Supporting Information

CO_2 Reduction Promoted by Imidazole Supported on a Phosphonium-Type Ionic Liquid-Modified Au Electrode at a Low Overpotential

Go Iijima,[†] Tatsuya Kitagawa,[¶] Akira Katayama,[¶] Tomohiko Inomata,[¶] Hitoshi Yamaguchi,[†] Kazunori Suzuki,[†] Kazuki Hirata,[†] Yoshimasa Hijikata,[†] Miho Ito,[†] and Hideki Masuda[¶*]

[†] Advanced Research and Innovation Center, DENSO CORPORATION, 500-1 Minamiyama, Komenoki-cho, Nisshin 470-0111, Japan

[¶] Graduate School of Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa, Nagoya 466-8555, Japan

*Corresponding email: masuda.hideki@nitech.ac.jp

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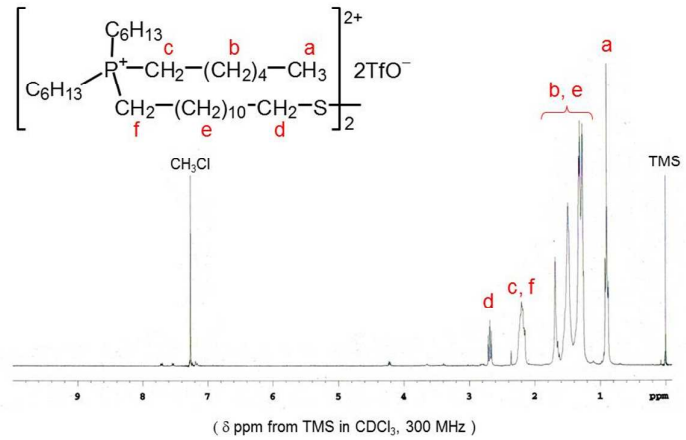
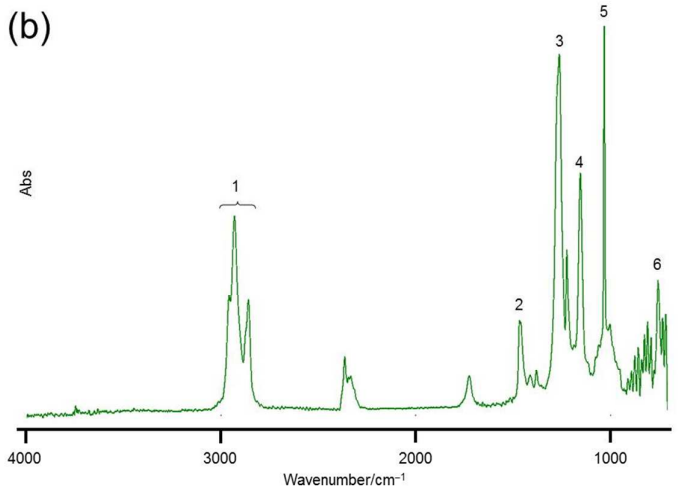
(a)



peak	chemical shift
a	0.90 (m, 9H, CH_3)
b, e	1.25-1.69 (m, 88H, -CH_2-)
c, f	2.20 (m, 8H, P^+CH_2-)
d	2.69 (t, 4H, SCH_2-)

(b)



	wavenumber/cm^{-1}	vibration mode
1	2957, 2927, 2855	ν(C-H), ν_{as}(C-H), ν_s(C-H)
2	1465	δ(C-H)
3	1260	ν(C-F)
4	1153	ν(SO_3^-)
5	1030	ν(S=O)
6	754	ν(C-S)

Figure S1. Characterization of IL, (a) ^{1}H-NMR and (b) FT-IR spectra.

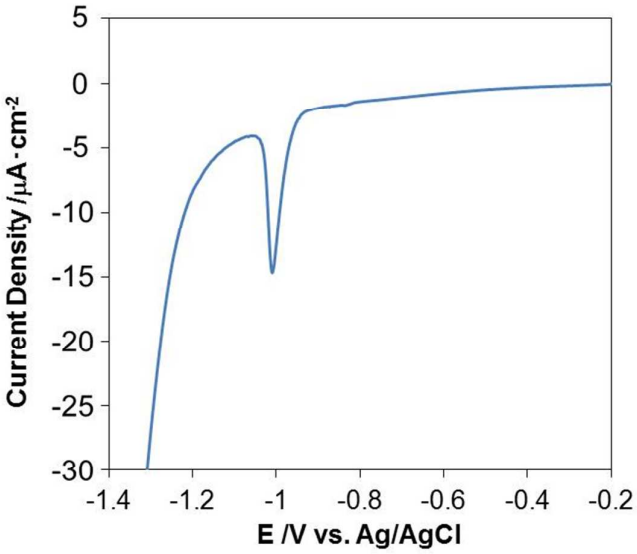


Figure S2. Electrochemical desorption of IL modified on the Au(111) electrode.

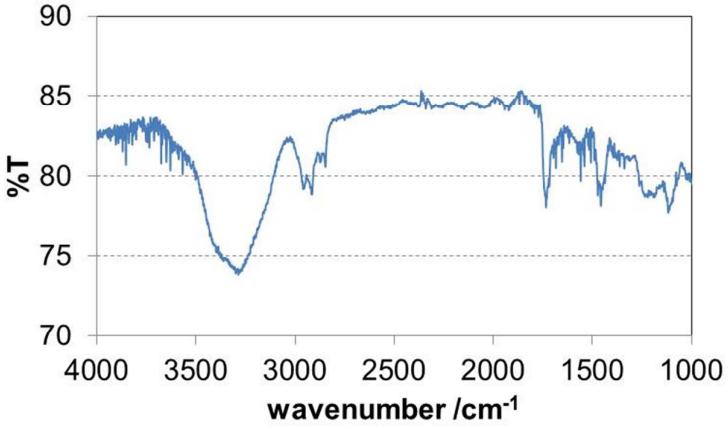
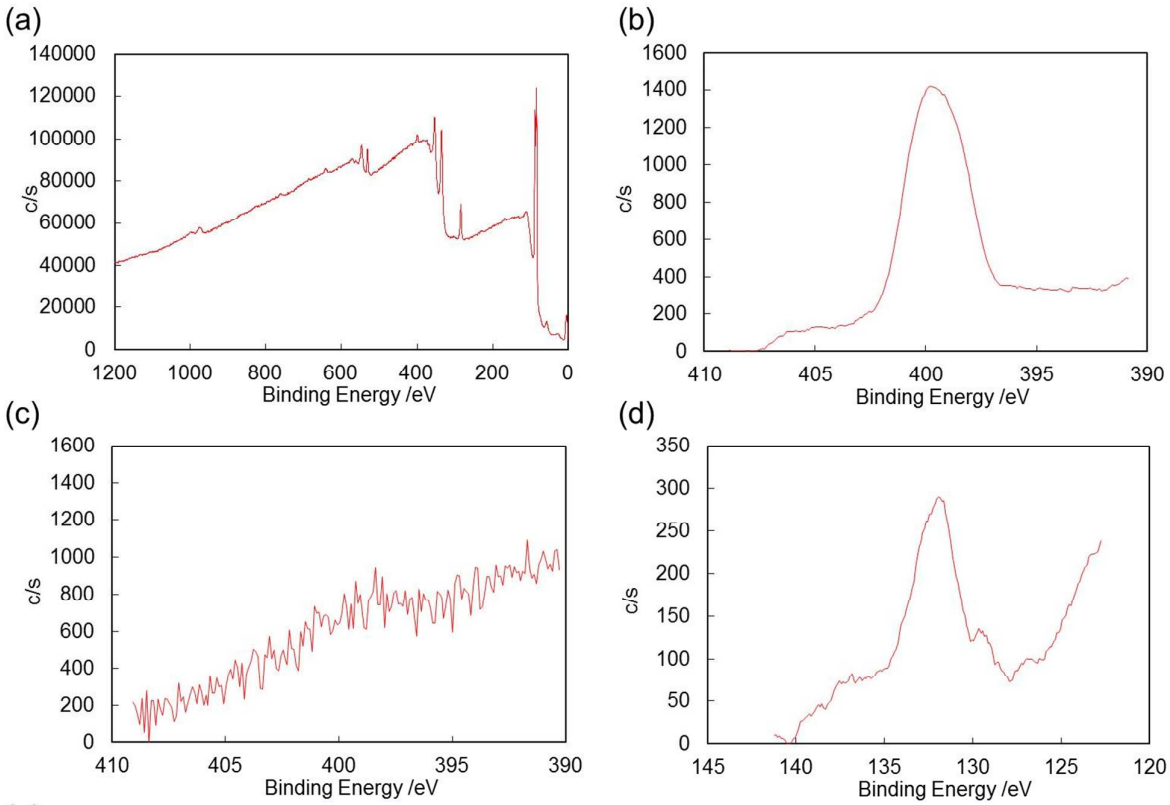


Figure S3. FT-IR spectrum of **imidazole@IL/Au** by RAS measurement.



(e)

electrode	N1s/P2p
imidazole@IL/Au(−120℃)	17.0
imidazole@IL/Au(r. t.)	2.4

Figure S4. XPS analysis of **imidazole@IL/Au.** (a) Wide range spectrum as measured at −120 °C, (b) spectrum in the range of 390 - 408 eV as measured at −120 °C, (c) spectrum in the range of 390 - 408 eV as measured at room temperature, (d) spectrum in the range of 124 - 140 eV as measured at −120 °C, (e) peak intensity ratio of N1s to P2p as performed at each temperature.

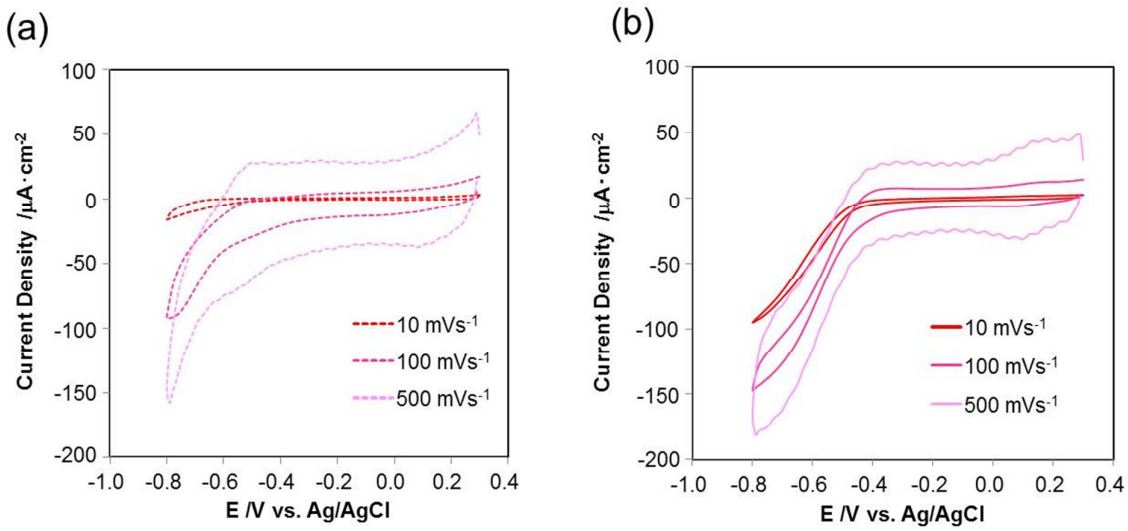


Figure S5. CV measurements of **imidazole@IL/Au** under (a) Ar and (b) CO_2 at various sweep rates.

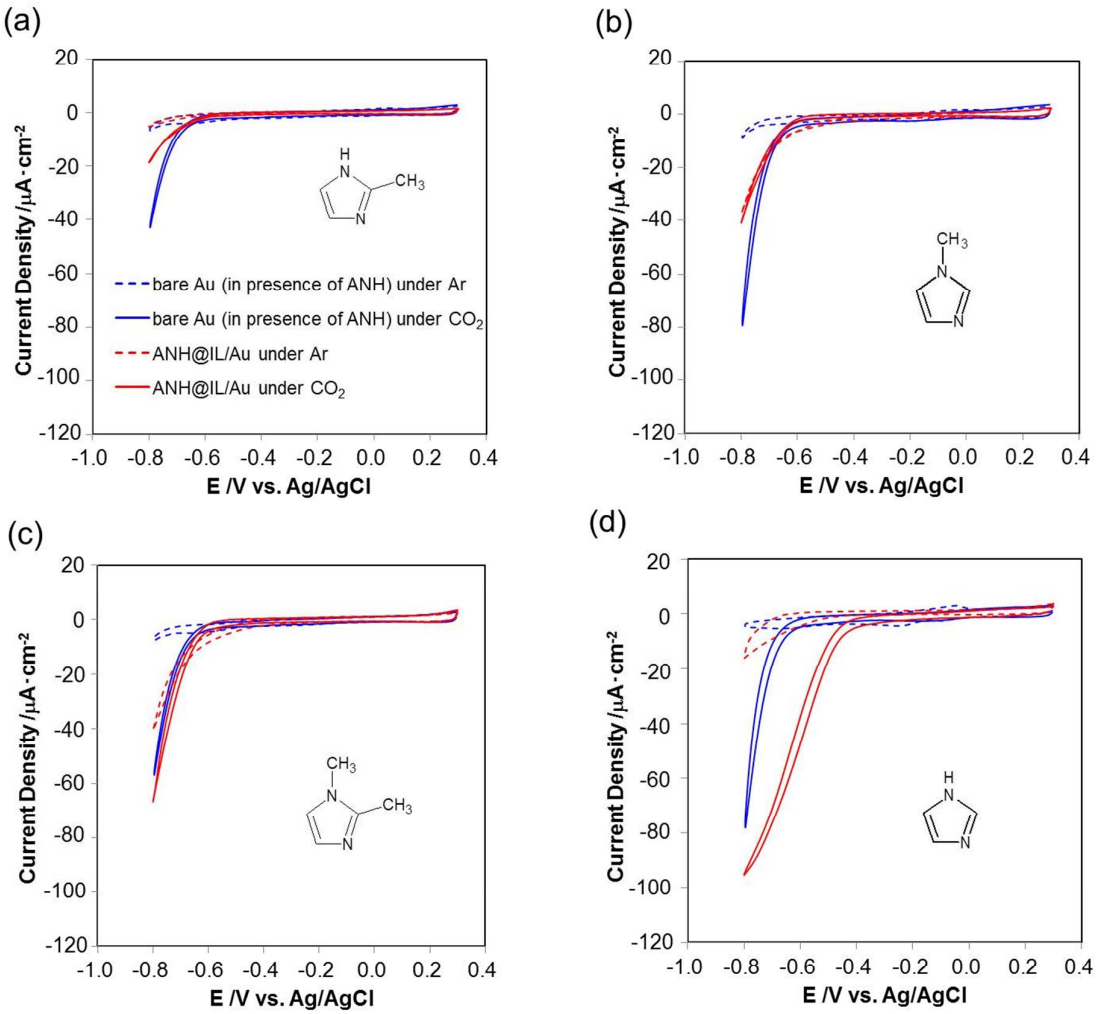


Figure S6. CV measurements of the **ANH@IL/Au** systems containing (a) 2-methylimidazole, (b) 1-methylimidazole, (c) 1,2-dimethylimidazole and (d) imidazole as ANH, as measured with a sweep rate of 10 mV/sec.

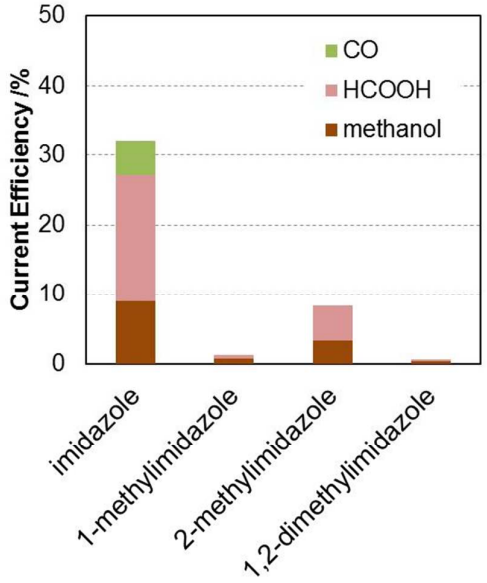


Figure S7. Current efficiencies of formate, methanol and CO produced using several different **ANH@IL/Au** electrodes (imidazole, 1-methylimidazole, 2-methylimidazole and 1,2-dimethylimidazole as ANH) as measured at −0.8 V vs. Ag/AgCl.

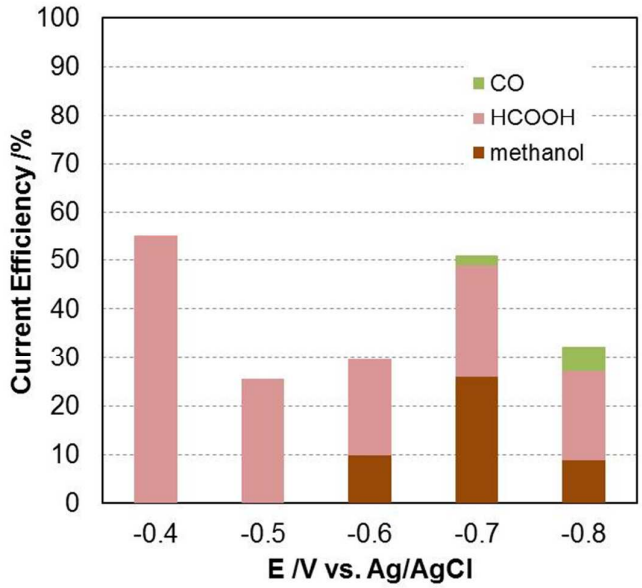


Figure S8. Current efficiencies of formate, methanol and CO produced using the **imidazole@IL/Au** electrode as measured at various electrochemical potentials.

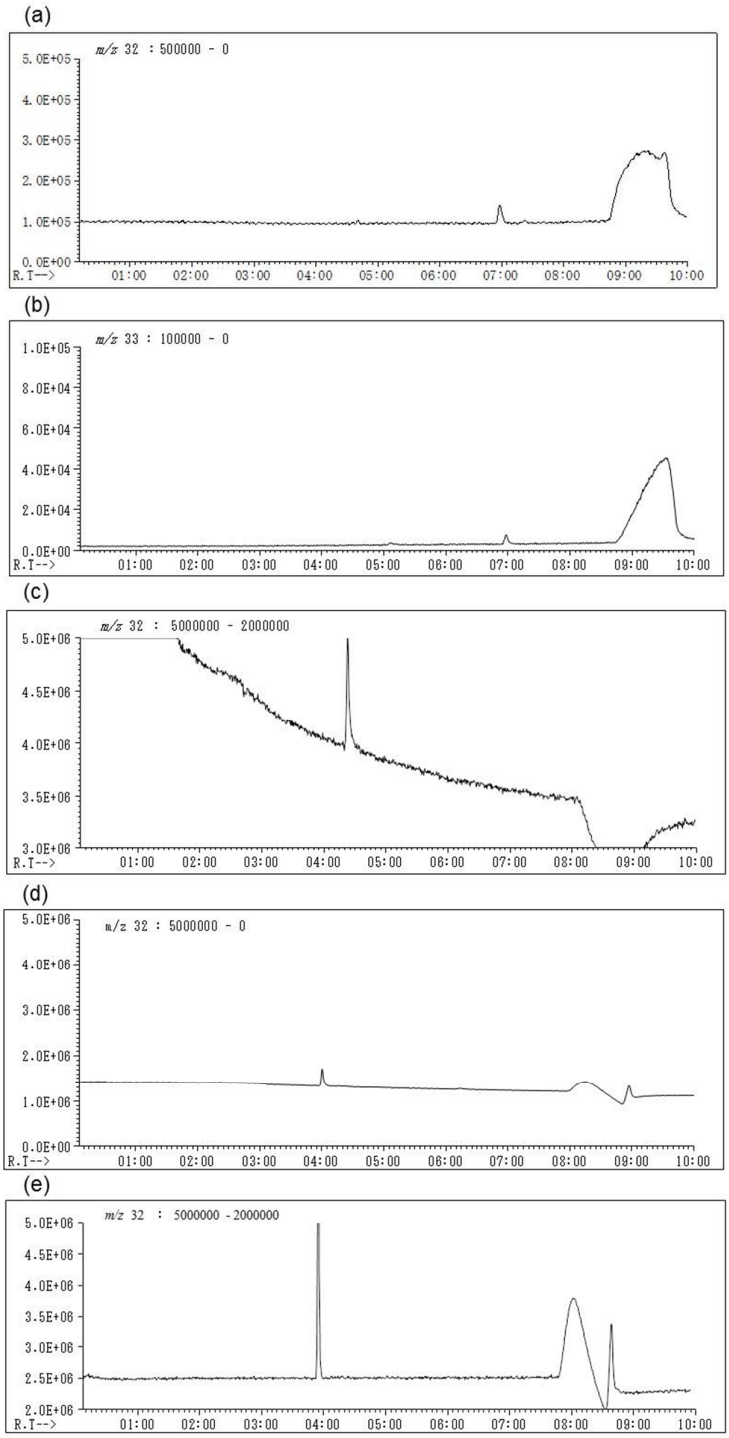


Figure S9. GC-MS spectra of (a) $^{12}CH_3OH$ and (b)$^{13}CH_3OH$ as analyzed at a retention time of 7 minutes performed at −0.8 V vs. Ag/AgCl under CO_2 and $^{13}CO_2$, respectively. (c), (d) and (e) are GC-MS spectra performed using IL/Au electrode, homogeneous system of imidazole at −0.8 V vs. Ag/AgCl or using **imidazole@IL/Au** electrode at −0.4 V vs. Ag/AgCl under CO_2. All spectra obtained from (c), (d) and (e) did not give any peaks derived from CH_3OH as analyzed at a retention time of 7 minutes (other peaks of (c), (d) and (e) are attributed to contamination from instruments.).

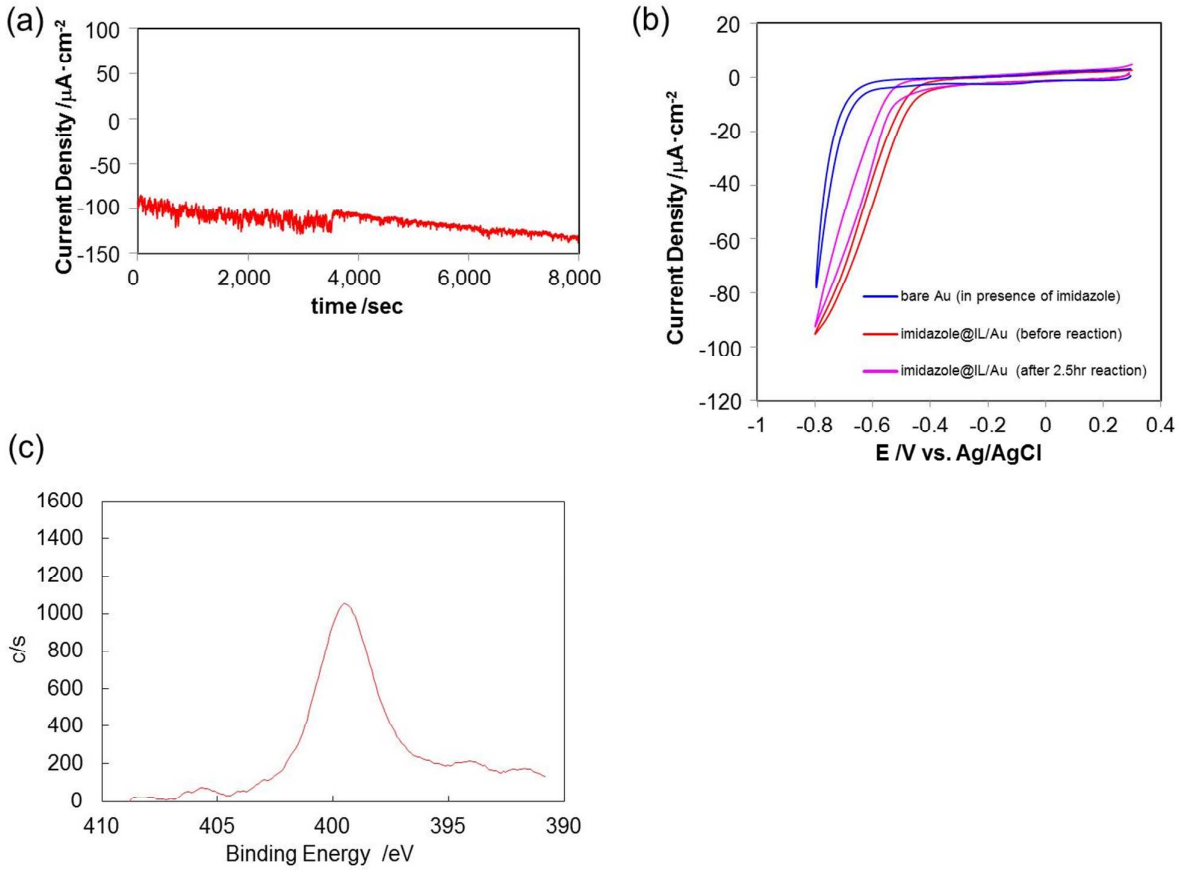


Figure S10. (a) Current density vs. time of **imidazole@IL/Au** under CO_2 at −0.8 V vs. Ag/AgCl, (b) CV measurement of **imidazole@IL/Au** under CO_2 before and after electrolysis and (c) XPS analysis of **imidazole@IL/Au** after electrolysis, in the range of 390 - 408 eV as measured at −120 °C.

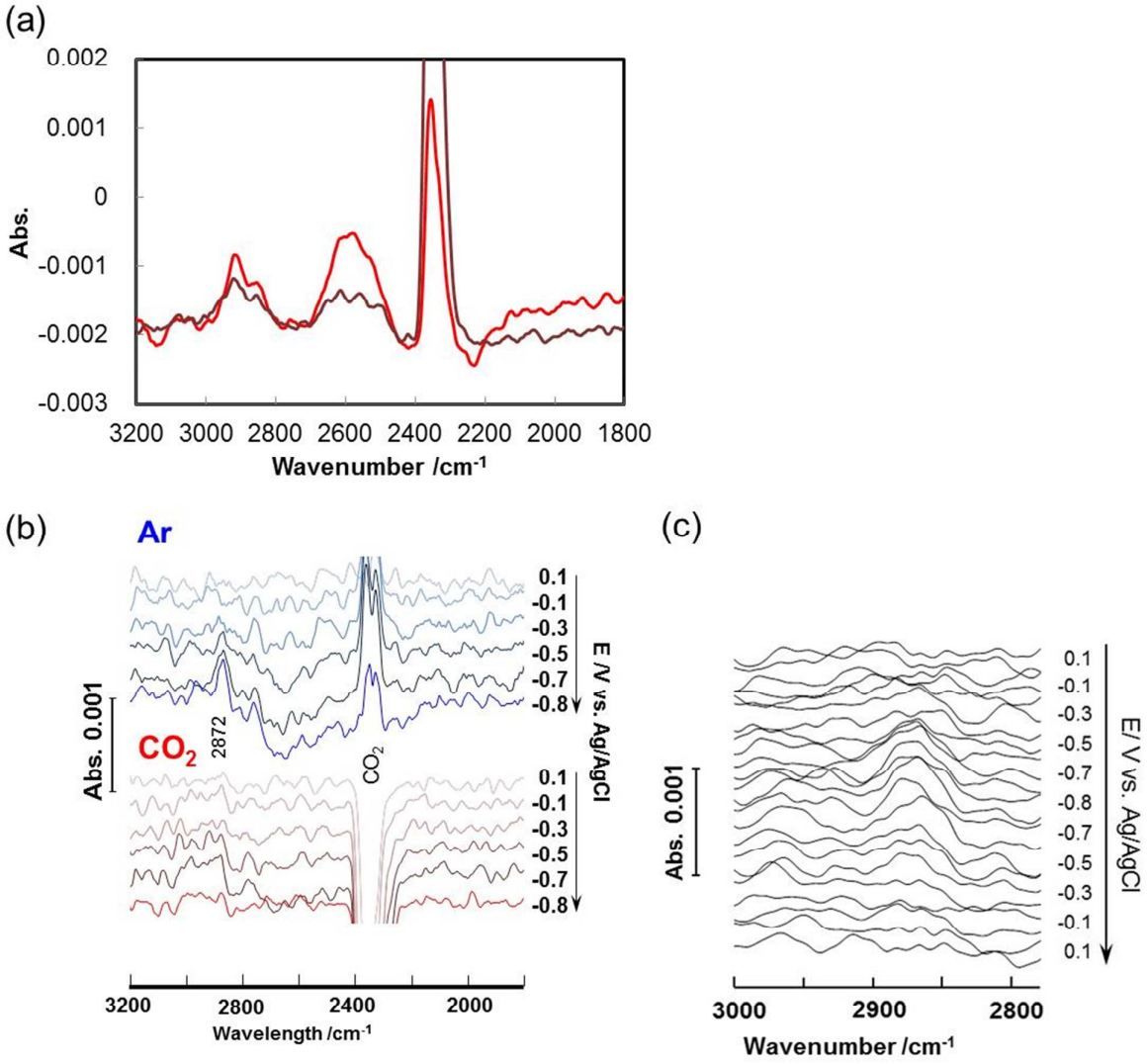


Figure S11. Potential dependent *in-situ* ATR-SEIRAS (a) at -0.8 V using the bare Au electrode under CO_2 in D_2O solutions containing imidazole-d_4 (brown) and imidazole (red), (b) using the IL/Au electrode in 0.1 M $NaClO_4$ under Ar (blue) and CO_2 (red), (c) using the IL/Au electrode under Ar in the range of 2775 – 3000 cm^{-1}.

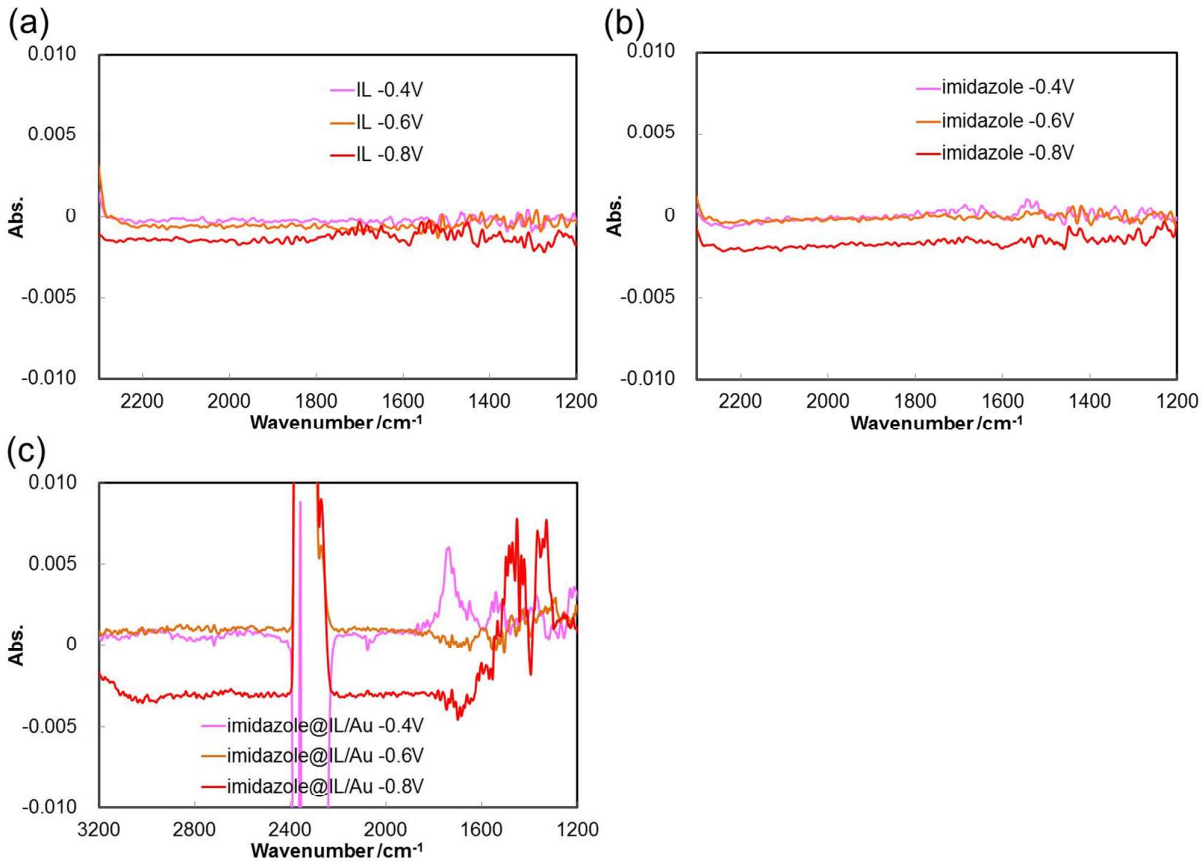


Figure S12. SEIRAS spectra coupled with constant potential electrolysis (−0.4V, −0.6 V, −0.8 V) at 600 sec. (a) using the IL/Au electrode in 0.1 M $NaClO_4$ D_2O solution under CO_2, (b) using the bare Au electrode in 0.1 M $NaClO_4$ D_2O solution containing 0.01 M imidazole under CO_2, and (c) wide range spectra (1200-3200cm^{-1}) using the **imidazole@IL/Au** electrode in 0.1 M $NaClO_4$ D_2O solution under CO_2.

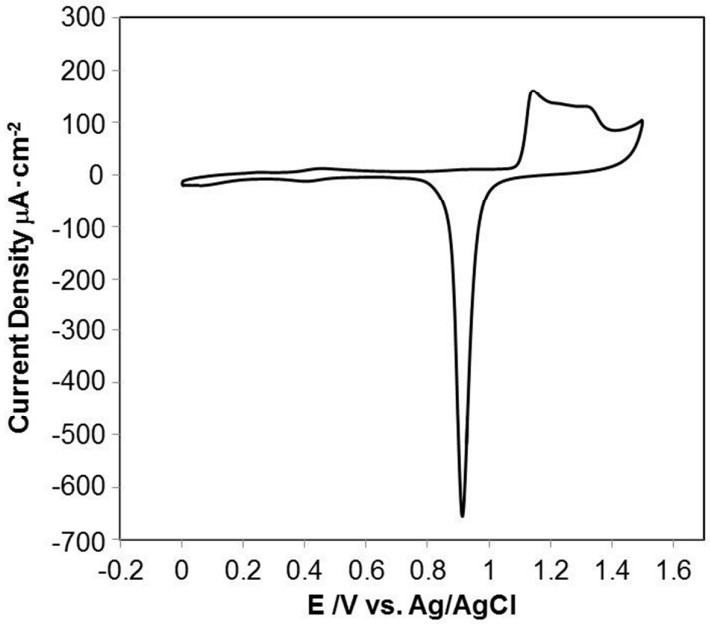
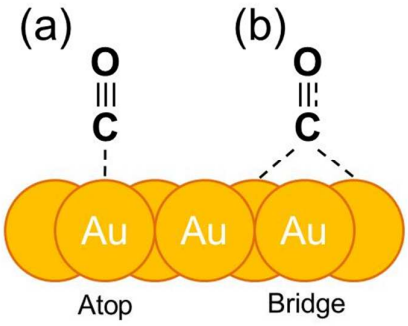
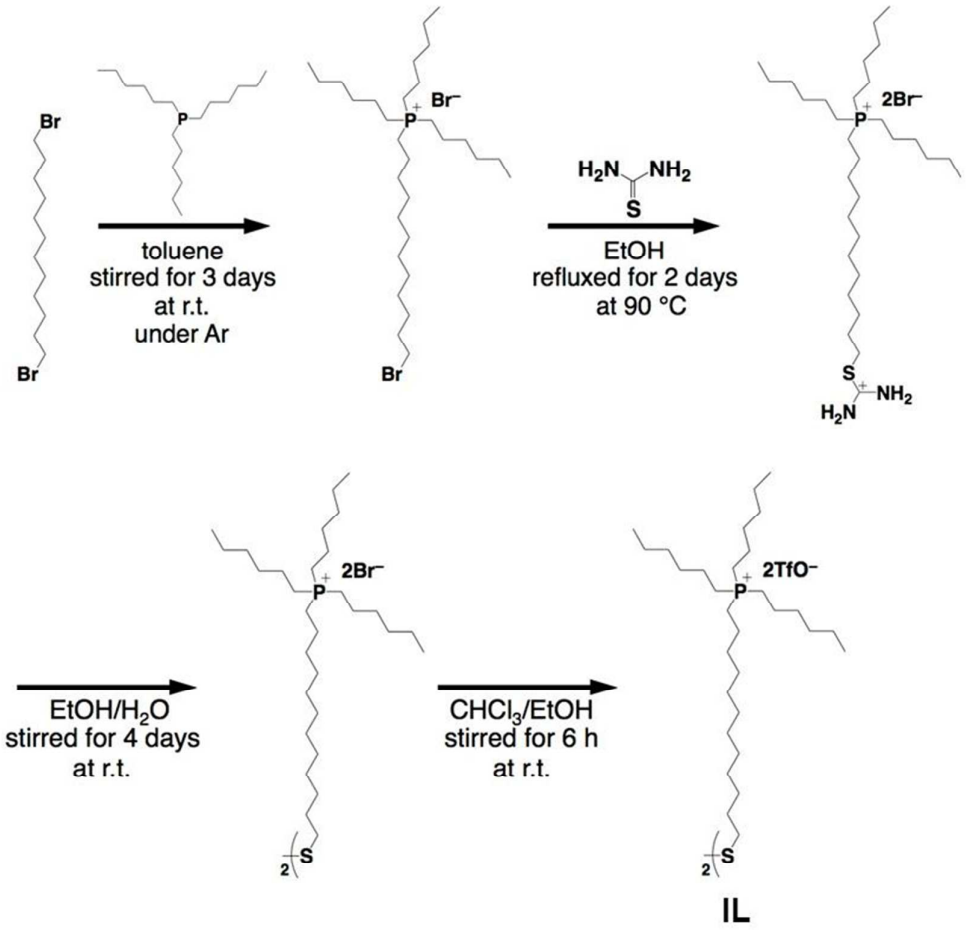


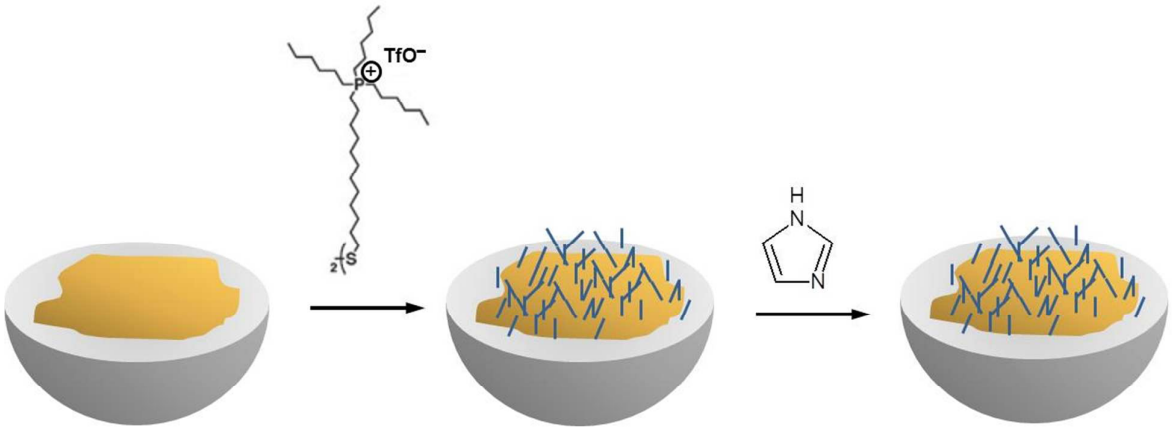
Figure S13. Cyclic voltammogram measured with SEIRAS for Au film prepared on a Si ATR prism in 0.1 M H_2SO_4 aqueous solution. Scan rate is 20 mV s^{-1}. Active surface area was calculated by integrating the charge of Au oxide reduction peak with a theoretical value of 444 μC/cm^2 required for reducing a monolayer of Au oxide. The roughness factor of Au film employed for SEIRAS measurement was estimated as 4.18.



Scheme S1. Possible CO adsorption sites on Au, (a) atop and (b) 2-fold bridge.



Scheme S2. Synthetic scheme of the ionic liquid containing the disulfide group, **IL**.



Scheme S3. Preparation of the prism for SEIRAS measurements.