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Photoelectrochemical Reduction of Carbon Dioxide at Si(111) Electrode Modified by Viologen Molecular Layer with Metal Complex

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Photoelectrochemical carbon dioxide reduction was carried out at a p-type Si(111) electrode modified with a viologen molecular layer and $[AuCl_4]^-$ or $[PdCl_4]^{2-}$. It was proven that the reduction reaction was mediated by viologen moiety and while CO_2 reduction was dominant at the Si(111) electrode modified with $[PdCl_4]^{2-}$ in the potential region where viologen moiety was in the first reduced state, it became dominant at the electrode modified with $[AuCl_4]^-$ when viologen moiety became the second reduced state. FT-IR measurement confirmed the formation of formic acid/formate ion at the $[PdCl_4]^{2-}$/viologen-modified Si electrode.

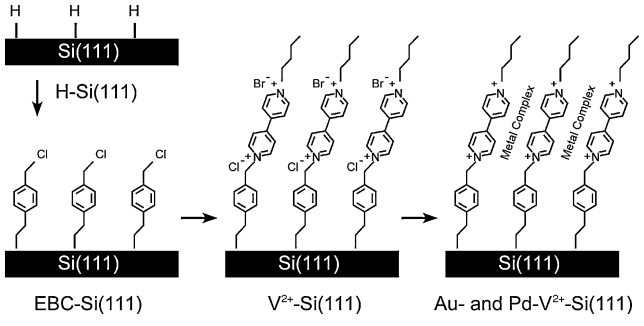
Carbon dioxide fixation attracts much interest of many scientists and engineers not only because CO_2 is considered to be one of the main causes of global warming[1] but also because it is scientifically very challenging to convert CO_2, one of the most stable molecules, to fuels and useful chemicals.[2] Electrochemical reduction of CO_2 is one of the most studied systems,[2–4] but very large overpotential and low current efficiency prevent its practical use. Moreover, if electricity is generated by using fossil fuel, more CO_2 is produced. Photoelectrochemical and photocatalytic reduction of CO_2 using a semiconductor is ideal as solar energy can be utilized to reduce CO_2.[2] Unfortunately, however, most of the semiconductors, which have a suitable band gap for solar energy conversion, are corrosive in aqueous solutions.[5] Furthermore, most of the semiconductor surfaces are not catalytically active for multi-electron-transfer reactions such as hydrogen evolution and CO_2 reduction, because they do not adsorb reaction intermediates with suitable strength.[6–8] One method to solve these problems is to modify the semiconductor surface with metal or metal ions, which act as catalyst. But this approach has one severe problem that surface states, which act as charge recombination centers, are often introduced at the metal–semiconductor interface as a result of the surface modification by metal.[9]

Several groups have used organic molecular layers to separate catalytic metals and semiconductor surfaces so that the introduction of surface states, which is the result of direct contact between catalytic metals and semiconductor surface, can be avoided and demonstrated that efficiencies of photoelectrochemical reactions are significantly enhanced, although the position and amount of catalyst are not well controlled.[8d,10,11] Recently, we have demonstrated that very efficient photoelectrochemical hydrogen evolution reaction (HER) can be achieved at a Si(111) electrode modified with a highly ordered organic molecular layer with viologen moieties, which is directly bonded to Si surface via Si–C bond, as an electron mediator and Pt complex, which is confined within the molecular layer as a catalyst.[12,13]

In this paper, we have extended this approach to photoelectrochemical carbon dioxide reduction at p-type Si(111) electrode modified with viologen molecular layer and various metal complexes. $[AuCl_4]^-$ and $[PdCl_4]^{2-}$ are chosen as complexes as electrochemical CO_2 reduction is known to proceed efficiently at Au and Pd electrodes while H_2 generation is dominant at Pt electrode in CO_2-saturated solution.[14]

Surface modification was carried out as schematically shown in Scheme 1. Details of the procedure for the modification by organic layers and characterization of modified surfaces have been reported before.[12] Briefly, a freshly prepared hydrogen-terminated (H-) Si(111) surface[15] was sequentially treated to yield a viologen monolayer-modified (V^{2+}-) Si(111) substrate: (1) H-Si(111) surface was illuminated with 254-nm light for 2 h in deaerated 4-vinylbenzyl chloride to yield a 4-ethylbenzyl chloride-modified (EBC-) Si(111) surface, (2) the substrate was then kept in benzene solution saturated with 4,4′-bipyridine and then in 1-bromobutane, both at 70 °C for 12 h to obtain a V^{2+}-Si(111) surface. The V^{2+}-Si(111) was immersed in an aqueous solution containing 10 mM of $Na[AuCl_4]$ or $K_2[PdCl_4]$ for 20 min at room temperature to yield Au- or Pd-V^{2+}-Si(111) surfaces, respectively.

X-ray photoelectron spectra (XP spectra) obtained using a Rigaku model XPS-7000 with monochromic Mg Kα for the (A) Au- and (B) Pd-V^{2+}-Si(111) surfaces in Au4f and Pd3d regions, respectively, confirm the incorporation of the metals.[16]



Scheme 1. Schematic illustration of the modification steps of hydrogen-terminated (H-) Si(111) surface to obtain Au- and Pd-V^{2+}-Si(111) surfaces. Metal Complex: $[AuCl_4]^-$ and $[PdCl_4]^{2-}$. See the text for the detail.[12]

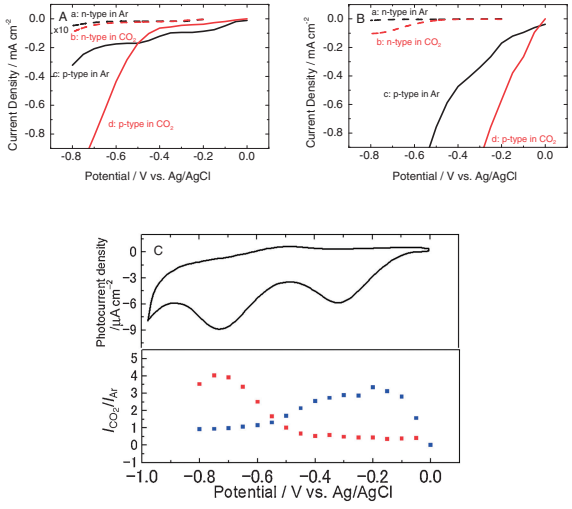


Figure 1. Current–voltage relations of (A) Au- and (B) Pd-V^{2+}-Si(111) electrodes in 0.1 M aqueous Na_2SO_4 solutions saturated with Ar (black; a, c) and CO_2 (red; b, d) in dark (n-type, broken line; a, b) and under illumination (p-type, solid line; c, d) with a light intensity of 0.12 mW cm^{-2}. Scan rate: 1 mV s^{-1}. (C) Top panel: Cyclic voltammogram of p-type V^{2+}-Si(111) electrode in a 0.1 M aqueous Na_2SO_4 solution saturated with Ar under illumination with a light intensity of 0.12 mW cm^{-2}. Scan rate: 100 mV s^{-1}. Bottom panel: Ratio between currents at Au- (red) and Pd-V^{2+}-Si(111) electrodes (blue) in CO_2-saturated solution and that in Ar-saturated solution (I_{CO_2}/I_{Ar}) as a function of potential.

Figure 1 shows *I–V* curves of the (A) Au- and (B) Pd-V^{2+}-Si(111) electrodes in Ar- and CO_2-saturated 0.1 M aqueous Na_2SO_4 solutions. The pH of the Ar-saturated 0.1 M Na_2SO_4 solution was adjusted to 4.4 by adding H_2SO_4, since the pH of 0.1 M Na_2SO_4 changed from 5.9 to 4.4 by CO_2 saturation. Relatively small current flowed at the n-Si(111) electrodes modified with viologen layer/metal complexes in the dark both in Ar- and CO_2-saturated solutions. However, currents in CO_2-saturated solution were clearly larger than those in Ar-saturated solution at potentials more negative than ca. −0.5 V.

Cathodic currents in both the Ar- and CO_2-saturated solutions started to flow at much more positive potentials at the p-Si(111) electrodes modified with viologen layer/metal complexes under illumination[17] than those at the modified n-Si(111) electrode in the dark, although only negligibly small currents flowed in the dark (<5 μA cm^{-2} at −0.8 V) as expected because electrons are the minority carrier of p-type semiconductors. At the p-type Pd-V^{2+}-Si(111) electrode, photocurrent started to flow at potential as positive as 0 V and increased significantly as potential became more negative both in the Ar- and CO_2-saturated solutions. Photocurrent in the CO_2-saturated solution was larger than that in the Ar-saturated solution in the potential region shown in Figure 1, but both became almost the same as potential became more negative than ca. −0.6 V. On the other hand, although photocurrent started to flow also at around 0 V at the Au-V^{2+}-p-Si(111) electrode in both solutions, it did not increase much even when potential was made more negative, particularly in the Ar-saturated solution. Photocurrent in the CO_2-saturated solution significantly increased and became larger than that in the Ar-saturated solution when potential became more negative than ca. −0.55 V.

These trends are more clearly seen in the bottom panel of Figure 1C, which shows potential dependencies of the ratio between photocurrents in the CO_2 (I_{CO_2}) and Ar-saturated solutions (I_{Ar}) at the Au-V^{2+}- and Pd-V^{2+}-Si(111) electrodes. At the Pd-modified Si electrode, I_{CO_2} became larger than I_{Ar} as soon as photocurrent started to flow at 0 V, but I_{CO_2}/I_{Ar} gradually decreased as potential became more negative than ca. −0.2 V and became 1 as potential became more negative than ca. −0.6 V as mentioned before. At the Au-modified Si electrode, I_{CO_2} was smaller than I_{Ar} in the relatively positive potential region, but I_{CO_2}/I_{Ar} increased significantly as potential became more negative than ca. −0.5 V and reached 4 at −0.7 V. The top panel of Figure 1C is the cyclic voltammogram (CV) of V^{2+}-Si(111) electrode without metal complex under illumination obtained with very fast scan rate (50 mV s^{-1}). Reduction peaks of viologen moiety are clearly observed at −0.25 and −0.7 V for the reduction of V^{2+} to $V^{\bullet+}$ and of $V^{\bullet+}$ to $V^{\bullet\bullet}$, respectively. Positions of these peaks were more positive than those observed at n-type V^{2+}-Si(111) electrode in the dark as expected.[12b] Potential dependencies of photocurrent and I_{CO_2}/I_{Ar} seem to be related to the reduced state of viologen moiety. While at the Pd-V^{2+}-Si(111) electrode, large photocurrent flowed in both Ar- and CO_2-saturated solution as soon as the reduction of V^{2+} to $V^{\bullet+}$ started, at the Au-V^{2+}-Si(111) electrode, only relatively small and almost no photocurrent were observed in Ar- and CO_2-saturated solutions, respectively, in potential region where viologen moiety was in $V^{\bullet+}$, and significant increase of photocurrent was observed in CO_2-saturated solution as soon as $V^{\bullet+}$ was reduced to $V^{\bullet\bullet}$. This difference should be due to the difference in the energy to form adsorbed intermediate states on the metal catalysts.

As a qualitative analysis of the products of CO_2 reduction, in situ FT-IR measurements were performed at the Au- and Pd-V^{2+}-Si(111) electrodes in 0.1 M Na_2SO_4 solution saturated with CO_2.[18] Figure 2A shows IR spectra (s-polarization) obtained at the Pd-V^{2+}-Si(111) electrode in the CO_2-saturated 0.1 M Na_2SO_4 solution keeping the potential at −0.7 V for a given period of time under illumination with a spectrum measured in dark before illumination as a reference.

No significant difference was noticed between the p- and s-polarized spectra.[20] Negative peaks due to the consumption in the thin layer were observed at around 1600, 2350, and 3200 cm^{-1}, corresponding to bending of OH of water, CO stretching of dissolved CO_2, and OH stretching of water, respectively, showing that HER and CO_2 reduction proceeded. A small positive peak due to the accumulation of reduction product was observed at around 1410 cm^{-1}, which corresponds to symmetric stretch of carboxylate group. The growth of this peak with time is more clearly seen in Figure 2B, which shows IR spectra in 1325–1475 cm^{-1} region with correction of background due to a strong negative OH bending peak. This agrees with previous reports that the main product of electrochemical carbon dioxide reduction reaction at Pd electrode is formic acid/formate ion.[21] Asymmetric stretching peak of carboxylate group, which should be present at around 1610 cm^{-1} is not visible because of a strong negative OH bending peak at this potential. IR spectra obtained at various potentials shown in Figure 2C indicate that at −0.2 V, the negative OH bending peak is

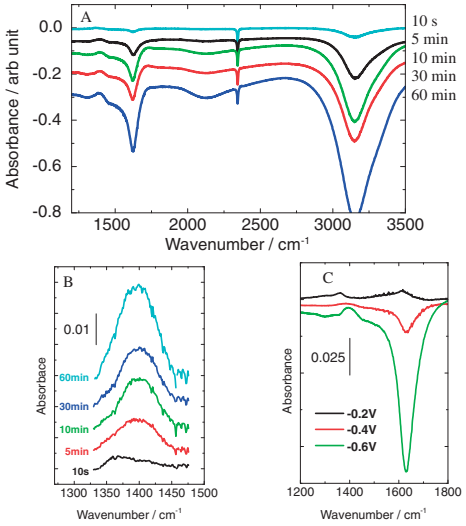


Figure 2. IR spectra at the Pd-V^{2+}-Si(111) electrode in a CO_2-saturated 0.1 M Na_2SO_4 solution (A, B) with keeping the potential at −0.7 V for a given period of time under illumination in (A) 1250–3500 and (B) 1325–1475 cm^{-1} regions with background correction, and (C) at various potentials in 1200–1800 cm^{-1} region.

not visible and that small positive peaks due to symmetric and asymmetric stretch of carboxylate are observed. This is in good agreement with the result shown in Figure 1B that the dominant reaction at this potential is CO_2 reduction.

In situ FT-IR measurements obtained at the Au-V^{2+}-Si(111) electrode in 0.1 M Na_2SO_4 solution saturated with CO_2 shows only negative peaks due to the consumption in the thin layer at around 1600, 2350, and 3200 cm^{-1}, corresponding to bending of OH of water, CO stretching of dissolved CO_2, and OH stretching of water, respectively, and no positive peaks were observed. Thus, although it is confirmed that HER and CO_2 reduction proceeded at the Au-V^{2+}-Si(111) electrode, no product was determined. According to previous reports, the main product of CO_2 reduction at gold electrode is CO.[14]

In conclusion, photoelectrochemical carbon dioxide reduction was significantly enhanced by modifying Si(111) surfaces by the organic molecular layer with viologen moieties and $[AuCl_4]^-$ or $[PdCl_4]^{2-}$. It was confirmed that viologen moiety plays an important role for mediating electron transfer from Si to metal catalysts. While CO_2 reduction was dominant at the Si(111) electrode modified with $[PdCl_4]^{2-}$ in the potential region where viologen moiety was in the first reduced state, the second reduced state is required to reduce CO_2 at the electrode modified with $[AuCl_4]^-$. FT-IR measurements confirmed the formation of formic acid/formate ion as a product of CO_2 reduction, and selectivity of CO_2 reduction to HER is high at the positive potential at Pd-V^{2+}-Si(111) electrode. The decrease of selectivity for CO_2 reduction at the Pd-V^{2+}-Si(111) electrode as potential became negative should simply be due to the low surface concentration of CO_2 with respect to H_2O (H^+) for HER. More detailed analysis including gaseous products is under way.

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