

X-ray absorption and emission studies of the electronic states of visible-light semiconductor photocatalyst: Rh-doped SrTiO₃

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Rh-doped SrTiO₃ is a visible-light semiconductor photocatalyst, and the valence states of Rh are closely related to the reactivity of photocatalyst [1]. However, the electronic states of valence and conduction band have not been directly determined yet. In this study, we investigated both occupied and unoccupied states of Rh-doped SrTiO₃ samples as a function of Rh amount and the valence of Rh using X-ray emission spectroscopy (XES) and absorption spectroscopy (XAS) at BL07LSU in SPring8.

Rh:SrTiO₃ powders with Rh doping levels of 0, 1, 3, and 5 at% were prepared in the following way. Mixtures of SrCO₃ (baked at 300°C for 1 hour before use), TiO₂, and Rh₂O₃ were pre-calcined at 900°C for 5 hours, followed by heating at 1100°C for 10 hours. An excess amount of Sr (7 at%) was used in the starting materials. The powders were pressed into thin pellets at 10 MPa and calcined at 1200°C for 12 hours. This synthesis process produced samples with Rh⁴⁺ substituting at the Ti⁴⁺ site. Valence control of Rh was made by annealing a Rh⁴⁺:SrTiO₃ pellet in a H₂ atmosphere at 300°C for 2 hours, reducing Rh⁴⁺ to Rh³⁺. A color difference between the Rh⁴⁺ (purple) and Rh³⁺ (yellow) samples are observed visually, as shown in Figure 1. Each sample was confirmed to be single phase by x-ray diffraction.

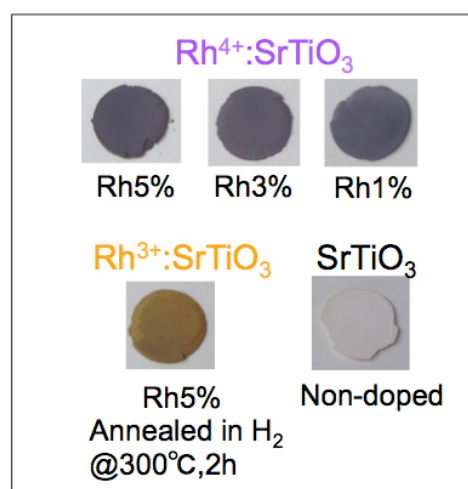


Figure 1. Photos of prepared Rh:SrTiO₃ thin pellets

Figure 2 shows a series of O1s XAS spectra of Rh^{4+/3+}:SrTiO₃ and non-doped SrTiO₃. According to the dipole selection rules, the O1s XAS of Rh:SrTiO₃ corresponds to a transition from the O1s core level to an unoccupied O2p state that is hybridized with Ti3d or Rh4d states. The main peak at ~531 eV is composed mainly of Ti3d states hybridized with the O2p states, forming the conduction band of SrTiO₃. The spectral intensity in the gap region is shown on an expanded (×2) scale above each spectrum. The intensity of the unoccupied in-gap peak at ~1.5 eV below the CB minimum increased with increasing the Rh⁴⁺

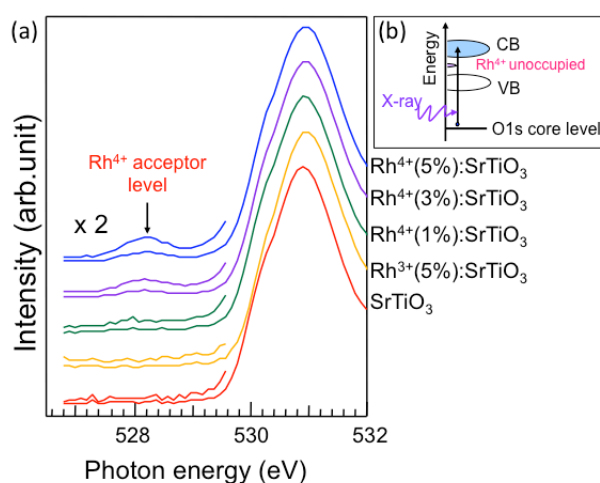


Figure 2. (a) O1s XAS spectra of Rh⁴⁺(x at%):SrTiO₃ (x = 0, 1, 3, 5) and Rh³⁺(5 at%):SrTiO₃. (b) Energy level diagram for the transitions probed by O1s XAS.

doping level. Note that no absorption peak was observed in a 5 at% $\text{Rh}^{3+}:\text{SrTiO}_3$ sample. Thus, we assign the peak at 528.2 eV to a Rh^{4+} acceptor level, in accordance with the original interpretation of the UV-Vis-NIR absorption spectra [2,3].

Figure 3 shows a series of O1s XES spectra of $\text{Rh}^{4+/3+}:\text{SrTiO}_3$ and non-doped SrTiO_3 samples with the excitation energy of 530.9 eV. The two main peaks at 523.5 and 526 eV are assigned to fluorescence related to transitions from bonding and non-bonding O2p states to the O1s core level, respectively [5]. The small peak located at 530.9 eV was an elastically scattered incident x-ray. A small but systematic emission increases in the VB shoulder region from 527 to 528.3 eV with increasing Rh content could be assigned to the $\text{Rh}^{4+/3+}$ donor levels. A spectral weight shift to higher emission energy by ~ 0.5 eV is evident for the reduced $\text{Rh}^{3+}:\text{SrTiO}_3$ sample. Note that the Rh donor levels close to the VB maximum of SrTiO_3 were observed as a shoulder close to the band-gap excitation energy in the UV-Vis-NIR absorption spectra of the $\text{Rh}^{4+/3+}:\text{SrTiO}_3$ samples [2,3].

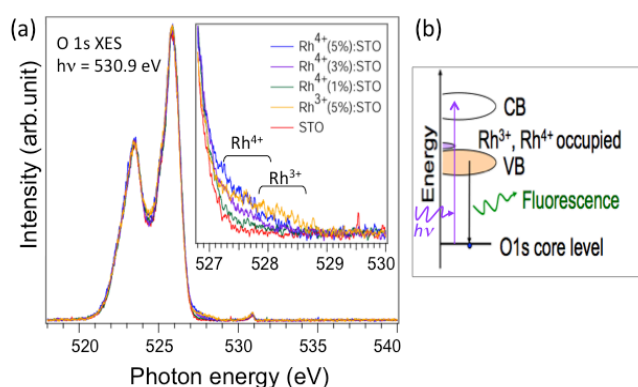


Figure 3. (a) O1s XAS of $\text{Rh}^{4+}(x \text{ at}\%):\text{SrTiO}_3$ ($x = 0, 1, 3, 5$), $\text{Rh}^{3+}(5 \text{ at}\%):\text{SrTiO}_3$, and non-doped SrTiO_3 , taken with the x-ray energy of 530.9 eV. The inset shows an expansion of the top of the valence band. (b) A schematic view of the transitions involved in O1s XES.

Based on the present XAS and XES results, the main difference in the photocatalytic activity between Rh^{4+} and $\text{Rh}^{3+}:\text{SrTiO}_3$ can be explained by the difference in the in-gap Rh states. It is known that the photocatalytic activity of $\text{Rh}:\text{SrTiO}_3$ increases during the induction period, when Rh^{4+} is partially converted to Rh^{3+} [2]. We can conclude that the lower photocatalytic efficiency of $\text{Rh}^{4+}:\text{SrTiO}_3$ is related to the appearance of the unoccupied mid-gap state that may serve as a recombination center for the photoexcited carriers.

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