Effects of electron doping with oxygen defect introduction on photocatalytic hydrogen/oxygen evolution activity of non-stoichiometric $SrTiO_{3-\delta}$

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Abstract: The non-stoichiometry of $SrTiO_{3-\delta}$ powder was precisely controlled by annealing oxygen partial pressure without changing other physicochemical properties. The photocatalytic activities of $SrTiO_{3-\delta}$ for hydrogen and oxygen evolution were enhanced respectively forty-fold and three-fold with an increase in the density of oxygen defects. Increasing the defect density increases the electron density of the samples due to the principle of charge compensation. Electron doping accompanied with the defect formation prolonged the lifetime of photoexcited electron and expanded the degree of surface band bending. The improvements of photocatalytic activities correlated well with these two factors generated the electron doping.

Keywords: Oxide semiconductor, Oxygen defect, Electron density.

1. Introduction

Defects in photocatalysts have a significant impact on photocatalytic activity for overall water splitting[1] and the half reactions of hydrogen or oxygen evolution.[2] Although some reports clearly showed evidence for enhanced photocatalytic activity by the introduction of defects, no quantitative correlation between defects and photocatalytic activity has been obtained in any of reported powder-based semiconductors. The lack of such information has hindered a fundamental understanding of defect effects on the photocatalytic activity and how to rationally improve the activity.

In this study, we present a quantitative evaluation of photocatalytic hydrogen and oxygen evolution in a half reaction using strontium titanate ($SrTiO_{3-\delta}$) powder by precise control of the oxide non-stoichiometry. For the purpose of quantitative investigation, we have focused on the electron density, which increased with the density of oxygen defects due to the principle of charge compensation of the system.

2. Experimental

Non-stoichiometric $SrTiO_{3-\delta}$ powder samples were prepared by a polymerized complex method followed by annealing under different oxygen partial pressure. The electron densities of $SrTiO_{3-\delta}$ powders were approximated from the measurement using $SrTiO_{3-\delta}$ single crystals annealed with different oxygen partial pressure, as shown in Figure 1(a). The prepared samples were studied by powder X-ray diffraction (XRD), UV-visible diffuse reflectance spectroscopy (DRS), scanning electron microscopy (SEM), scanning transmission electron microscopy (STEM), X-ray photoelectron spectroscopy (XPS), the Brunauer-Emmett-Teller (BET) surface area measurement and inductively coupled plasma mass spectrometry (ICP-MS). The photogenerated charge carrier dynamics was observed by time-resolved absorption spectroscopy.

Photocatalytic reactions were conducted at room temperature using a top-irradiation type cell that was connected to a closed gas circulation system made of glass. 100 mg of $SrTiO_{3-\delta}$ powder was dispersed in 10 vol% methanol aqueous solution or 50 mM $AgNO_3$ aqueous solution (140 mL). After outgassing the reactant solution by a vacuum pump, the solution was irradiated under a 300 W Xe lamp. The irradiation wavelength was collected by the combination of a total reflection mirror and water filter (λ >300 nm).

3. Results and discussion

In X-ray diffraction patterns, all of the prepared samples showed single-phase diffraction patterns attributed to perovskite $SrTiO_3$, and no significant difference of structure with electron density. Also, no significant variance in morphology, surface area, surface electronic structure and chemical compositions were confirmed by SEM and STEM images, XPS spectra, BET measurement and ICP-MS measurement, respectively. However, in DRS, the samples having electron density larger than 10^{18} cm^{-3} were gray powder, exhibiting a visible light absorption band longer than 400 nm. This absorption is more pronounced with increasing electron density. The visible light absorption band can be assigned to the formation of reduced titanium species accompanied with electron doping. In addition, increasing the electron density prolonged the lifetime of photogenerated electron, as revealed by transient absorption spectroscopy.

The photocatalytic activities of the prepared $SrTiO_{3-\delta}$ powders were evaluated under UV light irradiation, and the results are shown in Figure 1(b). To understand the sole impact of electron doping, no cocatalyst was included in the $SrTiO_{3-\delta}$ powders. To further avoid complexity in the carrier separation dynamics towards the proton reduction and water oxidation reaction sites, the half reaction was investigated using methanol or $AgNO_3$ aqueous solution. As shown in Figure 1(b), both the hydrogen and oxygen evolution activities were significantly enhanced with an increase in the electron density. The highest electron density sample exhibited a forty-fold improvement in hydrogen evolution. Transient absorption spectroscopy indicated that the lifetime of photoexcited electrons was prolonged with an increase in the electron density, which correlated well with the improved hydrogen evolution activity. The oxygen evolution activity was also enhanced three-fold with electron doping. This enhancement correlated well with the degree of surface band bending that resulted from different electron densities within the material.

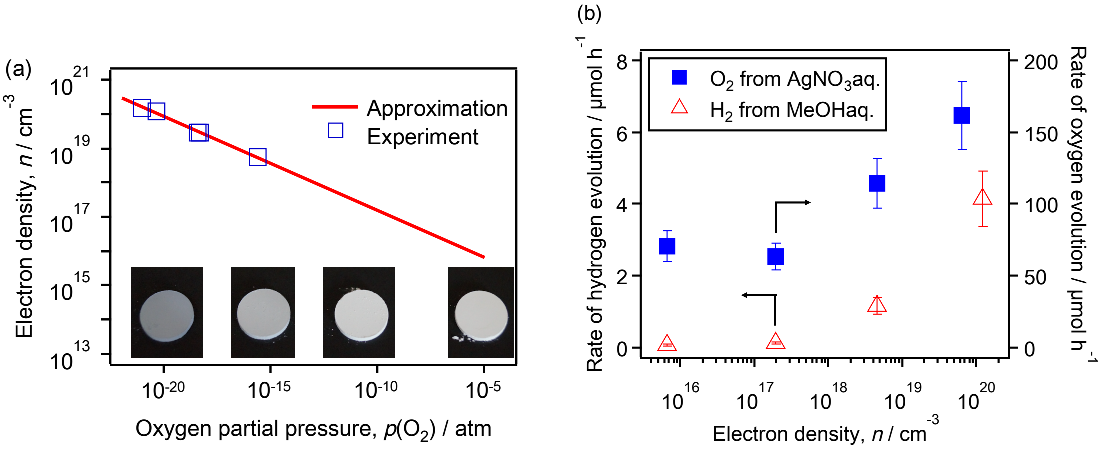

Figure 1. (a) Electron densities obtained using $SrTiO_{3-\delta}$ single crystals annealed at 1423 K with different oxygen partial pressure. The line and square represent the approximated and measured values, respectively, while the inset images show the colors of samples annealed under the corresponding. (b) Rate of gas evolution from methanol aqueous solution (10 vol%) and $AgNO_3$ aqueous solution (50 mM) using $SrTiO_{3-\delta}$ under UV light (λ >300 nm) as a function of the electron density in $SrTiO_{3-\delta}$. Reaction conditions: catalyst, 100 mg; solution, 140 mL; light source, xenon lamp (300 W); reaction vessel, Pyrex top-irradiation type.

4. Conclusions

Non-stoichiometric $SrTiO_{3-\delta}$ samples that possessed precisely controlled electron density without changing other physicochemical characteristics such as the crystallinity, morphology and surface electronic state were prepared by annealing with different oxygen partial pressure. Using these $SrTiO_{3-\delta}$ powders, the quantitative discussion between defect density and photocatalytic activity was realized. The quantitative investigation revealed that photocatalytic activities for hydrogen/oxygen evolution were correlated strongly with the lifetime of photoexcited electron and the degree of surface band bending.

References

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