

## Supporting information

### The role of electrode wettability in electrochemical reduction of carbon dioxide

Mengran Li<sup>\*,a,b,†</sup>, Mohamed Nazmi Idros<sup>a,†</sup>, Yuming Wu<sup>a</sup>, Thomas Burdyny<sup>b</sup>, Sahil Garg<sup>c</sup>, Xiu Song Zhao<sup>a</sup>, Geoff Wang<sup>a</sup>, Thomas E. Rufford<sup>a,\*</sup>

a. School of Chemical Engineering, the University of Queensland, St Lucia, 4072, Brisbane, Queensland, Australia

b. Materials for Energy Conversion and Storage (MECS), Department of Chemical Engineering, Faculty of Applied Sciences, Delft University of Technology, van der Maasweg 9, 2629 HZ Delft, The Netherlands

c. Surface Physics and Catalysis (SurfCat) Section, Department of Physics, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark

† M.Li. and M.N. Idros contributed equally to this work.

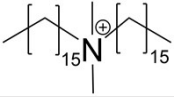
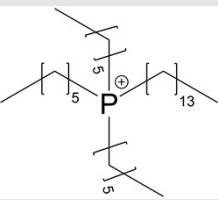
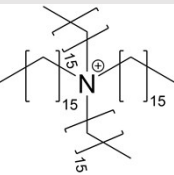
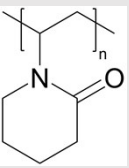
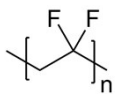
Corresponding authors: M. Li: [m.li6@uq.edu.au](mailto:m.li6@uq.edu.au); T.E. Rufford: [t.rufford@uq.edu.au](mailto:t.rufford@uq.edu.au)

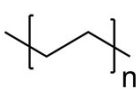
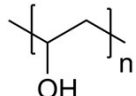
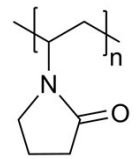
Table S 1 A summary of recent advances in modifying catalyst surface wettability via additives for CO<sub>2</sub> electrochemical reduction.

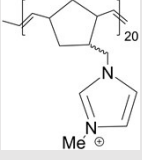
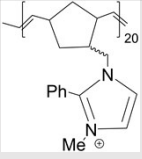
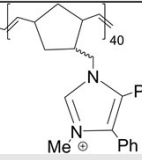
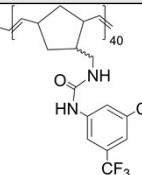
Catalyst	Substrate	Additives	Preparation methods	Contact angle (°)	Potential (V vs RHE)	Faradaic Efficiency (%)							Peak current density (mA cm <sup>-2</sup> )	Catholyte	Membrane	References
						Hydrogen	Formate/formic acid	Carbon monoxide	Methane	Ethylene	Ethanol	Acetate				

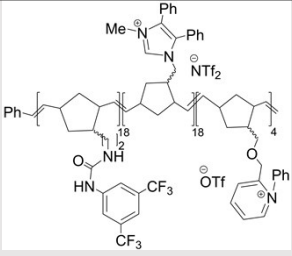
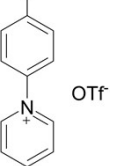
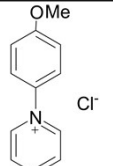
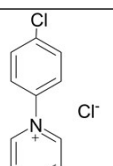
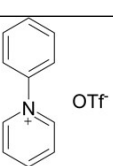
PTFE-treated Ni-embedded nitrogen-doped carbon nanotubes	carbon fibre	PTFE (1wt%)	Vertically aligned Ni(OH) <sub>2</sub> nanosheets were first grown on the CNF via hydrothermal method; growth of Ni-embedded nitrogen-doped carbon nanotubes via calcination with melamine followed being soaked in concentrated HCl at 85 °C; after washed with water, the obtained samples were immersed in PTFE aqueous solution, followed by heating at 350 °C.	147	-0.78	6.41		95.6						4.56	0.5M KHCO <sub>3</sub>	Nafion	1
		PTFE(0.25wt%)		0	-0.78	24.6		68.4					5.8				
		PTFE (0.5wt%)		16	-0.78	18		73.8					6.5				
		PTFE (0.75wt%)		121	-0.78	16.8		70.6					7.2				
		PTFE (1.25 wt%)		153	-0.78	5.28		90.5					4.6				
		PTFE (1.5 wt%)		146	-0.78	3.86		93.4					2.2				
Oxide-derived Cu	Metal foil	N.A	Drop casting solution of the organics onto the metal surface. Nafion was there after drop cast onto the surface.	27	-0.7	28	34	28						0.7	0.05 M K <sub>2</sub> CO <sub>3</sub> and 4 mM KCl aqueous solution	Selemon AMV	2

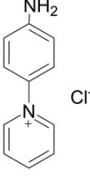
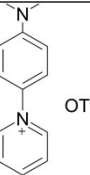
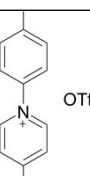
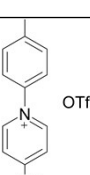
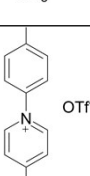
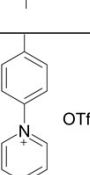


		<p>Dihexadecyl demethylammonium bromide</p> 		48	-0.7	3	18	76								0.3			
		<p>Trihexyltetra decyphosponium bromide</p> 		48	-0.7	27	11	49								0.1			
		<p>Tetrahexadecylammonium bromide</p> 		65	-0.7	27	30.5	33.8								0.7			
		<p>Polyvinyl pyrrolidone</p> 		11	-0.7	43	45	10								0.8			
CuO-derived Cu nanoparticles	Carbon paper Toray 060	<p>PVDF</p> 	First CuO nanoparticles were drop casted onto carbon paper, followed by drop casting of the polymers and/or Nafions	126	-1.12	28				32.7						12.3	0.5M KHCO <sub>3</sub>	N/A	3

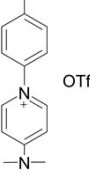
		PE 		127	-1.12	28.5				29.5					12.6			
		PVA 		68	-1.12	49.5		3	8.4	22.7					7			
		PVA + Nafion		85	-1.12	51.5		4.1	5.8	17.4					7.1			
		PVP 		71	-1.12	52.1		6.4	2.3	12.8					8.5			
		PVP + Nafion		84	-1.12	50.3		5.9	2.2	15.1					9.3			
Cu nano dendrites	Cu foil	N.A		17	-1.6	71	7.3	0.6		8.7	4.5	0.3	0.5			0.1M CsHCO <sub>3</sub>	Nafion	4
		Alkanethiol	Submerged the Cu nano dendrite into 1-octadecanethiol under vacuum at 60 °C	153	-1.6	9.64	1.88	3.38	6.94	56.3	16.1	3.44	9.64					

CuO-derived nonawire array	Cu foil	N.A		33	-1.1	38.5	10	4.1		23.8	10.6		2.4	14.8	20.7	0.1M KHCO <sub>3</sub>	N.A	5	
		PTFE	Soak the catalyst in PTFE solution the, followed by annealing at 350 °C	137	-1.1	17.1	26.7	23.8			13.5	10							18.85
Cu surface modified with organic modifiers	Cu foil		The Cu foil was spin coated with polymer methanol solution followed by annealed at 70 °C for 10 min	73	-1.08	94.6	0.7		1.5						12.2	0.1M KHCO <sub>3</sub>	Selemon AMV AEM	6	
				78	-1.08	69.3	6.6	1	14.1	5.3					3.9				
				88	-1.08	37.8	11.1	2.8	14	21.5	3.4				2.6				2.75
				90	-1.08	33.6	1.1	0.5	28.1	25.5	6				1.1				4.64

				104	-1.08	17.4	1.9	0.7	1.9	11.9	17.4			4.3	4.66			
Cu surface modified with the organic modifier	PTFE GDL		Cu was sputtered on to the PTFE membrane, followed by electrodeposition of the organic film on the surface in 0.1M KHCO <sub>3</sub> solution containing 10mM additives	51	-0.83	7.9	2.2	5.3	0.3	64.6	16.7	3.5		2.1	N.A.	1M KHCO <sub>3</sub>	Fumapem FAA-3-PK-130	z
				67	-0.83	10.1	2.1	8.8	0.5	57.3	16.2	1.9		1.8	N.A.			
				51	-0.83	5.1	3.3	6.3	1.8	63.1	17.6	1.1		4.7	N.A.			
				61	-0.84	10.5	1.4	6.3	0.5	59.9	15.6	1.1		2.5	N.A.			

		 <chem>Nc1ccc(cc1)[N+]1ccncc1.[Cl-]</chem>	58	-0.82	22.2	3.5	4.8	0.4	50.4	15.6	2.8		2.7	N.A.			
		 <chem>COc1ccc(cc1)[N+]1ccncc1.[OTf-]</chem>	60	-0.83	24.8	1.6	3.4	2.2	43.9	18.7	4.2		1.1	N.A.			
		 <chem>COc1ccc(cc1)[N+]1ccncc1.[OTf-]</chem>	68	-0.83	7.5	1.9	10.1	0.8	57	16.2	2.1		2.5	N.A.			
		 <chem>C(F)(F)Fc1ccc(cc1)[N+]1ccncc1.[OTf-]</chem>	60	-0.84	12.6	1.6	12.5	0.7	55.1	11.7	2		2.3	N.A.			
		 <chem>COc1ccc(cc1)[N+]1ccncc1.[OTf-]</chem>	60	-0.83	13.4	1.5	12.6	0.2	55.2	12.5	1.4		2.8	N.A.			
		 <chem>COc1ccc(cc1)[N+]1ccncc1.[OTf-]</chem>	56	-0.83	22	1.4	4.6	1.1	51.8	13.6	1.3		2.4	N.A.			



				57	-0.82	36.7	3.7	3.5	0.3	37.5	13.9	0.9		4.4	N.A.			
--	--	---	--	----	-------	------	-----	-----	-----	------	------	-----	--	-----	------	--	--	--

## References

- Chen, R.; Tian, W.; Jia, Y.; Xu, W.; Chen, F.; Duan, X.; Xie, Q.; Hu, C.; Liu, W.; Zhao, Y.; Kuang, Y.; Zhang, Y.; Sun, X., Engineering Interfacial Aerophilicity of Nickel-Embedded Nitrogen-Doped CNTs for Electrochemical CO<sub>2</sub> Reduction. *ACS Applied Energy Materials* **2019**, *2* (6), 3991-3998.
- Buckley, A. K.; Lee, M.; Cheng, T.; Kazantsev, R. V.; Larson, D. M.; Goddard Iii, W. A.; Toste, F. D.; Toma, F. M., Electrocatalysis at Organic–Metal Interfaces: Identification of Structure–Reactivity Relationships for CO<sub>2</sub> Reduction at Modified Cu Surfaces. *Journal of the American Chemical Society* **2019**, *141* (18), 7355-7364.
- Liang, H.-Q.; Zhao, S.; Hu, X.-M.; Ceccato, M.; Skrydstrup, T.; Daasbjerg, K., Hydrophobic Copper Interfaces Boost Electroreduction of Carbon Dioxide to Ethylene in Water. *ACS Catalysis* **2021**, *11* (2), 958-966.
- Wakerley, D.; Lamaison, S.; Ozanam, F.; Menguy, N.; Mercier, D.; Marcus, P.; Fontecave, M.; Mougel, V., Bio-inspired hydrophobicity promotes CO<sub>2</sub> reduction on a Cu surface. *Nature Materials* **2019**, *18* (11), 1222-1227.
- Cai, Z.; Zhang, Y.; Zhao, Y.; Wu, Y.; Xu, W.; Wen, X.; Zhong, Y.; Zhang, Y.; Liu, W.; Wang, H.; Kuang, Y.; Sun, X., Selectivity regulation of CO<sub>2</sub> electroreduction through contact interface engineering on superwetting Cu nanoarray electrodes. *Nano Research* **2019**, *12* (2), 345-349.
- Wang, J.; Cheng, T.; Fenwick, A. Q.; Baroud, T. N.; Rosas-Hernández, A.; Ko, J. H.; Gan, Q.; Goddard Iii, W. A.; Grubbs, R. H., Selective CO<sub>2</sub> Electrochemical Reduction Enabled by a Tricomponent Copolymer Modifier on a Copper Surface. *Journal of the American Chemical Society* **2021**, *143* (7), 2857-2865.
- Li, F.; Thevenon, A.; Rosas-Hernández, A.; Wang, Z.; Li, Y.; Gabardo, C. M.; Ozden, A.; Dinh, C. T.; Li, J.; Wang, Y.; Edwards, J. P.; Xu, Y.; McCallum, C.; Tao, L.; Liang, Z.-Q.; Luo, M.; Wang, X.; Li, H.; O'Brien, C. P.; Tan, C.-S.; Nam, D.-H.; Quintero-Bermudez, R.; Zhuang, T.-T.; Li, Y. C.; Han, Z.; Britt, R. D.; Sinton, D.; Agapie, T.; Peters, J. C.; Sargent, E. H., Molecular tuning of CO<sub>2</sub>-to-ethylene conversion. *Nature* **2020**, *577* (7791), 509-513.