

Supporting Information

Si₃N₄ whiskers modified with Titanium as stable Pt electrocatalysts supports for methanol oxidation and oxygen reduction

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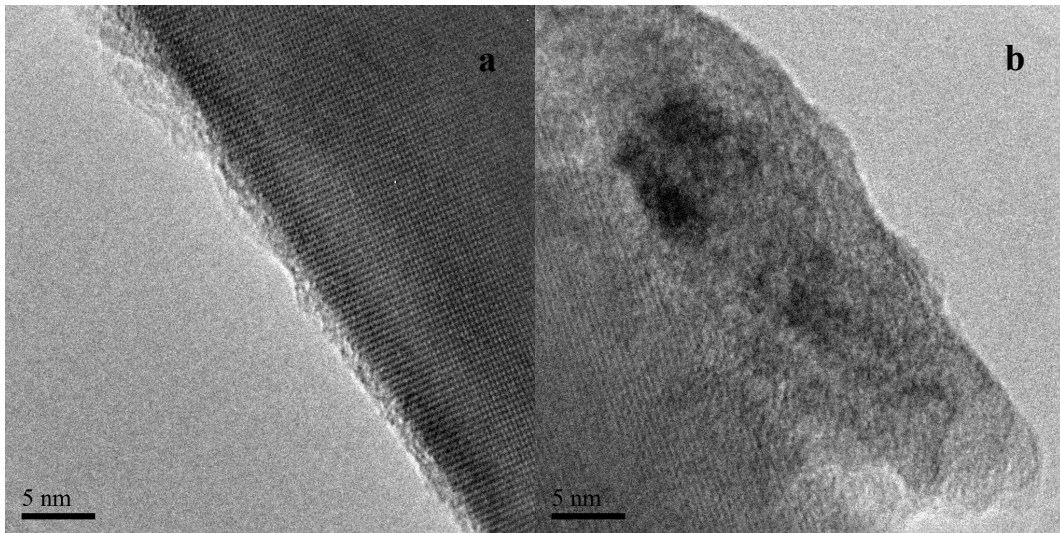


Fig. S1 HRTEM images of Ti/Si₃N₄ (a, b).

As shown in the Fig. S1a, uniformly nanoscale coating was formed over the Si₃N₄ whisker after the one-pot deposition process. The coating was continuous with particles as shown in the Fig. S1a. A clearer image of the particles showed in the Fig. S1b.

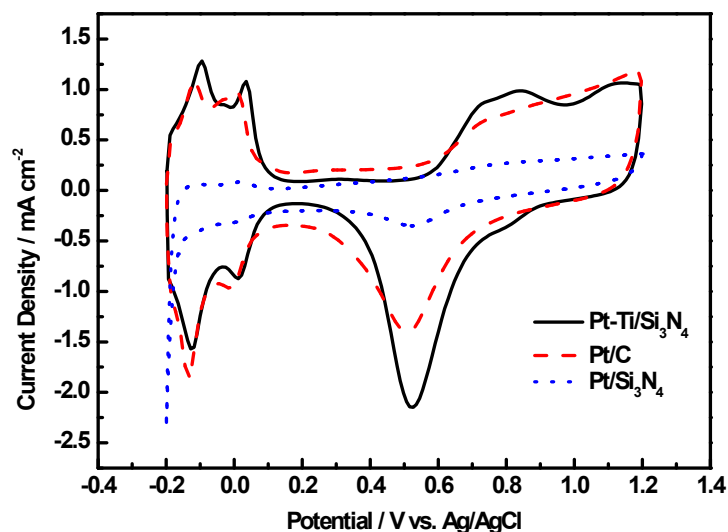


Fig. S2 CVs of Pt-Ti/Si₃N₄, Pt/C and Pt/Si₃N₄ electrocatalysts tested in 0.5 M H₂SO₄ at a scan rate of 50 mV s⁻¹.

As shown in Fig. S2, the CVs exhibited adsorption-desorption peaks of hydrogen from the surface of Pt between -0.2 to 0.1 V (vs. Ag/AgCl). The ECSA of the electrocatalysts can be calculated by integrating the charge collected in the hydrogen adsorption/desorption region after double-layer correction, and normalizing the integrated values with the scan rate, Pt loading, and the charge value of 210 $\mu\text{C cm}^{-2}$ for the adsorption of a hydrogen monolayer. The ECSA value of the Pt-Ti/Si₃N₄ (70.50 m² g⁻¹) electrocatalysts was greater than that of the Pt/C (58.67 m² g⁻¹) and Pt/Si₃N₄ (8.83 m² g⁻¹) electrocatalysts.

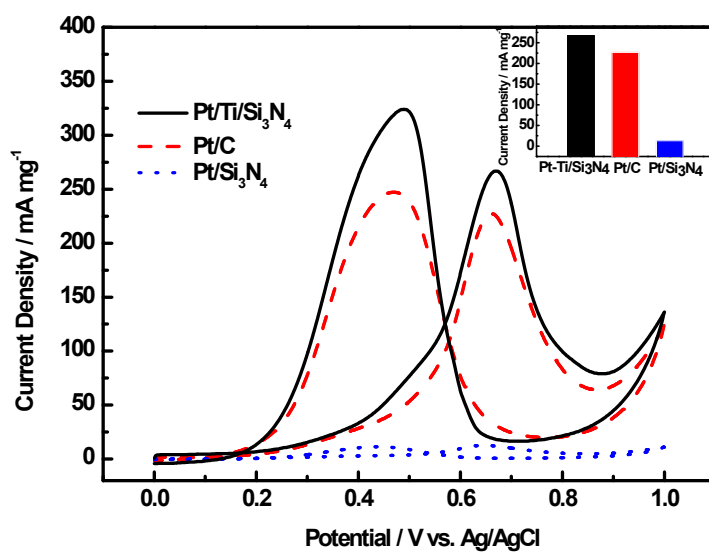


Fig. S3 CVs of Pt-Ti/Si₃N₄, Pt/C and Pt/Si₃N₄ electrocatalysts tested in 1.0 M CH₃OH + 0.5 M H₂SO₄ at a scan rate of 50 mV s⁻¹; The inset shows the mass-normalized current density.

As shown in Fig. S3, the Pt-Ti/Si₃N₄ (267.35 mA mg⁻¹) showed the highest mass-normalized current density at peak potential that was obviously higher than that on the Pt/C (226.70 mA mg⁻¹) and Pt/Si₃N₄ (12.96 mA mg⁻¹).

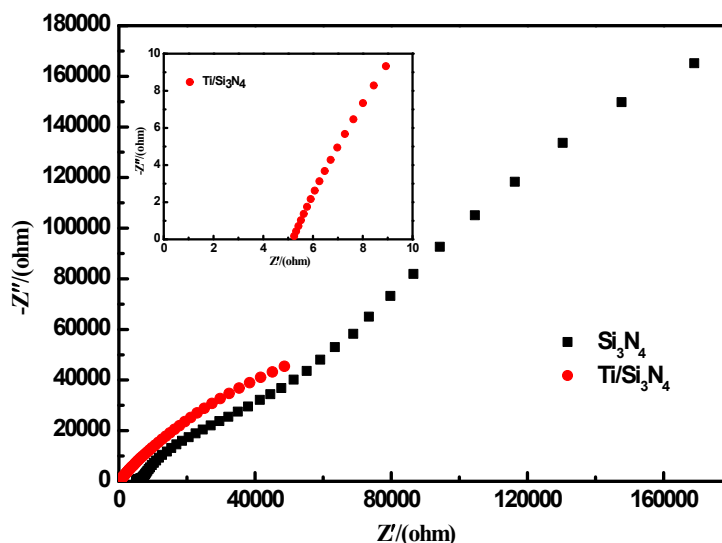


Fig. S4 Nyquist plots of the experimental impedance data the pristine Si₃N₄ and Ti/Si₃N₄ in 0.5 M H₂SO₄ solution measured in the range of 10 mHz to 100 kHz with a 5 mV amplitude.

We measured the electrochemical impedance spectra of the pristine Si₃N₄ and Ti/Si₃N₄ through the powder electrode. A piece of platinum wire (0.1 mm in diameter) was sealed in a small pipette and a small cavity was left at the tip (0.5 mm in diameter). The cavity was filled with powder by grinding the tip on a glass slide over which the powder was spread about 1.5mm in depth.

The impedance spectra for the Si₃N₄ and Ti/Si₃N₄ tested in the frequency range of 10 mHz to 100 kHz at the open circuit potential with a 5 mV amplitude in 0.5 M H₂SO₄ are shown in Fig. S4. It can be seen that the internal resistance of Ti/Si₃N₄ (5.22 Ω) is smaller than that of Si₃N₄ (5.19 kΩ), which suggests that the Ti/Si₃N₄ electrode has better conductive properties and consequent electrochemical properties.

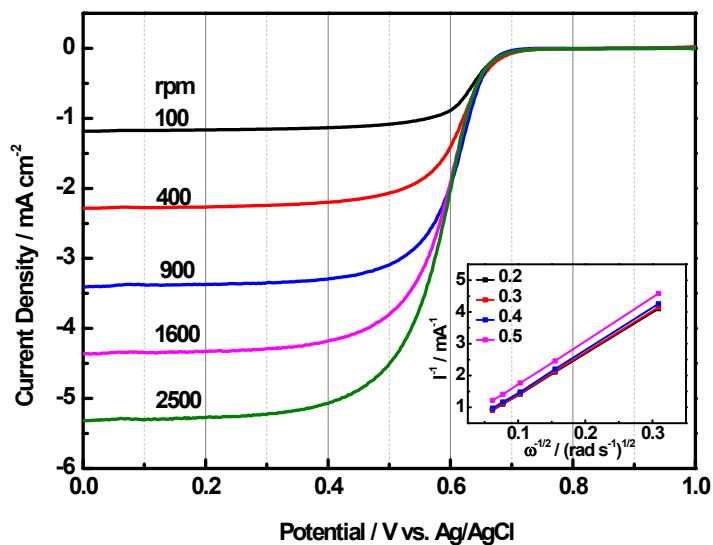


Fig. S5 LSVs of Pt/C electrocatalysts on the RDE at different rotation rates in the O₂-saturated 0.5 M H₂SO₄ solution (scan rate: 10 mV s⁻¹); the inset shows K–L curves.

The LSVs of the Pt/C electrocatalysts tested on the RDE at different rotation rates sweep from 1.0 to 0.1 V (vs. Ag/AgCl) at the scan rate of 10 mV s⁻¹ in the O₂-saturated 0.5 M H₂SO₄ solution. The slopes remain approximately constant over the potential between 0.2 and 0.5 V vs. Ag/AgCl. The average number of electrons transferred (*n*) for ORR on Pt/C can be estimated on the basis of the K–L equation was 3.82.

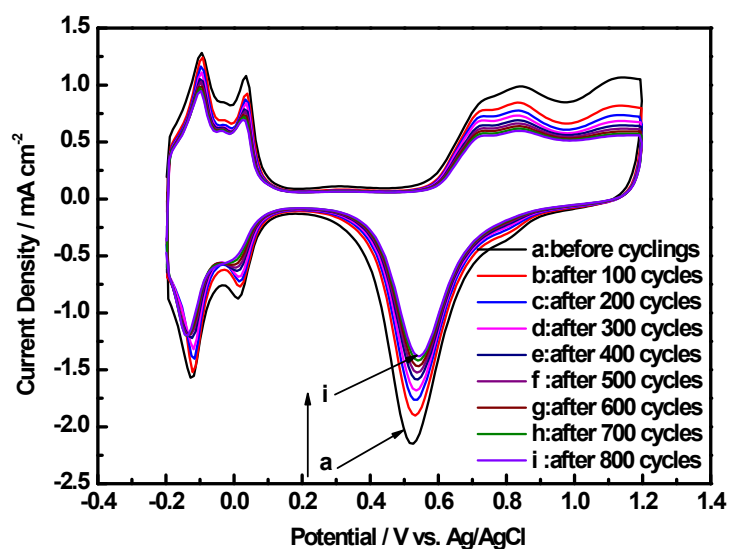


Fig. S6 CV curve of Pt-Ti/Si₃N₄ electrocatalysts recorded in 0.5 M H₂SO₄ between -0.2 and 1.2 V (vs. Ag/AgCl) with a 50 mV s⁻¹ sweep rate at room temperature, the currents were normalized by the geometric electrode area (0.19 cm²).

Fig. S6 shows the CVs of the Pt-Ti/Si₃N₄ electrocatalysts before and after 800 cycles. After 800 cycles, the ECSA of the Pt-Ti/Si₃N₄ retained 72.85%, indicating an excellent stability of the Pt-Ti/Si₃N₄.

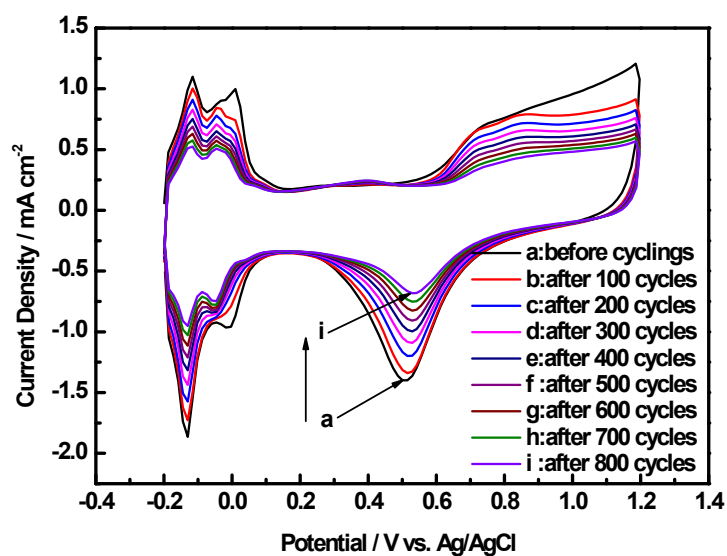


Fig. S7 CV curve of Pt/C electrocatalysts recorded in 0.5 M H₂SO₄ between -0.2 and 1.2 V (vs. Ag/AgCl) with a 50 mV s⁻¹ sweep rate at room temperature, the currents were normalized by the geometric electrode area (0.19 cm²).

Fig. S7 shows the CVs of the Pt/C electrocatalysts before and after 800 cycles in 0.5 M H₂SO₄ between -0.2 and 1.2 V (vs. Ag/AgCl). After the 800 cycles, the ECSA of the Pt/C retained only 42.23%.

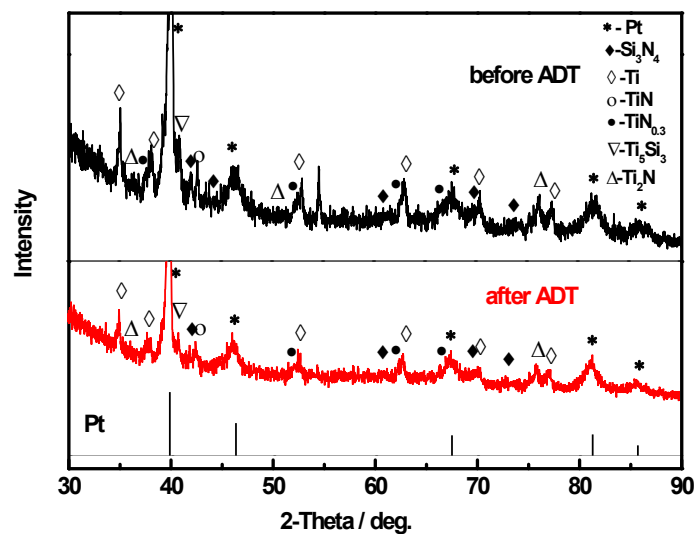


Fig. S8 XRD patterns of Pt-Ti/Si₃N₄ before and after the ADT test.

As shown in Fig. S8, the XRD pattern of Pt-Ti/Si₃N₄ showed no obvious change of the phase as well as the size of the Pt particles after the test, which consistent with the results of electrochemical. In other words, the Pt-Ti/Si₃N₄ electrocatalyst had outstanding stability during the test.

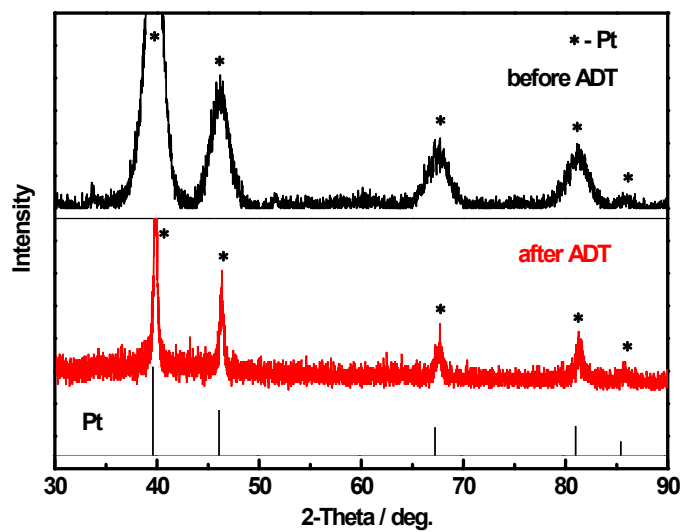


Fig. S9 XRD patterns of Pt /C before and after the ADT test.

The size of the Pt particles of Pt/C increased obviously from 4.67 nm to 26.12 nm (calculated via the Scherrer equation) as shown in the Fig. S9, which consistent with the results of electrochemical test.