XAFS Characterization of Metal Catalysts Embedded within Viologen Multilayers Formed on Si(111) Surfaces

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Abstract

Organic molecular layers with viologen moieties as electron transfer mediators and various metal complexes such as $PtCl_4^{2-}$, $PdCl_4^{2-}$ and $AuCl_4^-$ as catalysts for multi-electron transfer reactions were constructed on hydrogen terminated Si(111) surfaces and their photoelectrochemical hydrogen evolution and carbon dioxide reduction properties were examined.

High selectivity for CO_2 reduction in preference to the hydrogen evolution was achieved at the Si(111) electrodes modified by molecular layers with Pd and Au complexes. This is reasonably understood because both Pd and Au metal nanoparticles are known to be good electrocatalysts for CO_2 reduction. Surprisingly, high selectivity for CO_2 reduction was also achieved at the Si(111) electrode modified by molecular layer with Pt complex despite the fact that hydrogen evolution reaction is dominant at Pt metal nanoparticle even in CO_2 saturated solution.

To clarify the reason for this anomalously high selectivity for CO_2 reduction at the Pt-modified Si(111) electrode, the local structures and oxidation states of the metal catalysts were determined by X-ray photoelectron spectroscopy (XPS) and polarization-dependent total reflection fluorescence (PTRF)- X-ray absorption fine structure (XAFS). It was found that Pt complex was not reduced to metallic nanoparticle under operation, and therefore, Pt complex acts as a confined molecular catalyst for CO_2 reduction, whereas Pd and Au complexes were reduced to form nanoparticles.

References

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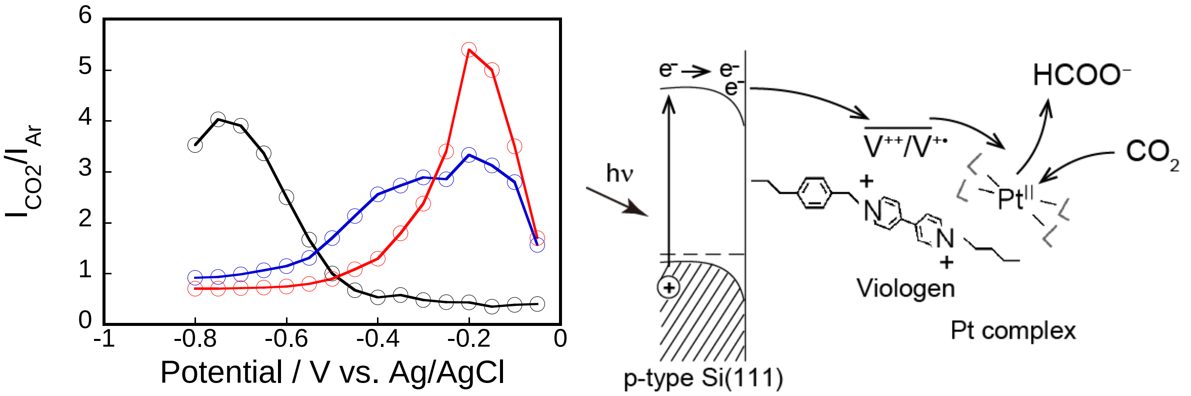
Figures



(left) Ratio between photocurrents at the Pt- (red), Pd- (blue) and Au-modified (black) Si(111) electrodes in the CO_2-saturated solution and that in the Ar-saturated solution (I_{CO2}/I_{Ar}) as a function of potential. (right) Schematic model of the confined molecular catalyst.