Enhanced catalytic activity and stability of copper and nitrogen doped titania nanorods supported Pt electrocatalyst for oxygen reduction reaction in polymer electrolyte fuel cells

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Name	Temperature	Solution	Phase formation	Nanostructure
P-25 (TiO ₂)	180 °C/ 4h	10 M KOH	Anatase	Spherical
P-25	180 °C/ 8h	10 M KOH	Anatase	Spherical+ wires
P-25	180 °C/ 24h	10 M KOH	Anatase	nanowires
Titanium isopropoxide	180 °C/24h	10 M KOH	Anatase	Irregular shape
Titanium isopropoxide	180 °C/4h	5 M HCl	Rutile	Spherical + Nanorods
		ITO plate		
Titanium	180 °C/6h	5 M HCl	Rutile	Nanorods
isopropoxide		ITO plate		
Titanium isopropoxide	180 °C/6h	5 M HCl	Rutile	Nanorods
		Glass plate		

Table 1S: Optimization of Rutile TiO₂ during preparation of nanorods



Fig. 1S Various stages of colour change observed during preparation of ORR catalyst.



Fig. 2S (a) FE-SEM image for (a) TiO₂, (b) TiON, (c) TiON-Cu 1 and (d) TiON-Cu 3.



Fig. 2S (b) FE-SEM mapping for Pt deposited on TiON-Cu 2 nanorods support.



Fig. 3S (a) TEM of Pt deposited on TiO_2 nanorods with different scale.



Fig. 3S (b) TEM and STEM image of Pt deposited on TiO₂ nanorods. (a & b) Pt/TiO₂,
(c) overall elemental mapping image and individual STEM mapping (d) Oxygen,
(e) Titanium and (f) Platinum.



Fig. 4S (a) XRD refinement for both TiO_2 and TiON-Cu framework.

Parameter	TiO ₂	TiON-Cu 2
Space group	136	136
Hermann-Mauguin	P42/mnm	P42/mnm
symbol		
Hall symbol	-P 4n 2n	-P 4n 2n
Crystal structure	Tetragonal	Tetragonal
a	4.6013	4.5946
b	4.6013	4.5946
С	2.9587	2.9610
α	90	90
β	90	90
Ŷ	90	90
Volume	62.39	62.37
Bragg R-factor	3.82	3.86
RF-factor	3.58	3.62
X ²	3.16	3.26

The refined structural parameters of TiO_2 and TiON-Cu 2 sample.



Fig. 4S (b) XRD pattern for (a) TiO_2 , (b) TiON, (c) TiO_2 -Cu 2, (d) TiON-Cu 1, (e) TiON-Cu 2 and TiON-Cu 3 framework. Right side expended region from 32 to 40 (2 θ) asterisks peak indicated that un-doped Cu in the form of CuO (confirm from JCPDS No:89-5899).



Fig. 5S Steady state polarization of different prepared electrocatalysts.



Fig. 6S XRD pattern for (a) Pt/C before AST, (b) after AST-1 for support durability and (c) after AST -2 catalyst durability.



Fig. 7S XRD pattern for (a) Before AST for Pt/TiON-Cu 2 nanorods, (b) after AST-1 and (c) after AST-2.



Fig. 8S FE-SEM cross sectional image of MEAs comprising Pt/C before and after AST-1 (a & b) and Pt/TiON-Cu 2 nanorods before and after AST-1 (c & d).



Fig. 9S FE-SEM cross sectional image of MEA comprising Pt/C before and after AST-2 (a & b) and Pt/TiON-Cu 2 nanorods before and after AST-2 (c & d).



Fig. 10S TEM image for (a) Pt/C before AST, (b) after 1,000 AST-1 cycles and (c) after 10,000 AST-2 cycles.



Fig. 11S TEM image for Pt/TiON-Cu 2 nanorods (a) Before AST, (b) AST-1 after 6,000 cycles and (c) AST-2 after 18,000 cycles (for catalyst).



Fig. 12S XPS spectra of Pt 4f orbital state for Pt/C: (a) Before AST, (b) AST -1 after 1,000 cycles and (c) AST-2 after 10,000 cycles.



Fig. 13S XPS spectra of Pt 4f orbital state for Pt/TiON-Cu 2: (a) before AST (b) AST-1 after 6,000 cycles and (c) AST-2 after 10,000 cycles.