### **Electronic Supplementary Information**

# Deuteration of organic compounds by electrolysis of glucoseheavy water using a graphene oxide membrane reactor

Le Mai Hong Tham,<sup>‡a</sup> Imam Sahroni, <sup>‡bc</sup> Ghina Kifayah Putri,<sup>b</sup> Taiga Kodama,<sup>b</sup> Muhammad Fadil,<sup>b</sup> Takeru Nakahara,<sup>b</sup> Ami Takase,<sup>b</sup> Muhammad Sohail Ahmad,<sup>de</sup> Armando T. Ouitain,<sup>f</sup>

Yusuke Inomata,<sup>b</sup> Prasert Reubroycharoen,<sup>\*a</sup> and Tetsuya Kida,<sup>\*bde</sup>

<sup>a</sup>Center of Excellence in Catalysis for Bioenergy and Renewable Chemicals (CBRC), Department of Chemical Technology, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand.

<sup>b</sup>Graduate School of Science and Technology, Department of Applied Chemistry and Biochemistry, Faculty of Advanced Science and Technology, Kumamoto University, Kumamoto 860-8655, Japan.

<sup>c</sup>Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Islam Indonesia, Yogyakarta 55584, Indonesia.

<sup>d</sup>Institute of Industrial Nanomaterials (IINa), Kumamoto University, Kumamoto 860-8555, Japan.

<sup>e</sup>International Research Organization for Advanced Science and Technology (IROAST), Kumamoto University, Kumamoto 860-8555, Japan.

<sup>f</sup>Center for International Education, Kumamoto University, Kumamoto 860-8555, Japan.

\*Corresponding authors: tetsuya@kumamoto-u.ac.jp, prasert.r@chula.ac.th.

#### **Experimental Section**

#### **Graphene Oxide synthesis**

Graphene oxide (GO) was synthesized via a modified Tour's method. Briefly, a mixture of 3 g expanded graphite (EC500 and EC1000), 360 mL of concentrated H<sub>2</sub>SO<sub>4</sub>/H<sub>3</sub>PO<sub>4</sub>, and 18 g KMnO<sub>4</sub> were placed in a boiling flask. The boiling flask was then connected to a condenser, and the mixture was stirred for 12 h at 50 °C. After completing the reaction, the mixture was slowly poured into 400 mL DI water and cooled with an ice bath. While the mixture was stirred, 3 mL of 30% H<sub>2</sub>O<sub>2</sub> was added to reduce the residual permanganate. The gas formation occurred during the addition of H<sub>2</sub>O<sub>2</sub>, making the solution's color slowly brown. After cooling down, the mixture containing graphite oxide was transferred to centrifuge tubes and centrifuged for 15 min. The precipitates were then washed with an aqueous solution of HCl (5%) to remove the remaining K<sup>+</sup> and Mn<sup>+</sup>. The mixture was centrifuged at 4000 rpm for 20 min (three times). The mixture was washed with DI water and sonicated for 12 hours to produce GO nanosheets. The resulting mixture was centrifuged again at 1000 rpm for 30 min.

#### **Graphene Oxide Membrane Fabrication**

We fabricated three different types of GO membranes; (1) GOM, (2) Ce ion doped-GOM (Ce-GOM), and (3) Ce ion and 2-hydroxyethanesulfonic acid-doped GOM (S-Ce-GOM). We fabricated (1) GOM by filtering a GO suspension (5 mL) in stacking two membrane filters with 180  $\mu$ m and 0.4  $\mu$ m pore size for 12 h. (2) Ce-GOM was fabricated by filtering a mixture of Ce(SO<sub>4</sub>)<sub>2</sub> (0.005 mmol) and GO suspension (5 mL) and (3) S-Ce-GO membrane was fabricated by filtering a mixture of 2-hydroxyethanesulfonic acid (0.01 mmol), Ce(SO<sub>4</sub>)<sub>2</sub> (0.005 mmol), and GO suspension

(5 mL), respectively. Finally, the GOMs were removed from the supporting membrane filters to form self-standing GOMs.

#### Analysis of Permeated Gases from the GOM Reactor

To evaluate the evolution rate of hydrogen and deuterium gas from the reactor, glucose–D<sub>2</sub>O electrolysis was performed at room temperature using GOM, Ce-GOM, and S-Ce-GOM membrane reactor fitted with an IrO<sub>2</sub>(40 wt%)/Al<sub>2</sub>O<sub>3</sub> catalyst on anode and Pt (36.8 wt%)/C catalyst on the cathode. D<sub>2</sub>O or glucose-containing D<sub>2</sub>O (0.5 M) was charged into the anode tank, and Ar as carrier gas was flowed into the cathode cell at a rate of 50 mL/min. An IrO<sub>2</sub>(40 wt%)/Al<sub>2</sub>O<sub>3</sub> electrode catalyst was employed at the anode, while Pt(36.8 wt%)/C electrode catalyst was used at the cathode. The electrolysis was performed using a potentiostat. The GOM separated the anode and cathode cells. The rate of H<sub>2</sub>–D<sub>2</sub> production was investigated while increasing the current density ( $I_{cell}$ ) at the cell voltage ( $V_{cell}$ ) of 1.0–3.0 V. Ar gas flowed to the empty cathode cell, and the gas generated at the cathode was analyzed by gas chromatography-thermal conductivity detector (GC-TCD).

The  $D_2/H_2$  ratio of the gas produced at the cathode was also measured using an FTIR spectroscopy (FTIR-4000 JASCO, Tokyo, Japan) system equipped with a long-path gas cell (PIKE Technology, Madison, Madison, USA), as shown in Fig. S6. The gas generated from the cathode cell was introduced into a cold trap, where water vapor was removed. Then, synthetic oxygen was mixed with this gas at a flow rate of 20 mL/min, and  $D_2$  and  $H_2$  in the gas were combusted on a platinum catalyst at 150 °C to produce  $D_2O$  and  $H_2O$ , which were introduced into the gas cell. The D/H ratio of the gas was determined from the peak areas of the D–O and H–O vibrations in the FTIR spectra.

## Procedures for Deuteration of Organic Molecules Using Electrochemical GOMs Reactor

Electrochemical deuteration was conducted in air at room temperature in an electrochemical GOM reactor. The GOM electrode assembly (MEA) consisted of an anode cell, carbon separator made of isotropic graphite (current collector), carbon paper, IrO<sub>2</sub> (40 wt%)/Al<sub>2</sub>O<sub>3</sub> anode catalyst, GO membrane, Pt(36.8 wt%)/C cathode catalyst, and cathode cell. The anode and cathode were tank-type cells made of acrylic. The Pt/C catalysts were coated onto the GO membranes using a drop-coating method. Catalyst inks were prepared by mixing Pt (36.8 wt%)/C powder (TEC10E50E; Tanaka Holdings Co., Ltd., Japan) in isopropyl alcohol (reagent grade, Wako Pure Chemical Industry, Ltd., Japan). The GOMs coated with IrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and Pt/C electrodes were sandwiched between carbon papers, carbon separators, and anode/cathode cells. In the anode cell, 5 mL of D<sub>2</sub>O containing 0.5 M glucose was loaded, whereas organic molecules were used as the substrate in the cathode cell. The electrochemical reaction was performed in the potentiostat mode, where a constant applied potential (3V) was applied to the electrochemical cell using an instrument (Gamry 1010B, Philadelphia, Pennsylvania, USA).

An aliquot of the substrate solvent (200  $\mu$ L) in the cathode cell was taken out every eight hours and analyzed by <sup>1</sup>H NMR and <sup>2</sup>H NMR to monitor the deuterium incorporation (%) and the reaction profiles over time. After 24 hours of deuteration, the product was concentrated in vacuo to determine the yield (%). NMR spectra were recorded using an NMR spectrometer (JNM-ECZ400R, JEOL) operated at 400 MHz (<sup>1</sup>H NMR) and 61 MHz (<sup>2</sup>H NMR). Chemical shifts were reported in parts per million (ppm) downfield of the internal tetramethylsilane. The multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), d (doublet), and br (broad).

#### **Deuterium Incorporation (%) and Yield (%)**

Deuterium incorporation (%) in the deuterated product was quantified by the decrease in <sup>1</sup>H NMR integral intensities at the specified positions compared with the starting material. We introduced the internal standard dimethyl sulfone (DMSO<sub>2</sub>) (6H) for a quantitative NMR, TraceCERT® (Wako Pure Chemical Industry, Ltd., Japan), to determine the amount of (H) integral in the product. For example, if the <sup>1</sup>H NMR peak corresponding to the proton in terminal toluene ( $\delta = 2.29$ ) has an integration of 0.60 H compared to the starting material integration of 3.00 H. In this case, a simple subtraction indicates that 80 of 100% hydrogen atoms were exchanged for deuterium, corresponding to 80% D incorporation.

The yields of the isolated products are listed in Fig. 4. The yield was calculated by dividing the millimoles of experimental deuterated products by the millimoles of theoretical deuterated product with the equation (1) as follows:

Yield (%) = 
$$\frac{n(\text{obtained products})}{n(\text{theoretical deuterated products})} \times 100\%$$
 (1)



Fig. S1 Graphene Oxide membrane (GOM) properties. Solid state <sup>13</sup>C NMR spectra of (a) GOM, (b) Ce-GOM, and (c) S-Ce-GOM. (d) Percentage (%) of functional groups in GOM, Ce-GOM, and S-Ce-GOM.



Fig. S2 Graphene Oxide membrane (GOM) properties. (a) X-ray diffraction (XRD) patterns of GOM, Ce-GOM, and S-Ce-GOM. (b) Cross-sectional SEM images of GOM, (c) Ce-GOM, (d) S-Ce-GOM. (e) A Nyquist plot of the GOM in RH 90% at room temperature, together with the equivalent circuit, where Rs is bulk resistance, CPE is constant phase element,  $R_{ct}$  is charge transfer resistance,  $W_{s1}$  is diffusion element, and  $W_s$  is Warburg impedance.

The proton conductivity was calculated using Eq. 2,

$$\sigma = \frac{1}{A. Rs}$$
(2)

 $\sigma$ : proton conductivity, *l*: the distance between the two electrodes (cm), Rs: the membrane resistance (S), A: the cross-sectional area of the membrane (cm<sup>2</sup>). Proton conductivity for GO, Ce-GO, and S-Ce-GO were determined to be 0.14 (mS cm<sup>-1</sup>), 0.32 (mS cm<sup>-1</sup>), and 0.82 (mS cm<sup>-1</sup>), respectively.



Fig. S3 (a) Schematic experimental setup of hydrogen and deuterium production from  $D_2O$  electrolysis using graphene oxide membrane reactors. (b) Deuterium production assisted by glucose electrolysis in  $D_2O$  and its application for deuteration of toluene- $d_3$ .



Fig. S4 Photo images of a GOM reactor cell and experimental setup.



Fig. S5 (a) I-V curve of D<sub>2</sub>O electrolysis and (b) glucose–D<sub>2</sub>O electrolysis.



Fig. S6 Schematic of the FT-IR gas cell system equipped with a water vapor trap and a catalytic combustor.



Scheme S1. Electrochemical deuteration of toluene to toluene- $d_3$ 

#### **Procedure for Electrochemical Deuteration of** C(sp<sup>3</sup>)**-H bonds in Methyl Aromatic Sites**

**Deuteration of Toluene**- $d_3$  (1b). Toluene (92.14 mg, 1 mmol) was dissolved in methanol (5 mL) and loaded onto the cathode of the GOM reactor. The electrochemical deuteration reaction was performed at ambient temperature and open air at a constant cell voltage of V = 3V. After 24 h, the reaction mixture at cathode cell was concentrated in vacuo to obtain the desired product as a clear liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  [ppm] 7.19-7.23 (m, 2H), 7.08-7.18 (m, 3H), 3.88 (s, H<sub>2</sub>O), 3.53 (s, Internal Standard=DMSO<sub>2</sub>, 6H), 2.41 (m, DMSO-d<sub>6</sub>), 2.29 (s, 0.60 H). <sup>2</sup>H NMR (61 MHz, CHCl<sub>3</sub>):  $\delta$  [ppm] 2.40 (s, 3D), 4.27 (s, D<sub>2</sub>O). D% incorporation: 80%, Yield: 82%.

**2-methylnaphthalene**-*d*<sub>3</sub> (**2b**). 2-methylnaphthalene (142.20 mg, 1 mmol) was dissolved in methanol (5 mL) and loaded in the cathode of the GOM reactor. The electrochemical deuteration reaction was performed at ambient temperature and open air at a constant cell voltage of V = 3V. After 24 h, the reaction mixture at cathode cell was concentrated in vacuo to obtain the desired product as a clear liquid. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  [ppm] 7.74-7.81 (m, 1H), 7.44-7.60 (m, 2H), 7.28-7.43 (m, 4H), 3.51 (s, Internal Standard=1,4-dioxane, 8H), 2.63 (s, 0.5 H), 2.46 (m, DMSO-d<sub>6</sub>). (b) <sup>2</sup>H NMR (61 MHz, CHCl<sub>3</sub>):  $\delta$  [ppm] 2.68 (s, 3D). D% incorporation: 83%, Yield: 80%.

**4-methylanisole**-*d*<sub>3</sub> (**3b**). 4-methylanisole (122.16 mg, 1 mmol) was dissolved in methanol (5 mL) and loaded in the cathode of the GOM reactor. The electrochemical deuteration reaction was performed at ambient temperature and open air at a constant cell voltage of V = 3V. After 24 h, the reaction mixture at cathode cell was concentrated in vacuo to obtain the desired product as a clear liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  [ppm] 6.62-6.90 (m, 2H), 6.91-6.93 (m, 2H), 3.61 (s, 3H), 3.52 (s, Internal Standard=1,4-dioxane, 8H), 2.11 (s, 0.45H). (b) <sup>2</sup>H NMR (61 MHz, CHCl<sub>3</sub>):  $\delta$  [ppm] 7.26 (CDCl<sub>3</sub>), 2.11 (s, 3D). D% incorporation: 85%, Yield: 85%.

*p*-tolunitrile-*d*<sub>3</sub> (4b). *p*-tolunitrile (117.15 mg, 1 mmol) was dissolved in methanol (5 mL) and loaded in the cathode of the GOM reactor. The electrochemical deuteration reaction was performed at ambient temperature and open air at a constant cell voltage of V = 3V. After 24 h, the reaction mixture at cathode cell was concentrated in vacuo to obtain the desired product as a clear liquid. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  [ppm] 7.38-7.70 (m, 2H), 7.35-7.37 (m, 2H), 3.52 (s, Internal Standard=1,4-dioxane, 8H), 2.46-2.48 (m, DMSO-d<sub>6</sub>), 2.36 (s, 0.55H). (b) <sup>2</sup>H NMR (61 MHz, CHCl<sub>3</sub>):  $\delta$  [ppm] 2.36 (s, 3D). D% incorporation: 82%, Yield: 81%.

**O-xylene-***d*<sub>6</sub> (**5b**). O-xylene (106.17 mg, 1 mmol) was dissolved in ethanol (5 mL) and loaded onto the GOM reactor cathode. The electrochemical deuteration reaction was performed at ambient temperature and open air at a constant cell voltage of V = 3V. After 24 h, the reaction mixture at cathode cell was concentrated in vacuo to obtain the desired product as a clear liquid. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  [ppm] 7.00-7.07 (m, 4H), 3.51 (s, Internal Standard=1,4-dioxane, 8H), 2.46-2.47 (m, DMSO-d<sub>6</sub>), 2.18 (s, 1.15 H). (b) <sup>2</sup>H NMR (61 MHz, CHCl<sub>3</sub>):  $\delta$  [ppm] 2.18 (s, 6D), 4.5 (s, D<sub>2</sub>O). D% incorporation: 80%, Yield: 80%.

**1,3,5-trimethylbenzene**-*d*<sup>9</sup> (**6b**). 1,3,5-trimethylbenzene (120.19 mg, 1 mmol) was dissolved in ethanol (10 mL) and loaded in the cathode of the GOM reactor. The electrochemical deuteration reaction was performed at ambient temperature and open air at a constant cell voltage of V = 3V. After 24 h, the reaction mixture at cathode cell was concentrated in vacuo to obtain the desired product as a clear liquid. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  [ppm] 76.71 (s, 3H), 3.51 (s, Internal Standard=1,4-dioxane, 8H), 2.46-2.47 (m, DMSO-d<sub>6</sub>), 2.18 (s, 2.25 H). (b) <sup>2</sup>H NMR (61 MHz, CHCl<sub>3</sub>):  $\delta$  [ppm] 2.18 (s, 6D), 4.5 (s, D<sub>2</sub>O). D% incorporation: 75%, Yield: 72%.



Fig. S7 (a) <sup>1</sup>H NMR and b) <sup>2</sup>H NMR spectra of Toluene-*d*<sub>3</sub>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ
[ppm] 7.19-7.23 (m, 2H), 7.08-7.18 (m, 3H), 3.88 (s, H<sub>2</sub>O), 3.53 (s, Internal Standard=DMSO<sub>2</sub>,
6H), 2.41 (m, DMSO-d<sub>6</sub>), 2.29 (s, 0.60 H). <sup>2</sup>H NMR (61 MHz, CHCl<sub>3</sub>): δ [ppm] 2.30 (s, 3D),
4.27 (s, D<sub>2</sub>O). D% incorporation: 80%, Yield: 82%.



Fig. S8 (a) <sup>1</sup>H NMR and b) <sup>2</sup>H NMR spectra of Toluene- $d_3$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  [ppm] 7.19-7.23 (m, 2H), 7.10-7.18 (m, 3H), 3.52 (s, Internal Standard=DMSO<sub>2</sub>, 6H), 2.41 (m, DMSO-d<sub>6</sub>), 2.25 (s, 0.65 H). <sup>2</sup>H NMR (61 MHz, CHCl<sub>3</sub>):  $\delta$  [ppm] 2.25 (s, 3D). D% incorporation: 79%, Yield: 80%.



Fig. S9 (a) <sup>1</sup>H NMR and (b) <sup>2</sup>H NMR spectra of Toluene- $d_3$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ [ppm] 7.19-7.23 (m, 2H), 7.08-7.18 (m, 3H), 3.88 (s, H<sub>2</sub>O), 3.53 (s, Internal Standard=DMSO<sub>2</sub>, 6H), 2.46 (m, DMSO-d<sub>6</sub>), 2.25 (s, 1.10 H). <sup>2</sup>H NMR (61 MHz, CHCl<sub>3</sub>): δ [ppm] 2.40 (s, 3D), 4.85 (s, D<sub>2</sub>O). D% incorporation: 63%, Yield: 60%.



Fig. S10 (a) <sup>1</sup>H NMR and (b) <sup>2</sup>H NMR spectra of 2-methylnaphthalene-*d*<sub>3</sub>. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ [ppm] 7.74-7.81 (m, 1H), 7.44-7.60 (m, 2H), 7.28-7.43 (m, 4H), 3.51 (s, Internal Standard=1,4-dioxane, 8H), 2.63 (s, 0.5 H), 2.46 (m, DMSO-d<sub>6</sub>). (b) <sup>2</sup>H NMR (61 MHz, CHCl<sub>3</sub>): δ [ppm] 2.68 (s, 3D). D% incorporation: 83%, Yield: 80%.



Fig. S11 (a) <sup>1</sup>H NMR and (b) <sup>2</sup>H NMR spectra of 4-methylanisole- $d_3$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  [ppm] 6.62-6.90 (m, 2H), 6.91-6.93 (m, 2H), 3.61 (s, 3H), 3.52 (s, Internal Standard=1,4-dioxane, 8H), 2.11 (s, 0.45H). (b) <sup>2</sup>H NMR (61 MHz, CHCl<sub>3</sub>):  $\delta$  [ppm] 7.26 (CDCl<sub>3</sub>), 2.11 (s, 3D). D% incorporation: 85%, Yield: 85%.



Fig. S12 (a) <sup>1</sup>H NMR and (b) <sup>2</sup>H NMR spectra of *p*-tolunitrile-*d*<sub>3</sub>. <sup>1</sup>H NMR (400 MHz, DMSOd<sub>6</sub>): δ [ppm] 7.38-7.70 (m, 2H), 7.35-7.37 (m, 2H), 3.52 (s, Internal Standard=1,4-dioxane, 8H), 2.46-2.48 (m, DMSO-d<sub>6</sub>), 2.36 (s, 0.55H). (b) <sup>2</sup>H NMR (61 MHz, CHCl<sub>3</sub>): δ [ppm] 2.36 (s, 3D). D% incorporation: 82%, Yield: 81%.



Fig. S13 (a) <sup>1</sup>H NMR and (b) <sup>2</sup>H NMR spectra of O-xylene-*d*<sub>6</sub>. <sup>1</sup>H NMR (400 MHz, DMSOd<sub>6</sub>): δ [ppm] 7.00-7.07 (m, 4H), 3.51 (s, Internal Standard=1,4-dioxane, 8H), 2.46-2.47 (m, DMSO-d<sub>6</sub>), 2.18 (s, 1.15 H). (b) <sup>2</sup>H NMR (61 MHz, CHCl<sub>3</sub>): δ [ppm] 2.18 (s, 6D), 4.5 (s, D<sub>2</sub>O). D% incorporation: 80%, Yield: 80%.



Fig. S14 (a) <sup>1</sup>H NMR and (b) <sup>2</sup>H NMR spectra of Mesitylene- $d_9$ . <sup>1</sup>H NMR (400 MHz, DMSOd<sub>6</sub>):  $\delta$  [ppm] 76.71 (s, 3H), 3.51 (s, Internal Standard=1,4-dioxane, 8H), 2.46-2.47 (m, DMSOd<sub>6</sub>), 2.18 (s, 2.25 H). (b) <sup>2</sup>H NMR (61 MHz, CHCl<sub>3</sub>):  $\delta$  [ppm] 2.18 (s, 6D), 4.5 (s, D<sub>2</sub>O). D% incorporation: 75%, Yield: 72%.



Fig. S15 (a) <sup>1</sup>H NMR spectrum of 0.5 M glucose in D<sub>2</sub>O before electrolysis; <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O):  $\delta$  [ppm] 5.08-5.09 (d, 1H), 4.51 (s, D<sub>2</sub>O), 4.48-4.49 (d, 1H), 3.50-3.54 (m, 2H), 3.28-3.33 (m, 2H), 3.25-3.27 (m, 2H), 3.12-3.24 (m, 2H), 3.08-3.10 (m, 1H). (b) <sup>1</sup>H NMR spectrum of 0.5 M glucose in D<sub>2</sub>O after electrolysis under an applied potential of 3 V for 24 h; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  [ppm] 4.85-4.87 (d, 1H), 4.58 (s, D<sub>2</sub>O), 4.56-4.57 (d, 1H), 4.31-4.33 (d, 2H), 4.30-4.31 (m, 1H), 3.50-3.53 (m, 2H), 3.34-3.38 (m, 3H), 3.06-3.07 (m, 1H), 3.00-3.04 (m, 1H).

Glucose shows absorption peaks from 3.00 to 3.80 ppm assigned to the ring protons.<sup>1, 2</sup> The proton signals at 4.51 ppm and 5.08 ppm are associated with  $\alpha$ -H1 and  $\beta$ -H1 bound to the anomeric carbon atom (C1 position) of glucose. When electrolysis proceeded at an applied voltage of 3 V, the presence of gluconic acid in the mixture was revealed by the appearance of a 4.29 ppm proton signal typical of 1H at the C2 position.<sup>3-5</sup>



Fig. S16 CO<sub>2</sub> detection during the electrolysis of 0.5 M glucose in D<sub>2</sub>O under applied potential  $V_{cell} = 3.0 V$  for 60 minutes.

#### REFERENCES

- 1. B. E. Lewis and V. L. Schramm, J. Am. Chem. Soc., 2001, 123, 1327-1336.
- 2. S. Dash and N. Munichandraiah, J. Electrochem. Soc., 2013, 160, H858.
- 3. N. Nordin, L. Bordonali, H. Davoodi, N. D. Ratnawati, G. Gygli, J. G. Korvink, V. Badilita and N. MacKinnon, *Angew. Chem. Int. Ed.*, 2021, **60**, 19176-19182.
- 4. M. Varničić, I. N. Zasheva, E. Haak, K. Sundmacher and T. Vidaković-Koch, *Catalysts*, 2020, **10**, 269.
- 5. R. D. Armstrong, J. Hirayama, D. W. Knight and G. J. Hutchings, ACS Catal., 2019, 9, 325-335.