Supporting Information

Enzyme-Mimicking Redox-Active Vitamin B12 Functionalized MWCNT-Catalyst for Nearly 100% Faradaic Efficiency in Electrochemical CO_2 Reduction

Yashly Yesudas K,[a,b] Mani Balamurugan,[c] Ki Tae Nam,[c] Buvaneswari Gopal,[b]* Annamalai Senthil Kumar[a,b] *

[a]Carbon Dioxide Research and Green Technology Centre, Vellore Institute of Technology University,
Vellore 632 014, India

[b]Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology University, Vellore 632 014, India

[c]Department of Materials Science and Engineering, Seoul National University, Seoul 151-742, Korea.

**Corresponding Author's email addresses: askumar@vit.ac.in & askumarchem@yahoo.com*

1. Calculation for the Turnover Number and Turnover Frequency

1.1. Turnover Number (TON)

The Turnover Number (TON) is a measure of the catalytic efficiency of the MWCNT@B12 surface. It is calculated as the ratio of the number of moles of CO formed to the number of moles of active B12 catalyst.

TON = (Number of moles of CO formed)/(Number of moles of active B12)

Given values:

- CO concentration: 36.02 μmol (obtained by bulk electrolysis experiment at an optimal potential, -1.35 V vs Ag/AgCl (-0.727 V vs RHE) and product measured by GC technique, where nearly 100% Faradaic efficiency (FE) for CO_2 conversion to CO is achieved. Total time of electrolysis =1800s)

- Active B12 concentration: 7.91 nmol (Derived from the charge of the CV redox-peak of the CP/MWCNT@B12)

Calculation for the TON:

TON = $(36.02 \times 10^{-6}$ mol$)/(7.91\times10^{-9}$ mol$) = 4559$

1.2. ***Turnover Frequency (TOF)***

The Turnover Frequency (TOF) is a measure of the rate of CO_2-to-CO conversion. It is calculated as the ratio of the TON to the reaction time.

TOF = TON/time (s^{-1})

Given values:

- TON: 4559

- Electrolysis time: 1800s

Calculation:

TOF = 4559/1800 s = 2.5 s^{-1}

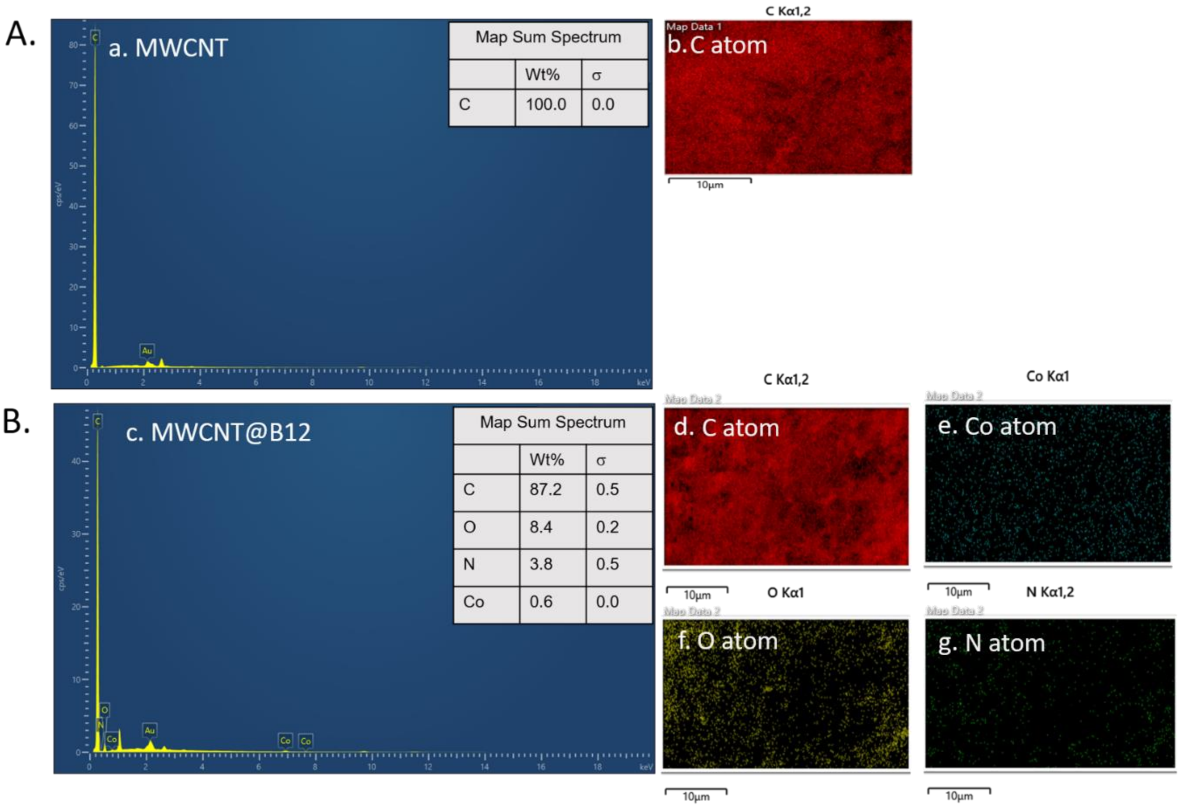

Figure S1. EDAX spectrum and corresponding elemental mapping of (A) MWCNT (a) and (B) MWCNT@B12(c). Elemental mapping of Carbon from MWCNT (b), and Carbon (d), Cobalt (e), Oxygen (f) and Nitrogen (g) from MWCNT@B12.

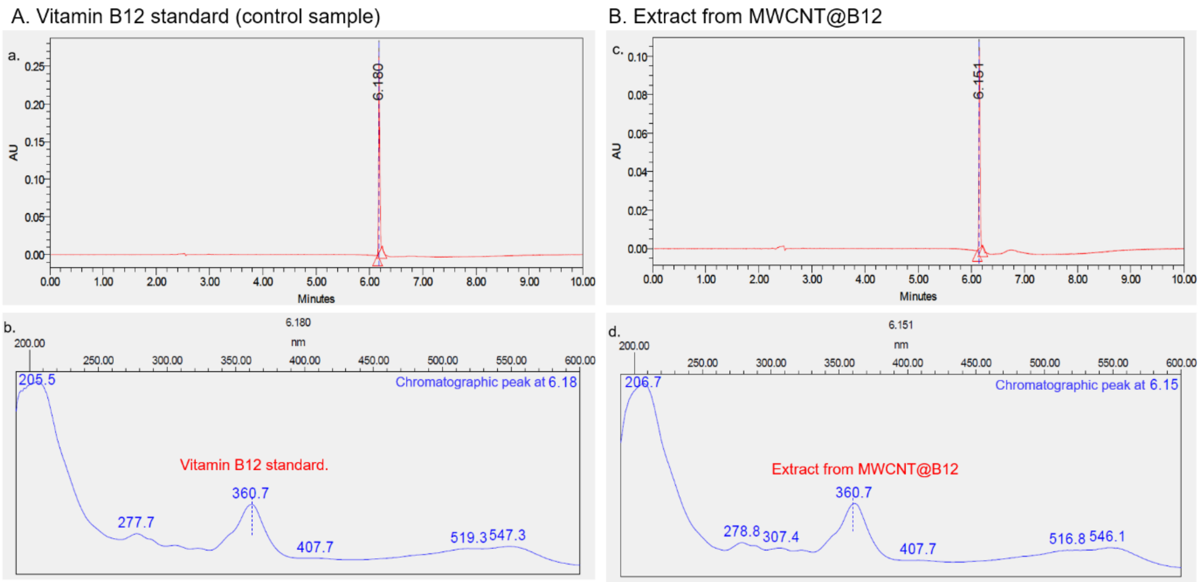

Figure S2. Confirmation for the Vitamin B12. UPLC chromatogram (a and c) and corresponding UV spectrum (b and d) of (A) Standard Vitamin B12 and (B) Aqueous extract of MWCNT@B12. Mobile phase, acetonitrile+(water+formic acid (0.025%)) under gradient condition.

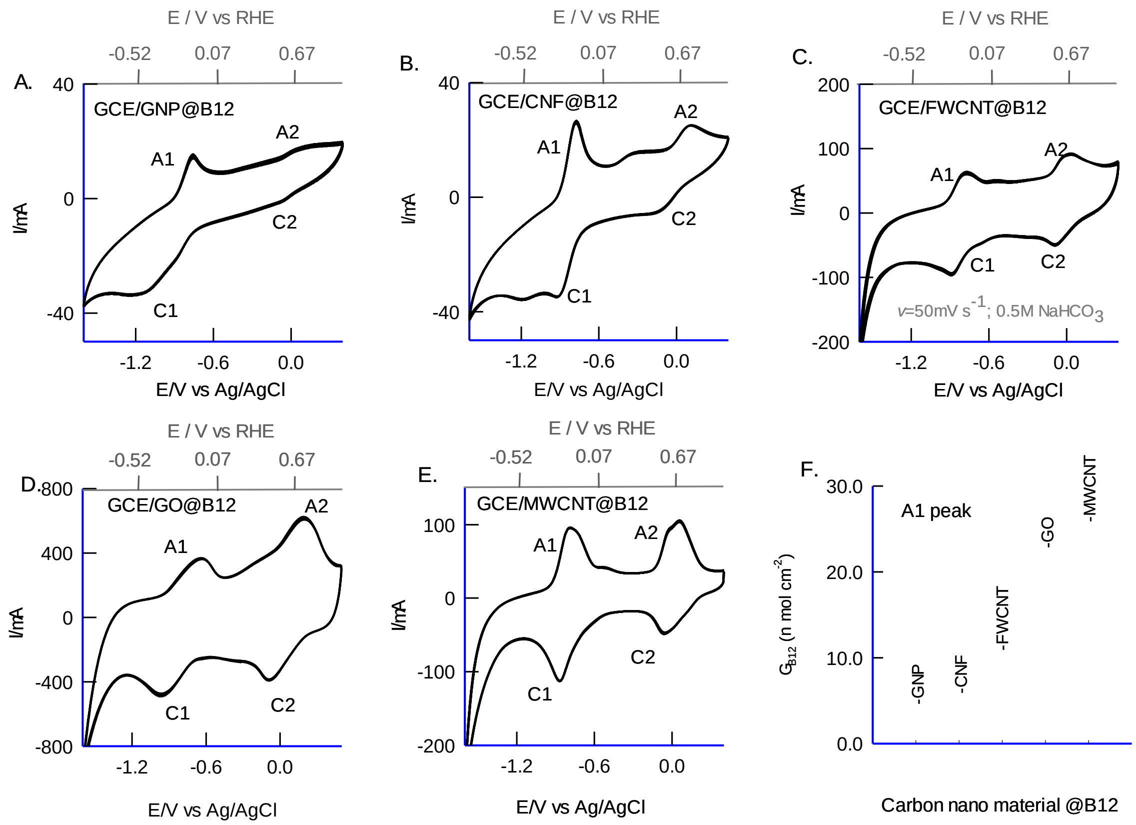

Figure S3. Comparative CV responses of B12 immobilized on various carbon nanomaterials modified GCE surfaces in 0.5 M $NaHCO_3$ solution (N_2= purged) at the scan rate of 50 mV s^{-1}. GNP = graphite nanopowder; CNF = Carbon Nanofiber; FWCNT = carboxylic acid functionalized multiwalled carbon nanotube; GO = Graphene oxide; MWCNT = multiwalled carbon Nanotube.

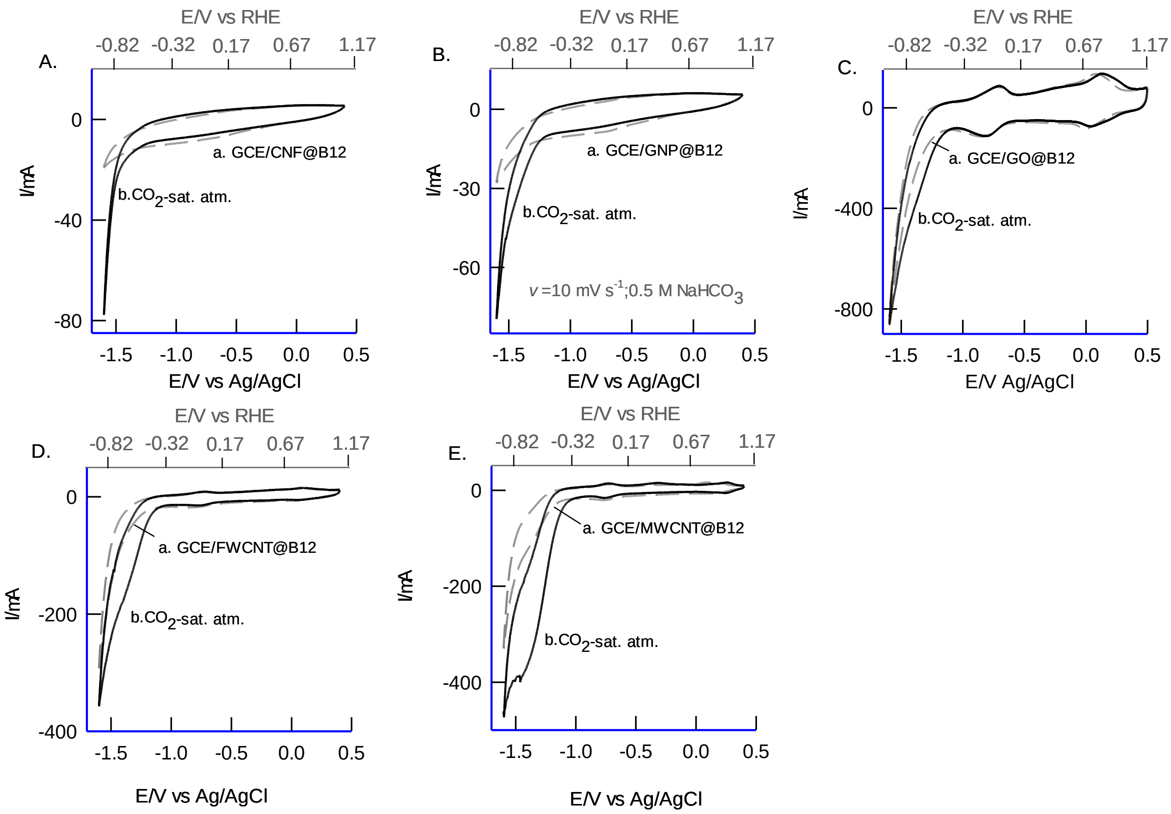

Figure S4. CV response of modified electrode in N_2 saturated atm (curve a) and in CO_2 saturated (curve b) in 0.5 M $NaHCO_3$ solution at $v = 10$ mV s^{-1}. (A) GCE/CNF@B12 (B) GCE/GNP@B12 (C) GCE/GO@B12 (D) GCE/FMWCNT@B12 (E) GCE/MWCNT@B12.

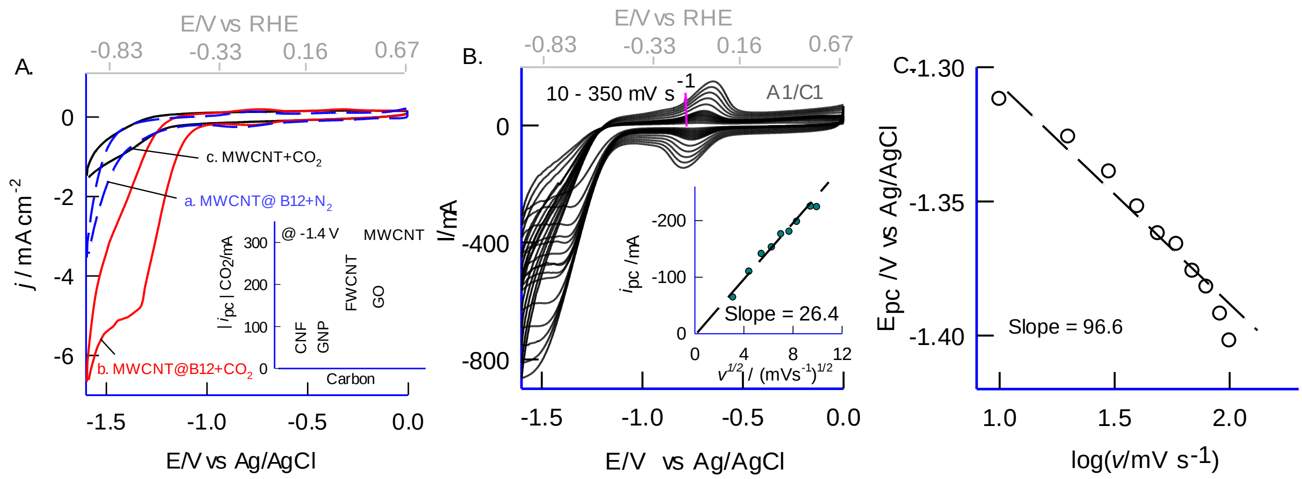

Figure S5. Comparative CV responses GCE/MWCNT@B12 with N_2 (a) and CO_2 (b) saturated 0.5 M $NaHCO_3$ at a scan rate of 10 mV s^{-1}. Curve c is a control CV of GCE/MWCNT with CO_2 saturated solution. Inset is a plot of $|i_{pc}|$ CO_2 (μA) versus B12 modified carbon electrodes; GCE/CNF@B12; GCE/GNP@ B12; GCE/FWCNT@B12; GCE/GO@B12; GCE/MWCNT@B12. (B) Effect of scan rate on CV response of GCE/MWCNT@B12 in saturated CO_2 in 0.5 M $NaHCO_3$. Inset is a plot of i_{pc} vs square root of scan rate $(v)^{1/2}$. (C) Plot of E_{pc} vs log of scan rate (v)

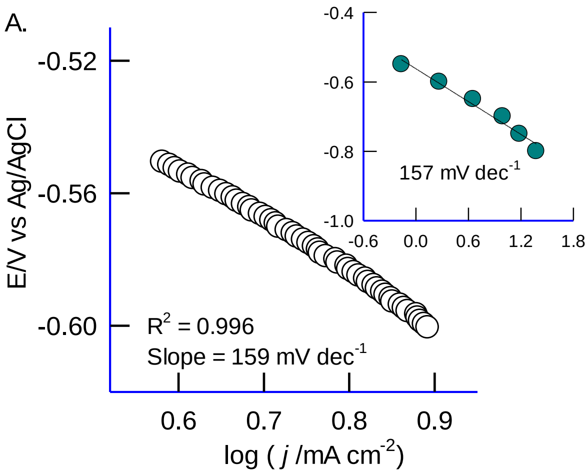

Figure S6. (A) Tafel plot for the CV data of electrochemical reduction of CO_2 on CP/MWCNT@B12 at $v = 10$ mV s^{-1} corresponding to the Figure 3A. Inset is the Tafel plot corresponding to the potentiometric polarization experimental's current density data as given in the Figure 3B.

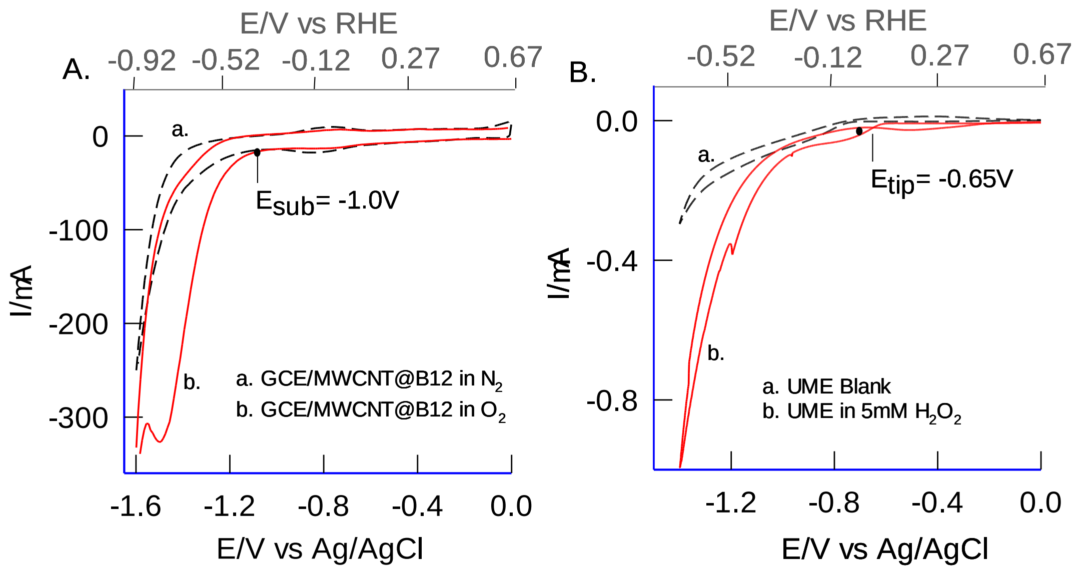

Figure S7. (A) CV response of GCE/MWCNT@B12 in N_2 saturated (curve a) and in O_2 saturated (curve b) atmosphere in 0.5 M $NaHCO_3$ solution at v = 10 mV s^{-1}. (B) CV response of platinum UME without (a) and with 5 mM H_2O_2 (b) in 0.5 M $NaHCO_3$ (curve b) at v = 10 mV s^{-1}

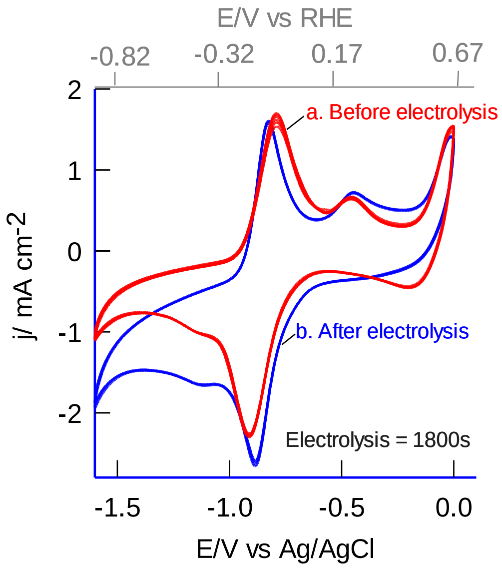

Figure S8. Stability of the modified electrode. Comparative CV responses of CP/MWCNT@B12 before (curve a) and after electrolysis (curve b) of saturated CO_2 in 0.5 M $NaHCO_3$ at v = 50 mV s^{-1}.