

An extraordinarily stable catalyst: Pt NPs supported on two-dimensional $\text{Ti}_3\text{C}_2\text{X}_2$ ($\text{X}=\text{OH}$, F) nanosheets for Oxygen Reduction Reaction

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Experimental Section

The $\text{Ti}_3\text{C}_2\text{X}_2$ nanosheet material was prepared by hydrofluoric acid leaching and surface modification. Briefly, 0.5 g Ti_3AlC_2 powder was immersed in 20 mL HF solution (40 wt%) and stirred for 10 h to remove the Al atoms from Ti_3AlC_2 . Further removal of Al atoms and the installation of hydroxyl groups on the supporting material was accomplished by soaking the $\text{Ti}_3\text{C}_2\text{X}_2$ in 40 mL 1 M H_2SO_4 at 80°C for 2 h. The material was then washed with ultrapure water and dried.

The Pt/ $\text{Ti}_3\text{C}_2\text{X}_2$ catalyst (20 wt% Pt loading) was synthesized using a previously reported ethylene glycol (EG) reduction method. Briefly, 320 mg $\text{Ti}_3\text{C}_2\text{X}_2$ was dispersed in an EG solution after sonication for 10 min. Next, an already-prepared mixture composed of 240 mg trisodium citrate dihydrate and 4 mL 40 mg/mL chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) was added. The obtained inky slurry was then stirred at room temperature for 48 h to achieve homogeneous adsorption of Pt ion precursors to the support and then refluxed at 160°C for 2 h under an atmosphere of highly purified nitrogen. When the reaction was complete, the sample was cooled to 80°C and the black precipitate was collected by repeated centrifugation. The solid was washed with ethanol and ultrapure water before drying under vacuum at 80°C overnight, which resulted in the formation of the Pt/ $\text{Ti}_3\text{C}_2\text{X}_2$.

The analyses of the electrical conductivity of $\text{Ti}_3\text{C}_2\text{X}_2$ were conducted using a homemade button cell (see the simple illustration in Figure S4) and confining the sample between two smooth polished steel discs; the electric conductivity of the sample was measured by electric impedance spectroscopy. A Solartron SI 1287 electrochemical interface equipped with a Solartron SI 1260 impedance/gain-phase analyzer coupling system was used. The operating frequency range was between 0.1 Hz and 100000 Hz, the AC amplitude was 10 mV, and the DC potential was 0 V compared to an open circuit. For a comparison, the electrical conductivity of the unmodified Ti_3AlC_2 , commercially available Vulcan carbon black and activated Vulcan carbon black (treated with boiling concentrated HNO_3 for 4 h) were also subjected to similar operating conditions. X-ray diffraction data were collected on a XRD-6000 using Cu KR radiation ($\lambda=1.5418 \text{ \AA}$) at a step rate of $2^\circ/\text{s}$. Both low-resolution transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were conducted on a FEI tecnai G² 20S-TWIN instrument operating at 120 kV. X-ray Photoelectron Spectroscopy was conducted on a Cratos XSAM800 spectrometer equipped with a monochromatic Al X-ray source (Al KR, 1.4866 keV). The vacuum in the analysis chamber was maintained at 10^{-7} Pa, and the binding energy was calibrated by using 285 eV as the C 1s peak energy.

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, 5 mm in diameter, PINE: AFEST050GC), a Ag/AgCl (saturated KNO_3)

reference electrode, and a platinum wire counter electrode. All potentials in this study were reported relative to the reversible hydrogen electrode (RHE). The working electrodes were prepared by applying the catalyst ink onto glassy carbon (GC) disk electrodes. In summary, 5 mm diameter GC disk electrodes, which were polished to a mirror finish before each experiment (0.05 μm alumina), were used as substrates for the catalysis. For the electrode preparation, the electrocatalyst was dispersed in ethanol and sonicated for 15 minutes to form a uniform catalyst ink (0.83 mg Pt mL^{-1}) and 20 μL of this ink was pipetted onto the GC disk (84.59 μg Pt cm^{-2}). After the solvent was evaporated, the deposited catalyst was covered with a drop of dilute aqueous 0.5 wt% Nafion solution; the resulting thin film was strong enough to attach the catalysts particles permanently to the GC RDE without producing any resistance. The prepared electrodes were dried at room temperature for 20 minutes before electrochemical tests.

The working electrode was first cycled between 0 and 1.2 V at a scan rate of 50 $\text{mV}\cdot\text{s}^{-1}$ 100 times in an N_2 -purged HClO_4 solution (0.1 M) at room temperature, which produced a clean electrode surface. Next, the cyclic voltammetry (CV) measurements were conducted by cycling the potential between 0 and 1.2 V with a sweep rate of 50 $\text{mV}\cdot\text{s}^{-1}$. The electrochemical surface areas (ECSA) were calculated by measuring the charge associated with the H_{ads} (Q_{H}) between 0 and 0.4 V and assuming $Q_{\text{ref}}=0.21 \text{ mC}\cdot\text{cm}^{-2}$, which corresponds to a surface density of 1.3×10^{15} Pt atoms per cm^2 ; this is the established value for polycrystalline Pt electrodes. The ECSA of Pt was calculated based on the equation $\text{ECSA}=Q_{\text{H}}/(Q_{\text{ref}}m)$, Where Q_{H}

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(mC) is the charge for H adsorption ($\text{mC}\cdot\text{cm}^{-2}$), $Q_{\text{ref}}=0.21 \text{ mC}\cdot\text{cm}^{-1}$ is the electrical charge associated with monolayer adsorption of hydrogen of Pt, and m is the loading of Pt ($\text{mg}\cdot\text{cm}^{-2}$) on the working electrode. The oxygen reduction reaction (ORR) experiments were performed in an oxygen-saturated HClO_4 solution (0.1 M) at room temperature. The RDE rotation rate was 1600 rpm and sweep rate was $10 \text{ mV}\cdot\text{s}^{-1}$. Current densities were normalized with respect to the geometric area of the GC RDE (0.196 cm^2). The specific kinetic current density (j_k) associated with the intrinsic activity of the catalysts can be obtained based on the equation $j_k = (j_d * j) / (j_d - j)$, where j is the measured current density, j_k is the kinetic current density, j_d is the diffusion-limited current density, respectively. The CV measurements for accelerated durability tests (ADT) were performed at potentials between 0.6 and 1.1 V against a reversible hydrogen electrode (RHE) at a scan rate of $50 \text{ mV}\cdot\text{s}^{-1}$ in oxygen-purged 0.1 M HClO_4 at room temperature for 10000 cycles. Meanwhile, full-scale voltammograms between 0.0 and 1.2 V in N_2 -saturated HClO_4 solution (0.1 M) and ORR measurements in O_2 -saturated HClO_4 solution (0.1 M) after the ADT cycling were also recorded to track the degradation of Pt catalysts.

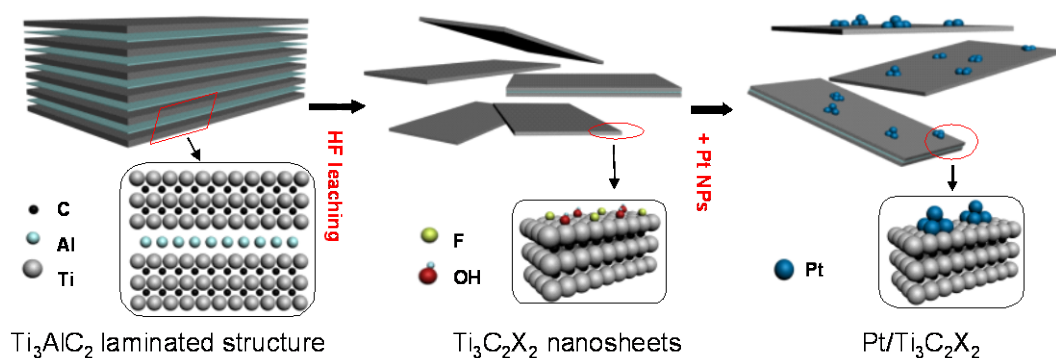


Fig.S1. Schematic illustration detailing all major steps involved in the preparation of Ti₃C₂X₂ (X = OH, F) and Pt/Ti₃C₂X₂.

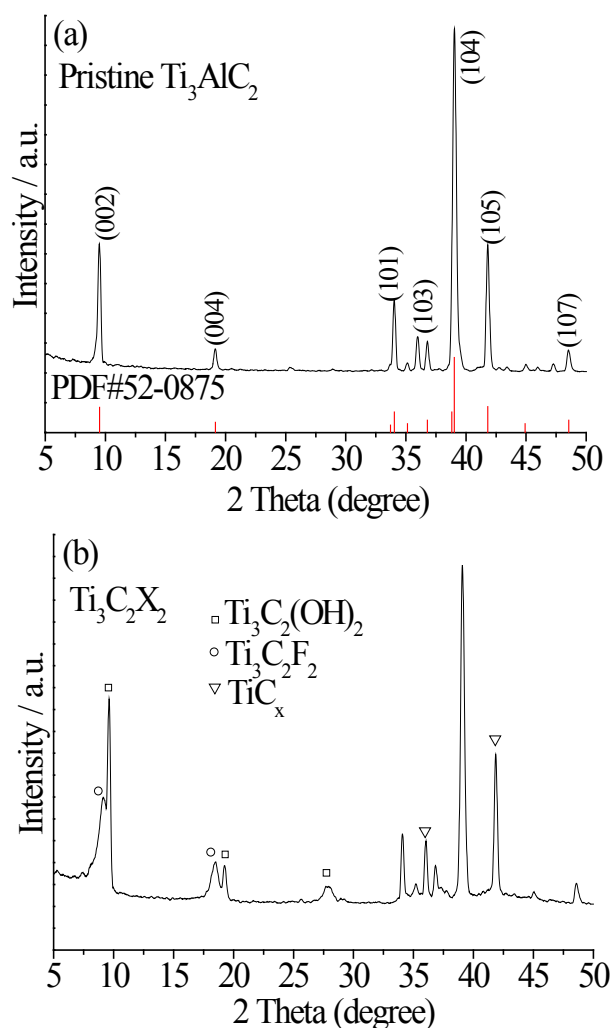


Fig.S2 X-ray diffraction patterns of (a) pristine Ti_3AlC_2 , (b) $\text{Ti}_3\text{C}_2\text{X}_2$.

The formation of Ti-O and Ti-F was confirmed by the peak division at $2\theta \approx 9^\circ$ and 19° , which belong to the diffraction peak of $\text{Ti}_3\text{C}_2\text{F}_2$ (9.2° and 18.5°) and $\text{Ti}_3\text{C}_2(\text{OH})_2$ (9.6° and 19.2°). Additionally, a diffraction peak detected at $2\theta \approx 27.5^\circ$ was attributed to the hydroxyl groups, which are vital to the formation of adsorption sites for the Pt ion precursor.

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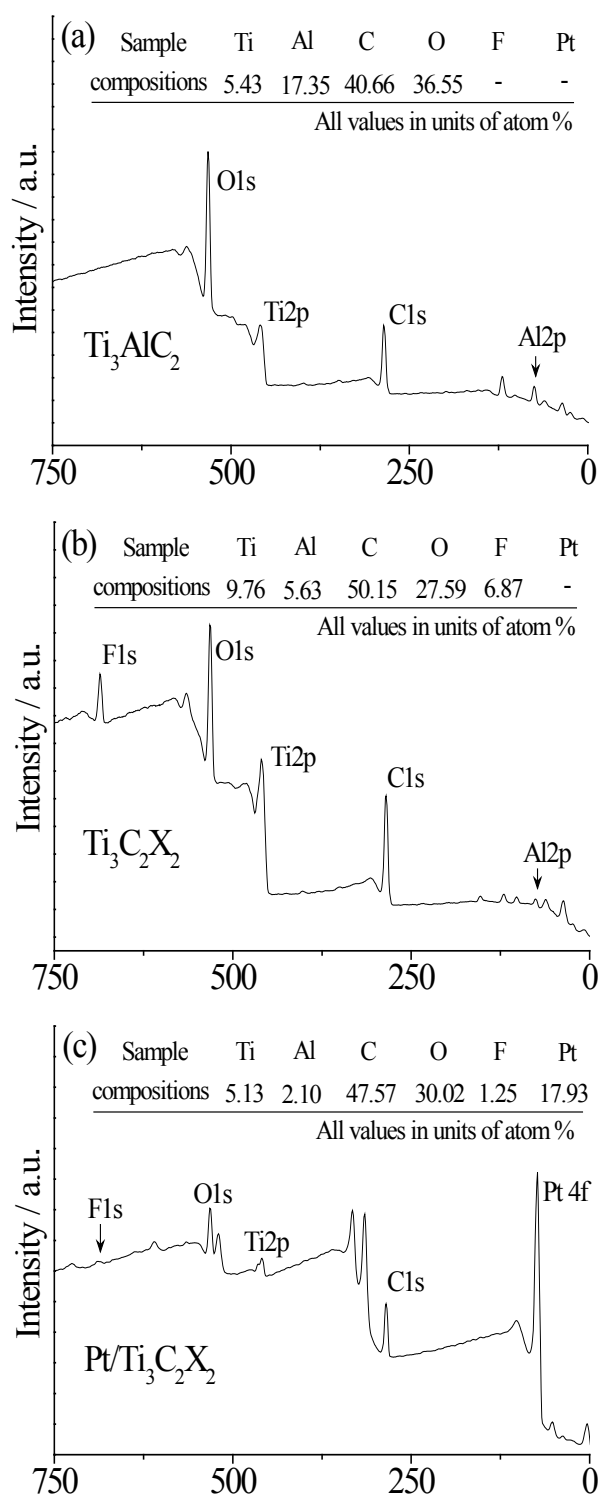


Fig.S3. XPS surveys of (a) Ti_3AlC_2 , (b) $\text{Ti}_3\text{C}_2\text{X}_2$ and (c) $\text{Pt/Ti}_3\text{C}_2\text{X}_2$ catalyst.

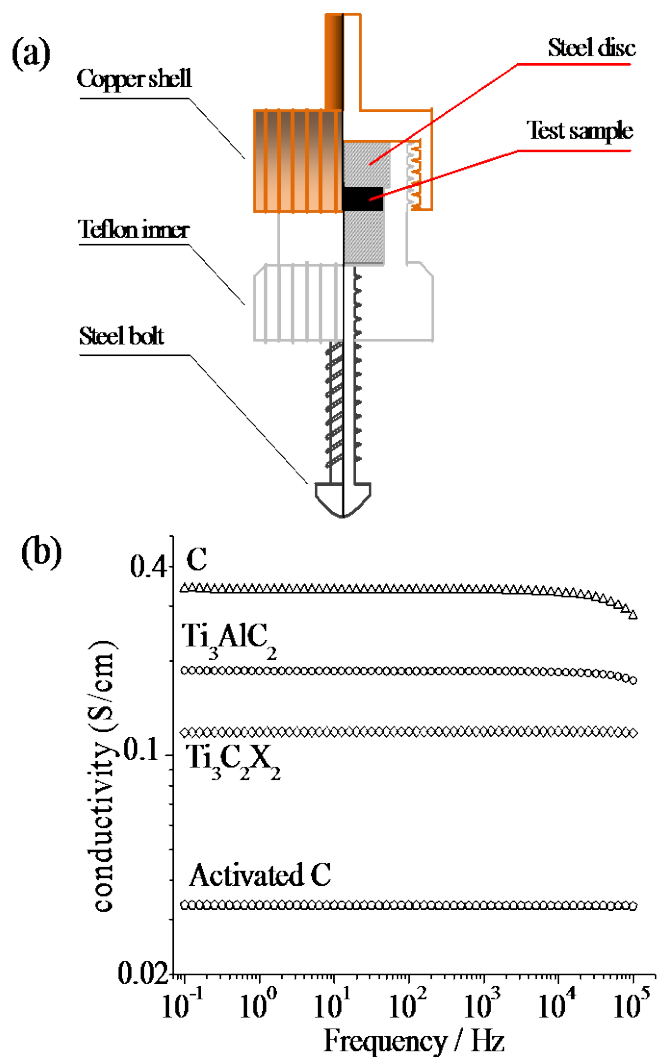


Fig.S4 (a) Diagram of the button cell, (b) Electrical conductivity of C, activated C, Ti_3AlC_2 and $\text{Ti}_3\text{C}_2\text{X}_2$.

The $\text{Ti}_3\text{C}_2\text{X}_2$ exhibit a relative lower conductivity than that of pristine Ti_3AlC_2 , the reduced conductivity can be attributed to the leaching of Al atoms interleaved in the Ti_3AlC_2 laminated structure and the formation of atom defects caused by the HF treatment, but can mainly be ascribed to the formation of oxygen and fluoride species on the nanosheet structure.

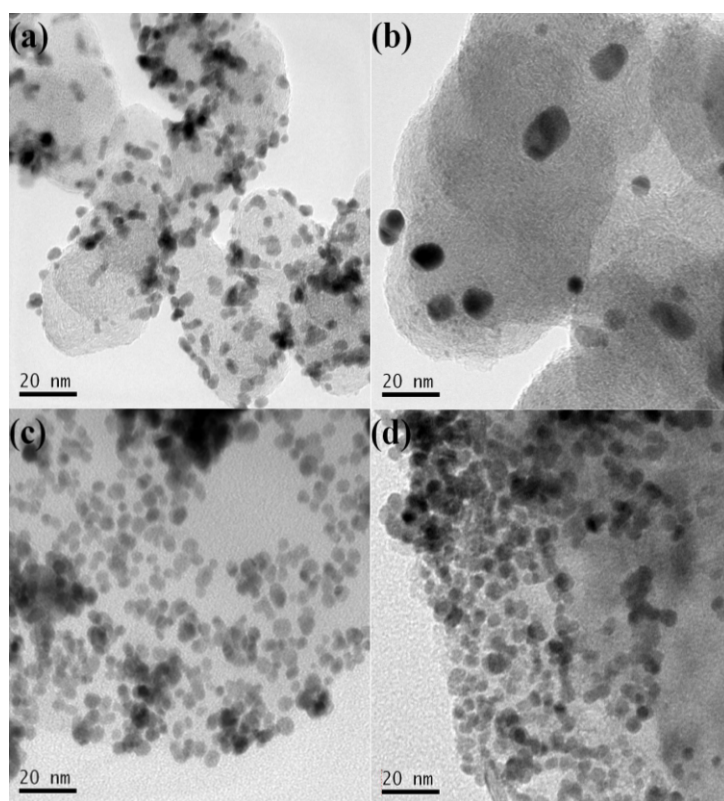


Fig.S5 TEM images of Pt/C catalyst (a) fresh and (b) after the ADT, and Pt/Ti₃C₂X₂ catalyst (c) fresh and (d) after the ADT.

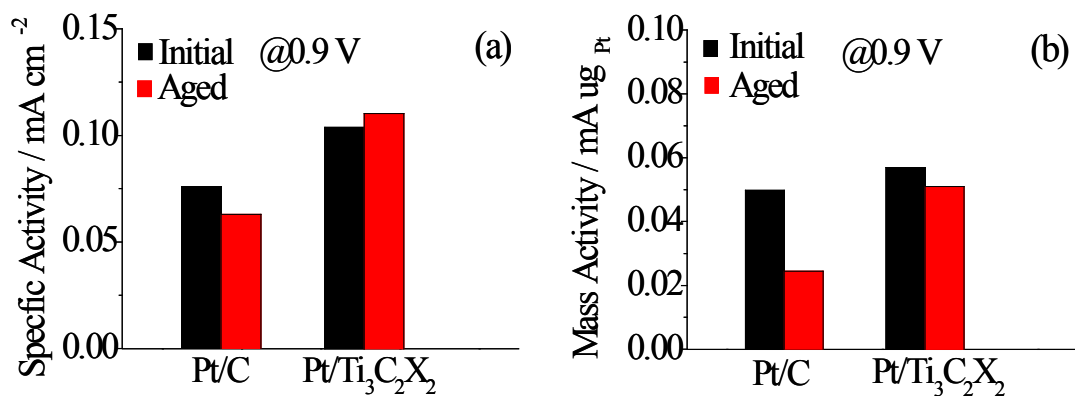


Fig.S6 Specific activity (a) and mass activity (b) at 0.9 V vs RHE for Pt/Ti₃C₂X₂ and Pt/C catalysts.

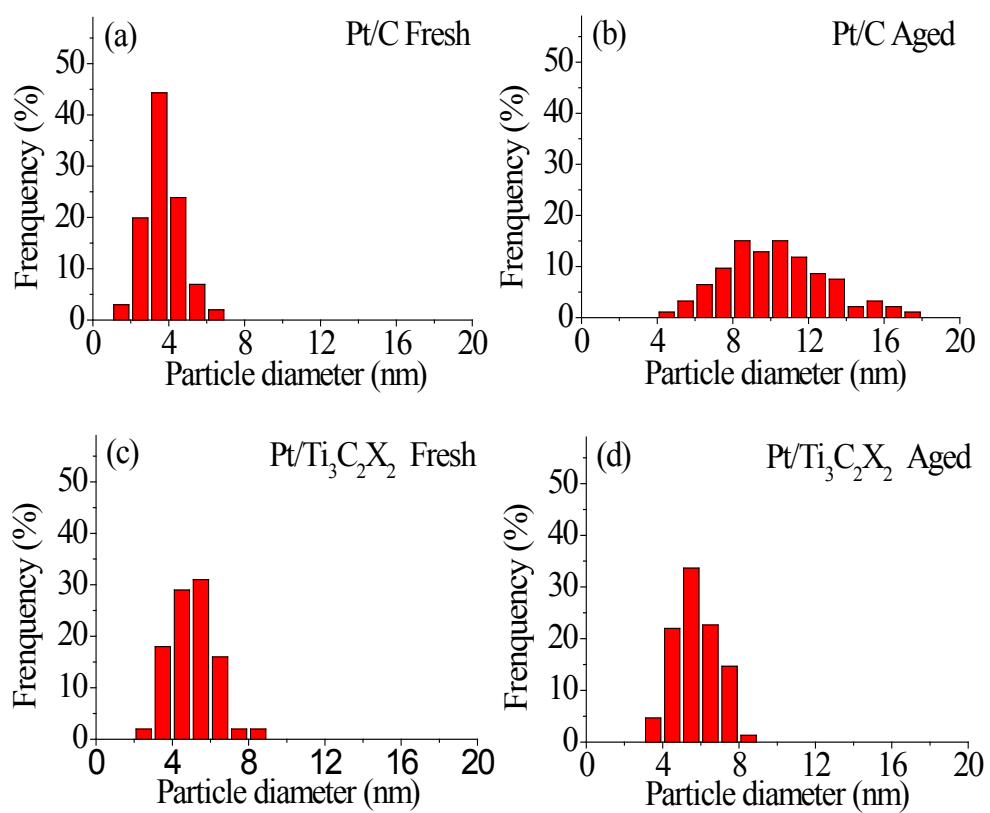


Fig.S6 Pt particle distribution histograms of (a) fresh JM-Pt/C catalyst, (b) aged JM-Pt/C catalyst, (c) fresh Pt/Ti₃C₂X₂ catalyst, and (d) aged Pt/Ti₃C₂X₂ catalyst.