

NaTaO₃ photocatalysts doubly doped with metal cations

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1 Introduction

Currently, the use of solar energy for hydrogen production via the water splitting reaction is of widespread importance as it is regarded as one of the most promising routes for the conversion of solar energy into chemical energy [1]. Such a conversion route mimics photosynthesis in nature, and it demonstrates immense potential to be the pinnacle of sustainable energy. Only light, water, and a catalyst are required. Thus, the selection of an appropriate photocatalyst is key to achieving a high solar energy conversion efficiency.

Among the photocatalyst materials investigated in the last two decades, alkali tantalates, particularly sodium tantalate (NaTaO₃), are excellent materials for the photocatalytic overall water splitting [2–5]. When properly doped with La cations through the solid-state route, NaTaO₃ shows a quantum efficiency of as high as 56% upon ultraviolet exposure at 270 nm [6]. Following their breakthrough, a lot of efforts have been made in the world to build a library of highly efficient photocatalysts based on metal-doped NaTaO₃.

While La-doped NaTaO₃ (La-NTO) has showed developments in engineering for artificial photosynthesis, questions in science remain to be answered. The mechanism behind enhancement of water splitting efficiency induced by the La doping is unknown. The decisive properties of the dopant in relation with photoexcited electrons and holes remain nearly unexplored. Without understanding science of the highly efficient photocatalysts, how and why water efficiently splits on La-NTO, proper research direction can never be achieved.

Another important issue to be addressed is sensitizing La-NTO to visible light. Visible light accounts for approximately 45% of total solar radiation reaching the Earth's surface. Doping metals with half-filled *d* states is a well-known method to produce filled or empty electronic states in the band gap for visible light sensitization. Double doping with half-filled transition metal (TM) together with La is suggested to be a suitable way of visible light sensitization of NTO. With this double doping system, cationic charge is balanced without need for oxygen vacancy. Therefore, undesired, negative contribution coming from oxygen vacancy formation can be avoided.

2 Methodology

The first purpose to be achieved in this research project is to understand the detailed bulk structure of La-NTO and its photocatalytic behavior for water splitting reaction under ultraviolet irradiation. The insights obtained is expected to be transferable to design visible-light-

sensitized NTO through double doping with La and TMs. To achieve the first purpose, three topics are studied. The first topic is the mechanism of enhanced water splitting activity upon La doping into NTO. Here, a plausible mechanism of photoactivity enhancement is proposed. The occupation preference of La cations in the host NTO lattice is also elucidated. The second topic is the role of core and shell structure in dictating the water splitting activity of La-NTO. Core-shell structure forms in the highly active La-NTO prepared through the solid-state route [6]. Understanding the role of such a unique nanoarchitecture is thus important for designing highly active perovskite-structured tantalate photocatalysts which are likely featured with such a core-shell structure. The third topic is the role of spatial La distribution in controlling the water splitting activity of La-NTO. When prepared with the solid-state method, the distribution of La dopants is also different in space from the surface to the bulk region. The water splitting activity is potentially sensitive to the spatial dopant distribution in the solid-state prepared La-NTO.

Herein, the detailed structure and photocatalytic behavior of La-NTO are investigated with a number of microscopy and spectroscopy techniques, such as scanning transmission electron microscopy, X-ray absorption spectroscopy, light-induced infrared absorption spectroscopy, microwave conductivity, and photoacoustic spectroscopy to unravel the key insights into the structure-photoactivity relationship.

The second purpose is visible-light sensitization of La-NTO with TMs, including Cr, Mn, Fe, Co, Ni, Rh, and Ir. Seven topics are thus studied according to the TM being employed for the sensitization. In most cases, the dopant concentrations are systematically varied to know the sensitization behavior with respect to the extent of doping (doping level). TMs in the same group and TMs in the same row are to be compared to get hidden insights into the sensitization behavior of TMs to La-NTO. X-ray absorption spectroscopy is employed to investigate the local environments around dopants, while infrared absorption spectroscopy induced by visible light is used to confirm whether electrons are photoproduced by the doubly doped samples upon visible light exposure.

3 Results and Discussion

A series of La-NTO samples have been successfully prepared through the solid-state method to reproduce the highly photoactive La-NTO reported earlier [6]. In La-NTO, the La cations sit in the Na site of the host lattice. At a low concentration of less than 5 mol%, La dopants effectively restrict electron-hole recombination to increase

the electron population. Energy gradient of the conduction band edge (CBB) is proposed to be responsible for the restricted recombination. A concentration gradient of the La dopants decreasing gradually from the surface to the bulk is suggested to exist. The concentration gradient of dopants simultaneously induces an energy gradient of the CBB. The energy gradient of the CBB separates the excited electrons to the bulk away from holes populating the surface to restrict recombination. Because the upward shift of the CBB is small enough relative to the thermal energy at room temperature, the separated electrons in the bulk can then return to the surface.

Herein, electron population is measured with light-induced infrared absorption spectroscopy. The order of electron population agrees with that of gas evolution rates. Given this fact, light-induced infrared absorption spectroscopy potentially offers a simple, straightforward manner to foresee the photocatalytic behavior of newly developed NTO materials.

Furthermore, a La-rich shell with the thickness of about 3 nm forms heteroepitaxially over La-poor core when La-NTO is prepared through the solid-state route. The formed core and shell structure present in the La-NTO particle play a role in governing the water splitting activity. In the case of La-NTO, the presence of La-rich shell is detrimental to the restriction of recombination. Systematic etching of La-NTO with HF is then carried out to verify the roles of core and shell. Etching gradually diminishes the shell. Increasing the etching time decreases the particle size and alters the particle shape to remove the typical step-edge structure on the surface. Increased etching time leads to the decreased electron population and hence the water splitting rate. Systematic etching also confirms the presence of a La concentration gradient, which agrees well with the results of element maps by the scanning transmission electron microscopy coupled with energy dispersive X-ray spectroscopy.

Given the fact that the La dopant distribution is spatially different across the particle; decreasing in the La concentration from the surface to the bulk region, this feature may importantly contribute to the water splitting activity. If this is indeed the case, designing water splitting activity through controlling the spatial dopant distribution is thus possible and should be a convenient approach. To confirm this supposition, two La-NTO samples with an identical dopant concentration yet possessing different spatial La distribution are prepared. Less homogeneous sample shows a noticeably higher water splitting activity. The higher water splitting activity of this sample is proposed to be caused by the higher electron population due to a better restriction of recombination. The better restriction of recombination is suggested to be due to a sufficiently larger energy gradient of the CBB that separates electrons to the bulk region away from holes populating the surface. The less homogeneous sample also shows a considerably higher electron trap density around the CBB. These shallow electron traps may beneficially affect the water splitting activity. Specifically, the shallow electron traps capture a large portion of photoexcited

electrons. The shallowly trapped electrons remain reactive to contribute to the higher hydrogen evolution rate [7].

Visible light sensitization is then performed on La-NTO by coupling with TMs. It is found upon the double doping that not only is light absorption extended to visible light, the doubly doped samples can also produce electrons under visible light irradiation. These photoproducted electrons should be usable to drive redox reaction on the surface upon exposure to visible light. Low doping levels of less than 10 mol% generally give large electron population, although the light extensions to visible region are lower than samples with high doping levels. This finding supports the interpretation that extending light absorption does not necessarily increase the electron population.

Furthermore, X-ray absorption fine structure confirms that in the doubly doped samples La cations occupy the Na site while TM cations occupy the Ta site, most likely forming LaTMO-NaTaO₃ solid solutions. In this case, oxygen vacancy is not required to balance the cationic charge. At an identical dopant concentrations, there is no systematic trend recognized on the sensitization feature among the TMs in the same group or those in the same row in terms of electron population. The difference in the spatial dopant distributions at the same doping level can be one reason to make finding the trend of the sensitization behavior difficult.

It is to be noted that in the doubly doped samples, for instance, La+Co co-doped NTO and La+Rh co-doped NTO, the dopant distributions can also be spatially tuned to result in varied electron population. Less homogeneous samples show higher electron population, similar to those observed with single doping La-NTO. Given this fact, an identical mechanism of restricted electron recombination may be the case for both the singly doped and doubly doped NTO samples.

The mechanism of restricted electron-hole recombination proposed here for NTO singly doped with La and doubly doped with La and TMs may also be applicable to interpret the restricted recombination and enhanced water splitting activity in metal-doped perovskite metal oxides such as SrTiO₃. As is well known, SrTiO₃ is also an important water splitting photocatalyst.

A part of results of this research project have been reported in peer-reviewed journals. The results of studying La+Cr co-doped NTO has been published in [8]. Visible light sensitization of La-NTO with Mn is reported in [9], while that with Fe is reported in [10]. Upon coupling with those TMs, La-NTO is able to absorb visible light to produce electrons. Restriction of electron-hole recombination in La+TM co-doped NTOs is optimized at a low doping level of less than 8 mol%, similar to those observed in La-NTO. Given this fact, the mechanism of the restricted recombination in those singly doped and doubly doped NTOs may be identical.

Revealing mechanisms behind the world-record efficiency for photocatalytic water splitting such as that over La-NTO provides us rich knowledge about creation, transport, and reactivity of electronically excited states in multi-element semiconductors. These issues are

undoubtedly in a frontier of chemistry today. Moreover, physical insights yielded in this research can potentially be transferred to innovate highly efficient, visible-light sensitized photocatalysts for artificial photosynthesis in a practical scale. On broader impact, this research can contribute to science in Indonesia, since photocatalysis is highly relevant for tropical countries blessed with sunlight all year round.

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