Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information For:

2D Ultrathin Core-shell Pd@$Pt_{monolayer}$ Nanosheets: Defect-Mediated Thin Film Growth and Enhanced Oxygen Reduction Performance

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Experimental Section

Materials and methods

Pd@$Pt_{monolayer}$ ultrathin nanoplate fabrication

Pd nanoplates were synthesized by a colloidal method proposed by Zheng and co-workers[1]. $Pd(acac)_2$ (50.0 mg), CTAB (185.0 mg), PVP (160.0 mg) and 10 mL benzyl alcohol were mixed at room temperature and saturated with carbon monoxide (CO) gas. After heating the mixture for 3h at 70 °C, the dark blue precipitates were separated by centrifugation and further purified by ethanol for several times. These Pd nanoplates were loaded onto a polished glassy carbon electrode (diameter = 5 mm, without Nafion®) for surface modification via a defect-mediated thin film growth method[2].

The surface modification was performed on a CHI 760D electrochemical workstation (Shanghai Chenhua Co., China), using a conventional three electrode cell with Pt foil as the counter electrode and reversible hydrogen electrode (RHE) as the reference electrode. Before cyclic voltammetry measurement, one cycle of potential sweep between 0.2 to 1.2 V at a sweep rate of 10 mV s^{-1} was applied to clean the surfactant adsorbed on the Pd surface. According to the voltammetry curves for Cu UPD on Pd nanoplates, Pt was deposited by repeated potential cycles between 0.40 (bulk deposition potential of Cu) and 0.67 V (bulk deposition potential of Pt) for 15 times, followed by a final linear potential sweep to 1 V to remove Cu. After the treatment, Pd@$Pt_{monolayer}$ materials were collected for subsequent characterization.

Physicochemical characterization

Power X-ray diffraction (XRD) pattern was measured by a Bruker D8 Advance X-ray diffractometer using Cu Kα radiation (λ=1.5418 Å) with a scan rate of $0.04°s^{-1}$. Transmission electron microscopy (TEM, JEM 1011) was operated at an acceleration voltage of 100 kV. Fine structure analyses were carried out with the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) operated at 300 kV, attached with energy-dispersive X-ray spectroscopy (EDS). All TEM samples were prepared by depositing a drop of diluted suspension in ethanol on carbon film coated molybdenum grid. To measure the sample thickness, Pd nanoplates were dropped onto a mica substrate for atomic force microscopy (AFM, NanoScope IIIA) analyses under the tapping mode. Composition analyses of Pd and Pt were further confirmed with the inductively coupled plasma mass spectrometry (ICP-MS, IRIS Advantage spectrometer). Surface structures of Pd@Pt$_{\text{monolayer}}$ were analyzed by means of X-ray photoelectron spectrometer (XPS, ESCALAB 250), using a monochromatized MgKα X-ray as the excitation source and choosing C1s (284.60 eV) as the reference line.

Electrochemical Testing

Pd@Pt$_{\text{monolayer}}$ catalyst ink was prepared by mixing 200μL as-prepared ethanol suspension into 1 mL ethanol. The prepared catalyst ink solution (8μL) was then deposited onto a polished glassy carbon disc electrode (geometric surface area of 0.19625 cm^{-2}) leading to a loading of 48.2 μg cm^{-2}, followed by complete dry under ambient conditions. The electrode was then immersed into 50 mM H_2SO_4 at 30 °C by a circulating water bath, and all electrochemical surface modification and testing were carried out using a reference hydrogen electrode (RHE) and a platinum wire counter electrode. For CO stripping voltammetry, CO gas (99.99 %) was bubbled for 30 min first, following by N_2 gas bubbling for additional 30 min at 0.4 V. ORR activities were measured by using a PAR model 636 rotating disk electrode system in an O_2-saturated 0.1 M $HClO_4$ solution at 30 °C, and the electrode rotation rate varied from 400 to 2500 rpm. Prior to the electrochemical measurements, the electrolytes were deoxygenated by bubbling N_2 for 20 min. Commercial carbon supported platinum (Pt/C) was tested for comparison with an electrode loading of 15μg_{Pt} cm^{-2}. As a result of substantial hydrogen adsorption, the electrochemical surface area (ECSA) from the hydrogen adsorption/desorption area was unreliable. Here we calculated ECSA of Pd nanoplates and Pd@$Pt_{monolayer}$ by integrating the charge associated with reduction of surface Pt-O and Pd-O in 0.1 M N_2-purged $HClO_4$ electrolyte, by assuming a charge of 420 $\mu C\ cm^{-2}$. For commercial Pt/C catalyst, ESA was calculated from the hydrogen adsorption / desorption charge in the CV curve, by assuming a charge of 210 $\mu C\ cm^{-2}$. The ECSAs of Pd@$Pt_{monolayer}$ and Pt/C were calculated to be 171.45 and 77.96 $m^2\ g_{Pt}^{-1}$, respectively. Accelerated durability test (ADT) was carried out by continuous potentiodynamic sweep between 0.6-1.0 V in oxygen-saturated 0.1 M $HClO_4$ solution for 5000 cycles at 30 °C, with a reversible hydrogen electrode (RHE) working as the reference electrode at a scan rate of 50 mV s^{-1}.

Reagents: Pd(II) acetylacetonate (Pd(acac)$_2$) and $HClO_4$ (G.R.) were produced by Aladdin Co. Ltd. Poly(vinylpyrrolidone) (PVP) (MW=30000), Cetyltrimethylammonium bromide (CTAB), benzyl alcohol, H_2SO_4 (A.R.), $CuSO_4$□$5H_2O$ (A.R.), H_2PtCl_4 (A.R.) were purchased from Sinopharm Chemical Reagent Co. Ltd. The Johnson Matthey Pt/C (20 wt%) catalysts was purchased from Alfa Aesar. The water used in all experiments was ultrapure (18.2 MΩ). All reagents were used as received without further purification.

References

1. X. Huang, S. Tang, X. Mu, Y. Dai, G. Chen, Z. Zhou, F. Ruan, Z. Yang and N. Zheng, *Nat. Nanotech.*, 2011, **6**, 28-32.
2. J. X. Wang, B. M. Ocko and R. R. Adzic, *Surf. Sci.*, 2003, **540**, 230-236.

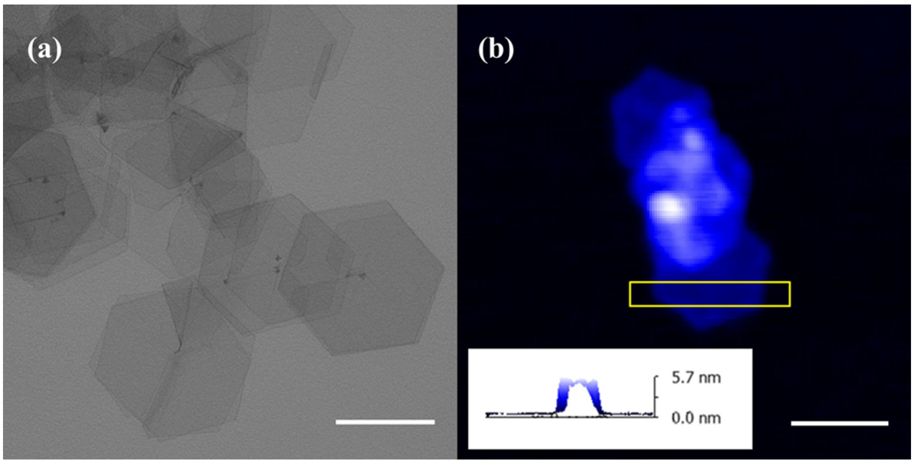

Figure S1. (a) TEM image of Pd nanoplates. The scale bar stands for 150 nm. (b) AFM images of Pd nanoplates. The inset picture shows the z-axis height at selected yellow region. The scale bar stands for 150 nm.

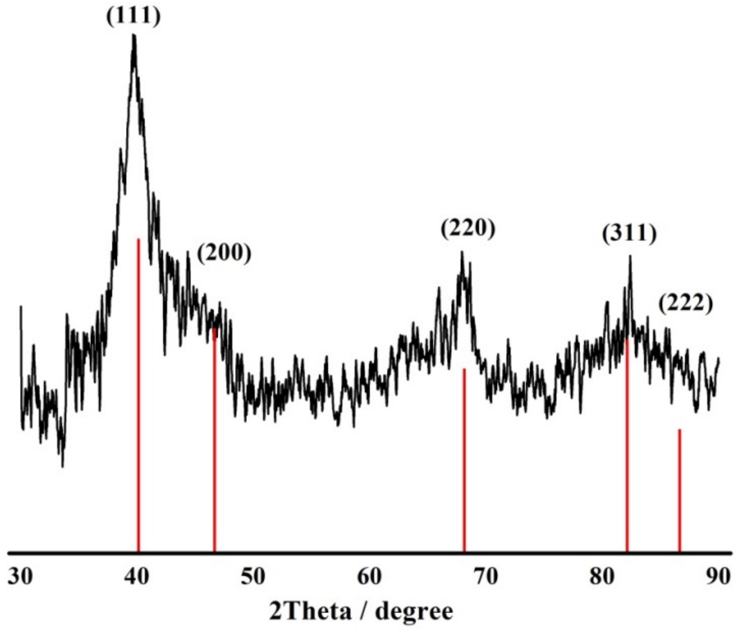

Figure S2. XRD pattern of as-prepared Pd nanoplates.

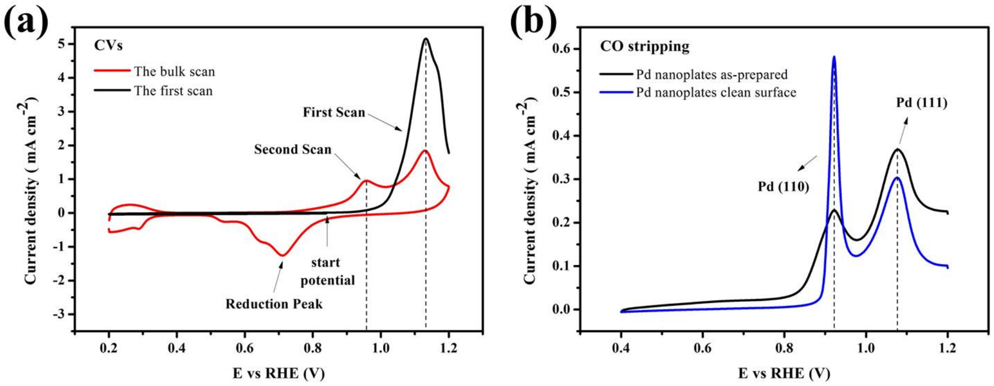

Figure S3. (a) CVs for Pd nanoplates in N_2-purged 50 mM H_2SO_4 solution at 10 mV s^{-1} scan rate. (b) CO stripping curves for Pd nanoplates before (black solid line) and after (blue solid line) electrochemical surface cleaning, measured in N_2-purged 50 mM H_2SO_4 solution at 2 mV s^{-1} scan rate.

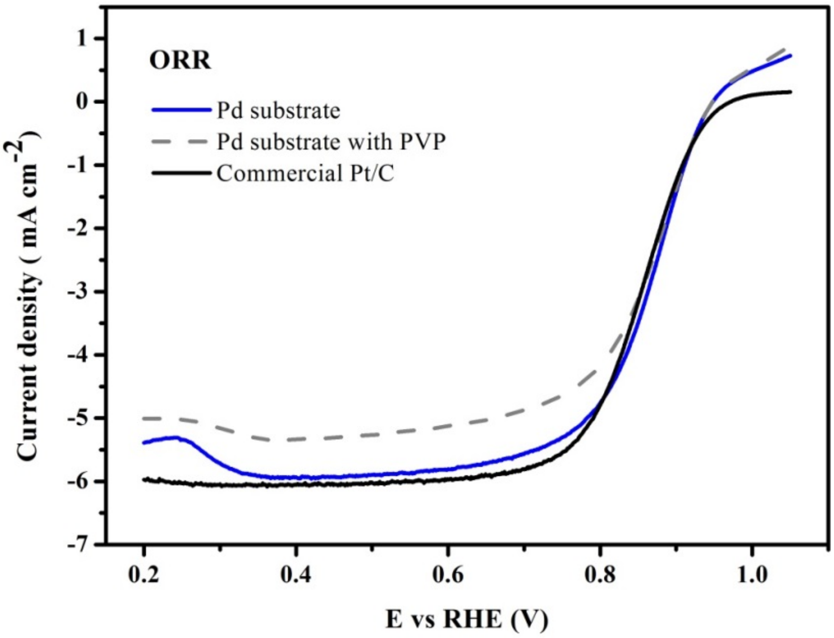

Figure S4. ORR activity differences of Pd substrates before and after PVP removal from the surface, in O_2 saturated 0.1 M $HClO_4$ solution, using commercial Pt/C as a reference.

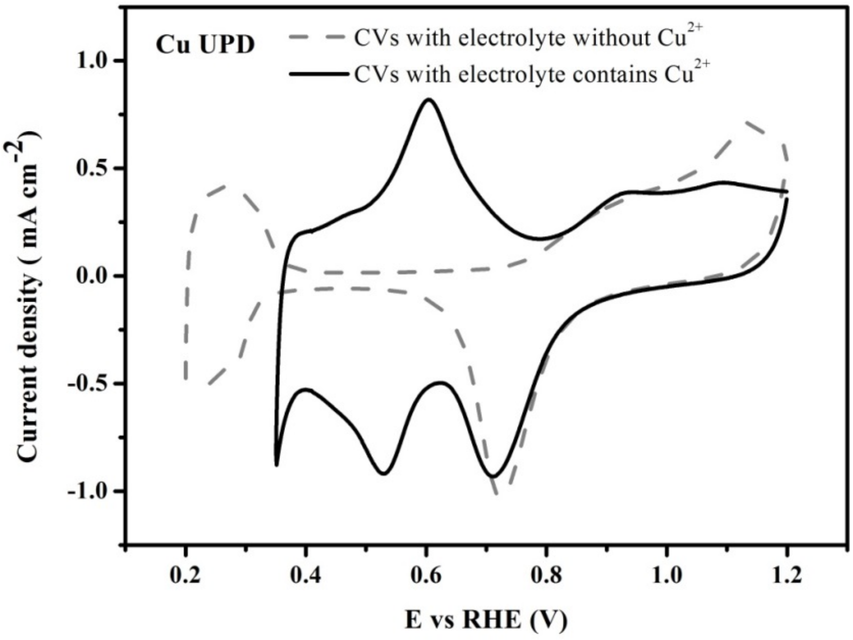

Figure S5. Voltammetry curves for Cu UPD on Pd nanoplates (solid line) in N_2-saturated solution containing 50 mM H_2SO_4 and 50 mM $CuSO_4$, together with a baseline voltammetric curve for Pd nanoplates in a solution without Cu (dash line). Scan rate 10 mV s^{-1}.

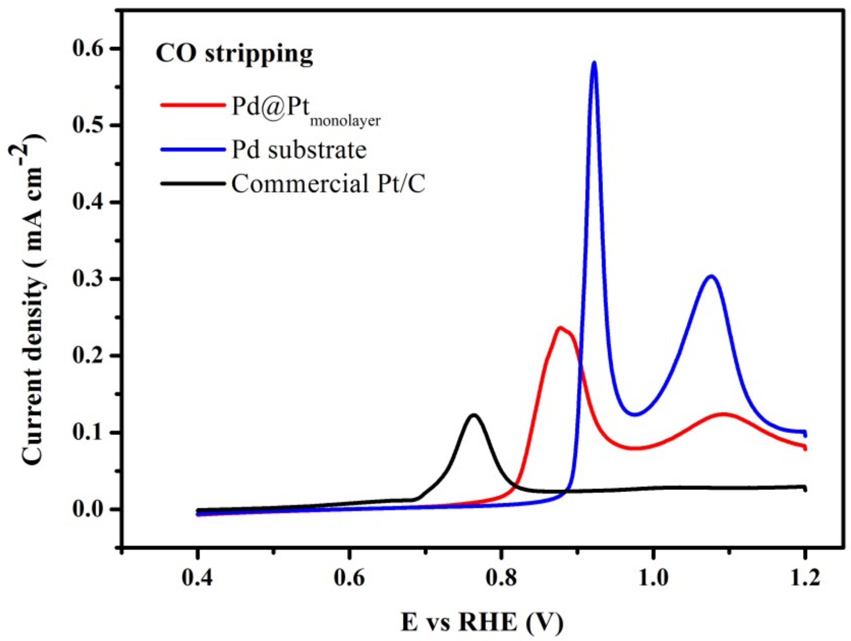

Figure S6. CO stripping voltammetry curves of different materials in 50 mM H_2SO_4 solution at a scan rate of 2 mV s^{-1}.

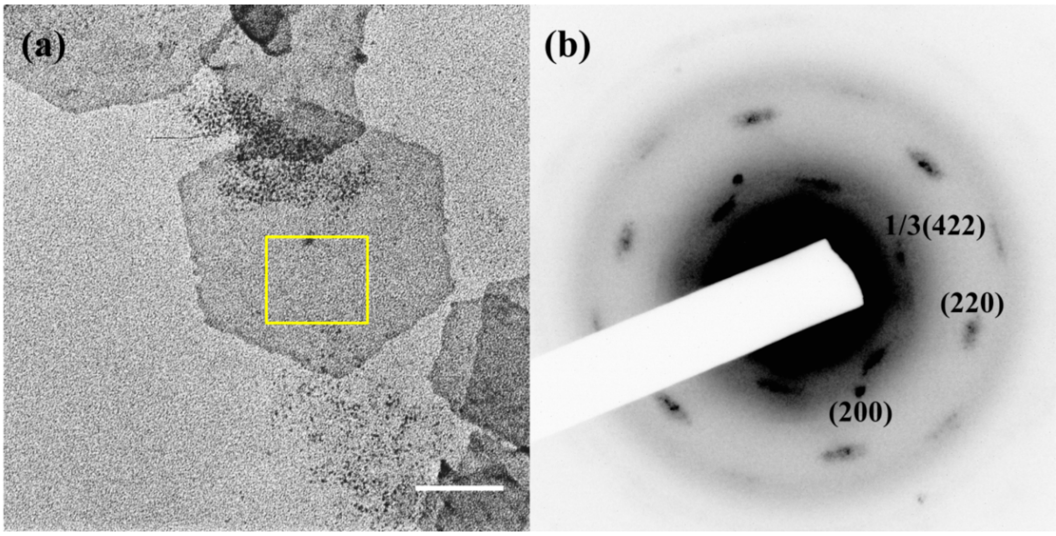

Figure S7. (a) TEM image and (b) SAED pattern of Pd@Pt$_{monolayer}$ catalyst. The scale bar stands for 50 nm.

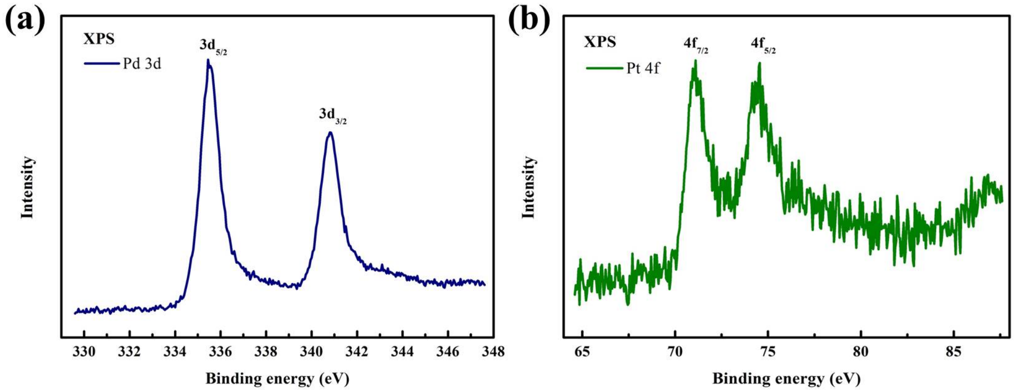

Figure S8. XPS spectra of (a) Pd 3*d* and (b) Pt 4*f* of Pd@Pt$_{monolayer}$.

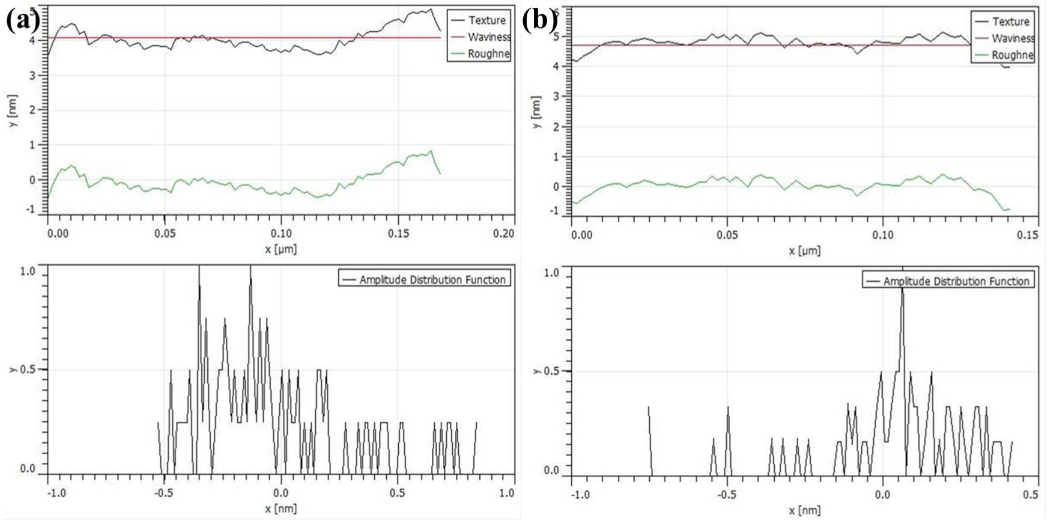

Figure S9. Roughness parameters based on AFM measurement of (a) Pd nanoplates and (b) Pd@Pt$_{monolayer}$. Roughness average values (R_a) of Pd substrate and Pd@Pt$_{monolayer}$ are 0.26 and 0.19 nm, respectively. And root mean square roughness values (R_q) of Pd substrate and Pd@Pt$_{monolayer}$ are 0.32 and 0.25 nm, respectively.

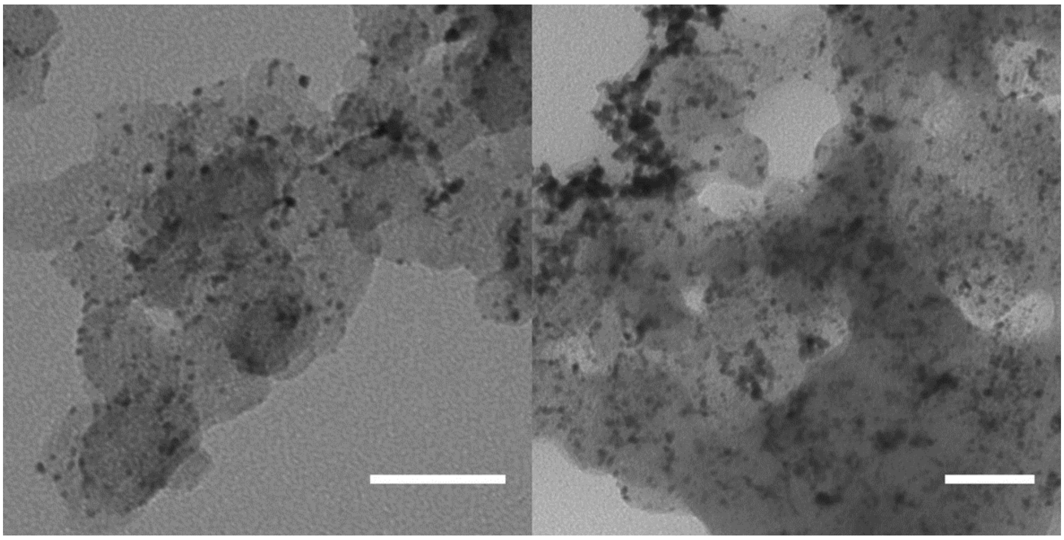

Figure S10. TEM images of commercial Pt/C before (left) and after (right) 5000 cycles durability measurement in 0.1 M $HClO_4$ solution. Scale bar stands for 50 nm.

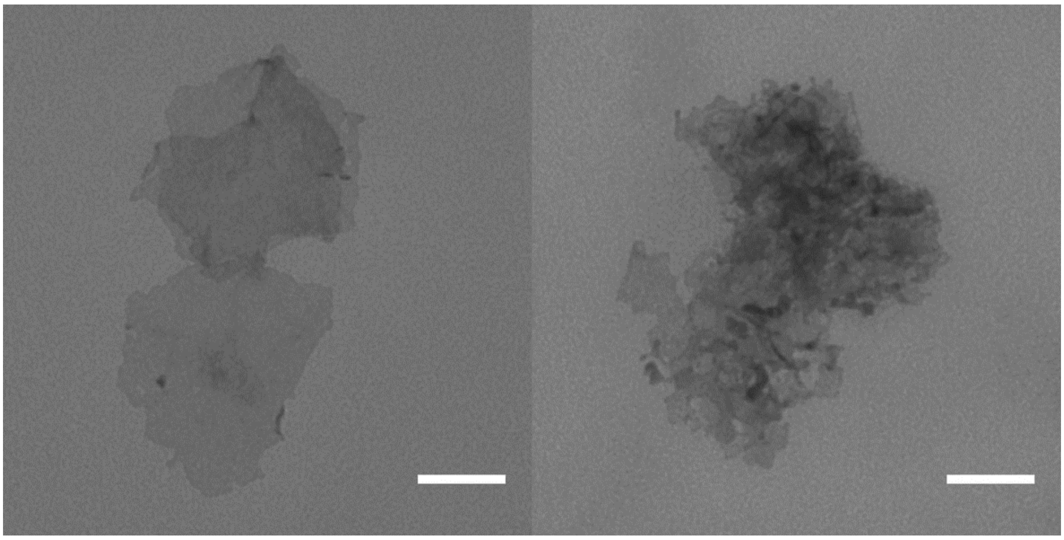

Figure S11. TEM images of Pd@Pt$_{monolayer}$ before (left) and after (right) 5000 cycles durability measurement in 0.1 M HClO$_4$ solution. Scale bar stands for 50 nm.