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Supporting Information

Nickel Carbonate ($Ni_2(CO_3)_3$) as an Electrocatalyst and Photo-electrocatalyst for Methanol Electro-oxidation

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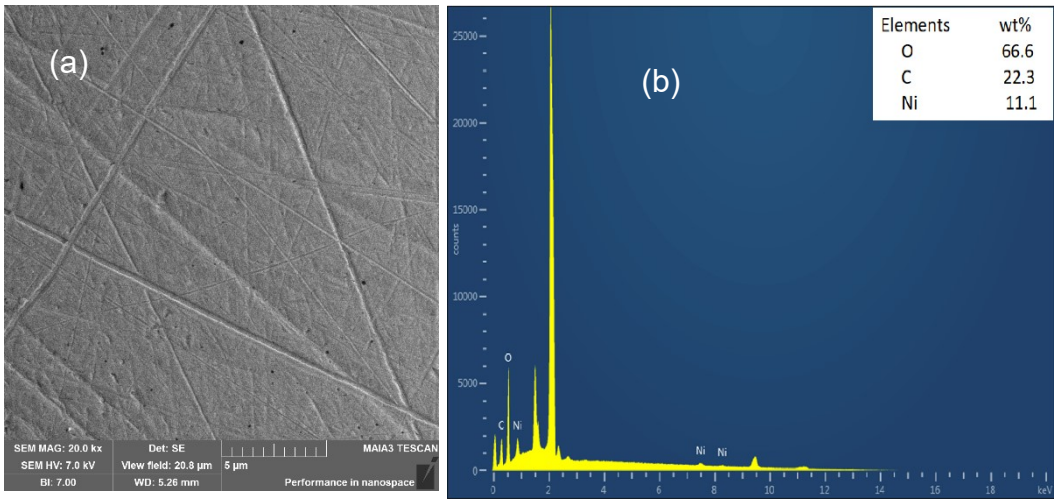

Figure S(1). SEM image of bare Pt electrode surface (a), EDX mapping of $Ni_2(CO_3)_3$ (b).

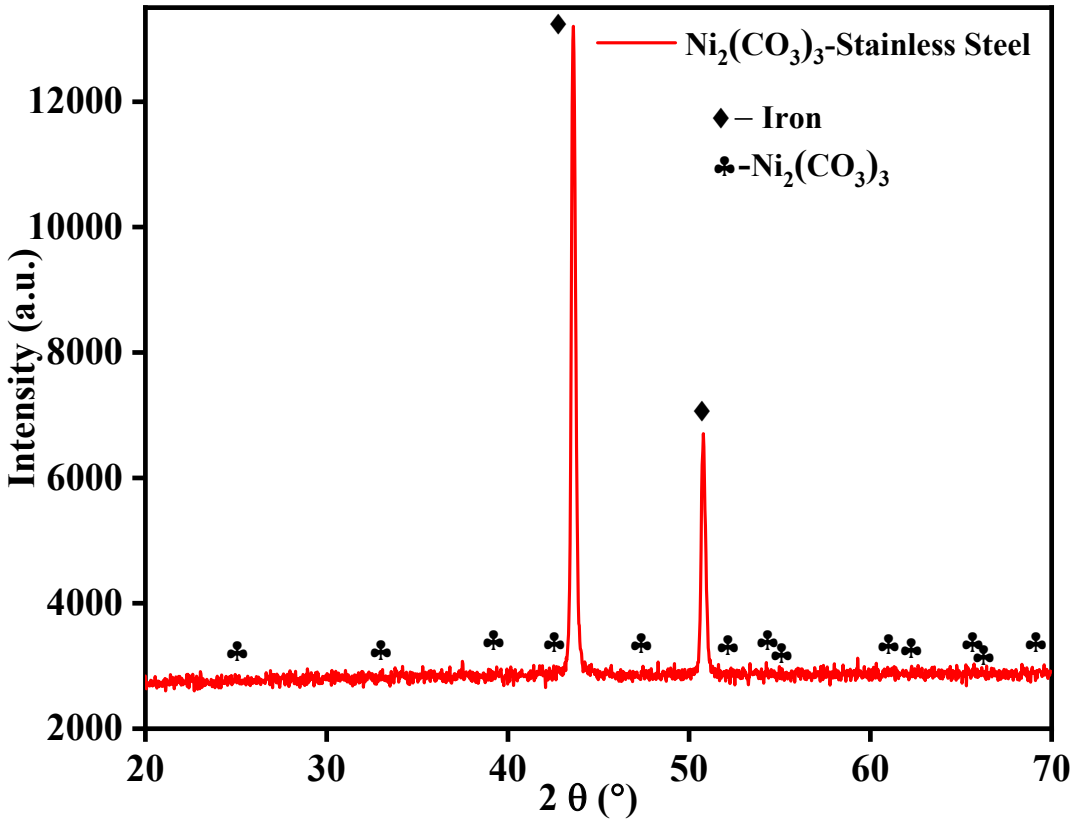

Figure S(2). X-ray diffraction pattern of $Ni_2(CO_3)_3$ on the Stainless-steel substrate

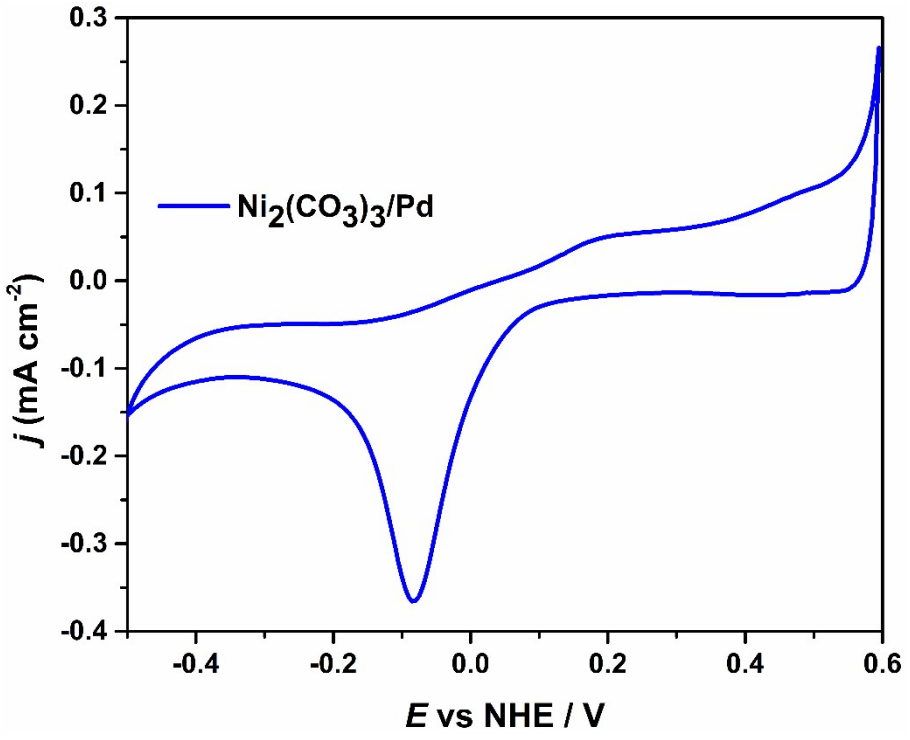

Figure S(3). CV of $Ni_2(CO_3)_3$/Pd in 0.10 M KOH (pH 13) solution at a scan rate of 50 $mV \cdot s^{-1}$ in the absence of CH_3OH.

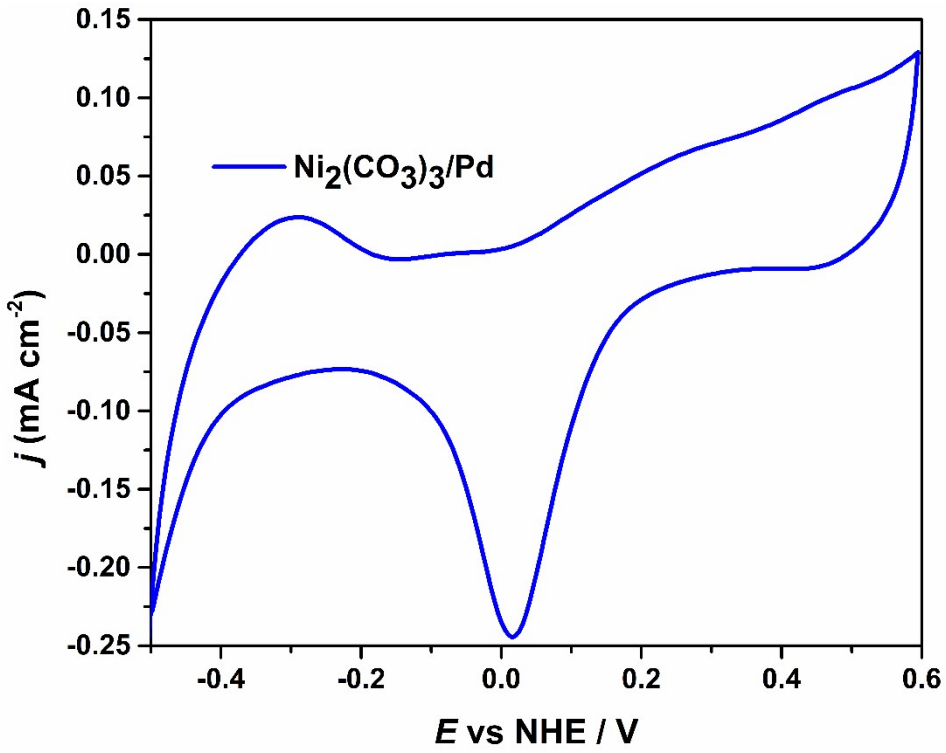

Figure S(4). CV of $Ni_2(CO_3)_3$/Pd in 1.0 M Na_2CO_3 (pH 10.3) solution at a scan rate of 50 $mV \cdot s^{-1}$ in the absence of CH_3OH.

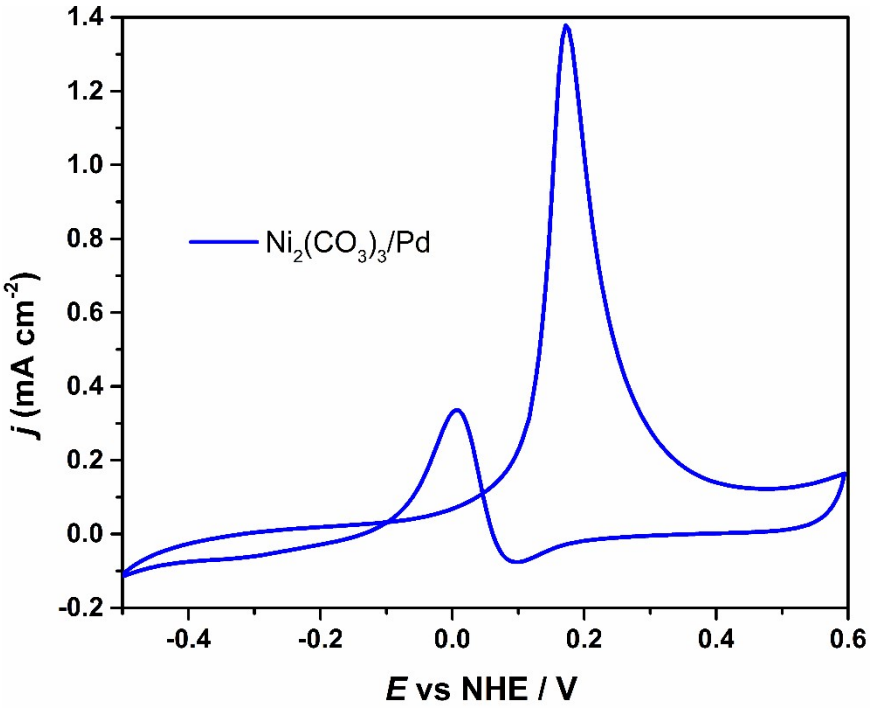

Figure S(5). CV of $Ni_2(CO_3)_3$/Pd in 1.0 M Na_2CO_3 (pH 10.3) containing 1.0 M CH_3OH solution at a scan rate of 50 $mV \cdot s^{-1}$.

Table 1. Comparison of methanol oxidation activity.

Electrodes and Catalyst	**Electrolytes**	**Methanol [M]**	**J ($mA \cdot cm^{-2}$)**	**$E_{p,a}$ a=anodic potential (NHE)**	**Ref.**
Pt	0.1 M KOH	1	0.310	0.07 V	Present work
	1 M Na_2CO_3	1	0.91	0.1 V	
Pd	0.1 M KOH	1	0.9	-0.01 V	Present work
$Na_3Co^{III}(CO_3)_3$/Pt	0.1 M KOH	1	19.7	0.1 V	[1]
	1 M Na_2CO_3	1	5.8	0.1 V	
$Na_3Co^{III}(CO_3)_3$/Pd	0.1 M KOH	1	4.3	-0.01 V	[1]
NiO/ITO	0.5 M NaOH	0.5	10.8	0.5 V	[2]
NiP/ITO	0.5 M NaOH	0.5	30.4	0.5 V	[2]
NiPR/ITO	0.5 M NaOH	0.5	62.6	0.5 V	[2]
Anodic NiO	0.1 M NaOH	1	65.0	0.74 V*	[3]
Urchin like $NiCo_2O_4$	0.1 M KOH	0.5	13.49	0.82 V*	[4]
NiO_x/MnO_x/GC	0.5 M NaOH	0.5	9.72	0.79 V*	[5]
NiO NTs-400	1.0 M KOH	0.5	24.3	1.5 V*	[6]
Mn doped $Ni(OH)_2$	1.0 M NaOH	0.5	14.18	0.5 V**	[7]
$NiMoO_4$ nanorod	1.0 M KOH	2	49	0.89 V*	[8]
$Ni_2(CO_3)_3$/Pt	0.1 M KOH	1	19.8	0.08 V	Present work
	1 M Na_2CO_3	1	6.3	0.12 V	
$Ni_2(CO_3)_3$/Pd	0.1 M KOH	1	5.2	0.1 V	Present

	1 M Na_2CO_3	1	1.39	0.18 V	work

*: Anodic potential vs. RHE, **: Anodic potential vs. Ag/AgCl

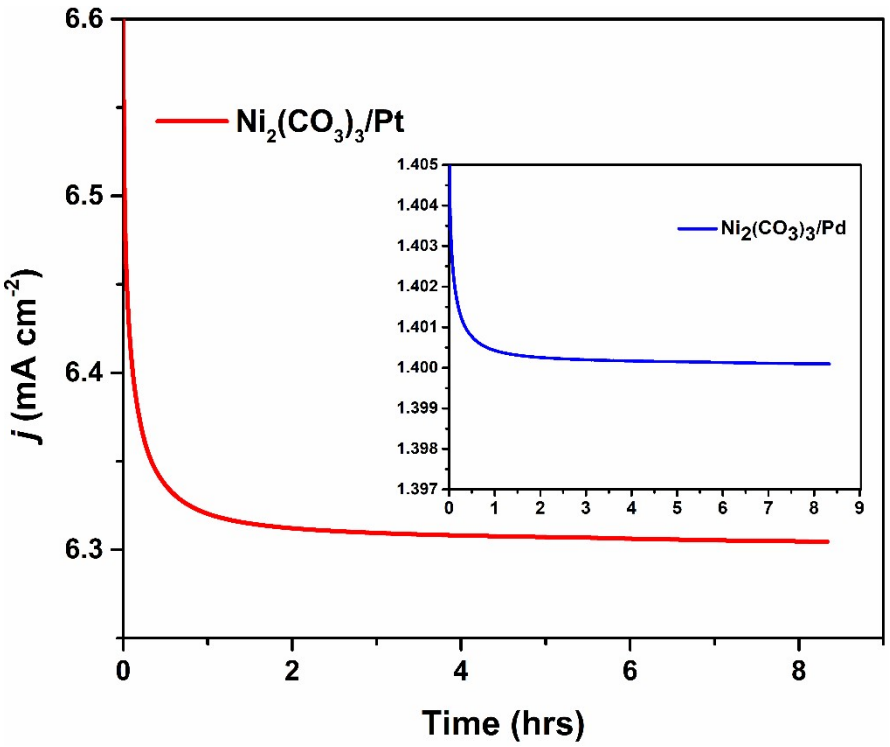

Figure S(6) Chronoamperometry study of $Ni_2(CO_3)_3$/Pt and $Ni_2(CO_3)_3$/Pd for methanol oxidation in 1.0 M Na_2CO_3 with 1.0 M CH_3OH at constant potential 0.1 V and 0.13V vs NHE

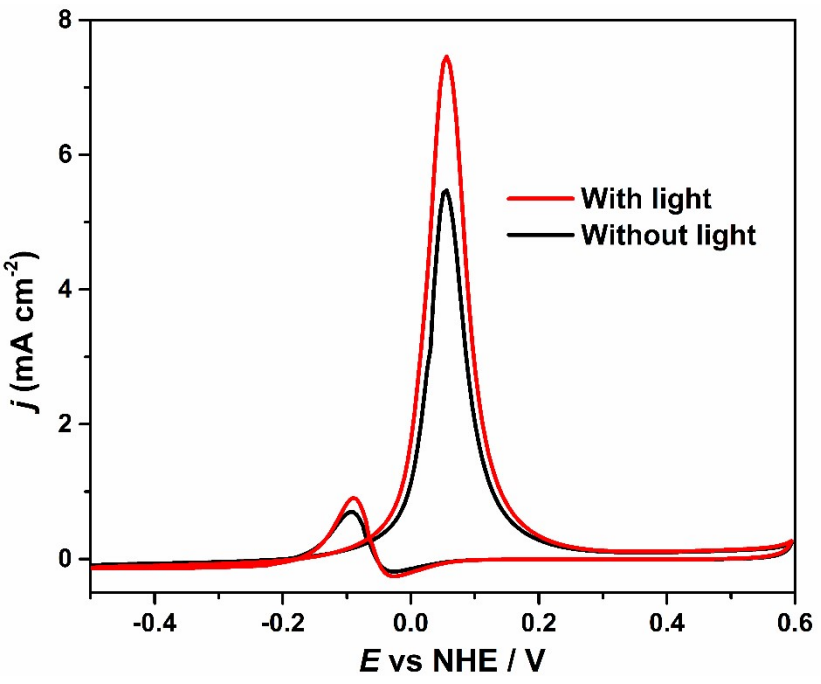

Figure S(7). CV curves of $Ni_2(CO_3)_3$/Pd in 0.10 M KOH with 1.0 M CH_3OH at the scan rate of 50 mV s^{-1} with light irradiation and without light

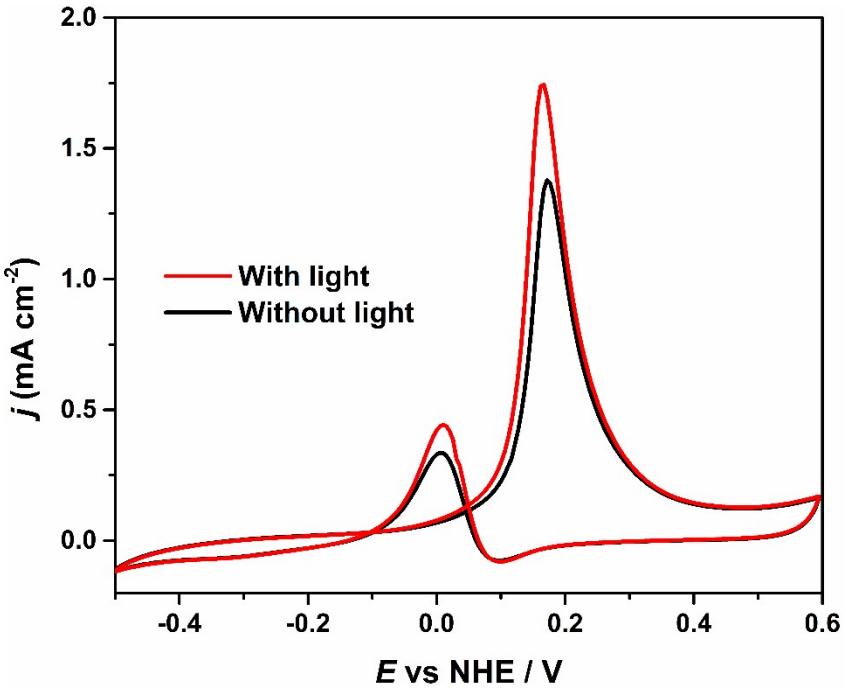

Figure S(8). CV curves of $Ni_2(CO_3)_3$/Pd in 1.0 M Na_2CO_3 with 1.0 M CH_3OH at the scan rate of 50 mV s^{-1} with light irradiation and without light

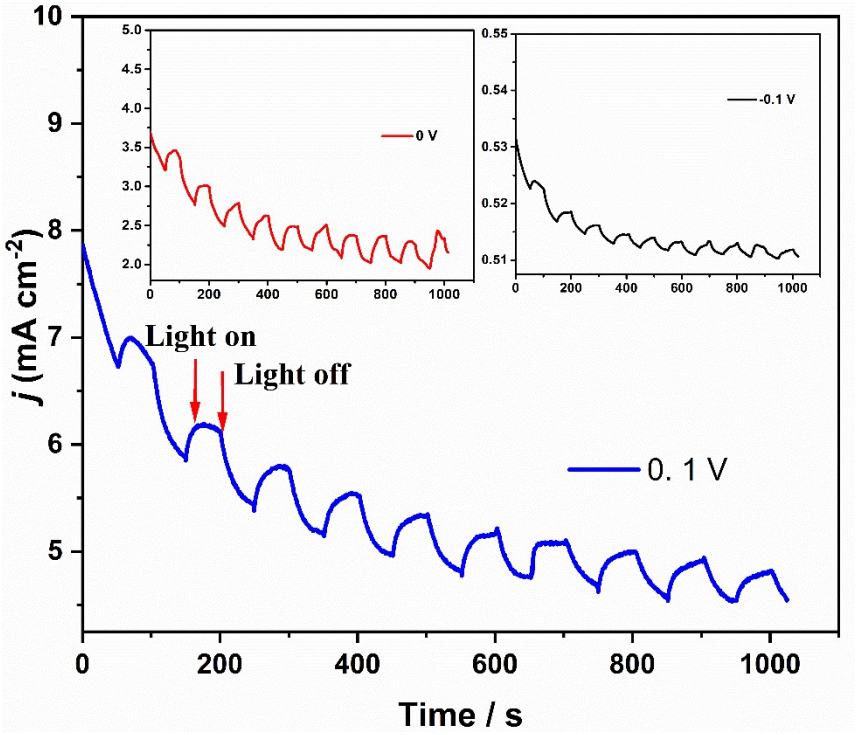

Figure S(9). Chronoamperometry curves of $Ni_2(CO_3)_3$/Pd in 0.10 M KOH with 1.0 M CH_3OH with light and dark at constant potentials.

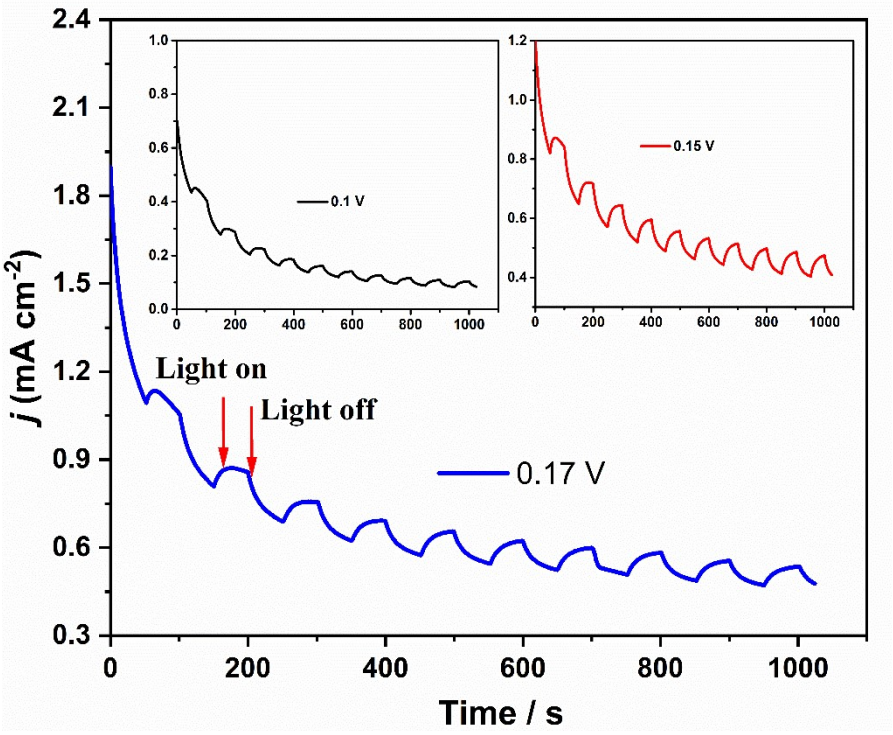

Figure S(10). Chronoamperometry curves of $Ni_2(CO_3)_3$/Pd in 1.0 M Na_2CO_3 with 1.0 M CH_3OH with light and dark at constant potentials.

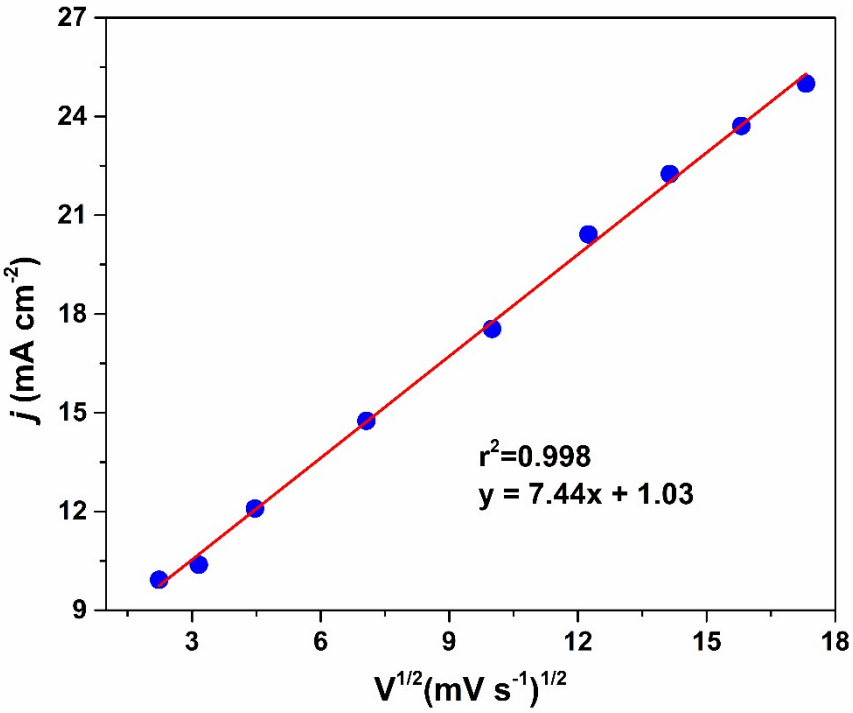

Figure S(11). Plot of anodic current density vs. the square root of the scan rate in 0.10 M KOH and 1.0 M CH_3OH.

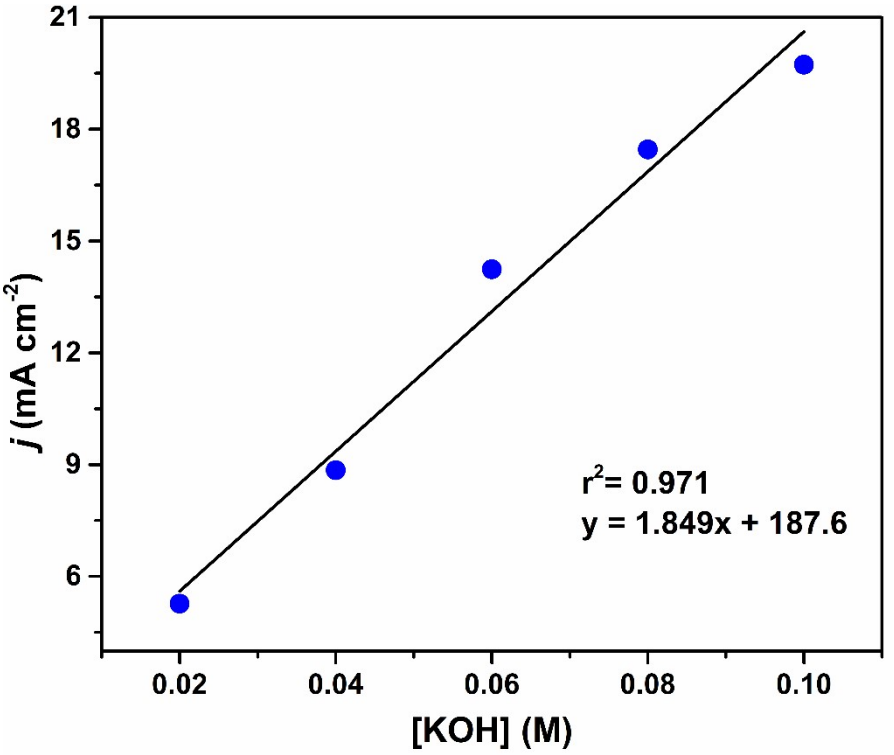

Figure S(12). Linear fit of the different concentration of KOH in the presence of methanol..

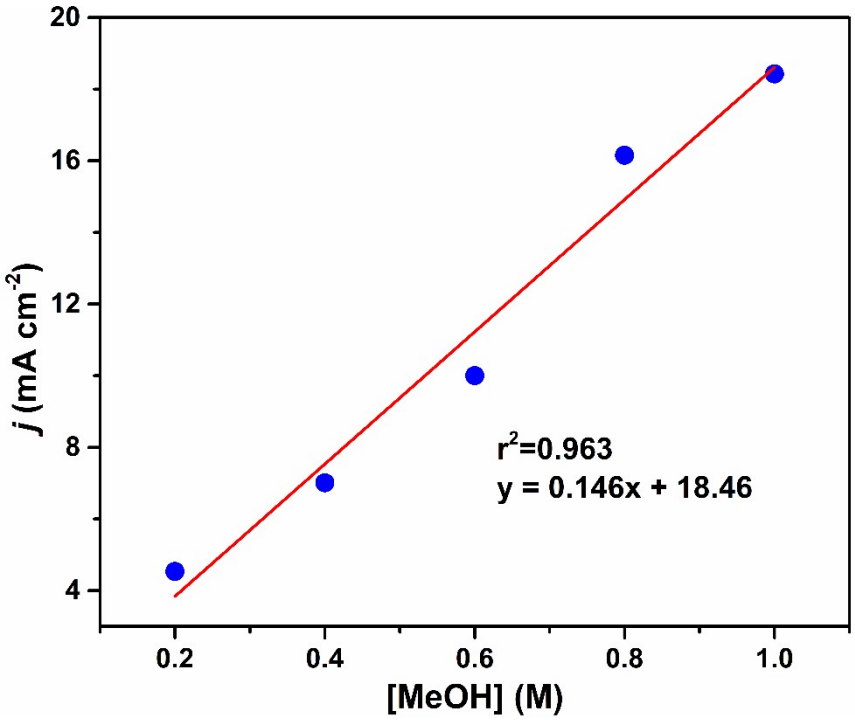

Figure S(13). Linear fit of the different concentration of methanol in KOH medium

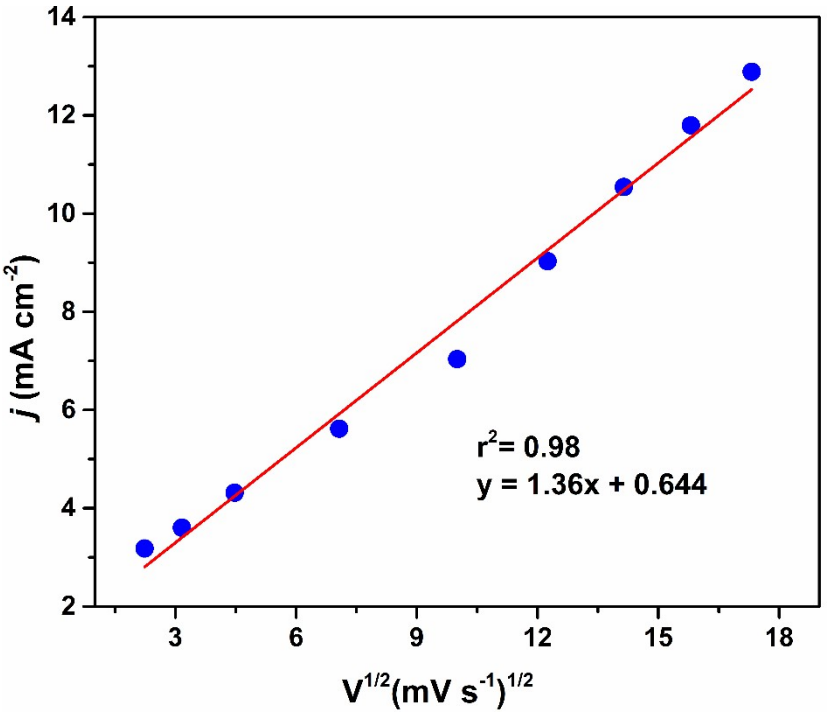

Figure S(14). The plot of anodic current density and the square root of the scan rate in 1.0 M Na_2CO_3 and 1.0 M CH_3OH.

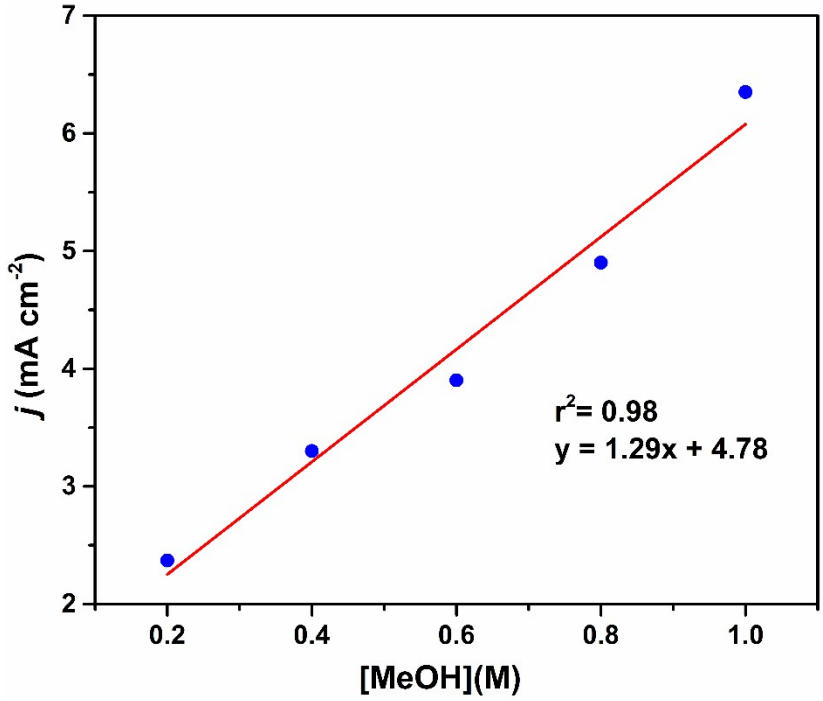

Figure S(15). Linear fit of the different concentration of methanol in Na_2CO_3 medium.

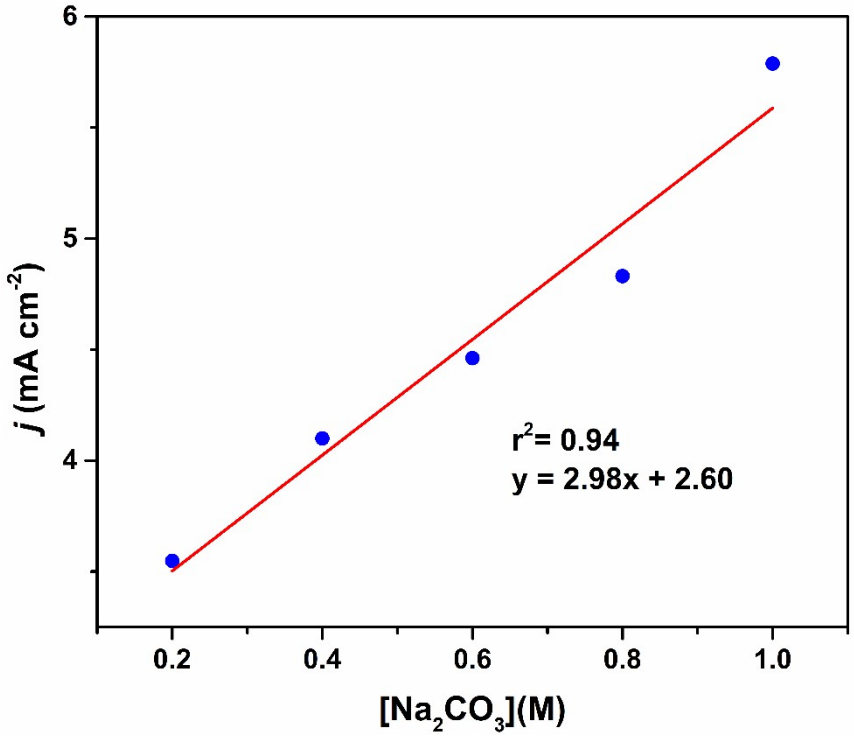

Figure S(16). Linear fit of the different concentration of Na_2CO_3 in the presence of methanol.

Product analysis

After the completion of reaction, the reaction mixture was analyzed by Gas chromatography. The samples were injected into the GC unit with the help of gastight syringe. The inlet used for the analysis comprised of split/splitless liner with the split ratio maintained at around 15:1 and the temperature maintained at around 140 °C. The temperature of oven was maintained at 40 °C. and was then heated to 60 °C with the ramp rate of 30 °C min^{-1} and maintained at same temperature for 4 and 2 min. Finally, the oven temperature was increased to 180 °C with ramp rate of 60 °C and held at the same temperature for another 5 min. The detector used to analyze the sample was TCD and the temperature was set to 250 °C for the efficient detection of the reactant medium. The products formed were determined by the confirmation with authentic sample. The results obtained by the GC are represented in Fig S16. The data obtained from Fig S 16, confirms that only CO_2 was formed from the oxidation of methanol with the retention time of around 11 min. This can be confirmed on comparison with the injected authentic CO_2 data.

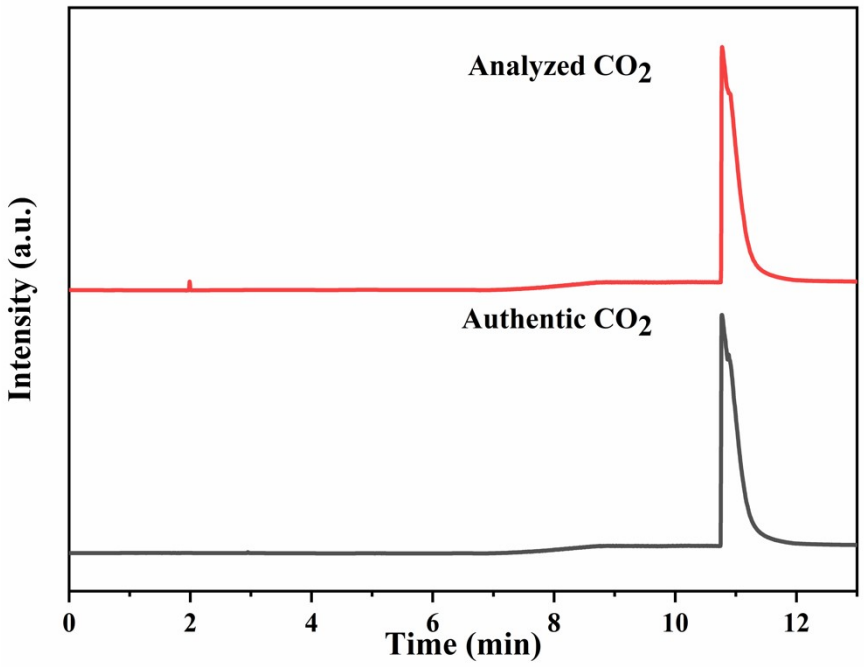

Figure S(17). Gas chromatogram of authentic CO_2 and methanol oxidation reaction sample.

References

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