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journal homepage: www.elsevier.com/locate/apcatbTensile strain for band engineering of SrTiO₃ for increasing photocatalytic activity to water splittingYoonyoung Kim^b, Motonori Watanabe^b, Junko Matsuda^b, Jun Tae Song^{a,b}, Atsushi Takagaki^{a,b}, Aleksandar Staykov^b, Tatsumi Ishihara^{a,b,*}^a Department of Applied Chemistry, Faculty of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka, 819-0395, Japan^b International Institute for Carbon-Neutral Energy Research (WPI-I²CNER), 744 Motooka, Nishi-ku, Fukuoka, 819-0395, Japan

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ABSTRACT

SrTiO₃ is a well-known highly active photocatalyst with high energy conversion efficiency. In this study, we investigated the formation of oxygen vacancy by using the chemo-mechanical effect that was introduced by the dispersion of metal particles into grain and photocatalytic activity to water splitting. Au dispersion on SrTiO₃ followed by sintering treatment was studied for introduction of chemo-mechanical strain because of a different thermal expansion coefficient; the introduced chemo-mechanical strain generated oxygen vacancy in SrTiO₃. Thus, induced chemo-mechanical strain shows change in electronic band structure resulting in increasing lowest unoccupied molecular orbital (LUMO) level with increasing Au content. Since photoluminescence was significantly decreased by sintering after Au dispersion, the introduced strain effects may work for increasing a charge separation efficiency and adsorption site in water splitting. Therefore, the photocatalytic activity was much increased by sintering treatment after Au dispersion on SrTiO₃.

1. Introduction

Photocatalytic water splitting is an attractive catalytic process of the formation of hydrogen as energy carrier and many materials such as oxide, oxynitride, and nitride have been studied [1–4]. SrTiO₃ is well-known photocatalyst with a perovskite structure that has high chemical stability and structural variety [5,6]. Furthermore, it has a wide bandgap which is controlled to utilize visible light by doping Rh [7,8], anion doping F [9], N [10], S [11], etc. For further increase in activity, doping various cations like Al [12] or Mo [13] is also reported for increasing apparent quantum yield (AQY). On the other hand, oxygen vacancy has unique properties in photocatalytic reaction; it works as a charge trap and also adsorption site and suppress the recombination of electron and hole in photocatalytic reaction [14–17]. Moreover, the oxygen vacancy constructs impurity level that assists to consist of narrow band gap in order to absorb visible light [18–22]. Therefore, recently, there is strong interest in oxygen vacancy in photocatalyst for increasing activity and also unique reactions like CO₂ convert into acetic acid [23–25]. In this research, we investigated the effects of oxygen vacancy introduced by chemo-mechanical effect on activity to water splitting on SrTiO₃. Since thermal expansion coefficient of Au and SrTiO₃ are 14×10^{-6} and $9 \times 10^{-6} \text{ K}^{-1}$, respectively, large tensile

strain will be induced when Au and SrTiO₃ are connected at high temperature and cooled down. In our previous study, chemo-mechanical strain effects on TiO₂ was studied and it was found that H₂ formation rate was much increased by chemo-mechanical effects of Au dispersed in TiO₂ followed by spark plasma sintering (SPS) [26]. This chemo-mechanical effect on water splitting is explained by narrowing band gap of TiO₂ and so it is expected that introduction of lattice strain is one of the effective method for increasing water splitting activity of inorganic photocatalyst. In this study, effects of Au dispersion in SrTiO₃ followed by SPS sintering treatment on photocatalytic water splitting activity were studied and in a similar manner with TiO₂, it was found that dispersion of Au into SrTiO₃ followed by SPS treatment is highly effective for increasing activity to photocatalytic water splitting and the electronic band structure in SrTiO₃ was also varied with lattice strain.

2. Experimental

2.1. Preparation of Au dispersed SrTiO₃

SrTiO₃ was synthesized by the solid-state reaction method after ball mill mixing. SrCO₃ and TiO₂ (Rutile) were used for the starting material of SrTiO₃. The stoichiometric ratio of starting reagents to SrTiO₃ were

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