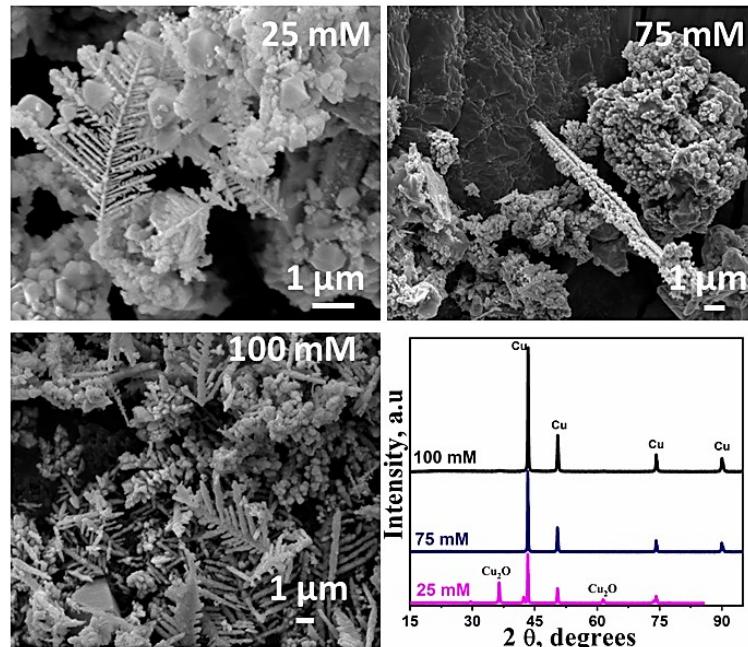


1           **Unravelling the Chemistry of Catalyst Surface and Solvent towards C-C Bond Formation**  
2           **through Activation and Electrochemical Conversion of CO<sub>2</sub> into Hydrocarbons over Micro-**  
3           **structured Dendritic Copper**

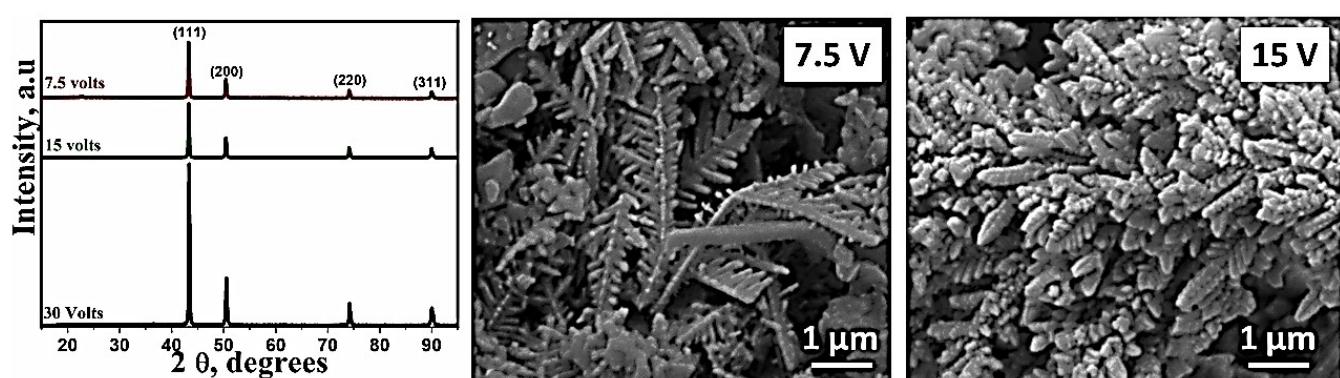
4           **Nusrat Rashid<sup>1</sup>, Mohsin Ahmad Bhat<sup>2</sup>, Pravin P. Ingole<sup>1\*</sup>**

5           <sup>1</sup>Department of Chemistry, Indian Institute of Technology Delhi, New Delhi, India 110016.

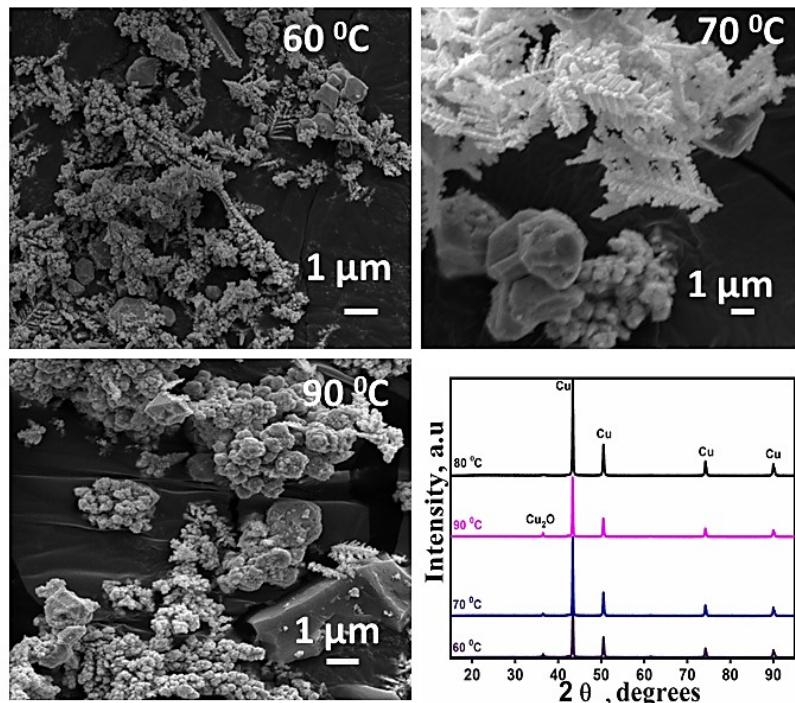
6           <sup>2</sup>Department of Chemistry, University of Kashmir, Srinagar, Jammu and Kashmir, India



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8       *Figure SI-1: The representative SEM images and XRD patterns of the Cu-microstructures prepared at*  
9       *varying AsH concentration used during the electrodeposition process.*

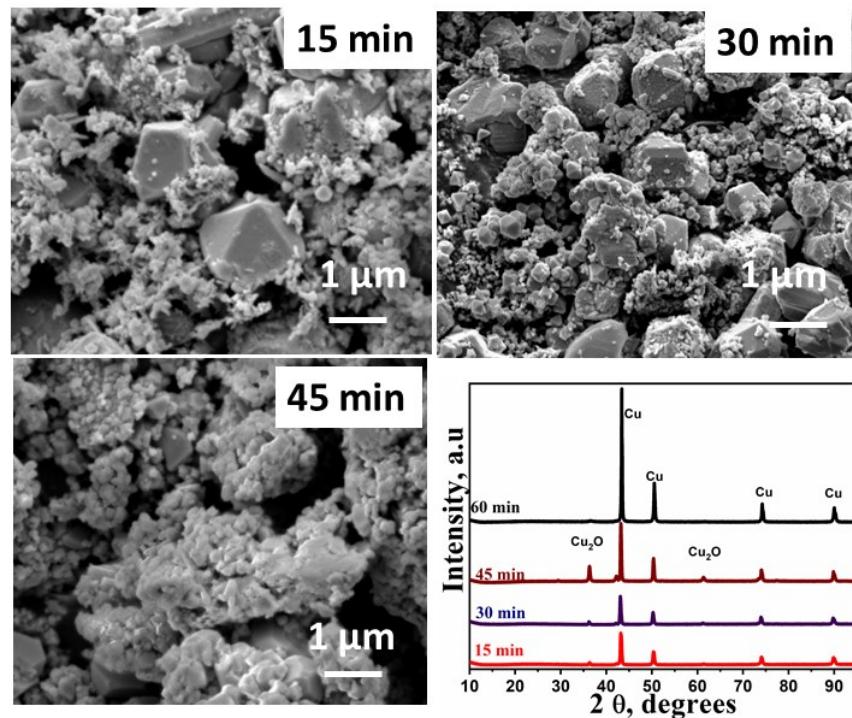


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11      *Figure SI-2: The representative XRD patterns and SEM images of the Cu-microstructures prepared at*  
12      *varying biases applied during the electrodeposition process. The SEM image for 30 V sample is not shown*  
13      *as it is the same sample obtained with 100 mM AsH concentration shown in Figure SI-2.*



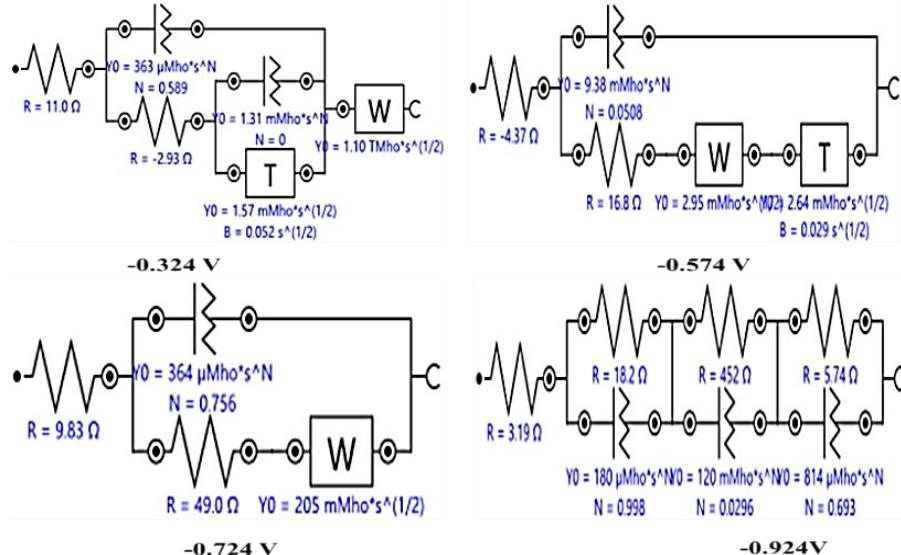
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15 *Figure SI-3: SEM images and XRD patterns of the Cu-microstructures prepared at varying*  
 16 *electrodeposition bath temperatures. The SEM image for 80 °C sample is not shown as it is the same*  
 17 *sample obtained with 30 V bias and 100 mM AsH concentration shown in Figure SI-2.*



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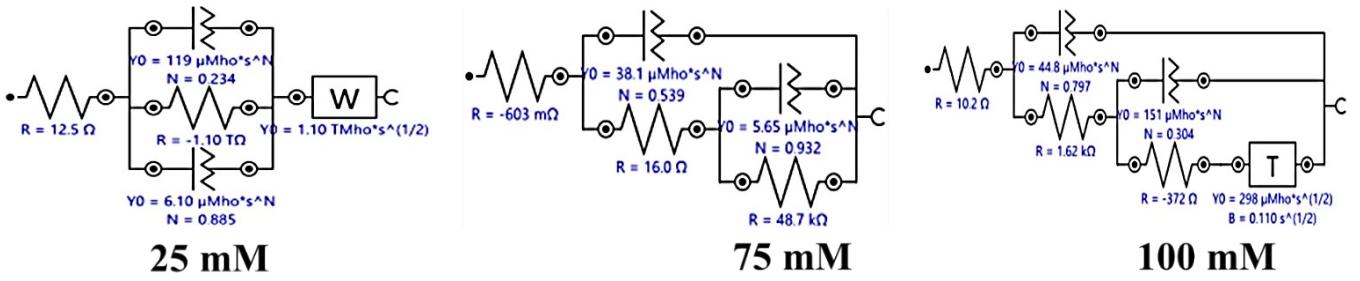
19 *Figure SI-4: SEM images and XRD patterns of the Cu-microstructures prepared at varying*  
 20 *electrodeposition times. The SEM image for 60 minutes sample is not shown as it is the same sample*  
 21 *obtained with 60 °C, 30 V bias and 100 mM AsH concentration shown in Figure SI-2.*



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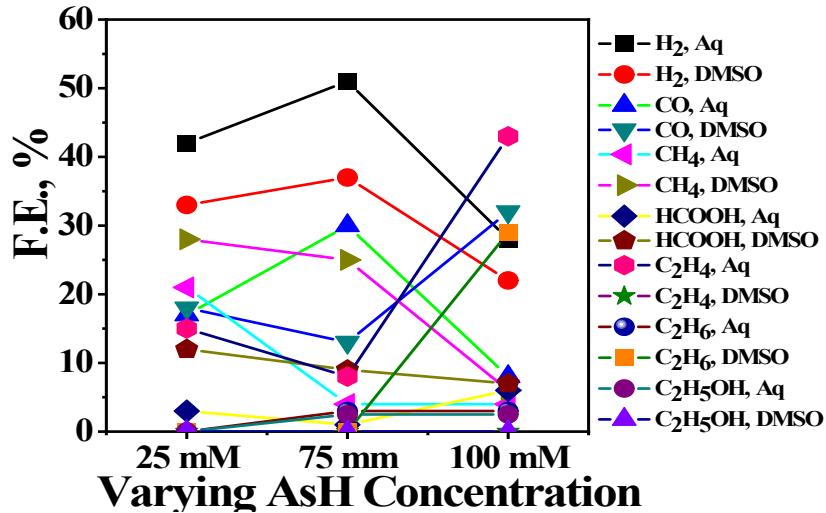
23 *Figure SI-5: An equivalent circuits fitted to the Nyquist plots obtained on the most active Cu-  
24 microstructures in  $\text{CO}_2$  saturated  $0.2 \text{ M KHCO}_3$  at different potentials.*

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27 *Figure SI-6: An equivalent circuits fitted to the Nyquist plots obtained on different Cu-microstructures in  $\text{CO}_2$  saturated  $0.2 \text{ M KHCO}_3$  at OCP. Due to different microstructure these catalysts behave differently,  
29 suggesting role of nano-morphology in charge transfer dynamics.*



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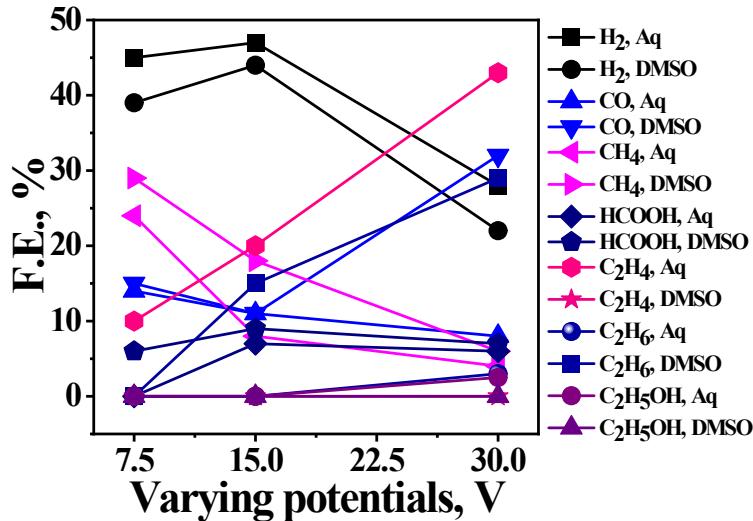
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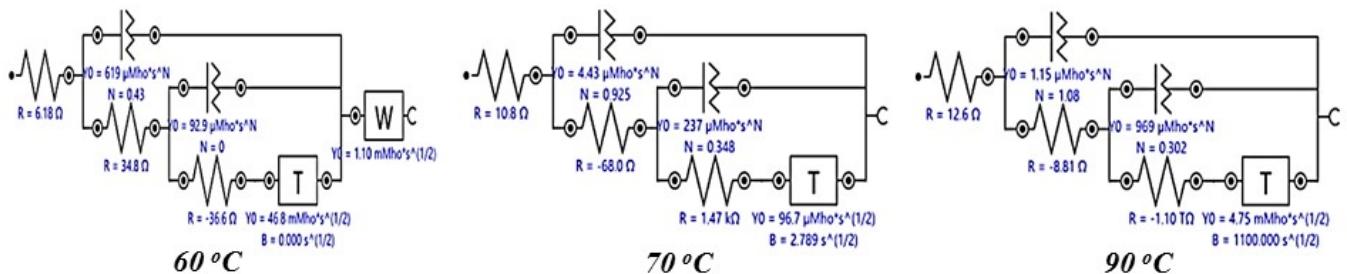
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40 *Figure SI-9.* A comparison of the trend in variation of F.E. values for Cu-microstructure catalysts  
 41 (prepared at varying applied bias) in DMSO and  $KHCO_3$  aqueous medium.

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44 *Figure SI-10:* An equivalent circuits fitted to the Nyquist plots obtained on different Cu-micrstructures in  
 45  $CO_2$  saturated 0.2 M  $KHCO_3$  at OCP. Except for the additional warburg element in 60°C, the  
 46 representative equivalent circuits for other ctalysts have similar elements, reinforcing that similar nano-  
 47 morphology behaves in similar ways albeit with different values for the elements constituting the circuit.

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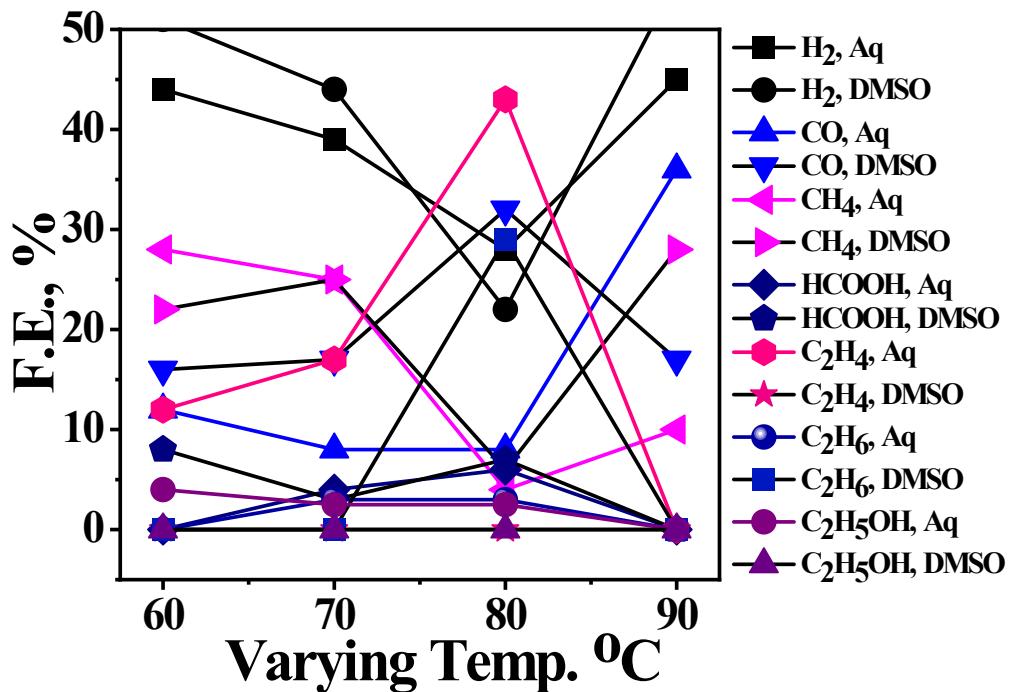
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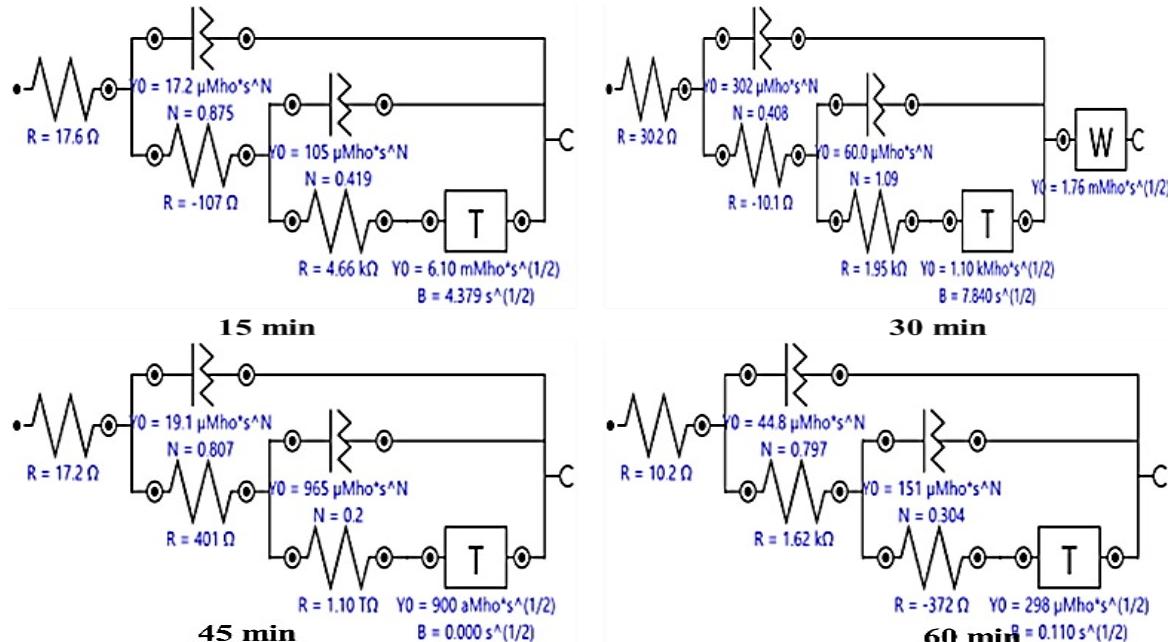
54 Table SI-1: Different products obtained at different surfaces in 0.2M  $KHCO_3$  and DMSO in a  $CO_2$ -  
 55 saturated solution at -1.0V (RHE) (NHE in DMSO). The table also shows the product selectivity

Samples	H <sub>2</sub>	CO	CH <sub>4</sub>	HCOOH	F.E. for C1	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>5</sub> OH	F.E. for C2	C1 + C2	Total	Selectivity (in %) For C1	Selectivity (in %) for C2
25 mM	42	17	21	3	24	15	0	0	15	39	98	61.5	38.5
<b>DMSO</b>	33	18	28	12	40	0	0	0	0	40	91	100	0
75 mM	51	30	4	1	5	8	3	2.5	13.5	18.5	99.5	27	73
<b>DMSO</b>	37	13	25	9	34	0	0	0	0	34	84	100	0
100 mM	28	8	4	6	10	43	3	2.5	48.5	58.5	94.5	17	83
<b>DMSO</b>	22	32	6	7	13	0	29	0	29	42	96	31	69
7.5 V	45	14	24	0	24	10	0	0	10	34	93	71	29
<b>DMSO</b>	39	15	29	6	35	0	0	0	0	35	89	100	0
15 V	47	11	8	7	15	20	0	0	20	35	93	43	57
<b>DMSO</b>	44	11	18	9	27	0	15	0	15	42	97	64	36
30 V	28	8	4	6	10	43	3	2.5	48.5	58.5	94.5	17	83
<b>DMSO</b>	22	32	6	7	13	0	29	0	29	42	96	31	69
60	44	12	28	0	28	12	0	4	16	44	100	63	37
<b>DMSO</b>	51	16	22	8	30	0	0	0	0	30	97	100	0
70	39	8	25	4	29	17	3	2.5	22.5	51.5	98.5	56	44
<b>DMSO</b>	44	17	25	3	28	0	0	0	0	28	89	100	0
80	28	8	4	6	10	43	3	2.5	48.5	58.5	94.5	17	83
<b>DMSO</b>	22	32	6	7	13	0	29	0	29	42	96	31	69
90	45	36	10	0	10	0	0	0	0	10	91	100	0
<b>DMSO</b>	55	17	28	0	28	0	0	0	0	28	100	100	0
15 min	37	49	0	5	5	0	0	0	0	5	91	100	0
<b>DMSO</b>	39	19	26	13	39	0	0	0	0	39	97	100	0
30 min	26	28	23	10	33	0	0	0	0	33	87	100	0
<b>DMSO</b>	31	17	24	19	43	0	0	0	0	43	91	100	0
45 min	35	20	15	2	17	12	3	2.5	17.5	34.5	89.5	49	51
<b>DMSO</b>	49	15	25	6	31	0	0	0	0	31	95	100	0
60 min	28	8	4	6	10	43	3	2.5	48.5	58.5	94.5	17	83
<b>DMSO</b>	22	32	6	7	13	0	29	0	29	42	96	31	69
	<b>For 60 min in 0.2 M <math>KHCO_3</math> at different applied potentials.</b>												
-0.32 V	28	41	3	0	3	0	0	0	0	3	72	100	0
-0.57 V	36	49	8	2	10	3	0	0	3	13	98	77	23
-0.72 V	41	21	17	0	17	12.5	0	0	12.5	29.5	91.5	58	42
-0.92 V	37	22	13	4	17	19	3	2	24	41	100	41	59
-1.00 V	28	8	4	6	10	43	3	2.5	48.5	58.5	94.5	17	83

56 dependence on the applied potential at 60 min catalyst (optimized dendritic structure).

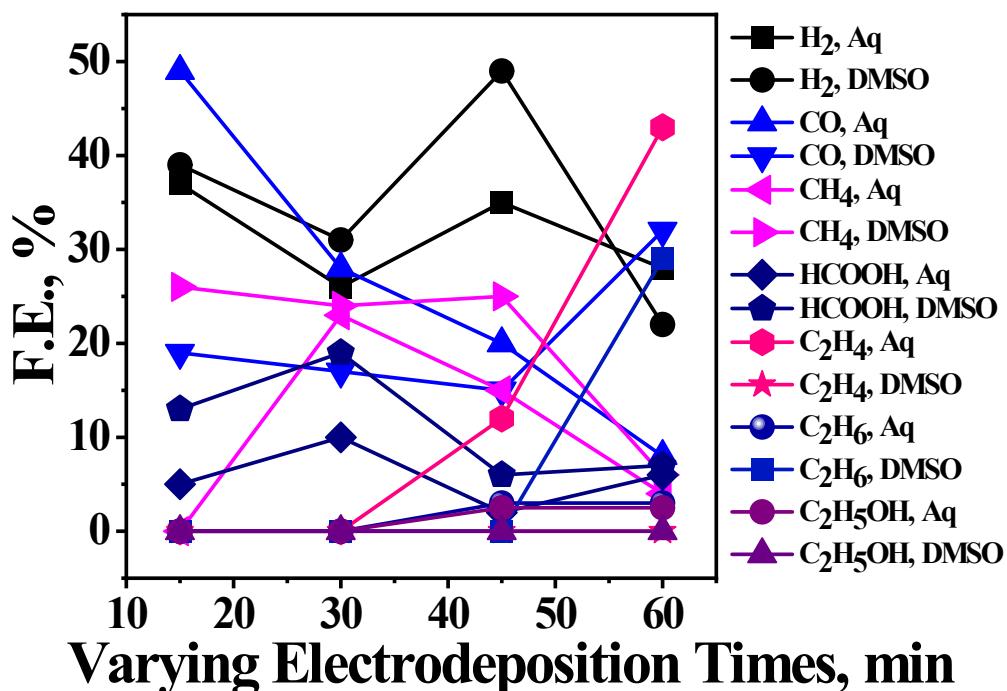


60 *Figure SI-11. A comparison of the trend in variation of F.E. values for Cu-microstructure catalysts*  
 61 *(prepared at varying electro-deposition temperatures) in DMSO and  $KHCO_3$  aqueous medium.*



64 Figure SI-12: An equivalent circuits fitted to the Nyquist plots obtained on different Cu-micrstructures  
65 (prepared at varying electrodeposition times) in  $\text{CO}_2$  saturated 0.2 M  $\text{KHCO}_3$  at OCP.

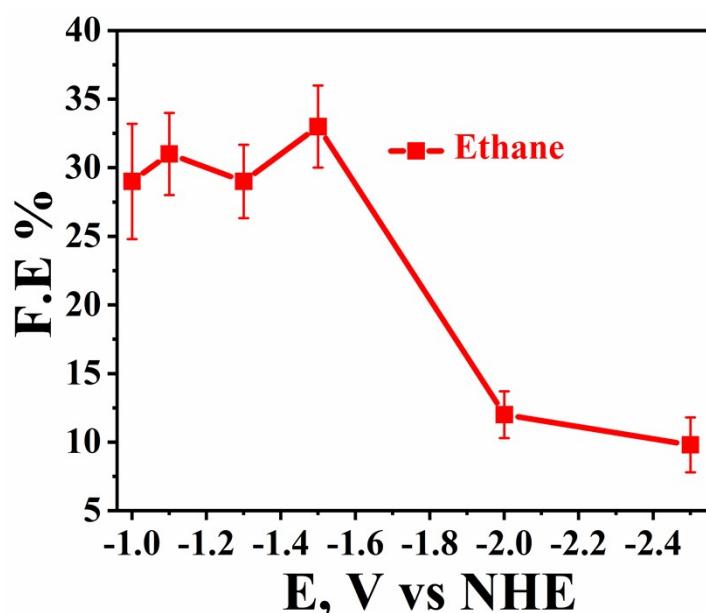
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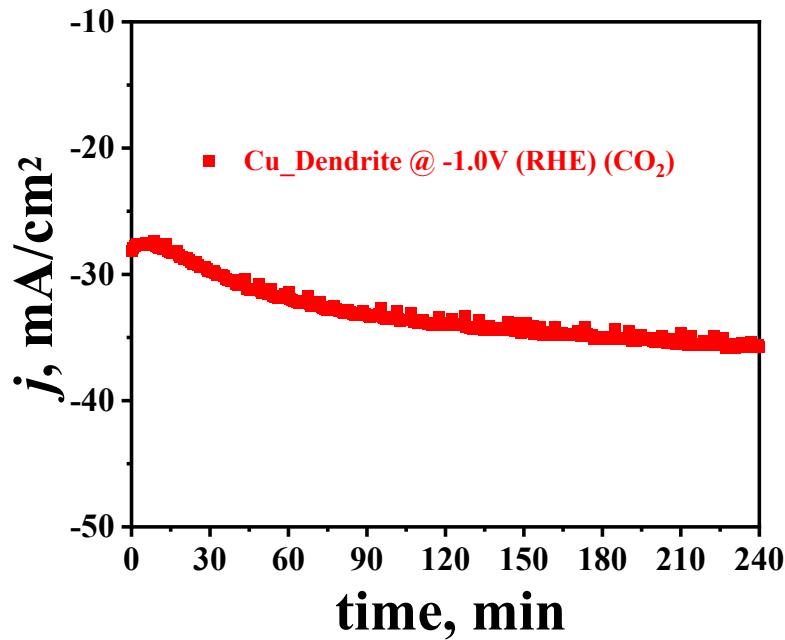
68 Figure SI-13. A comparison of the trend in variation of F.E. values for Cu-microstructure catalysts  
69 (prepared at varying electro-deposition times) in DMSO and  $\text{KHCO}_3$  aqueous medium.

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72 Figure SI-14: Change in ethane production with change in applied potential on optimised dendritic  
 73 structure in DMSO electrolyte.



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75 Figure SI-15: Stability of optimised copper dendrite (30V, 80 °C, 60 min and 100 mM AsH) in CO<sub>2</sub> for 3  
 76 hours.

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78 Table SI-2: EIS fitting parameters of different samples at OCP as derived from the circuit fit.

Sample	R1(ohm)	Q1(Mho*s*N)	R2 (ohm)	Q2(Mho*s*N)	R3 (ohm)	T1(Mho*s*1/2)	W1(Mho*s*1/2)
25 mM	12.5	119* 10 <sup>-6</sup>	-1.10* 10 <sup>12</sup>	6.10 * 10 <sup>-6</sup>	--	--	1.10*10 <sup>12</sup>
75 mM	603*10 <sup>-3</sup>	38.1*10 <sup>-6</sup>	16	5.65*10 <sup>-6</sup>	48.7*10 <sup>3</sup>	--	--
7.5 V	9.84	120*10 <sup>-6</sup>	1.71*10 <sup>3</sup>	179*10 <sup>-6</sup>	-526	365*10 <sup>-6</sup>	--
15 V	-74.1	781*10 <sup>-6</sup>	94.6	221*10 <sup>-6</sup>	- 1.10*10 <sup>12</sup>	1.1*10 <sup>3</sup>	6.01*10 <sup>-3</sup>
60 °C	6.18	619*10 <sup>-6</sup>	34.8	92.9*10 <sup>-6</sup>	-36.6	46.8*10 <sup>-3</sup>	1.1*10 <sup>-3</sup>
70 °C	10.8	4.43*10 <sup>-6</sup>	-68.0	237*10 <sup>-6</sup>	1.47*10 <sup>3</sup>	96.7*10 <sup>-6</sup>	--
90 °C	12.6	1.15*10 <sup>-6</sup>	-8.81	969*10 <sup>-6</sup>	-1.1*10 <sup>12</sup>	4.75*10 <sup>-3</sup>	--
15 min	17.6	17.2*10 <sup>-6</sup>	-107	105*10 <sup>-6</sup>	4.66*10 <sup>3</sup>	6.10*10 <sup>-3</sup>	--
30 min	30.2	302*10 <sup>-6</sup>	-10.1	60*10 <sup>-6</sup>	1.95*10 <sup>3</sup>	1.10*10 <sup>3</sup>	1.76*10 <sup>-3</sup>
45 min	17.2	19.1*10 <sup>-6</sup>	401	965*10 <sup>-6</sup>	1.1*10 <sup>12</sup>	900*10 <sup>-18</sup>	---
60 min	10.2	44.8*10 <sup>-6</sup>	1.62*10 <sup>3</sup>	151*10 <sup>-6</sup>	-372	298*10 <sup>-6</sup>	--

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82 *Table SI-3: EIS fitting parameters of optimised dendritic structure at different potentials as derived from*  
 83 *the circuit fit.*

Potential, V (RHE)	R1(ohm)	Q1(Mho*s*N)	R2 (ohm)	Q2(Mho*s*N)	R3 (ohm)	T1(Mho*s*1/2)	W1(Mho*s*1/2)
OCP	10.2	$44.8 \times 10^{-6}$	$1.62 \times 10^3$	$151 \times 10^{-6}$	-372	$298 \times 10^{-6}$	--
-0.324	11.0	$363 \times 10^{-6}$	-2.93	$1.31 \times 10^{-3}$	--	$1.57 \times 10^{-3}$	$1.1 \times 10^{12}$
-0.574	-4.37	$9.38 \times 10^{-3}$	16.8	--	--	$264 \times 10^{-3}$	$295 \times 10^{-3}$
-0.724	9.83	$364 \times 10^{-6}$	49.0	--	--	--	$205 \times 10^{-3}$
-0.924	3.19	$180 \times 10^{-6}$	18.2	$120 \times 10^{-3}$	452	R4=5.74(ohm)	$Q_3 = 814 \times 10^{-6}$ (Mho*s*N)

85 *Table SI-4: Morphology as a function of various synthetic parameters.*

Sets of samples	Synthesis variable	Crystalline phase	Morphology observed
Set I	<i>Conc. Of Ascorbic acid</i>		
	25 mM (80 °C, 60 min, 30 V)	Cu (0), Cu <sub>2</sub> O	Mixed (polygons and dendrites)
	75 mM (80 °C, 60 min, 30 V)	Cu (0)	Asymmetrical aggregates.
	100 mM (80 °C, 60 min, 30 V)	Cu (0)	Extensively branched dendrites.
Set II	<i>Applied voltage</i>		
	7.5 V (80°C, 60 min, 100mM)	Cu (0)	Dendrites with few branches.
	15 V (80°C, 60 min, 100mM)	Cu (0)	Coral reef structures with coupled dendrites.
	30 V (80°C, 60 min, 100mM)	Cu (0)	Extensively branched dendrites.
Set III	<i>Temperature of reactor</i>		
	60 °C (30V, 60 min, 100mM)	Cu (0), Cu <sub>2</sub> O	Mixed (polygons and small dendrites)
	70 °C (30V, 60 min, 100mM)	Cu (0), Cu <sub>2</sub> O	Mixed (polygons and small dendrites)
	80 °C (30V, 60 min, 100mM)	Cu (0)	Extensively branched dendrites.
	90 °C (30V, 60 min, 100mM)	Cu (0), Cu <sub>2</sub> O	Broken dendritic fragments and agglomerated structures.
Set IV	<i>Time of reaction</i>		
	10 min (30V, 80°C, 100mM)	Cu (0)	Spheres
	15 min (30V, 80°C, 100mM)	Cu (0), Cu <sub>2</sub> O	Polygons
	30 min (30V, 80°C, 100mM)	Cu (0), Cu <sub>2</sub> O	Edge covered polygons
	45 min (30V, 80°C, 100mM)	Cu (0), Cu <sub>2</sub> O	Dendritic stems

	60 min (30V, 80°C, 100mM)	Cu (0)	Extensively branched dendrites.
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