Supporting Information

Photo-reduction of CO_2 on p-type silicon using Re(bipy-Bu^t)(CO)$_3$Cl: Photovoltages exceeding 600 mV for the selective reduction of CO_2 to CO

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Photoelectrochemical (PEC) cell:-

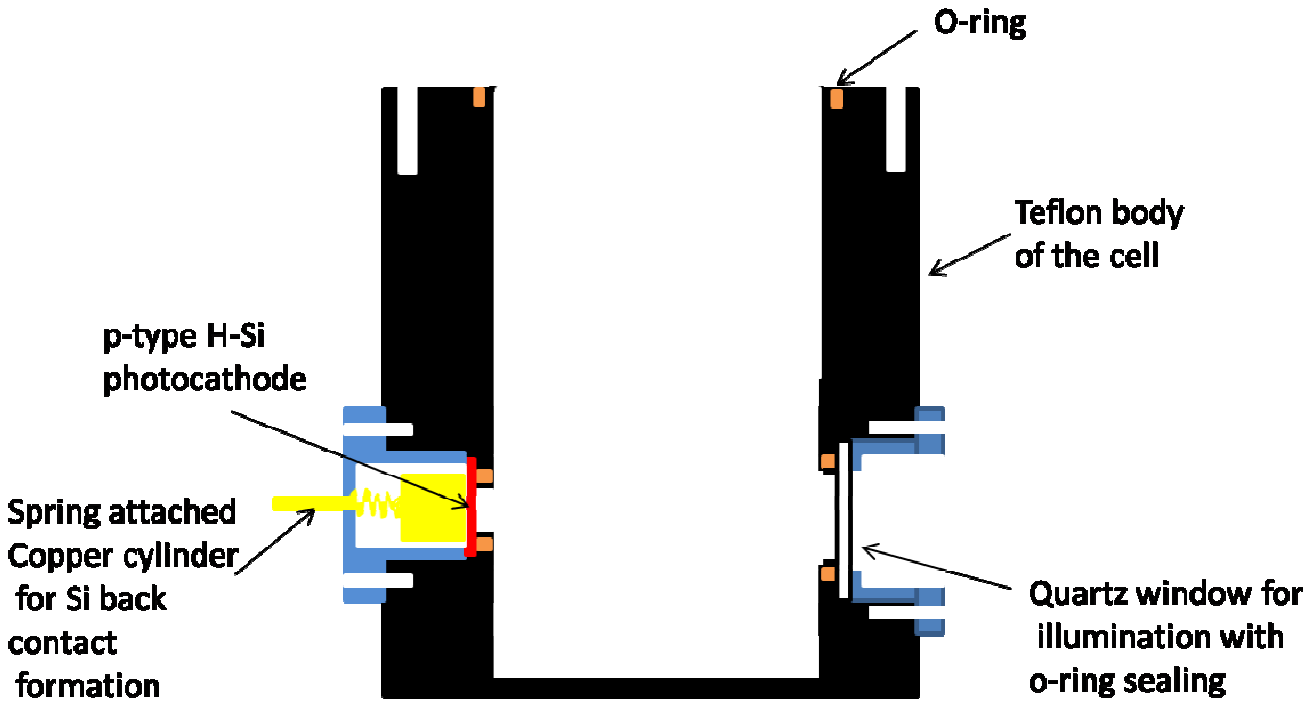

Figure S1. (a) Schematic diagram of photoelectrochemical (PEC) cell without the cap.

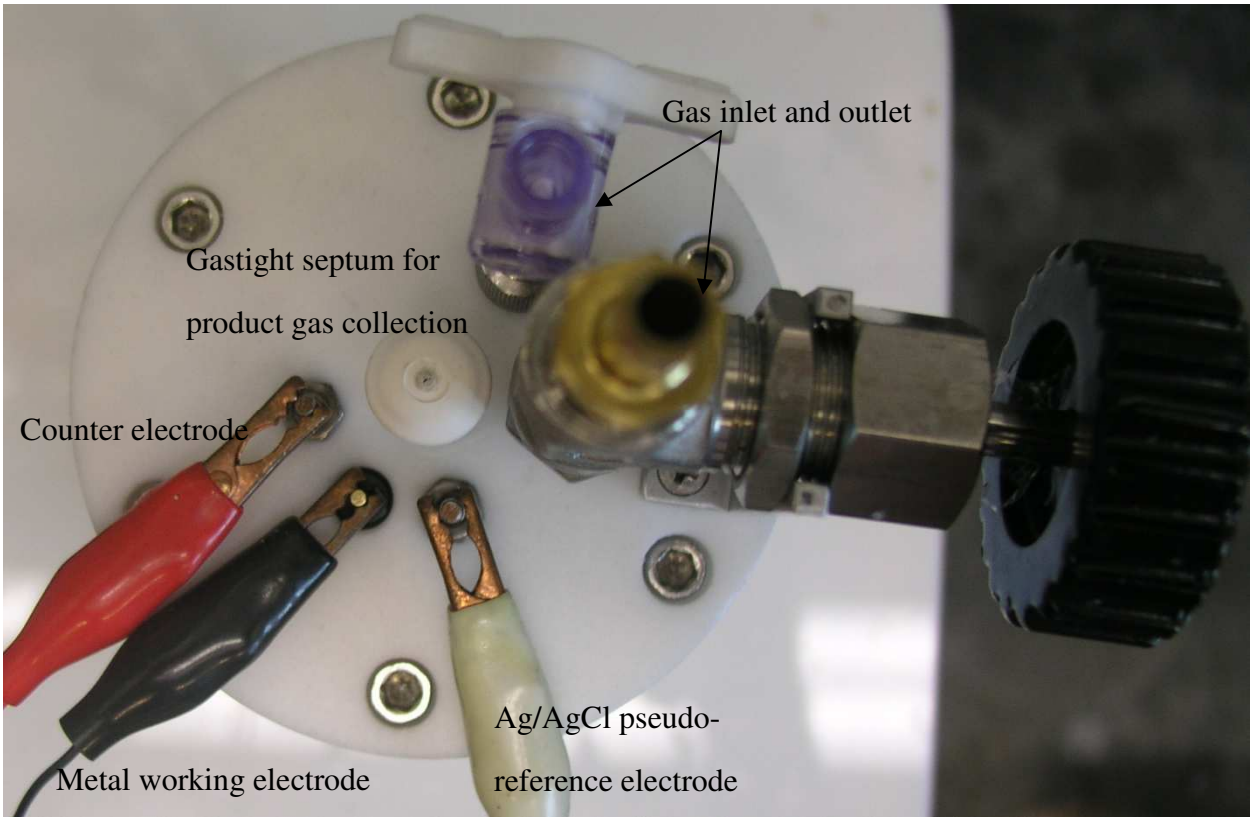

Figure S1. (b) Photograph of PEC cell cap with all the parts indicated.

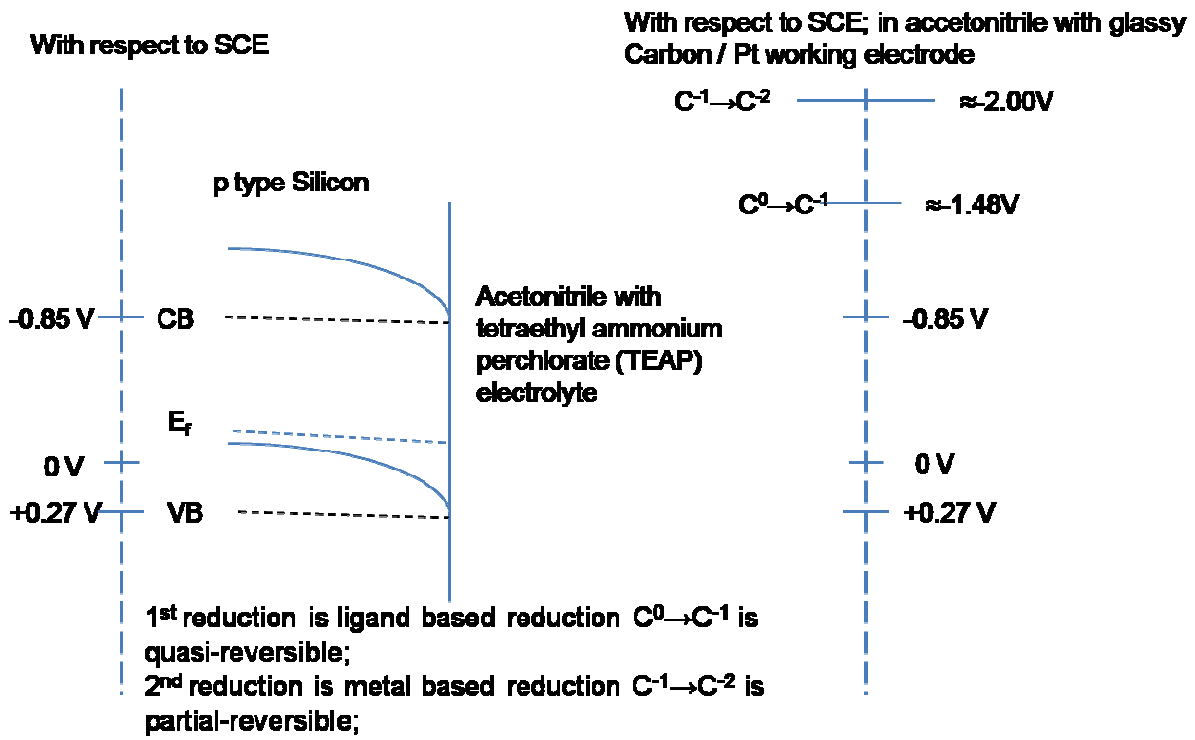

Figure S2. (a) Band edge position of conduction band (CB) and valence band (VB) of p type Si[1] and redox potentials of catalyst[2] before contact with respect to saturated calomel electrode (SCE); where E_f is Fermi level of p-type Si.

References:

(1) Turner, J. A.; Manassen, J.; Nozik, A. J. *Appl. Phys. Lett.* **1980**, *37*, 488.

(2) Smieja, J. M.; Kubiak, C. P. *Submitted Inorg. Chem.* **2010**.

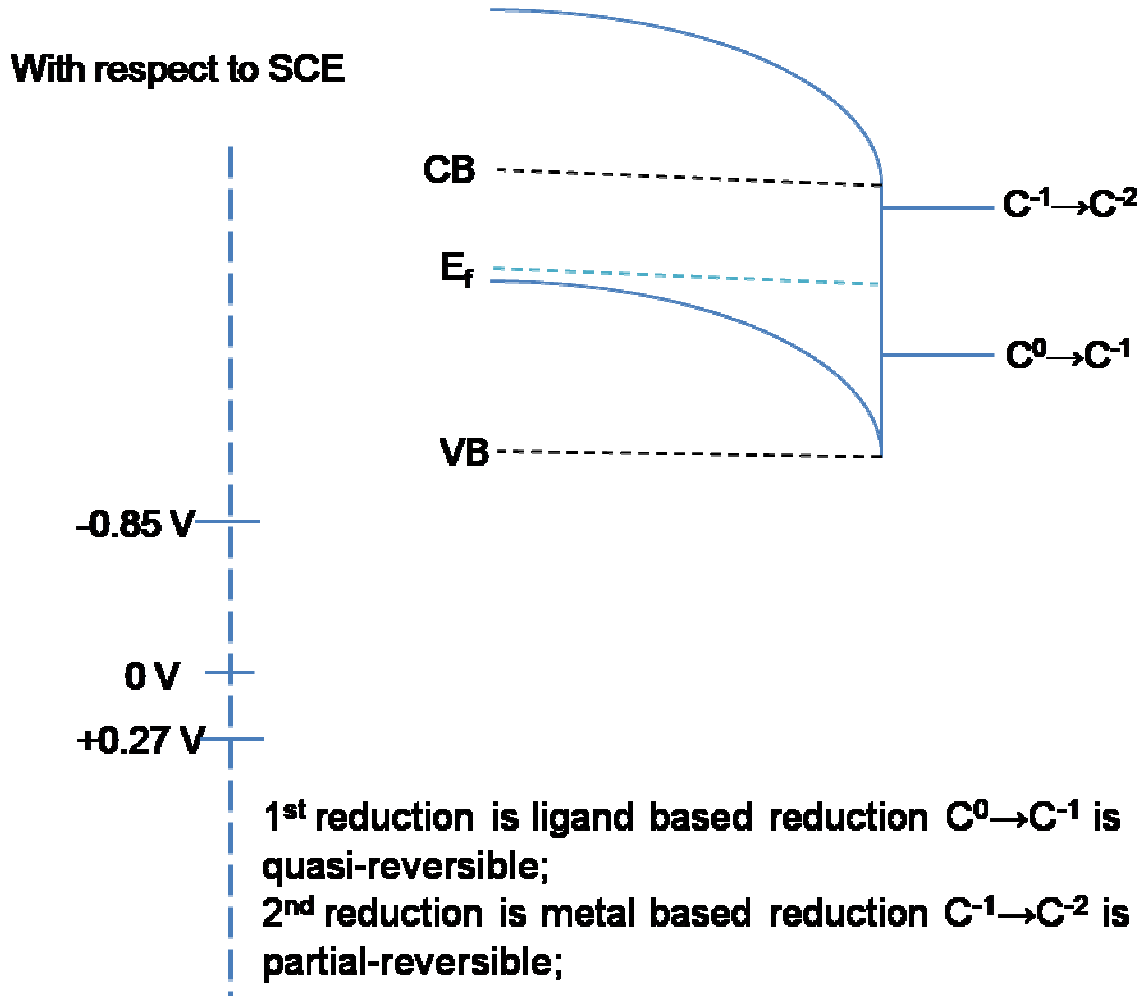

Figure S2. (b) Band edge position of conduction band (CB) and valence band (VB) of p type Si and redox potentials of catalyst after coming into contact with respect to saturated calomel electrode (SCE); where E_f is Fermi level of p-type Si.

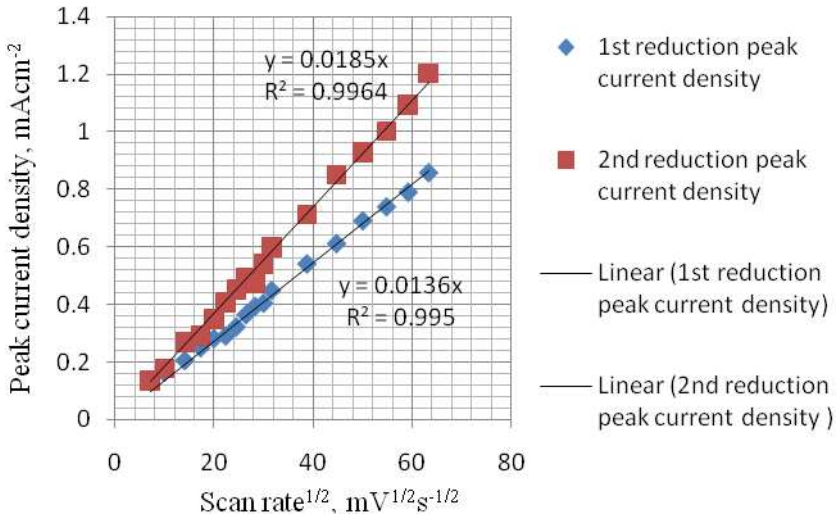

Figure S3. Scan rate dependence of peak current densities of 1st and 2nd reductions of **2** on illuminated p-type H-Si.

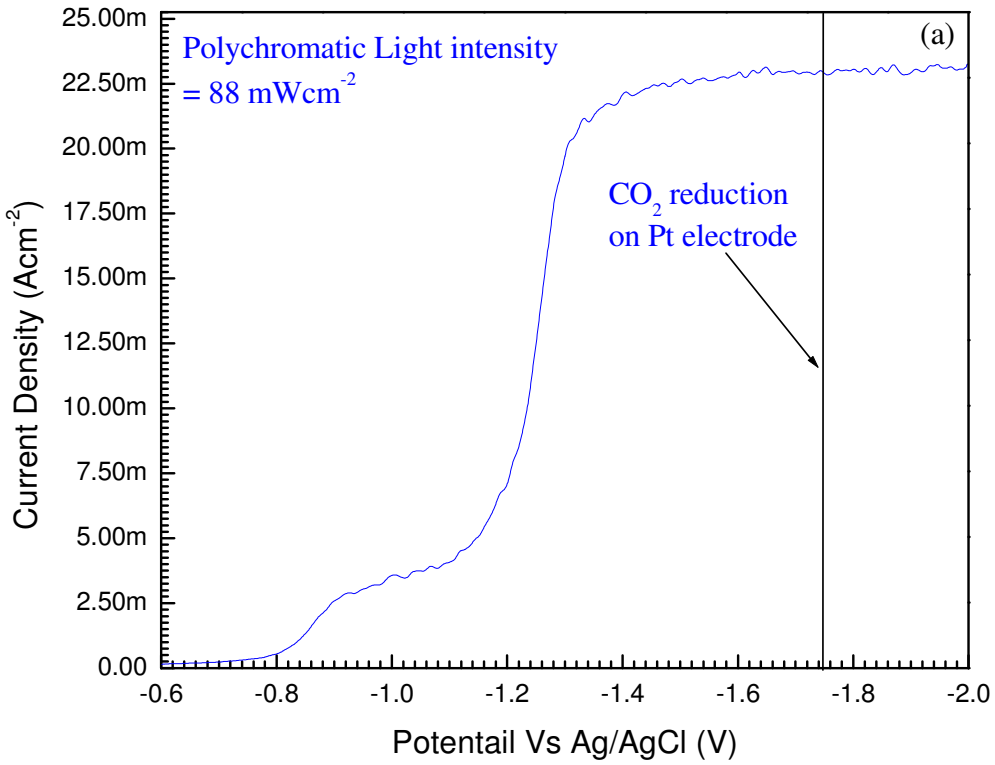

Figure S4. (a) Current density-voltage characteristic of p-type H-Si/**2** junction under CO_2. Open circuit voltage, V_{OC}, = 668 mV; Short circuit current density, J_{SC}, = 23 $mAcm^{-2}$; Fill factor ≈ 58 % and Overall conversion efficiency ≈ 10 %.

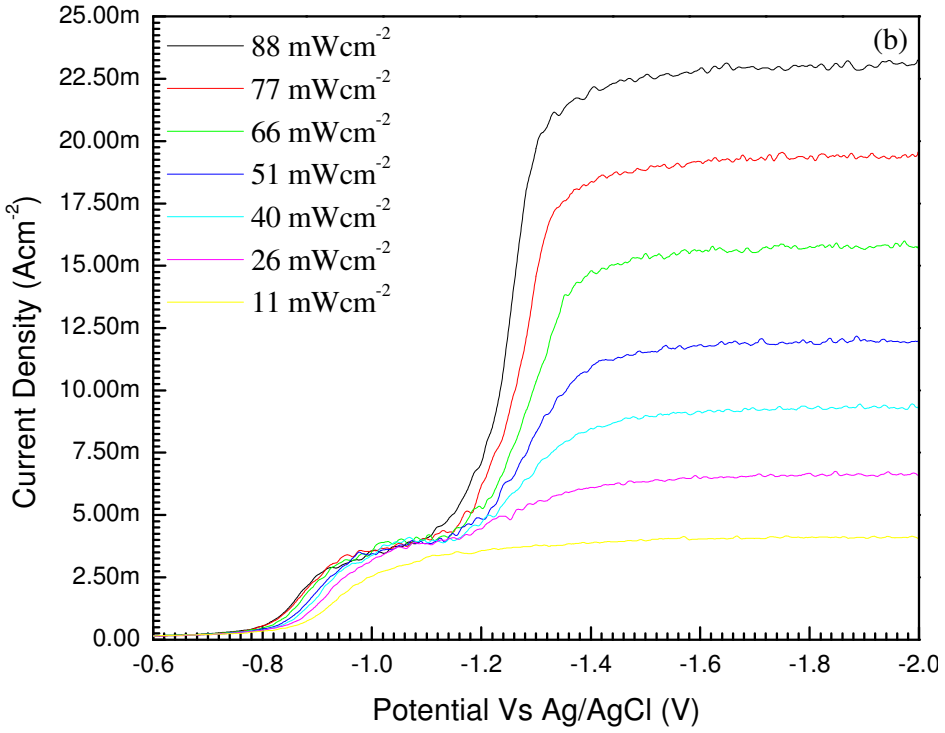

Figure S4. (b) Light intensity dependence of catalytic current density under polychromatic illumination of p-type H-Si photocathode.