

## Supplementary Information

### NanoPorous Hollow PtCu Nanoparticles for Oxygen Reduction Reaction

Meng Wang,<sup>a</sup> Weimin Zhang,<sup>b</sup> Jiazhao Wang,<sup>c</sup> Andrew Minett,<sup>b</sup> Victor Lo,<sup>b</sup>  
Huakun Liu,<sup>c</sup> and Jun Chen<sup>\*a</sup>

<sup>a</sup> *Intelligent Polymer Research Institute (IPRI), University of Wollongong,  
Wollongong, NSW, Australia,*

<sup>b</sup> *School of Chemical and Biomolecular Engineering., University of Sydney,  
Sydney, NSW, Australia*

<sup>c</sup> *Institute for Superconducting and Electronic Material (ISEM), University of  
Wollongong, Wollongong, NSW, Australia*

\*To whom correspondence should be addressed. E-mail: [junc@uow.edu.au](mailto:junc@uow.edu.au)

### Experimental

#### Synthesis

Copper nanoparticles were synthesized according to the procedures as the reported elsewhere<sup>1</sup>. Typically, 37 mg cetyltrimethylammonium bromide (CTAB, 99.9+%, Fluka) was dissolved in 20 ml aqueous solution containing 100  $\mu$ L 0.1 M cupric chloride (BDH Anala R). The pH was adjusted to 10 by ammonia solution (Ajax Finechem). Then another aqueous solution containing the same concentration CTAB and 60  $\mu$ l hydrazine (35 wt% in water, Sigma Aldrich) was added slowing under vigorous stirring. After 3 hours a red wine colour appeared which indicated the copper nanoparticles formed. Once copper nanoparticles were formed, 50  $\mu$ L 0.1 M  $H_2PtCl_6 \cdot xH_2O$  in 20 ml deoxygenated Milli-Q water was added dropwise, and the solution was allowed to react for another 3 hours. To avoid particle aggregation, the alloyed PtCu nanoparticles were supported on carbon black (CB, Vulcan XC-72 R, Cabot Corp.). This was achieved by mixing the above synthesised colloids with certain amount of acid treated CB and stirring overnight. The final product with 20 wt% Pt loading was collect by filtration and washed with acetone and hot water for several times to remove residue hydrazine and surfactant, and then dried in a vacuum oven at 80 °C for overnight. This sample is denoted as Pt<sub>0.5</sub>Cu<sub>1</sub>/C. To explore an optimized composition for electrocatalysis, PtCu nanoparticles with various molar ratio (Pt/Cu) of 1, 0.75, 0.5, and 0.25:1 were synthesised with the controlled concentrations of the precursors.

## TEM, HRTEM, STEM-EDS, XRD, and ICP-MS Measurements

Transmission electron microscope (TEM) images of the samples were collected using a JEOL JEM-2100 F transmission electron microscope operated at 200 kV. Energy dispersive spectroscopy (EDS) in the scanning TEM (STEM) mode was employed to determine the elemental composition. High resolution TEM (HRTEM) was conducted on a JEOL JEM-3000F transmission electron microscope operated at 300 kV. Powder X-ray diffraction (XRD) measurements were conducted with a Bruker D8-advanced X-ray powder diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Energy dispersive spectroscopy (EDS, Bruker) was used to determine the elemental composition and distribution of the catalysts. Inductively coupled plasma – mass spectrometry (ICP-MS 7500CS, Agilent Technologies) was used to determine the metal contents of the products.

## Electrochemical measurements

Electrochemical measurements were conducted in a standard three-electrode using a CHI 720C Bipotentiostat (CH Instruments, Inc., USA). Cyclic voltammograms (CV) (Figure S6) and linear sweep voltammograms (LSV) (Figure S7) testings were carried out using a glassy carbon disk-platinum ring rotating ring disk electrode (RRDE,  $0.2475 \text{ cm}^2$ , Pine Research Instrumentation, USA) connected to a 636 rotating disk electrode system (Princeton Applied Research, USA). The reference electrode was an Ag/AgCl in saturated AgCl-KCl solution and the counter electrode was platinum wire. For the electrodes preparation, required amount of carbon support PtCu catalysts was ultrasonically dispersed in 5% Nafion<sup>®</sup>/H<sub>2</sub>O/isopropanol (1:1 by volume) to obtain a 1 mg/ml uniform ink. Then 30  $\mu\text{L}$  of the ink was dropped on the RRDE electrode and dried in the air before the electrochemical tests. Given that the copper is unstable during electrochemical testing, the electrode film was cycled 200 times between -0.28 and 0.962 V at 0.5 V/s to achieve stable current-voltage curves in nitrogen saturated electrolyte. Evaluation of ORR activity was performed in 0.1 M HClO<sub>4</sub> solution. Accelerated durability tests were carried out in oxygen saturated 0.1 M perchloride acid by applying cyclic potential sweep between 0.4 and 1 V (vs. Ag/AgCl) for 10 000 cycles, with a sweep rate of 100 mV/s.

The transferred electron number ( $n$ ) for per O<sub>2</sub> molecular and the percentage of hydrogen peroxide (% H<sub>2</sub>O<sub>2</sub>) in the ORR can be estimated using the following equations:

$$n = \frac{4I_D}{I_D + \left(\frac{I_R}{N}\right)} \quad (1)$$

$$\%H_2O_2 = 100(4 - n)/2 \quad (2)$$

(where  $I_D$  is the disk current,  $I_R$  is the ring current, and  $N$  is the collection efficiency of the RRDE apparatus used in this study, which is 0.37, as determined using the  $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$  redox system in a solution containing 1 mM  $\text{K}_3\text{Fe}(\text{CN})_6$  and 0.1 M  $\text{NaNO}_3$ ).

For a detailed study of the electrochemical activities of the PtCu/C and Pt/C, the kinetic current was calculated from the ORR polarization curves with mass-transport effect corrected using the Levich-Koutecky equation ( $\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_d}$ , where  $i_k$  is the kinetic current and  $i_d$  is the diffusion limiting current) and normalized by the electrochemical surface area and mass of platinum for the specific area activities and mass activities comparisons.<sup>2</sup>

### Single Fuel Cell Test

Membrane electrode assemblies (MEAs) were prepared by the brush technique as the described elsewhere<sup>3</sup>. Typically, the anode was a 5 cm<sup>2</sup> electrode prepared with 20 wt% commercial Pt/C (E-TEK, Natick, MA) with a platinum loading of 0.2 mg cm<sup>-2</sup>. The cathodes were prepared with PtCu/C and E-TEK Pt/C, respectively, with a platinum loading of 0.4 mg cm<sup>-2</sup>. The assembled MEAs were tested using a 850e fuel cell test system (Scribner Associate, Inc., USA) in a single fuel cell hardware assembly (Fuel cell Technologies, Inc., USA) fed with humidified hydrogen and oxygen, respectively. The gas flow was controlled at 0.08 mL min<sup>-1</sup>. The fuel cell measurements were carried out at 80°C under 15 psi (103.42 kPa) back pressure. The MEAs were activated and electro-dealloyed by the method previously reported<sup>4</sup>. The polarization curves were recorded using a potential scan method that involved holding the cell at each potential for 60 s in order to obtain the steady-state current value with a scan rate of 25 mV s<sup>-1</sup> from 0.95 V to 0.65 V.

## Results

Table S1 Metal contents of the synthesized PtCu nanostructures.

Reactant Ratio (Pt:Cu)	Analysed from ICP-MS			Derived From XRD			
	Pt (wt%)	Cu (wt%)	Pt/Cu atomic ratio	Lattice Parameter (Å)	Pt molar fraction	Cu molar fraction	Pt/Cu atomic ratio
1	9.16	2.05	1.46	3.832	0.61	0.39	1.56
0.75	4.21	1.13	1.21	3.830	0.60	0.40	1.50
0.5	2.14	0.95	0.73	3.829	0.59	0.41	1.43
0.25	3.06	4.64	0.22	3.828	0.58	0.42	1.38

Table S2 Metal Contents of PtCu nanoparticles (Precursor ratio Pt:Cu=0.5:1) derived from ICP-MS before and after acid treatment.

	Pt(wt%)	Cu(wt%)	Pt/Cu atomic ratio
Before acid treatment	2.14	0.75	0.73
after acid treatment	4.65	1.14	1.33

\*The lattice parameters are the average lattice spacing calculated from the three major phases ((111), (200) and (220)) of PtCu alloyed nanoparticles; the Pt molar fraction were obtained by Vegard's law<sup>5</sup>.

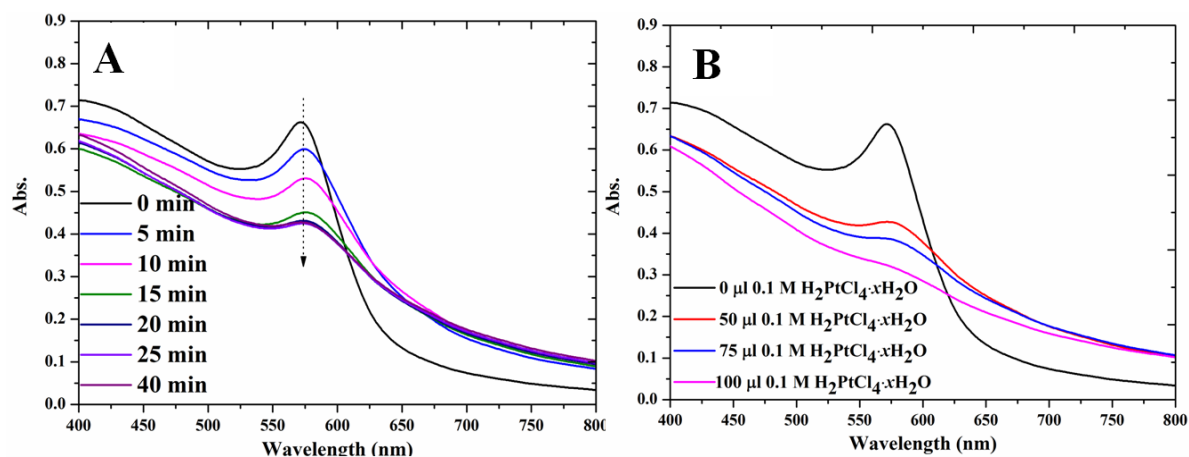


Fig. S1 (A) UV-Vis spectra of copper nanoparticles before (0 min) and at intervals of 1 min – 40 min after starting to add 50 µL 0.1 M  $H_2PtCl_6 \cdot xH_2O$  (adding rate 1 mL/min, with addition completed after 20 min); (B) UV-Vis spectra of copper nanoparticle colloids (0.5 mmol  $CuCl_2 \cdot 2H_2O$ , 37 mg CTAB, 60 µL hydrazine),  $Pt_{0.5}Cu_1$  nanoparticles (50 µL 0.1 M  $H_2PtCl_6 \cdot xH_2O$  added),  $Pt_{0.75}Cu_1$  nanoparticles (75 µL 0.1 M  $H_2PtCl_6 \cdot xH_2O$  added), and  $Pt_1Cu_1$  nanoparticles (100 µL 0.1 M  $H_2PtCl_6 \cdot xH_2O$  added).



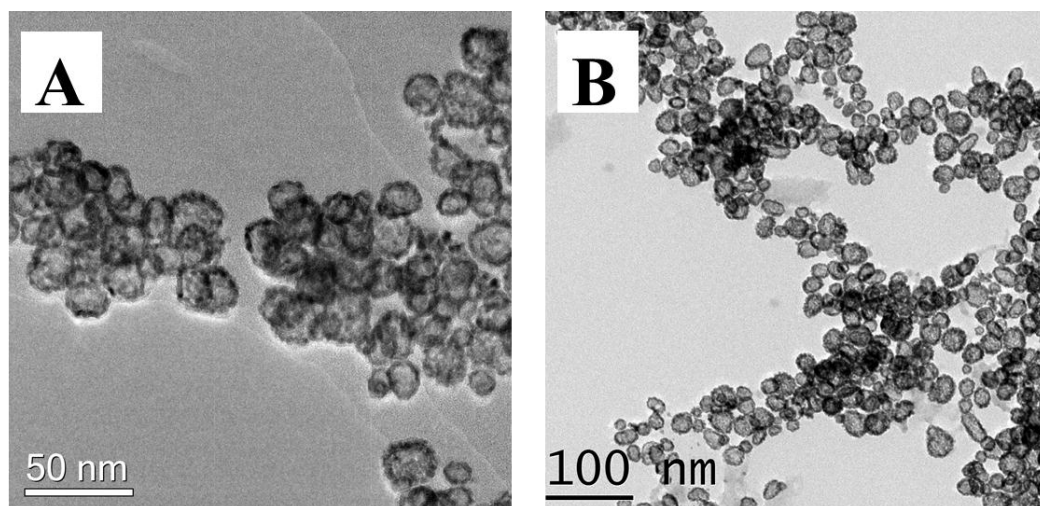


Fig. S2 TEM images of the hollow  $\text{Pt}_{0.5}\text{Cu}_1$  nanostructures at low magnifications.

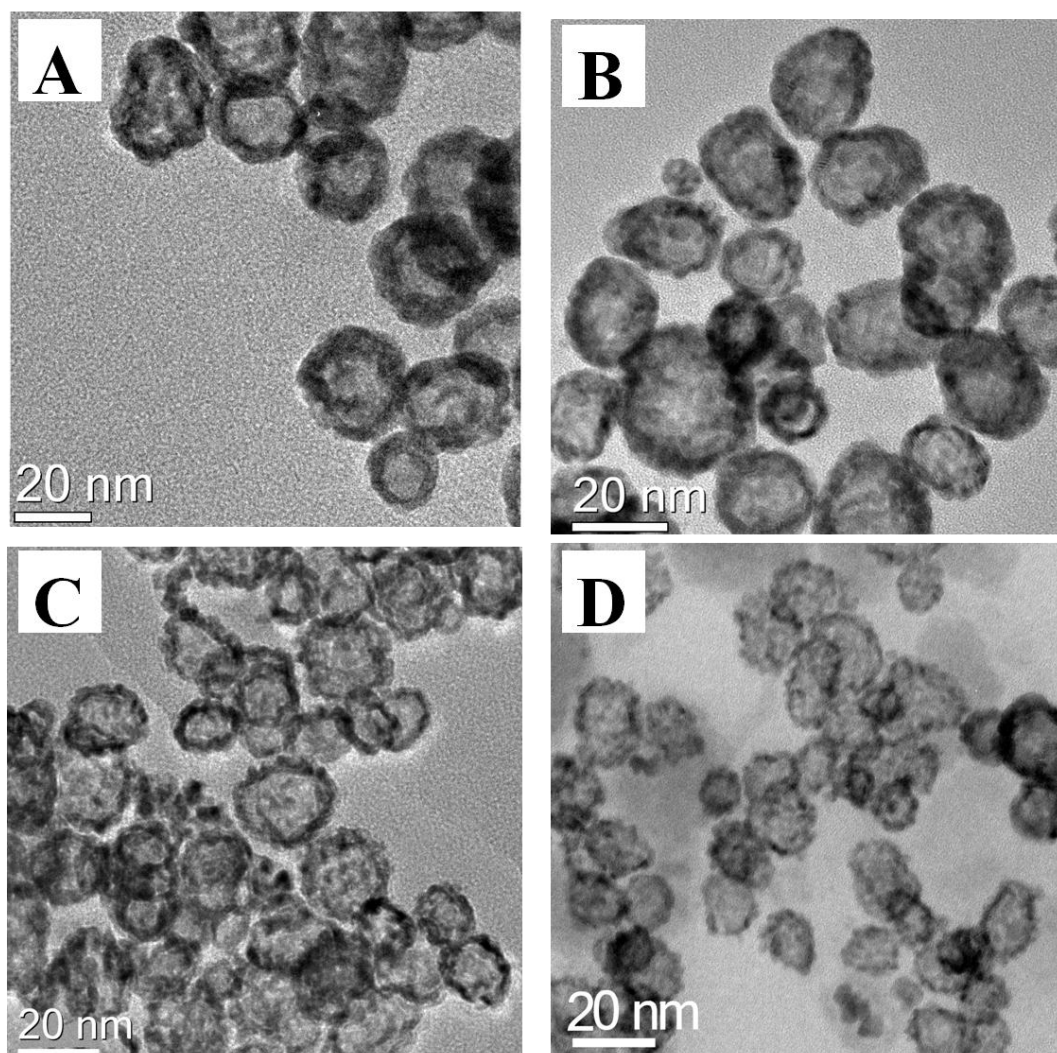


Fig. S3 TEM images of the hollow PtCu nanostructures with various ratios of Pt and Cu precursor: from A-D, the ratios are 1, 0.75, 0.5, and 0.25.

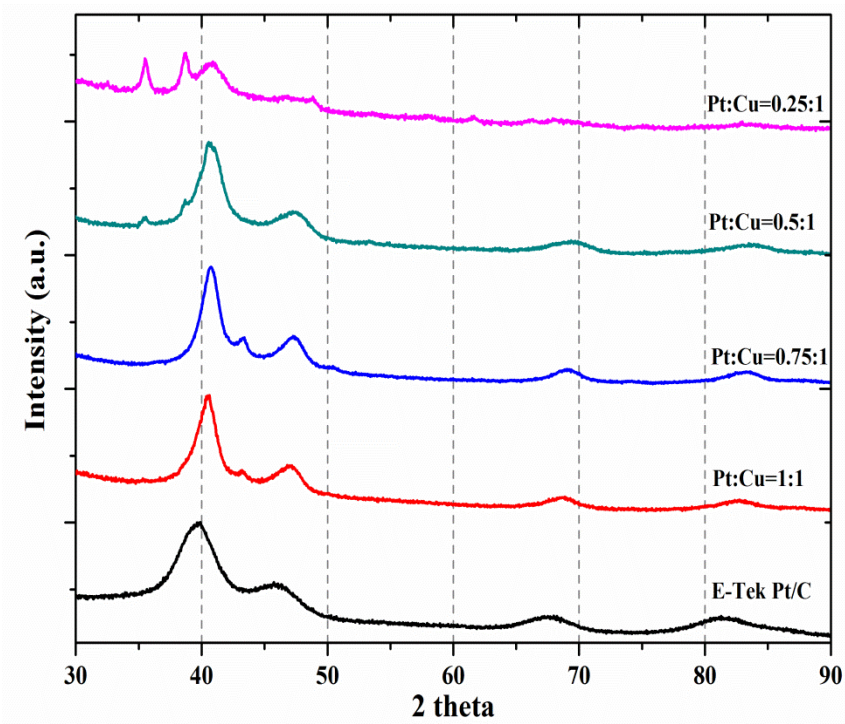


Fig..S4 XRD patterns of the hollow PtCu/C with various Pt/Cu ratios and of commercial E-Tek Pt/C.

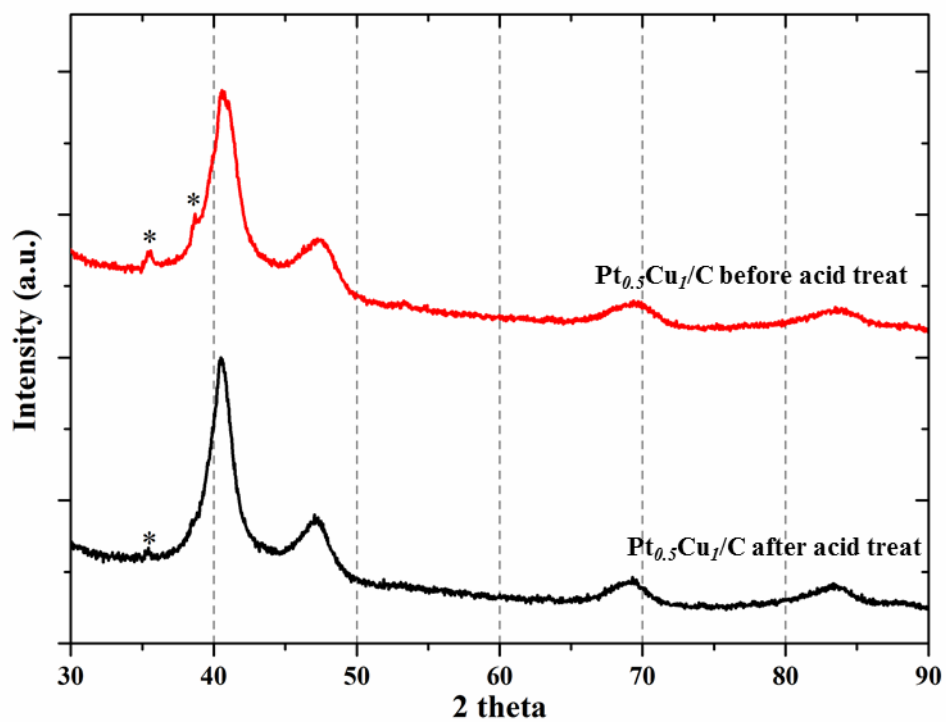


Fig. S5 XRD patterns of the Pt<sub>0.5</sub>Cu<sub>1</sub>/C before and after acetic acid treatment.

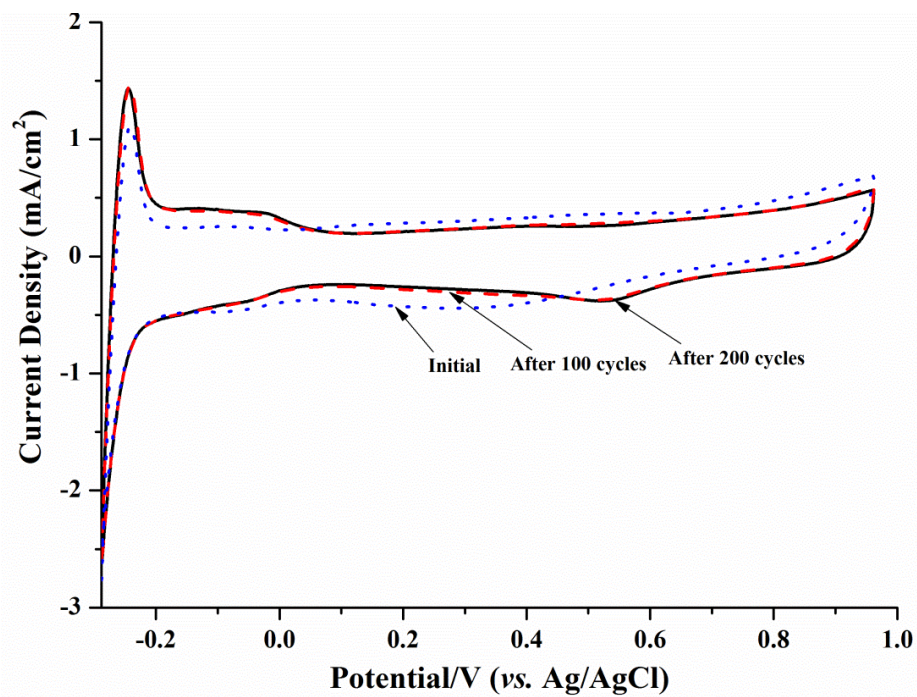


Fig. S6 CV curves of the Pt<sub>0.5</sub>Cu<sub>1</sub>/C before (initial) and after electro-dealloying for 100 cycles and 200 cycles.

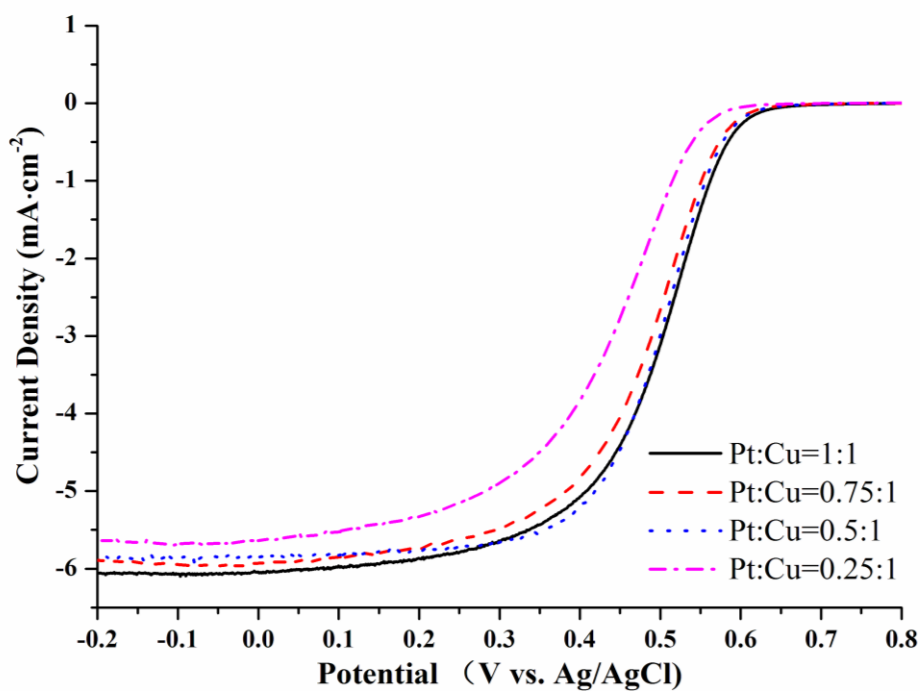


Fig. S7 Polarisation curves of PtCu hollow nanostructures with various ratios of Pt and Cu precursor using the RRDE technique in oxygen saturated electrolyte (0.1 M HClO<sub>4</sub>).

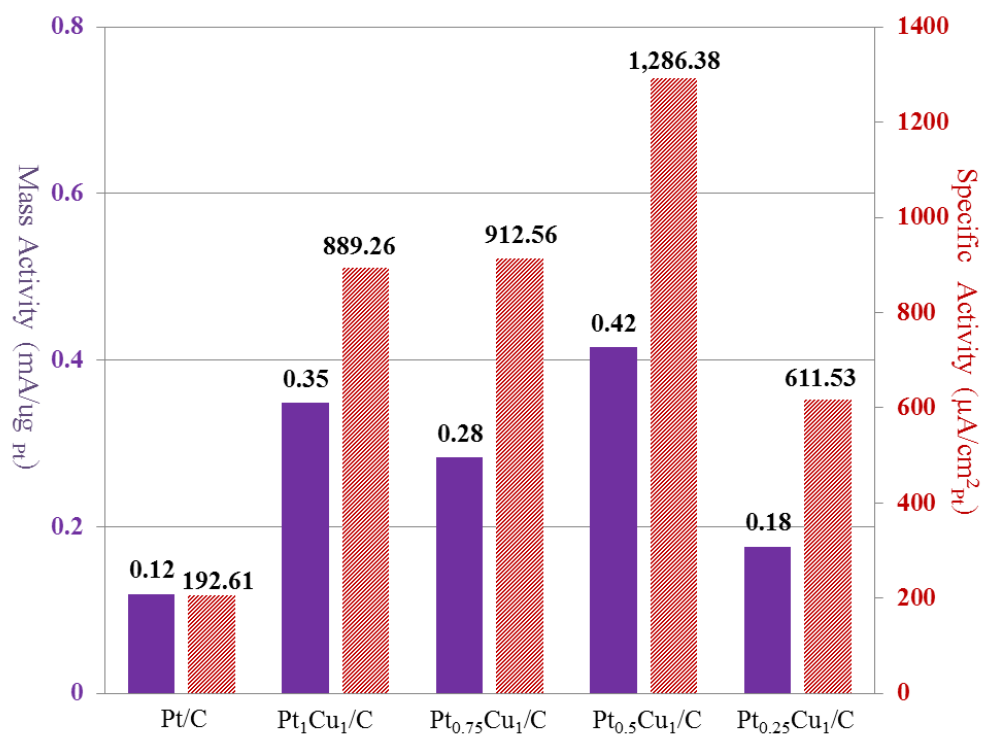


Fig. S8. Mass activities (solid columns) and specific area activities (diagonal pattern filled columns) of the hollow PtCu/C with different molar ratios and the E-Tek Pt/C.



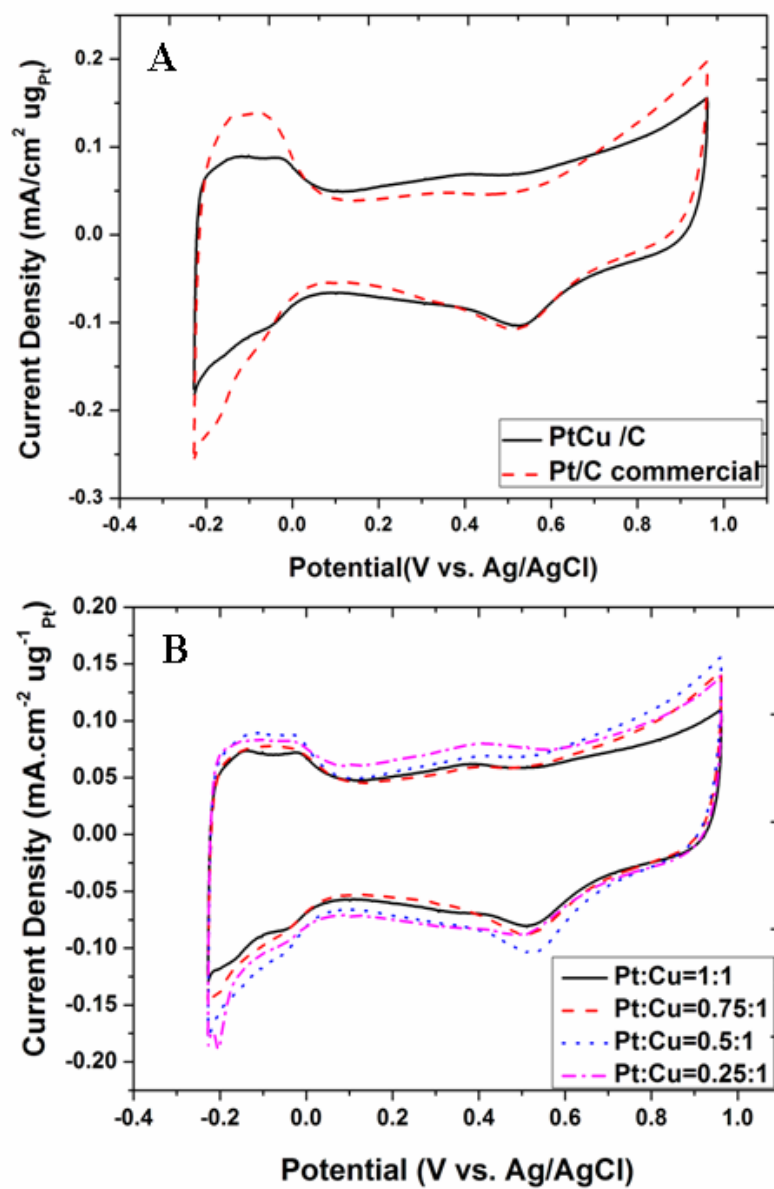


Fig. S9 CV curves of (A) Pt<sub>0.5</sub>Cu<sub>1</sub>/C and Pt/C; (B) PtCu/C hollow nanostructures with various ratios of Pt and Cu precursor.

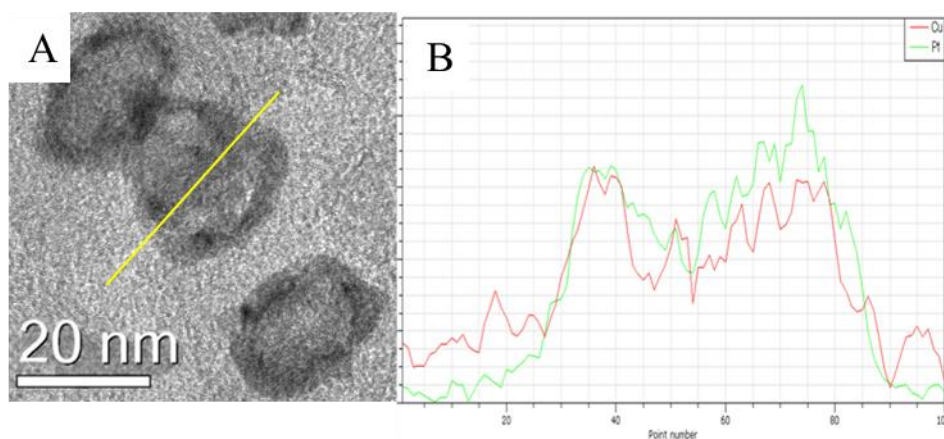


Fig. S10 (A) TEM image; (B) EDX line scan profiles of the  $\text{Pt}_{0.5}\text{Cu}_1/\text{C}$  along the line shown in (A) after durability testing.

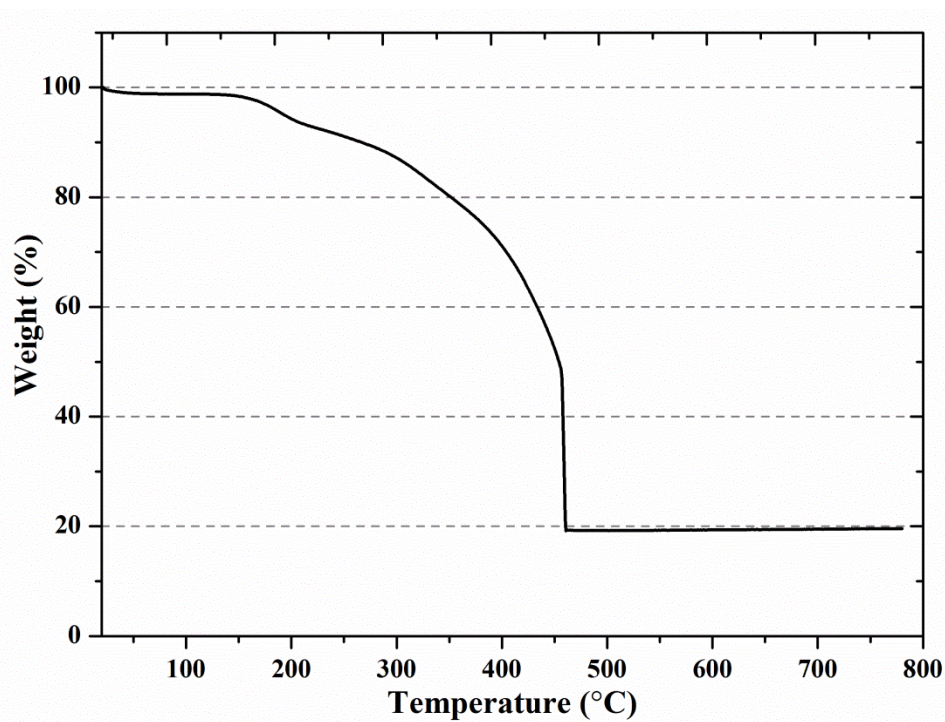


Fig. S11 Thermogravimetry curves of the  $\text{Pt}_{0.5}\text{Cu}_1/\text{C}$  calcinated in air atmosphere.

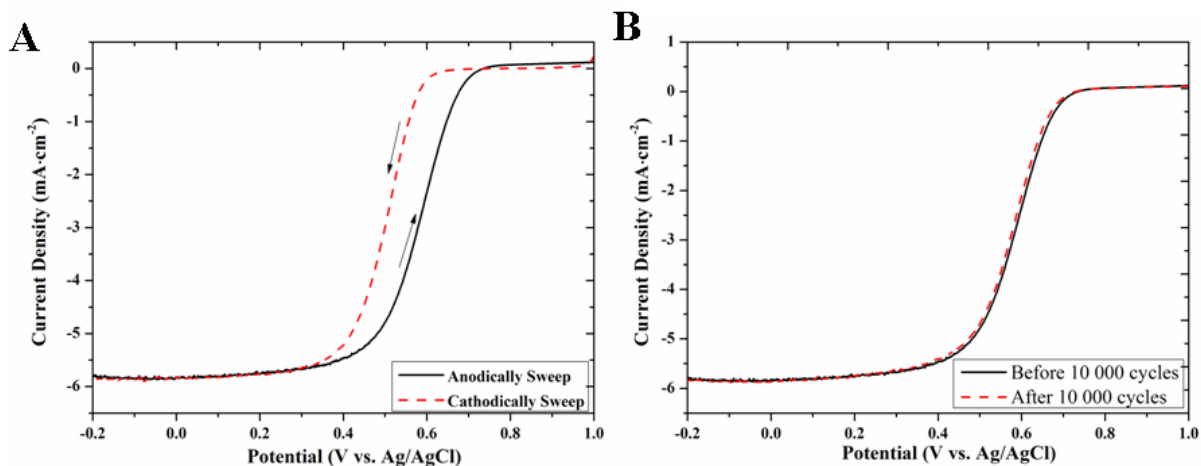


Fig. S12 (A) Comparison of ORR curves swept cathodically and anodically of the Pt<sub>0.5</sub>Cu<sub>1</sub>/C, and (B) ORR curves swept anodically of the Pt<sub>0.5</sub>Cu<sub>1</sub>/C before and after 10 000 cycle potential scan.

1. S.-H. Wu and D.-H. Chen, *J. Colloid Interface Sci.*, 2004, **273**, 165.
2. B. Lim, M. Jiang, P. H. C. Camargo, E. C. Cho, J. Tao, X. Lu, Y. Zhu and Y. Xia, *Science*, 2009, **324**, 1302.
3. W. Zhang, J. Chen, G. F. Swiegers, Z.-F. Ma and G. G. Wallace, *Nanoscale*, 2010, **2**, 282.
4. P. Mani, R. Srivastava and P. Strasser, *Journal of Physical Chemistry C*, 2008, **112**, 2770.
5. Z. Liu, S. Koh, C. Yu and P. Strasser, *J. Electrochem. Soc.*, 2007, **154**, B1192.