Enhanced CO₂ reduction with hydrophobic cationic-ionomer layer modified zero-gap MEA in acidic electrolyte

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1. Chemicals and materials

Commercial Ag powders (99%, 60-120 nm) and PTFE powders (average diameter of about 200 nm) were purchased from Macklin and used without further treatments. SiO_2 microsphere (about 300 nm) was synthesized under the Stöber process (J. Phys. Chem. C 2007, 111, 30, 11223–11230). The Nafion 115 membrane (DuPont), Nafion solution (DuPont, 5 wt%) and carbon paper (SGL 36BB) were obtained from Suzhou Sinro Technology CO., Ltd. The quaternary ammonia poly(N-methyl-piperidine-co-p-terphenyl) (QAPPT, 5 wt%) was purchased from Yiwei New Energy Research Institute, the structural formula and some properties are shown in Table S1). Commercial iridium-tantalum/titanium (IrO_2-TaO_5/Ti, 100 mesh) was obtained from Utron Technology. K_2SO_4 (AR) and H_2SO_4 (98%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Ultrapure water (18.2 MΩ) was used to prepare aqueous solutions.

2. Experimental sections

2.1 Preparation of electrodes

To fabricate the bare Ag electrode, 10 mg Ag powder was dispersed into the mixture of 0.5 mL isopropanol and 0.5 mL water and subjected to vigorous ultrasonic till obtaining a homogeneous catalyst ink. 0.18 mL catalyst ink was spray-coated onto the carbon paper (1.5 × 1.5 cm) on a heating plate (80°C).

To prepare the modified electrodes, typically, 10 mg PTFE powders or SiO_2 microsphere were dispersed in the mixture of 0.5 mL water, 0.45 mL isopropanol and 0.05 mL ionomer solution. Following ultrasonic treatment, 0.18 mL of obtained homogeneous ink was spray-coated onto the above bare Ag electrode (1.5 × 1.5 cm) on the heating plate at 80°C (In order to minimize the error of catalyst loading caused by the preparation process of different batches, a 6 × 6 cm carbon paper was spay coated with Ag catalyst at once, and then cut into 16 pieces). The sample coated with PTFE and QAPPT was marked as PTFE-Q, the sample coated with PTFE and Nafion was marked as PTFE-N, and the sample coated with SiO_2 and QAPPT was marked as SiO_2-Q. The Mix electrode was fabricated by spray-coat 0.18 mL mix ink of 10 mg Ag powder, 10 mg PTFE powder, 0.05 mL QAPPT solution, 0.5 mL water and 0.45 mL isopropanol under the same method.

To investigate the influence of hydrophobicity for the modification layer on the electrocatalysis performance, the factors of hydrophilia, layer thickness, conductivity and particle size were considered as the main index for choosing the solid framework. As a result, the non-conducting and hydrophilic SiO_2 microspheres were employed

to build the adlayer replacing the hydrophobic PTFE, as the diameter of SiO_2 used in this experiment is about 250 nm and the material density is about 2.3 g cm^{-3}, which is comparable to that of the PTFE nanoparticles (diameter about 220 nm, 2.1 -2.3 g cm^{-3}). Recent studies have shown that the doped Si atom could affect the electronic structure and the stability of nanoparticles, and the hydroxyl group on the surface of the electrode or the substrate of loaded catalyst could affect the micro-environment of the catalyst surface to influence the electrocatalysis performance. [1,2] However, the layer-by-layer coating program at < 100°C did not involve element doping and led the catalysts to less contact with the modifications for the GDE, in contrast to the electrode constructed with the mixture ink of catalyst and the modifications. Therefore, it was considered that SiO_2 mainly affects the hydrophilicity of the modification layer, and the other influencing factors may not be the main cause of the differences for the electrodes in ECR performance.

1. W. Guo, X. Tan, S. Jia, S. Liu, X. Song, X. Ma, L. Wu, L. Zheng, X. Sun and B. Han, *CCS Chemistry*, 2023, 1-9. DOI: 10.31635/ccschem.023.202303138.

2. S. G. Ji, H. C. Kwon, T.-H. Kim, U. Sim and C. H. Choi, *ACS Catalysis*, 2022, **12**, 7317-7325.

2.2 Characterizations

The morphologies of the powders and electrodes were characterized by a field emission scanning electron microscope (SEM, Phenom Phaors G2). The X-ray diffraction (XRD) measurements were operated with a Miniflex 600 system (Rigaku, Japan), using Cu Kα radiation, and the sweep velocity is 8° min^{-1}. The static contact angle of electrodes was measured with a JY-82C contact angle meter (Chengde Dingsheng testing machine testing equipment Co., LTD, China).

2.3 Electrochemical measurements

An Auto-lab M204 electrochemical workstation with a 10 A booster (Metrohm) was used for the electrochemical measurements. All the electrochemical experiments were carried out in a zero-gap membrane electrode assembly (MEA) electrolyzer (1 cm^2, Titanium material, from Gaoss Union company, China). IrO_2-Ta_2O_5/Ti mesh (1 × 1 cm) was employed as the anode. The cathode and anode were placed inside the MEA chamber and tightly pressed with a piece of Nafion 115 membrane as the separator. Humidified CO_2 (99.999%) was fed to the cathodic chamber at 20 sccm. Except for obvious labels, 0.1 M K_2SO_4 and 0.1 mM H_2SO_4 were used as the single-pass anolyte with a flow rate of 2 mL min^{-1}. The gas inflow was controlled by a digital mass flow controller (Horiba), and the out-flow rate of gas was measured by a digital soap-membrane flowmeter (YT-100ML, Yuntang Technology,

China). The gas from the cathodic outlet first flowed through a cold hydrazine and then into a $CaCl_2$ dryer, and was finally analyzed with online gas chromatography (GC, Fuli 9790Plus). For the electrochemical impedance spectroscopy (EIS) measurements, the electrodes were placed in the MEA reactor and tested at the open circuit potential, 20 sccm humid CO_2 and 2 mL min^{-1} anolyte (0.1 M K_2SO_4 and 0.1 mM H_2SO_4) were fed to the cathodic chamber and anodic chamber, respectively.

2.4 Analysis

The voltage reported in this work was recorded without iR correction. The EIS results were fitted by the software of Zview 3.1.

The Faradic efficiency was calculated as follows:

$$FE(\%) = \frac{c \times v \times n \times F \times p}{R \times T \times j} \times 100\%$$

Where c is the volume fraction of detected gas product from GC, v is the out-flow rate of gas, n is the number of electron transfers for certain gas products, F is Faradic constant, p is the standard atmosphere pressure (101.325 kPa), R is the gas constant, T is 298.15 K, j is the applied current.

For the K^+ measurements, the liquid outcome from the cathodic chamber was collected by a cold trap during the electrolysis, and the chamber was washed sufficiently with ultrapure water after the ECR reaction. All the collected liquid was moved to a 100 mL volumetric flask and determined with ion chromatography (ECO, Metrohm).
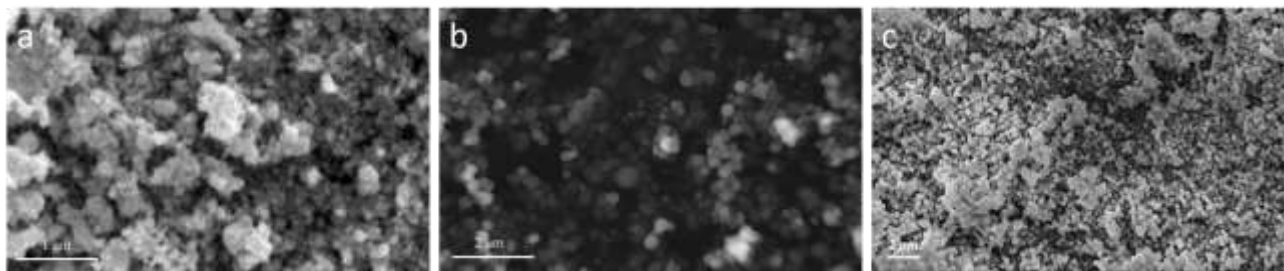
Fig. S1 SEM image of (a) commercial Ag powder, (b) commercial PTFE powder, and (c) SiO$_2$ microsphere.
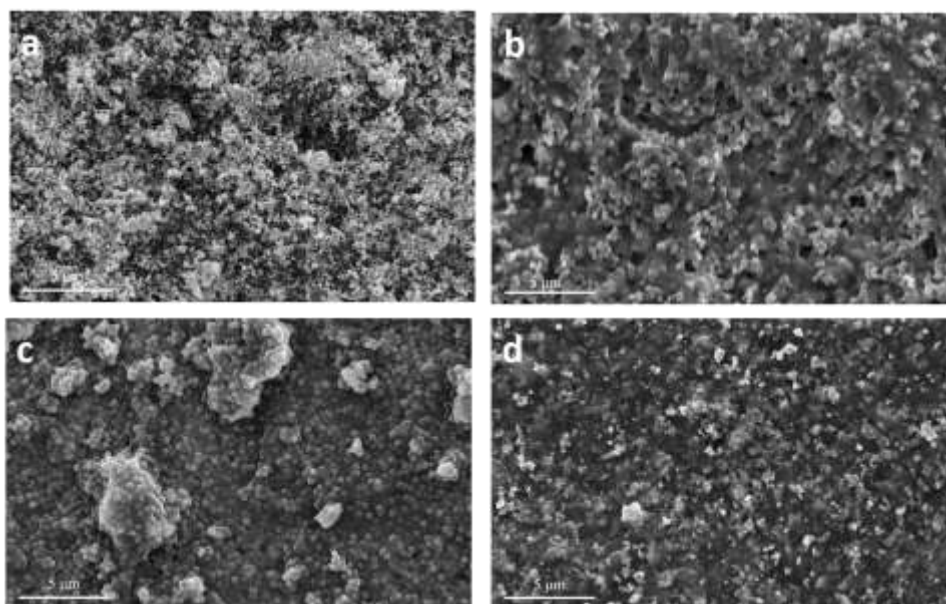

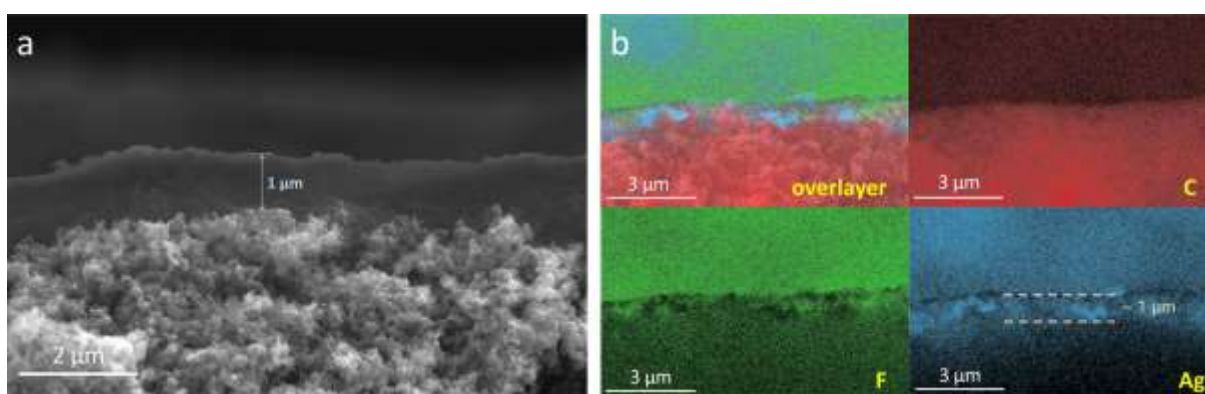**Fig. S2** SEM images of (a) Bare Ag, (b) PTFE-Q, (c) SiO$_2$-Q, and (d) Mix electrode.

Fig. S3 (a) Side view of PTFE-Q electrode, (b) elements mapping of Bare Ag electrode.
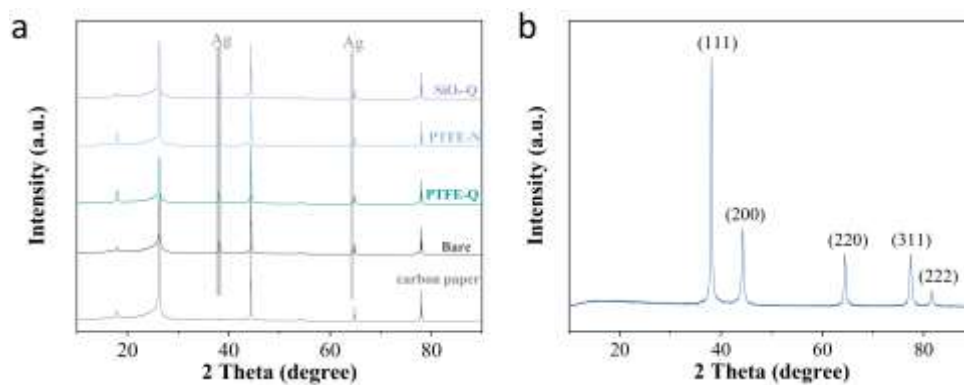
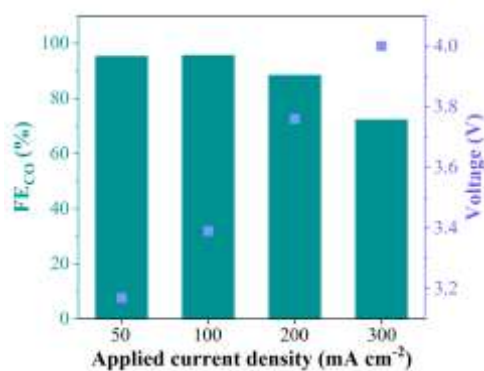**Fig. S4** XRD patterns of (a) the prepared GDEs, and (b) commercial Ag powders.

Fig. S5 FE_{CO} and the full-cell voltage of ECR on PTFE-Q with different applied current densities in 0.1 M K_2SO_4.
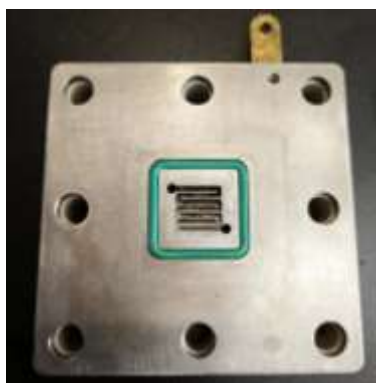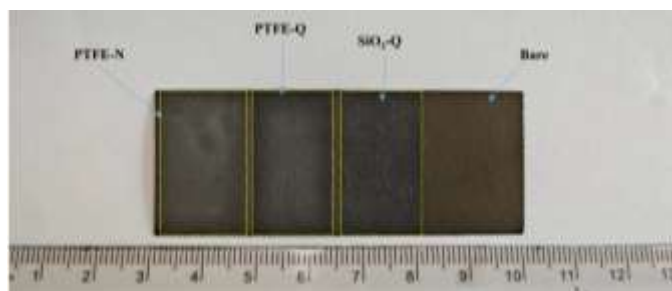

Fig. S6 Image of cathodic chamber.

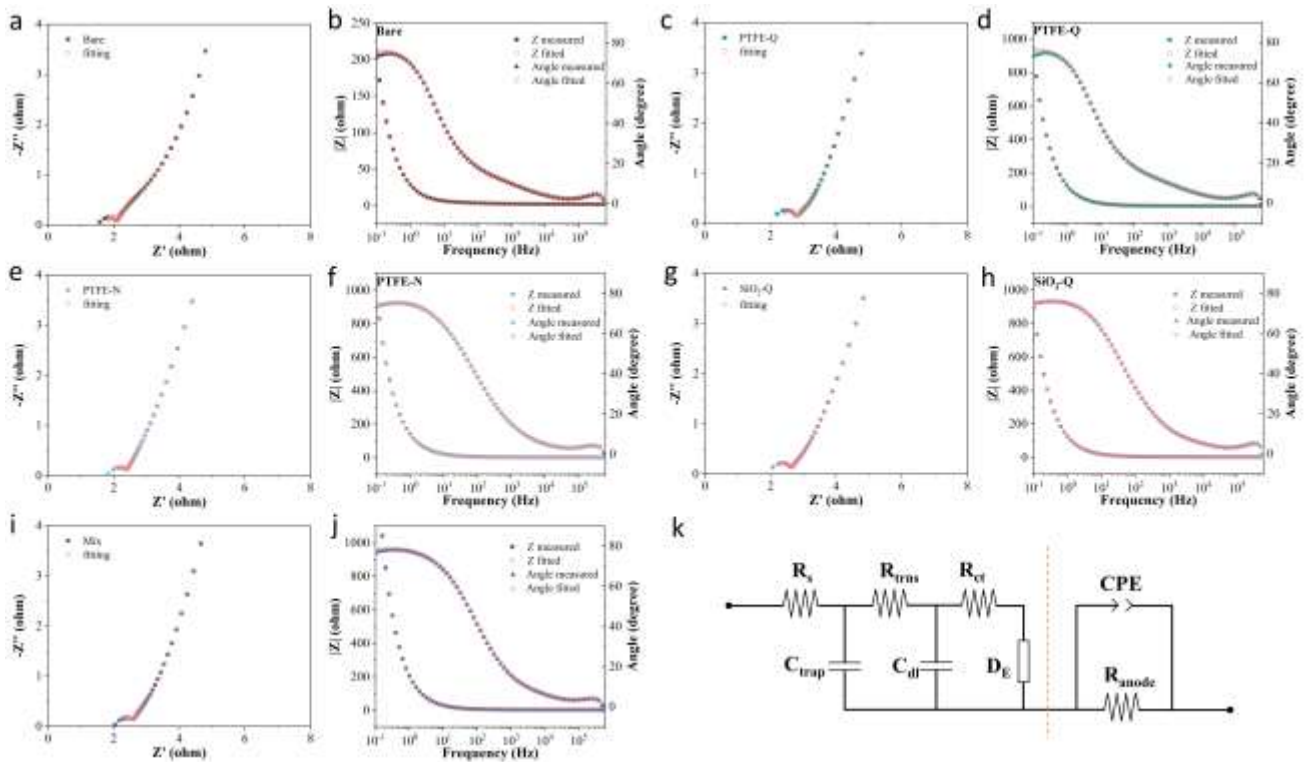**Fig. S7** Image of the prepared GDEs.

Fig. S8 Fitting of the EIS patterns. Fitting on the Nyquist and Bode plots for (a, b) the Bare electrode, (c, d) PTFE-Q electrode, (e, f) PTFE-N electrode, (g, h) SiO$_2$-Q electrode, (i, j) the Mix electrode. (k) the proposed circuit model for the fabricated MEA, where R_s represents the internal resistance of cathodic Ti and carbon fiber, R_{trns} and C_{trap} represent electron transport resistance in the micro-porous carbon layer, R_{ct} and C_{dl} represent charge transfer resistance and double layer capacitance at the catalysts and ionomer interface, DE represents the diffusion impedance, R_{anode} and *CPE* represent the internal resistance and constant phase angle element of the anode.
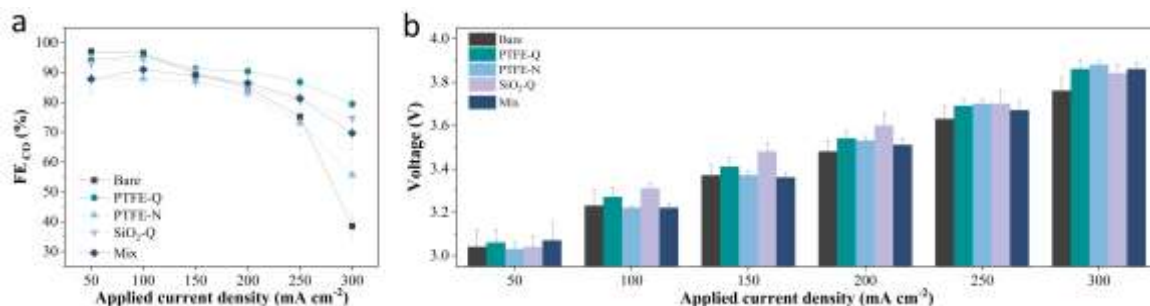

Fig. S9 (a) FE$_{CO}$ and (b) the cell voltage of different electrodes (anolyte: 0.1 mol L^{-1} K$_2$SO$_4$ and 0.1 mmol L^{-1} H$_2$SO$_4$).

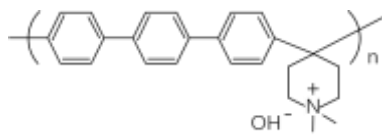**Table S1.** The structural formula and basic properties of QAPPT (Energy Environmental Science 2019, 12, 2455)

QAPPT	

Ion exchange capacity (mmol g^{-1})	2.65
Swelling degree (%) @ 60°C	9.0
Water uptake (%) @ 60°C	55
σ (mS/cm) @60°C	98

Table S2. Fitting parameters of the proposed circuit model for the EIS patterns.

	Bare	PTFE-Q	PTFE-N	SiO$_2$-Q	Mix
R_{anode}	3.112	40.48	12.95	9.136	58.27
CPE1-T	0.0131	0.016746	0.01336	0.016153	0.015129
CPE1-P	0.64686	0.50316	0.51151	0.4886	0.47976
R_s	1.799	2.309	2.05	2.195	2.264
R_{ct}	0.22747	0.18199	0.39769	0.16315	0.22745
DE2	2-CPE #1				
DE2-R	0.6539	0.000261	3.7923E-8	2.0122E-6	4.014E-7
DE2-T	0.0040877	0.00053234	0.00083858	0.0010028	0.00041119
DE2-P	0.76309	0.62994	0.71786	0.75531	0.72757
DE2-U	0.003173	0.00099647	0.00017498	0.00049966	0.0004008
C_{dl}	0.00012298	0.00014443	0.00050087	0.00020284	0.00019088
R_{trns}	0.26459	0.44017	0.26094	0.36147	0.236
C_{trap}	2.5701E-6	1.1676E-6	2.5507E-6	1.206E-6	2.8476E-6
Chi-Squared	0.0011952	0.00043604	0.00033005	0.0001844	0.0002926
Sum of Sqr	0.1482	0.055377	0.040266	0.022128	0.035698