

## ホスホン基を介したプロトン供給促進による光触媒的水素生成活性向上の pH 依存性

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pH dependence of photocatalytic hydrogen evolution activity improved by the accelerated proton supply thorough phosphonate groups (<sup>1</sup>*Faculty of Engineering, Shinshu University*, <sup>2</sup>*Research Initiative for Supra-Materials*, <sup>3</sup>*The University of Tokyo*) ○Masataka Yamamoto,<sup>1</sup> Tomoya Mizukami,<sup>1</sup> Yosuke Kageshima,<sup>1,2</sup> Katsuya Teshima,<sup>1,2</sup> Kazunari Domen,<sup>2,3</sup> Hiromasa Nishikiori<sup>1,2</sup>

We have reported that the photocatalytic hydrogen evolution activity of La,Rh-codoped SrTiO<sub>3</sub> (La,Rh:STO) can be improved by modifying the surface of La,Rh:STO with the silane coupling reagent containing phosphonate groups<sup>1)</sup>. The phosphonate groups might contribute to accelerated proton supply to the active sites. In this study, we evaluated the dependence of photocatalytic hydrogen evolution activities of the phosphonate-modified La,Rh:STO on pH of reaction solution to elucidate the mechanisms of improved proton supply through the phosphonate groups.

The pH dependence of hydrogen evolution rate from methanol aqueous solution are summarized in Fig. 1. The hydrogen evolution rate obtained over La,Rh:STO increased according to increasing of pH. The phosphonate modification certainly contributed to the improved photocatalytic activities within all pH range, while the improvement was especially notable in the alkaline condition. In the presentation, characterizations of the photocatalytic materials before and after the reaction as well as the possible mechanism will be also discussed. **Keywords** : Photocatalyst; Hydrogen Evolution; Proton Supply; Phosphonate Groups; Silane Coupling Reagent

これまでに、La,Rh 共ドーパ SrTiO<sub>3</sub> (La,Rh:STO)粉末光触媒表面にホスホン基を有するシランカップリング剤を修飾することで、水素生成活性が向上することを報告している<sup>1)</sup>。ホスホン基は、活性点へのプロトン供給促進に寄与していると考えられる。本研究では、ホスホン基を介したプロトン供給促進の機構解明を目的とし、ホスホン基修飾 La,Rh:STO の水素生成活性の反応溶液の pH 依存性を検討した。

メタノール水溶液からの水素生成速度の pH 依存性を Fig. 1 に示す。pH の上昇に伴って La,Rh:STO の水素生成速度は上昇した。全ての pH 域においてホスホン基修飾によって水素生成速度は向上したが、特に塩基性条件で活性向上が顕著であった。発表では、反応前後の光触媒材料のキャラクタリゼーションや想定される反応機構等についても議論する。

1) Y. Kageshima, *et. al.*, *Angew. Chem. Int. Ed.* **2021**, 60, 3654-3660.

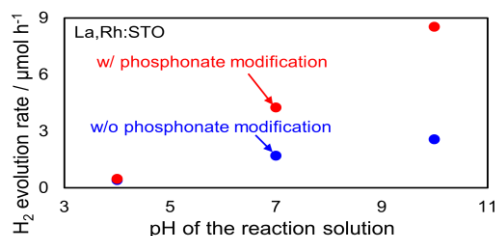


Fig. 1 Hydrogen evolution rate obtained over La,Rh:STO as a function of pH of the reaction solution .