

Figure S5 TEM images (A-H) of Pt-Pd bimetallic nanotubes with petal-like surface at different magnifications. A-D: 100 μL Na_2PdCl_4 (93.75 mM); E-H: 50 μL Na_2PdCl_4 (93.75 mM).

Table S1 Catalyst Characterization and Catalytic Performance (ethanol oxidation) Characteristics of Different PBNPSs, PNPSs and E-TEK Pd/C Catalyst.

Catalyst	Loading (μg/cm^2)	I_{peak} (mA/cm^2)	I_{peak} (mA/mg$_{metal}$)
Sample 1	103.1	8.21	1001
Sample 2	85.7	9.25	901.2
Sample 3	77.0	9.59	863.8
PNPSs	68.3	2.20	324.3
E-TEK Pd/C	90.5	2.69	269.2

18 H.-W. Liang, S. Liu, J.-Y. Gong, S.-B. Wang, L. Wang and S.-H. Yu, Adv. Mater., 2009, 21, 1850.