Electronic Supplementary Information

Hollow PtCu Nanoparticles Encapsulated into Carbon Shell *via* Mild Annealing of Cu Metal-Organic Frameworks

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Fig. S1 Guanjun Chen et al.

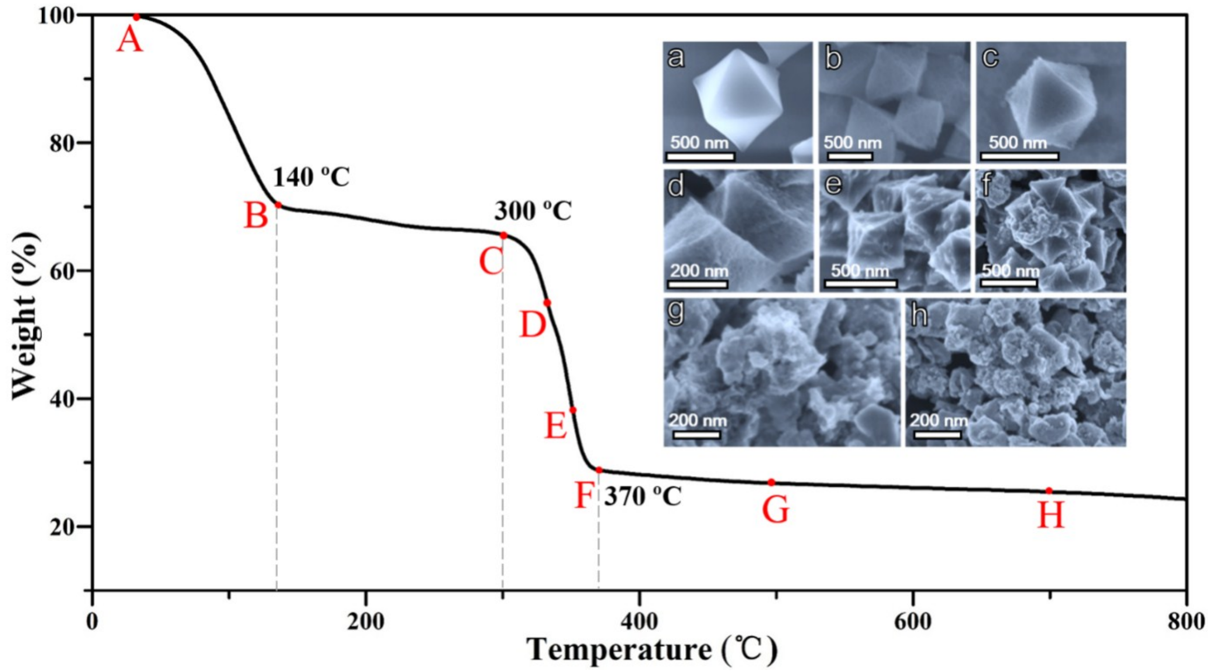

Fig. S1 TGA plots for Cu-BTC, the insets a-g correspond to the SEM images of A-G in TGA, respectively.

Fig. S2 Guanjun Chen et al.

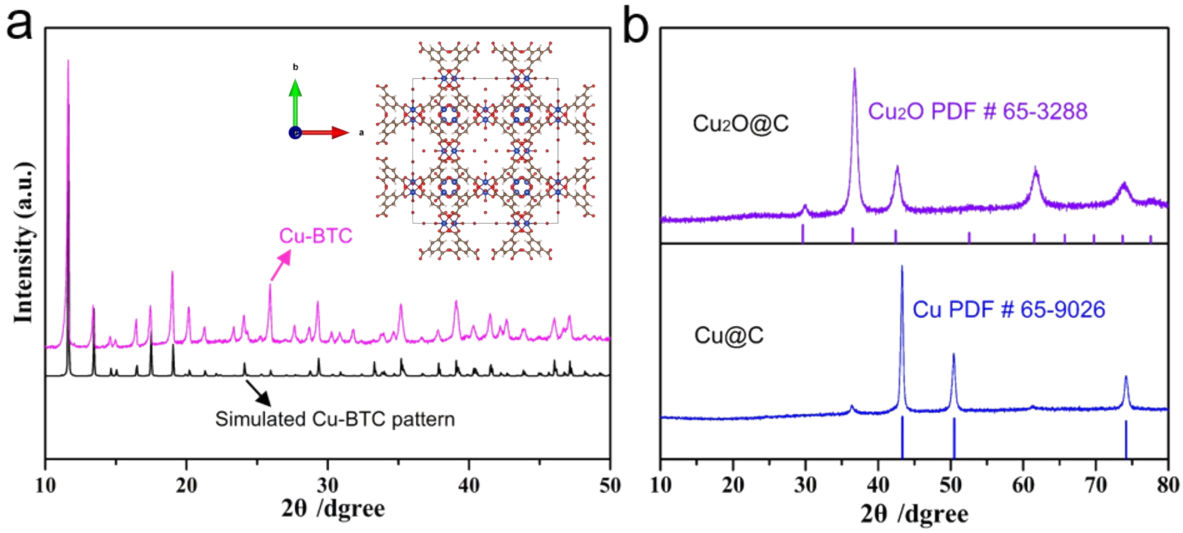

Fig. S2 (a) XRD patterns of Cu-BTC and the simulated XRD pattern of Cu-BTC by Materials Studio 7.0, the insets show the crystal structure of Cu-BTC (blue, gray, red and pink spheres represent Cu, C, O and H atoms, respectively). (b) XRD patterns of Cu@C and Cu_2O@C.

Fig. S3 Guanjun Chen et al.

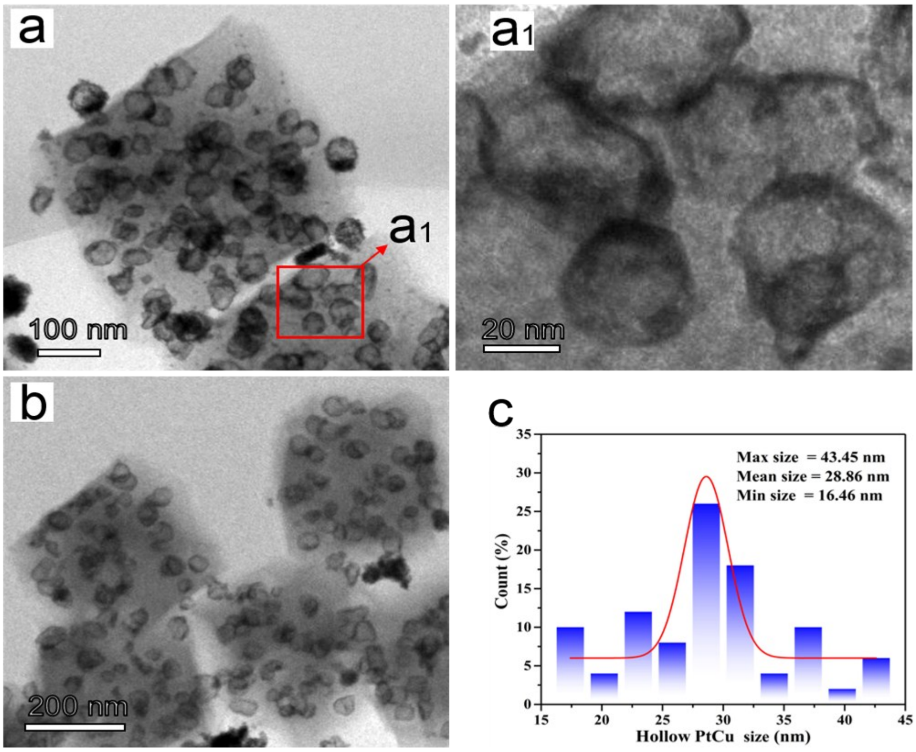

Fig. S3 (a-b) TEM images of S-H-Pt_xCu_y@C. (a_1) Enlarged TEM image of selected area labelled in (a). (c) The diameter distribution histograms of spherical hollow PtCu alloy statistics from (b).

Fig. S4 Guanjun Chen et al.

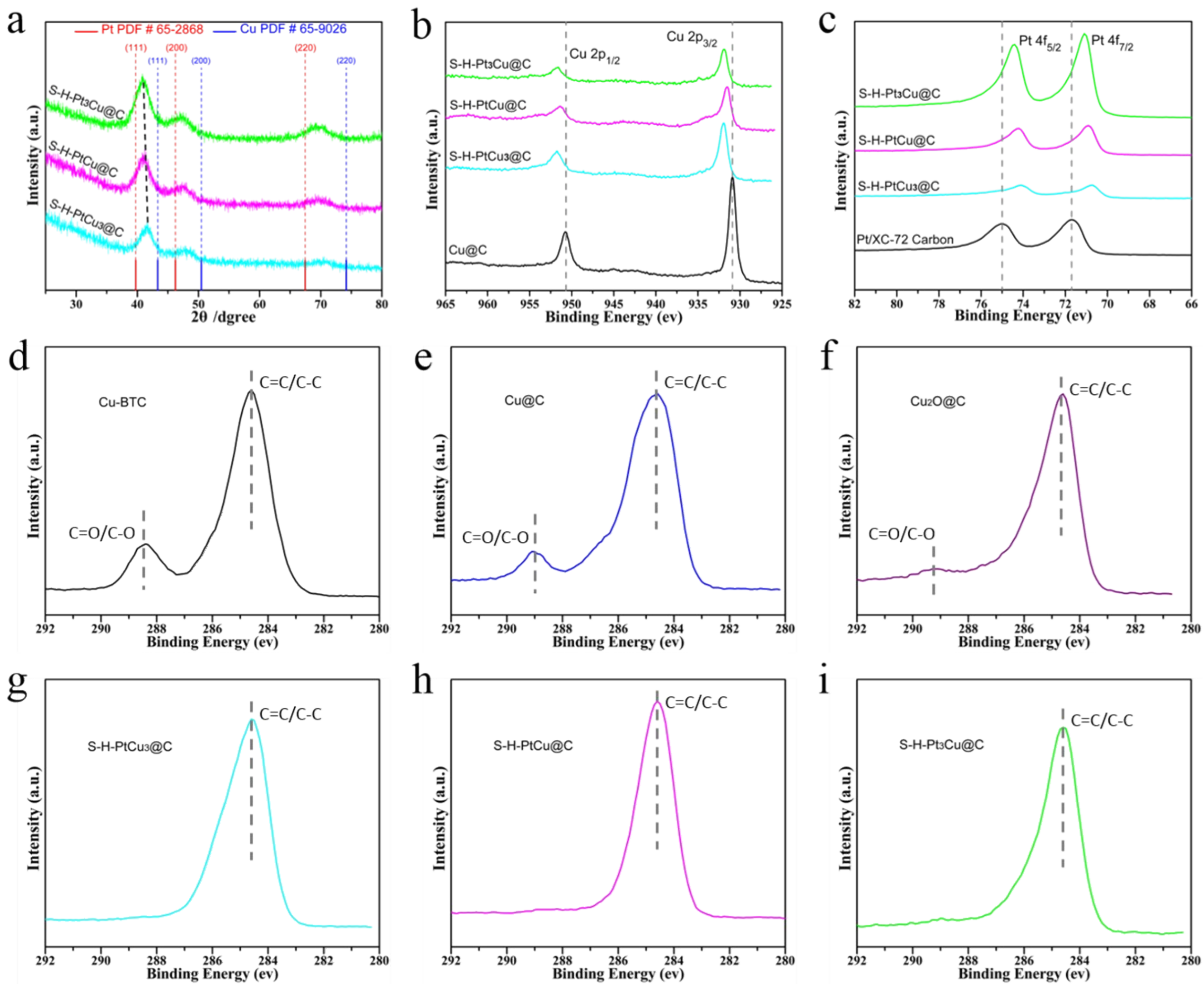

Fig. S4 (a) XRD pattern of S-H-Pt_xCu_y@C. (b) Cu 2p XPS spectra of S-H-Pt_xCu_y@C and Cu@C. (c) Pt 4f XPS spectra of S-H-Pt_xCu_y@C and Pt/XC-72 Carbon. (d-i) C 1s XPS spectra of Cu-BTC, Cu@C, Cu_2O@C, S-H-$PtCu_3$@C, S-H-PtCu@C and S-H-Pt_3Cu@C.

Fig. S5 Guanjun Chen et al.

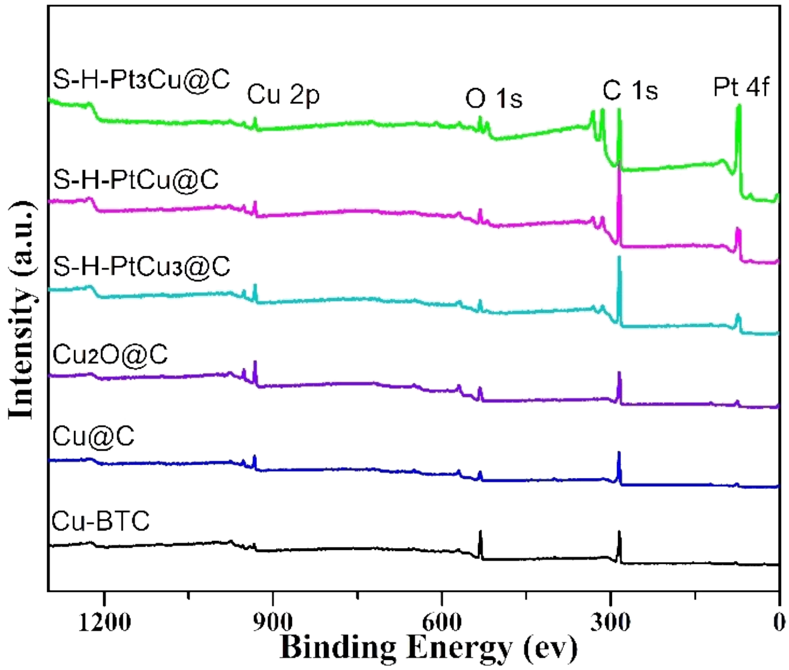

Fig. S5 Full range XPS spectrum of Cu-BTC, Cu@C, Cu_2O@C and S-H-Pt_xCu_y@C.

Fig. S6 Guanjun Chen et al

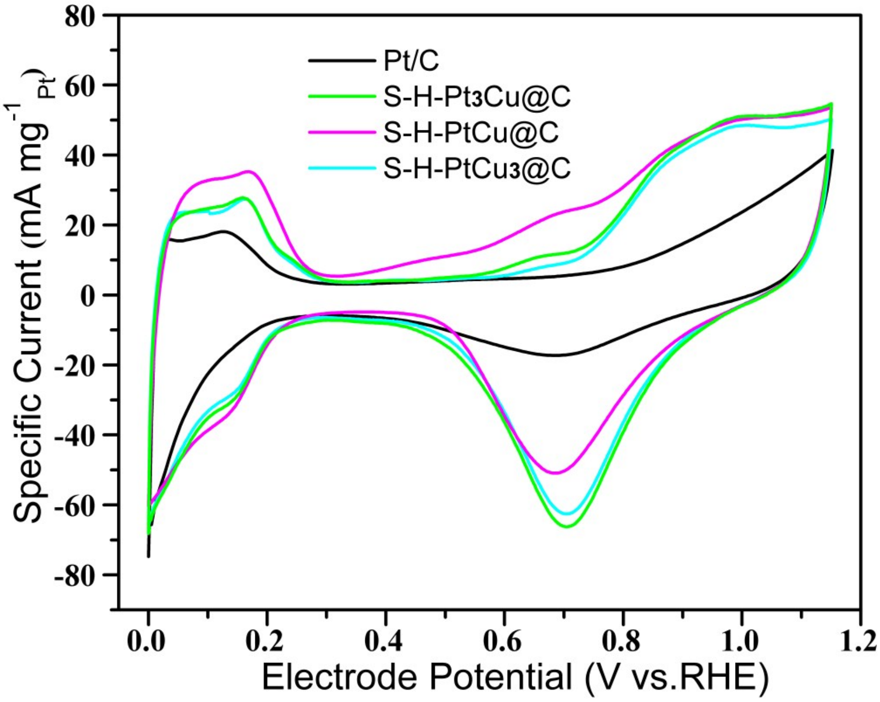

Fig. S6 CV curves of S-H-Pt_xCu_y@C and commercial Pt/C catalysts in 0.5 M H_2SO_4.

Fig. S7 Guanjun Chen et al.

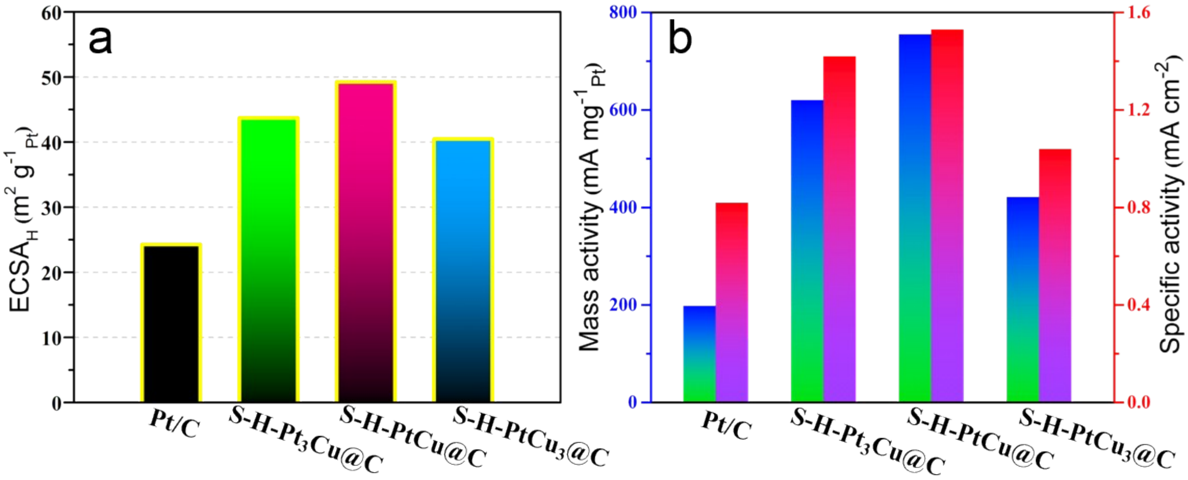

Fig. S7 (a) The electrochemically active surface area of S-H-Pt_xCu_y@C and commercial Pt/C catalysts. (b) Mass activity and Specific activity of S-H-Pt_xCu_y@C and commercial Pt/C catalysts

Fig. S8 Guanjun Chen et al.

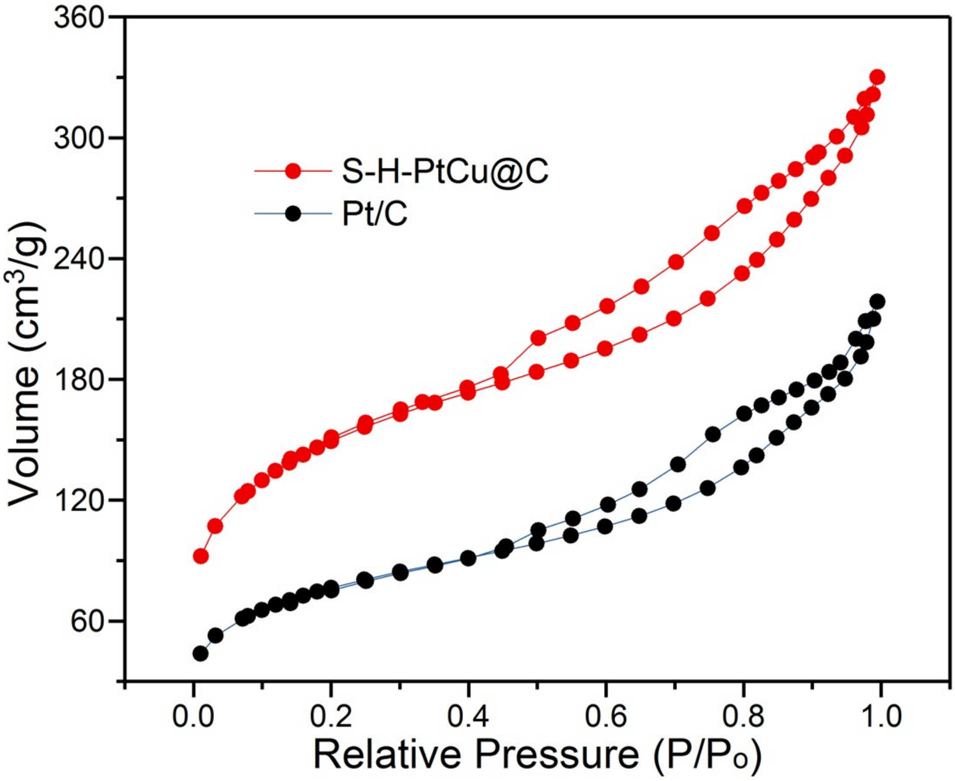

Fig. S8 Nitrogen adsorption and desorption isotherms of S-H-PtCu@C and commercial Pt/C.

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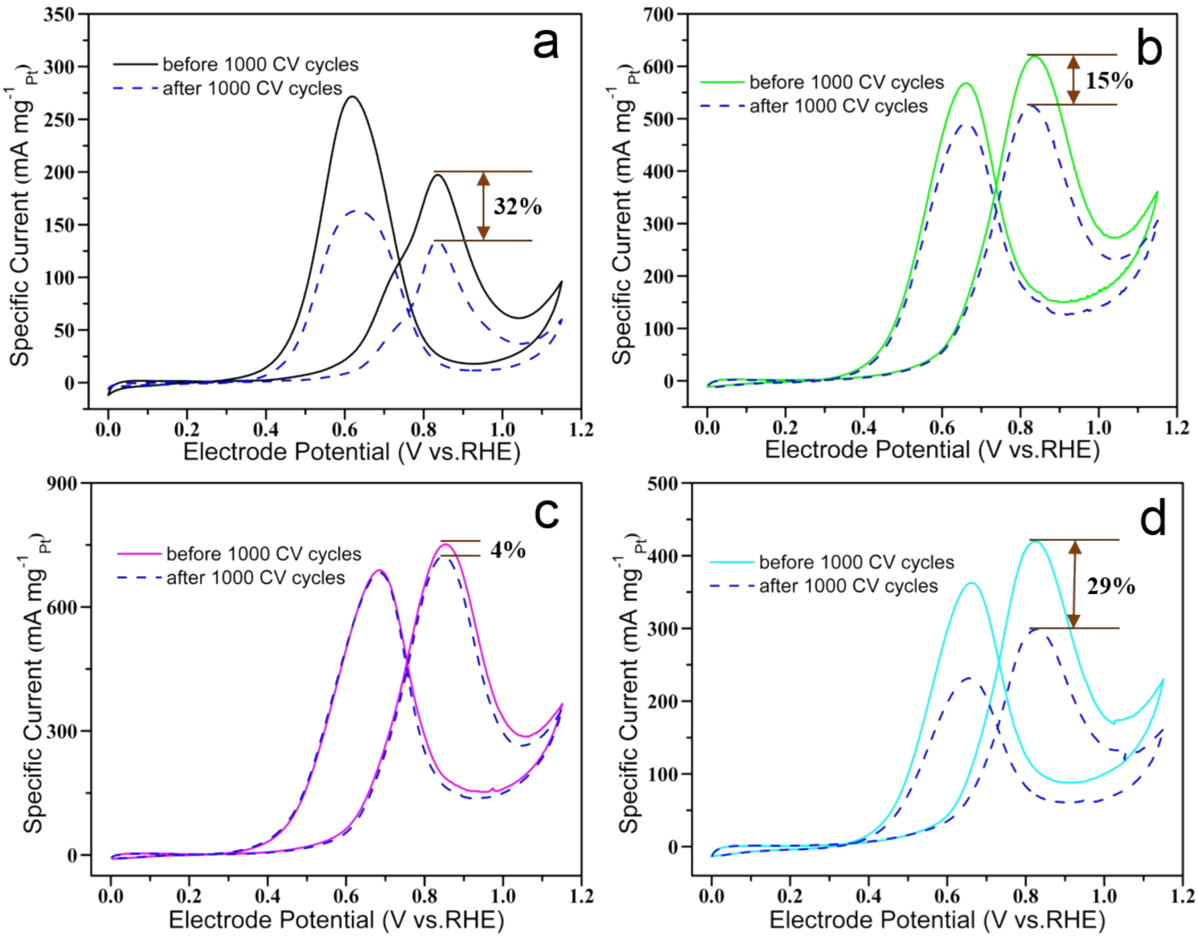

Fig. S9 (a-d) CV curves of commercial Pt/C, S-H-Pt_3Cu@C, S-H-PtCu@C and S-H-$PtCu_3$@C catalysts before and after 1000 potential cycles.

Fig. S10 Guanjun Chen et al.

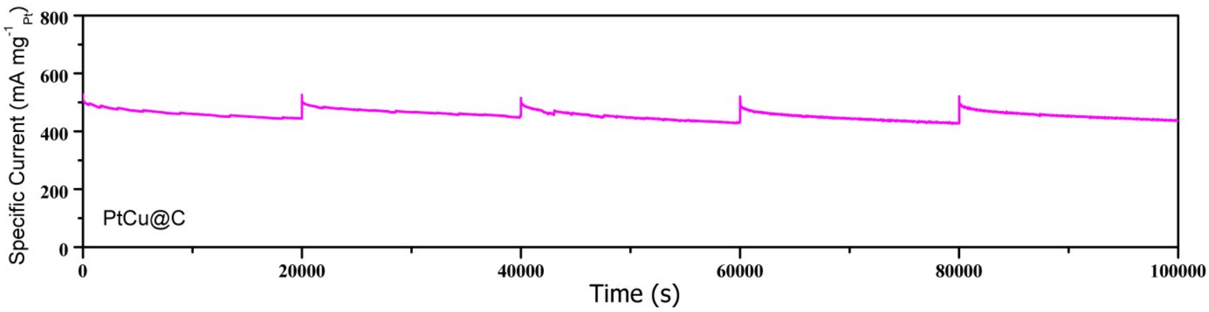

Fig. S10 Long-term durability measurements of S-H-PtCu@C catalyst, the arrows indicate when electrocatalysts were reactivated in clean 0.5 M H_2SO4.

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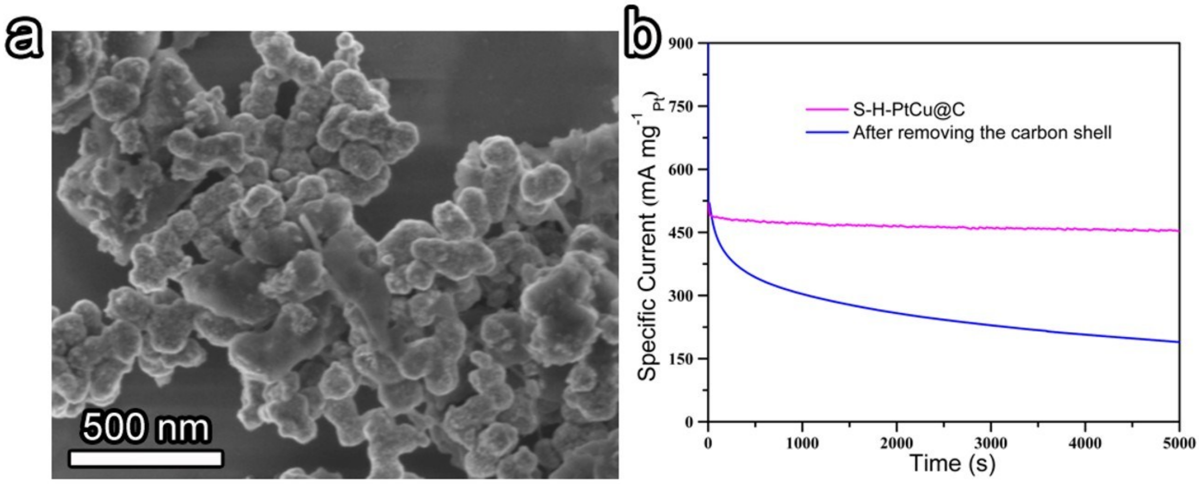

Fig. S11 (a) TEM characterization of S-H-PtCu@C after removing the carbon shell. (b) Chronoamperometric measurement result.

Fig. S12 Guanjun Chen et al.

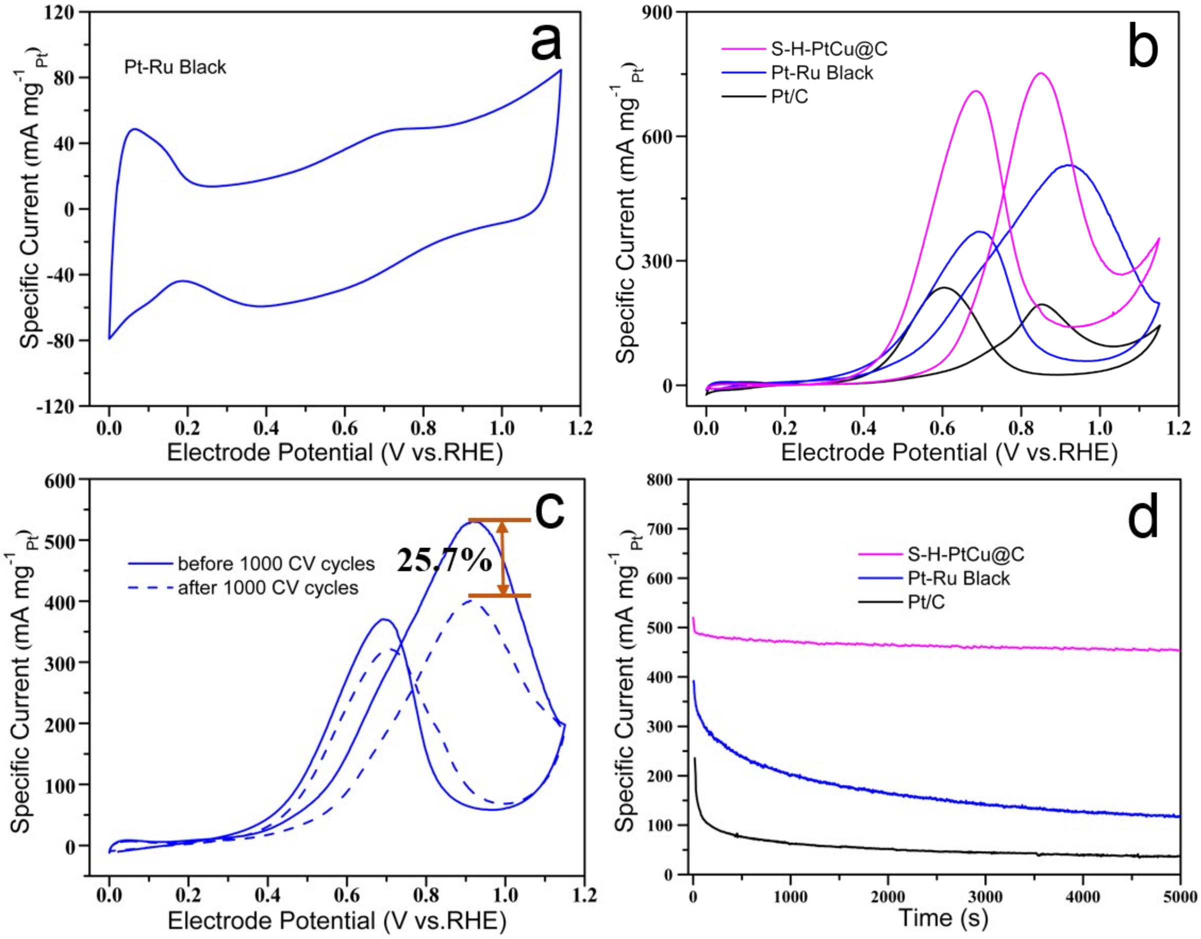

Fig. S12 (a) CV curves of S-H-PtCu@C, commercial Pt-Ru Black and commercial PtRu catalysts in 0.5 M H_2SO_4. (b) CV curves of S-H-PtCu@C, commercial Pt-Ru Black and commercial PtRu catalysts in 0.5 M H_2SO_4 + 1 M methanol. (c) CV curves of commercial Pt-Ru Black before and after 1000 potential cycles. (d) Chronoamperometric measurements.

Fig. S13 Guanjun Chen et al.

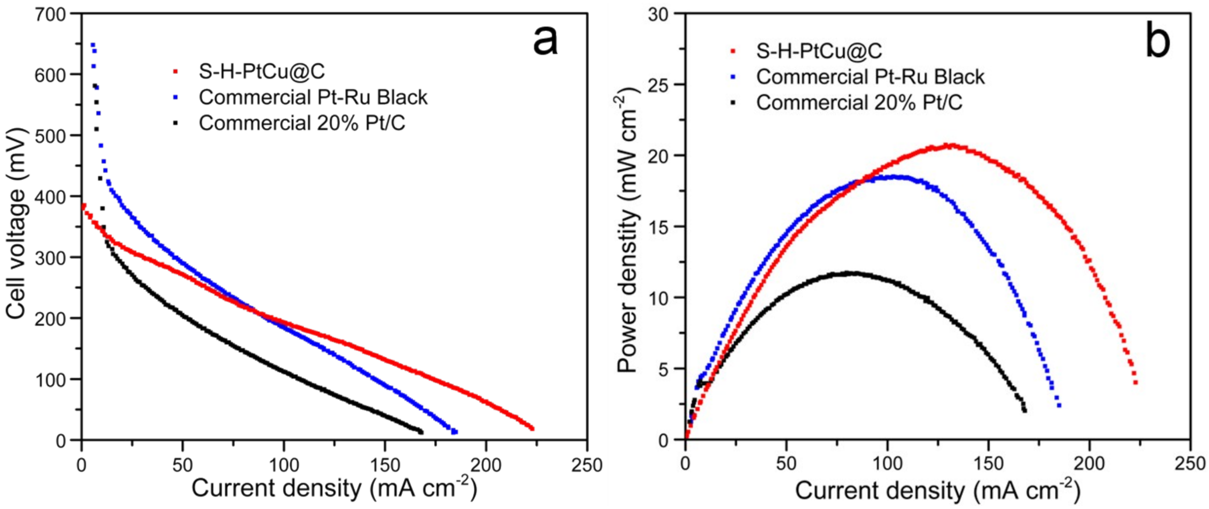

Fig. S13 (a) Polarization curves and (b) power density of S-H-PtCu@C, commercial Pt-Ru Black and commercial 20% Pt/C in DMFCs.

Fig. S14 Guanjun Chen et al.

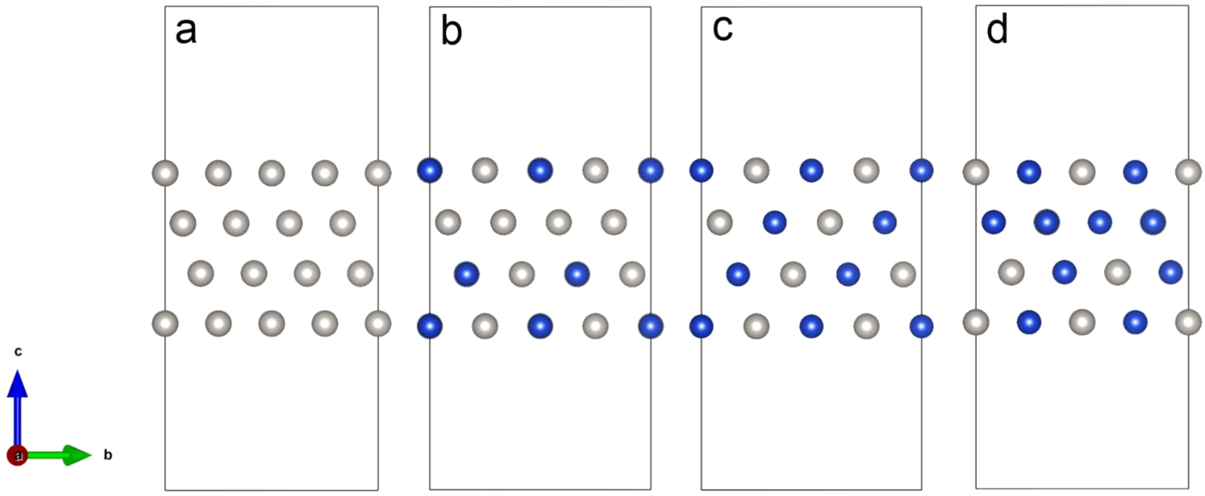

Fig. S14 (a-d) Structural models of Pt (111), Pt_3Cu (111), PtCu (111) and $PtCu_3$ (111) slabs.

Table S1 The atomic fraction of Pt and Cu in the sample.

Specimen	Pt (wt %)	Cu (wt %)	Pt : Cu (at %)
S-H-Pt_3Cu@C	76	9	73.4 : 26.6 ≈ 3 : 1
S-H-PtCu@C	57	20	48.2 : 51.8 ≈ 1 : 1
S-H-$PtCu_3$@C	36	37	24.1 : 75.9 ≈ 1 : 3

Table S2 A summary of the activity and stability of Pt-based electrocatalysts during MOR available in literature.

Electrocatalyst	Electrolyte	Mass activity (mA mg^{-1})	Specific activity (mA cm^{-2})	Scan rate (mV s^{-1})	Durability	Reference
S-H-PtCu@C	0.5 M H_2SO_4 + 1.0 M methanol	755.27	1.42	50	89 % activity retention after 5000s	**This work**
AL-Pt/Pt_3Ga	0.5 M H_2SO_4 + 1.0 M methanol	--	7.195	50	25 % activity retention after 1000s	*J. Am. Chem. Soc.* **2018**, *140*, 2773
$Pt_{69}Ni_{16}Rh_{15}$ NWs	0.1 M HClO4 + 0.5 M methanol	--	2.49	50	30 % activity retention after 5000s	*Adv. Mater.* **2019**, *31*, 1805833
Pt-8-92	0.5 M H_2SO_4 + 0.5 M methanol	405	1.29	100	30 % activity retention after 3000s	*Angew. Chem. Int. Ed.* **2016**, *55*, 1
octahedral Pt-Ag NCs	0.1 M $HClO_4$ + 0.5 M methanol	608.3	3.66	50	45 % activity retention after 2000s	*Nano Energy* **2019**, *61*, 397
PtBi nanoplates /C	0.1 M $HClO_4$ + 0.1 M methanol	1100	3.18	50	12 % activity retention after 4000s	*ACS Catal.* **2018**, *8*, 5581
Pt_3CoRu/C@NC	0.1 M $HClO_4$ + 0.5 M methanol	970	1.6	50	40 % activity retention after 6000s	*J. Mater. Chem. A* **2019**, *7*, 18143
Pt/e-RGO-SWCNT	0.5 M H_2SO_4 + 1.0 M methanol	190	1.45	50	15 % activity retention after 4000s	*Appl. Catal. B- Environ.* **2019**, *257*, 3117886
Pt-Fe_2P	0.5 M H_2SO_4 + 1.0 M methanol	1039	1.29	20	28 % activity retention after 3500s	*ACS Appl. Mater. Interfaces* **2019**, *11*, 9496
PtNiPb NPs	0.1 M $HClO_4$ + 0.5 M methanol	--	2.4	50	30 % activity retention after 5000s	*Nanoscale* **2019**, *11*, 16945

Table S3 A summary of the activity and stability of PtCu-alloy electrocatalysts during MOR available in literature.

Electrocatalyst	Electrolyte	Mass activity ($mA\ mg^{-1}$)	Specific activity ($mA\ cm^{-2}$)	Scan rate ($mV\ s^{-1}$)	Durability	Reference
S-H-PtCu@C	0.5 M H_2SO_4 + 1.0 M methanol	755.27	1.42	50	89 % activity retention after 10000s; 86 % activity retention after 20000s	**This work**
$PtCu_3$ cubic nanocages	0.1 M $HClO_4$ + 1.0 M methanol	--	14.1	20	20 % activity retention after 1000s	*J. Am. Chem. Soc.* **2012**, *134*, 13934
Au@PtCu/C	0.1 M $HClO_4$ + 0.5 M methanol	927	1.41	50	30 % activity retention after 800s	*Appl. Catal. B- Environ.* **2015**, *174-175*, 361
$Pt_{50}Cu_{50}$/G	1.0 M H_2SO_4 + 2.0 M methanol	--	55.2	50	50 % activity retention after 2000s	*J. Mater. Chem. A* **2015**, *3*, 15882
$Pt_{45}Cu_{35}Co_{20}$	0.1 M H_2SO_4 + 0.5 M methanol	--	18.24	50	20 % activity retention after 3600s	*ACS Appl. Mater. Interfaces* **2019**, *11*, 32282
PtCu nanostars	0.5 M H_2SO_4 + 1.0 M methanol	574	3.45	50	20 % activity retention after 2000s	*Nano Res.* **2019**, *12*, 1147
$Pt_{34.5}Cu_{65.5}$ octahedra	0.1 M H_2SO_4 + 0.5 M methanol	420	4.12	50	25 % activity retention after 3000s	*Nanoscale* **2018**, *10*, 4670
Cu@PtCu(Gly)	0.5 M H_2SO_4 + 1.0 M methanol	1568	3.56	100	15 % activity retention after 5000s	*Chem. Commun.* **2017**, *53*, 7457
$Pt_{84}Cu_{16}$	0.5 M H_2SO_4 + 0.5 M methanol	314	1.39	50	12 % activity retention after 4000s	*Chem. Eur. J.* **2019**, *25*, 343

Table S4 The DFT calculated formation energies (ΔH_{alloy}) of fcc Pt, $PtCu_3$, PtCu and Pt_3Cu, d band center (ε_d) and Bader charge of surface Pt atoms for Pt, $PtCu_3$, PtCu and Pt_3Cu alloy slabs.

	ΔH_{alloy} (eV)	Bader charge (e) [a]	ε_d (eV) [a]	$\Delta\varepsilon_d$ (eV)
Pt	--	--	-1.70	--
Pt_3Cu	-2.36	0.19	-1.96	-0.26
PtCu	-1.87	0.37	-2.17	-0.47
$PtCu_3$	-1.53	0.60	-1.80	-0.10

[a] The selected Pt atom will host CO after CO adsorption

$\Delta\varepsilon_d$ (eV) represents difference of the d-band center