

Supporting Information

Cation transport phenomena during CO₂ electroreduction in H-type cell with Nafion membrane

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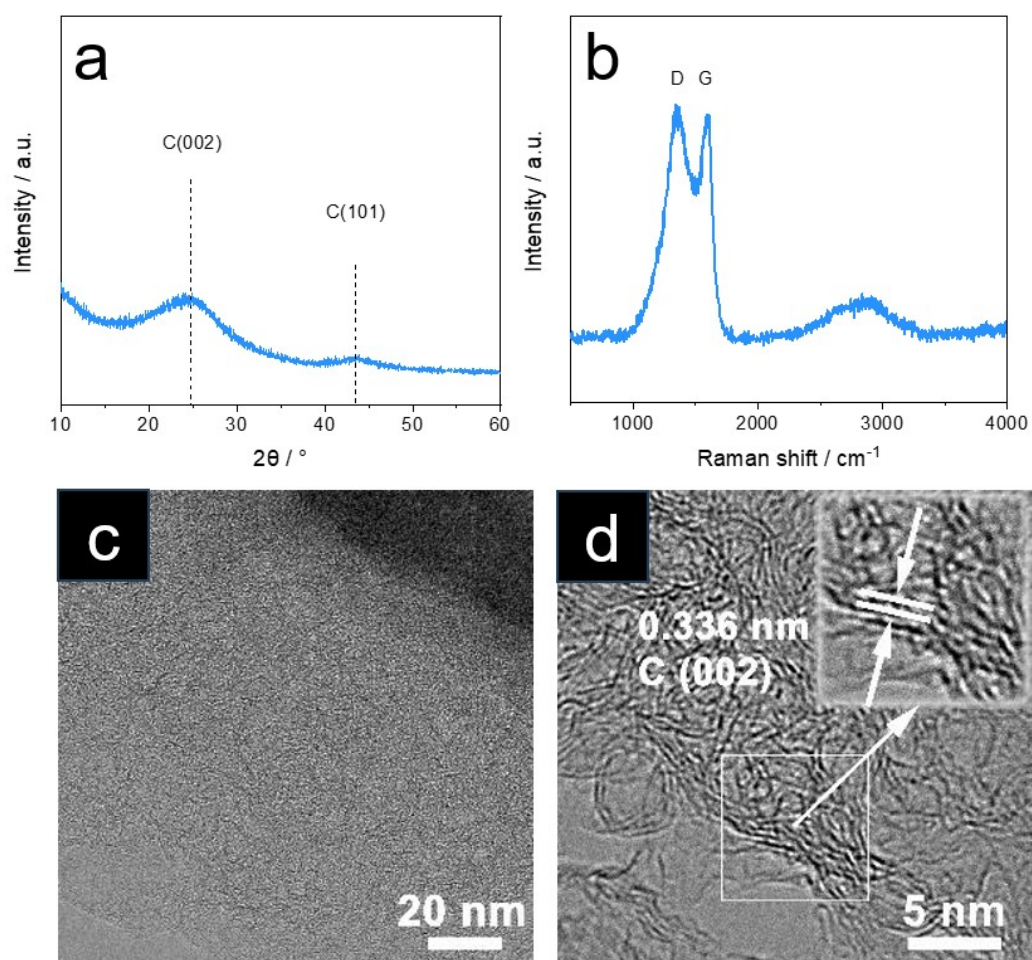


Figure S1 (a) XRD pattern, (b) Raman spectrum and (c, d) high resolution TEM images of N, S and Cl decorated carbon material.

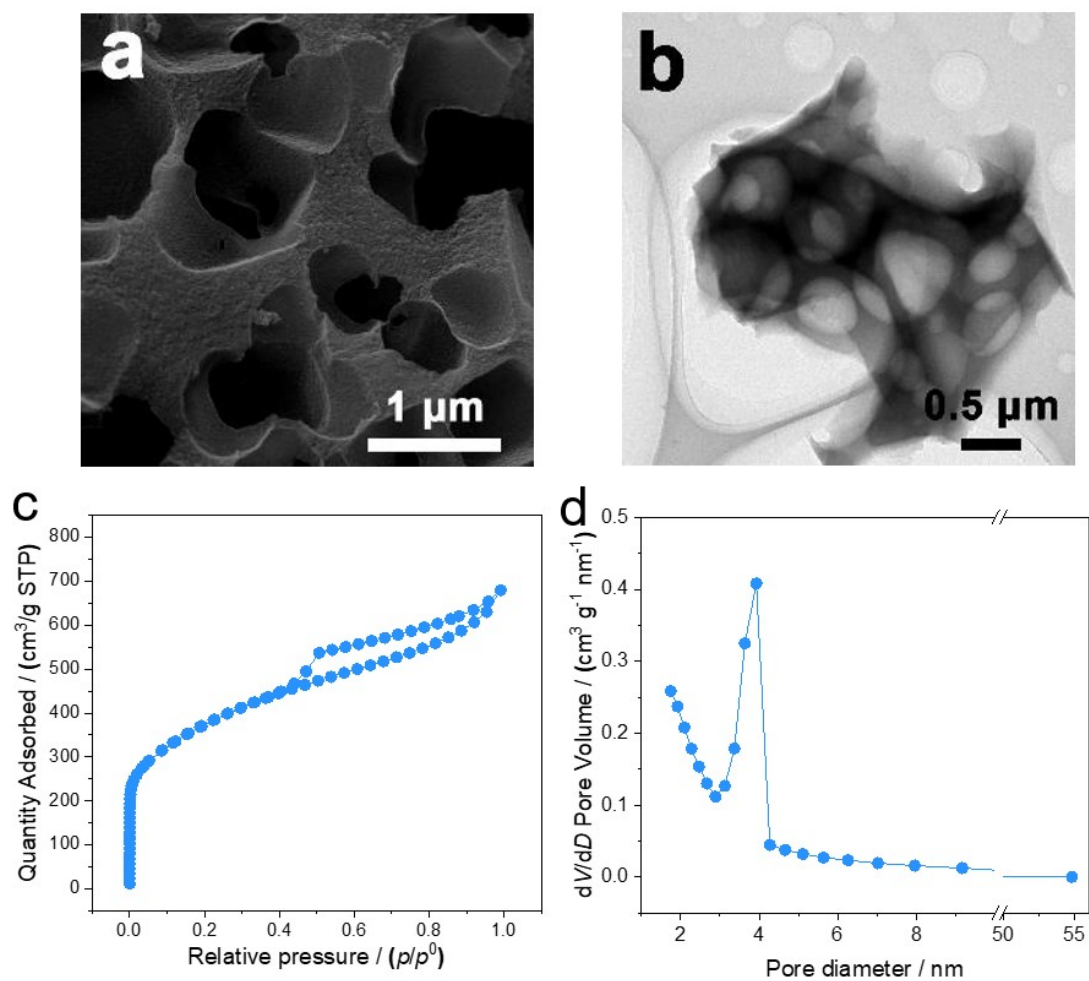


Figure S2 (a) SEM image, (b) Regular TEM image and (c) Nitrogen adsorption-desorption curves, pore distribution based on (d) Barrett-Joyner-Halenda (BJH) method of CM

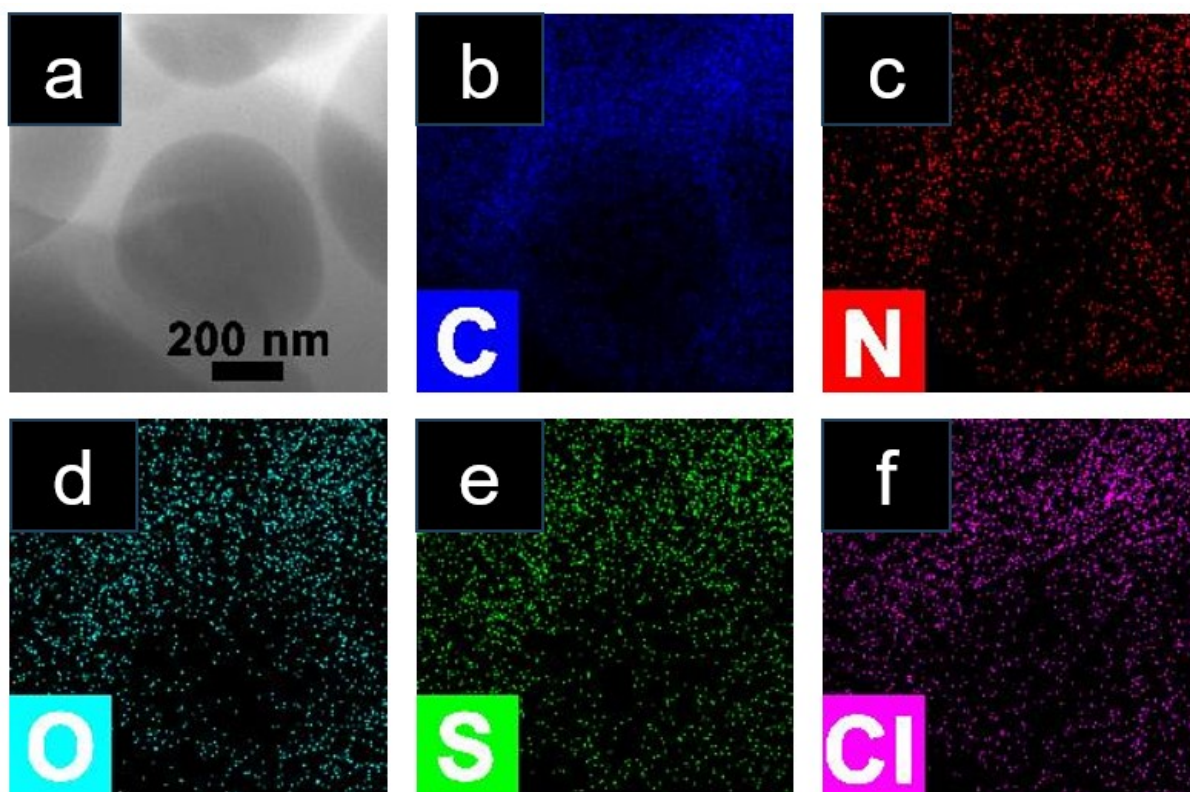


Figure S3 (a) Dark field TEM images and elemental mapping of (b) C, (c) N, (d) O, (e) S, (f) Cl of CM.

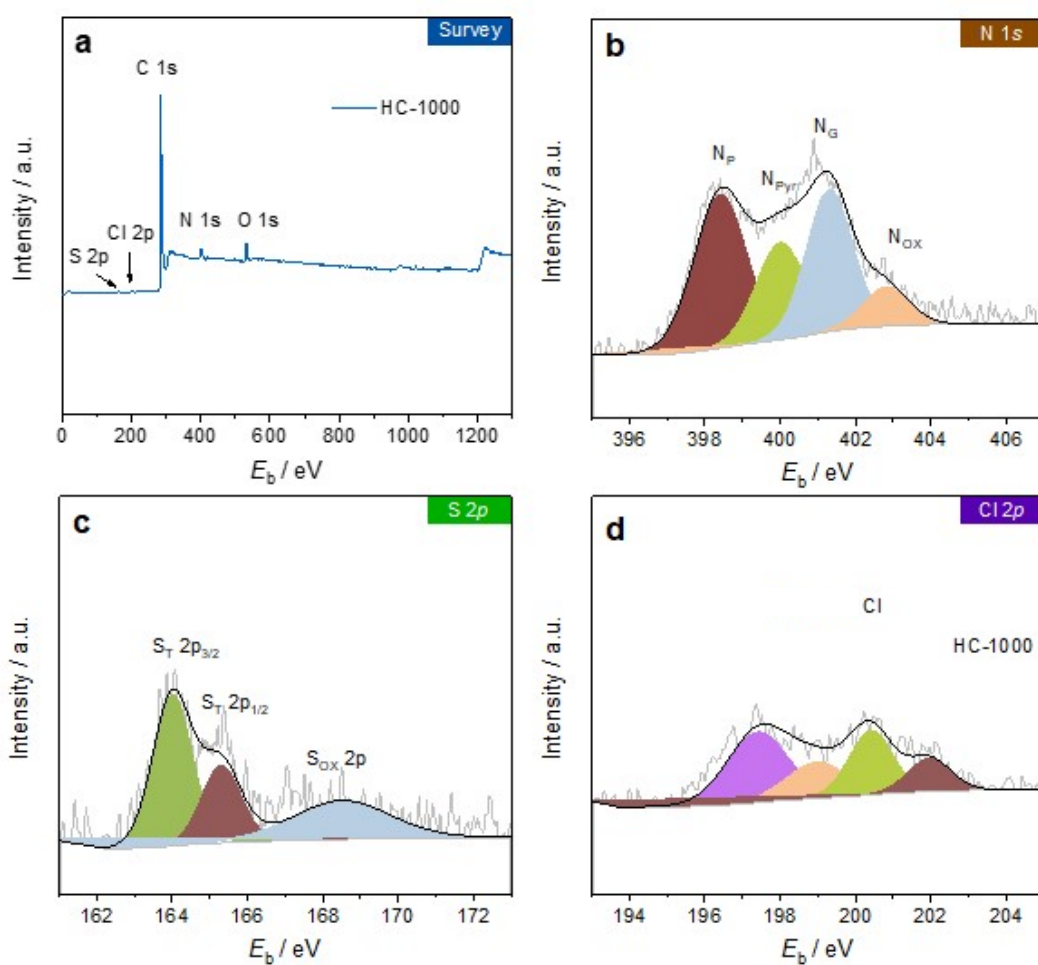


Figure S4 XPS spectra of N, S, and Cl of CM. (a) survey spectrum; fine spectra of (b) N1s, (c) S2p, and (d) Cl2p.

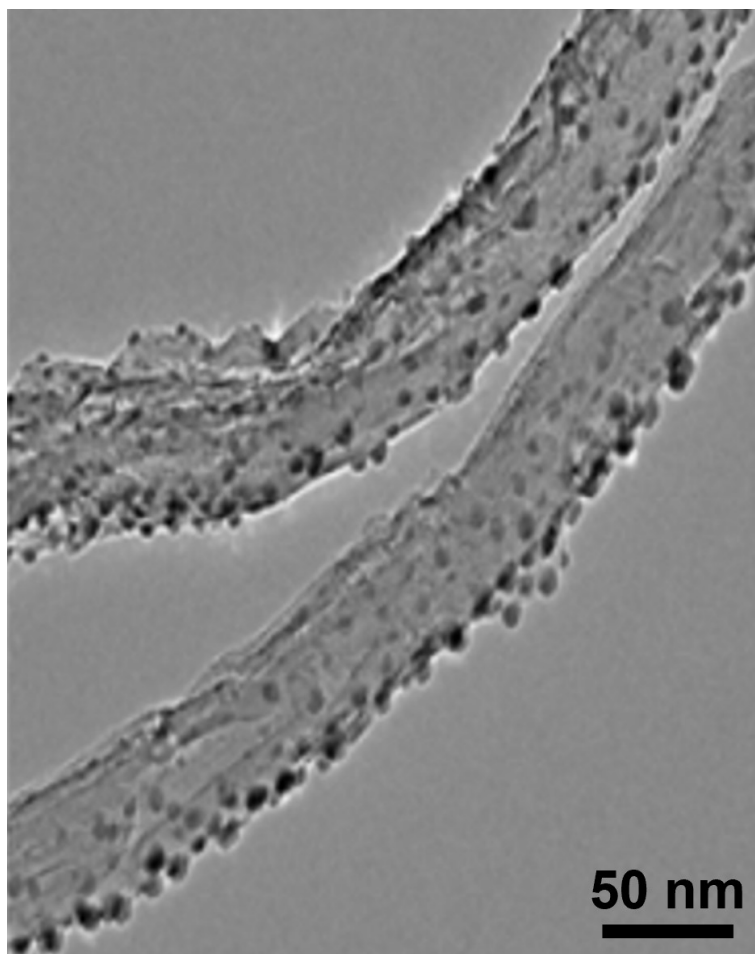


Figure S5 TEM image of Bi@CNTs.

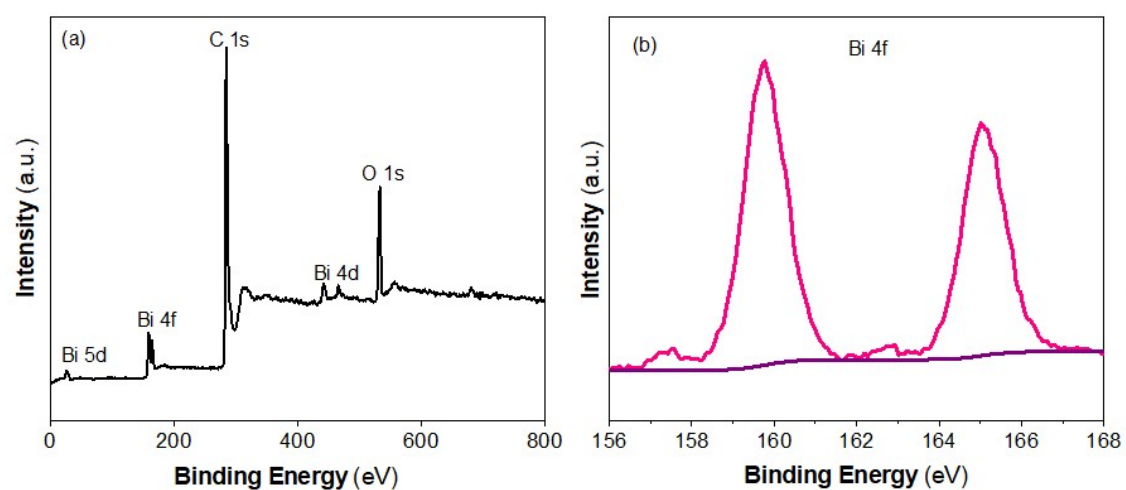


Figure S6 XPS spectra of Bi@CNTs: (a) survey spectrum, (b) fine spectrum of Bi 4f,

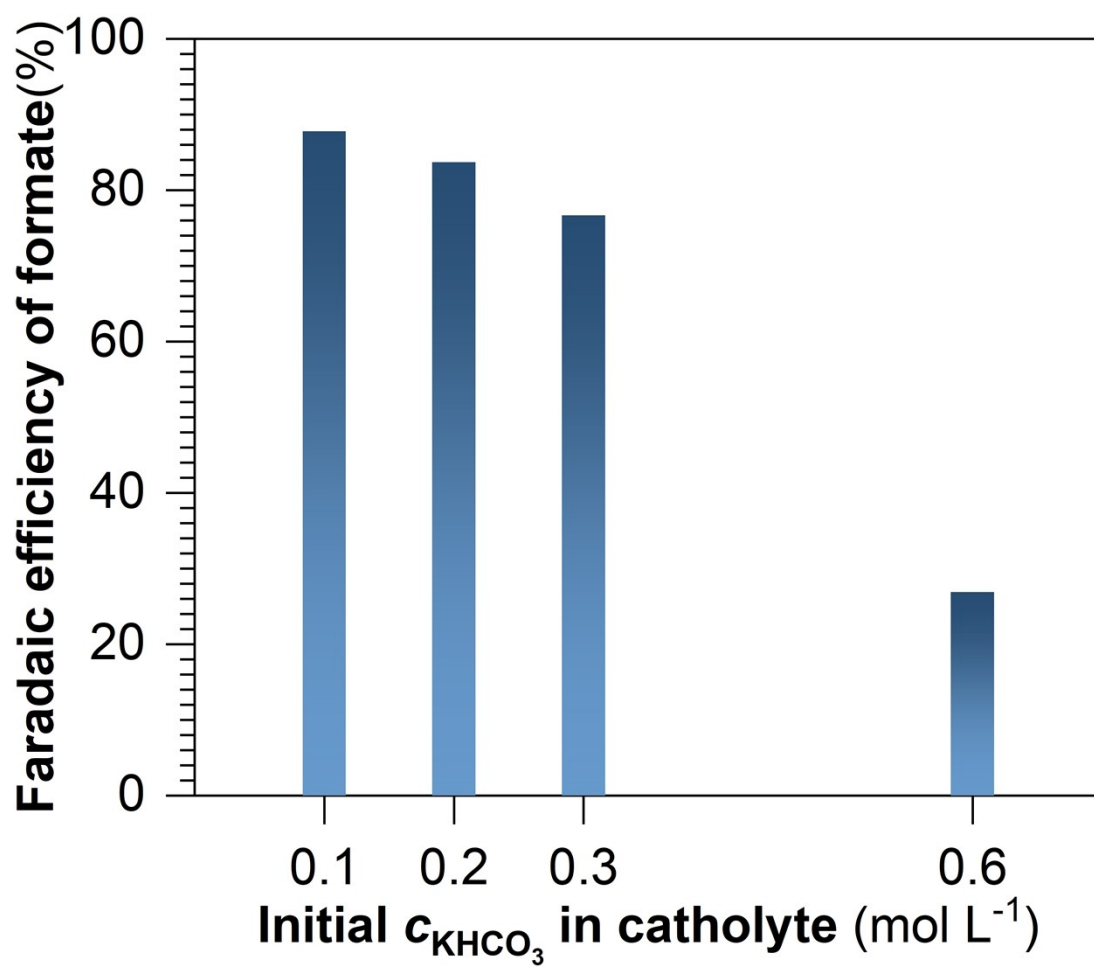


Figure S7 Faradaic efficiency of formate at different KHCO_3 concentration in catholyte.

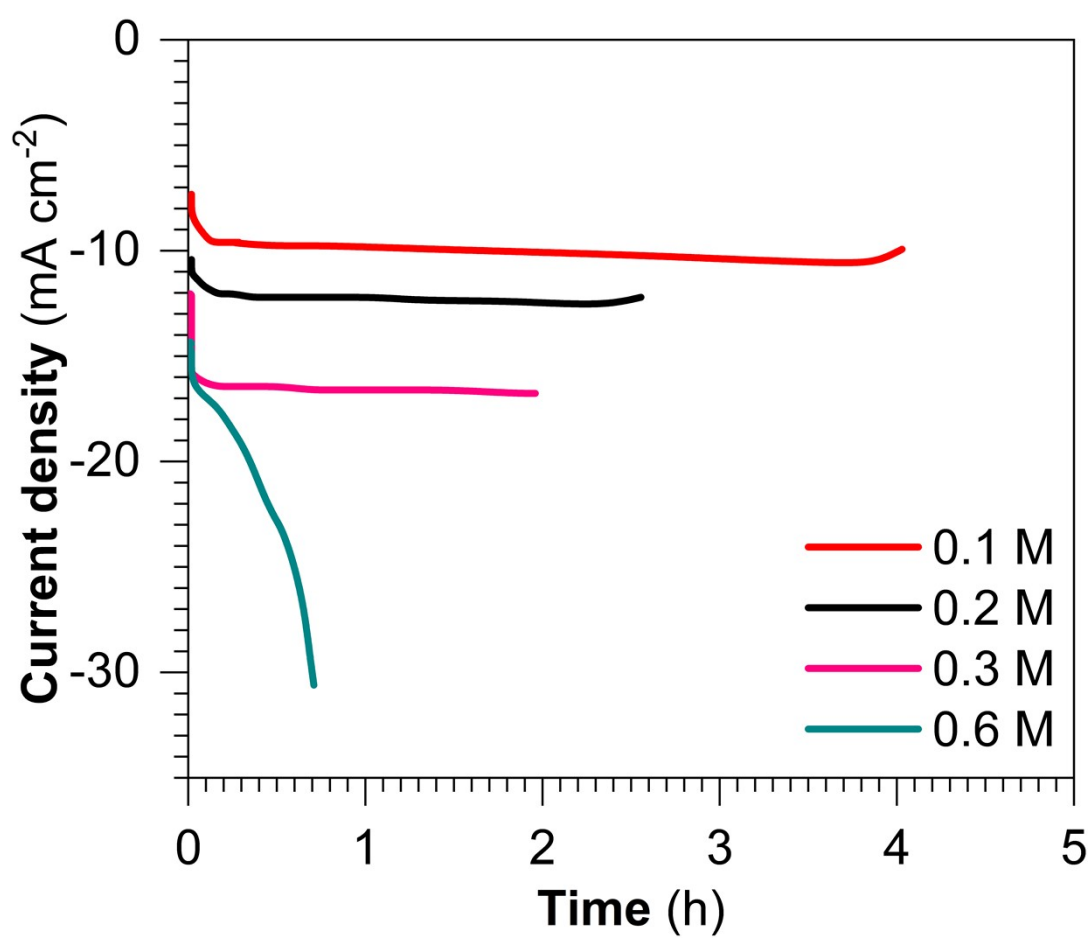


Figure S8 Recorded current in catholyte with different KHCO₃ concentration.

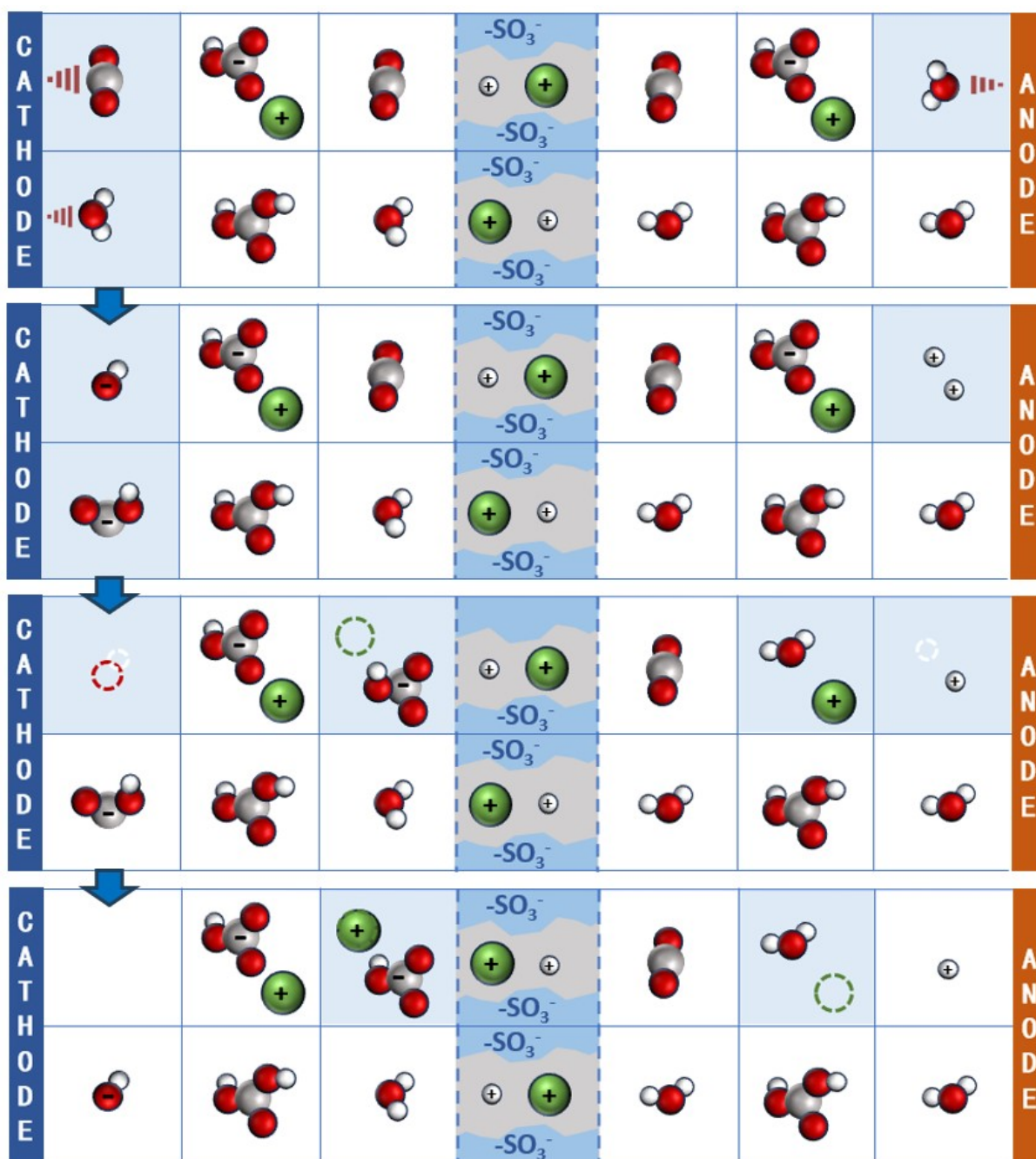


Figure S9 Schematic illustration of electrocatalytic reactions, nonfaradaic reactions, and transport of ions during CO₂ reduction on Bi@CNTs for producing formate.

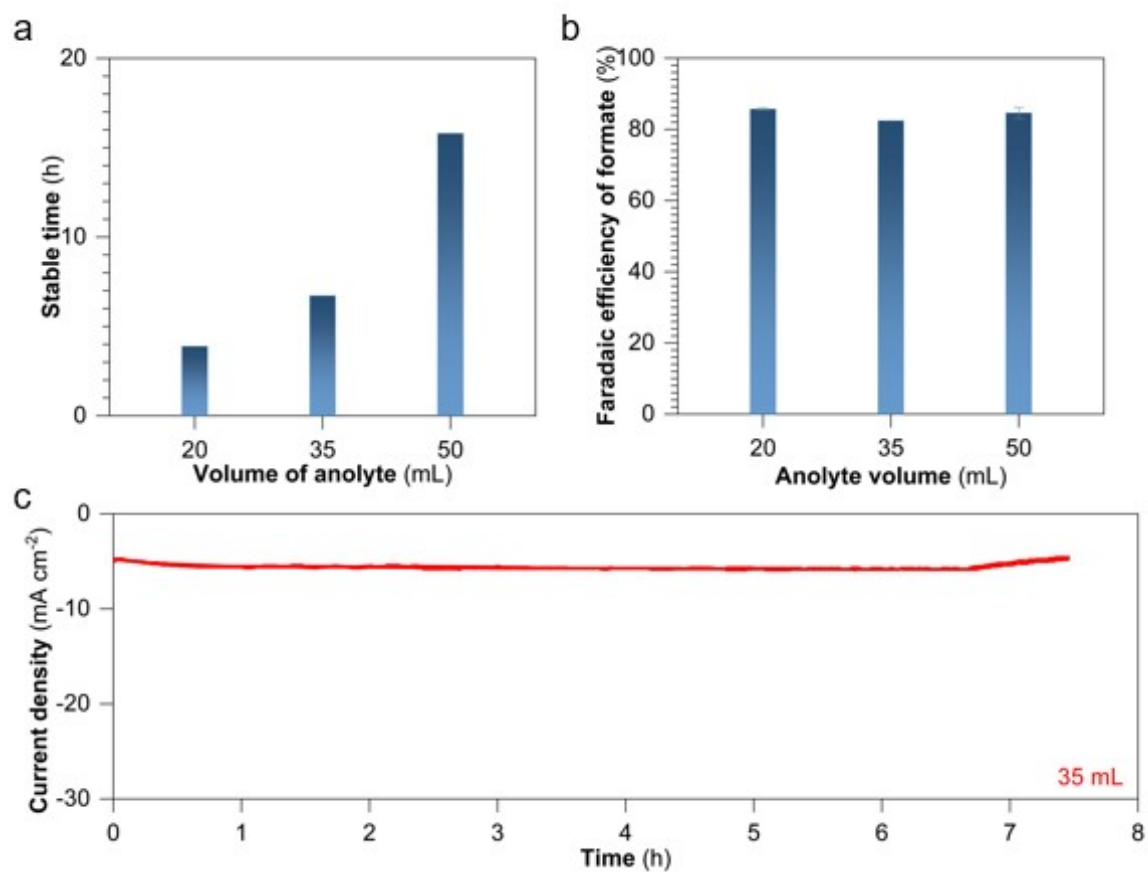


Figure S10 (a) Stable time at different volumes of anolyte, (b) Faradaic efficiency of formate at different anolyte volume, (c) Time-dependent current on Bi@CNTs in a H-type cell with 35 mL of anolyte.

Table S1 Amount of N, S and Cl elements calculated by XPS spectra of CM

<i>Sample</i>	<i>N</i>	<i>S</i>	<i>Cl</i>
	(%)	(%)	(%)
<i>Carbon material</i>	5.52	0.41	0.52

Table S2 Titration of $\text{HCO}_3^-/\text{OH}^-$ with HCl solution

A) Titration of HCO_3^- in CO_2 saturated KHCO_3 solution with HCl solution				
Electrode	Result	Experiment		
		1	2	3
Anode	V (HCl) (mL)	11.72	11.72	11.72
	c (HCO_3^-) (mol L ⁻¹)	0.1149	0.1149	0.1149
	$\bar{c}$ (HCO_3^-) (mol L ⁻¹)	0.1149		
	Phenomenon	The solution changes from yellow to orange		
B) Titration of $\text{HCO}_3^-/\text{OH}^-$ with HCl solution when the stability begins to decrease				
Electrode	Result	Experiment		
		1	2	3
Anode	V (HCl) (mL)	0.64	0.68	0.68
	c (HCO_3^-) (mol L ⁻¹)	0.0063	0.0067	0.0067
	$\bar{c}$ (HCO_3^-) (mol L ⁻¹)	0.0065		
	Phenomenon	The solution changes from yellow to orange		
Cathode	V (HCl) (mL)	21.14	21.12	21.02
	c ($\text{HCO}_3^-/\text{OH}^-$) (mol L ⁻¹)	0.2072	0.2070	0.2060
	$\bar{c}$ ($\text{HCO}_3^-/\text{OH}^-$) (mol L ⁻¹)	0.2067		
	Phenomenon	The solution changes from yellow to orange		
C) Titration of HCO_3^- with HCl solution when the stability drops to remain stable				
Electrode	Result	Experiment		
Anode	Phenomenon	1 drop of HCl		
		The solution changes from yellow to red		

