

Photocatalytic Activity of Oxygen Deficient SrTiO_{3-δ} Prepared by Reduced Atmosphere Calcination

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Photocatalytic water splitting by semiconductors has drawn significant attention as a potential means of H₂ production using solar energy. Metal oxide photocatalysts have been widely studied because of high stability in water under irradiation. Metal oxides are easy to form oxygen defects by calcination in reductive condition, which have been studied in defect chemistry. However, there are very few that deal with quantitative discussion about the relationship between oxygen defect density and photocatalytic activity.

SrTiO₃ is a typical non-stoichiometric compound that has oxygen vacancies depending on the oxygen partial pressure [1]. With decreasing the oxygen partial pressure, the density of electrons in SrTiO_{3-δ} is increased. With this fact in mind, we synthesized several SrTiO_{3-δ} samples with different electron densities, and examined photocatalytic activities.

Non-stoichiometric SrTiO_{3-δ} samples were prepared by a polymerized complex method followed by calcination in different oxygen partial pressure. The prepared samples were studied by powder X-ray diffraction, UV-visible diffuse reflectance spectroscopy, scanning electron microscopy and so on. Photocatalytic reactions were conducted using a top-irradiation type cell that was connected to a closed gas circulation system. 100 mg of SrTiO_{3-δ} was dispersed in MeOH aqueous solution or AgNO₃ aqueous solution. After outgassing, the solution was irradiated under a 300 W Xe lamp ($\lambda > 300$ nm).

In X-ray diffraction patterns, all of the prepared samples showed single-phase diffraction patterns attributed to perovskite SrTiO₃, and no significant difference of structure with calcining oxygen partial pressure. Also, no significant variance in surface morphology, surface area and chemical compositions were confirmed by SEM images, BET measurement and ICP-MS measurement, respectively. However, in diffuse reflectance spectroscopy, the samples calcining in lower oxygen partial pressure than 10⁻¹⁶ atm were gray powder, exhibiting a visible light absorption band longer than 400 nm. This absorption is more pronounced with decreasing oxygen partial pressure. The visible light absorption band can be assigned to reduced titanium due to formation oxygen defects. In addition, samples prepared in lower oxygen partial pressure prolonged the lifetime of photogenerated electron, as revealed by transient IR absorption spectroscopy.

Then we evaluated photocatalytic activities of the prepared SrTiO_{3-δ} samples. As shown in Fig. 1, H₂ evolution and O₂ evolution half reactions were enhanced with decreasing oxygen partial pressure. Samples prepared in lower oxygen partial pressure have a high oxygen defect density, which increase the electron density of the samples. The high electron density shifts the Fermi level to more negative directions. The results of photocatalytic reactions suggest that the Fermi level shift and longer lifetime of photogenerated electron contributed the high photocatalytic activities.

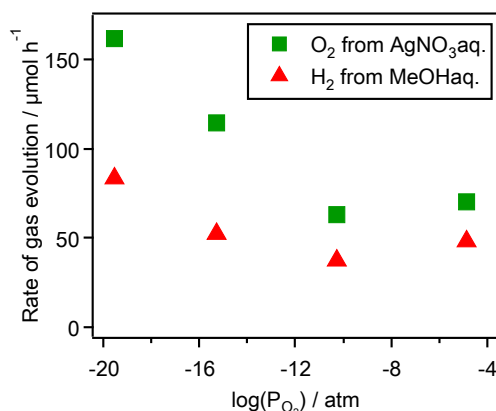


Fig. 1. Dependence of amount of evolved gases from reaction solution using SrTiO_{3-δ} on oxygen partial pressure.

REFERENCES

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