

## Electronic Supplementary Information

# Photoelectrochemical production of useful fuels from carbon dioxide on polypyrrole-coated p-ZnTe photocathode under visible light irradiation

Da Hye Won<sup>a</sup>, Jaehoon Chung<sup>a</sup>, Sung Hyeon Park<sup>a</sup>, Eun-Hee Kim<sup>c</sup> and Seong Ihl Woo<sup>a,b\*</sup>

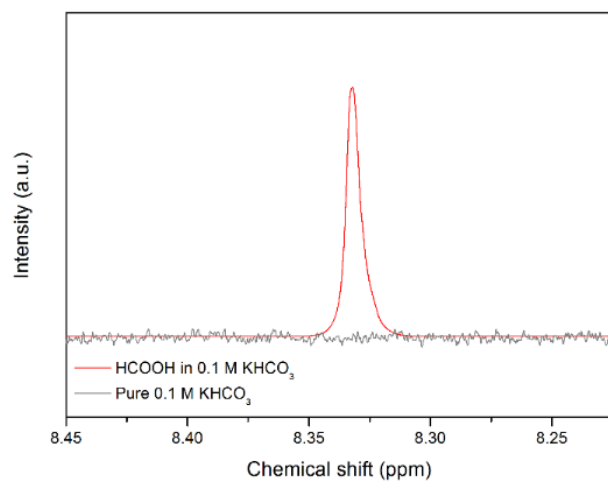
<sup>a</sup> *Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, Daejeon (305-701), Republic of Korea.*

<sup>b</sup> *Graduate School of EEWS, Korea Advanced Institute of Science and Technology, Daejeon (305-701), Republic of Korea.*

<sup>c</sup> *Division of Magnetic Resonance Research, Korea Basic Science Institute, Cheongju (363-883), Republic of Korea*

\* Corresponding author:

Tel: +82-42-350-3918; Fax: +82-42-350-8890; E-mail: siwoo@kaist.ac.kr.



**Fig. S1** <sup>1</sup>H NMR peak positions calibrated by purchased formic acid (red) dissolved in 0.1 M KHCO<sub>3</sub> aqueous solutions, containing the standard solution (in D<sub>2</sub>O solvent)

**Table S1** Calculated thickness of polypyrrole depending on CV cycles.

cycle	1 CV	2 CV	3 CV
$Q_{form}$ (mC/cm <sup>2</sup> )	16.72	22.43	26.75
PPy thickness (nm)	30.33	40.68	48.51

PPy thickness was calculated by the following equation.

$$d = (M.Wt) Q_{form} / nF\rho A$$

$M.Wt$  is the molar mass of repeating pyrrole unit = 69.3 g mol<sup>-1</sup>

$n$  is the number of electrons associated with polymer formation = 2

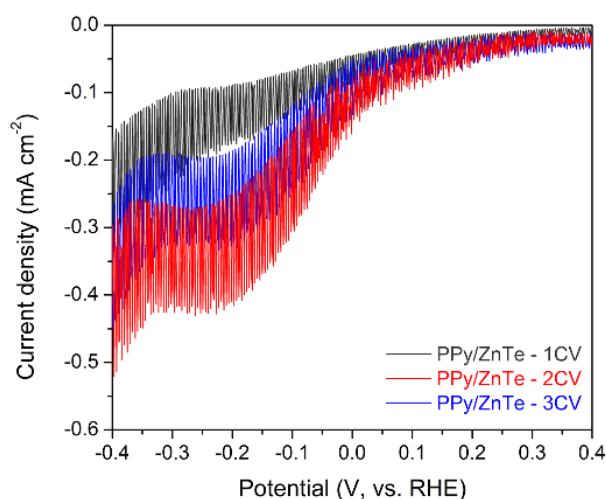
$F$  is the faradaic constant = 96485 C mol<sup>-1</sup>

$\rho$  is the estimated density of the film = 1.5 g cm<sup>-3</sup>

$A$  is the active area = 1.32 cm<sup>2</sup>

$Q_{form}$  is the charge associated with formation of the polymer

As shown in Table S1, the  $Q_{form}$  was calculated from the anodic charge of the background-subtracted CV results, which are obtained during electro-polymerization. The thickness of deposited PPy was varied depending on the number of CV cycles

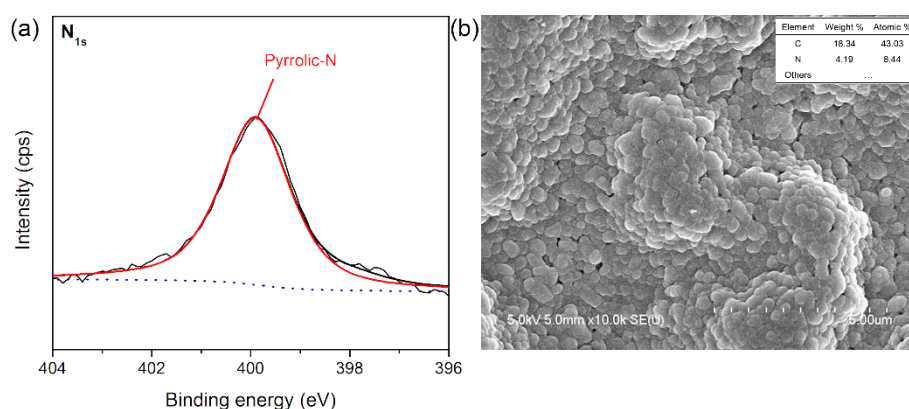


**Fig. S2** Compared CO<sub>2</sub> photoreduction activity by LSV in CO<sub>2</sub>- bubbled 0.1 M KHCO<sub>3</sub> aqueous solution under irradiation of chopped visible light at various PPy/ZnTe photoelectrodes, which was prepared depending on CV cycles.

## Preparation of PPy electrode

Single PPy electrode was prepared onto the FTO glass by electro-polymerization of pyrrole in three electrode system. The SCE and Pt coil were used as the reference and the counter electrode, respectively. 0.1 M KCl ( $\geq 99.0\%$ , Aldrich) solution containing 0.3 M pyrrole (98%, Aldrich) was used as electrolyte and the pH was adjusted to 3.50. The cyclic voltammetry (CV) was performed for electro-polymerization with potential range from -1.0 V to 0.8 V (vs. SCE) and  $20 \text{ mV}\cdot\text{sec}^{-1}$  of scan rate. After CV with 5 cycles, the rinsed PPy electrode was further oxidized in pure 0.1 M KCl electrolyte with constantly applied potential of 0.6 V (vs. SCE) for 30 sec to complete polymerization.

Since PPy is an electrocatalyst for  $\text{CO}_2$  reduction which cannot utilize photoenergy, it only can produce formic acid under its thermodynamic standard redox potential, which is confirmed from the single PPy electrode which started to produce small amount of formic acid under -0.2 V (Table. S2). However, when the PPy was deposited on the surface of p-ZnTe, PPy/ZnTe electrode exhibited superior  $\text{CO}_2$  reduction performance, especially at the potential of 0 and -0.1 V where PPy cannot produce any product (Fig. S4). Furthermore, the production rates of PPy/ZnTe electrode on various potentials were even higher than the sum of the production rates for p-ZnTe and single PPy electrode which definitely indicates the synergic effect between PPy and p-ZnTe.



**Fig. S3** Characterizations of prepared single PPy with (a) XPS analysis and (b) FESEM (Top-down image) and EDS analyses.

**Table S2** The results of electrochemical CO<sub>2</sub> reduction in CO<sub>2</sub>-bubbled 0.1 M KHCO<sub>3</sub> aqueous solution using prepared PPy electrode at applied constant potentials.

Potential (V)	Charge (C) <sup>a</sup>	HCOOH	
		Production rate <sup>b</sup>	F.E. (%)
0	0.04	ND <sup>c</sup>	
-0.1	0.06	ND	
-0.2	0.08	10.3	14.9
-0.3	0.06	10.9	21.1

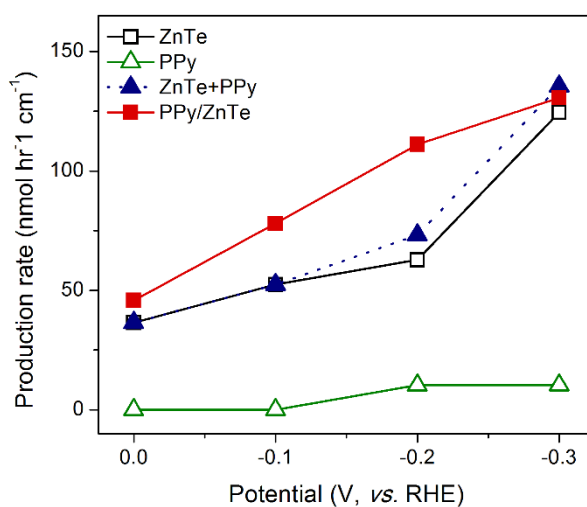
<sup>a</sup>Total charge used in CO<sub>2</sub> reduction reaction ( $= \int I dt$ ; where  $I$  is the measured current and  $t$  is the reaction time)

for 6 h

<sup>b</sup>Production rate of HCOOH (nmol·hr<sup>-1</sup>·cm<sup>-2</sup>)

<sup>c</sup>Not detected

\*Trace amount of H<sub>2</sub> was detected.

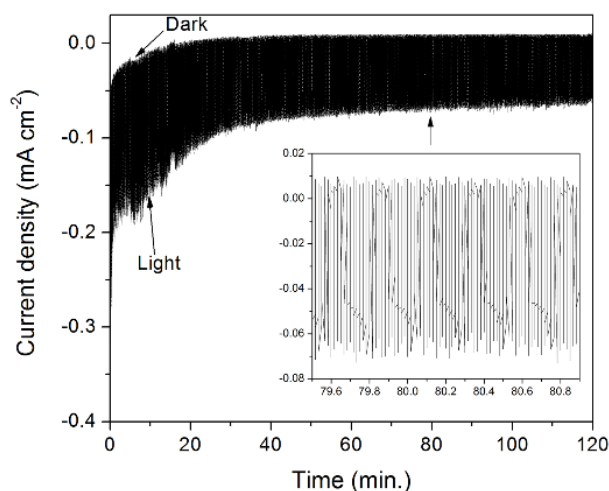


**Fig. S4** Comparison of the production rates of HCOOH using prepared ZnTe (blank square), PPy/ZnTe (filled square) and PPy electrode (blank triangle) in CO<sub>2</sub> reduction reaction (filled triangle means the sum of production rates of bare ZnTe and PPy).

## The stability of ZnTe and PPy/ZnTe as a photocathode

In previous research, II-VI compounds such as CdTe and ZnTe are well-known to be unstable towards photocorrosion when in contact with aqueous electrolytes.<sup>1</sup> Furthermore, the phenomenon of ZnTe photodegradation during photoelectrochemical CO<sub>2</sub> reduction was observed.<sup>2</sup> As shown in Fig. S5, the prepared ZnTe was also degraded during the photoelectrochemical CO<sub>2</sub> reduction by photocorrosion in our case and it might cause the low total Faradaic efficiency (Table 1). Nevertheless, it is worth noting that the prepared ZnTe exhibited relatively stable photocurrent and the product formation rates compared to other ZnTe electrodes and photocathodes.<sup>2,3</sup>

In that sense, the photocurrent and production rate decreased when the photocathode was repeatedly used (Table S3). This phenomenon was probably due to the photodegradation of ZnTe rather than the contamination or decomposition of PPy. It was also confirmed that PPy was still remain on ZnTe surface after CO<sub>2</sub> reduction reaction using XPS analysis (Fig. S6). Similarly, the stability of PPy, which often used as the electrocatalyst, was reported by Aydin *et al.* and their group showed that PPy was not changed and damaged during CO<sub>2</sub> reduction reaction.<sup>4</sup>



**Fig. S5** Photocurrent change of p-ZnTe photocathode under chopped visible light irradiation

in CO<sub>2</sub>-bubbled 0.1 M KHCO<sub>3</sub> at -0.3 V.

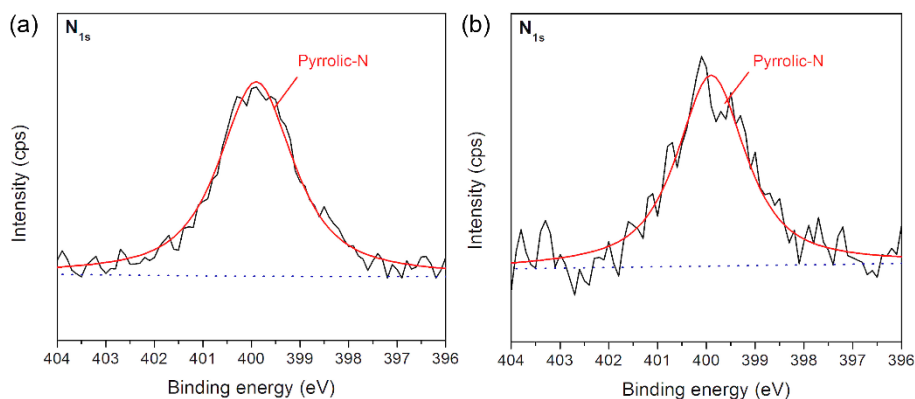
**Table S3** The repeatability of PPy/ZnTe photocathode in CO<sub>2</sub>-bubbled 0.1 M KHCO<sub>3</sub> aqueous solution under visible light irradiation at -0.3 V for 6 h.

Electrode	Charge <sup>b</sup> (C)	HCOOH		PPy/ZnTe CO		H <sub>2</sub>		Total F.E. (%)
		Rate*	F.E. (%)	Rate*	F.E. (%)	Rate*	F.E. (%)	
First reaction	0.58	130.6	26.1	50.4	10.1	107.8	21.5	57.7
Second reaction <sup>a</sup>	0.34	55.5	18.9	35.6	12.1	70.0	23.8	54.9

<sup>a</sup>The same photocathode after 6 h reaction

<sup>b</sup>Total charge used in CO<sub>2</sub> reduction reaction ( $= \int I dt$ ; where  $I$  is the measured current and  $t$  is the reaction time) for 6 h

\*Production rate of products such as HCOOH, CO and H<sub>2</sub> (nmol·hr<sup>-1</sup>·cm<sup>-2</sup>)



**Fig. S6** Comparison of XPS results of prepared PPy/ZnTe (a) before and (b) after reaction condition.

## Reference

- 1 M. F. Lichterman, A. I. Carim, M. T. McDowell, S. Hu, H. B. Gray, B. S. Brunschwig and N. S. Lewis, *Energ. Environ. Sci.*, 2014, 7, 3334-3337.
- 2 J.-W. Jang, S. Cho, G. Magesh, Y. J. Jang, J. Y. Kim, W. Y. Kim, J. K. Seo, S. Kim, K.-H. Lee and J. S. Lee, *Angew. Chem. Int. Edit.*, 2014, DOI: 10.1002/anie.201310461, n/a-n/a.
- 3 D. H. Won, C. H. Choi, J. Chung and S. I. Woo, *Appl. Catal. B: Environ.*, 2014, 158–159, 217-223.
- 4 R. Aydın, H. Ö. Doğan and F. Köleli, *Appl. Catal. B: Environ.*, 2013, 140–141, 478-482.

