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# Visible light driven photocatalytic hydrogen evolution and photophysical properties of Bi<sup>3+</sup> doped NaTaO<sub>3</sub>

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## ABSTRACT

Visible light active Bismuth doped NaTaO<sub>3</sub> powders were synthesized by the conventional solid state route for different Bi concentrations (2.5%, 5.0%, and 7.5% by moles). The optical properties of the doped samples were tuned by changing the molar ratio of Na and Ta in the initial reactants. The doped samples prepared with Na/Ta ratio close to unity (1.01–1.03) resulted in the highest band gap narrowing compared to the other synthesis conditions. It was shown that the photocatalytic hydrogen evolution occurred from these samples under the visible light irradiation ( $\lambda > 390$  nm) after loading of appropriate amount of platinum co-catalyst. The other synthesis conditions (Na/Ta = 1/1-x; x = 0.025, 0.05, 0.075 and Ta/Na = 1/1-x; x = 0.025, 0.05, 0.075; x is bismuth content) were not useful for the photocatalytic hydrogen evolution. The structural characterization suggested that the samples prepared with Na/Ta ratio close to unity, contain Bi ions located at both Na and Ta sites in the lattice. The Mott–Schottky plots revealed that the flat band potential of the pristine NaTaO<sub>3</sub> is highly negative to the H<sub>2</sub>/H<sub>2</sub>O reduction potential (-1.19 eV vs. SCE, pH = 7) and for all Bi doped NaTaO<sub>3</sub> samples, the flat band potential was sufficient for the hydrogen generation.

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## 1. Introduction

Solar hydrogen is considered as one of the most promising and sustainable ways to generate clean energy [1–4]. In order to commercialize the solar hydrogen production, 10–15% energy conversion efficiency is desired from the photocatalytic material system, under the solar radiation [5,6]. However, suitable material systems which meet this target efficiency under visible radiation are still lacking and efforts are needed to explore the photophysical properties of novel materials. In the past a few years, several materials systems such as SrTiO<sub>3</sub>, NaTaO<sub>3</sub>, TiO<sub>2</sub>, ZnS etc. have been thoroughly studied for the photocatalytic hydrogen production [6–10]. Various strategies have been adapted to achieve and enhance

the visible light photocatalytic activity. Doping in wide band gap photocatalysts such as Fe or Cr-doped TiO<sub>2</sub> [11], V-doped TiO<sub>2</sub> [12], preparing composites such as ZnO–CdS core shell nanostructures [13], TiO<sub>2</sub>/CdS nano-composites [14], Pt/Cr<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> [15], utilizing surface plasmonic effects as in Ag loaded TiO<sub>2</sub> [16–18] have been recently reported to gain the visible light hydrogen evolution. Among these strategies, doping in highly efficient wide band gap photocatalysts, is one of the most successful approaches to develop new compounds. Of the various photocatalysts studied, NaTaO<sub>3</sub> has been identified as an excellent photocatalyst for the water splitting reaction under UV radiation [19–22]. NaTaO<sub>3</sub> has sufficiently negative conduction band edge potential vs. H<sub>2</sub>/H<sub>2</sub>O reduction level (as indicated by empirical calculations) and possesses

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delocalized nature of photoexcited electrons which are highly beneficial for the photocatalytic hydrogen generation [20]. The photocatalytic activity of NaTaO<sub>3</sub> has been further enhanced by doping of ions such as La, Sr, Ca, and Ba [23,24]. Particularly, 2% La doped NaTaO<sub>3</sub> nanoparticles loaded with (0.2 wt. %) NiO have demonstrated superior photocatalytic behavior under 270 nm radiation [25]. In addition, La doped NaTaO<sub>3</sub> system, synthesized by sol-gel method has been further improved by RuO<sub>2</sub> loading to achieve stoichiometric water splitting reaction [26]. However, NaTaO<sub>3</sub> has a large band gap value (~4.0 eV) and thus the material systems like La doped NaTaO<sub>3</sub> are not useful in the solar spectrum. Nevertheless, due to its unique set of properties and high activity under UV radiation, NaTaO<sub>3</sub> is considered as a good host material to modify the electronic structure and to potentially achieve the visible light photocatalysis. Recent studies have shown that doping of elements like Bismuth [27,28], Nitrogen [29] and co-doping of elements like La–Co [30], La–Cr [31,32], and La–Ir [33] in NaTaO<sub>3</sub> is useful in inducing visible light absorption and subsequent photocatalytic activities. The photocatalytic hydrogen evolution by Bismuth doped NaTaO<sub>3</sub> powders prepared by hydrothermal method has been studied by Li et al [27]. Further, small concentration of Bi doping in NaTaO<sub>3</sub> and its photocatalytic activity has been reported by Wang et al. [34]. Although Li and co-workers [27] have shown that Bi doped NaTaO<sub>3</sub> solid solution is useful for photocatalytic hydrogen generation, a complete understanding of Bi doped NaTaO<sub>3</sub> system is needed for further development. Oxides of Bismuth have narrow band gaps on account of Bi 6s orbital and earlier studies show that doping of Bi<sup>3+</sup> in wide band gap photocatalysts has produced visible light absorption [35–37]. Therefore, it is essential to study the effect of Bi<sup>3+</sup> doping in NaTaO<sub>3</sub> on the photophysical properties and photocatalytic hydrogen evolution. Further, NaTaO<sub>3</sub> is an important photocatalyst and the measurement of flat band potentials (on SCE scale) of pristine and Bi doped NaTaO<sub>3</sub> is essential to contribute to the further understanding of this phase. In our earlier work, we showed that the optical properties of Bi doped NaTaO<sub>3</sub> can be significantly changed by changing the synthesis conditions [28]. Bismuth doped NaTaO<sub>3</sub> system shows significant absorption in the visible region and thus holds a promise to develop visible light sensitive photocatalysts with high activity. In this study, we report the visible light driven ( $\lambda > 390$  nm) photocatalytic hydrogen evolution from Bismuth doped NaTaO<sub>3</sub> powders up to 7.5% Bi doping. It was found that the doping concentration, synthesis conditions, and the amount of platinum co-catalyst loading significantly affect the photocatalytic properties. Further, the flat band potential of the pristine and Bi doped powders was estimated using Mott–Schottky plots. It was shown that doped NaTaO<sub>3</sub> powders can be potentially useful photocatalysts under the visible radiation.

## 2. Experimental details

### 2.1. Synthesis of materials

Pristine and Bi doped NaTaO<sub>3</sub> powders were prepared by the conventional solid-state method. The starting materials,

Ta<sub>2</sub>O<sub>5</sub> (Alfa Aesar 99%), Bi<sub>2</sub>O<sub>3</sub> (Sigma Aldrich 99%) and Na<sub>2</sub>CO<sub>3</sub> (Univar 99.8%) were mixed in an agate type mortar, pressed into pellets and fired at 1173 K for 10 h using a platinum crucible in a muffle furnace in ambient atmosphere. In all, Bi doped NaTaO<sub>3</sub> powders with increasing Bi content (2.5%, 5.0%, 7.5%, and 10%) were synthesized with three different molar ratios of the starting materials. The molar ratios of Ta:Na:Bi are summarized in Table 1. In short, Na rich, Na deficient, and near stoichiometric conditions were maintained by adjusting the amount of Na<sub>2</sub>CO<sub>3</sub> and Ta<sub>2</sub>O<sub>5</sub>. The series of samples synthesized under Na rich, Na deficient and near stoichiometric conditions are referred to as S1, S2, and S3, respectively. The purpose of applying different Na/Ta ratio is to adjust the optical properties of the final products through Bi site occupancy [28]. However since Na<sub>2</sub>O evaporates more easily during synthesis, a small amount of excessive Na<sub>2</sub>CO<sub>3</sub> was added as compensation. For example in the S3 samples, 1–3% more Na was used in the starting reagents to achieve targeted equal occupancy of Bi in both Na and Ta sites. Platinum nanoparticles were loaded on the surface of doped NaTaO<sub>3</sub> by chemical impregnation method. Appropriate amount of catalyst powder and platinum precursor (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, Sigma–Aldrich) were mixed in the agate type mortar. The suspension was continuously stirred and heated at 75 °C till it dried. The powder was further heated at 300 °C for 1 h.

### 2.2. Characterization

The phase and crystal structure were studied by analysis of X-ray diffraction patterns. (Bruker D8 Advance; Cu K $\alpha$  = 1.54 Å). The XRD patterns were recorded within 2 $\theta$  range of 20°–100° with the steps of 0.03° and time of 1 s per step. The optical properties of the powders were studied by diffused reflectance spectroscopy (DRS) using ultraviolet–visible absorption spectrometer (Shimadzu 2051 PC). The band gap values of the samples were estimated by Kubelka–Munk analysis, assuming direct band gaps. The morphology of the samples was analyzed by scanning electron microscope (JOEL 6400F) and the quantitative chemical analysis was done by EDS attachment using standard-less ZAF method. The flat band potentials of the photocatalysts were estimated by Mott–Schottky plots (1/C<sup>2</sup> vs. V). The electrochemical cell contained the working electrode made up of photocatalyst coated on FTO (surface, area = 3.5 cm<sup>2</sup>), counter electrode (platinum plate, area = 1.5 cm<sup>2</sup>) and reference electrode (saturated calomel electrode). The electrochemical measurements were carried out in dilute NaOH electrolyte of pH 10.5. A small AC signal of 100 Hz was applied between the working and counter electrodes and modulated DC bias was

**Table 1 – The ratios of initial reactants used to synthesize Bi doped NaTaO<sub>3</sub> samples.**

|              | Ta  | Na        | Bi |
|--------------|-----|-----------|----|
| Series 1(S1) | 1–x | 1         | x  |
| Series 2(S2) | 1   | 1–x       | x  |
| Series 3(S3) | 1   | 1.01–1.03 | x  |

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