

## **Supporting Information**

### **Alkaline Polymer Electrolyte CO<sub>2</sub> Electrolyzer Operated with Pure Water**

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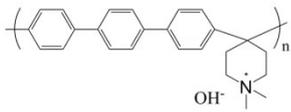
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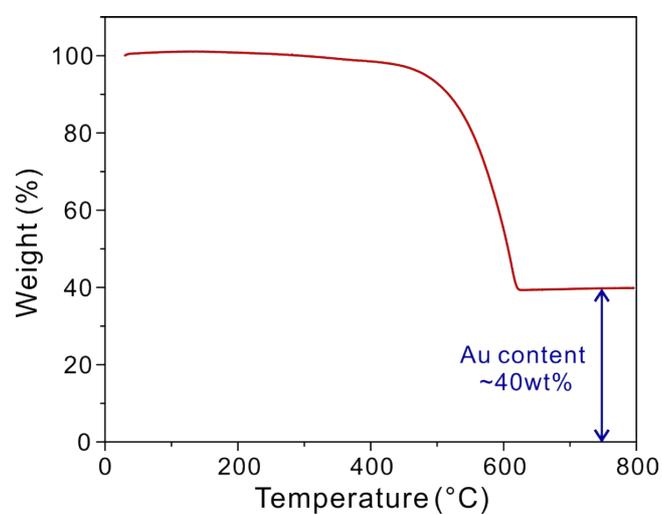
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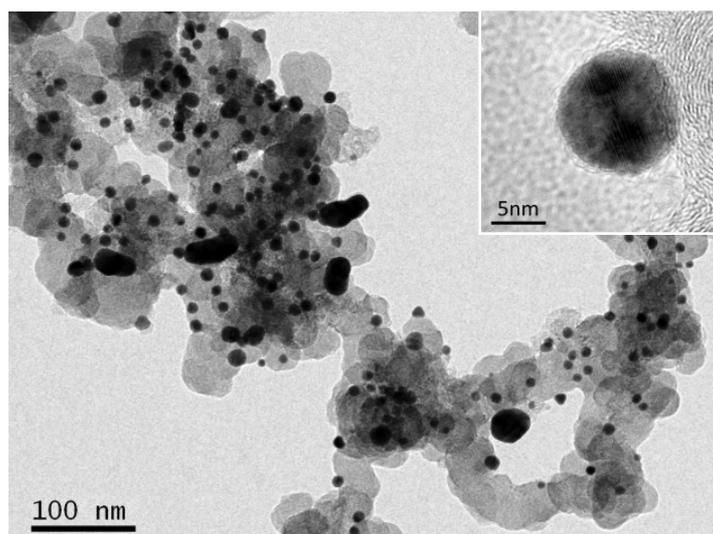
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**Table S1** Properties of the APE applied in this work.

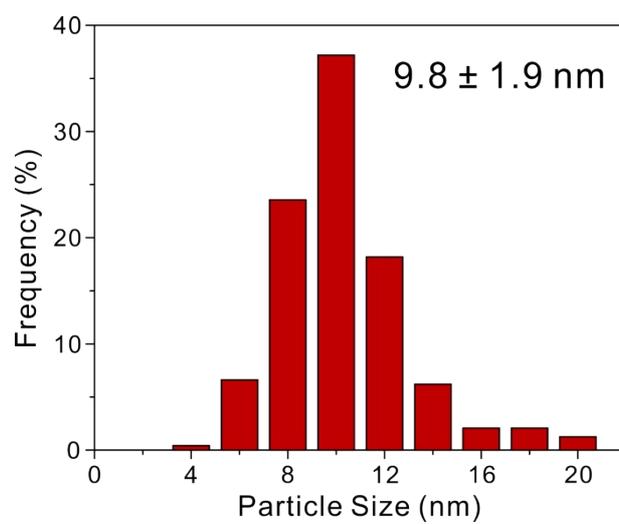
QAPPT	
IEC (mmol/g)	2.65
Swelling degree (%) @ 60°C	9.0
Water uptake (%) @ 60°C	55
$\sigma$ (mS/cm) @ 60°C	98



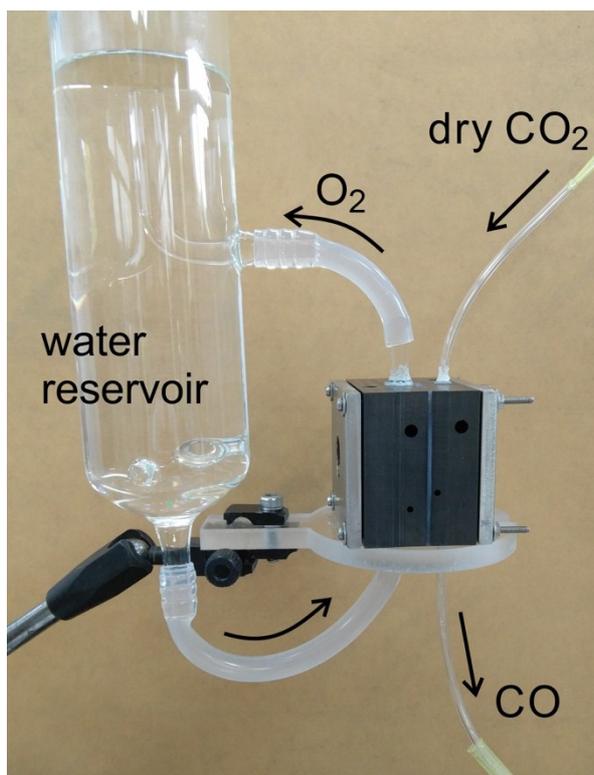
**Fig. S1** Thermogravimetric analysis for as-synthesized Au/C catalyst under air atmosphere, with temperature ramping at 10°C/min.



**Fig. S2** TEM image of the homemade Au/C catalyst. The inset shows a high-resolution view of a single Au nanoparticle.



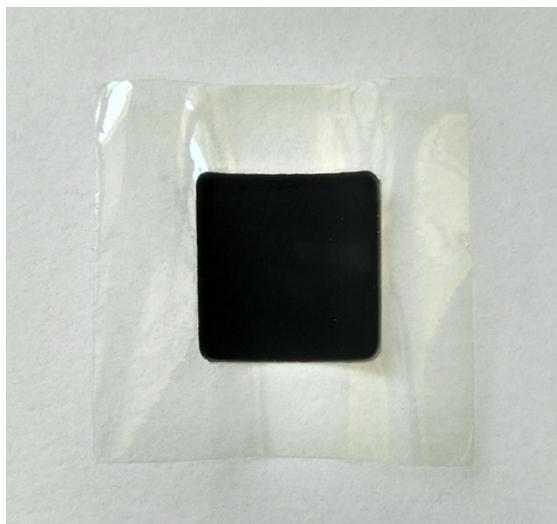
**Fig. S3** TEM histogram for the size distribution of Au NPs.



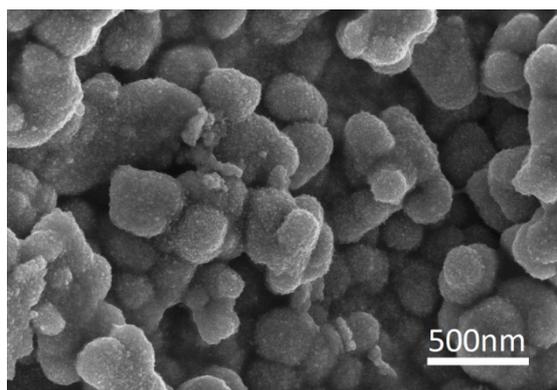
**Fig. S4** Photo of the lab device for APE CO<sub>2</sub> electrolysis.



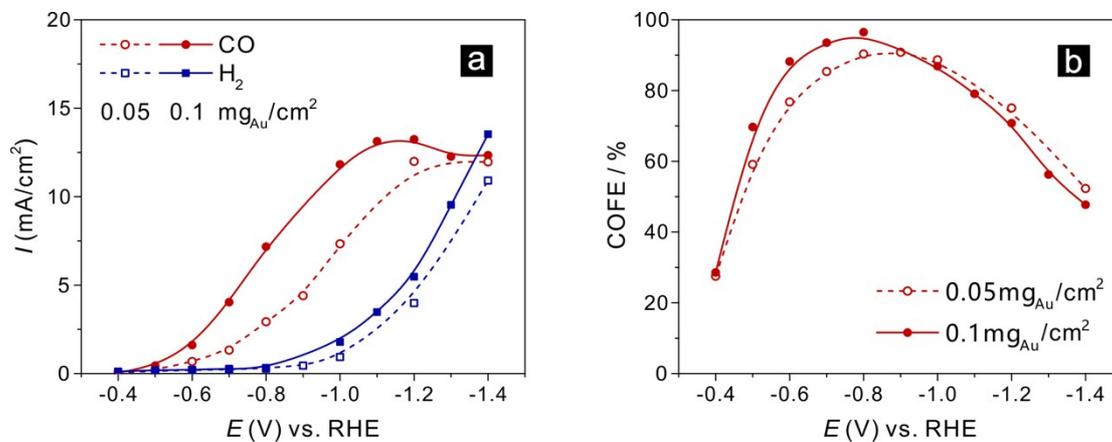
**Fig. S5** Photo of the porous Ti sheet, used as the anode GDL in this work.



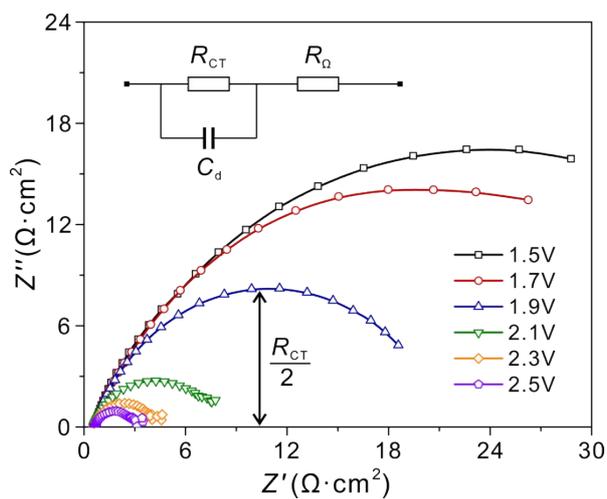
**Fig. S6** Photo of the Au/C catalyst layer on QAPPT membrane.



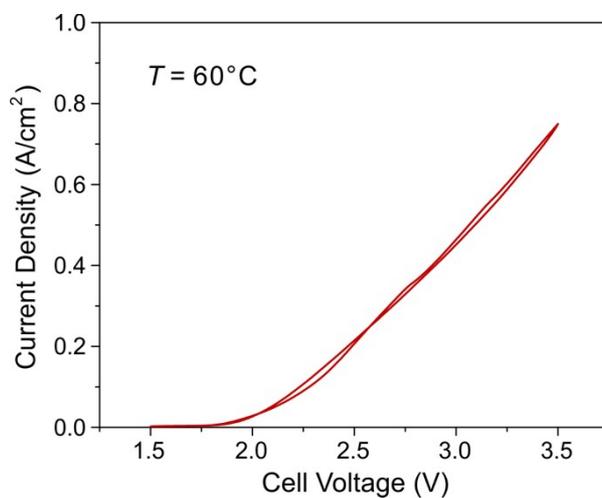
**Fig. S7** SEM image of the ionomer-impregnated IrO<sub>2</sub> catalyst layer on anode GDL.



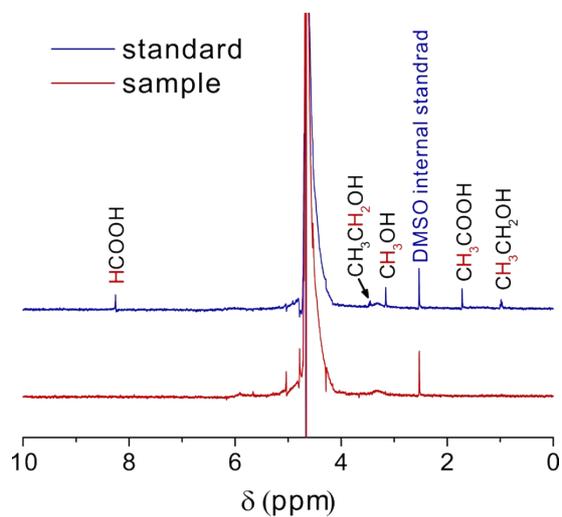
**Fig. S8** Regular CO<sub>2</sub>RR tests in 0.1 M KHCO<sub>3</sub> solution with different catalyst loadings. (a) Partial current densities of H<sub>2</sub> and CO. (b) The changes in COFE. The geometric area was 0.8 cm<sup>2</sup> and CO<sub>2</sub> flow rate was set to 5 sccm.



**Fig. S9** AC impedance spectra of the CO<sub>2</sub> electrolyzer at 60°C, indicating that the charge-transfer resistance ( $R_{CT}$ ) reduces quickly upon increasing the cell voltage.



**Fig. S10** Cyclic voltammogram of the CO<sub>2</sub> electrolyzer using Au/C. Au loading = 0.4 mg/cm<sup>2</sup>, scan rate = 100 mV/s.



**Fig. S11** <sup>1</sup>H NMR spectra of a standard solution of possible liquid products (blue line) and the water sampled from the anode water reservoir after longtime electrolysis (red line). DMSO was used as internal standard in both cases.