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Supporting Information

Hollow and porous palladium nanocrystals: synthesis and electrocatalytic application

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Experimental

Reagents and Chemicals

Palladium chloride ($PdCl_2$), urea (carbamide), polyvinylpyrrolidone (PVP, Mw = 30000) and methanol (CH_3OH) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Commercial Pd black was purchased from Johnson Matthey Corporation. All reagents were of analytical reagent grade and used without further purification.

Synthesis of Pd nanocrystals

In a typical synthesis of Pd nanobowls (Pd-NBs), 0.5 mL of 0.05 M $PdCl_2$ solution and 2.0 mL of 0.05 M urea were added into 7.5 ml deionized water with continuous ultrasonic for 10 minutes at room temperature. Then, 50 mg PVP (Mw = 30000) was added into $PdCl_2$-urea mixture solution with another continuous ultrasonic for 10 minutes. After adjusting solution pH to 12.0 using NaOH solution, the resulting homogeneous solution was transferred to a 20 mL Teflon-lined stainless-steel autoclave. The stainless-steel autoclave was heated at 140 °C for 4 h. After cooling to room temperature, the products were separated by centrifugation at 15000 rpm for 15 min and further purified by washing with ethanol three times. The Pd nanocages (Pd-NCs) and solid Pd nanoparticles (Pd-SNPs) were obtained using the same process but with the lower pH at 8.0 and 2.0, respectively.

Electrochemical Measurements

Prior to the electrochemical tests, all Pd nanocrystals were treated by UV irradiation (wavelength at 185 and 254 nm) in air for 4 h to further remove the capping agents.[1-4] After UV irradiation, the morphology and size of the various Pd nanocrystals still remained, as demonstrated by the TEM images (Figure S15). All electrochemical experiments were performed using a CHI 760 D electrochemical analyzer at 30 ±1 ^{o}C. A standard three-electrode system was used for all electrochemical experiments, which consisted of a platinum wire as the auxiliary electrode, a saturated calomel reference electrode (SCE) protected by Luggin capillary with KCl solution as the reference electrode, and a catalyst modified glassy carbon electrode as the working electrode. Potentials in this study were reported with respect to the SCE.

An evenly distributed suspension of catalyst was prepared by ultrasonic the mixture of 10 mg catalyst and 5 mL H_2O for 30 min, and 6 μL of the resulting suspension was drop-cast onto the surface of the glassy carbon electrode. After drying at room temperature, 3 μL of Nafion solution (5 wt. %) was covered on the modified electrode surface and allowed drying again. Thus, the working electrode was obtained, and the specific loading of metal on the electrode surface was about 170 μg cm^{-2}. Electrochemical measurements were conducted in N_2-saturated 0.1 M NaOH solution or N_2-saturated 0.1 M NaOH solution with 0.5 M CH_3OH. The electrochemically active surface areas (ECSA) of Pd catalysts was calculated from the following equation (ECSA=Q/mC, m was the loading amount of Pd metal) by integrating the reduction charge (Q) of surface $Pd(OH)_2$ and assuming a value of 420 μC cm^{-2} (C) for the reduction charge of a $Pd(OH)_2$ monolayer on the Pd surface because ECSA of Pd catalysts could not be precisely assessed by coulometry in the "hydrogen region" due to the interference of hydrogen absorption in bulk Pd.

The The continuous CV measurements were conducted by continuously cycling the potential between -0.8 and 0.4 V (vs. SCE) in N_2-saturated 0.1 M NaOH solution at a scan rate of 100 mV s^{-1}. Meanwhile, full-scale voltammogram between -0.8 and 0.4 V (vs. SCE) in N_2-saturated 0.1 M NaOH solution were recorded periodically to track the degradation of Pd electrocatalysts.

Characterization

X-ray diffraction (XRD) patterns were obtained with a Model D/max-rC X-ray diffractometer using Cu Ka radiation source (λ=1.5406 Å) and operating at 40 kV and 100 mA. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo VG Scientific ESCALAB 250 spectrometer. The binding energy was calibrated by means of the C 1s peak energy of 284.6 eV. Transmission electron microscopy (TEM) images were taken using a JEOL JEM-2100F transmission electron microscopy operated at 200 kV. High-resolution TEM (HRTEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) measurements were performed on FEI Tecnai G2 F20 microscope equipped with an EDAX X-ray detector. Scanning electron microscopy (SEM) images were captured on a JSM-2010 microscope at an accelerating voltage of 20 kV. Nitrogen adsorption−desorption isotherms (SADI) experiments were performed at 77 K on Micromeritics ASAP 2020MC instrument to determine the Brunauer−Emmett−Teller (BET) surface area and pore size distribution.

Figure section

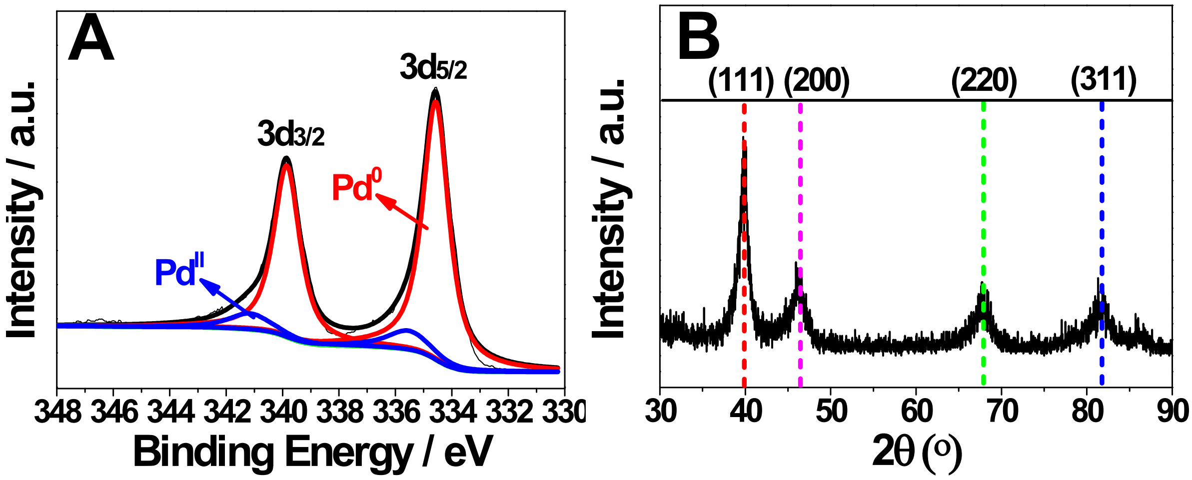

Fig. S1 (A) Pd 3d XPS spectrum and (B) XRD pattern of Pd-NBs.

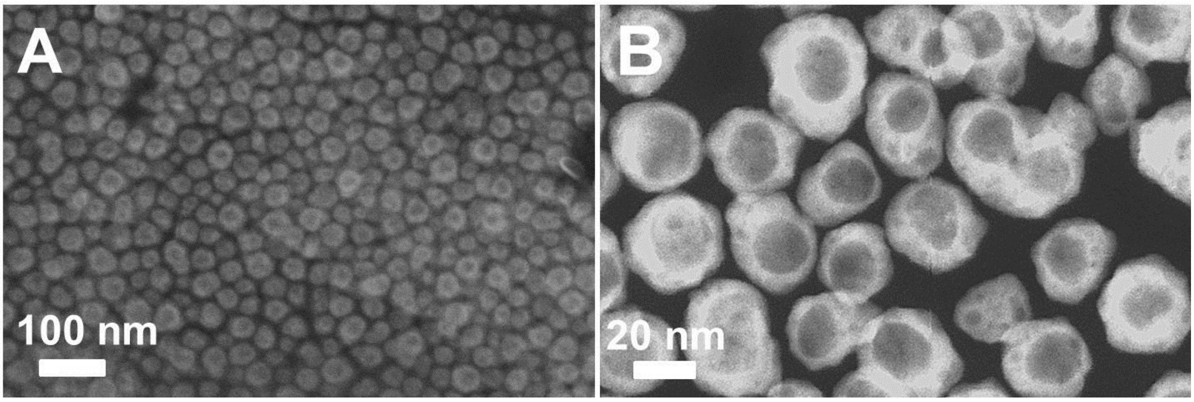

Fig. S2 Typical SEM and HAADF-STEM images of Pd-NBs.

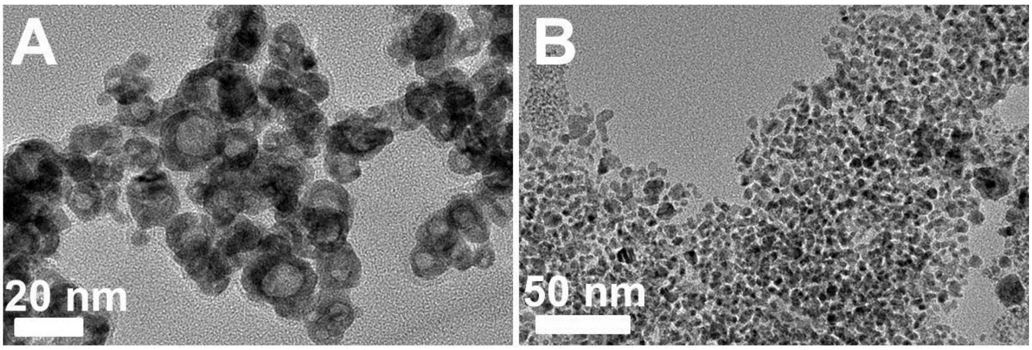

Fig. S3 TEM images of obtained Pd nanocrystals under the standard procedures except (A) without PVP and (B) without urea.

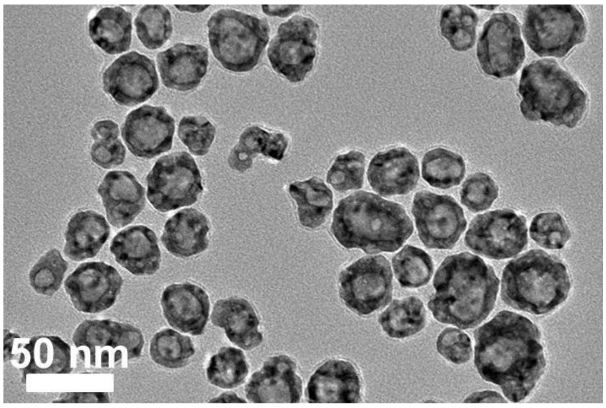

Fig. S4 TEM image of Pd nanocrystals prepared by displacing the air with N_2 to eliminate typical etchant O_2.

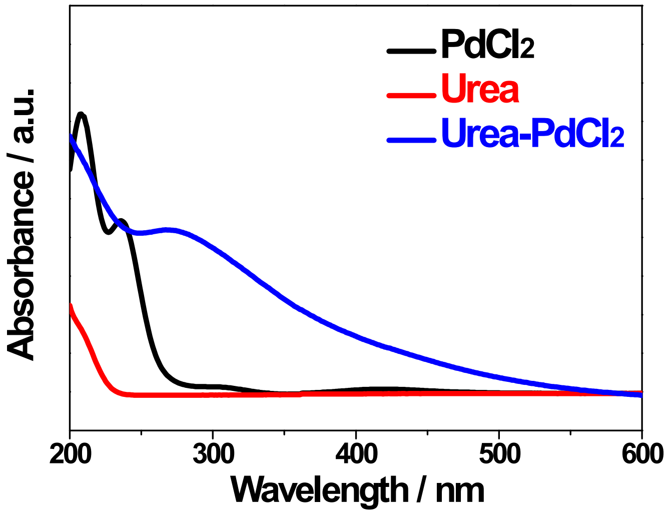

Fig. S5 UV–vis spectra of $PdCl_2$ solution, urea solution and the mixture solution of urea and $PdCl_2$.

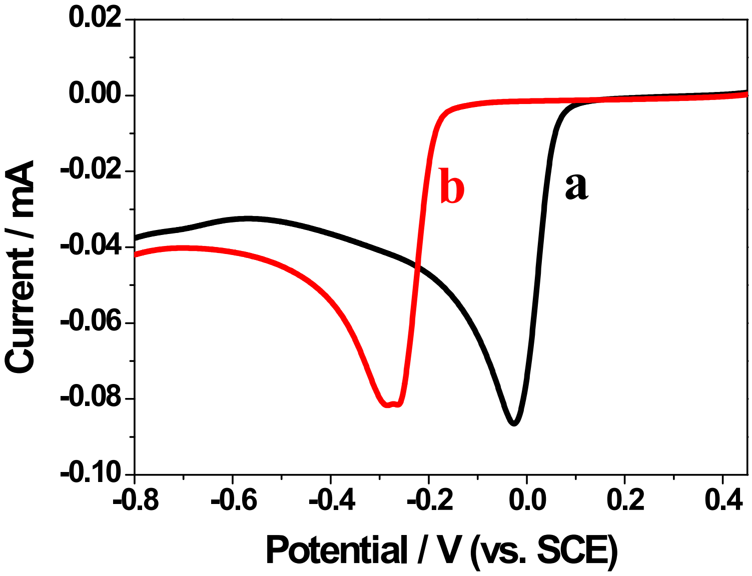

Fig. S6 Linear sweeping voltammograms of N_2-saturated 0.5 M KCl solution containing (a) 0.0025 M $PdCl_2$ (pH 2.0) and (b) 0.0025 M $PdCl_2$ + 0.4 M urea solution (pH 2.0) at the glassy carbon electrode at a scan rate of 100 mV s^{-1}, respectively.

As observed, the reduction peak potential of mixture solution containing urea and $PdCl_2$ shows the negatively shifts compared with the single-component $PdCl_2$ solution, also confirming that the interaction between $PdCl_2$ and urea. For the kinetically controlled synthesis of noble metal nanocrystals, the slow reduction rate of the metal precursor is crucial for the generation of high-quality nanocrystals, because a fast reduction rate generally results in the aggregation of metal nanostructures. According to thermodynamical view, the lower reduction potential results in the slower reduction rate. Thus, the low reduction potential of the urea–Pd^{II} complex facilitates the formation of the monodisperse Pd nanostructures, owing to the slow reduction rate.

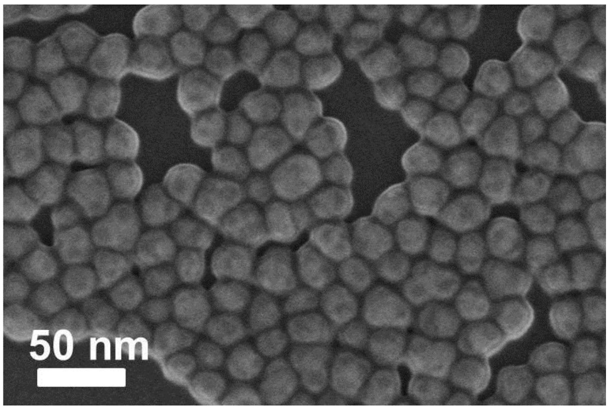

Fig. S7 Typical SEM image of Pd-NCs.

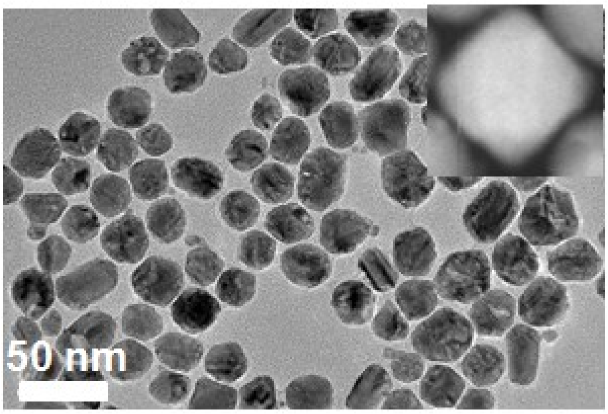

Fig. S8 TEM image of Pd-SNPs, the insert is the corresponding HAADF-STEM image.

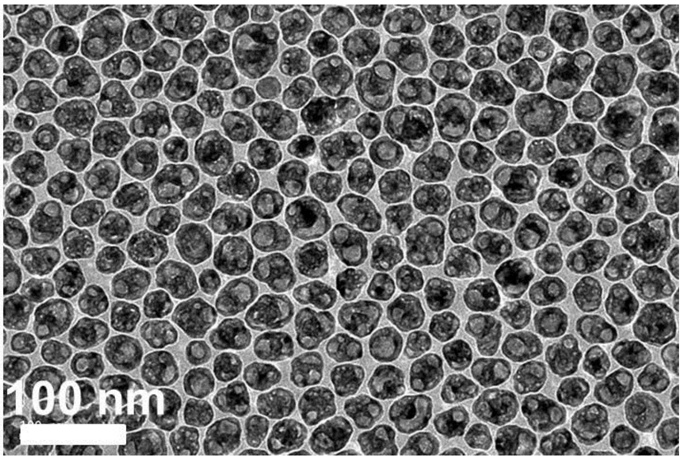

Fig. S9 TEM image of Pd-NCs after re-heating treatment at 140 °C for 12 h.

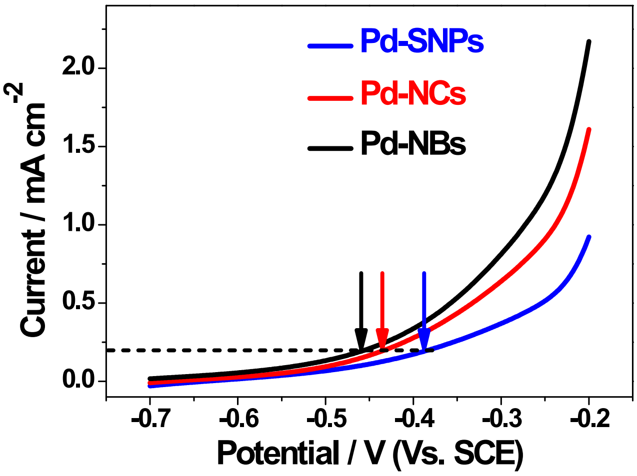

Fig. S10 CVs at low potential region for Pd-NBs, Pd-NCs and Pd-SNPs in N_2-saturated 0.1 M NaOH + 0.5 M CH_3OH solution at the scan rate of 50 mV s^{-1}.

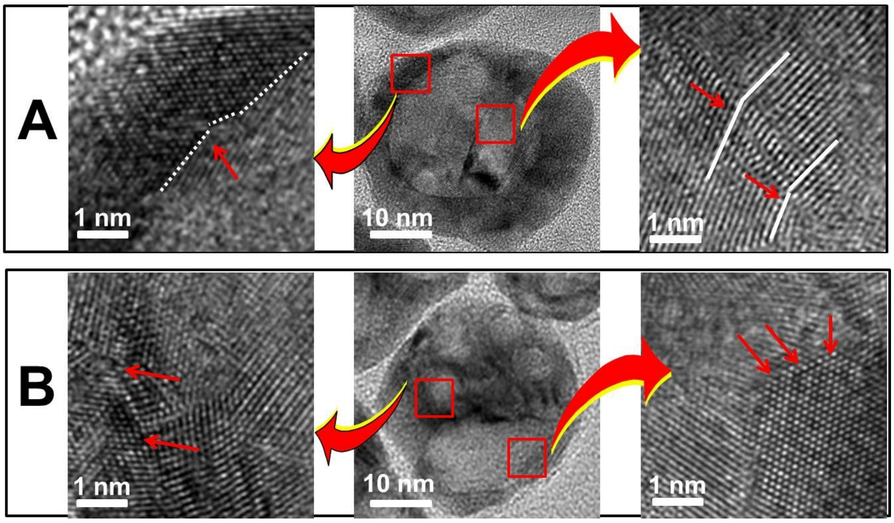

Fig. S11 HRTEM images of the (A) Pd-NBs and (B) Pd-NCs.

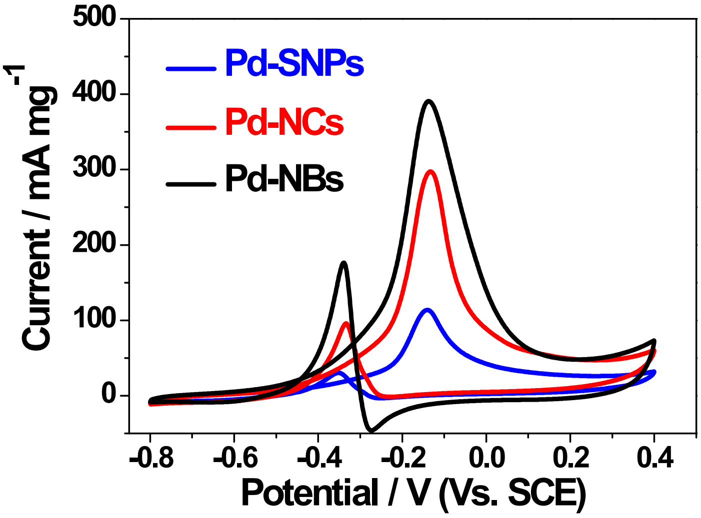

Fig. S12 Mass-normalized CVs for the Pd-NBs, Pd-NCs, and Pd-SNPs in N_2-saturated 0.1 M NaOH + 0.5 M CH_3OH solution at the scan rate of 50 mV s^{-1}.

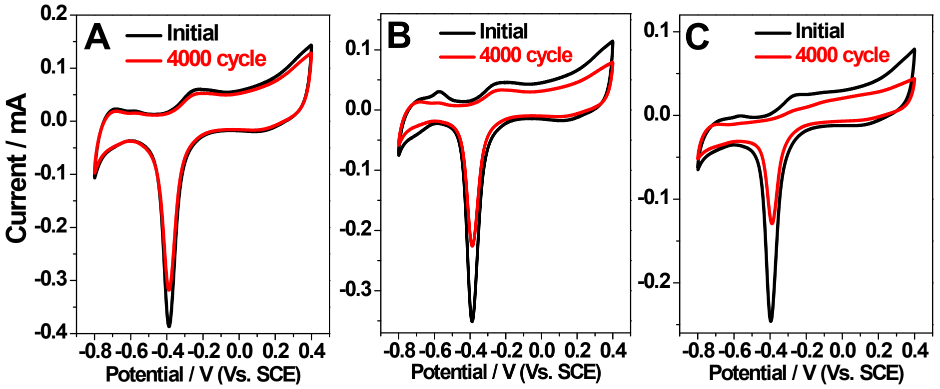

Fig. S13. CV curves for (A) Pd-NBs, (B) Pd-NCs and (C) Pd-SNPs in before and after 4000 cycles at a scan rate of 100 mV s^{-1}.

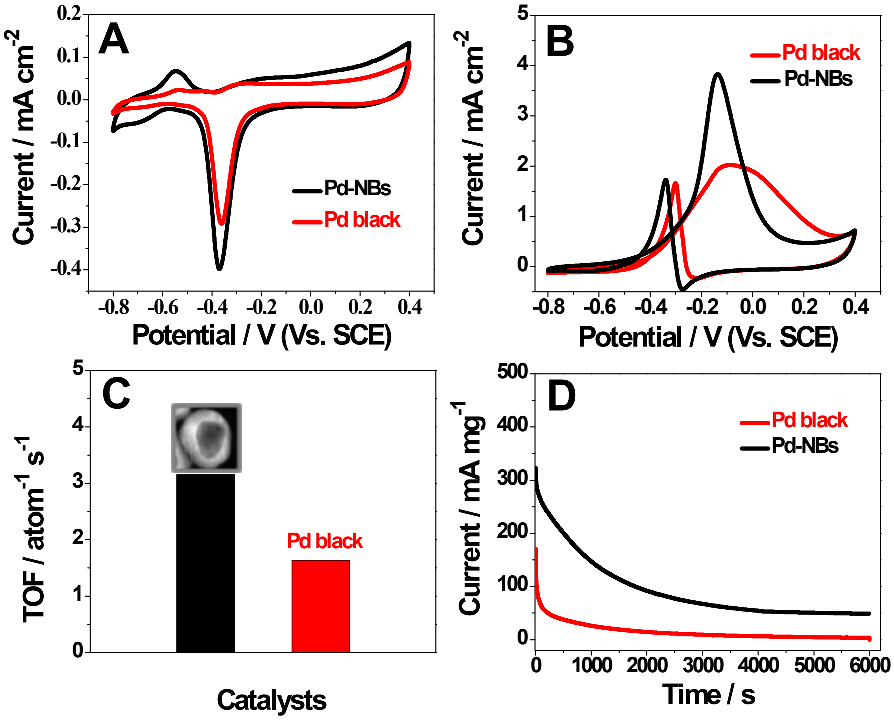

Fig. S14 (A) Cyclic voltammograms of Pd-NBs and Pd black in N_2-saturated 0.1 M NaOH solution at a scan rate of 50 mV s^{-1}. (B) ESCA-normalized CVs for Pd-NBs and Pd black in N_2-saturated 0.1 M NaOH + 0.5 M CH_3OH solution at the scan rate of 50 mV s^{-1}. (C) The TOF of Pd-NBs and Pd black at −0.15 V potential. (D) Chronoamperometry curves for Pd-NBs and Pd black in N_2-saturated 0.1 M NaOH + 0.5 M CH_3OH solution solution for 6000 s at −0.1 V potential.

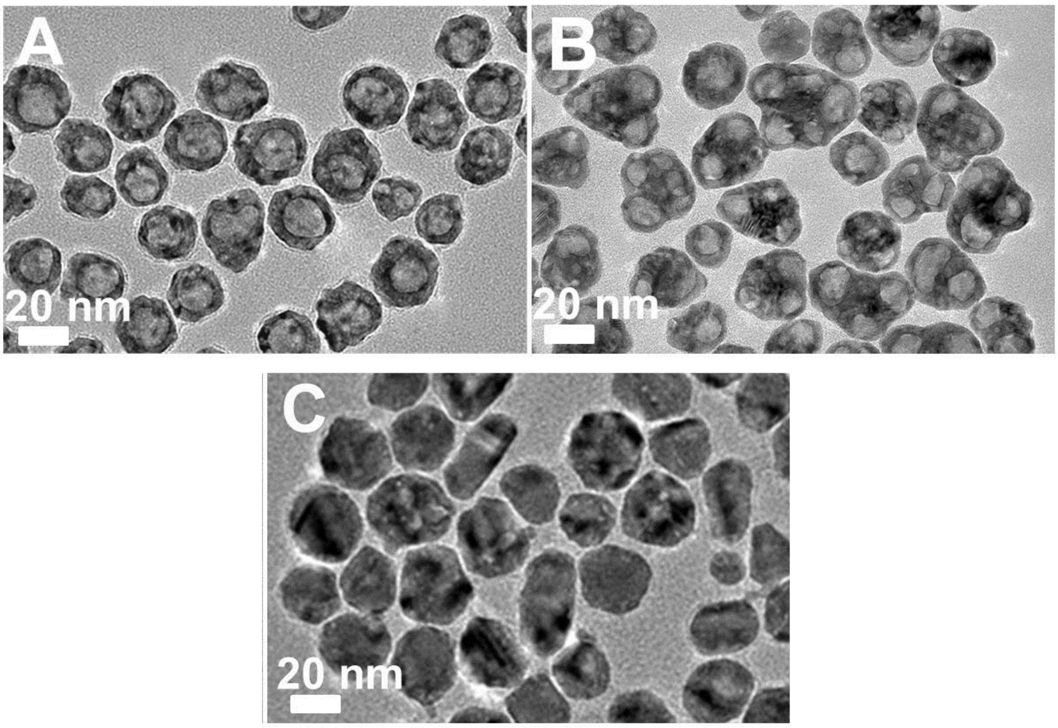

Fig. S15 TEM images of (A) Pd-NBs, (B) Pd-NCs and (C) Pd-SNPs after 4 h of UV treatment.

Reference

1. M. Crespo-Quesada, J. M. Andanson, A. Yarulin, B. Lim, Y. Xia and L. Kiwi-Minsker, *Langmuir*, 2011, **27** 7909–7916.
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3. Z. C. Zhang, J. F. Hui, Z. C. Liu, X. Zhang, J. Zhuang and X. Wang, *Langmuir*, 2012, **28**, 14845-14848.
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