

論文の内容の要旨

論文題目 Spectroscopic and Electrochemical Study on Hydrogen Evolution Sites of Photocatalysts for Water Splitting

(赤外分光法と電気化学を利用した水分解光触媒の水素発生サイトについての研究)

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In order to clarify the transfer of photoexcited electrons in photocatalyst and the function of different cocatalyst, in situ infrared spectroscopy (IR) using CO as probe molecules combined with electrochemical method was used as a tool to study the potential change of Pt or Rh particles deposited on the photocatalysts particles. By frequency shift of Pt-CO and Rh-CO adsorption peaks between dark and visible light irradiation conditions, potential change of cocatalyst particles were represented and analyzed.

Also, to enhance the hydrogen evolution reaction (HER), photodeposited Pt particles were introduced as reaction sites for HER. The effects of FeO_x layers deposited on p-Si electrodes were assessed and detailed analysis revealed that the increase in photocurrent was due to the effects of surface orientation and tailing of the removed FeO_x.

1. IR spectra of Pt/TaON, Pt/GaN:ZnO and Pt/LaTiO₂N

For Pt/GaN:ZnO and Pt/TaON, the C-O stretching vibrations of adsorbed CO on Pt shifted to a lower frequency under visible light irradiation, as shown in Figure 1. In case of Pt/GaN:ZnO, the peak frequency of linearly-bonded CO (CO_L) to the Pt cocatalyst was at 2047 cm⁻¹ under dark conditions. Under the maximum irradiation of 2.5×10^{17} photon cm⁻¹ s⁻¹, the CO_L peak shifted to 2039 cm⁻¹. In case of Pt/TaON, the CO_L frequency under dark conditions was 2053 cm⁻¹. Under the maximum irradiation, the absorption peak of CO_L shifted to 2042 cm⁻¹. The observed frequency shift of -8 cm⁻¹ and -11 cm⁻¹ indicates that the potential of the Pt cocatalyst particles was shifted to a more negative value by the excitation light irradiation on GaN:ZnO and TaON. On the other hand, no frequency shift was observed for Pt/LaTiO₂N under irradiation.

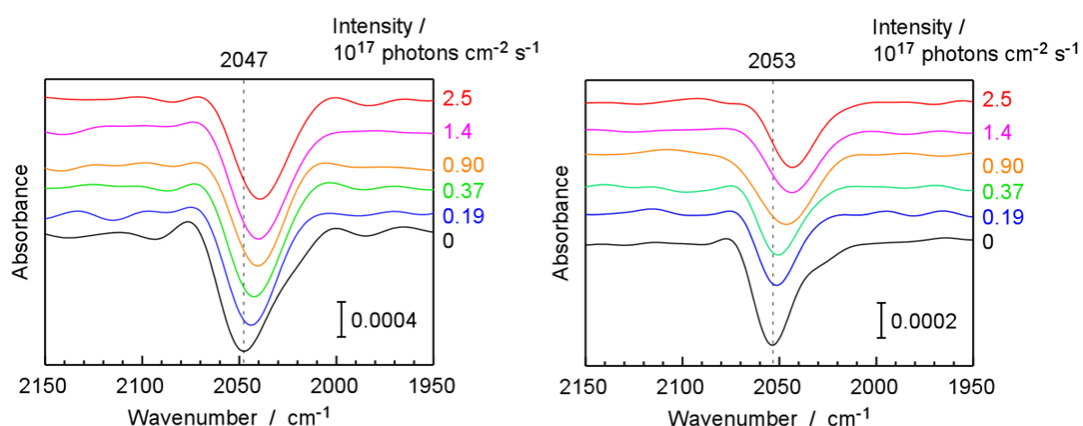


Figure 1 Infrared spectra of CO adsorbed on Pt in Pt/GaN:ZnO (left) and Pt/TaON (right) with changing excitation light intensity. Pt/GaN:ZnO or Pt/TaON was pasted onto ITO/sapphire, and the potential of the ITO was kept at the rest potential. The sample was immersed in a 0.1 M Na₂SO₄ aqueous solution at pH=6 and was irradiated with 385–740 nm light.

GaN:ZnO, TaON, and LaTiO₂N are n-type semiconductors, and upward band bending is expected at the photocatalyst/electrolyte interface. The Fermi levels (E_F) of the photocatalyst and the Pt should be the same. When the excitation light irradiates the photocatalyst particle, electrons in the valence band are excited to the conduction band along with the formation of a hole in the valence band. The photogenerated holes migrate to the photocatalyst/electrolyte interface by band bending at the photocatalyst/electrolyte interface, initiating an oxidation reaction at the interface. The photogenerated electrons migrate to Pt cocatalyst particles and negatively shift the potential. While Pt particles on GaN:ZnO and TaON were negatively shifted in potential by the irradiation, those on LaTiO₂N did not show this shift, indicating that the photoexcited carriers in Pt/LaTiO₂N did not behave as described above.

Besides, the obvious differences were observed between the slopes of Pt/GaN:ZnO and Pt/TaON. From the infrared measurements, a slope of -0.09 V/decade was observed for Pt/GaN:ZnO compared to -0.21 V/decade for Pt/TaON. A similar trend with estimated potential was also observed in the rest potential. The difference of dependent slopes suggests that the different recombination process is dominant for the Pt/GaN:ZnO and Pt/TaON system. It is most likely that this recombination pathway is related to the difficulty of overall water splitting on TaON. Improving the crystallinity and decreasing the number of defects in TaON should suppress the rate of recombination of photogenerated carriers in this pathway.

2. Comparison of potential shift between Pt and Rh

Some similarities and differences of IR spectra from Pt-deposited samples were observed in

Rh-deposited oxynitrides. In the case of Rh/GaN:ZnO, very similar photo-response frequency shift and light intensity dependence was confirmed with Pt/GaN:ZnO. In the case of Rh/TaON, although obvious shift also showed, slope of potential change on irradiation intensity dependence decreased to almost half of the Pt-deposited sample. In case of LaTiO₂N, despite frequency shift could not observed on Pt-deposited sample; obvious frequency shift and irradiation intensity dependence were observed on Rh-deposited one. The IR spectra for Rh/LaTiO₂N under dark and a series of light intensity are shown in Figure 2, together with spectra of Pt/LaTiO₂N as comparison. The reasons were partly ascribed to the different work function between Pt and Rh, as well as different size of cocatalyst particles between Pt/LaTiO₂N and Rh/LaTiO₂N.

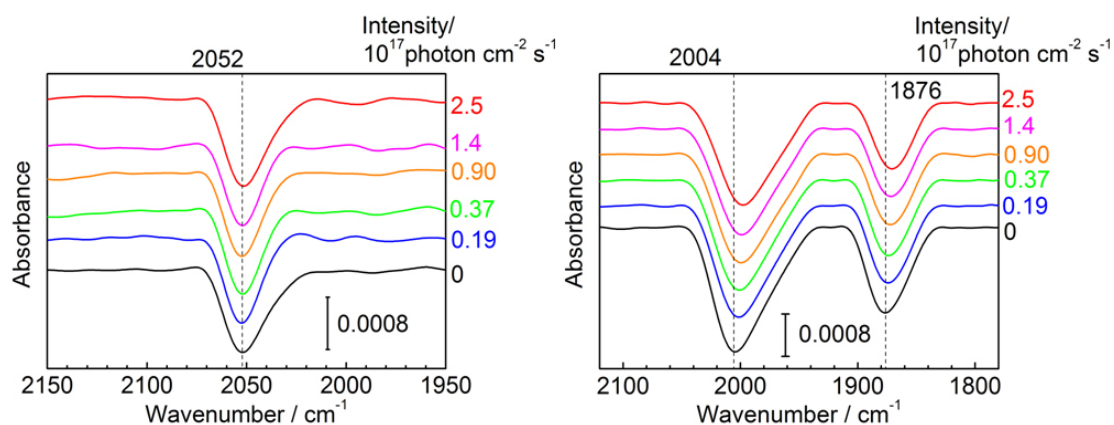


Figure 2 Infrared spectra of CO adsorbed on Pt (left) and Rh (right) deposited on LaTiO₂N with a changing intensity of excitation light. Pt or Rh deposited LaTiO₂N was pasted on ITO/sapphire, and the potential of the ITO was kept at the rest potential. The sample was immersed in a 0.1 M Na₂SO₄ aqueous solution at pH=6 and was irradiated with 385–740 nm light.

3. Effects of surface modification on p-Si

The PEC properties of bare and Pt-loaded p-Si (100) were examined first. Cathodic photocurrents were observed for both samples under irradiation, indicating that these electrodes are p-type semiconductors. Upon modification with Pt, both the photocurrent and onset potential showed a marked increase, from 0.2 $\mu\text{A}/\text{cm}^2$ to 0.28 mA/cm^2 (at 0 V_{RHE}) and from 0.15 V_{RHE} to 0.50 V_{RHE} , respectively. The apparent improvement in J - E properties by noble metal modification is likely due to the decrease of overpotential in hydrogen evolution.

To investigate the effects of FeO_x modifications, J - E measurements were performed on $\text{FeO}_x/\text{p-Si}(100)$ and $\text{Pt}/\text{FeO}_x/\text{p-Si}(100)$ electrodes. Before the measurements, the samples were aged for 10 h at $-0.28 V_{\text{RHE}}$ under illumination to bypass the induction period in the J - E measurements. Both the cathodic photocurrent and the onset potential of $\text{FeO}_x/\text{p-Si}(100)$ were higher than those of p-Si, at $0.15 \text{ mA}/\text{cm}^2$ (at $0 V_{\text{RHE}}$) and $0.52 V_{\text{RHE}}$, respectively. Pt modification of $\text{FeO}_x/\text{p-Si}(100)$ further improved the J - E properties: the onset potential shifted to $0.85 V_{\text{RHE}}$, which is 0.35 V more positive than that of $\text{Pt}/\text{p-Si}(100)$, and the photocurrent increased to $2.45 \text{ mA}/\text{cm}^2$ at $0 V_{\text{RHE}}$ (see Figure 3)

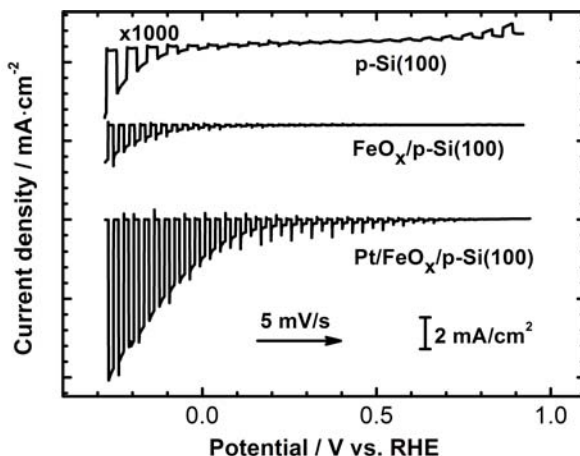


Figure 3. J - E curves of p-Si (100), $\text{FeO}_x/\text{p-Si}$ (100) and $\text{Pt}/\text{FeO}_x/\text{p-Si}$ (100) electrodes in $0.1 \text{ M Na}_2\text{SO}_4$ under intermittent illumination.

The present experimental results indicate that the improvement in J - E properties of aged $\text{Pt}/\text{FeO}_x/\text{p-Si}$ (100) is caused first by the formation of surface pyramids with $\{111\}$ facets. The FeO_x layer, which is removed during the aging treatment, promotes the formation of $\{111\}$ facets and produces surface properties conducive to hydrogen generation. This can be verified by the better photoresponse of p-Si(111) compared to p-Si(100) and the similarity in PEC properties between $\text{Pt}/\text{FeO}_x/\text{p-Si}(111)$ and $\text{Pt}/\text{FeO}_x/\text{p-Si}(100)$ with surface pyramids. One other possible factor is the tailing of FeO_x , which leads to the formation of a modulated carrier concentration structure in the depth direction. The depletion layer is thus thickened, which in turn enhances charge separation and PEC properties of p-Si.

4. Conclusions

This thesis describes the study on the potential change of Pt and Rh particles deposited on oxynitride photocatalysts by infrared absorption spectroscopy using adsorbed CO as a probe molecule. The different behavior of noble metal particles deposited on photocatalysts has been found. This thesis also includes the study on the surface modification of silicon by metal oxide thin layer to improve its PEC performance. These results clarify some of the reasons for the activities of various photocatalytic materials for overall water splitting under visible light irradiation, and effect of surface modification on p-Si photoelectrode.