

Electronic Supplementary Information

Atomic Layer Deposition of Ultra-trace Pt Catalysts onto Titanium Nitride

Nanowire Arrays for Electrocatalytic Methanol Oxidation

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Experimental section

Reagents: Carbon cloth (CC) used in this study was purchased from CeTech. Titanium (IV) n-butoxide (TBT) was purchased from Macklin Reagent Co., Ltd. Hydrochloric acid (HCl), sulphuric acid (H₂SO₄), nitric acid (HNO₃), acetone, methanol (CH₃OH), and ethanol were bought from Sinopharm Chemical Reagent Corp. Pt/C (20 wt %) was purchased from MERYER Co., Ltd. Nafion (5 wt %), (methylcyclopentadienyl)-trimethyl platinum (MeCpPtMe₃) and anatase particles (325 mesh) were purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. All the reagents were used as received without further purification.

Characterization: Field emission scanning electron microscope (JSM-7001F, JEOL, Tokyo, Japan) and transmission electron microscope (JEM-2100F, JEOL, Tokyo, Japan) were used to characterize the morphologies and structures of all the samples. Powder X-ray diffraction data was obtained from a Bruker-AXS Micro-diffractometer (D8 ADVANCE) for the crystal structural characterization. X-ray photoelectron spectroscopy experiments were performed on a Thermo ESCALAB 250Xi Multifunctional imaging electron spectrometer. Inductively coupled plasma mass spectrometry (ICP-MS) analysis was performed on Thermo ICAP 6300.

Pre-treatment of carbon cloth (CC): Typically, to ensure the surface of CC was well cleaned, CC was put into a 50 mL Teflon container containing 30 mL of concentrated HNO₃ and annealed at 120 °C for 2 h in oven. After cooling down to room temperature, the treated CC was washed under sonication in absolute ethanol and deionized water for several times respectively in order to obtain the cleaned CC.

The synthesis of TiN/CC: The dense TiO₂ nanowires were fabricated onto cleaned CC by a seed-assistant hydrothermal method. Briefly, the cleaned CC (2.5 × 3 cm²) was immersed in the mixture solution of TBT (5 mM) and ethanol under sonication for 40 min, which was subsequently annealed in air at 400 °C for 30 min to obtain the TiO₂ seeded CC for further

hydrothermal reaction. The TiO₂ seeded CC was immersed in a 50 mL Teflon container containing the mixture solution of acetone (15 mL), concentrated HCl (15 mL) and TBT (1.5 mL), and further heated at 200 °C for 80 min in oven to generate TiO₂ nanowires on CC (TiO₂/CC). After cooling down to room temperature, the TiO₂/CC was collected, washed, and dried respectively. TiO₂/CC was converted to TiN/CC by nitridation in ammonia at 900 °C for 2 h (heat to 900 °C at a rate of 5 °C/min, and stand at 900 °C for 2 h).

Fabrication of Pt/TiN/CC: The fabrication of Pt on TiN/CC was carried out in a hot-wall, closed chamber-type atomic layer deposition (ALD) reactor (D100-4P8C8H2F). The TiN/CC was placed in the ALD chamber and during the reaction process, nitrogen acted as the carrier gas, (methylcyclopentadienyl)-trimethyl platinum (MeCpPtMe₃) and ozone (produced using an ozone generator, China Guolin) act as precursor of Pt element. The pulse, exposure, and purge time for the precursor was 0.5, 10, and 20 s, respectively, and for ozone, the time was 1, 12, and 25 s, respectively. The typical deposition cycles were 5, 10, and 20.

The preparation of Pt/C electrode: To prepare Pt/C electrode, 8 mg Pt/C (20 wt %) and 20 μL (5 wt %) Nafion solution were dispersed in 990 μL 1:1 v water/ethanol solvent by 30 min sonication to form an ink. Then 30 μL catalyst ink was loaded on CC (0.5 cm × 0.5 cm) and air-dried at room temperature.

Preparation of TiN powder electrode: The TiN powder was fabricated according to a previous report.¹ To prepare TiN powder electrode, 10 mg TiN and 10 μL 5 wt % Nafion solution were dispersed in 990 μL 1:1 (V:V) water/ethanol solvent by 2 hours sonication to form an ink. Then 4 μL catalyst ink was dropped onto the 3 mm glassy carbon electrode and then air-dried at room temperature.

Electrochemical measurements: Electrochemical measurements were performed with a Bio-Logic VSP-300 electrochemical workstation with a standard three-electrode system. The as-fabricated sample was served as the working electrode with Hg/Hg₂SO₄ and Pt wire as the

reference electrode and the auxiliary electrode, respectively. The cyclic voltammetry (CV) curves for electrochemical active areas (ECSA) of Pt/TiN/CC (0.5 cm × 0.5 cm) and commercial Pt/C catalyst on the carbon cloth (0.5 cm × 0.5 cm) were recorded between -0.7V and 0.9V vs. Hg/Hg₂SO₄ at the rate of 50 mVs⁻¹ in 0.5M H₂SO₄ solution. CV tests of methanol oxidation were studied between -0.6 V and 0.5 V vs. Hg/Hg₂SO₄ at the rate of 50 mVs⁻¹ in 1M CH₃OH and 0.5M H₂SO₄ solution. Carbon monoxide (CO) stripping experiments were carried out in 0.5M H₂SO₄ solution. Before the measurement, purified Ar gas was purged into the electrolyte for 20 min to remove oxygen (O₂) from the solution, and then CO gas (99.99%) was bubbled into the solution for 20 min. In the meantime, the potential was maintained at 0 V to achieve maximum coverage of CO at the Pt samples. Finally, the redundant CO was removed by bubbling Ar gas (99.99%) for 15 min. Chronoamperometry curves for the stability tests of 10C-Pt/TiN/CC (0.5 cm × 0.5 cm) and Pt/C (0.5 cm × 0.5 cm) were recorded at 0.2 V vs. Hg/Hg₂SO₄ in 1M CH₃OH and 0.5M H₂SO₄ mixed solution.

The electrochemical impedance spectroscopy (EIS) was recorded over frequency ranging from 1 MHz to 0.1 Hz in in 0.5M H₂SO₄ and 1M CH₃OH solution with a Princeton A4000 electrochemical workstation. EIS experiments under the same frequency range were also tested in 5mM [Fe(CN)₆]^{3-/4-} and 0.1M KCl solution.

The calculation of ECSA: The ECSA of the electro-catalysts can be calculated by the equation:

$$ECSA = Q_H / (210 \times W_{Pt})$$

Where Q_H is the total charge (μC) for hydrogen desorption, and 210 represents the charge (μC/cm²_{Pt}) required to oxidize a monolayer of hydrogen on a clean Pt surface, W_{Pt} represents the Pt loading (μg/cm²) on the electrode. The loading of Pt element was measured by inductively ICP-MS.

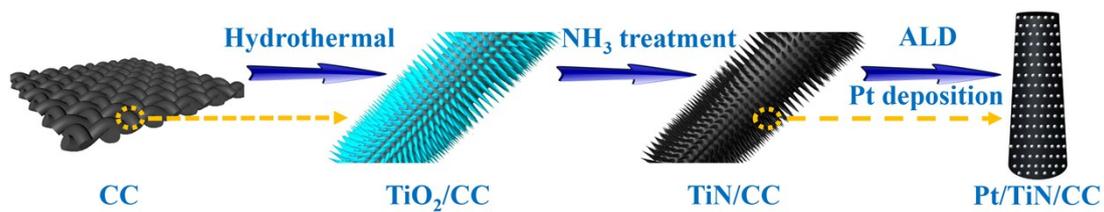


Fig. S1. The schematic illustration of fabrication of Pt/TiN/CC catalyst.

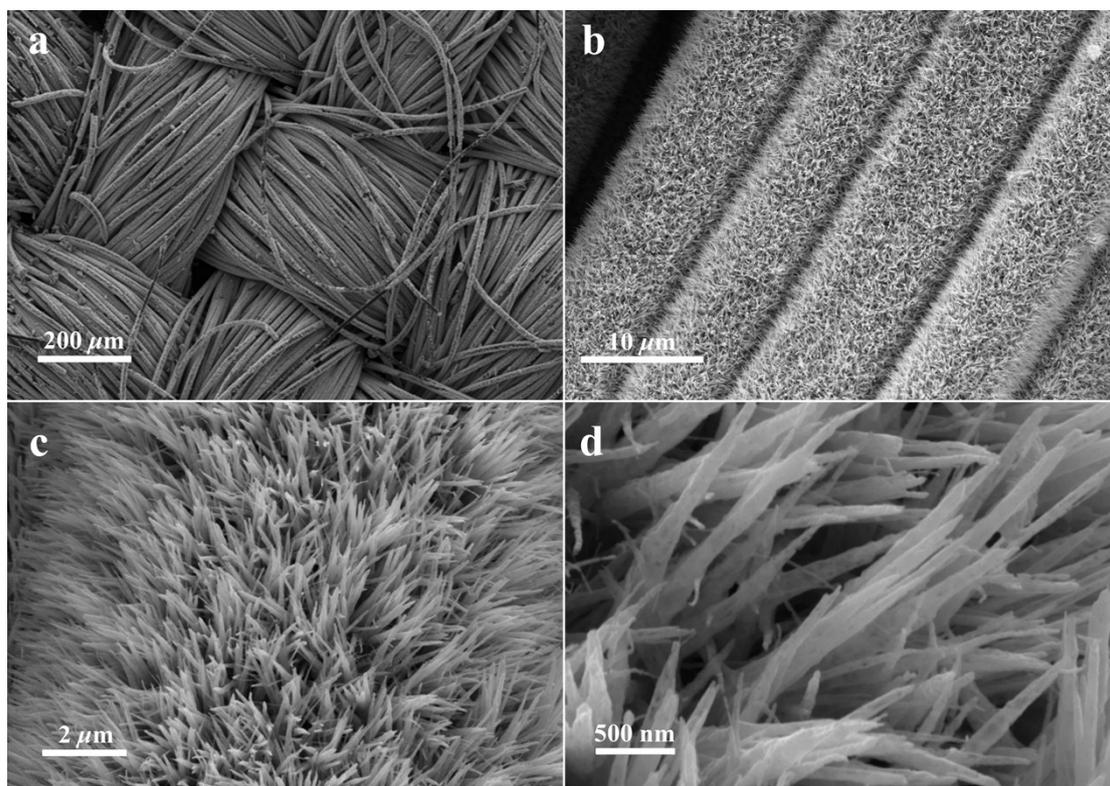


Fig S2. (a) SEM image of TiN/CC nanowires, and (b, c, d) the SEM images of 10C-Pt/TiN/CC.

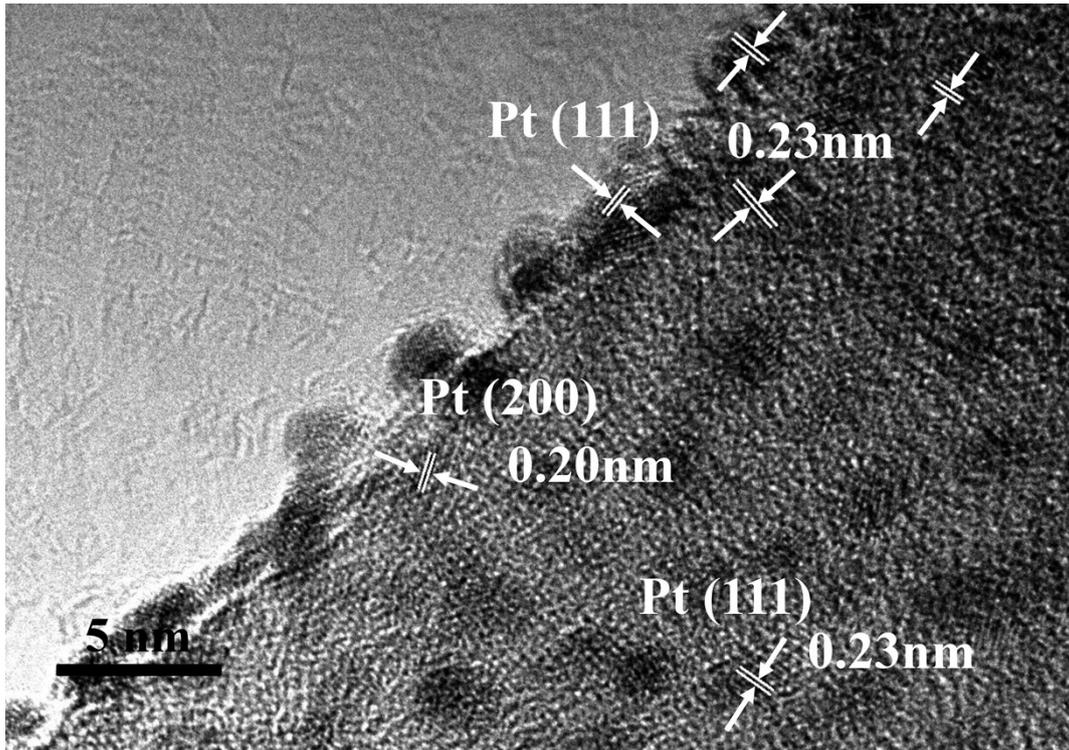


Fig. S3. The high-resolution TEM image of 10C-Pt/TiN/CC.

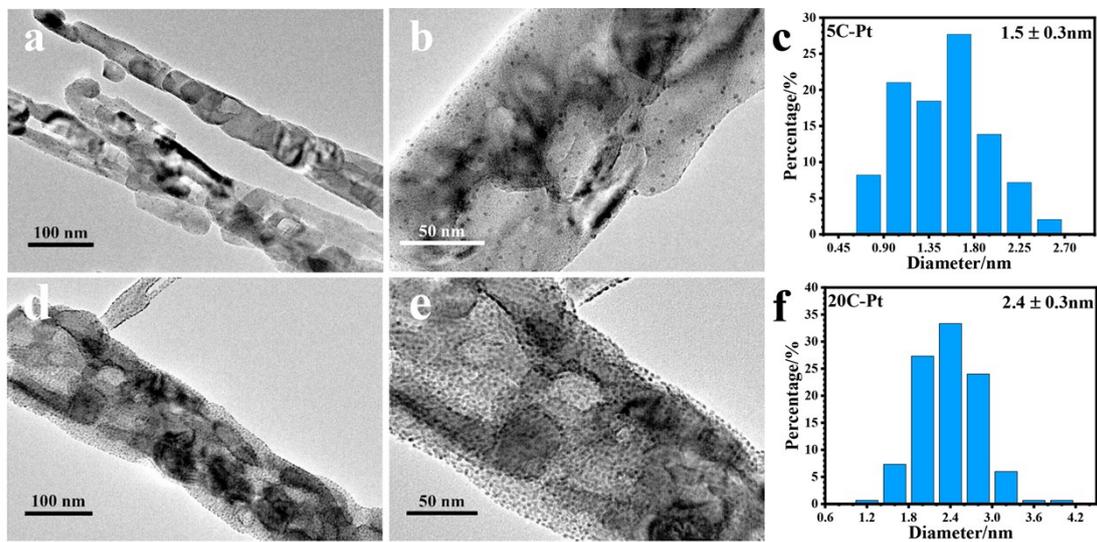


Fig. S4. (a, b) The typical TEM images of 5C-Pt/TiN/CC and (c) size distribution of Pt nanoparticles in 5C-Pt/TiN/CC sample. (d, e) The typical TEM images of 20C-Pt/TiN/CC and (f) size distribution of Pt nanoparticles in 20C-Pt/TiN/CC.

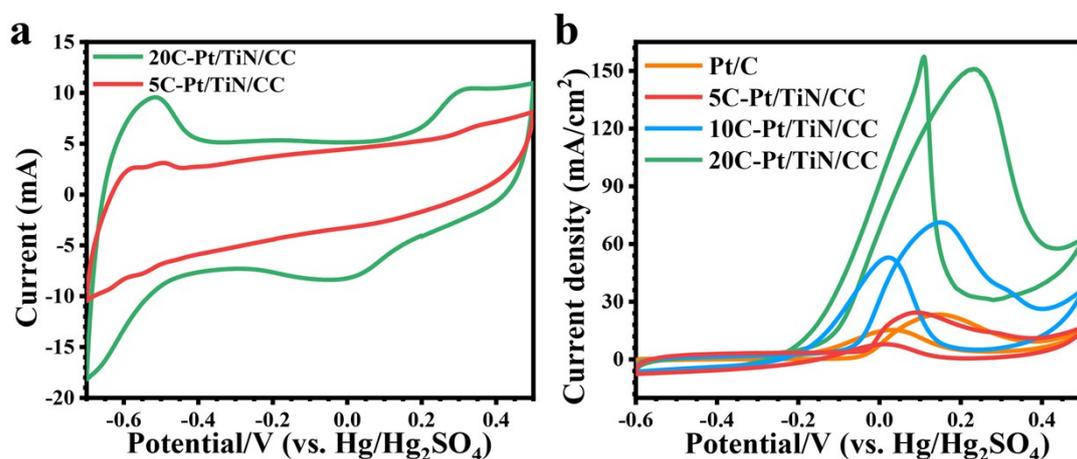


Fig. S5. (a) CV curves of 5C-Pt/TiN/CC and 20C-Pt/TiN/CC in 0.5M H₂SO₄ at a scan rate of 50 mVs⁻¹. (b) The current density (normalized to the geometric area of the electrode) of Pt/C, 5C-Pt/TiN/CC, 10C-Pt/TiN/CC and 20C-Pt/TiN/CC toward the methanol oxidation in 0.5M H₂SO₄ and 1M CH₃OH solution at a scan rate of 5 mVs⁻¹.

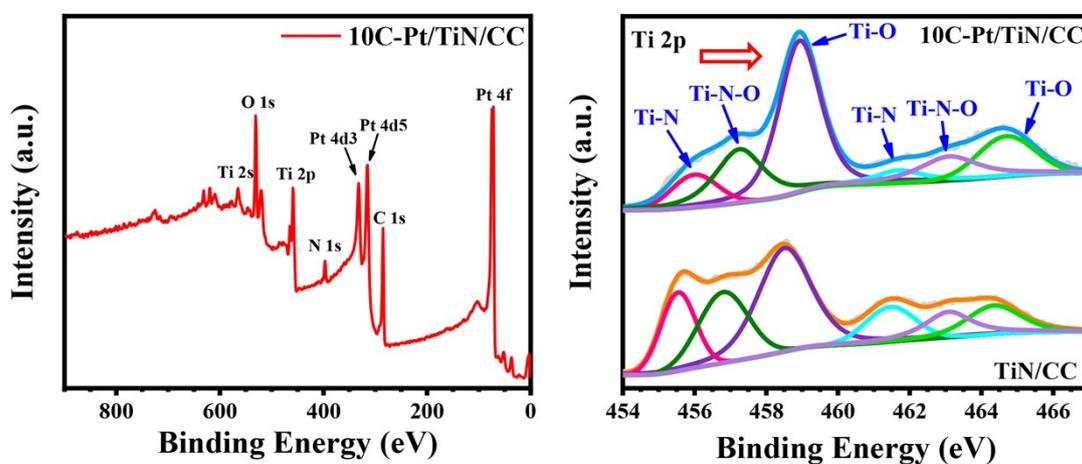


Fig. S6. (a) XPS survey of 10C-Pt/TiN/CC. (b) The high-resolution XPS spectra for Ti 2p of 10C-Pt/TiN and TiN/CC.

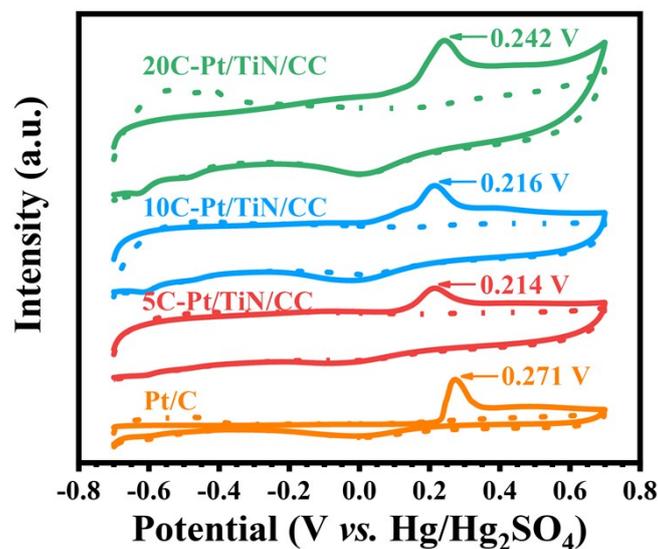


Fig. S7. CO stripping curves of Pt/TiN/CC samples and commercial Pt/C in 0.5M H_2SO_4 at 50 mVs^{-1} .

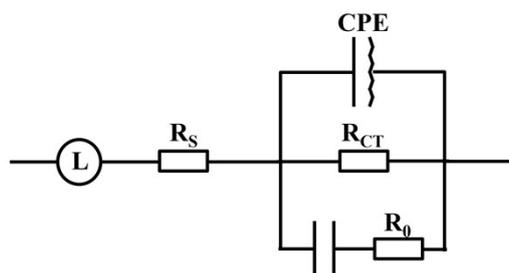


Fig. S8. The equivalent circuit for the EIS data fitting for 10C-Pt/TiN/CC and Pt/C in 0.5M H_2SO_4 and 1M CH_3OH . As to the equivalent circuit, R_{CT} represents the charge-transfer resistance; R_{S} is the uncompensated solution resistance; CPE is the constant phase element component; R_0 is associated with the contact resistance between the catalyst material and the carbon cloth; and L comes from the external circuit inductance and normally does not participate in electrochemical reactions.

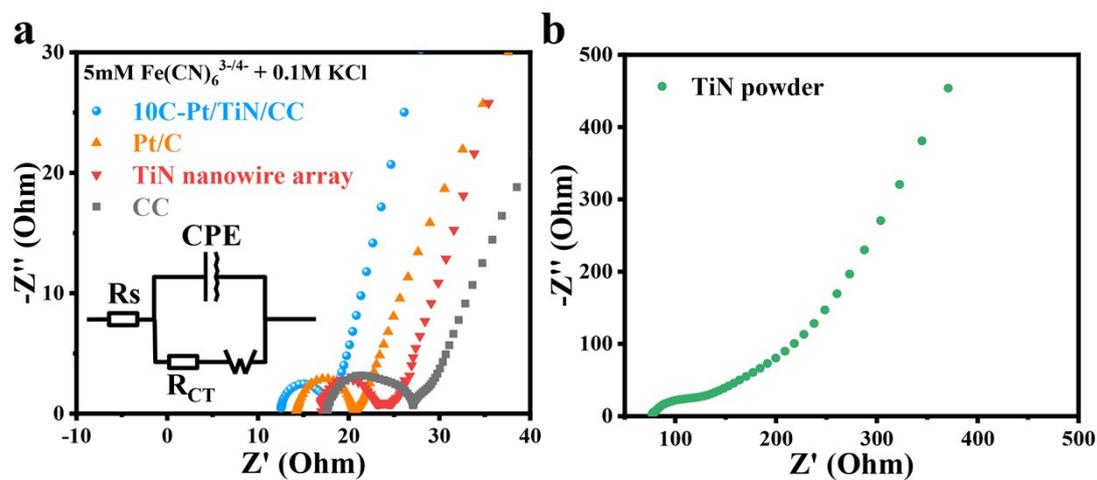


Fig. S9. The Nyquist plots of (a) 10C-Pt/TiN/CC, Pt/C, TiN nanowire array, CC (inset is the equivalent circuit) and (b) TiN powder on glassy carbon in 5mM $\text{Fe}(\text{CN})_6^{3-/4-}$ and 0.1M KCl solution.

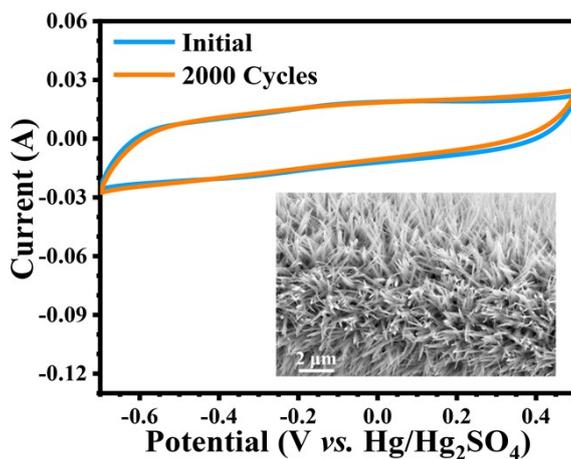


Fig. S10. The 1st and 2000th CV curves of TiN nanowire array in 0.5M H_2SO_4 solution at a scan rate of 200 mVs^{-1} (Inset is the SEM image of TiN/CC after 2000 CV cycles).

Table S1. Comparison of the MOR catalytic activity with other Pt-based electrocatalysts reported recently.

| Catalyst | Current density (A/mg _{Pt} @0.147V vs. Hg/Hg ₂ SO ₄) | Current density (A/mg _{Pt} @peak potential) | Peak potential (V vs. Hg/Hg ₂ SO ₄) | Ref. |
|--|--|--|--|-----------|
| Pt/TiN | ~ 0.67 | 0.68 | ~ 0.15 | 2 |
| Pt/Ti _{0.95} Co _{0.05} N | ~ 0.72 | 0.84 | ~ 0.22 | 3 |
| PtRu-Ni ₂ P/C-40% | ~ 0.48 | 0.52 | ~ 0.08 | 4 |
| Pt/TiN | ~ 0.17 | 0.23 | ~ 0.21 | 5 |
| Pt/Ti _{0.8} Mo _{0.2} N | 0.61 | 0.61 | 0.15 | 6 |
| Pt/3D graphene | ~ 1.2 | 1.63 | ~ 0.21 | 7* |
| 10C-Pt/TiN/CC | 1.67 | 1.70 | 0.15 | This work |

*The catalyst in [7] was tested in 1M H₂SO₄ and 0.5M CH₃OH, and all the catalysts in [2] - [6] and this work were tested in 0.5M H₂SO₄ and 1M CH₃OH.

Table S2. Values of charge transfer resistance in the equivalent circuit used for fitting the EIS experimental curve of 10C-Pt/TiN/CC, Pt/C, TiN/CC, bare CC and TiN on GC.

| Fitted value | 10C-Pt/TiN/CC | Pt/C | TiN/CC | CC | TiN on GC |
|---------------------------|---------------|------|--------|------|-----------|
| R_{ct} (Ω) | 5.84 | 6.38 | 7.25 | 9.89 | 58.15 |

References:

- 1 X. Zhu, X. Yang, C. Lv, S. Guo, J. Li, Z. Zheng, H. Zhu and D. Yang, *ACS Appl. Mater. Interfaces*, 2016, **8**, 18815-18821.
- 2 Y. Xiao, G. Zhan, Z. Fu, Z. Pan, C. Xiao, S. Wu, C. Chen, G. Hu and Z. Wei, *Electrochim. Acta*, 2014, **141**, 279-285.
- 3 X. Chen, W. Li, Z. Pan, Y. Xu, G. Liu, G. Hu, S. Wu, J. Li, C. Chen and Y. Lin, *Appl. Surf. Sci.*, 2018, **440**, 193-201.
- 4 J. Chang, L. Feng, C. Liu and W. Xing, *ChemSusChem*, 2015, **8**, 3340-3347.
- 5 M. Yang, Z. Cuiw and F. J. DiSalvo, *Phys. Chem. Chem. Phys.*, 2013, **15**, 1088-1092.
- 6 Y. Xiao, Z. Fu, G. Zhan, Z. Pan, C. Xiao, S. Wu, C. Chen, G. Hu and Z. Wei, *J. Power Sources*, 2015, **273**, 33-40.
- 7 Y. Qin, L. Chao, J. Yuan, Y. Liu, F. Chu, Y. Kong, Y. Tao and M. Liu, *Chem. Commun.*, 2016, **52**, 382-385.