

Efficient electrosynthesis of dimethyl carbonate from urea and methanol under mild conditions

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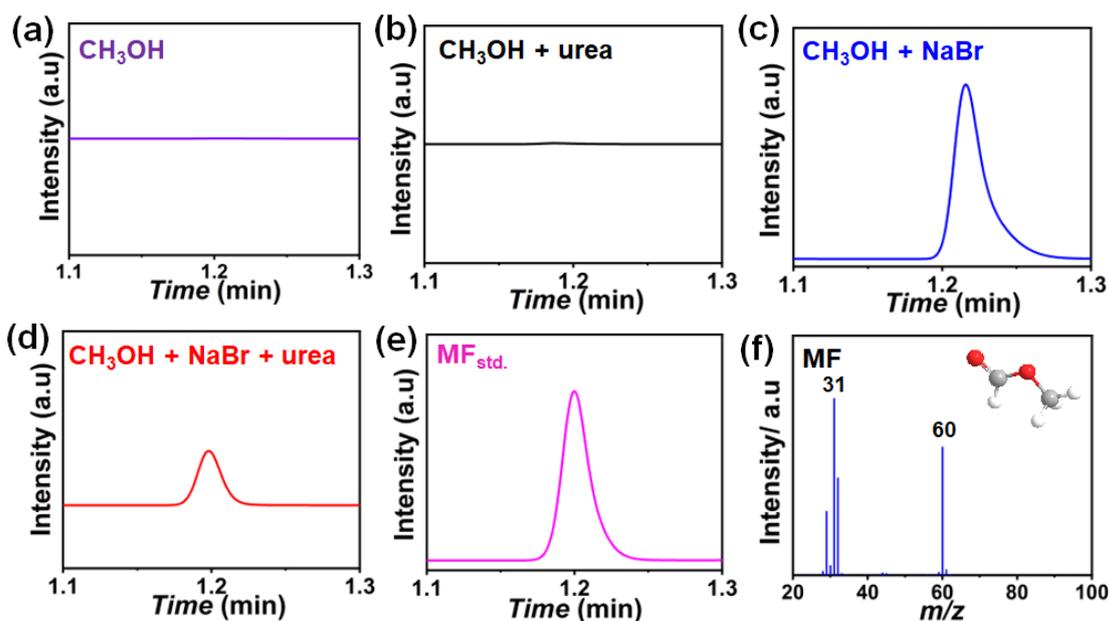


Fig. S1 Comparison of gas chromatograms of different electrochemical reactions of (a) pure CH₃OH (20 mL), (b) CH₃OH (20 mL) + urea (0.15 mol L⁻¹), (c) CH₃OH (20 mL) + NaBr (0.15 mol L⁻¹), and (d) CH₃OH (20 mL) + urea (0.15 mol L⁻¹) + NaBr (0.15 mol L⁻¹) over Pt (+)|Ti (-) electrodes under the conditions of 298 K, 20 mA cm⁻², and 36 h with that of (e) MF standard (MF_{std.}); (f) Mass spectrum of MF obtained from the experiment of “CH₃OH + urea + NaBr”.

It can be seen that in the absence of NaBr supporting electrolyte, MF was hardly produced in the methanol solution (a) or the mixed solution containing methanol and urea (b). In contrast, MF was obviously observed in the experiments of “CH₃OH + NaBr” and “CH₃OH + urea + NaBr”, indicating that NaBr is also crucial for the formation of MF.

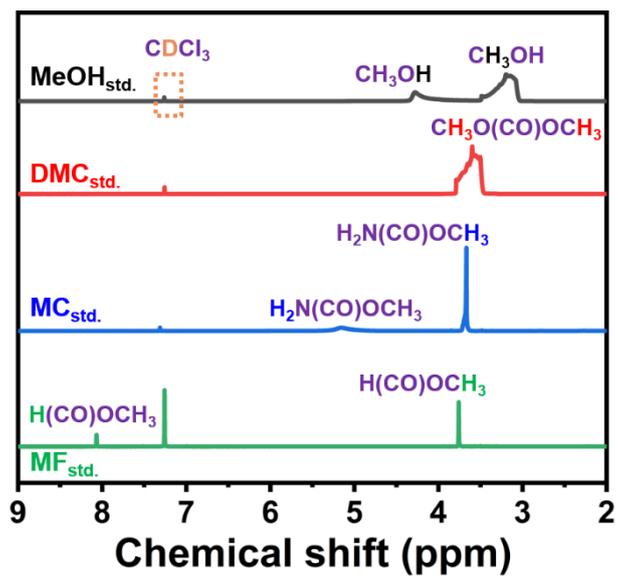


Fig. S2 ¹H NMR spectra of standard chemicals.

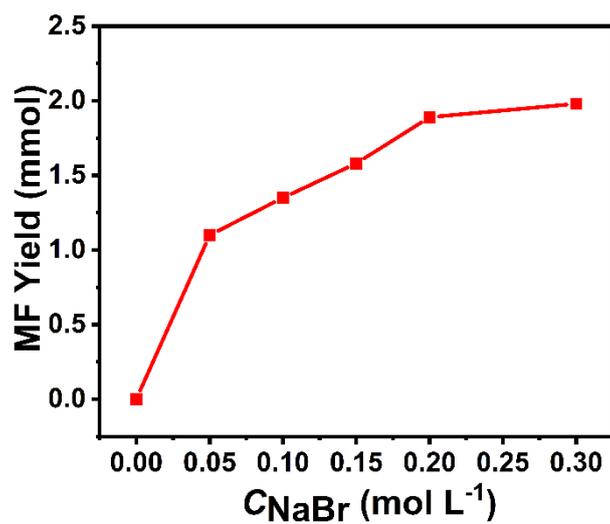


Fig. S3 Effect of NaBr concentration on MF yield over Pt (+)|Ti (-) electrodes. Reaction conditions: $C_{\text{urea}} = 0.15 \text{ mol L}^{-1}$, methanol (20 mL), $T = 298 \text{ K}$, *Current Density* = 20 mA cm^{-2} , *Time* = 36 h.

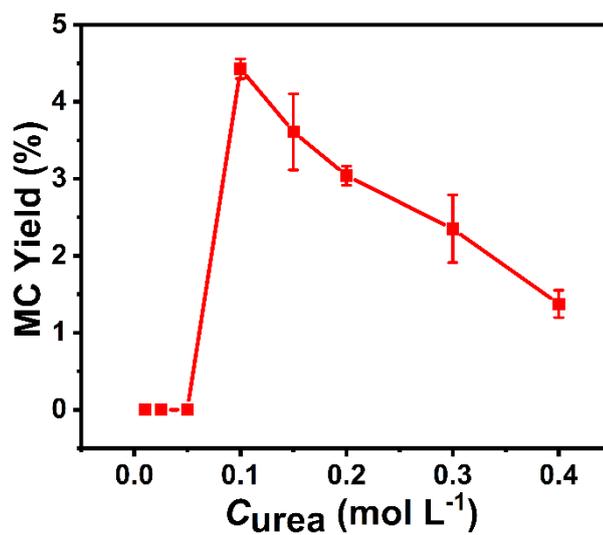


Fig. S4 Effect of urea concentration on MC yield over Pt (+)|Ti (-) electrodes. Reaction conditions: $C_{\text{NaBr}} = 0.15 \text{ mol L}^{-1}$, methanol (20 mL), $T = 298 \text{ K}$, *Current Density* = 20 mA cm^{-2} , *Time* = 36 h.

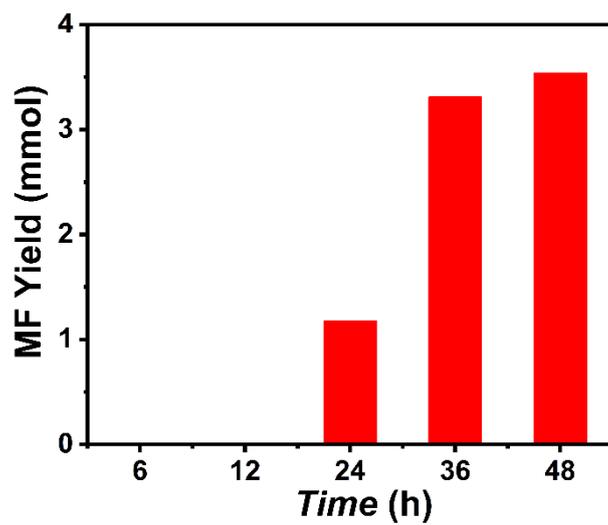


Fig. S5. Effect of reaction time on MF yield over Pt (+)|Ti (-) electrodes. Reaction conditions: $C_{\text{urea}} = 0.05 \text{ mol L}^{-1}$, $C_{\text{NaBr}} = 0.15 \text{ mol L}^{-1}$, methanol (20 mL), *Current Density* = 20 mA cm^{-2} , $T = 288 \text{ K}$.

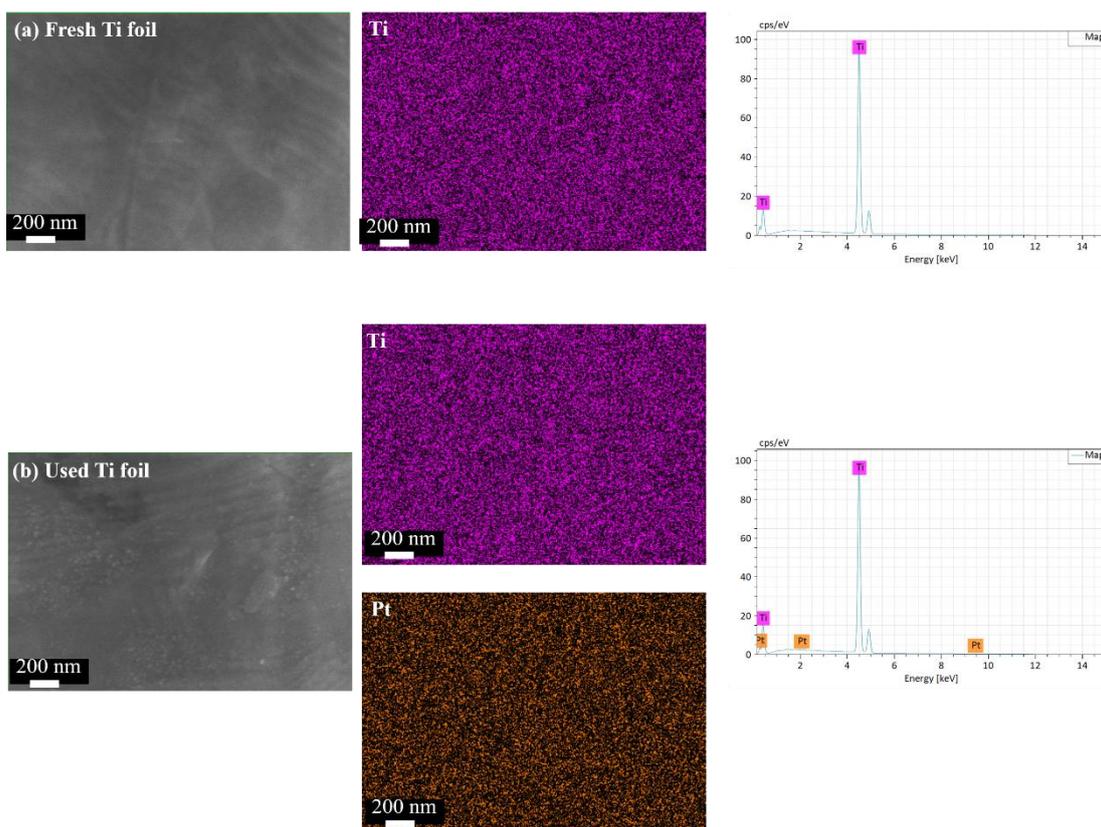


Fig. S6 SEM images, the corresponding EDX spectra and element mapping of the fresh Ti foil cathode (a) and the used one after the optimized electrosynthesis experiment (b).

It can be seen that there is a tiny difference in the morphologies of the fresh and used Ti foil cathode, indicative of the high stability of Ti foil cathode in this electrosynthesis system. In addition, the content of Pt element in the used Ti foil cathode can be neglected, suggesting that Pt element is hardly dissolved and deposited on the surface of Ti foil cathode.

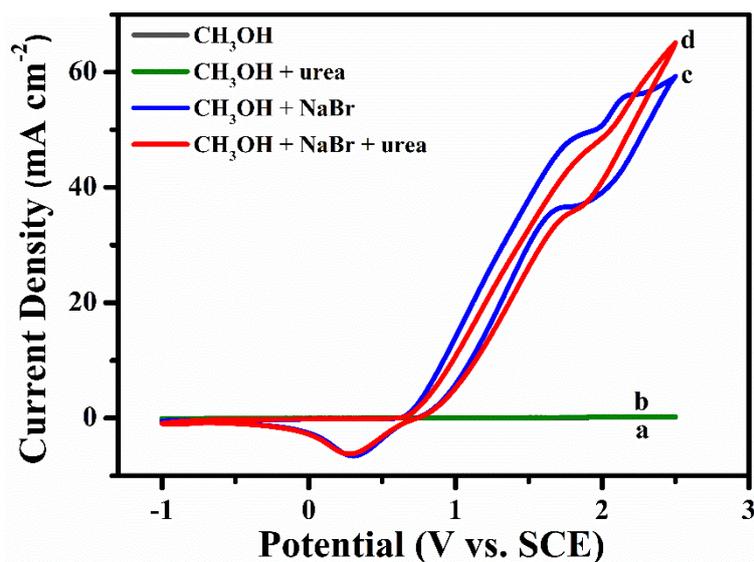


Fig. S7 CVs of (a) CH₃OH, (b) CH₃OH + urea, (c) CH₃OH + NaBr, and (d) CH₃OH + NaBr + urea at room temperature, using glassy carbon, platinum plate and saturated calomel (SCE) as the working electrode, the counter electrode, and the reference electrode, respectively.

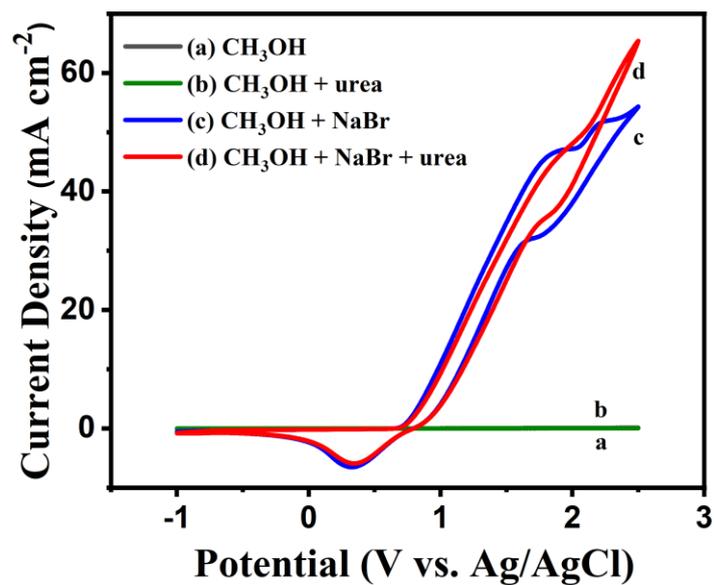


Fig. S8 CVs of (a) CH₃OH, (b) CH₃OH + urea, (c) CH₃OH + NaBr, and (d) CH₃OH + NaBr + urea at room temperature, using glassy carbon, platinum plate and Ag/AgCl as the working electrode, the counter electrode, and the reference electrode, respectively.

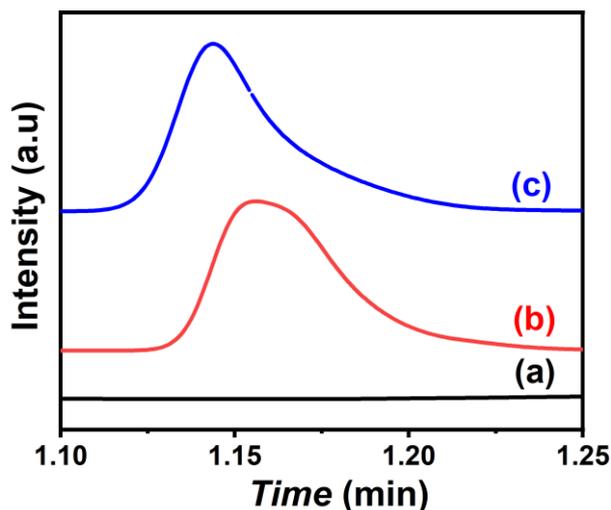


Fig S9. The GC results of different solutions: (a) the “CH₃OH + NaBr + urea” experiment under the conditions of $C_{\text{urea}} = 0.05 \text{ mol L}^{-1}$, $C_{\text{NaBr}} = 0.15 \text{ mol L}^{-1}$, methanol (20 mL), $T = 288 \text{ K}$, $\text{Current Density} = 20 \text{ mA cm}^{-2}$, $\text{Time} = 12 \text{ h}$; (b) adding 1-iodobutane into solution (a); butyl methyl ether standard (c).

There was an obviously peak at near 1.15 min after adding the 1-iodobutane into the cathode solution, which can be assigned to butyl methyl ether, suggesting that butyl methyl ether (C₄H₉OCH₃) was produced via the reaction of C₄H₉I + CH₃O⁻ → C₄H₉OCH₃ + I⁻, indicative of the existence of CH₃O⁻. Therefore, it can be concluded that conversion from CH₃OH to CH₃O⁻ happened in this non-aqueous electrosynthesis system.

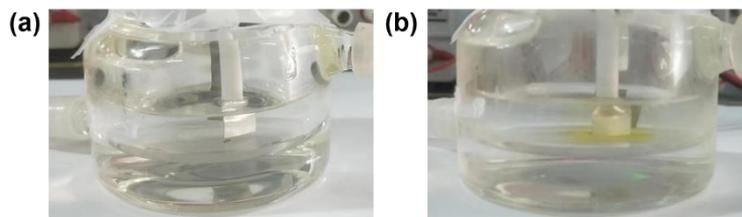


Fig. S10. Photographs of (a) the mixture before the electro-synthesis, and (b) the mixture during the electro-synthesis process of DMC from CH_3OH , urea and NaBr over Pt (+)|Ti (-) electrodes under the conditions of 0.05 mol L^{-1} urea, 20 mL methanol, 0.15 mol L^{-1} NaBr , 288 K , 20 mA cm^{-2} .



Fig. S11. Photographs of different mixtures. (a) The mixture obtained after the electro-synthesis of DMC for 0.5 h from CH_3OH , urea and NaBr over Pt (+)|Ti (-) electrodes under the conditions of 0.05 mol L^{-1} urea, 20 mL methanol, 0.15 mol L^{-1} NaBr , 288 K , 20 mA cm^{-2} ; (b) Immediately adding NaI into the mixture (a), when no electricity was supplied; (c) The mixture of CH_3OH , urea, NaBr , and NaI (0.05 mol L^{-1} urea, 20 mL methanol, 0.15 mol L^{-1} NaBr , and 0.15 mol L^{-1} NaI), when no electricity was supplied; (d) The mixture of CH_3OH , urea, and NaI (0.05 mol L^{-1} urea, 20 mL methanol, 0.15 mol L^{-1} NaI), when no electricity was supplied.

In order to confirm the formation of Br_2 in this electro-synthesis system, the color changes of the mixture were monitored under different states. As shown in **Fig. S10a**, the mixture was transparent before the electro-synthesis process started. However, during the electro-synthesis process, the color of the mixture became yellow near the Pt anode due to the evolution of Br_2 from the oxidation of Br^- (**Fig. S10b**). After the electro-synthesis was proceeded for 0.5 h , the power supply was turned off, and the color of the mixture suddenly faded and became transparent (**Fig. S11a**). These results

indicated the oxidation of Br⁻ to generate Br₂ actually happened in the Pt anode, and most of the formed Br₂ might be consumed by reaction with CH₃O⁻ to produce CH₃OBr after the power supply was turned off, accounting for the faded yellow color after the electricity was turned off.

In addition, to further verify the formation of Br₂ during the electrosynthesis process, we added NaI into the mixture in **Fig. S11a**. As obviously observed in **Fig. S11b**, the color of the mixture suddenly became much darker. In comparison with the mixture (c) (**Fig. S11c**) and the mixture (d) (**Fig. S11d**) without electricity supplied, it could be concluded that the reaction of Br₂ and NaI proceeded to form I₂ and NaBr (Br₂ + 2NaI = 2NaBr + I₂), again suggesting that a minimal amount of Br₂ was left in the mixture in **Fig. S11a**.

To sum up, with the help of electricity, the Br⁻ ion was easily oxidized to Br₂ in the Pt anode. The formed Br₂ could be further reduced to Br⁻ in the Ti cathode during the electrosynthesis process. After the power supply was turned off, the majority of the formed Br₂ might be consumed to produce CH₃OBr by reaction with CH₃O⁻.

Table S1 The electrosynthesis of DMC from urea and methanol with (i) and without (ii) Ar was used to purge air out of the cell before electrosynthesis.

Entry	Condition	DMC Yield
i	With Ar	50.4%
ii	Without Ar	44.6%

Reaction Conditions: Pt plate anode, Ti foil cathode, urea (0.05 mol L^{-1}), NaBr (0.15 mol L^{-1}), methanol (20 mL), Current Density = 20 mA cm^{-2} , 288 K, 12 h, 1 atm.

The effect of air on the electrosynthesis of DMC from urea and methanol was also investigated by comparing the results with/without Ar. As shown in **Table S1**, the obtained DMC yield without Ar was slightly lower than that using Ar. Therefore, Ar was used to purge air out of the cell, and the cell was sealed to ensure an oxygen-free environment.

Table S2 Effect of NaBr concentration on the conductivity of the mixture of CH₃OH + urea + NaBr at 298 K and 1 atm.

Entry	NaBr concentration (mol L ⁻¹)	Conductivity of mixture (ms cm ⁻¹)
1	0.05	3.25
2	0.10	5.94
3	0.15	8.94
4	0.20	10.92
5	0.30	13.31

Table S3 Effects of I₂ on the electrosynthesis of DMC from urea and methanol in an undivided cell.^a

Entry	Conditions	DMC Yield ^b
1	Without electricity	n. d.
2	With a current density of 20 mA cm ⁻²	n. d.

^a Pt plate anode, Ti foil cathode, 0.05 mol L⁻¹ urea, 20 mL methanol, 0.075 mol L⁻¹ I₂, 288 K, 12 h, 1 atm.
^b Yield was analyzed by GC-MS and GC with an internal standard, n. d. = not detected.

Table S4 Effects of Br₂ on the electrosynthesis of DMC from urea and methanol in an undivided cell.^a

Entry	Conditions	DMC Yield ^b
1	Without electricity	n. d.
2	With a current density of 20 mA cm ⁻²	n. d.

^a Pt plate anode, Ti foil cathode, 0.05 mol L⁻¹ urea, 20 mL methanol, 0.075 mol L⁻¹ Br₂, 288 K, 12 h, 1 atm.
^b Yield was analyzed by GC-MS and GC with an internal standard, n. d. = not detected.

Table S5 Effects of anode materials on the electrosynthesis of DMC from urea and methanol in an undivided cell.^a

Entry	Anode material	DMC Yield^b
1	Pt plate	50.4%
2	graphite plate	45.0%
3	glassy carbon (GC)	25.7%

^aTi foil cathode, urea (0.05 mol L⁻¹), NaBr (0.15 mol L⁻¹), methanol (20 mL), Current Density = 20 mA cm⁻², 288 K, 12 h, 1 atm.

^b Yield was analyzed by GC-MS and GC with an internal standard, n. d. = not detected.

Table S6 Determination of Pt content in the solution after the electrosynthesis of DMC from urea and methanol over Pt (+)|Ti (-) electrodes under the conditions of 0.05 mol L⁻¹ urea, 20 mL methanol, 0.15 mol L⁻¹ NaBr, 20 mA cm⁻², 288 K, 12 h, 1 atm.

Element	Concentration ($\mu\text{g L}^{-1}$) ^a	Wt (%) ^b
Pt	3.6×10^{-2}	4.5×10^{-9}

^a Obtained by inductively coupled plasma mass spectrometry (ICP-MS) using a PerkinElmer NexION 1000

^b Based on the total weight of the solution after the electrosynthesis experiment

As shown **Table S6**, the content of Pt element in the solution after the electrosynthesis experiment can be negligible, indicating Pt anode is very stable in our non-aqueous system.

Table S7 Comparison of electrosynthesis of DMC from urea and methanol with reported thermo-synthesis results.

Types	Catalysts	Starting Materials	Temperature (K)	Pressure	Time (h)	DMC Yield (%)	Ref.
Thermo-synthesis	ZnO-SrO	n(methanol) : n(urea) = 15	443	No mention	6	35	1
	ZnO(0.54)-Nb ₂ O ₅ (0.20)TiO ₂ (0.26)	n(methanol) : n(urea) = 20	413	No mention	4	39.1	2
	ZnO	n(methanol) : n(urea) = 20	443	No mention	8	~30	3
	Zn/Al mixed oxides	n(methanol) : n(urea) = 20	453	No mention	10	~36.5	4
	ZnO(0.7)-CeO ₂ (0.3)	n(methanol) : n(urea) = 20	443	No mention	4	28.9	5
	ZnO(0.64)-CeO ₂ (0.26)-La ₂ O ₃ (0.1)	n(methanol) : n(urea) = 20	443	20 bar	4	50.4	6
	ZnO-CaO	n(methanol) : n(urea) = 20	453	No mention	10	41.2	7
	Fe ₂ O ₃ /HMCM-49	n(methanol) : n(urea) = 160	453	No mention	8	33.4	8
Electrosynthesis	None	0.05 mol L⁻¹ urea in methanol	288	1 atm	12	50.4	This work

Table S8 Comparison of electrosynthesis of DMC from urea and methanol with the reported literatures on electrosynthesis of DMC from CO₂ and methanol.

Entry	Electrochemical cell	Conditions	Reactants and Supporting Electrolyte	Time (h)	Temperature (K)	DMC Yield (%)	Ref.
1	Undivided cell	Nanoporous copper incorporated platinum, Mg rod, -2.2 V vs. Ag	CO ₂ , CH ₃ OH, BmimBF ₄ , CH ₃ I	6	298	81	9
2	Undivided cell	Pt (-) Pt (+), 5.5 V (cell potential)	CO ₂ , CH ₃ OH, BmimBr, epoxide	48	303	75.5	10
3	Undivided cell	In, Pt foil, -1.7 V vs. Ag	CO ₂ , CH ₃ OH, BmimBF ₄ , CH ₃ I	6	313	76	11
4	Undivided cell	Cu (-) Mg (+), -1.8 V vs. Ag/AgI	CO ₂ , CH ₃ OH, BmimBF ₄ , CH ₃ I	6	298	33	12
5	Undivided cell	Pt (-) Pt (+), 5.5 V (cell potential)	CO ₂ , CH ₃ OH, BmimBr, CH ₃ OK	48	303	3.9	13
6	Undivided cell	Graphite (-) Pt (+), 4.0 V (cell potential)	CO ₂ , CH ₃ OH, BzmimCl CO ₂ , CH ₃ OH, BmimCl CO ₂ , CH ₃ OH, BmimOH CO ₂ , CH ₃ OH, BmimBr CO ₂ , CH ₃ OH, BmimBF ₄ CO ₂ , CH ₃ OH, EmimBF ₄ CO ₂ , CH ₃ OH, EmimBr	60	293	3.8 3.7 3.1 2.1 0.3 1.3 0.6	14
7	Divided cell	Pt/Nb plate (-) Pt/Nb plate (+), 1.2 V vs. Ag/AgCl	CO ₂ , CH ₃ OH, BmimBr, CH ₃ OK	48	279	12.5	15
8	Undivided cell	Graphite (-) Pt (+),	CO ₂ , CH ₃ OH, BmimOH	40	293	0.85	16

		3.5 V (cell potential)	CO ₂ , CH ₃ OH, ApmimBr			1.06	
			CO ₂ , CH ₃ OH, BmimBr			0.43	
			CO ₂ , CH ₃ OH, BmimBF ₄			0.2	
9	Undivided cell	Au (-) glassy carbon (+), Pd/C catalyst, 12 mA cm ⁻²	CO ₂ , CH ₃ OH, NaBr	-	room temperature	FE 60%	17
10	Undivided cell	Ti (-) Pt (+), 20 mA cm⁻²	Urea, CH₃OH, NaBr	12	288	50.4	This work

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