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Supporting Information

The heat-promoted metal-support interaction of PtCu/SiO_2 carbon-free catalyst for methanol oxidation and oxygen reduction reactions

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1. Chemicals

Ethanol, ammonium hydroxide (28 wt.%), ethylsilicate, Chloroplatinic acid hexahydrate [$H_2PtCl_6 \cdot 6H_2O$)], copper nitrate hydrate [$Cu(NO_3)_3 \cdot 3H_2O$] and ethylene glycol (EG) were of analytical reagent (A.R.) grade and purchased from Sinopharm Chemical Reagent Co., Ltd. Commercial 20 wt.% Pt/C was self-made in lab. All chemicals were used as received. Deionized water (DI water, Millipore, 18.2 MΩ at 25 ºC) was used in all processes.

2. Characterizations

The morphology was observed by scanning electron microscope (SEM，SUPRA 55,Carl Zeiss), and the structure was identified by transmission electron microscope(TEM, Titan G2 60-300 with image corrector).The X-ray diffraction (XRD, Ultima III, Rigaku) was performed to identify the crystal structure. FTIR was tested using */AVATAR360. X-ray photoelectron spectroscopy (XPS) was carried out on ESCALAB 250 (Thermo Scientific) to probe the surface chemical information of catalysts.

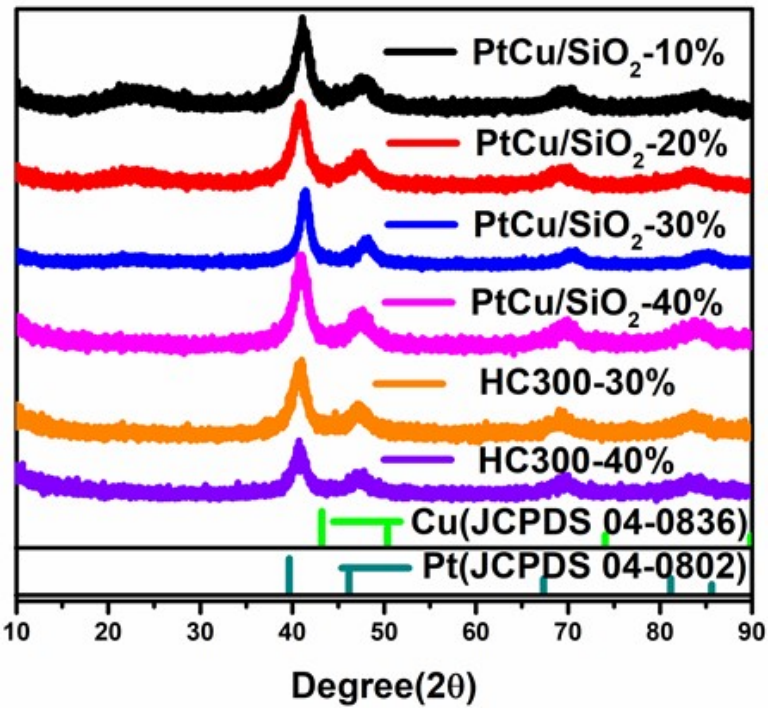

Figure S1. XRD pattern of $PtCu/SiO_2$ with 10, 20, 30, 40 wt.% Pt loading ($PtCu/SiO_2$-10%, $PtCu/SiO_2$-20%, $PtCu/SiO_2$-30% and $PtCu/SiO_2$-40%), HC300-30% and HC300-40% represent the catalysts $PtCu/SiO_2$-30% and $PtCu/SiO_2$-40% calcined at 300 ℃.

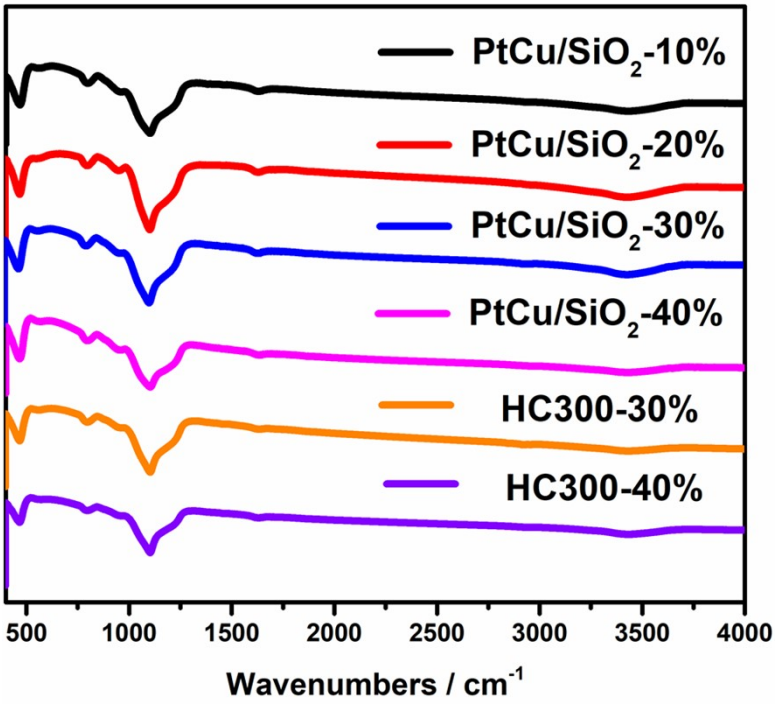

Figure S2. FTIR spectra of $PtCu/SiO_2$ with different Pt loading ($PtCu/SiO_2$-10%, $PtCu/SiO_2$-20%, $PtCu/SiO_2$-30% and $PtCu/SiO_2$-40%), HC300-30%, and HC300-40%.

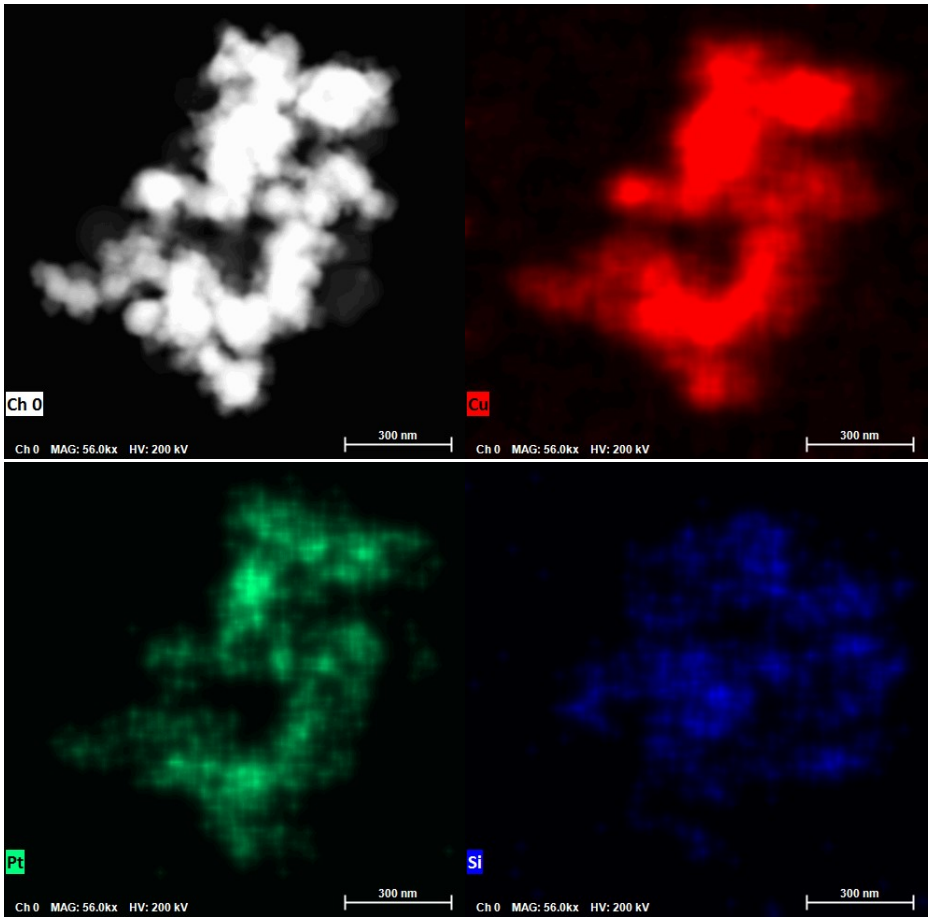

Figure S3 The elemental mapping of HC300-40%.

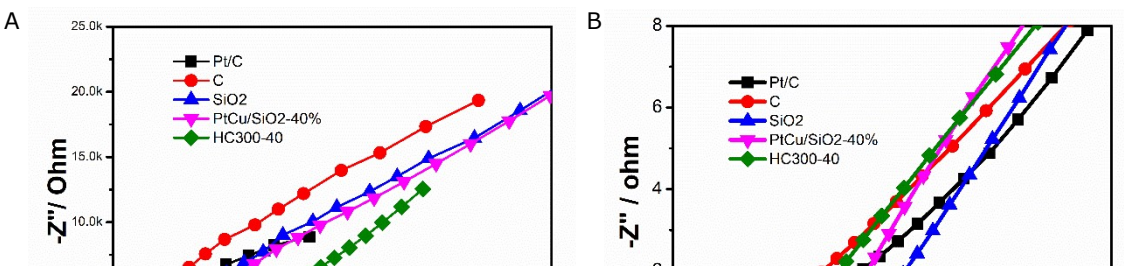

Figure S4 A, the Nyquist plots of carbon (XC-72), SiO_2 nanospheres, PtCu/SiO_2-40%, and HC300-40%; B, the plots from 4~7 Ohm of horizontal coordinate.

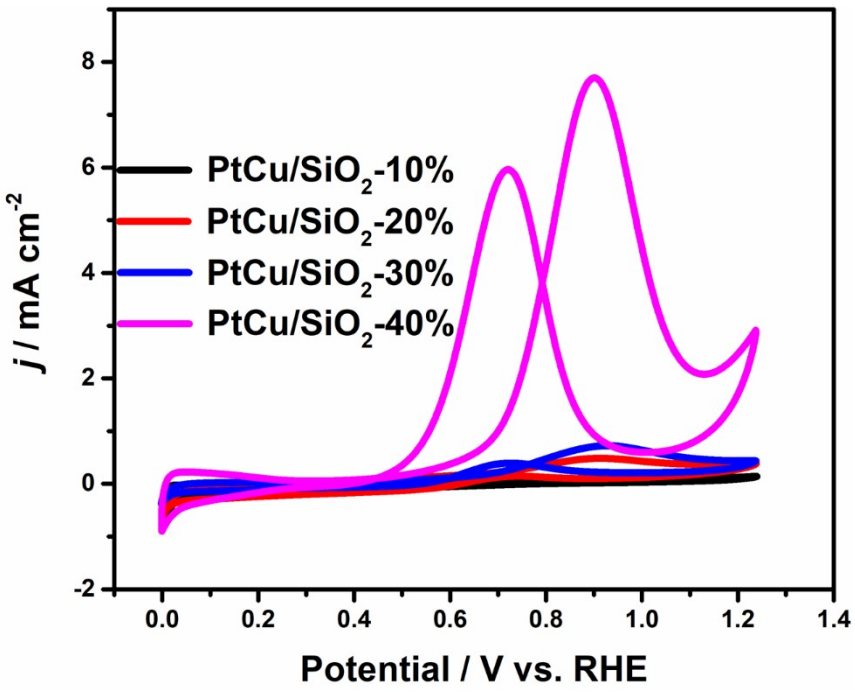

Figure S5. MOR activities of $PtCu/SiO_2$-10%, $PtCu/SiO_2$-20%, $PtCu/SiO_2$-30%, and $PtCu/SiO_2$-40%.

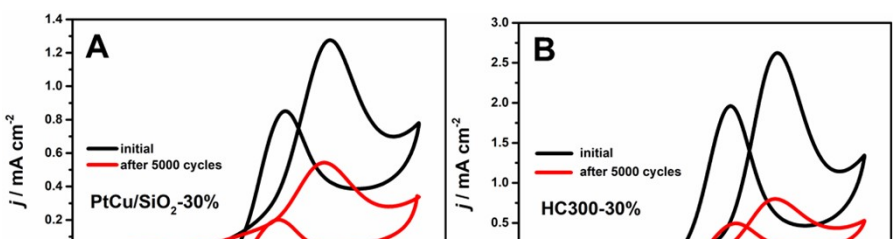

Figure S6. MOR durability of PtCu/SiO_2-30% (A), HC300-30% (B), PtCu/SiO_2-40% (C), HC300-40% (D), and Pt/C (E).

Table S1 The composition detected by ICP-AES

Sample	SiO_2 (wt %)	Pt (wt %)	Cu (wt %)	Pt:Cu (at %)
PtCu/SiO_2-10%	88.1	8.1	3.7	0.72
PtCu/SiO_2-20%	60	32	7.9	1.33
PtCu/SiO_2-30%	45.2	38.9	15.8	0.81
PtCu/SiO_2-40%	29	58	13	1.46
HC300-30%	37.3	50	12	1.36
HC300-40%	43	46.6	10.4	1.47

Table S2 The binding energy of all catalysts detected by XPS

Sample	Si 2p (eV)	Cu $2p_{3/2}$ (eV)	Cu $2p_{1/2}$ (eV)	Pt $4f_{7/2}$ (eV)	Pt $4f_{5/2}$ (eV)
$PtCu/SiO_2$-30%	103.68	932.08	951.68	71.28	74.48
HC300-30%	103.48	932.28	951.78	71.58	74.78
$PtCu/SiO_2$-40%	103.68	931.88	951.68	71.38	74.58
HC300-40%	103.48	932.48	952.18	71.68	74.88

Sample	ECSA (m^2/g_{pt})	MA (A mg_{Pt}^{-1})	SA (mA cm^{-2})	I_f:I_b
$PtCu/SiO_2$-30%	1.84	0.032	1.785	1.49
HC300-30%	1.83	0.051	2.79	1.34
$PtCu/SiO_2$-40%	3.53	0.13	3.66	1.30
HC300-40%	4.38	0.28	6.35	1.27
Pt/C	30.8	0.29	0.945	0.93

Table S3 The MOR test results of all catalysts