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N-doped $NaTaO_3$ synthesized from a hydrothermal method for photocatalytic water splitting under visible light irradiation

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ABSTRACT

$NaTaO_{3-x}N_x$ catalysts were synthesized by a hydrothermal (H) and a solid-state (S) method in this study. The H- and S-$NaTaO_{3-x}N_x$ samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), UV-visible (UV-vis) diffuse reflectance spectroscopy, and photoluminescence (PL) spectroscopy. The XRD patterns of the H- and S-samples showed peaks indexed to the pure phase of perovskite $NaTaO_3$ and minor peaks assignable to Ta_3N_5 at various synthesis temperatures. Substitution of oxygen by nitrogen ions causes the light absorption of the H- and S-$NaTaO_{3-x}N_x$ samples to be extended to the 600–650 nm region, thus making the samples visible-light active. The $NaTaO_{3-x}N_x$ samples exhibited photocatalytic activity for H_2 and O_2 evolution from aqueous methanol and silver nitrate solutions under visible-light irradiation. The UV-vis and PL spectra of the H- and S-catalysts revealed the presence of cationic vacancies and reduced metallic species, which acted as recombination centers. These results demonstrated that the preparation method plays a critical role in the formation of defect states, thereby governing the photocatalytic activity of the $NaTaO_{3-x}N_x$ catalysts.

1. Introduction

In the past few decades, the photocatalytic decomposition of water has emerged as a promising technique to produce H_2 and O_2 as fuels for sustainable energy [1–7]. In 1972, Honda and Fujishima first explored photocatalysis using TiO_2 and Pt as photoelectrodes under UV light irradiation [8]. Since then, considerable research has been devoted to the development of photocatalysts with unique semiconducting properties, such as, TiO_2 [9,10], $SrTiO_3$ [11,12], $K_4Nb_6O_{17}$ [13], and $NaTaO_3$ [14–17]. In the late 1990 s, Kudo et al. reported that $NaTaO_3$, which has a wide band gap of 4.0 eV, shows outstanding photocatalytic activity for the production of H_2 and O_2 in a stoichiometric ratio of 2:1, upon NiO loading and doping with La ions [18]. The photocatalytic performance of $NaTaO_3$ is significantly influenced by its crystalline structure, i.e., monoclinic and orthorhombic phases [19]. In the monoclinic structure, the photo-excited electron and holes separated efficiently because of the cubic-like Ta–O–Ta bond linkage, thus improving its photocatalytic activity [20]. On the other hand, $NaTaO_3$ was activated only in the UV region (< 300 nm) because of its large band gap, thereby limiting its practical application in photocatalysis.

Several efforts have been made to improve the light absorption efficiency of Ta-based compounds [21–27]. Among the synthesis methods to obtain these Ta derivatives, the simplest route is calcination under ammonia atmosphere via a solid-state reaction. Ammonolysis at high temperature is a facile method to substitute O ions with N ions and thereby induce an extensive O/N hybridization for altering the band gap energy [28,29]. Nitrides and oxynitrides such as tantalum oxynitride (TaON) [30–32] and tantalum nitride (Ta_3N_5) [33–36] have attracted considerable attention as visible-light-active photocatalysts. TaON and Ta_3N_5 were prepared by nitriding Ta_2O_5 under NH_3 flow at 1123 K for 15 h; the quantum efficiency of TaON and Ta_3N_5 for water splitting was up to 34% and 10%, respectively [37]. Schmuki et al. reported that Na-doped Ta_3N_5 has a smaller band gap and shows a higher photoelectrochemical current response than does pure Ta_3N_5 [38]. Recently, Yao prepared N-doped TaO_xN_y by the sol-gel method and successfully reduced its band gap, so that light absorption could be extended to the visible region [39]. They also found that the N doping level and reduced Ta^{4+} species in TaO_xN_y would affect its photocatalytic activity. N doping introduces localized N 2p states above the valence band, which is responsible for the red shift of the absorption; on the other hand, Ta^{4+} defects act as donor states and the electrons in these states are excited to the conduction band for the photocatalytic reaction [39]. Oxynitride solid solutions, $Na_xLa_{1-x}TaO_{1+2x}N_{2-2x}$, were synthesized by ammonolysis

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under NH_3 atmosphere at 1273 K, which showed photocatalytic activity for both H_2 and O_2 evolution under visible-light irradiation in the presence of sacrificial reagents [40]. Moreover, a series of perovskite and Ruddlesden-Popper tantalum oxynitrides such as $SrTaO_2N$, $BaTaO_2N$, Sr_2TaO_3N, and Ba_2TaO_3N, have been reported [41–46]. These studies support the fact that O/N disorder is thermodynamically favored in perovskite-structured materials at high temperature.

Nitrogen-doped $NaTaO_3$, with a cubic morphology and high crystallinity, has been synthesized using a hydrothermal method [47,48]. Under UV and visible light irradiation, the photocurrent density of the N-doped $NaTaO_3$ improved significantly compared to that of the undoped $NaTaO_3$. The visible light response originated from the introduction of nitrogen, which formed hybridized N 2p and O 2p states. These localized states with the higher energy level in the band gap give rise to an additional shoulder in absorption spectrum, which is responsible for the enhancement in photocatalytic activity [49,50]. Although nitridation is a favorable approach to prepare oxynitride and nitride photocatalysts, there are only a few reports on the synthesis of nitrogen-doped $NaTaO_3$. Thus far, the chemical properties, photocatalysis, and photoluminescence performances of the nitrogen-doped $NaTaO_3$ catalyst synthesized by the hydrothermal methods remain elusive.

In this study, a visible-light-driven nitrogen-doped $NaTaO_3$ is successfully prepared by the hydrothermal method. The catalyst exhibits photocatalytic activity for H_2 and O_2 production in the presence of sacrificial reagents, under visible light irradiation. The crystalline structure, optical properties, and photoluminescence (PL) mechanism of the visible-light-active $NaTaO_{3-x}N_x$ are examined to guide the development of an efficient catalyst for the photocatalytic splitting of water under visible-light irradiation.

2. Experimental

$NaTaO_{3-x}N_x$ photocatalysts were prepared by the hydrothermal and solid-state methods. In the hydrothermal synthesis, the precursor Ta_3N_5 (referred to as H-precursor), was prepared by the nitridation of commercial Ta_2O_5 powder at 850 °C under NH_3 flow (at a flow rate of 10 mL/min) for 15 h. Then, the H-precursor was suspended in 10 M NaOH solution and stirred at room temperature. A reddish powder was obtained after autoclaving the as-prepared solution at 200 °C or 240 °C for 6 and 24 h, followed by filtration and drying at 60 °C for 24 h. Hereinafter, the samples thus obtained will be designated as H20-6, H24-6, H20-24, and H24-24, in which 20 and 24 indicate the temperatures of 200 °C and 240 °C, and 6 and 24 refer to the reaction time.

For the solid-state synthesis of $NaTaO_{3-x}N_x$, the precursor $NaTaO_3$ (referred to as S-precursor) was first prepared by the previously reported sol-gel method [20]. The sol-gel synthesized $NaTaO_3$ was subjected to calcination in a tubular furnace under NH_3 atmosphere at 825°C or 850°C for 5, 10, and 20 h. The resulting powders were washed several times with deionized water and dried at 60°C for 24 h. Hereinafter, the products obtained will be referred to as S825-5, S850-10, and S850-20, in which 825 and 850 indicate the calcination temperature, and 5, 10, and 20 refer to the reaction time.

The crystalline structures of these samples were determined by powder X-ray diffractometry (XRD, Rigaku RINT 2100, Japan) with Cu Kα radiation ($\lambda = 1.5418$ Å) at 40 kV and 40 mA. The XRD patterns were collected at a step interval of 0.01° and a scan rate of 4 min^{-1} in the 2θ range of 20–70°. The surface morphology and microstructure were examined using scanning electron microscopy (SEM; JEOL JSM-6700F, Japan) and high-resolution transmission electron microscopy (HR-TEM; FEI Tecnai, G2 F20, Philips, USA). Diffuse reflection spectra of the specimens were obtained using an ultraviolet-visible-near infrared spectrometer (Hitachi, U-4100, Japan) equipped with an integration sphere. These spectra were converted from reflection to absorbance using the Kubelka-Munk method [51]. The N_2 surface area was determined with the Brunauer–Emmet–Teller (BET) equation at −196 °C using an adsorption apparatus (Micromeritics ASAP 2010, USA). The photoluminescence (PL) spectra of the resulting powder were measured at −196 °C using a fluorescence spectrophotometer (Hitachi, F-7000, Japan).

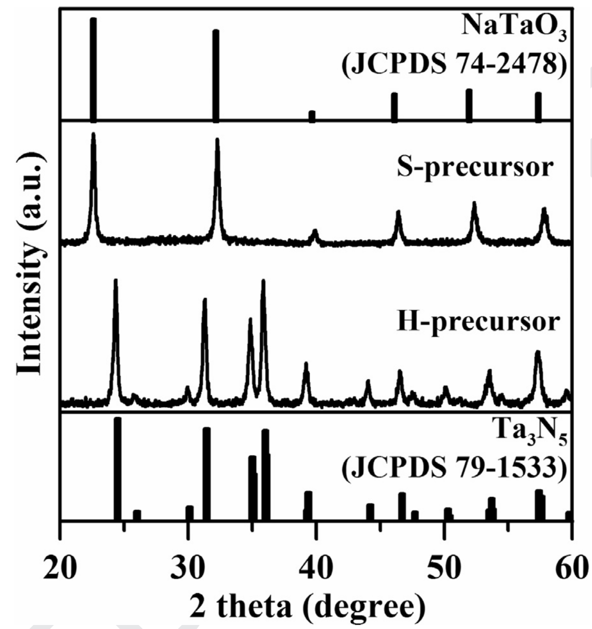

Fig. 1. Powder XRD patterns of H- and S-precursors. Standard diffraction patterns of Ta_3N_5 (JPCDS 79-1533) and $NaTaO_3$ (JCPDS 74-2478) are shown at the bottom and top of the figure, respectively.

The photocatalysts were photo-deposited using nanoparticulate Pt metal as a co-catalyst. Photodeposition was performed using a 400 W high-pressure mercury lamp (SEN HL400EH-5, Japan) as the light source. The lamp spectrum was obtained using a photodetector (Oriel, model 71,964, USA) coupled with a Cornerstone 130 monochromator (Oriel) with a 10 nm bandwidth. The total photon flux, light power, and radiation flux on the reaction system were calculated. The catalyst (0.5 g) was magnetically stirred in an aqueous methanol solution (1 L, 20 vol%) containing 6.64 mg of H_2PtCl_6•$6H_2O$ (Alfa Aesar, USA) for 3 h. The resulting Pt-deposited photocatalyst was filtered and subjected to photocatalytic reaction measurements.

The photocatalytic reactions were conducted using the photocatalysts suspended in a gas-closed inner-irradiated reaction chamber under UV light and visible light irradiation, separately. The jacket between the reaction chamber and the lamp was filled with flowing cool water and aqueous 1 M of $NaNO_2$ solution for UV and visible light irradiation, respectively. The light source was a 400 W high-pressure mercury lamp. In these experiments, 20 vol% of methanol and 1 M of $AgNO_3$ solution were used as sacrificial reagents for H_2 and O_2 productions, respectively. The quantities of the evolved H_2 and O_2 were determined using gas chromatography (Hewlett-Packard 7890, USA; molecular sieve 5A column, thermal conductivity detector, argon carrier gas).

3. Results and discussion

The XRD patterns of the H- and S-precursors, Ta_3N_5, and $NaTaO_3$, respectively, are shown in Fig. 1. All distinct diffraction peaks were indexed to the pure phases of orthorhombic Ta_3N_5 (JCPDS 79-1533) and monoclinic $NaTaO_3$ (JCPDS 74-2478),

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