A TiN@C core-shell support for improving Pt catalyst corrosion resistance

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1. Experimental and measurement

1.1 Synthesis of the TiN@C support.

Firstly, TiO_2 nanoparticles (Macklin, anatase, 5-10 nm, 99.8%) and the GuHCl (Aladdin, 99.5%) with a mass ratio of 1:10 were weighed and mixed well. Then the above samples were spread in the alumina ark and placed in a tubular furnace. Vacuum environment is settled up after vacuum pump working 3-5 minutes. The temperature was heated to 900 °C for 2 h at a heating rate of 10 °C/min, and then naturally cooled to room temperature, the TiN@C support was obtained after grinding finally. The catalyst support synthesized at 900℃ with a mass ratio of 1:5,1:10 and 1:15 were written as TiN@C-1:5, TiN@C-1:10 and TiN@C-1:15, respectively. The sample synthesized by 1:10 at 900 °C is the most representative.

1.2 Synthesis of the Pt/TiN@C catalyst.

Pt/TiN@C catalyst was prepared by a typical Microwave-EG method as reported in our recent work[1]. Firstly, 27 mg TiN@C support powder was placed in a three necked flask containing 50 ml EG. The TiN@C support powder was dispersed evenly in ice water bath by ultrasonic wave for 2 h. Then 400 μL 38.6 mol/mL EG solution of [$H_2PtCl_6·6H_2O$] was slowly added into the mixed solution, then the PH value was adjusted to 9-10 slowly by 0.5 mol/L EG of NaOH. The mixed solution above was placed in a microwave machine, the microwave power was set to 500W, and the temperature was kept at 180 °C for 10 min at rotating speed 500 rpm with condensing reflux. After natural cooling to room temperature, suction filtration was carried out, and repeatedly washing with 80 °C ultrapure water and ethanol to remove Cl^- and residual glycol solution. The filtrated product was dried in vacuum at 60 °C overnight, and Pt/TiN@C catalyst was synthesized finally. Unless otherwise noted, Pt load is 9.05 wt% in all catalysts in this paper.

1.3 Physical characterization of the support and catalysts.

XRD (X-ray powder diffraction) patterns were characterized on a Bruker D8 ADVANCE through a Cu Kα radiation source in a 2θ range of 5°–85° at a scanning rate of 5° min^{-1}. A Thermo Fisher Scientific XI is used to test

XPS. A FEI Talos-S was used to record TEM images. The system was equipped within EDX detector.

1.4 Electrochemical measurement of the support and catalysts.

All the electrochemical measurements involved in this paper were tested on an shanghai Chenhua CHI760E electrochemical work-station at 25°C, which uses a three-electrode consist of counter electrode-Carbon rod, reference electrode-Ag/AgCl (saturated KCl，reference electrode vs. reversible hydrogen electrode (RHE), $E_{Ag/AgCl}$ = E_{RHE} + 0.26 V, and a rotating disk electrode (RDE) system (Pine Research Instrumentation) with working electrode (glassy carbon area is 0.19625 cm^2).

All the catalyst ink involved in this paper was prepared as follows. 6mg catalyst ink was put into a mixture solution made up of 2682 μL absolute ethyl alcohol ethanol, 300 μL ultrapure water and 18 μL 5% Nafion solution. The catalyst ink obtained above was ultrasonicated to fully disperse with ice water bath for 30 minutes. After that, a pipette gun was used to drop 10 μL catalyst ink onto the glassy carbon electrode surface at 350 rpm. Finally, the glassy carbon electrode was dried under an infrared lamp for 5 min.

The Pt loading of all the catalysts involved in this paper refers to the proportion of Pt element mass to the whole catalyst. Pt/C mentioned in this paper refers to 20% JM Pt/C catalyst whose support is Vulcan XC - 72. And current-time test result is normalized to 20% Pt load.

All the RDE chemical tests were measured at 25 °C in N_2-saturated or O_2-saturated 0.1 M $HClO_4$ solution. cyclic voltammetry (CV) tests of the electrocatalysts were characterized at a positive scan rate of 100 mV s^{-1} in O_2-saturated solution and 50 mV s^{-1} N_2-saturated solution at the range of 0 - 1.2 V (vs. RHE). The polarization curves of RDE were recorded at a rate of 1600 rpm and a positive scan rate of 10 mV s^{-1} in O_2-saturated solution. Current-method was carried out in O_2-saturated 0.1 M $HClO_4$ solution at 1.2V (vs. RHE) with the rotation of 500 rpm at the room temperature.

2. DFT calculation

Slab models are used as basic model in this study[2], an orthorhombic supercell of 8.51 ✕ 8.51 ✕ 22.0 Å, and a hexagonal supercell of 7.39 ✕ 7.39 ✕ 30 Å with periodic boundary conditions were used for the TiN-supported, graphite-supported single Pt atom. According to the results of the interaction between Pt and N obtained by XPS, A Pt single atom was directly placed above the N site of TiN (1 0 0), and Pt/C is represented by placing a Pt Single atom on graphite. The vacuum spaces for the systems were larger than 12.5 Å. The TiN system consisted of 32 Ti and 32 N atoms and the graphite consisted of 72 carbon atoms[3]. We illustrate the strength of the interaction between Pt nanoparticles and support by calculating the energy of Pt/TiN (Pt single atom on TiN bulk) and Pt/C (Pt single atom on graphite), which indirectly represents the stability of two catalysts.

All calculations were performed using the Vienna ab initio simulation package (VASP) code. The electron–ion interactions were described by projector augmented wave potentials. The exchange-correlation function was described by the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE). The electron wave function was expanded using plane waves with a cutoff energy for the plane wave basis set at 400 eV. 4×4×1 k-point sampling was adopted for the slabs. Geometric optimization was performed until the energy and forces were less than 10-4 eV and 0.05 eV/Å, respectively. Vacuum layers of ~ 12.5 Å were employed. All of the atoms were fully relaxed[3].
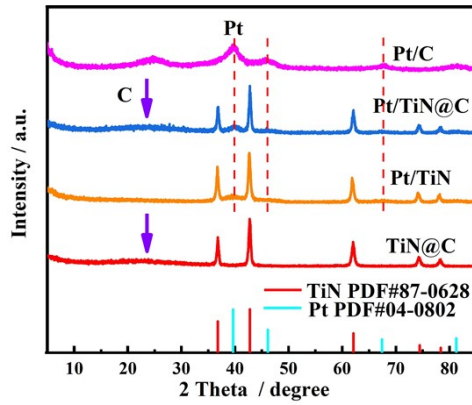
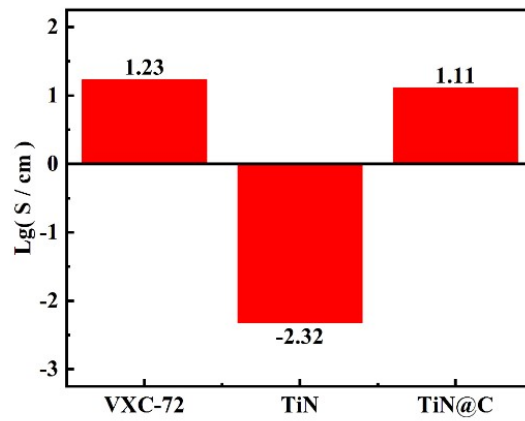Figure S1. The XRD of Pt/C, Pt/TiN@C, Pt/TiN, and TiN@C.

Figure S2. The conductivity of the VXC-72, TiN, and TiN@C, and the ordinate is the logarithm of the conductivity.

Table S1. The element tested by XPS

element/atomic%	Pt	Ti	N	C	O
TiN	-	31.12	24.17	11.86	32.74
TiN@C	-	34.86	31.21	9.13	24.81
Pt/TiN@C	8.61	28.05	24.56	12.93	25.85

Table S2. The interaction of Pt and support in Pt/TiN and Pt/graphite

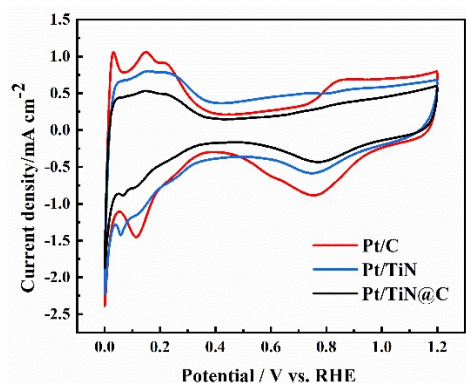| Samples	$E_{Pt/support}$ / eV	$E_{support}$ / eV	$E_{detachment}$ / eV
Pt/TiN	-620.63	-616.25	4.38
Pt/C	-666.67	-664.54	2.13

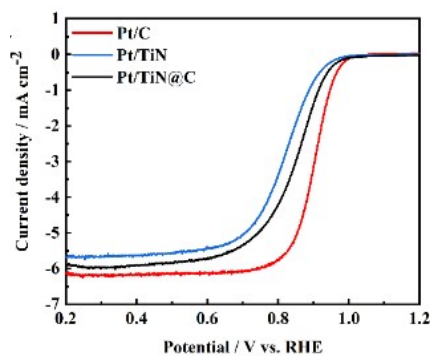Figure S3. The CV curves in N_2-saturated $HClO_4$ at the speed of 50 mV s^{-1} of Pt/C, Pt/TiN and Pt/TiN@C.

Figure S4. The LSV curves in O_2-saturated $HClO_4$ at the speed of 10 mV s^{-1} of Pt/C, Pt/TiN and Pt/TiN@C at the speed of 1600 r·min^{-1}.
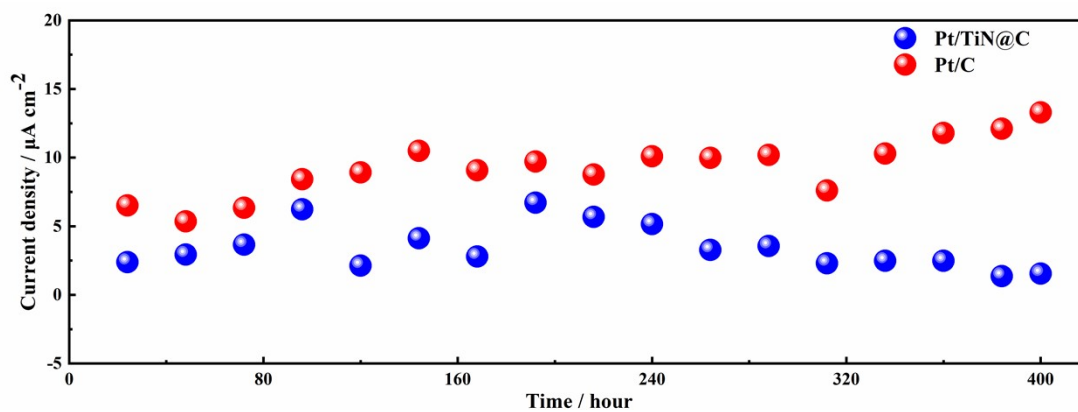

Figure S5. The corrosion current density of Pt/C and Pt/TiN@C in the current-time test

Table S3. The MA change of Pt/C and Pt/TiN@C (mA mg_{Pt}^{-1})

Time / h	Initial	100	200	300	400
Pt/C	176.62	133.41	127.15	120.23	85.82
Pt/TiN@C	154.28	149.35	104.16	89.30	82.98

Table S4. The ECSA change of Pt/C and Pt/TiN@C ($m^2\ g_{Pt}^{-1}$)

Time / h	Initial	100	200	300	400
Pt/C	71.42	54.76	36.31	23.06	21.42
Pt/TiN@C	69.18	59.21	42.37	39.88	35.30

Reference

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3. J. A. Kwon, M. S. Kim, D. Y. Shin, J. Y. Kim and D. H. Lim, J. Ind. Eng. Chem., 2017, 49, 69-75.