SUPPLEMENTARY INFORMATION

Cu(II)/Cu(0) Electrocatalyzed CO_2 and H_2O Splitting

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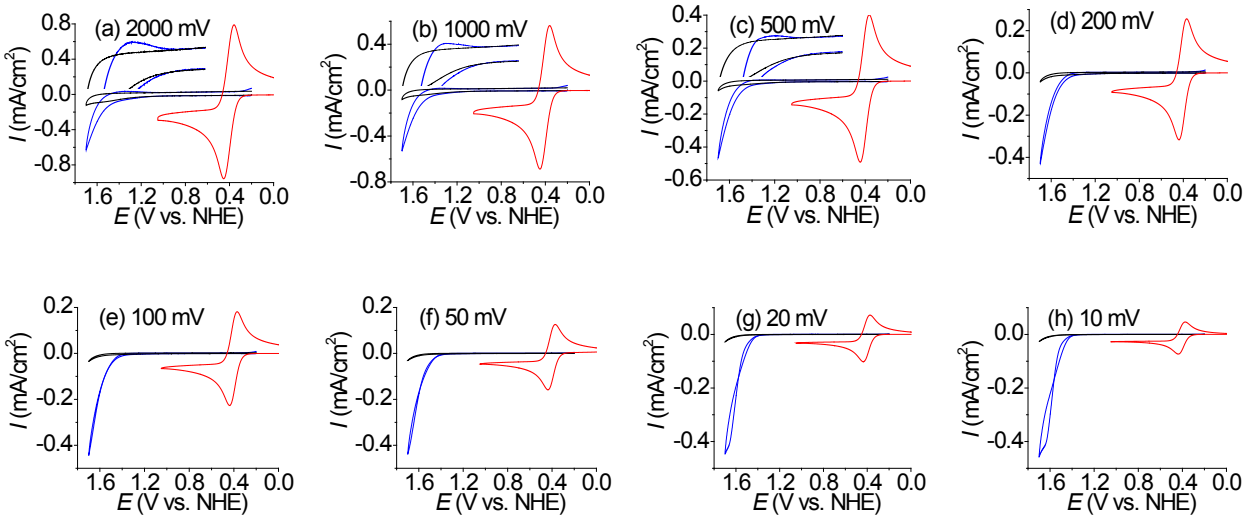

Figure S1. CVs of 0 mM (black) and 1.2 mM (blue) $CuSO_4$ at a BDD disk electrode in 1 atm CO_2-saturated 0.1 M $NaHCO_3$ solution (pH ~6.7) at different scan rates. Insets in (a)-(c) show the magnified views for the re-reduction of higher oxidation state Cu species to Cu(II) at fast scan rates. Red lines represent CVs of 1.2 mM $K_4Fe^{II}(CN)_6$ under identical conditions.

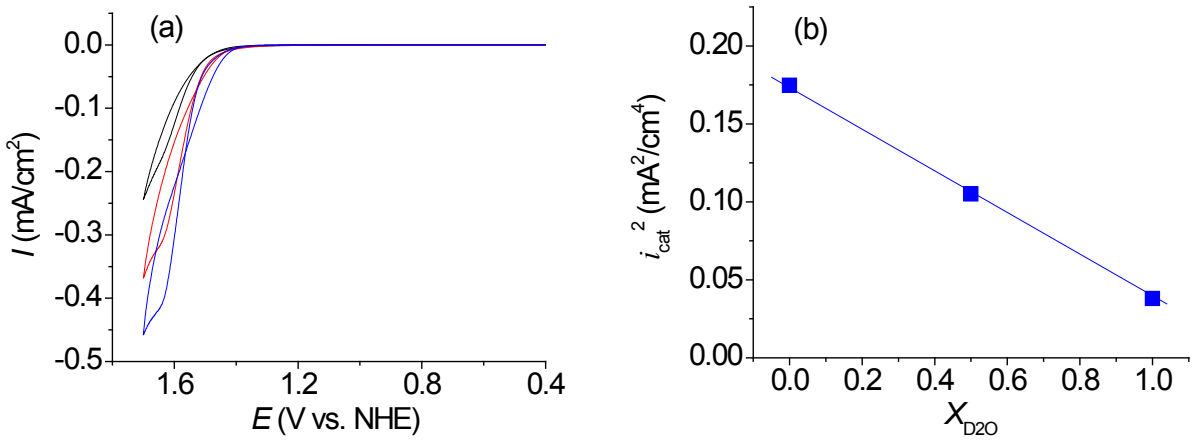

Figure S2. (a) CVs of 1.2 mM $CuSO_4$ in 1 atm CO_2-saturated 0.1 M $NaHCO_3$ solution (pH ~6.7) in D_2O (black), 1:1 H_2O/D_2O (red), and H_2O (blue). (b) Dependence of $i_{cat}^2(X_{D2O})$ at 1.65 V on X_{D2O}, the mole fraction of D_2O. Electrode, BDD (0.071 cm^2); scan rate, 10 mV/s.

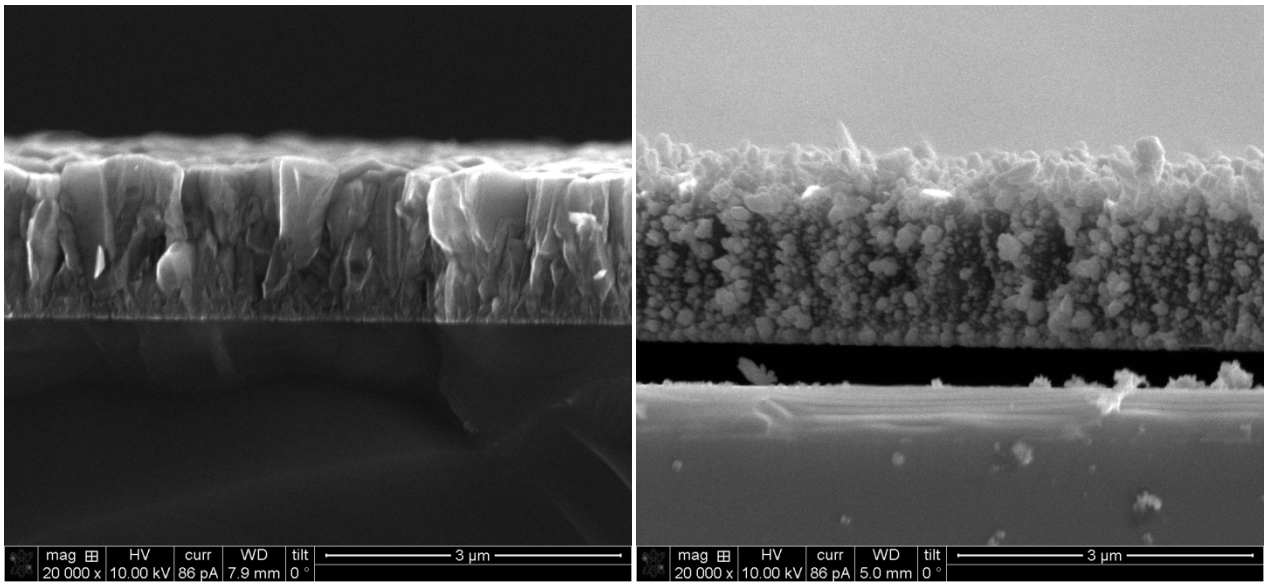

Figure S3. Cross-sectional FESEM images of the BDD|Si electrode and the Cu(0) cluster film deposited on BDD|Si..

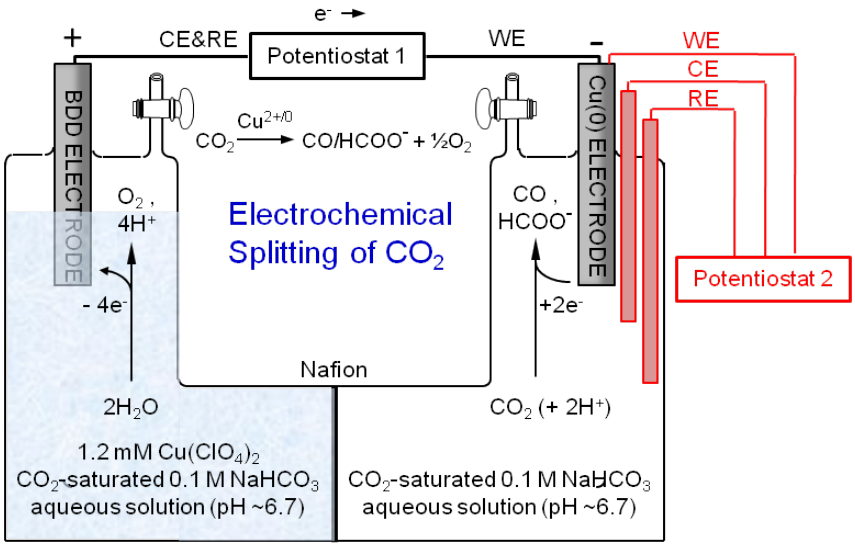

Figure S4. As in Figure 4 in the paper, potentiostat 2 (in red) was included to monitor (technique: open circuit potential - time) the potential applied at the cathode working electrode by potentiostat 1 and vice versa for monitoring the anode working electrode. For potentiostat 2: WE, working electrode; CE, counter electrode (Pt wire); RE, reference electrode (SCE).