

## Catalytic Reduction and Reductive Functionalisation of Carbon Dioxide with Waste Silicon from Solar Panel as the Reducing Agent

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## 1 Experimental Section

### 1.1 General Methods

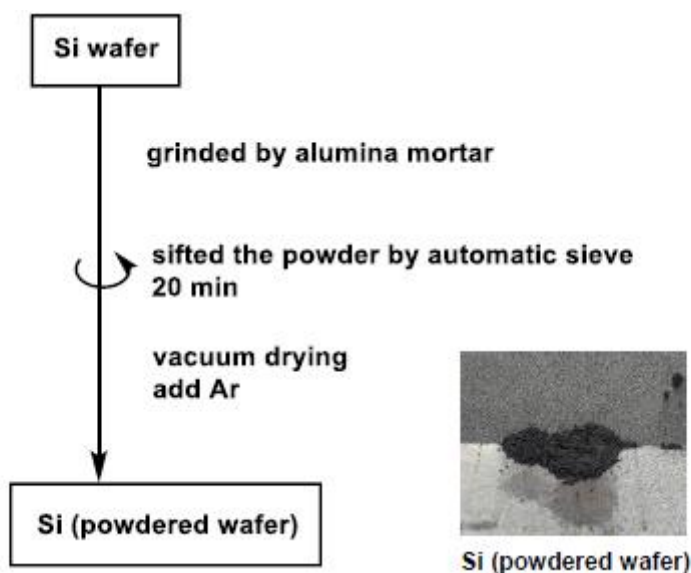
Czochralski monocrystalline silicon wafers (solar grade, Si: >99.9999%) obtained from solar panel production process were gifted from National Institute of Advanced Industrial Science and Technology (AIST). Tetrabutylammonium fluoride trihydrate (TBAF.3H<sub>2</sub>O, >99%) was purchased from Kanto Chemical, Co. Inc. without further purification. <sup>13</sup>CO<sub>2</sub> (<sup>13</sup>C, 99%, <1% <sup>18</sup>O) was purchased from Cambridge Isotope Laboratories. D<sub>2</sub>O was purchased from Kanto Chemical, Co. Inc. CDCl<sub>3</sub> (>99.8%) was purchased from Kanto Chemical, Co. Inc. Dimethylsulfoxide (DMSO, dehydrated, >99%) was purchased from Kanto Chemical, Co. Inc. and used without further purification. Unless otherwise mentioned, all other materials were purchased from Tokyo Chemical Industry Co., Ltd. Kanto Chemical Co., Inc. and Aldrich Inc.

The liquid <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured with CDCl<sub>3</sub> as the solvent using Bruker AVANCE 400 (operating frequency are 400 and 100 MHz for <sup>1</sup>H and <sup>13</sup>C NMR measurement, respectively) and Bruker AVANCE HD500 (operating frequency are 500 and 125 MHz for <sup>1</sup>H and <sup>13</sup>C NMR measurement, respectively). Shimadzu QP2010 SE gas chromatograph-mass spectrometer (GC-MS) equipped with a DB-1 column and Shimadzu GC2025 gas chromatograph with flame ionization detection (GC-FID) were used for product characterization. Initially, the temperature was hold at 50°C for 6 minutes, then raised with a rate of 10°C/min to 280°C, then the temperature was hold at 280°C for the final 10 minutes. XPS analyses were conducted on an ULVAC-PHI ESCA1700R system equipped with a dual Mg/Al X-ray source and a hemispherical analyzer operating in the field analyzer transmission mode. Al K<sub>α</sub> X-ray source was operated at 350 W and 14 kV. Excess charges on the samples were neutralized. The analysis chamber was conditioned to be less than 10<sup>-7</sup> Pa during measurement. Spectra were acquired in the O 1s, C 1s, N 1s, F 1s, and Si 2p regions with pass energies of 58.7 eV. Samples were powdered and attached to a stainless-steel plate with a carbon double tape. The C 1s peak at a binding energy (BE) of 285 eV was taken as an internal reference. Powder X-ray diffraction (XRD) patterns were recorded using a Rigaku SmartLab diffractometer with Cu K<sub>α</sub> radiation. SEM-EDS analysis of powdered silicon samples was performed by HITACHI SU8010.

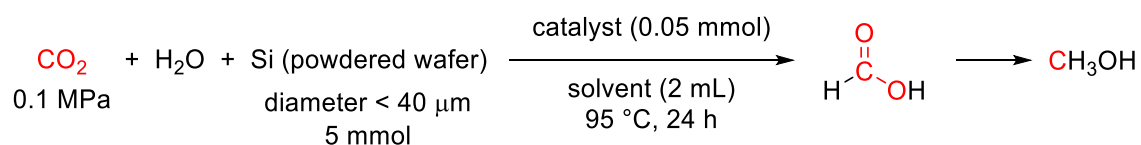
### 1.2 Preparation of silicon powder as the reducing agent

Silicon wafers were crushed with alumina mortar to powdered form and sifted by automatic sieve with 300, 90, 40, and 20 μm mesh sizes. The different sizes of silicon powders were stored in

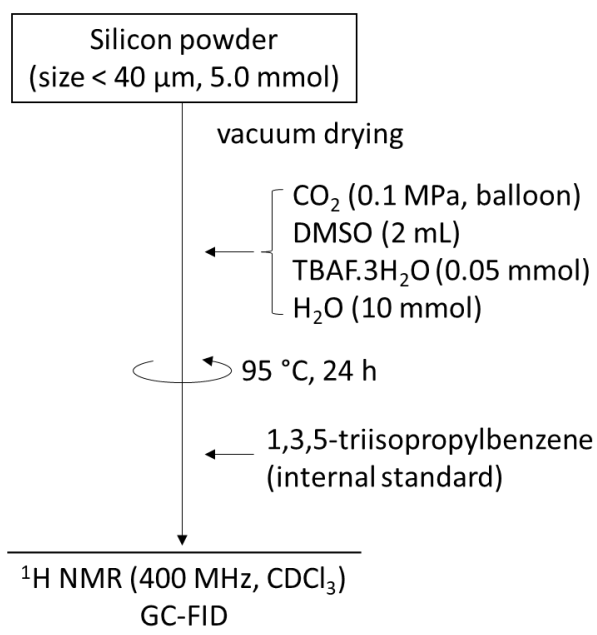
containers with Argon atmosphere and moisture was kept low by storing the container inside a desiccator.



### 1.3 Typical procedure for fluoride-catalyzed CO<sub>2</sub> reduction with silicon powder and H<sub>2</sub>O

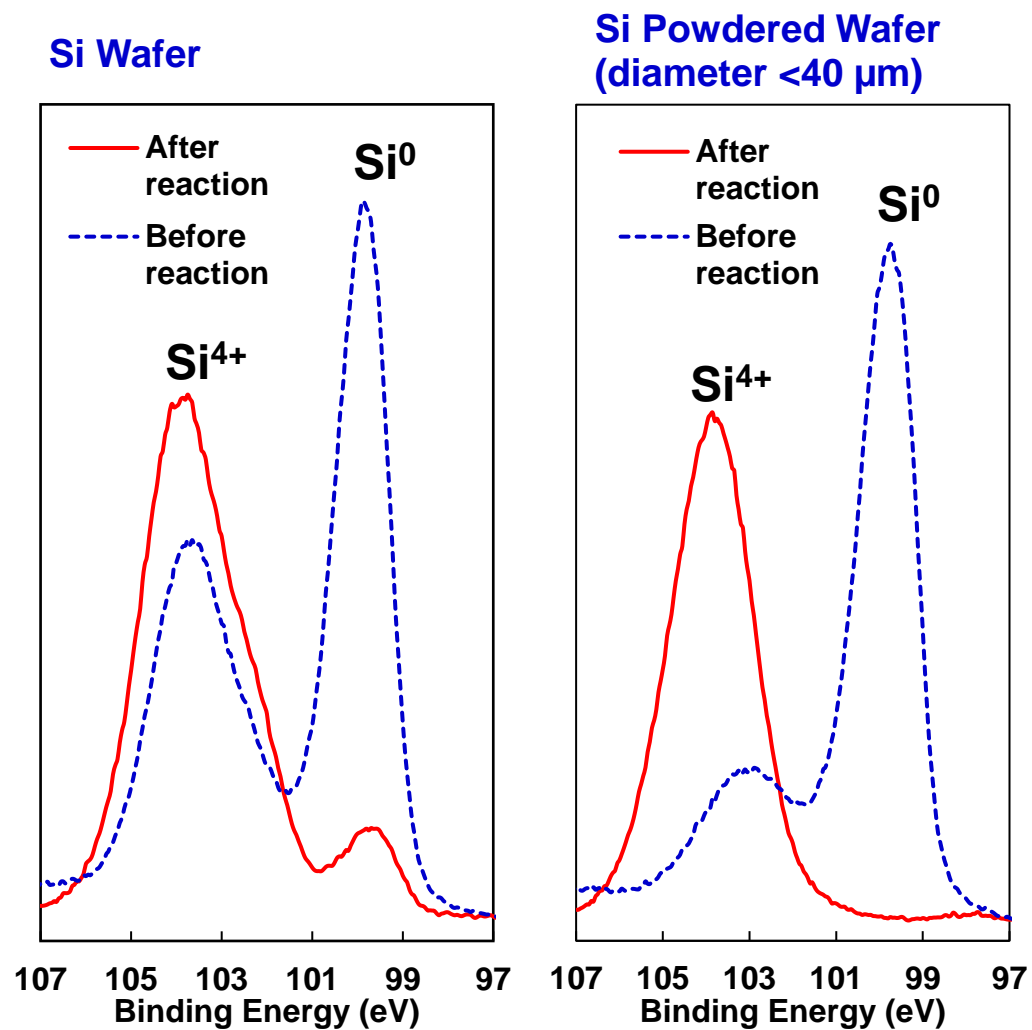


To a balloon-connected Schlenk tube, powdered silicon wafer (diameter < 40  $\mu\text{m}$  or 20  $\mu\text{m}$ , 140 mg, 5.0 mmol) was added and vacuum dried. Afterwards, CO<sub>2</sub> (0.1 MPa) was introduced. In a vial, catalyst (typically TBAF.3H<sub>2</sub>O, 0.05 mmol), solvent (typically DMSO, 2 mL), and a definite amount of deionized water (typically 10 mmol) were mixed and introduced to the Schlenk tube by 2 mL syringe. For pressurized reaction (0.2-0.9 MPa), a SUS autoclave was used as a reactor. The resulting mixture was stirred vigorously at 95  $^\circ\text{C}$  for 24 h. the reaction products were confirmed through GC-MS and <sup>1</sup>H NMR spectrometry. The formic acid yield was determined by the liquid <sup>1</sup>H NMR in CDCl<sub>3</sub> solvent using the internal standard technique with 1,3,5-triisopropylbenzene as the internal standard. The quantitative correlation of <sup>1</sup>H NMR peak area of formic acid and internal standard (triisopropylbenzene) was confirmed by standard samples. Simultaneously, methanol yield was determined by GC-FID analysis after dissolving a part of the reaction mixture in diethylether and hydrochloric acid followed by filtration.

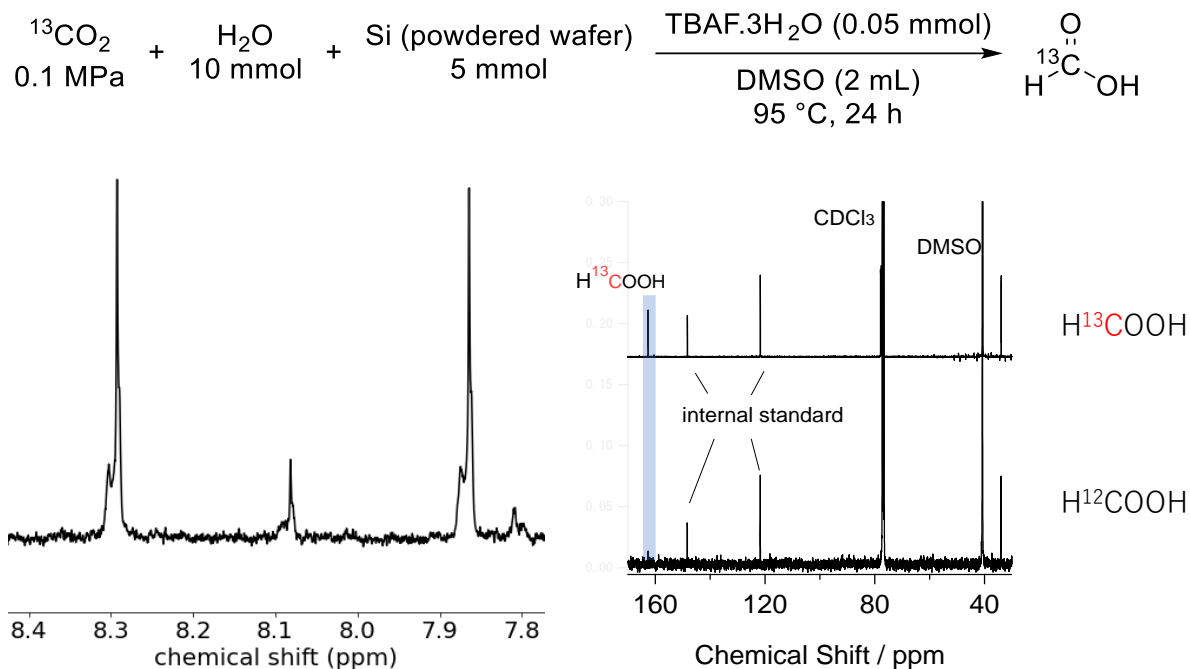


#### 1.4 Typical procedure for fluoride-catalyzed formamide synthesis with silicon powder, amine, and $\text{H}_2\text{O}$

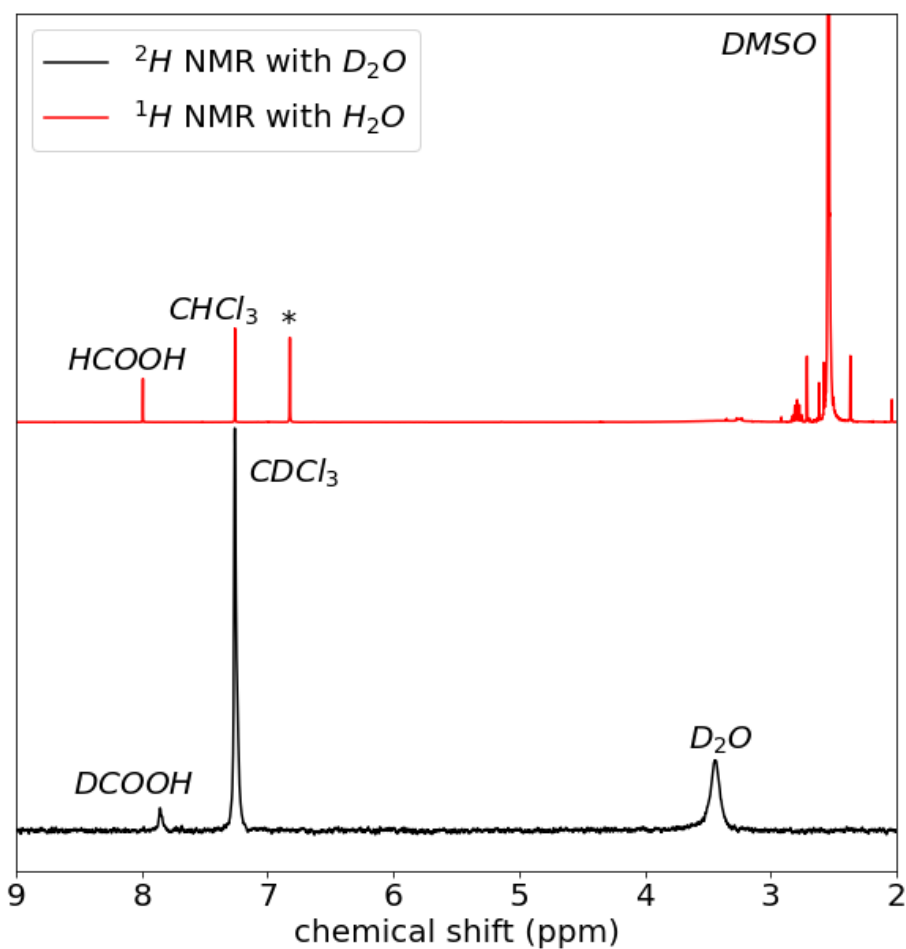
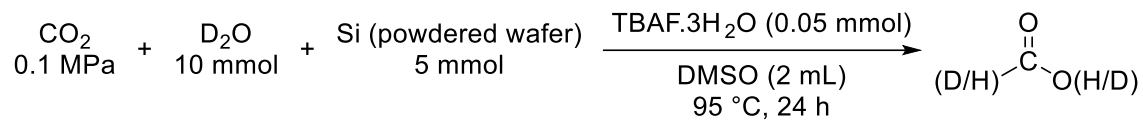
In a vial, TBAF·3 $\text{H}_2\text{O}$  (0.05 mmol), DMSO (2 mL), morpholine (1.0 mmol), and a definite amount of deionized water (10 mmol) were mixed and introduced to a SUS autoclave. To a SUS autoclave, powdered silicon wafer (diameter <math>< 20 \mu\text{m}</math>, 5.0 mmol) was added. Afterwards,  $\text{CO}_2$  was introduced and pressurized to 0.5MPa. The resulting mixture was stirred vigorously at 120 °C for 72 h. the reaction products were confirmed through GC-MS and  $^1\text{H}$  NMR spectrometry. The formamide yield was determined by the liquid  $^1\text{H}$  NMR in  $\text{CDCl}_3$  solvent using the internal standard technique with 1,3,5-triisopropylbenzene as the internal standard.



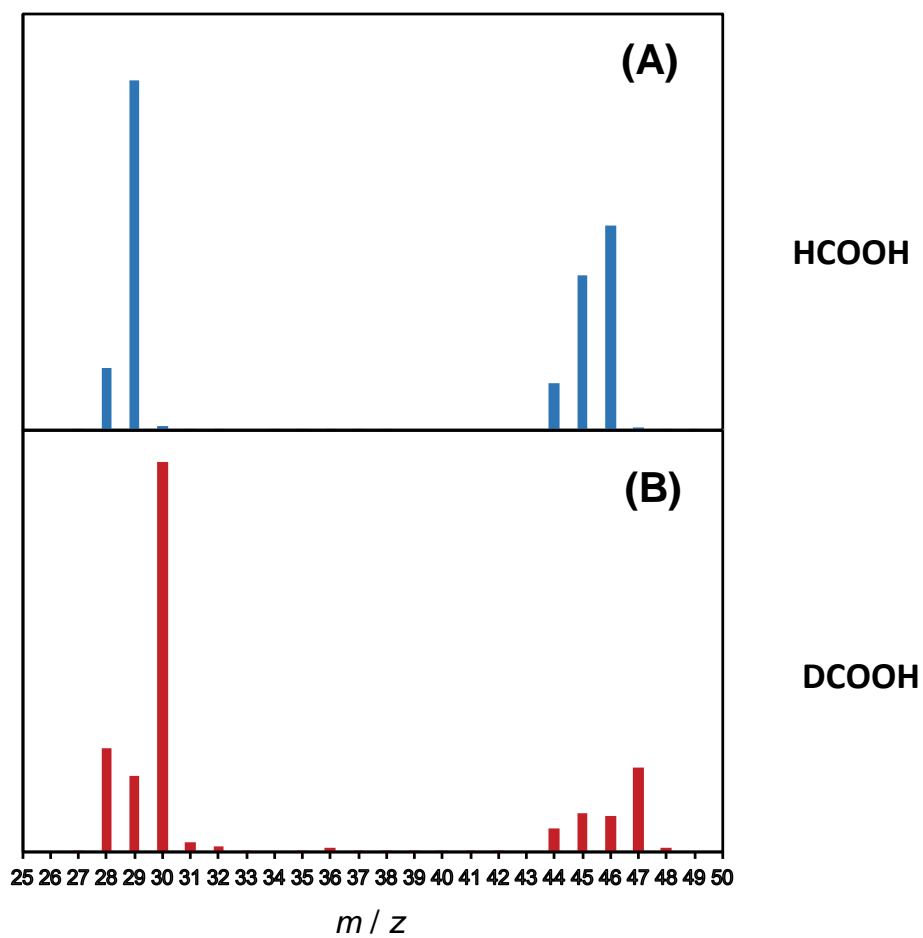
**Fig. S1** Si 2p XPS spectra of silicon wafer and powdered silicon wafer before and after the formic acid synthesis. Reaction conditions: powdered silicon wafer (5 mmol), CO<sub>2</sub> (0.1 MPa, balloon), H<sub>2</sub>O (10 mmol), catalyst (0.05 mmol), DMSO (2 mL), 95 °C, 24 h.



**Fig. S2**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the reaction mixture of formic acid synthesis using  $^{13}\text{CO}_2$  as the carbon source. Reaction conditions: powdered silicon wafer (5 mmol),  $^{13}\text{CO}_2$  (0.1 MPa, balloon),  $\text{H}_2\text{O}$  (10 mmol),  $\text{TBAF}\cdot 3\text{H}_2\text{O}$  (0.05 mmol), DMSO (2 mL),  $95^\circ\text{C}$ , 24 h.

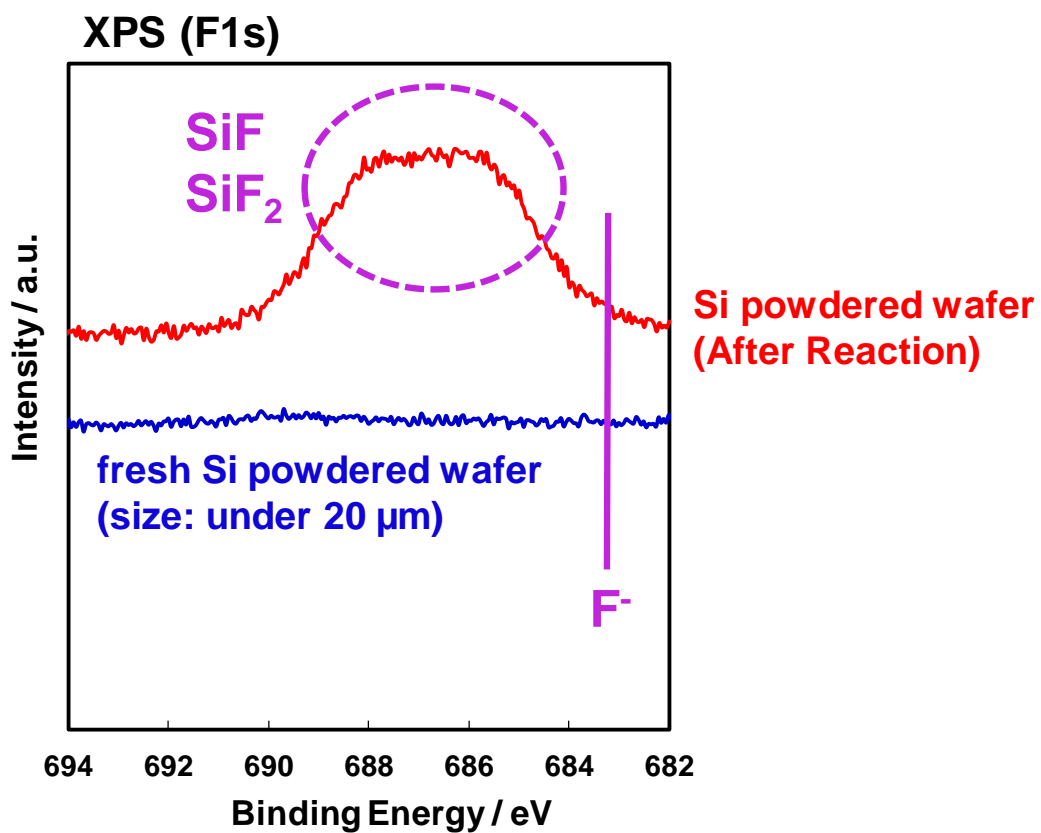


**Fig. S3** (top)  $^1\text{H}$  NMR spectrum of the reaction mixture of formic acid synthesis using  $\text{H}_2\text{O}$  as the hydrogen source and (bottom)  $^2\text{H}$  NMR spectrum of similar reaction using  $\text{D}_2\text{O}$  as the hydrogen source. Reaction conditions: powdered silicon wafer (5 mmol),  $\text{CO}_2$  (0.1 MPa, balloon),  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$  (10 mmol), TBAF $\cdot$ 3 $\text{H}_2\text{O}$  (0.05 mmol), DMSO (2 mL), 95  $^\circ\text{C}$ , 24 h. (\*) indicated internal standard peak



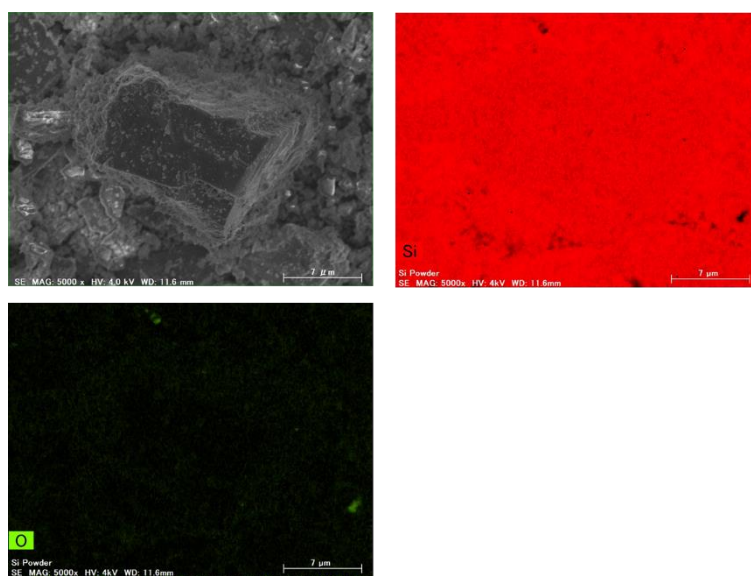
**Fig. S4** Mass spectra of (A) pure formic acid and (B) the reaction mixture of formic acid synthesis using  $D_2O$  as the hydrogen source. Reaction conditions: powdered silicon wafer (5 mmol),  $CO_2$  (0.1 MPa, balloon),  $D_2O$  (10 mmol), TBAF. $3H_2O$  (0.05 mmol), DMSO (2 mL), 95 °C, 24 h.



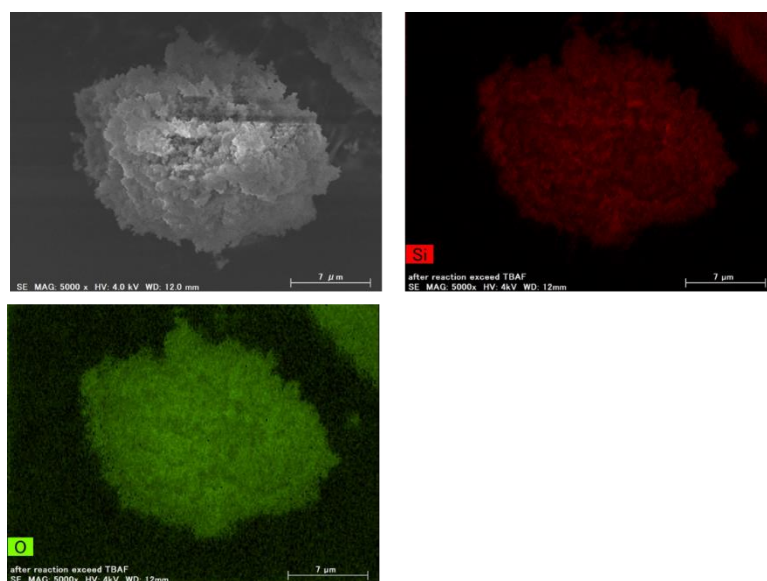


**Fig. S5** F 1s XPS spectra of silicon wafer and powdered silicon wafer before and after the formic acid synthesis. Reaction conditions: powdered silicon wafer (5 mmol), CO<sub>2</sub> (0.1 MPa, balloon), H<sub>2</sub>O (10 mmol), catalyst (0.05 mmol), DMSO (2 mL), 95 °C, 24 h.

(A)



(B)



**Fig. S6** SEM image and EDS mapping of (A) fresh Si powder and (B) recovered solid after the catalysis.