Synergism between CdTe semiconductor and pyridine photo-electrocatalysis for CO_2 reduction to formic acid

Ji Hoon Jeon, Paulpandian Muthu Mareeswaran, Chang Hyuck Choi, and Seong Ihl Woo*

Department of Chemical and Biomolecuar Engineering, Korea Advanced Institute of Science and Technology, Daejeon, South Korea.

Supporting Information

Experimental

Cadmium sulfate ($CdSO_4$) and Tellurium oxide (TeO_2) are purchased at Sigma-Aldrich. Deionized water is used throughout the study. Fluorine doped tinoxide (FTO) glass is purchased at Wooyang GMS (Korea). Three electrodes, single and H-cells (Fig. 1) are used for the photoelectrochemical experiments.

Synthesis of cadmium telluride thin film

CdTe (cadmium telluride) is synthesized by electrodepositing method. $CdSO_4$ is dissolved in deionized water at room temperature and then TeO_2 is added in portions. The pH was adjusted to pH 2 using 1 M of H_2SO_4. FTO glass is cleaned for 30 minutes with acetone using sonication and rinsed several times with deionized water. This FTO glass is placed in $CdSO_4$-TeO_2 solution and used as electrode. The electrodeposition is carried out on FTO glass at applied potential of -0.6 V with respect standard calomel electrode (SCE) at room temperature. Finally, the deposited FTO glass is calcinated at 400 °C for 2 hr in Ar atmosphere. The rate of change of temperature is 10°C/min.

This electrode is characterized by the SEM image, recorded from FEI field-emission scanning electron microscope(SEM) (Fig. 1) and LabRam HR UV/Vis/NIR high resolution Raman microscope with laser source 514 nm, and spectral range 100 ~ 700 cm^{-1} (Fig. 3). This is also characterised by Ragaku D/MAX-III X-ray diffraction (XRD) with nickel CuKα radiation (Fig. 4).

Characterisation

The CdTe/FTO electrode is further characterized using XRD and Raman spectroscopy. The Raman spectra and XRD are shown in Fig. S1 and S2 respectively. There are two sharp peaks in Raman spectra. The presence of a peak 124 and 143 cm^{-1} is considered as indication of CdTe formation.[1] CdTe is identified through the emergence of the sharp, high angle peak 23.7, 39.2 and 46.42 θ in the XRD pattern.[1] This peak may be attributed to the cubic zinc blended structure and the deposited CdTe thin film exhibits a preferred orientation along the (111) planes parallel to the substrate.[2] Other peaks are attributed to the tin oxide of FTO glass.[2] XRD and Raman spectrum contains typical patterns of the synthesized cadmium telluride which have been well documented.[1, 2] The UV-visible absorption spectrum of

CdTe/FTO is shown in Fig. S3. The CdTe/FTO have wide absorption in the visible region (300 nm – 677 nm), therefore it can utilize the maximum wavelength of the visible light available in the solar spectrum. The band gap energy of CdTe is small (1.47 eV) and it can be easily excited using the visible light irradiation.[3] The excited electron goes to the conduction band of the CdTe and its band position is -0.27 eV.[3]

Catalyst activity test by electrochemical test

The experimental setup is given in Fig. 1a. The photocathode is comprised of CdTe thin films synthesized as above with respect to SCE as reference electrode and Pt wire as counter electrode. The photocathode potential is measured with respect to SCE. Nitrogen is bubbled into the 0.1 M $NaHCO_3$ electrolyte with citric acid (citric acid and sodium citrate) buffer (0.1 M) at pH 5 (100 ml), for 1 hr to remove any dissolved carbon dioxide due to the reaction of citric acid with $NaHCO_3$ and this saturated electrolyte is electrochemically reduced at cathodic polarizations of 0 V ~ -0.6 V versus SCE. The CdTe modified electrode is irradiated for 6 hr with visible light from Xe-arc lamp (450W) containing UV cut-off filter. After irradiation finished the potential is scanned at 0 V ~ -0.6 V electrolytes under same condition. Finally, CO_2 gas is bubbled and saturated electrolyte is electrochemically reduced in both dark and light conditions. The observed current is analysed for the above four conditions.

Catalyst activity test by product analysis

A DuPont Nafion 117-type proton exchange membrane (0.18mm thickness) is used as diaphragm in the H-cell (Fig. 1b). A N_2 saturated 0.1 M solution of $NaHCO_3$ with citric buffer is used as electrolyte at pH 5 (100 ml). After saturation with N_2 the solution is saturated with CO_2 bubbling for another one hour. The irradiation experiment is carried out in the same conditions as above. The product obtained during the photoelectrochemical reduction is collected at every 30 minutes and analysed using Gas Chromatography (GC) with FID column.

Faradaic efficiency

Faradaic efficiency is calculated using the following equation.[4]

$$\varepsilon_{faradic} = nFM/Q \qquad (1)$$

Where, $\varepsilon_{faradic}$, n, F, M, Q are Faradic efficiency, number of electrons, Faraday's constant, number of moles of the product and charge passed, respectively.

References

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2. O. R. Ochoa, E. J. Witkowski Iii, C. Colajacomo, J. H. Simmons and B. G. Potter Jr, *J. Mat. Sci. Lett.* 1997, 16, 613-616.
3. B. Kumar, M. Llorente, J. Froehlich, T. Dang, A. Sathrum and C. P. Kubiak, *Annu. rev. phys. chem.* 2012, 63, 541-569.
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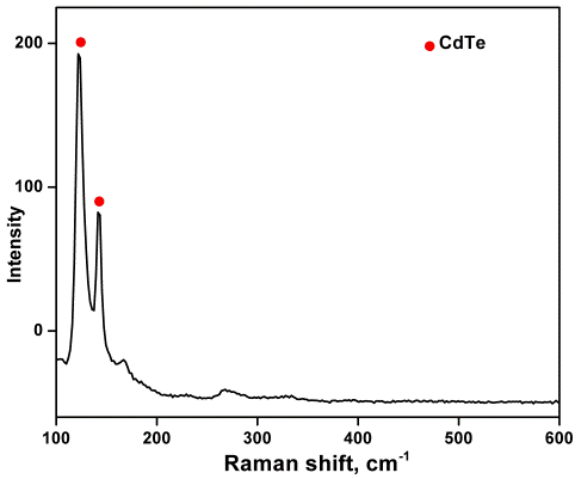

Fig. S1. Raman spectra of CdTe/FTO

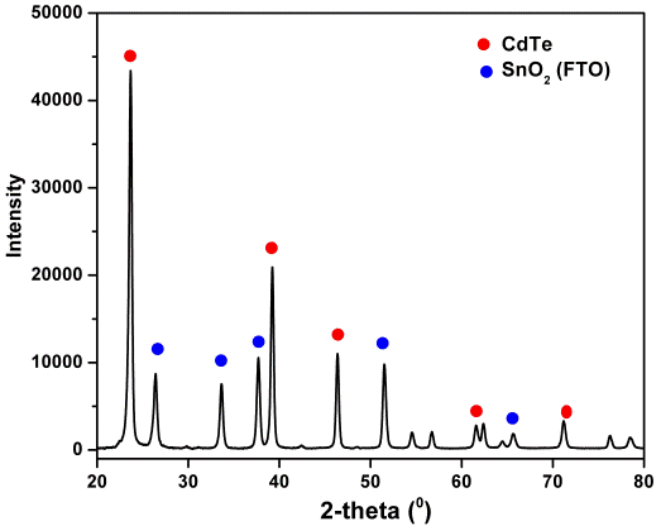

Fig S2. XRD spectra of CdTe/FTO

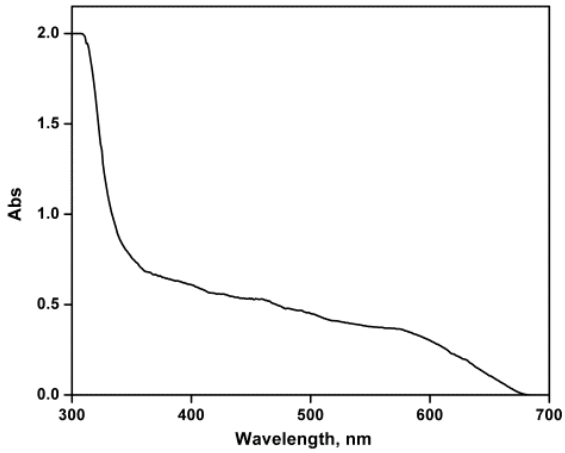

Fig. S3. UV-visible spectra of CdTe thin film deposited on FTO

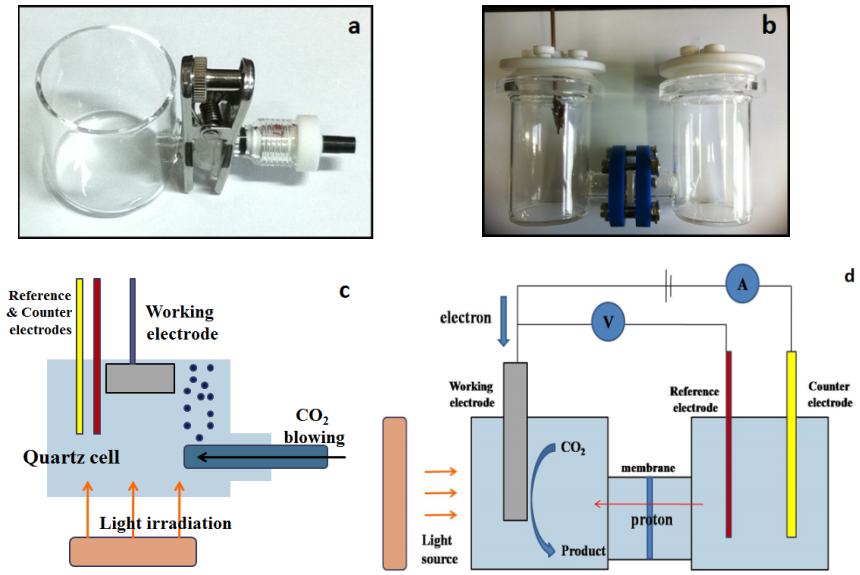

Fig. S4. (a) Experimental setup of the cell for carbon dioxide reduction (b) Experimental setup of the H-cell for product analysis (c) Scheme of photoelectrocatalytic cell for carbon dioxide reduction and (d) Scheme of photoelectrocatalytic cell for product analysis

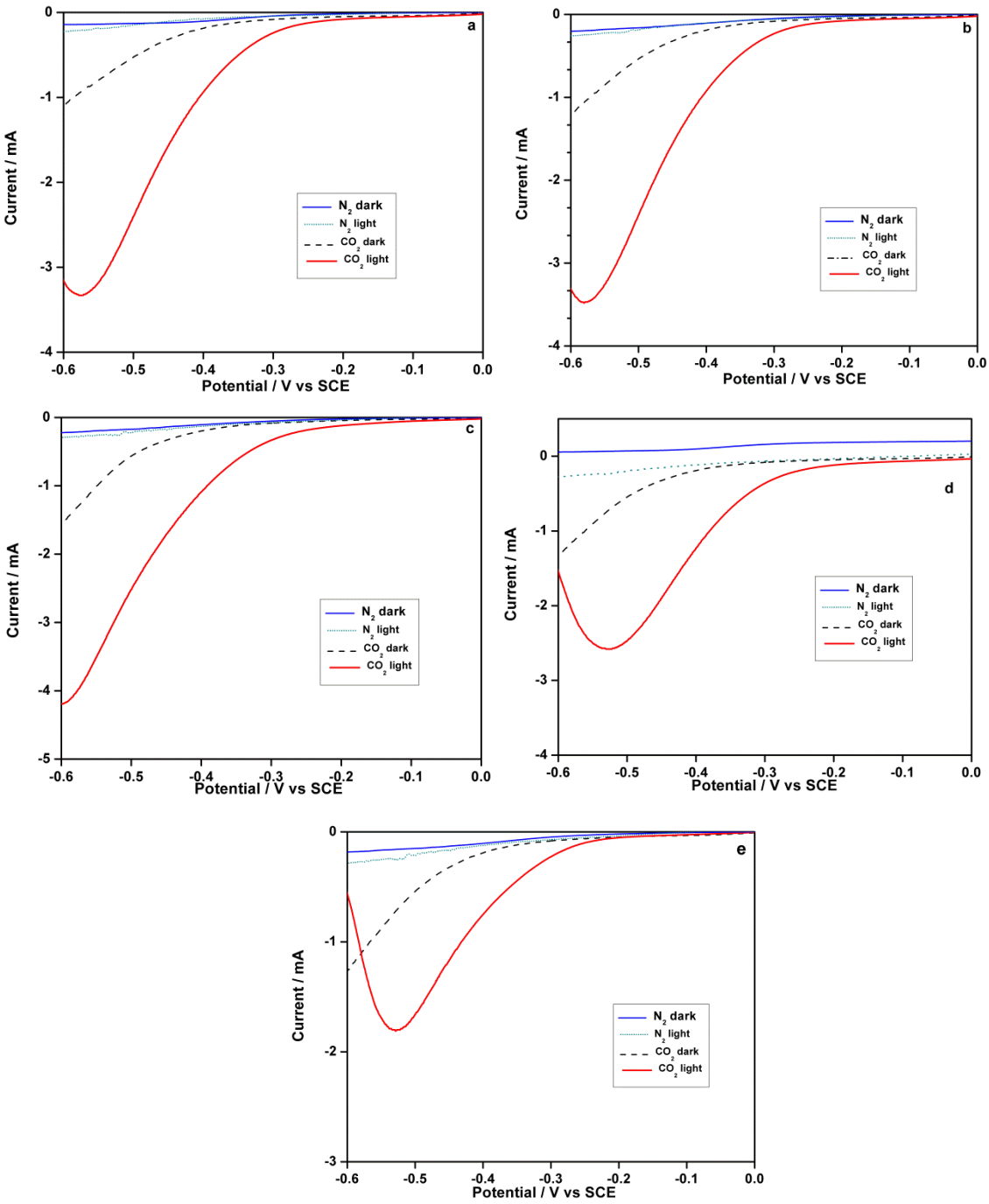

Fig. S5 Photo-electrochemical test using linear sweep volotametry (LSV) method (a) CdTe, (b) CdTe- 5 mM pyridine, (c) CdTe- 10 mM pyridine, (d) CdTe- 20 mM pyridine, (e) CdTe- 30 mM pyridine

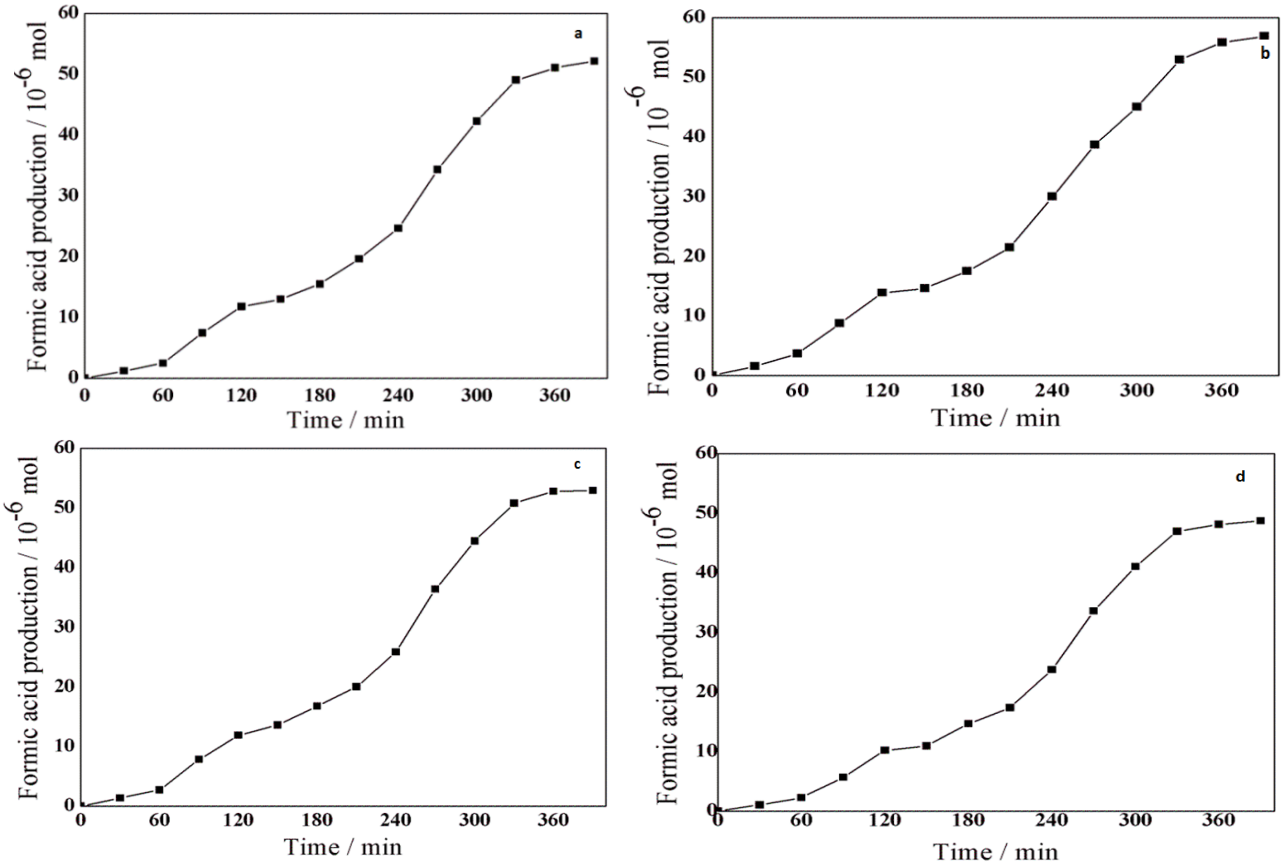

Fig S6. Formation of formic acid in the presence of pyridine (a) 5 mM, (b) 10 mM, (c) 20 mM and (d) 30 mM