Electronic Supplementary Information (ESI)

Facile synthesis of ultrathin single-crystalline palladiumnanowires with enhanced electrocatalytic activities

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Experimental Section

Chemicals and materials. Commercially available palladium (II) chloride (99.9 wt%), L-ascorbic acid, didodecyldimethylammonium chloride (DODAC) and palladium black were purchased from Alfa Aesar. Hydrochloric acid, formic acid and ethanol were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai). Copper sulfate and Nafion® solution were purchased from Sigma-Aldrich corporation. Deionized water (18.2 MΩ) was produced from a pure power water purification system (Aike, China). H_2PdCl_4 solution (10 mM) was prepared by dissolving 0.3550 g palladium (II) chloride in HCl solution (20 mL, 0.2 M) and further diluting to 200 mL with deionized water. All the reagents were of analytical reagent grade and used without further purification.

Synthesis of Pd nanowires. In a typical synthesis of single-crystalline Pd nanowires, 0.03 g DODAC was dissolved in 10 mL deionized water with vigorous magnetic stirring, then 1.0 ml H_2PdCl_4 solution (10 mM) was added. The above mixture was transferred into an oven and kept under 95 °C for 30 min. A freshly prepared L-ascorbic acid (AA, 0.3 M, 1.0 mL) was rapidly injected into the hot solution. Immediately, the color of the reaction solution changed from brownish yellow to black. After the reaction, Pd nanowires were collected by centrifugation using a sufficient ethanol and washed with ethanol three times. The other Pd nanostructures were obtained following the similar process except for the crystallization temperature.

Characterization. The transmission electron microscope (TEM) observation was performed with a JEOL JEM-2100 microscope operated at 200 kV (Cs 1.0 mm, point resolution 2.3 Å). Images were recorded with a KeenView CCD camera (resolution 1376 x 1032 pixels, pixel size 6.45 x 6.45 μm). X-ray diffraction patterns were recorded on a powder sample using a D/max 2500 VL/PC diffractometer (Japan) equipped with graphite-monochromatized Cu Kα radiation in 2θ ranging from 1° to 8° and 30° to 90°. Related work voltage and current were 40 kV and 100 mA, respectively.

Small-angle X-ray scattering (SAXS) measurements were performed on a SAXSess mc2 apparatus with Cu Kα radiation (Anton Paar).

Electrochemical measurements. The electrocatalytic tests were carried out on the CHI 660E electrochemical analyzer at room temperature. A standard three-electrode system was employed for all electrochemical tests, which consisted of a platinum gauze as the counter electrode, a KCl-saturated silver/silver chloride electrode (SSE) as the reference electrode, and a catalyst coated glassy carbon electrode (GCE) as the working electrode. Potentials in this study were reported with respect to the SSE.

A well dispersed suspension of Pd catalyst was prepared by mixing 2 mg Pd nanoparticle and 1 mL ethanol and H_2O (volume ratio of 1:3) under ultrasonic for 20 min. A total of 5 μL such catalyst ink was coated on pre-treated GCE using a microliter syringe. After drying in 50 °C, the electrode was illuminated by a UV/ozone cleaning instrument (100 W, with 185 nm and 254 nm emissions) at the distance of about 5 mm for 2 hours to remove the organic surfactants before electrochemical measurements. Then, 5 μL of 1.0 wt % Nafion® solution was dropped onto the electrode surface and allowed drying again. Electrochemical measurements were performed in a 0.5 M N_2-saturated H_2SO_4 solution with or without 0.5 M HCOOH at a scan rate of 50 $mV \cdot s^{-1}$. The electrochemically active surface areas (ECSA) of Pd catalysts were calculated based on the charges associated with the stripping of a Cu monolayer underpotentially deposited (UPD) on the Pd nanocrystals by assuming 420 $\mu C\ cm^{-2}$ for a full monolayer coverage of Cu.[1-2] The Cu underpotential deposition process was performed in 0.5 M H_2SO_4 and 0.01 M $CuSO_4$ solutions at a scan rate of 50 mV s^{-1}. Chronoamperometry curves were obtained in an N_2-saturated 0.5 M HCOOH and 0.5 M H_2SO_4 mixture solution for 3000 s at 0.2 V applied potential.

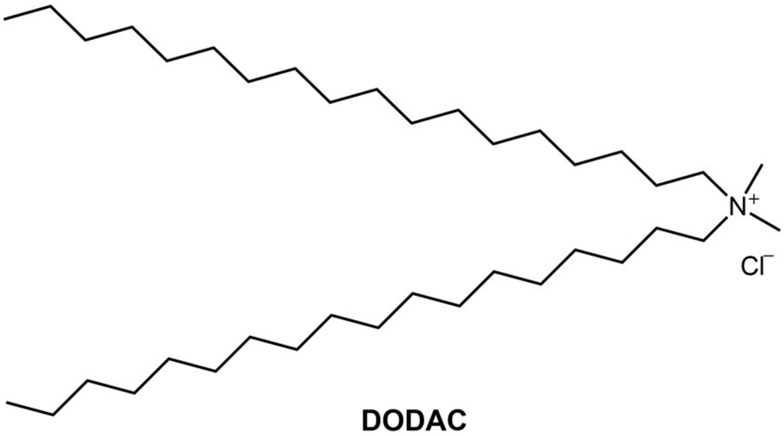

Fig. S1 The molecular structure of surfactant DODAC used in this work. This surfactant possesses double hydrophobic carbon chains which plays an important role in the subsequent directing-synthesis of Pd nanowires by the self-assembly process in the aqueous solution.

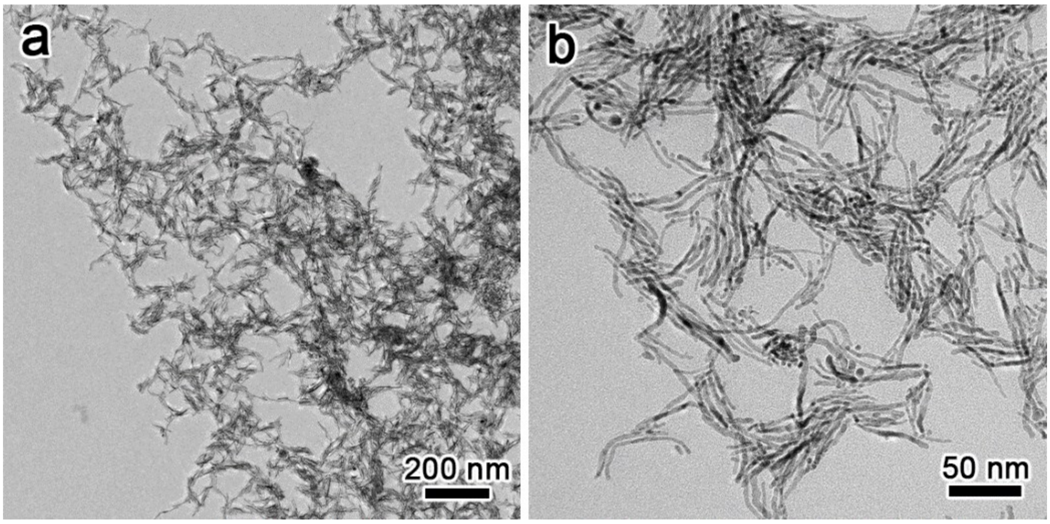

Fig. S2 TEM images of ultrathin Pd nanowires obtained immediately after the injection of AA (less than 2 s). It indicated that the crystalline growth of Pd nanostructure was quite rapid, resulting in the fail observation of the time evolution of Pd crystal structure.

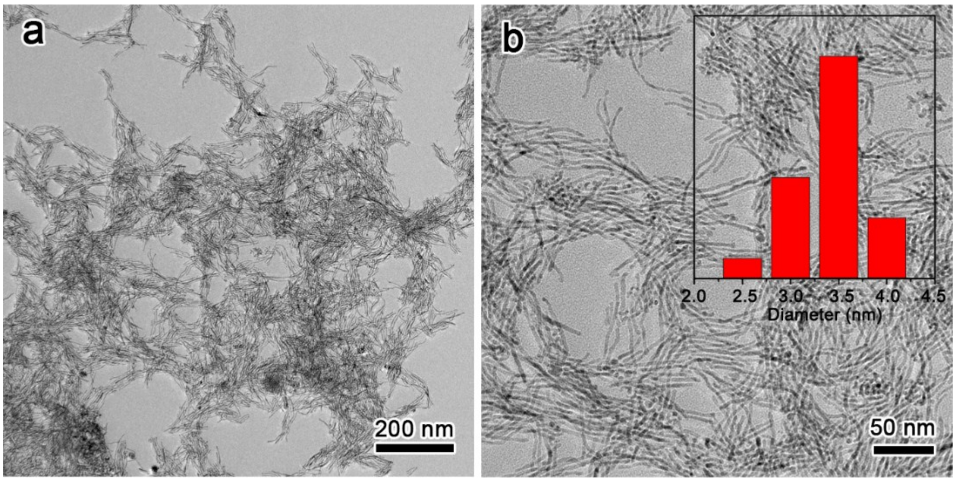

Fig. S3 Low-magnification TEM images (a and b) of Pd nanowires. The insert in b is the diameter distribution of these Pd nanowires, indicating that the obtained PdNWs have an average diameter about 3.5 nm although the length of individual wire seems to be not uniform from several tens to hundreds of nanometres.

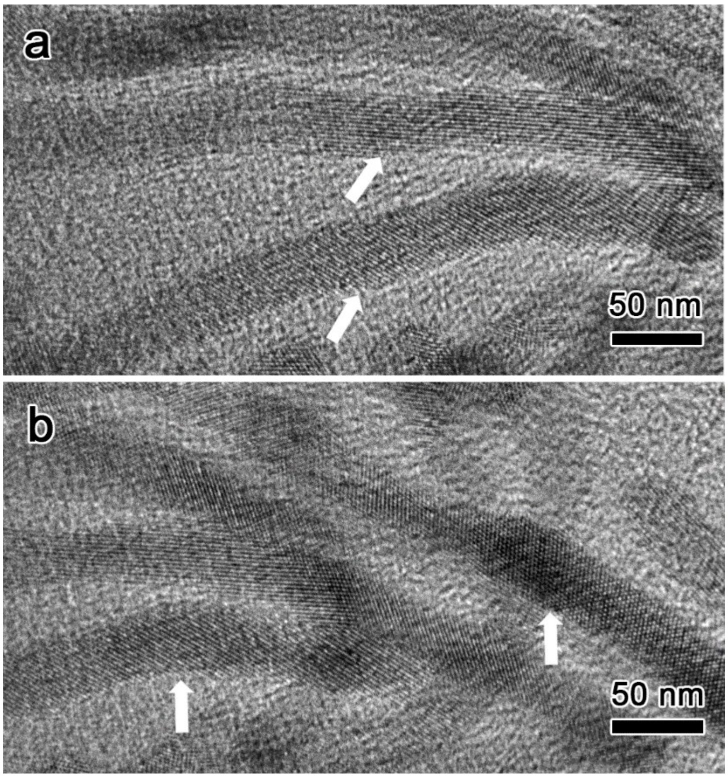

Fig. S4 HRTEM images of some other individual Pd nanowires (as shown by the white arrows) demonstrating that the Pd nanowires possess a single-crystalline property. However, from the fringes in the individual Pd nanowire, it demonstrates that the Pd nanowires do not grow along a fixed crystallographic orientation although all of them possess the obvious single-crystalline structure.

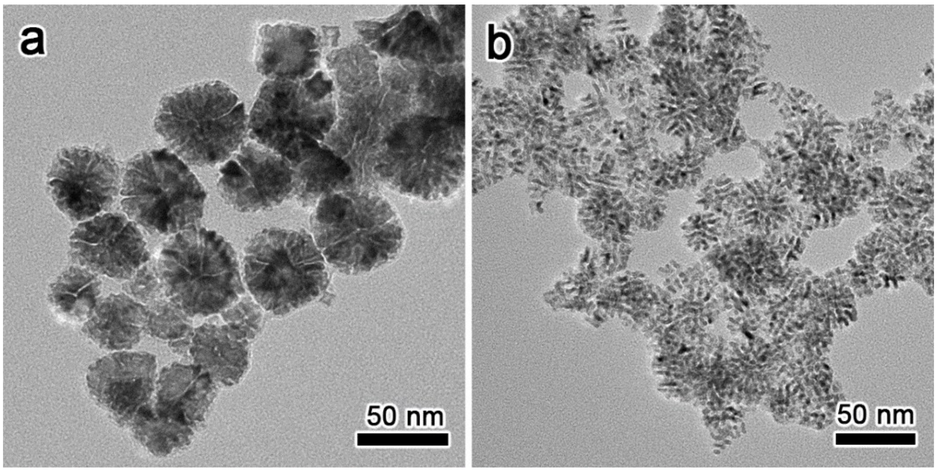

Fig. S5 TEM images of Pd nanomaterials synthesised by using the surfactants cetyltrimethylammonium chloride (CTAB, a) and cetylpyridinium chloride (CPC, b) under the same synthesis ratio and temperature with DODAC.

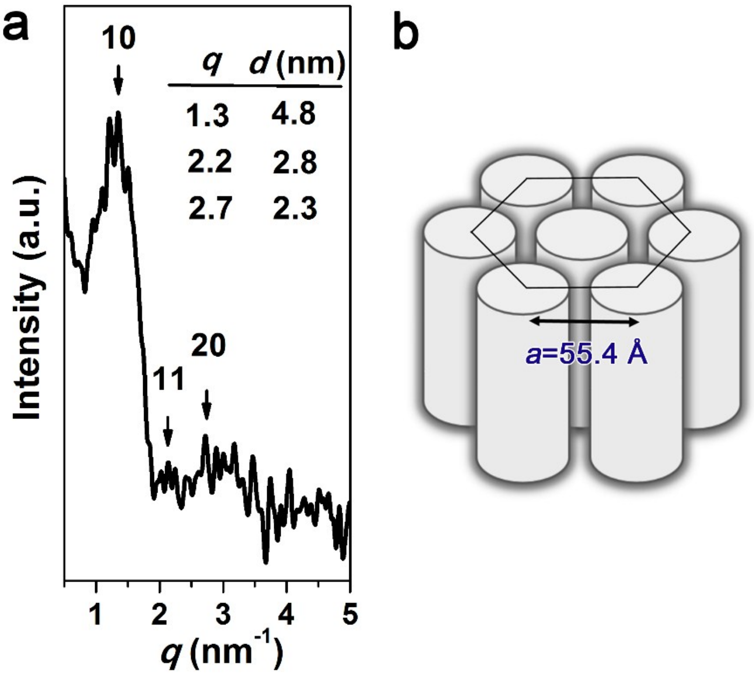

Fig. S6 SAXS spectra (a) of the liquid consisting of H_2O, DODAC, H_2PdCl_4. b) Structural representation of the corresponding mesostructure in the liquid. It indicated that the *p*6*mm* mesostructure indeed existed in the synthesis system although the mesoscopic order was not such fine as the solid one. The unit cell parameter based on the SAXS result was about 55.4 Å, similar with the data obtained via the small-angle XRD of the solid complex (Fig. 2).

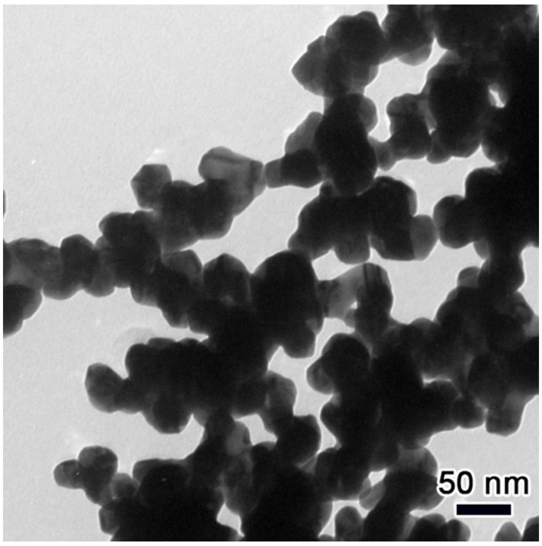

Fig. S7 Representative TEM image of commercial Pd black (PdB). It shows that the PdB has an average diameter about 50 nm and a relatively poor dispersion.

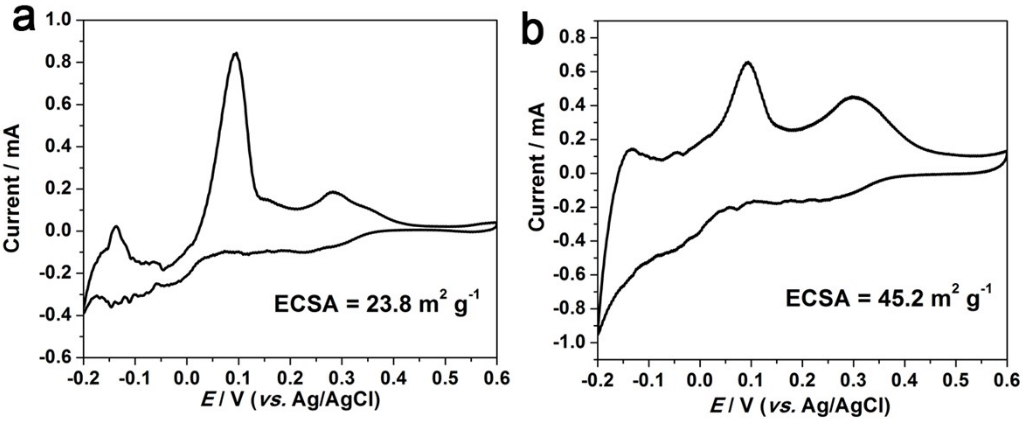

Fig. S8 Cyclic voltammograms (CV) of Cu monolayers underpotentially deposited on PdNWs and PdB in a solution contraining 0.5 M H_2SO_4 and 0.01 M $CuSO_4$ at a sweeping rate of 50 mV/s. The ECSAs were calculated to 23.8 $m^2\ g^{-1}$ and 45.2 $m^2\ g^{-1}$, respectively.

Reference

[1] Chierchie, T.; Mayer, C. *Electrochim. Acta* 1988, 33, 341.
[2] Jin, M., Zhang, H., Xie, Z., Xia, Y. *Energy Environ. Sci.*, 2012, 5, 6352.