

# Formation, Characterization and Catalytic Properties of Metal Nanoclusters within Molecular Layers

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Metal and semiconductor nanoclusters have been attracting much attention because of their unique optical, electronic, and catalytic properties. Metal nanocluster catalysts are important not only because the ratio of surface atoms/bulk atoms increases and more metal atoms are effectively used for catalytic reactions as the size of the cluster gets smaller but also because metal nanocluster catalysts sometimes show catalytic activity that the bulk metals do not have. The origin of the unique catalytic activity of metal nanocluster catalysts is, however, not clear yet.

Hydrogen is considered to be the most important clean fuel and production of hydrogen from water using solar energy is essential for hydrogen to be widely used in future. Photoelectrochemical and photocatalytic decomposition of water has been studied for long time but many problems are not solved. Surface of semiconductor, which is the photon absorber for both photoelectrochemical and photocatalytic reactions, is usually not suitable for multi-electron reactions such as hydrogen (HER) and oxygen (OER) evolution reactions, which are the key reactions of hydrogen production from water, and, therefore, surface modification by catalytic metals are required. Direct attachment of metal onto semiconductor surface often leads to the lower efficiency due to the formation of Schottky junction and/or the introduction of surface recombination center but we have recently demonstrated that the efficient photoelectrochemical hydrogen evolution at Si electrode can be achieved by separating Pt nanoclusters (hydrogen evolution catalyst) from Si surface using organic monolayers. In this study, we followed the formation processes of Pt nanoclusters and determined the structures of the nanoclusters during HER by x-ray absorption fine structure (XAFS).

Two methods were employed to form Pt nanoclusters. In the first method, (i) a thiol-terminated organic monolayer was constructed on a hydrogen-terminated (H-) Si(111) surface by UV-induced hydrosilylation reaction, (ii) the monolayer-covered substrate was then immersed in  $K_2PtCl_4$  aqueous solution, and (iii) finally the Pt complex attached to the monolayer was chemically or electrochemically reduced in a Pt ion free solution to form Pt clusters as shown in Scheme 1. XAFS measurements were performed at BL12C of Photon Factory after each modification step. XANES and EXAFS spectra after step (ii) show the disappearance of Pt-Cl bond and Pt coordination by more electronegative, i.e., oxygen, species. A model for the attachment of the complex to the thiol-terminated monolayer is shown in Fig. 2 (top panel). While XANES and EXAFS spectra after the chemical reduction showed the formation of Pt clusters of ca. 2 nm diameter, those after electrochemical reduction were exactly the same as those obtained before the reduction, showing the complex was not reduced, although HER is significantly accelerated at this surface compared with the surface without the Pt complex incorporation. This shows that the Pt complex is acting as HER catalyst. To see how the catalyst is working, in situ XAFS measurement is essential but not possible at this surface because the number of Pt species is too small.

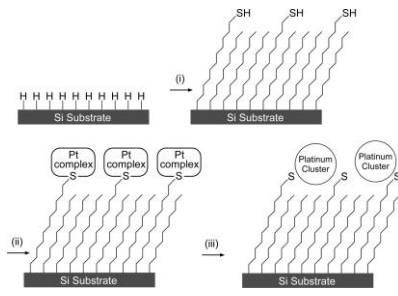
In situ XAFS study was carried out at a Si(111) electrode modified by the second method as shown in Scheme 2. After the molecular layer with viologen moiety was formed on a hydrogen-terminated Si(111) surface, the substrate was immersed in  $K_2PtCl_4$  aqueous solution so that the Pt complex was incorporated within the molecular layer by ion exchange reaction. Figure 4 shows a series of XANES and EXAFS spectra and FT of this sample. Ex situ XANES and EXAFS spectra measured after immersion in  $K_2PtCl_4$  solution showed typical features of  $PtCl_4^{2-}$  complex. Once the sample was placed in a solution and potential was swept negatively from 0 to -0.6 V vs. Ag/AgCl, Pt-Cl hybridization peak, which appears at 11572 eV, decreased and the white line (WL) intensity increased, suggesting the exchange of Cl ligands by O species such as  $H_2O$  or  $OH^-$ . At -0.8 V, where HER vigorously took place, WL intensity decreased, indicating the reduction of Pt, but no Pt-Pt bond was observed. The WL peak also became broad as a result of Pt-H interaction as previously reported. Pt-O bond became longer at this potential. When the electrode potential was returned to 0 V, where no HER takes place, the WL peak became sharper than that at -0.8 V, suggesting the Pt-H interaction was formed only when HER is taking place. These results suggest that Pt single atom acts as HER catalyst.

In conclusion, formation of Pt single atom/molecular HER catalysts on or within organic layers.

## References

- [1] T. Masuda, K. Shimazu, K. Uosaki, *J. Phys. Chem. C*, **112** (2008) 10923.
- [2] H. Fukumitsu, T. Masuda, D. Qu, Y. Waki, H. Noguchi, K. Shimazu and K. Uosaki, *Chem. Lett.*, **39** (2010) 768.

## Figures



Scheme 1. Formation of thiol-terminated monolayer (i), incorporation of Pt complex (ii), and reduction of the complex (iii) to form Pt nanoclusters on organic monolayer on Si(111).

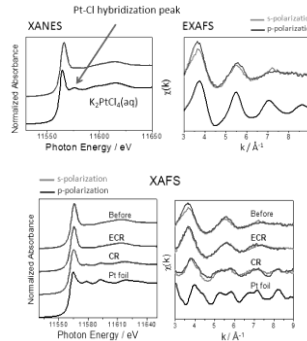


Figure 1. XANES and EXAFS spectra after step (ii) (top) and step (iii) (bottom).

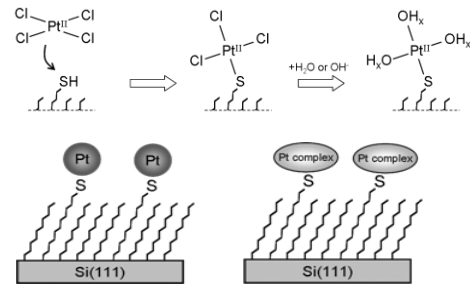
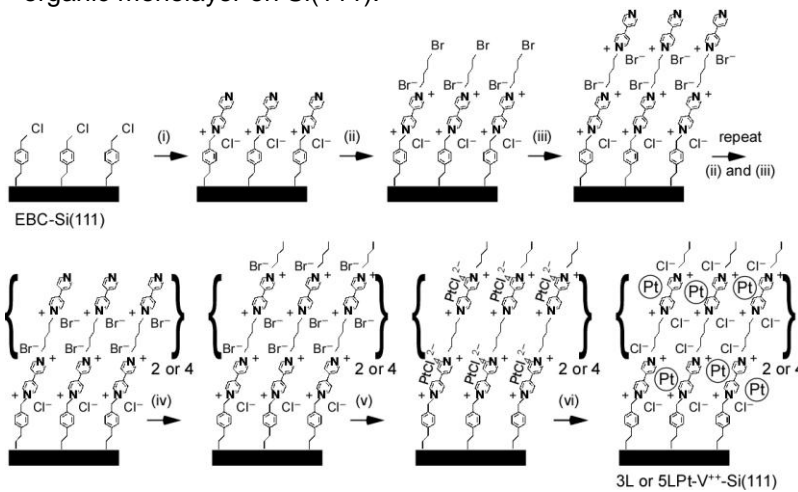


Figure 2. Schematic model for complex attachment to thiol group (top) and Pt structures (bottom) after chemical (left) and electrochemical reduction (right).



Scheme 2. Formation of viologen multilayers (i-iv), incorporation of Pt complex (v), and reduction of the complex (vi) to form Pt nanoclusters within the organic layers on Si(111).

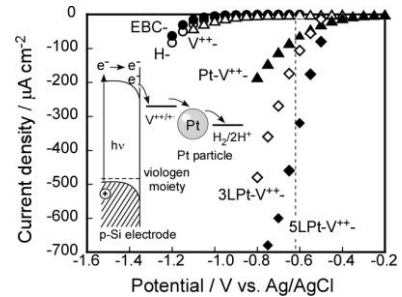


Figure 3. Steady state I-V curves of the p-type H<sup>-</sup> (○), EBC<sup>-</sup> (●), V<sup>++</sup> (Δ), Pt-V<sup>++</sup> (▲), 3LPt-V<sup>++</sup> (◇) and 5LPt-V<sup>++</sup>-Si(111) (◆) electrodes under illumination in 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution. Inset: Energy diagram for the HER at the p-Si(111) modified with Pt/viologen layers.

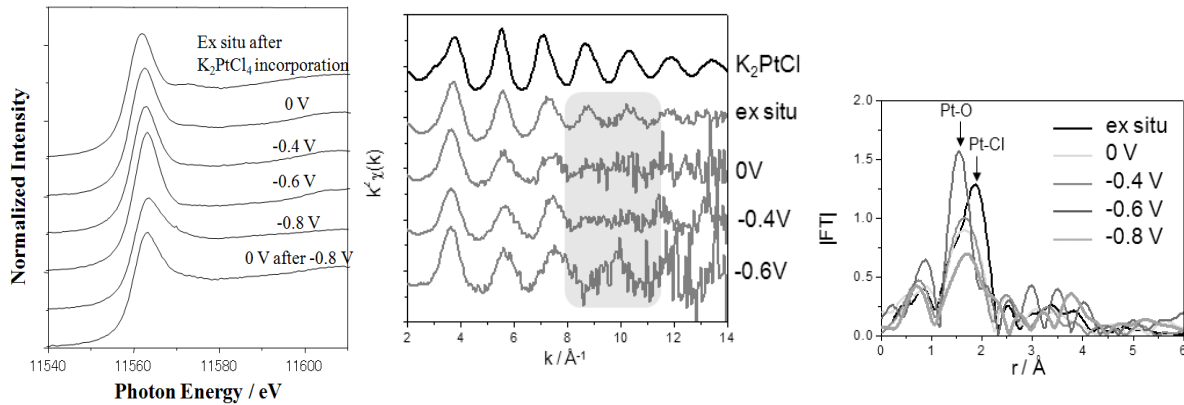


Figure 4. XANES (left) and EXAFS (middle) spectra and FT (right) obtained ex situ after immersion in K<sub>2</sub>PtCl<sub>4</sub> solution and in situ at various potentials.