

Supporting Information

Three-Dimensional TiO₂@C Nano-Network with High Porosity as Highly Efficient Pt-based Catalyst Support for Methanol Electrooxidation

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Experimental Details

Synthesis of Pt-based catalysts

Pt/TCN catalysts were prepared by the microwave-assisted ethylene glycol method. The theory value of Pt loading was 20 wt.%. Typically, 40 mg TCN was dispersed into 60 mL mixed solution of ethylene glycol and isopropyl alcohol (V/V=4:1) to obtain an uniform suspension. An appropriate amount of H₂PtCl₆-EG solution was then added into the suspension. After the suspension was adjusted to pH≈12.0, the suspension saturated with argon was heated by microwave for 55 s. For the purpose of the Pt deposition, the pH value of the cooled suspension was allowed to 2.0 by HNO₃. Finally, the suspension was filtered and washed with a large amount of deionized water. After dried under vacuum at 80 °C for 5 h, the catalysts were obtained. The 40 wt. % Pt/TCN-5v10 and 40 wt. % Pt/C catalysts used for single fuel cell were prepared in the similar way.

Preparation of membrane electrode assembly (MEA)

The anode catalysts of single fuel cell were compared by using the 40 wt. % Pt/TCN-5v10 and the as-prepared 40 wt. % Pt/C, respectively. The cathode catalysts were the same of homemade 40 wt. % Pt/C. The catalyst ink was produced by mixing the as-prepared catalysts and 5 wt. % Nafion ionomer solution in isopropanol alcohol solution. After ultrasonic dispersion, the catalyst ink was brushed onto the gas diffusion layers (GDLs) to form the catalyst layer. The metal loading was 2.5 mg·cm⁻² and the Nafion content was 20 wt. % for anode and cathode. The backing layer used the Teflon-treated carbon paper. The cathode gas diffusion layers (GDLs) were sprayed onto the 30 wt. % Teflon-treated carbon paper while the anode diffusion layer was sprayed onto the 15 wt. % Teflon-treated carbon paper. Nafion 117 membrane was used as the solid electrolyte. Before using, the membrane was treated by sequential immersion in 3 wt. % H₂O₂ solution, ultrapure water, 0.5 mol·L⁻¹ H₂SO₄ and ultrapure water at 80 °C for 1 h, respectively. Lastly, MEA was prepared by hot-pressing at

135 °C, 100 kg·cm⁻² for 90 s.

Electrochemical measurements

Electrochemical experiments were carried out in a typical cell with three electrodes at room temperature using the CHI 650E instrument. A platinum network was used as the counter electrode while Hg/Hg₂SO₄ electrode (MSE, 0.64 V relative to normal hydrogen electrode, NHE) was used as the reference electrode. A glassy carbon electrode was used as the working electrode. The Ar-saturated 0.5 mol·L⁻¹ H₂SO₄ solution was used as the supporting electrolyte while the Ar-saturated 0.5 mol·L⁻¹ H₂SO₄ containing 0.5 mol·L⁻¹ CH₃OH solution was used for methanol electrooxidation. The working electrode was prepared as follows. The uniform catalyst ink was made by dispersing 4.0 mg catalyst into 2 mL ultrapure water. The 5 μL catalyst ink was pipetted onto the glassy carbon electrode with 4 mm diameter. After drying, 5 μL dilute aqueous Nafion[®] solution was then pipetted onto the surface of the catalyst layer. After drying again, the working electrode was obtained.

The cyclic voltammograms (CV) and CO-stripping measurement were recorded from -0.64 to 0.51 V vs. MSE at the rate of 50 mV·s⁻¹. Before measurement, the working electrode was activated until a steady CV was obtained. Electrochemical impedance spectroscopy (EIS) was obtained at 0.6 V between 100 kHz and 0.01 Hz with the amplitude of 5 mV. The amperometric *i-t* curves were obtained at 0.6 V for 3600 s. EIS and *i-t* curves were both tested in methanol acidic medium. All tests above are at 25 °C.

MEA was installed between two graphite plates with serpentine flow fields. The single fuel cell tests were carried out by Fuel Cell Testing System (Scribner Associates Inc., Series 890E, Southern Pines, NC, USA). The 1.5 mol·L⁻¹ methanol solution was fed to the anode side with a flow rate of 3.0 mL·min⁻¹ while pure oxygen under ambient pressure was supplied to the cathode side with a flow rate of 200 mL·min⁻¹ at 80 °C. Before the single fuel cell tests, MEA should be fully activated at a fixed current of 30 mA·cm⁻² for 24 h. The polarization

curves and power density curves of the MEAs were plotted at the same time. In order to ensure a steady-state performance achieved, each point on the polarization curves and power density curves was obtained by continuous operation of about 3 min at a given voltage.

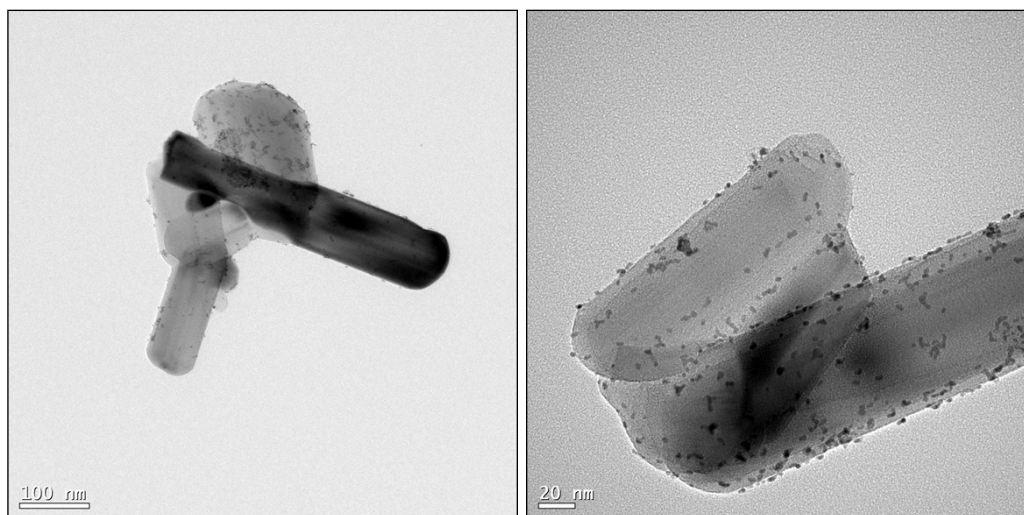


Figure S1. TEM images of Pt/TiO₂ with the absence of RF

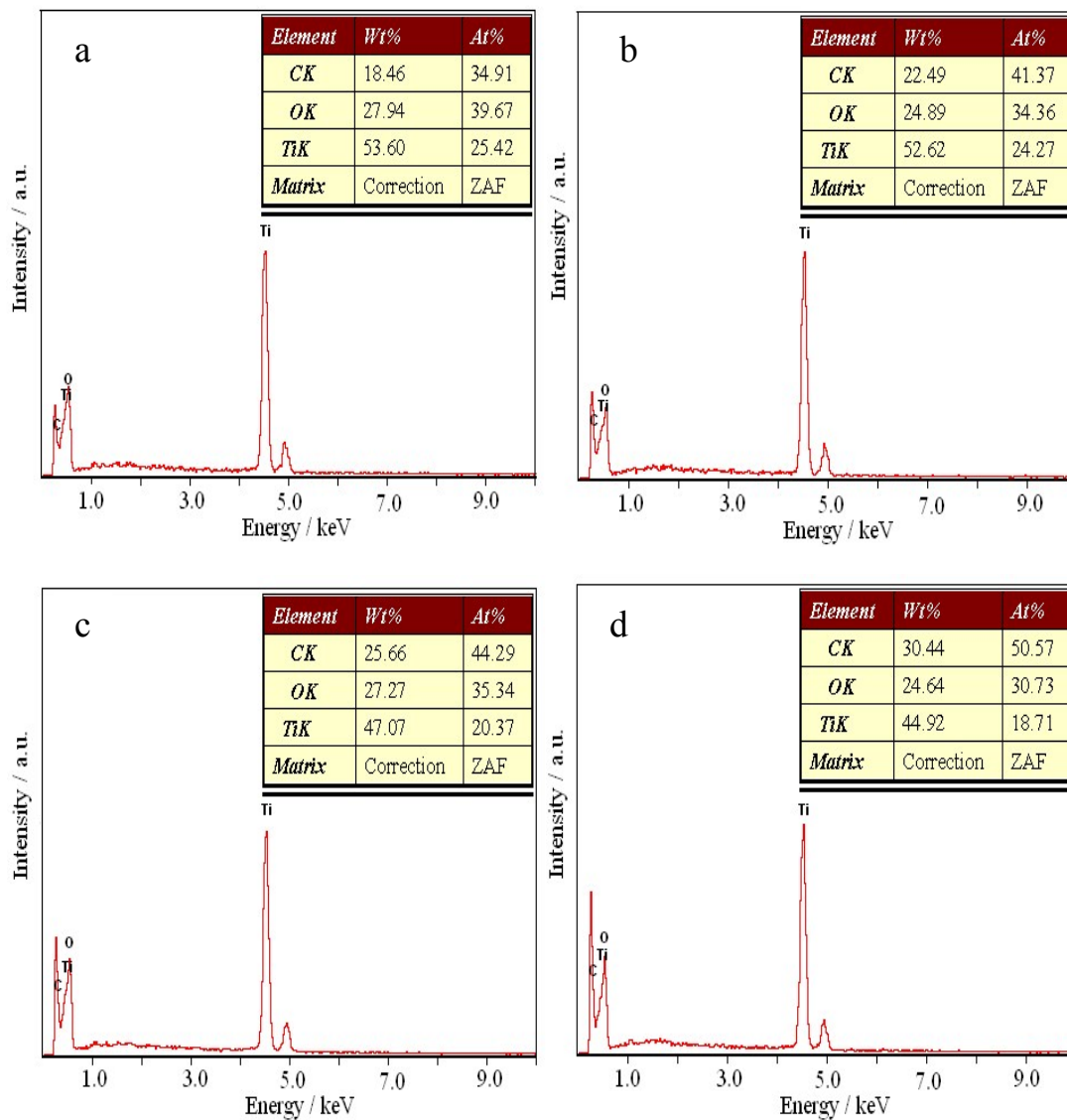


Figure S2. EDX of TCN with different mass ratio of TiO₂/RF: a) 5v6, b) 5v8, c) 5v10 and d) 5v12.

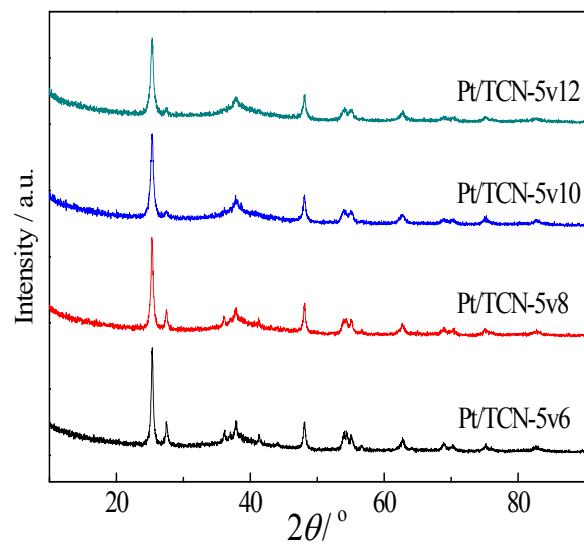


Figure S3. XRD of Pt/TCN with different mass ratio of TiO₂/RF.

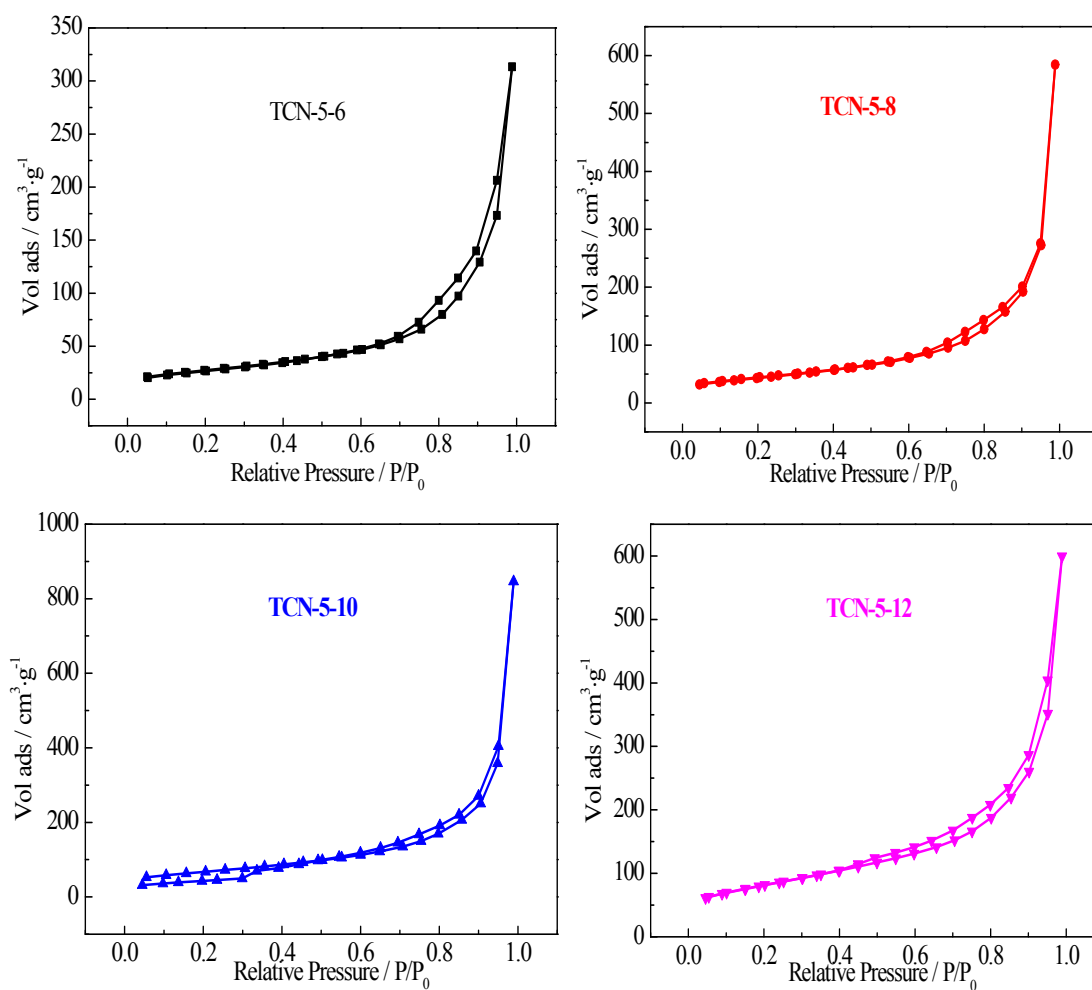


Figure S4. Adsorption-desorption isotherm of nitrogen on the different TCN supports.

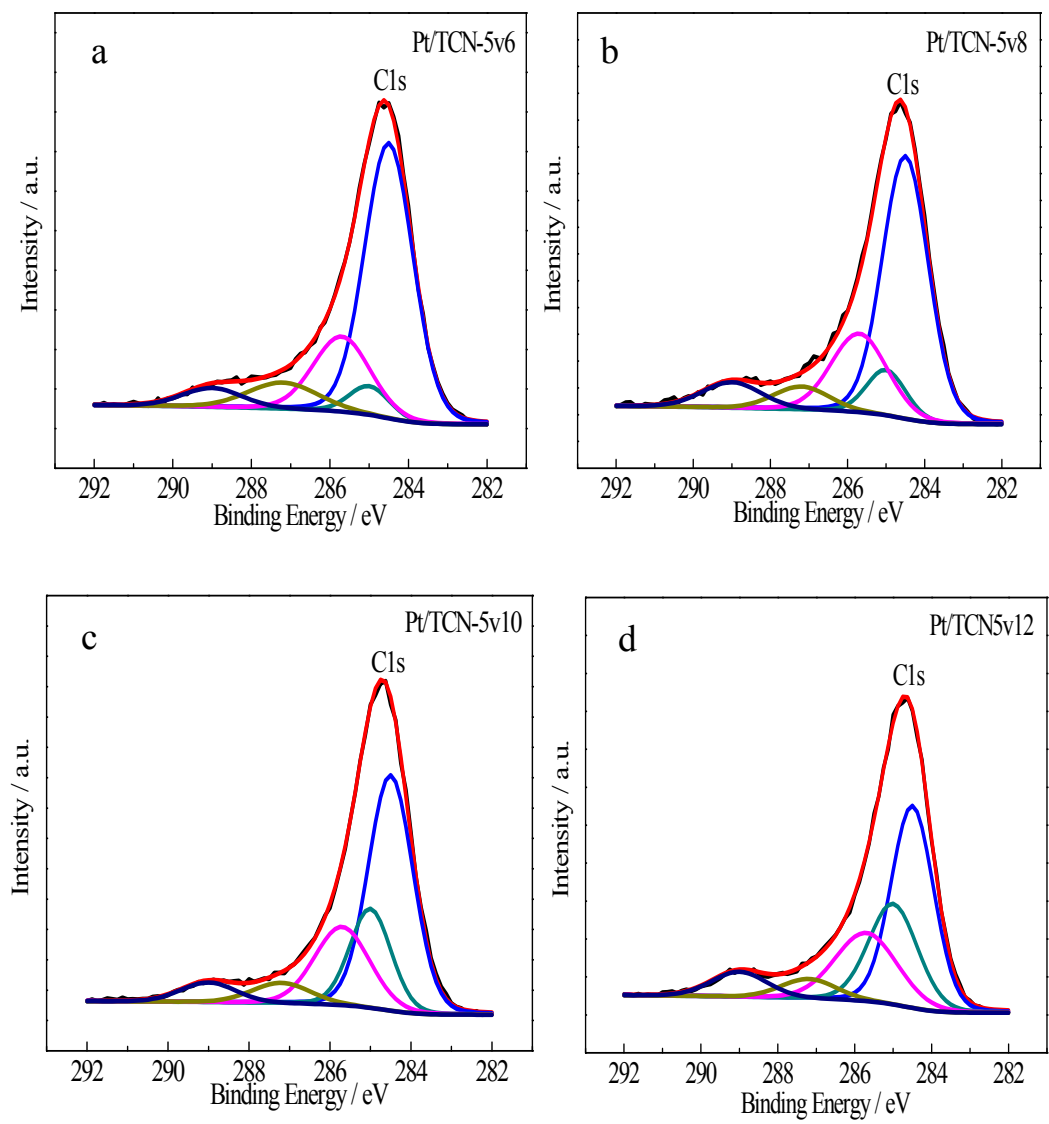


Figure S5. XPS curve fitting of C 1s peak for Pt/TCN with different mass ratio of TiO₂/RF: a) 5v6, b) 5v8, c) 5v10 and d) 5v12.

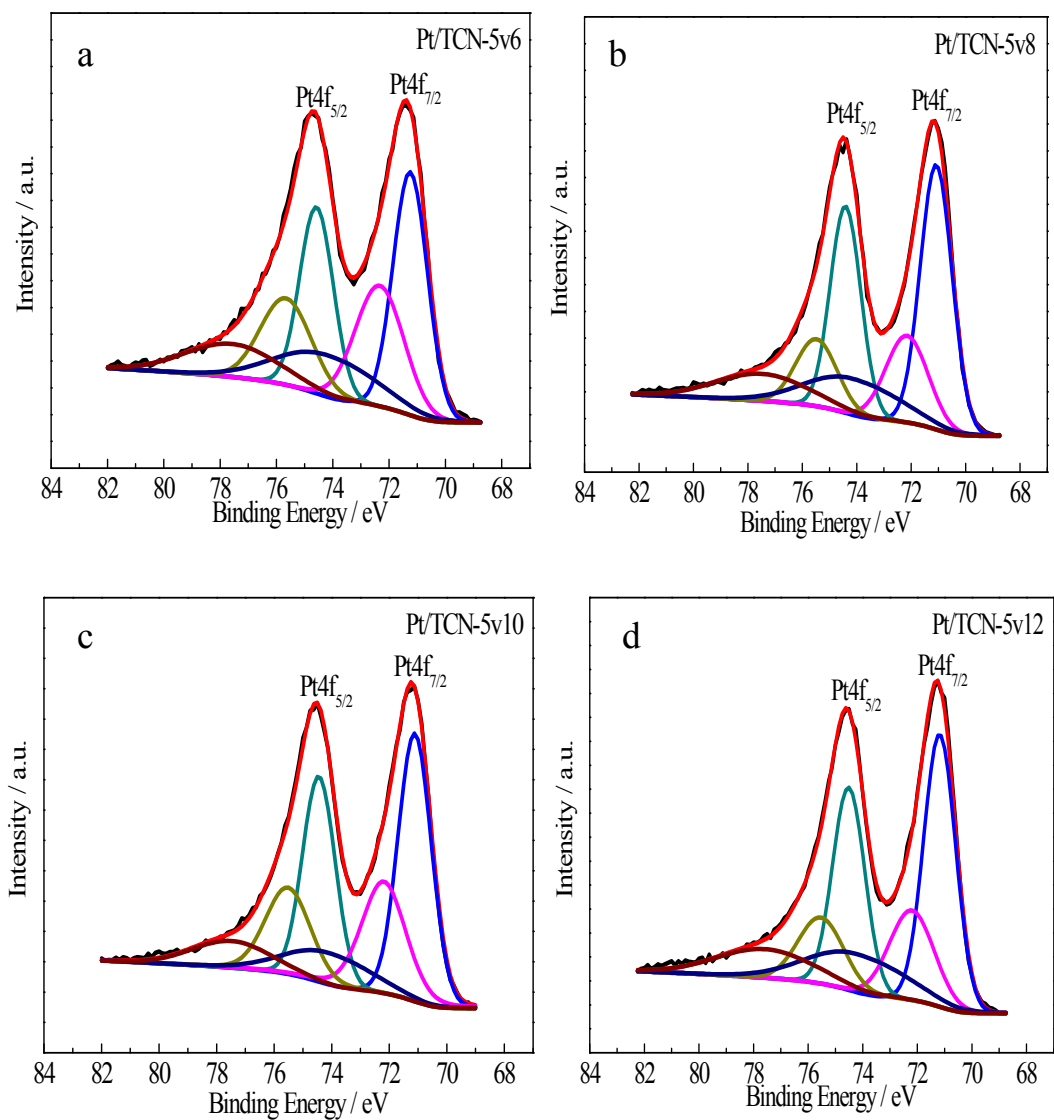


Figure S6. XPS curve fitting of Pt 4f peak for Pt/TCN with different mass ratio of TiO₂/RF: a) 5v6, b) 5v8, c) 5v10 and d) 5v12.

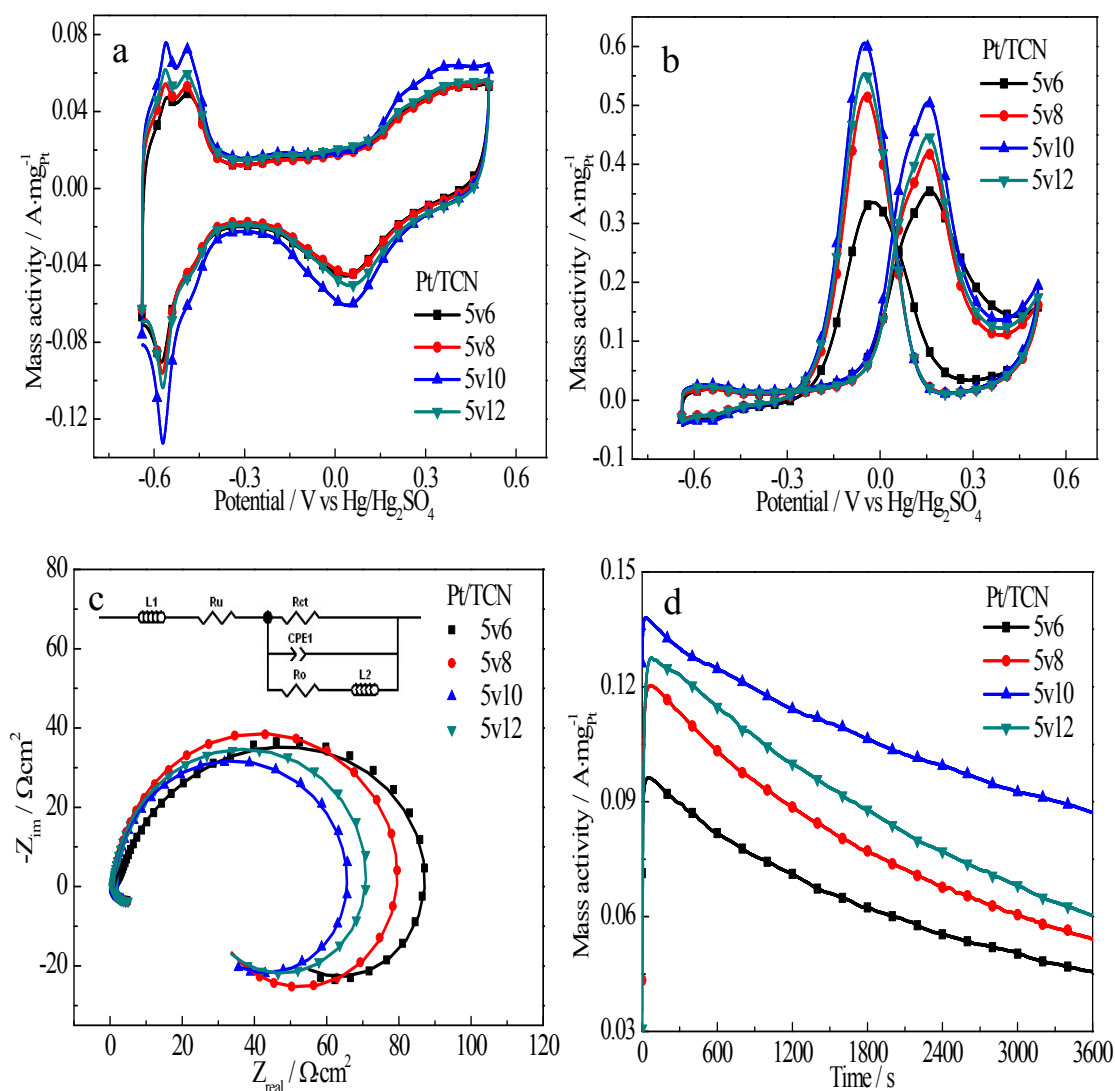


Figure S7. Electrocatalytic performance of Pt/TCN catalysts with different mass ratio of TiO₂/RF. a) Cyclic voltammogram at 25 °C in Ar-saturated 0.5 mol·L⁻¹H₂SO₄ solution with a sweep rate of 50 mV·s⁻¹. b) Cyclic voltammogram of methanol electro-oxidation at 25 °C in Ar-saturated solution of 0.5 mol·L⁻¹ CH₃OH and 0.5 mol·L⁻¹H₂SO₄ with a sweep rate of 50 mV·s⁻¹. c) Nyquist plot of methanol electro-oxidation at 0.6 V vs NHE at 25 °C in Ar-saturated solution of 0.5 mol·L⁻¹ CH₃OH and 0.5 mol·L⁻¹H₂SO₄. d) chronoamperometric current at 0.6 V vs NHE for 3600 s at 25 °C in Ar-saturated solution of 0.5 mol·L⁻¹ CH₃OH and 0.5 mol·L⁻¹H₂SO₄.

Table S1. Results of curve fitting of C 1s peak for Pt/TCN

Sample	sp ² -C	C	-C-OR	>C=O	-COOR
	284.5 eV	285.0 eV	285.7 eV	287.8 eV	288.9 eV
Pt/TCN-5v6	61.4 %	5.3 %	19.6 %	8.5 %	5.2 %
Pt/TCN-5v8	57.4 %	8.5 %	20.8 %	6.1 %	7.2 %
Pt/TCN-5v10	49.6 %	19.3 %	20.4 %	5.6 %	5.1 %
Pt/TCN-5v12	42.4 %	24.4 %	21.0 %	5.3 %	6.9 %

Table S2. Results of curve fitting of Pt 4f peak for Pt/TCN

Sample	Pt species	Binding energy	Relative content
Pt/TCN-5v6	Pt (0)	71.3 eV	45.6 %
	Pt (II)	72.3 eV	32.1 %
	Pt (IV)	74.3 eV	22.3 %
Pt/TCN-5v8	Pt (0)	71.1 eV	54.5 %
	Pt (II)	72.2 eV	23.8 %
	Pt (IV)	74.2 eV	21.7 %
Pt/TCN-5v10	Pt (0)	71.1 eV	52.5 %
	Pt (II)	72.2 eV	31.3 %
	Pt (IV)	74.2 eV	16.2 %
Pt/TCN-5v12	Pt (0)	71.2 eV	52.9 %
	Pt (II)	72.2 eV	24.5 %
	Pt (IV)	74.3 eV	22.6 %