Electronic Supplementary Information:

Selective electrochemical reduction of carbon dioxide to ethanol by relay catalytic platform

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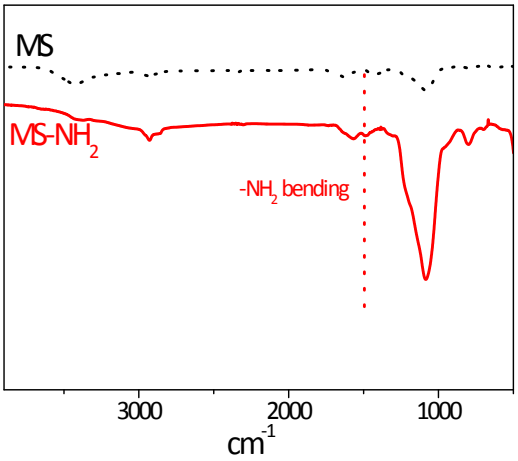

Fig. S1. IR spectrum of MS and MS-NH_2.

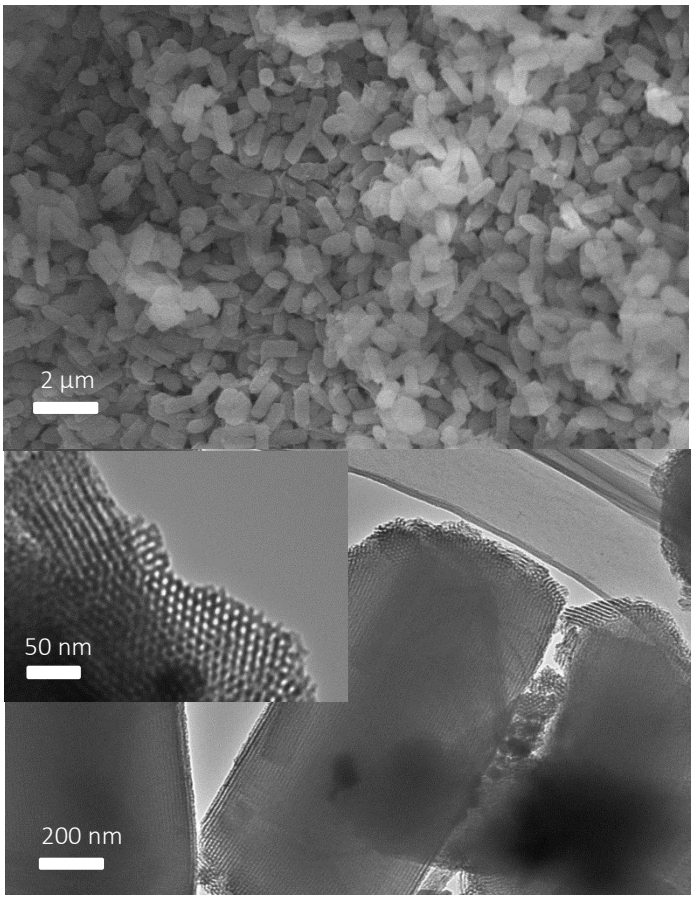

Fig. S2. SEM (a) and TEM (b) images of MS-NH_2.

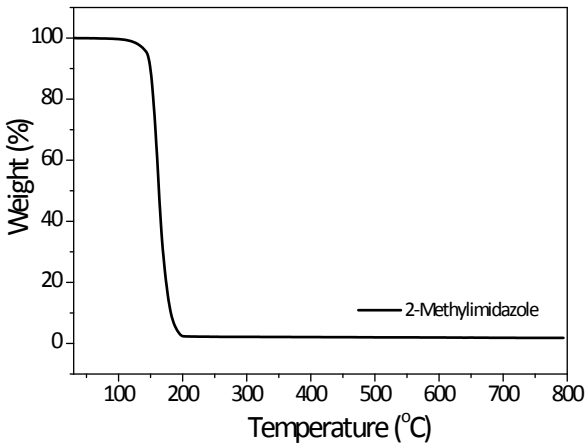

Fig. S3. TGA analysis of 2-methylimidazole in N_2, which shows that the 2-methylimidazole can be completely decomposed.

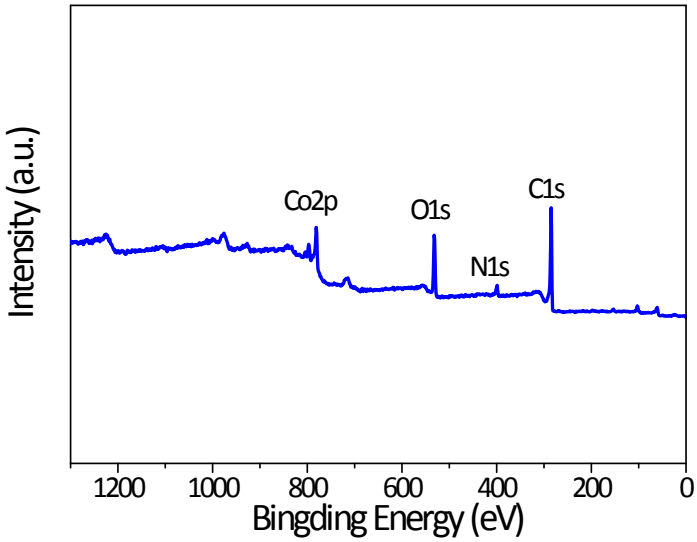

Fig. S4. XPS spectrum of CNT-MC/Co.

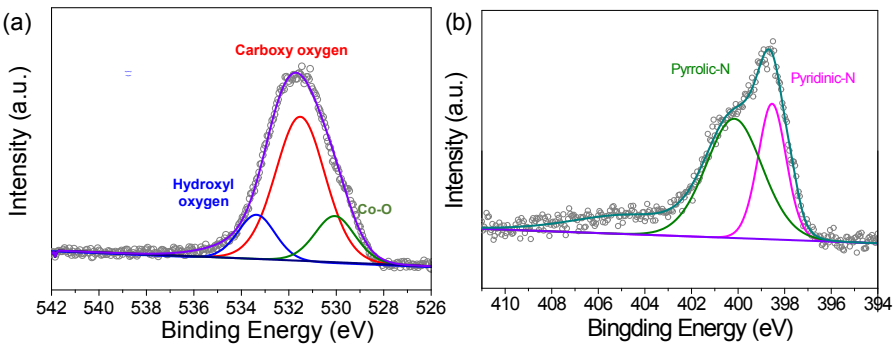

Fig. S5. O1s (a) and N1s (b) spectrum of MC-CNT/Co.

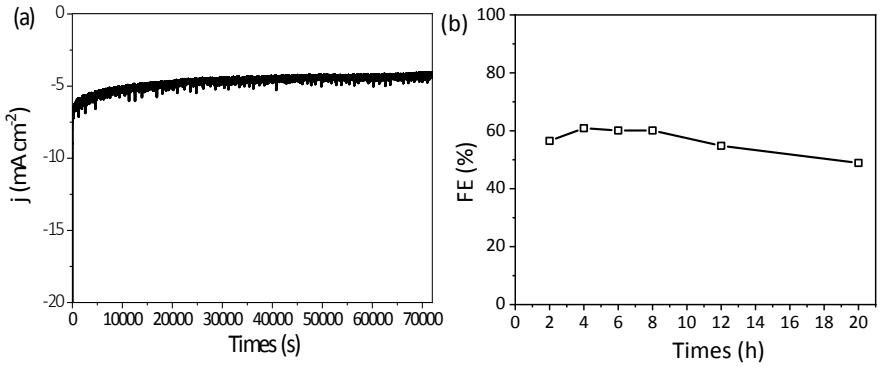

Fig. S6. Total current density (a) and FE (b) versus time in 0.5 M $KHCO_3$ under a CO_2 atmosphere on MC-CNT/Co.

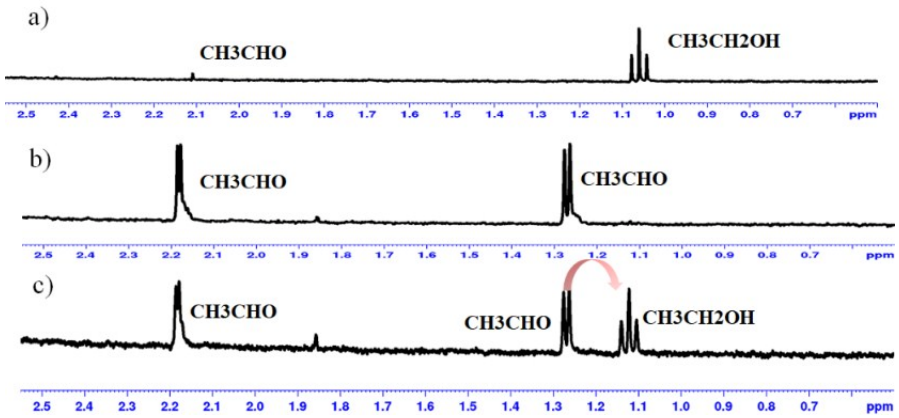

Fig. S7. Liquid product analysis (1H NMR spectra) over MC-CNT/Co catalyst at -0.32 V (vs RHE) in CO_2-saturated (a) and CH_3CHO-added (b and c) 0.5 M $KHCO_3$ solution.

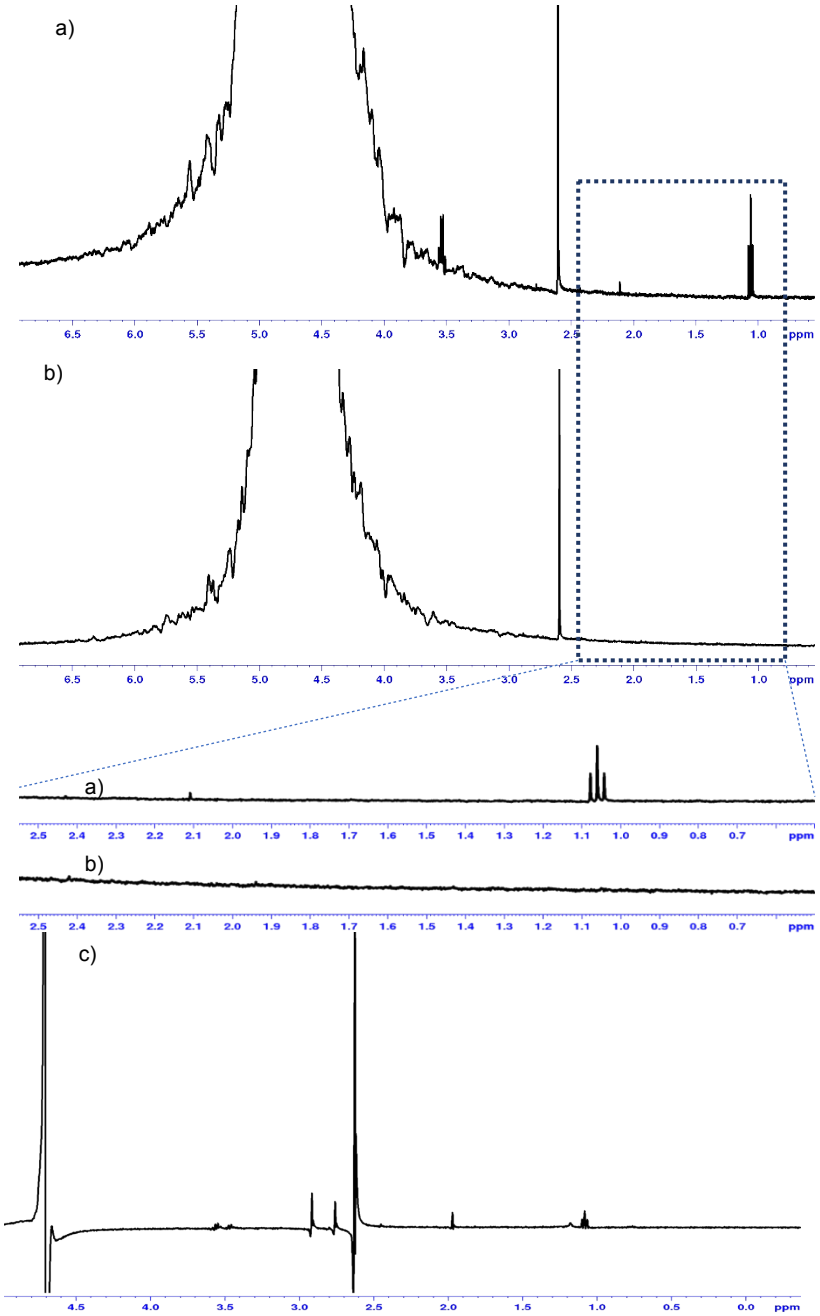

Fig. S8. Liquid product analysis (1H NMR spectra) over MC-CNT/Co catalyst at -0.32 V (vs RHE) in CO_2-saturated (a) and Ar-saturated (b) 0.5 M $KHCO_3$ solution; and liquid product analysis (1H NMR spectra using water suppression method) over MC-CNT/Co catalyst at -0.32 V (vs RHE) in CO_2-saturated (c).

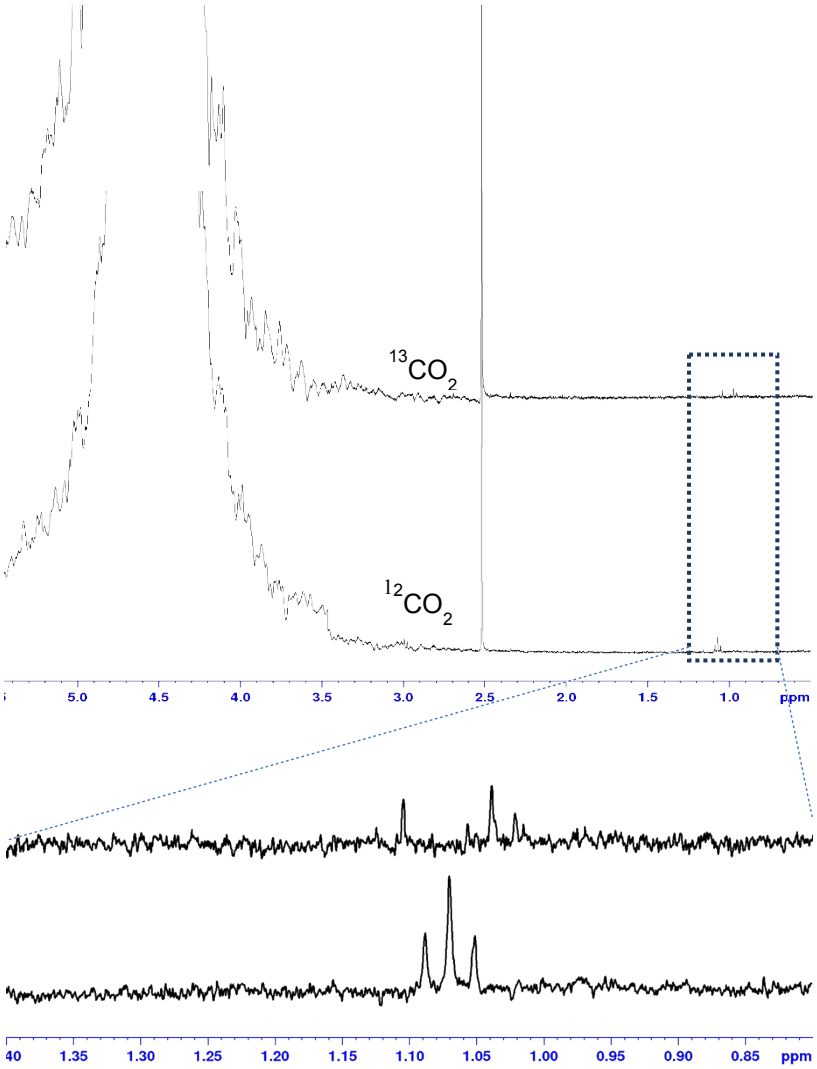

Fig. S9. Liquid product analysis (1H NMR spectra) over MC-CNT/Co catalyst over electrolysis at -0.32 V (vs RHE) in $^{12}CO_2$-saturated and $^{13}CO_2$-saturated 0.5 M $KHCO_3$ solution.

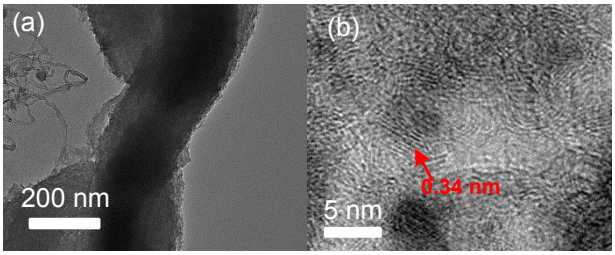

Fig. S10. TEM images of MC-CNT.

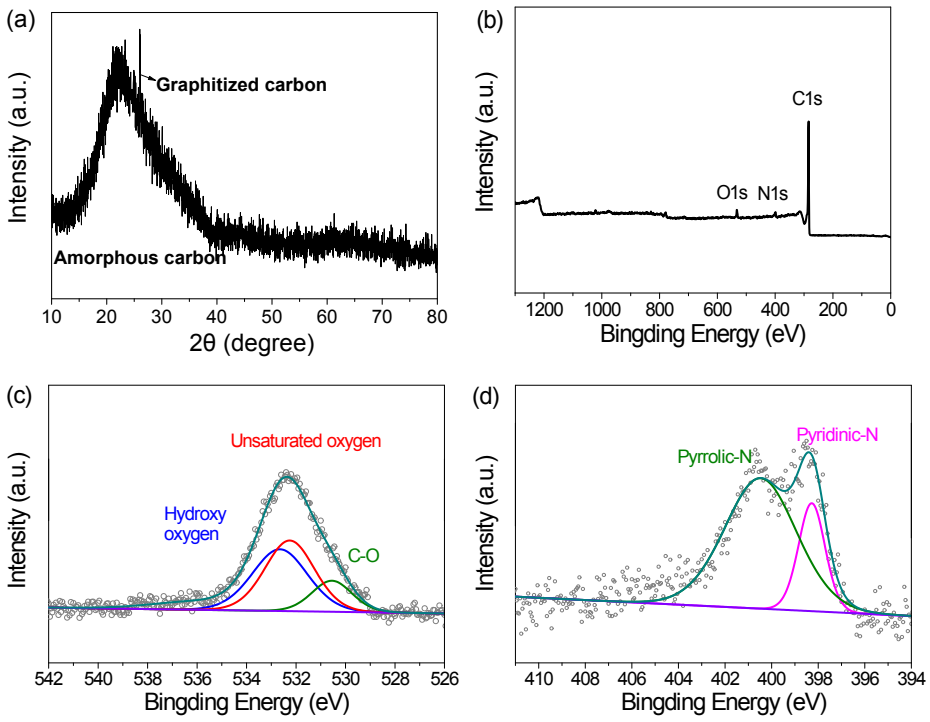

Fig. S11. XRD (a) and XPS (c-d) spectra of MC-CNT.

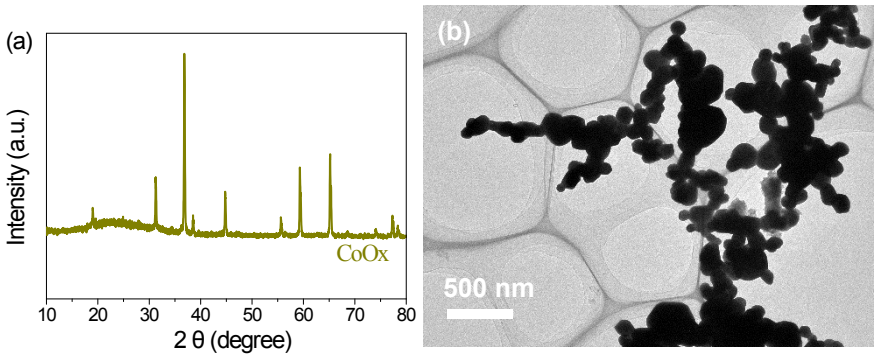

Fig. S12. XRD pattern(a) and TEM image (b) of Co-O*x* derived from $Co(NO_3)_2$ pyrolysis.

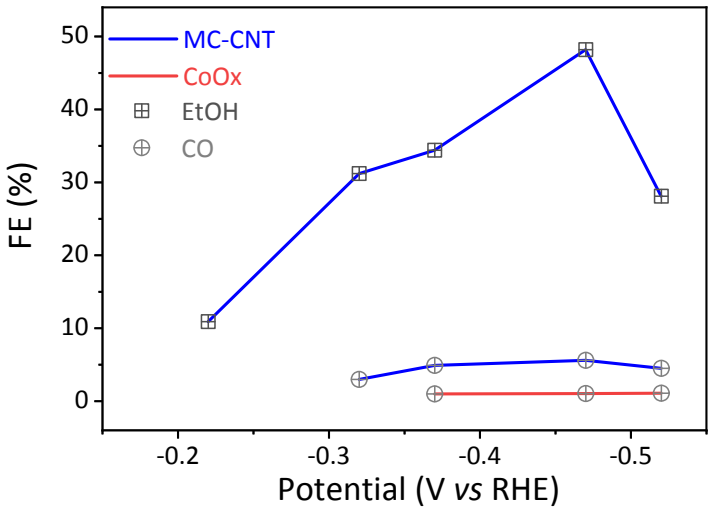

Fig. S13. Faradic efficiencies of EtOH and CO over CoOx and MC-CNT catalysts in CO_2-saturated 0.5 M $KHCO_3$ solution in the potential range from -0.2 V to -0.6 V (*vs* RHE).

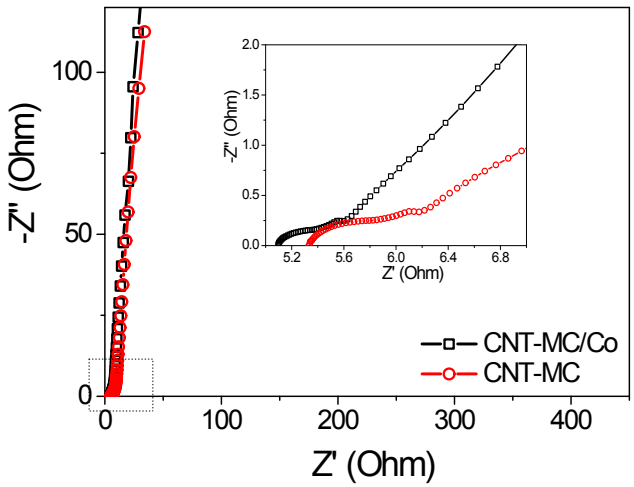

Fig. S14. The experimental and simulated EIS spectra of CNT-MC/Co and CNT-MC electrodes in CO_2-saturated 0.5 M $KHCO_3$.