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Supplementary Information

Enhanced Stability and Activity with Pd–O Junction Formation and Electronic Structure Modification of Palladium Nanoparticles Supported on Exfoliated Montmorillonite for the Oxygen Reduction Reaction

Wei Ding,† Zidong Wei,*† Siguo Chen,† Meirong Xia,† Jinsong Hu, ‡ Li-jun Wan,*‡ Xueqiang Qi†, Xiaohua Hu† and Li Li†

† The State Key Laboratory of Power Transmission Equipment & System Security and New Technology, College of Chemistry and Chemical Engineering, Chongqing University, Chongqing, 400044; China

‡ Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Sciences (CAS), Beijing 100190, China

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Table S1: Calculated adsorption energies (AE) of Oads on various metal surfaces.

Scheme S1. The structure of MMT.

Figure S1. TEM image of the edge of an ex-MMT nanoplatelet.

Figure S2. TEM image of Na-MMT.

Figure S3. (A) HRTEM of a typical Pd NPs with the PdOx or Pd-O-ex-MMT junction on ex-MMT nanoplatelets. (B) HRTEM of the junction (red) area.

Figure S4. XRD patterns of the Pd/C and the Pd/ex-MMT catalysts.

Figure S5. The ORR kinetic current densities of the Pd/ex-MMT, Pd/C and Pt/C calculated from the LSV in figure 4b.

Figure S6. LSV of Pd/ex-MMT in an O_2-saturated 0.1 M $HClO_4$ solution on various rotating speed; 10 mV/s scan rate.

Figure S7. LSV of Pd/ex-MMT (A) and Pd/C (B) in an O_2-saturated 0.1 M $HClO_4$ solution before (black) and after (red) stability tests; 10 mV/s scan rate.

1. Experimental

Preparation of ex-MMT

Exfoliated montmorillonite (ex-MMT) nanoplatelets were prepared by a double hydrothermal reaction. Ten grams of Na-MMT was stirred intensely in 200 mL of deionized water at 60 °C for 2 h. Twenty milliliters of 0.25 g/mL cetyltrimethylammonium bromide (CTAB) solution was slowly added to the suspension with vigorous stirring at 60 °C. After 10 min, the slurry was refluxed at 100 °C for 17 h. After being cooled, filtered, washed, and dried at 80 °C for 24 h, the gray modified montmorillonite (CTAC-MMT) was collected, and a double hydrothermal reaction was performed. Briefly, 1 g of CTAC-MMT was dispersed in 15 mL of a 0.2 g/mL CTAC water solution by being stirred for 1 h. After 15 mL of glycol was added to the CTAC-MMT suspension, the suspension was placed in a 50 mL autoclave with a Teflon lining and was maintained at 180 °C for 15 h. After being filtered, the residues were added to a 30 mL glycol–water (1:1 volume ratio) solution.

After being stirred for 1 h, the suspension was placed in a 50 mL autoclave and was maintained at 180 °C for another 15 h. After being centrifuged and vacuum dried at 80 °C for 24 h, the final product, ex-MMT nanoplatelets, was obtained.

Preparation of Pd/ex-MMT and Pd/C

Pd/ex-MMT and Pd/C were synthesized via the hydrothermal ethylene glycol (EG) reduction method. Briefly, 250 mg of ex-MMT sheets (or carbon) and 5 mL of 0.05 M $PdCl_2$ solution were mixed with 5 mL of EG, and the resulting mixture was stirred for 24 h to induce ion exchange. After another 20 mL of EG was added and the pH was adjusted to 10.0 using 1 M NaOH in EG solution, the mixture was placed into a Teflon-lined autoclave and then maintained at 160 °C for 2 h. The product was subsequently filtered, washed, and vacuum dried at 80 °C.

The content of Pd in the catalysts was determined by spectrophotometric determination. Briefly, Pd/ex-MMT catalyst was treated with 40% HF solution to remove MMT and was then dissolved in nitrohydrochloric acid. After the solvent was evaporated, the dissolved solid remained in HCl solution. The palladium-containing solution was placed in a 100 mL brown volumetric flask, and 2 mL of HCl (1:1), 3 mL of EDTA solution, 4 mL of sodium sulfite solution, and 2.5 mL of potassium iodide solution were added. The solution was diluted with water to the mark and kept in dark for 15 min before the absorbance was measured at a wavelength of 490 nm. The mass contents of Pd/ex-MMT and Pd/C were determined to be 9.60 wt% and 19.66 wt%, respectively.

Preparation of Pd/ex-MMT ink

Either 1 mg or 2 mg Pd/ex-MMT and the same weight of Vulcan XC-72 carbon black were dispersed in 200 or 300 μL of ethanol and ultrasonicated for 15 minutes to form a uniform catalyst ink.

Characterization

High-resolution transmission electron microscopy (HRTEM) was performed on a Zeiss LIBRA 200 FETEM instrument operated at 200 kV. XPS was performed using a Kratos XSAM800 spectrometer equipped with a monochromatic Al X-ray source (Al KR, 1.4866 keV). High-resolution elemental analyses were performed on the Pd 3d (330–350 eV) and O 1s (545–525 eV) regions with a pass energy of 20 eV, a 0.05 eV step, and an 800 ms dwell time. Each spectrum was constructed from an average of two scans. The pressure in the XPS analysis chamber was maintained at 10^{-7} Pa or less during data collection. In the data analysis, the binding energy (BE) of the core-level C 1s peak was set at 284.5 eV to compensate for surface-charging effects. The liner background was subtracted, and satellite peaks were removed for all element peaks prior to curve fitting. The experimental spectra were fitted into components with Gaussian line shapes. The surface elemental compositions were determined from the ratios of the peak areas corrected with empirical sensitivity factors. The XRD experiments were performed on an XRD-6000 (Japan) equipped with a Cu Kα (λ = 0.15418 nm) radiation source. The scanning range of the 2θ angle was from 2° to 90° at a scan speed of 2° per minute.

Electrochemical measurements

All electrochemical experiments were performed in a standard three-electrode cell at room temperature. The cell consisted of a glassy carbon working electrode (GC electrode, 3 mm in diameter, PINE: AFE3T050GC), an Ag/AgCl (saturated KCl) reference electrode, and a platinum foil counter electrode. All potentials in this study are given relative to the potential of the reversible hydrogen electrode (RHE). We prepared the working electrodes by applying catalyst ink onto glassy carbon (GC) disk electrodes. In brief, the electrocatalyst was dispersed in ethanol and ultrasonicated for 15 minutes to form a uniform catalyst ink. A total of 3 μL of well-dispersed catalyst ink was applied onto a pre-polished GC disk. After the disk was dried at room temperature, a drop of 0.05 wt% Nafion solution was applied onto the surface of the catalyst layer to form a thin protective film. The prepared electrodes were dried overnight at room temperature before electrochemical tests. The CV accelerating stress tests (AST) were performed at potentials between 0 and 1 V versus RHE at a scan rate of 50 mV s^{-1} in N_2-purged 0.1 M $HClO_4$ at room temperature. All of the electrodes were pretreated by being cycled at potentials between 0.05 and 1.1 V at a sweep rate of 50 mV s^{-1} for 50 cycles to remove any surface contamination prior to ORR activity testing. The ORR polarization curves were produced in an O_2-saturated 0.1 M $HClO_4$ solution at a 10 mV s^{-1} scan rate.

The kinetic current densities (j_k) (geometric surface area) of the catalysts can be obtained by the following relation:

$$j_k=j_d*j/(j-j_d)$$

Where j is the measured current density, j_k is the kinetic current density, j_d is the diffusion-limited current density, respectively.

2. **Computational Section**

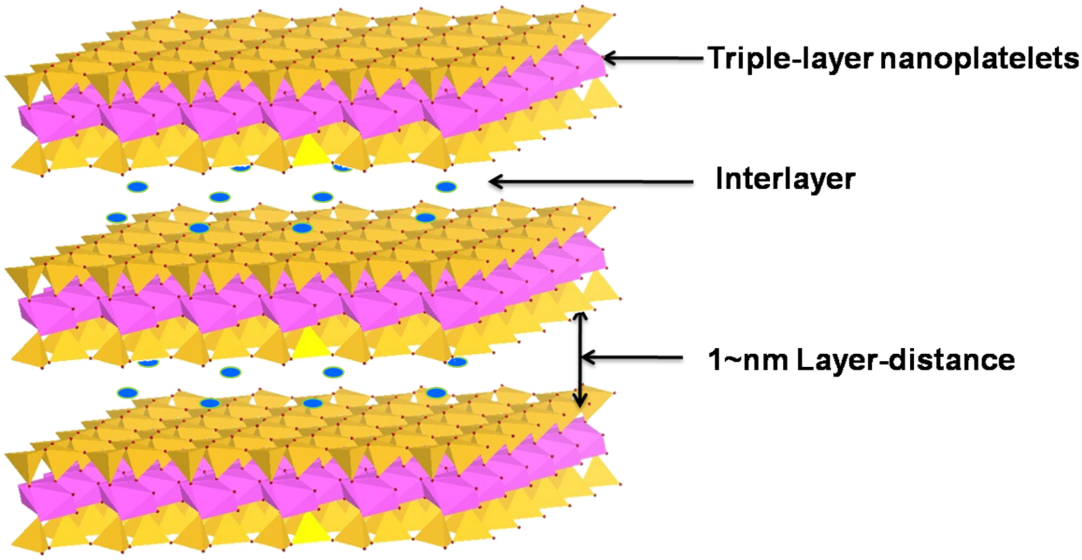
A slab model approach was used to investigate the Pd clusters on the MMT surface and graphene with the DMol3 Package. The DFT semi-core pseudopots approximation was used to replace core electrons by a single effective potential, thereby reducing the computational cost. Double numerical plus polarization (DNP) basis sets were employed for the valance orbitals, which provided accuracy at increased computational cost. The exchange correlation contributions have been treated using the generalized gradient approximation with the PW91 formulation. Full geometry optimizations were performed for all the models, and all atoms were fully relaxed. For MMT, its unit cell parameters area= 5.2 Å,b= 8.98 Å,c = 10.13 Å, and β=99°from the reported model structure. On the basis of the above unit cell parameters the supercell of MMT adopted in this work is 15.85×15.60×26.70 Å. For the Pd clusters adsorbed onto MMT, we applied the optimized cell for the *a*, *b*, and *c* lattice parameters of 15.85 Å, 15.60 Å, and 26.70 Å, respectively. The isolated Pd cluster was optimized in a 20 Å cubic supercell.

A supercell of MMT with surface defects was adopted to simulate the real surface of the ex-MMT. The defects include two different Si−O centers in the tetrahedral sheet and one AlVI−O−AlVI center in the octahedral sheet. A Pd cluster with 13 atoms was used to simulate Pd NPs. In fact, two configurations of Pd13 with icosahedral and cubo-octahedral structures were optimized on the MMT surface. We found that Pd13 with the icosahedral structure is more stable. Thus, only Pd13/ex-MMT with icosahedral structure is considered in the simulation. Although Pd13 cluster is quite large for simulation, it is still quite small relative to the real Pd NPs as shown in Figure 2c,d. The difference in size between the simulation model and the real NPs is generally accepted.

The AE of the O_{ads} is defined as the change in the potential energy E of the system (substrate + adsorbate) upon adsorption: AE = $(E_{(M/support)} - O_{ads}) - E_M - 1/2E(O_2)$.

Table S1: Calculated adsorption energies (AE) of Oads on various metal surfaces.

	Pd13/ex-MMT	Pd13/C	Pd13	Pt13
AE Oads (eV)	-2.04	-4.14	-4.35	-3.55
dO–O	1.38	1.38	1.35	1.39



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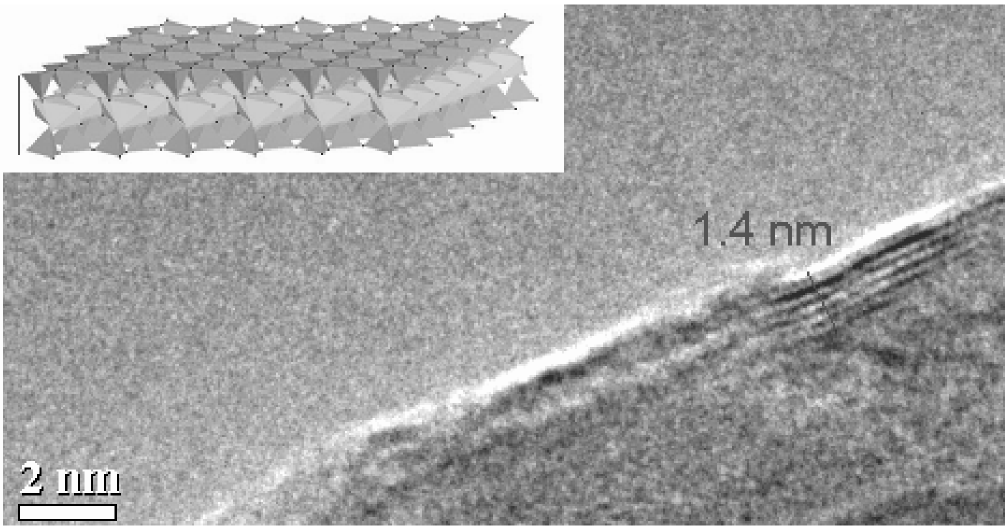

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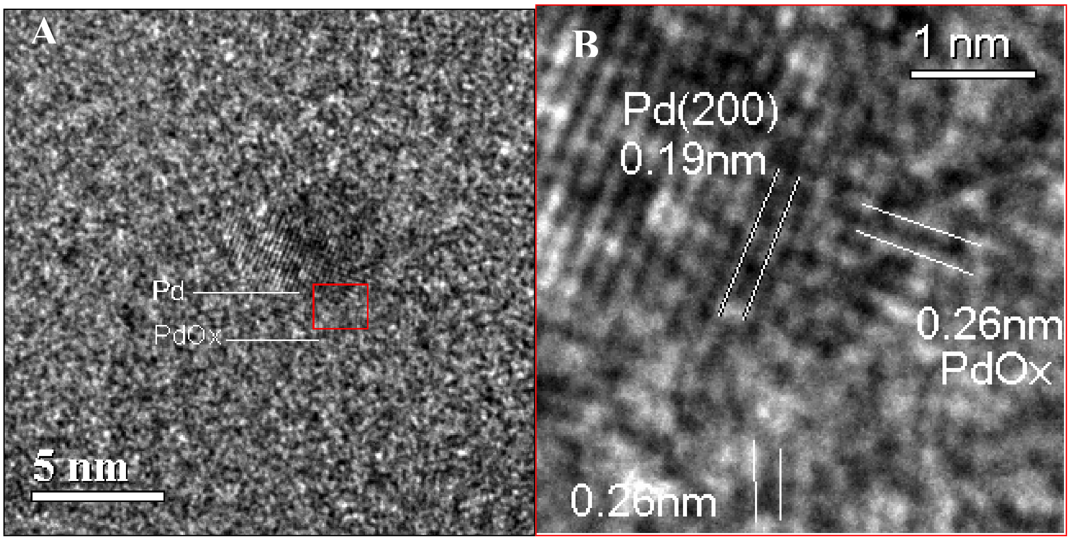

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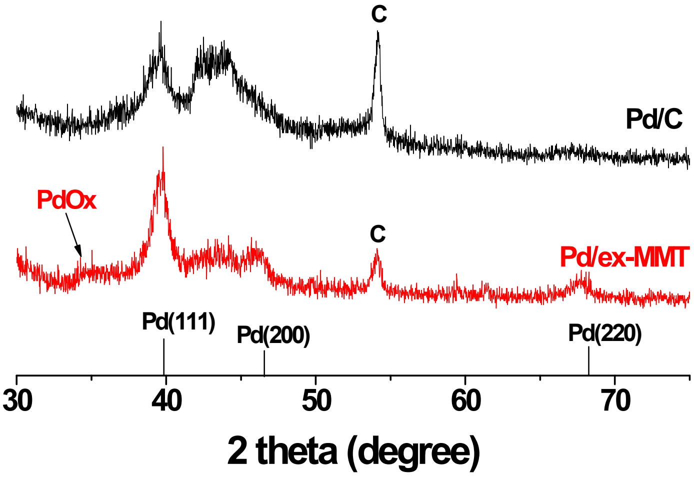

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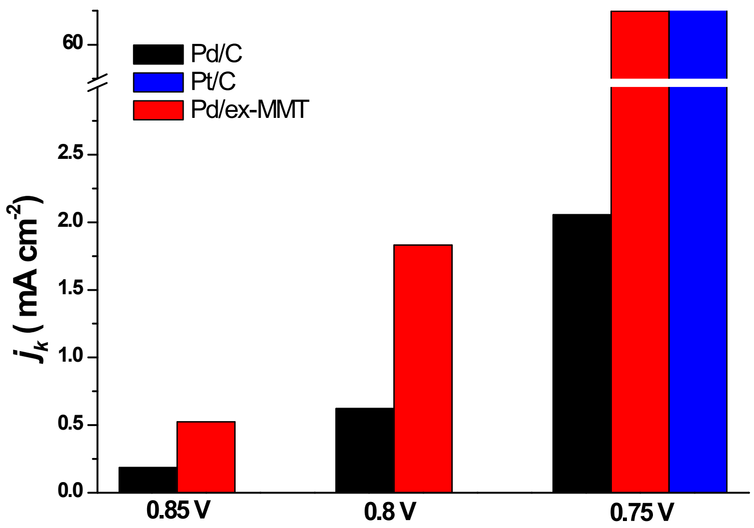

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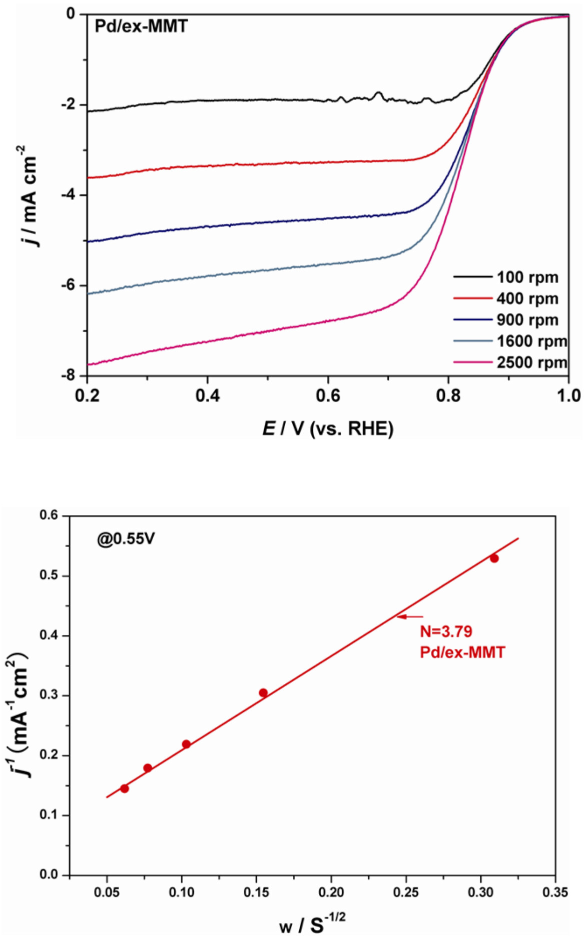

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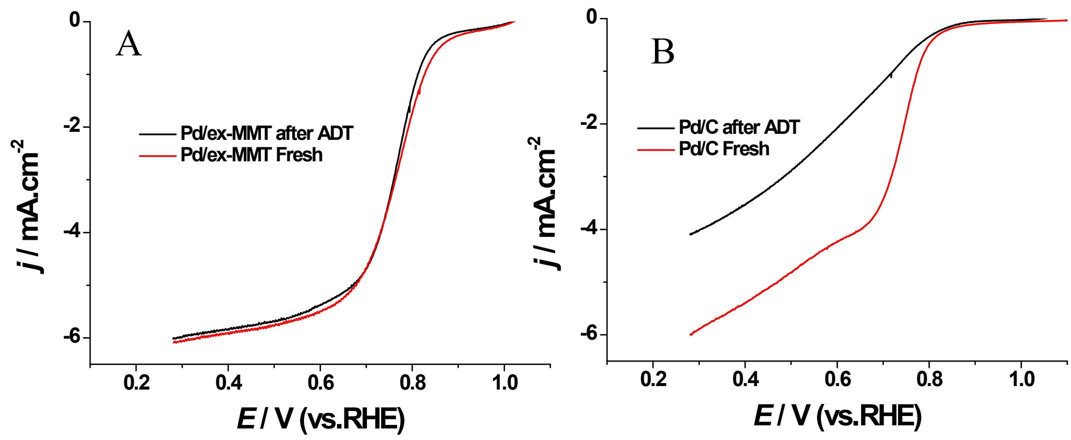

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