SrドープNaTaO$_3$の表面再構成と光触媒機能：よいドーパントを探す法則の探求

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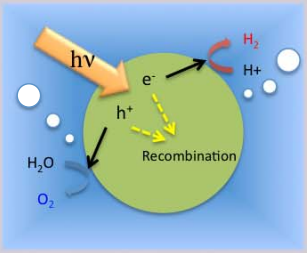
Introduction

$$2\,H_2O \xrightarrow[\text{Solar energy}]{\text{Photocatalyst}} H_2 + 1/2\,O_2$$

Electron-hole recombination should be restricted to increase photocatalytic activity.

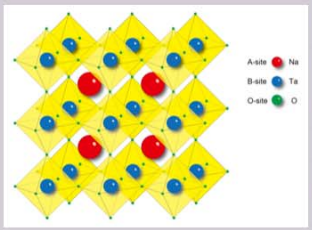
Metal dopants can somehow separate carriers (electrons and holes) to restrict electron-hole recombination.

Successful example



Water-splitting by photocatalysts

The Photocatalytic activity of $NaTaO_3$ increased a lot by metal dopants (Sr,Ba,La).[1,2] Perovskite-structured $NaTaO_3$ have two optional sites (A-site and B-site) for dopants to substitute. In the present research, Sr-doped $NaTaO_3$ have been mainly studied to finding relationship of substitutional sites of dopants with increased acitivity.



$NaTaO_3$ (Perovskite structure)

Experimental

Synthesis methods are as follow: [2,3]

Solid-state reaction (SSR): $Na_2CO_3 + Ta_2O_5 + SrCO_3$ → (1150 °C for 10 hours)

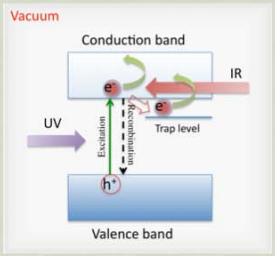
Hydrothermal reaction (HTR): $NaOH + Ta_2O_5 + SrCO_3$ → (160 °C for 24 hours, H_2O)

Successful doping were confirmed by energy-dispersive X-ray spectroscopy (EDX) on Sr/Ta molar ratio and by X-ray diffraction (XRD) on single XRD pattern of $NaTaO_3$.

Particle morphology of Sr-doped $NaTaO_3$ was observed by scanning electron microscopy (SEM). Raman spectroscopy was applied for identifying substitutional sites of dopants in perovskite-structured $NaTaO_3$.

Population of excited electrons were examined by Fourier transform infrared spectroscopy (FT-IR) upon ultraviolet (UV) irradiation.

Photocatalytic activity was studied by reduction rate of Ag^+ to Ag upon UV irradiation. $AgNO_3$ aqueous solution was used as testing reagent.



Mechanism of FT-IR / UV

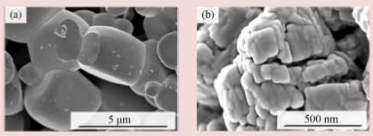
Results & Discussion

Sr-doped $NaTaO_3$

SSR	HTR

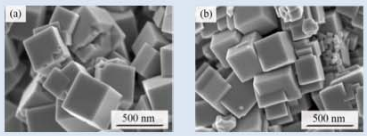
SEM images

Sr/Ta mol% : (a) 0, (b) 2.6



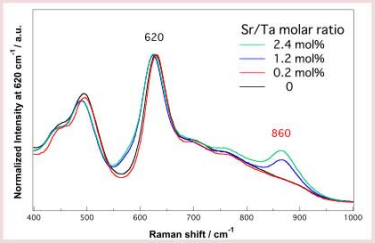
Surface reconstruction

Sr/Ta mol% : (a) 0, (b) 2.4

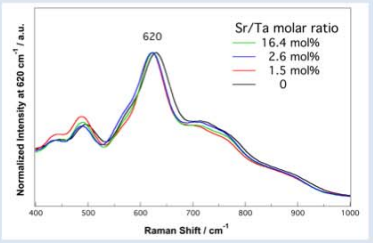


Unchanged

Raman spectra (Supporting information)

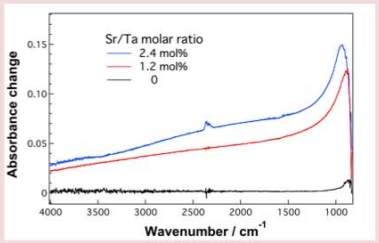


860 cm^{-1} Raman band – A_{1g} stretching (BO_6)
B-sites substitution

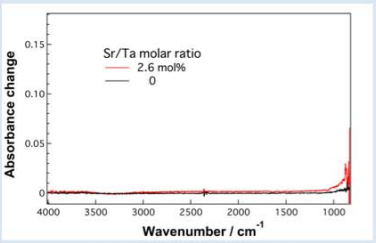


Not found any new Raman band
A-sites substitution

IR absorption / UV irradiation

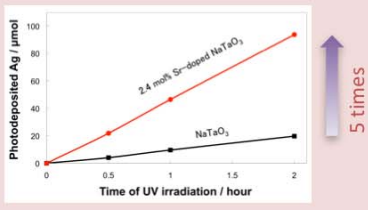


Population of electrons increased 1x times

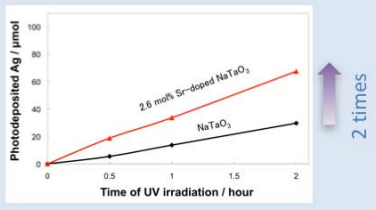


Population of electrons increased 3 times

Ag photodeposition rate



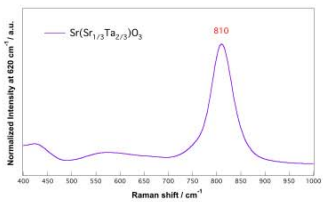
5 times

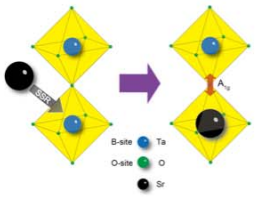


2 times

Supporting information

Raman spectrum of $Sr(Sr_{1/3}Ta_{2/3})O_3$





Perovskite structured materials said to show intensive Raman band at 800~900 cm^{-1} when two elements occupy B-sites.[4] Having B-sites doped perovskite structure, $Sr(Sr_{1/3}Ta_{2/3})O_3$ brings strong Raman band at 810 cm^{-1}. Model of corresponding A_{1g} stretching induced by B-site doped Sr is shown at right.

Conclusion

In SSR, Sr substitute in B-sites to reconstructing the surface morphology and further increase population of excited electrons for participating in the photocatalytic reaction. Rate of Ag^+ reduction increased by 5 times when doped by Sr in 2.4 mol%.

While in HTR, Sr substitute in A-sites and there were no clear change observed on particle morphology and on population of excited electrons. Activity increased by only 2 times.

Reference

[1] A, Kudo.; H, Kato.; *Chem. Phys. Lett*. **2000**, *331*, 373.
[2] M, Maruyama.; A, Iwase.; H, Kato.; A, Kudo.; H, Onishi.; *J. Phys. Chem. C* **2009**, *113*, 13918.
[3] Y, Lee.; T, Watanabe.; T, Takata.; M, Hara.; M, Yoshimura.; K, Domen.; *Bull. Chem. Soc. Jpn*. **2007**, *80*, 423.
[4] H, Zheng.; I, M, Reaney.; G, D, C, Csete.; R, Ubic.; J, Yarwood.; M, P, Seabra.; V, M, Ferreira.; *J. Mater. Res*. **2004**, *19*, 488.