## **Supporting information**

## Uniform Pt Nanoparticles Supported on Urchin-like Mesoporous TiO<sub>2</sub> Hollow Spheres as stable Electrocatalyst for Oxygen Reduction Reaction

Suqiong He,<sup>a,b</sup> Chuxin Wu, <sup>b</sup> Zhen Sun,<sup>a,b</sup> Yang Liu,<sup>b</sup> Rongtao Hu,<sup>b</sup> Lunhui Guan,<sup>b\*</sup> Hongbing Zhan<sup>a\*</sup> <sup>a</sup> Fuzhou University, College of Material Science & Engineering, Fuzhou 350108, Fujian, Peoples R China.

<sup>b</sup> CAS Key Laboratory of Design and Assembly of Functional Nanostructures, Fujian Key Laboratory of Nanomaterials, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350108, China.

## **Corresponding author:**

E-mail: guanlh@fjirsm.ac.cn (Lunhui Guan); hbzhan@fzu.edu.cn (Hongbing Zhan).



Fig. S1 XRD pattern obtained from AHTSS and UMTHS (scan rate: 5 °/min).



Fig. S2 (a) Low magnification SEM image of AHTSS. (b) Size distribution of AHTSS obtained by counting size of 100 NPs randomly in Fig. S2a. (c), (d) Magnifying SEM images of AHTSS.



Fig. S3 Low magnification SEM image of UMTHS.



Fig. S4 (a) Low magnification SEM image of UMTHS. (b) SEM image of UMTHS obtained by magnifying the selected area of the yellow solid rectangle in Fig. S4a.



Fig. S5 Low magnification TEM image of UMTHS.



Fig. S6 (a), (b) TEM images of AHTSS. (c) HR-TEM image obtained by magnifying the selected area of the yellow solid rectangle in figure S6b.



Fig. S7 Nitrogen sorption isotherm (a) and pore size distribution (b) obtained for AHTSS.



Fig. S8 XRD pattern obtained for Pt@C w/o UMTHS sample (scan rate: 1 °/min).



Fig. S9 XPS survey spectrum obtained for Pt@C w/o UMTHS sample.



Fig. S10 (a), (b) different magnification SEM images of Pt/UMTHS.



Fig. S11 Nitrogen sorption isotherm and pore size distribution (insetted) obtained for

Pt/UMTHS.



Fig. S12 (a) TEM of Pt@C w/o UMTHS sample. (b) Size distribution of Pt NPs obtained by counting size of 100 NPs randomly in Fig. S12a. (c) HR-TEM of Pt@C w/o UMTHS sample. (d) Magnified HR-TEM image acquired from the selected area in Fig. S12c (The circled area with yellow dash curve was the carbon layer).



Fig. S13 SEM image (a) and corresponding element mapping (b-d) of Pt/UMTHS.



Fig. S14 Raman spectra for Pt/UMTHS and Pt/C.



Fig. S15 LSV curve was obtained for Pt/UMTHS w/o CB at 1600 rpm (CB means acetylene carbon black which was added to the catalyst ink to further improve the conductivity of catalyst, Pt loading: 64.3 ug/cm<sup>2</sup>).



Fig. S16 LSV curves obtained at a rotation rate of 2500, 2000, 1600, 1200, 900 rpm in

O<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> electrolyte (10 mV/s).



Fig. S17 CV curves of Pt/UMTHS (a) and Pt/C (b) obtained before and after different potential cycles in  $N_2$ -saturated 0.1 M HClO<sub>4</sub> electrolyte at 0.6-1.0 V (100 mV/s, 25 °C). (c) Comparison and changes of ECSA obtained from Fig. S17a and S17b.



Fig. S18 TEM of Pt/UMTHS obtained after 10k potential cycles at 0.6-1.0 V. The mean size of Pt NPs after ADT was calculated by counting size of 100 NPs randomly in Fig. S18.



Fig. S19 TEM of Pt/C obtained before (a) and after 10 k potential cycles at 0.6-1.0 V(b). The mean size of Pt NPs before and after ADT was calculated by counting size of 100 NPs randomly in Fig. S19a and S19b, respectively.



Fig. S20 Comparison of the normalized  $E_h$  and ECSA (%) with corresponding literatures listed in Table S1.



Fig. S21 LSV curves of Pt/UMTHS (a) and the commercial Pt/C (b) obtained before and after 8k potential cycles at 1.0-1.4 V in  $O_2$ -saturated 0.1 M HClO<sub>4</sub> (1600 rpm, 10 mV/s, 25 °C).



Fig. S22 (a) XPS survey spectrum of UMTHS and Pt/UMTHS samples. (b) High resolution XPS of C 1s for UMTHS and Pt/UMTHS. (c) High resolution XPS of N 1s for Pt/UMTHS. (d) High resolution XPS of O 1s for UMTHS and Pt/UMTHS. The C emission peak appearing in the survey spectrum of UMTHS was ascribed to suitable amount of C added to the UMTHS sample before XPS analysis in order to calibrate all the emission peaks in UMTHS with C-C peak (284.8 eV).

<sup>a</sup> Catalyst	Cycling range,	<sup>b</sup> E <sub>h</sub> (V)	<sup>c</sup> ECSA	Pt loading	Electrolyte	Reference			
	cycles and gas	vs. RHE	$(m^2 g_{Pt}^{-1})$	(µg cm <sup>-2</sup> )					
CNT-Pt/TiO <sub>2</sub> nanofiber	0.6-1.0 V(vs. SHE)	0.84	85.69	400	0.5M H <sub>2</sub> SO <sub>4</sub>	Appl. Catal. B: Environ., 2017 <sup>1</sup>			
	10000 (N <sub>2</sub> )	0.78	59.98	400					
CNF/TiO <sub>2</sub> (R)-Pt	0.6-1.0 V	0.86	115.3	1	0.5M H <sub>2</sub> SO <sub>4</sub>	ACS nano, 2018 <sup>2</sup>			
	10000 (N <sub>2</sub> )	0.86	105	/					
$D_{4}(20 + 0/)/dT_{2}$ Ma O	0.2-0.8 V	0.84	53.6	107	$0.5M H_2 SO_4$	ACS Catal., 2016 <sup>3</sup>			
Pt (20 wt.%) /d- $\Pi_{0.9}MO_{0.1}O_y$	3000 (N <sub>2</sub> )	0.84	/	107					
Dt/Mh T:O non of them	0.6-1.1 V	0.896	/	(0		Sai Bar 2017 4			
$Pt/ND-11O_2$ hanomber	6000(O <sub>2</sub> )	0.878	/	60	0.1M HClO <sub>4</sub>	Sci. Kep., 2017			
	0.75-1.25 V	0.856	64.95	1.5	1.5	1.5		L Mater Cham A 2018 5	
Pt/11O <sub>2</sub>	10000(Ar)	0.816	38.97	15	0.1M HClO <sub>4</sub>	J. Mater. Chem. A, 2018			
	0.6-1.1 V	0.81	/	120.7	0.1M HClO <sub>4</sub>	Adv. Mater. Inter., 2017 <sup>6</sup>			
Pt/rGO/11O <sub>2</sub>	5000(Ar)	0.77	/	128.7					
	0.6-1.2 V(vs. SHE)	0.854	61	40					
Pt/CC1-30	10000(O <sub>2</sub> )	0.639	43	40	0.1M HClO <sub>4</sub>	Electrochim. Acta., 2018			
	0.6-1.0 V	0.867	42.95	745	0.1M HClO <sub>4</sub>	This work			
Pt/UM1HS	10000 (O <sub>2</sub> )	0.853	42.77	/0.5					

**Table S1** ORR stability comparison with other TiO<sub>2</sub>-supported Pt catalysts reported in recent five years.

<sup>*a*</sup> The catalyst comes from the corresponding reference; <sup>*b*</sup>  $E_h$  is the half-wave potential (V vs. RHE); <sup>*c*</sup> ECSA is the electrochemical surface area, which is calculated by  $H_{upd}$  method.

Table S2 Element content of Pt@C w/o UMTHS and Pt/UMTHS sample obtained from

XPS survey spectrum

Element (at.%) Sample	С	0	Ti	Pt	Ν
Pt@C w/o UMTHS	71.9	12.7	NA	7.7	7.7
Pt/UMTHS	47.70	26.93	10.00	9.39	5.99

## Reference

- 1. Y. Ji, Y. I. Cho, Y. Jeon, C. Lee, D.-H. Park and Y.-G. Shul, *Applied Catalysis B-Environmental*, 2017, **204**, 421-429.
- Y. Jeon, Y. Ji, Y. I. Cho, C. Lee, D.-H. Park and Y.-G. Shul, *Acs Nano*, 2018, **12**, 6819-6829.
- M.-C. Tsai, N. Trung-Thanh, N. G. Akalework, C.-J. Pan, J. Rick, Y.-F. Liao,
  W.-N. Su and B.-J. Hwang, *Acs Catalysis*, 2016, 6, 6551-6559.
- 4. M. Kim, C. Kwon, K. Eom, J. Kim and E. Cho, Scientific Reports, 2017, 7, 44411.
- 5. P. S. M. Kumar, V. K. Ponnusamy, K. R. Deepthi, G. Kumar, A. Pugazhendhi, H.

Abe, S. Thiripuranthagan, U. Pal and S. K. Krishnan, *Journal of Materials Chemistry* A, 2018, **6**, 23435-23444.

- C. H. Sung, R. Boppella, J.-W. Yoo, D.-H. Lim, B.-M. Moon, D. H. Kim and J. Y. Kim, *Advanced Materials Interfaces*, 2017, 4, 1700564.
- 7. P. Dhanasekaran, S. V. Selvaganesh, A. Shukla, N. Nagaraju and S. D. Bhat, *Electrochimica Acta*, 2018, **263**, 596-609.