

## Visible light driven photocatalytic hydrogen evolution by lanthanum and carbon-co-doped NaTaO<sub>3</sub> photocatalyst

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**Abstract.** This paper reports on the investigation of the application of lanthanum and carbon co-doped sodium tantalum oxide as a visible light responsive photocatalyst for hydrogen production. The catalyst was prepared by incorporating lanthanum and carbon into NaTaO<sub>3</sub> cluster via a sol-gel technique using sucrose as the carbon source. The La-C-NaTaO<sub>3</sub> sample was calcined at a temperature of 800 °C. Effects of carbon content on the crystal structure, shape, and optical absorption response as well as activity of hydrogen production of the sample were evaluated. The crystal of La-C-NaTaO<sub>3</sub> was characterized by XRD analysis. The results showed that the XRD pattern of the La-C-co-doped NaTaO<sub>3</sub> was found to be crystalline phase with orthorhombic structure. The analysis of SEM images illustrated that the particle size of the prepared powder was about 40-300 nm. The optical response was examined by diffuse reflectance spectra (DRS). It was depicted that the absorption edge of La-C-NaTaO<sub>3</sub> crystalline shifted to higher wavelength. The extension to the visible light absorption edge became drastic with the increasing carbon content in the sample. The photocatalytic activity of La-C-NaTaO<sub>3</sub> was examined from water-methanol aqueous solution under visible light irradiation. It was found that the photocatalytic activity of La-C-NaTaO<sub>3</sub> depended strongly on the doping content of C, and the La-C-NaTaO<sub>3</sub> sample shows the highest photocatalytic activity in water reduction. The optimum amounts of carbon to maximize the hydrogen evolution rate was to be 2.5 mol %. Under visible-light irradiation, the La-C-NaTaO<sub>3</sub> catalyst demonstrated high activity of H<sub>2</sub> evolution of 40.0 [ $\mu\text{mol h}^{-1}$ ], suggesting a promising utilization of such photocatalyst for hydrogen production. The La-C-co-doped NaTaO<sub>3</sub> photocatalyst could be further developed in order to produce hydrogen as a green energy.

### Introduction

Photocatalytic hydrogen production utilizing solar energy is believed to be one of ideal future green technologies for sustainable development of human beings [1]. Visible-light responsive photocatalytic technology has been considered as one of the most promising and sustainable ways to generate hydrogen production for clean energy and to eliminate undesired chemical substances for environmental conservation [2-3]. In recent years, several attempts have been made in developing heterogeneous photocatalysts with high activities, especially for the application in water decomposition into hydrogen and oxygen [4-5]. In the case of photo-decomposition of water for the production of hydrogen, NaTaO<sub>3</sub> has been identified as an excellent photocatalyst in the water splitting reaction under UV radiation due to its higher potential of conduction band arising from the more negative position of Ta 5d orbital [6]. However, its application is limited at the ultraviolet light region (wave length  $\lambda < 310$  nm) because of its optical absorption characteristic. Our previous works show that doping La<sup>3+</sup> ions in the NaTaO<sub>3</sub> lattice with 2 mol % could enhance the photocatalytic activity for hydrogen evolution markedly [7]. The material systems like La-doped NaTaO<sub>3</sub> are not useful in the solar spectrum.

A photocatalytic material active under visible light has long been expected from the viewpoint of efficient utilization of solar irradiation. The NaTaO<sub>3</sub> photocatalyst is required to be modified to reduce the band gap energy between conduction and valence bands for utilization under solar light. Recently, numerous efforts have been made to improve the efficiency of NaTaO<sub>3</sub> in harvesting

sunlight by shifting its spectral response into the visible region, mainly by cation or anion doping [8]. Various strategies have been adapted to achieve and enhance the visible light photocatalytic activity. Recent studies have shown that doping of elements like N and C doped NaTaO<sub>3</sub> are useful for inducing visible light absorption. The photocatalytic hydrogen evolution by N-doped NaTaO<sub>3</sub> powders prepared by sol-gel method has been studied by Fu et al [9]. Furthermore, carbon anion doping in NaTaO<sub>3</sub> and its photocatalytic activity have been reported by Kang and Park [10]. The band gap of NaTaO<sub>3</sub> has been narrowed successfully by doping with non-metal cations, by replacing lattice oxygen with N, C dopant. Nevertheless, their photocatalytic activities for split water were still very low. In semiconductor doping technology, co-doping of ions can overcome some limitations of single ion doping, such as poor crystallinity and more recombination centres for electron-hole pairs [11-12]. Thus, anion and cation doping can adjust the band structure of semiconductors, and it can also have an impact on the particle size and surface structure of materials [13], which usually results in a better photocatalytic activity [14]. Therefore, developing an active photocatalytic material at a wide range of visible light is still badly required for practical applications. Up to the present time, there have been very few investigations concerning the effects of carbon doping at La-NaTaO<sub>3</sub> and its photocatalytic performance.

In the present work, La and C co-doped NaTaO<sub>3</sub> were prepared by sol-gel process. The effects of carbon content in the La-NaTaO<sub>3</sub> on the photocatalytic activity were discussed for hydrogen production.

## Experimental Section

**Catalyst Preparation.** The La-C-NaTaO<sub>3</sub> powder photocatalyst was prepared by a sol-gel method [15]. A suitable amount of TaCl<sub>5</sub> (Aldrich, 99.9%) and NaOH (Merck, 99.0%) were dissolved in ethanol (Merck, 98.0%) and distilled water, separately. A solution containing 1.0 mol % of La(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O (Merck, 99.8%) was dissolved in 15 ml of water, then added dropwise into the above solution under vigorous stirring. The substitution of carbon onto the La-NaTaO<sub>3</sub> matrix was performed using sucrose as the carbon precursor. A required amount of sucrose (Merck, 99.5%) with various amounts of carbon (Carbon/Ta mol ratio,  $x = 0.50, 2.5, 3.0, 3.5, 4.0, 5.0$  and  $7.0$ ) was dissolved in 20 mL of absolute ethanol, and then added slowly to the above solution. Citric acid (Merck, 99.0%) was dissolved in 50 mL of water and then dropwise into the above solution under vigorous stirring for 2 h at room temperature. The mixture was stirred at 80 °C around 6 h to obtain the gel product by heating technique. The resultant gels were dried at a temperature of 120 °C for 6 h. The powders were ground by mortar and then subjected into a crucible and pre-treatment in a tube furnace at 400 °C for a period of 4 h. The obtained powders were then ground and calcined in air at 800 °C for 8 h in a tube furnace.

**Photocatalytic Hydrogen Production.** The photocatalytic activity for hydrogen production was evaluated under visible light condition. Typically 0.3 g of the catalyst was suspended in a solution of 400 mL ultra pure water in the presence of 10 vol. % methanol as sacrificial reagent in Pyrex glass cell. A 150W metal halide lamp was focused on the inside of the cell. The mixture was dispersed by magnetic stirring for 15 min, purged by Argon gas for 30 min in order to eliminate the dissolved oxygen prior to the photocatalytic reaction. The mixture was irradiated under visible light with magnetic stirring. The evolved H<sub>2</sub> was analyzed by a gas chromatography with a thermal conductivity detector and molecular sieve 5Å columns (GC-8A, Shimadzu Corp., Japan), with argon as a carrier gas.

## Results and Discussion

**Structural Characteristics.** The phase composition of the as-prepared samples was analysed by x-ray diffraction (XRD). Fig. 1 shows the XRD patterns of pure NaTaO<sub>3</sub>, La-doped NaTaO<sub>3</sub>, and La-C-co-doped NaTaO<sub>3</sub> prepared at various amounts of carbon doping levels calcined at 800 °C for 8 h. Compared with the XRD pattern of NaTaO<sub>3</sub>, it is interesting to learn that all diffraction peaks of

the samples could be easily indexed as a pure NaTaO<sub>3</sub> orthorhombic phase structure according to the standard card (JCPDS card no. 25-0863), as demonstrated in Fig. 1. All samples showed the presence of a single phase up to 5% carbon doping with no impurity phase, indicating that doping are uniformly incorporated into the NaTaO<sub>3</sub> lattice. Moreover, low concentration of La and C doping does not result in a significant change in the NaTaO<sub>3</sub> structure, and the samples have high crystallinity. The XRD pattern of higher percentage (>5%) of carbon doping is not presented in this paper due to the space limit.

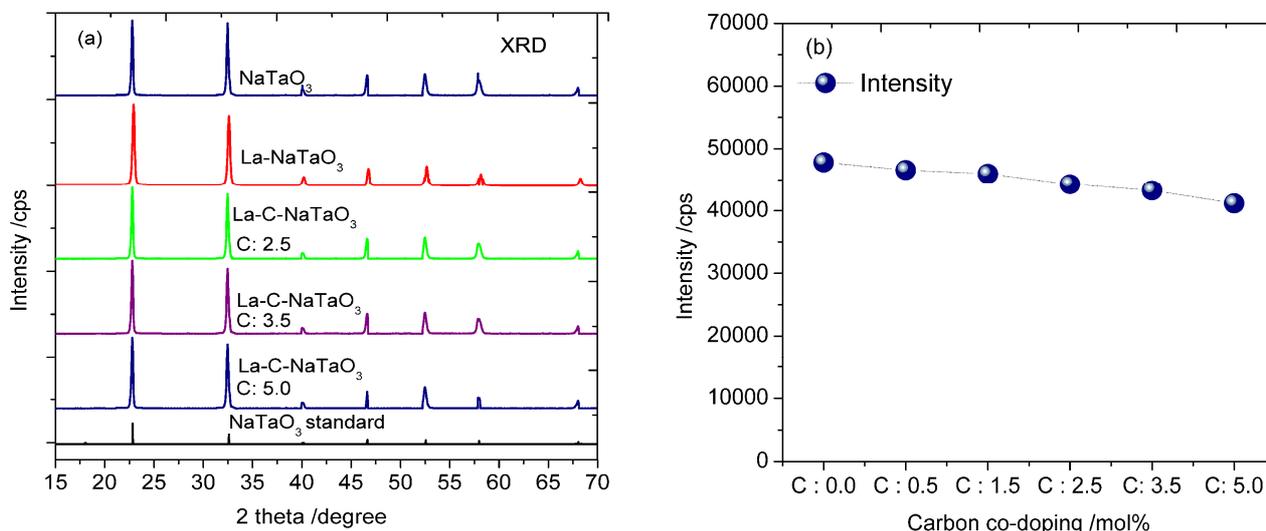


Fig. 1 (a) XRD patterns of La-C-co-doped NaTaO<sub>3</sub> prepared at various amounts of carbon content, (b) Intensity of XRD patterns at  $2\theta = 22.82^\circ$  with different carbon doping.

With respect to the presence of carbon in the prepared sample, the intensity (I) showing the peak of  $2\theta$  at around  $22.82^\circ$  corresponding to plane (020) is illustrated in Figure 1b. A gradual decrease in intensity was observed for the La-C-co-doped NaTaO<sub>3</sub> samples with the increase of the amount of carbon, implying that the presence of excessive carbon inhibits the grain growth. It seems that the C doping either decreases the band gap by mixing of C 2p states with O 2p states on the top of the valence band or creates a C-induced low-gap level. Similar result was reported by Park et al. that the model for visible-light absorption in doped TiO<sub>2</sub> is due to substitution of oxygen by another atom, such as N or C, which results in a mix of N,C 2p and O2p states [16].

**UV-Vis Absorption Spectra.** In an attempt to validate the crystalline phase of the synthesized La-C-co-doped NaTaO<sub>3</sub> with different carbon doping levels, additional UV-Vis absorption spectra (Fig. 2) was performed. The La-C-co-doped NaTaO<sub>3</sub> sample showed strong absorption in visible light region. The steep shape of the spectrum indicated that the visible light adsorption is due to the band-gap transition. The band gap values of the samples being transformed into absorbance units by Kubelka-Munk function [17]. The band gap energy ( $E_g$ ) values for different samples were calculated from the UV-vis spectra using equation  $E_g$  (eV) =  $1240/\lambda_g$  (nm). The band gap value of the La-doped NaTaO<sub>3</sub> was found to be 4.0 eV. The absorption spectra of all of carbon-co-doped samples showed a tendency towards longer wavelength in conjunction with the increase in carbon content, indicating that the change in the optical absorption is caused by carbon doping. Similar observation was also reported for C-doped TiO<sub>2</sub> demonstrating more intense and broad background absorption in the visible light region [18].

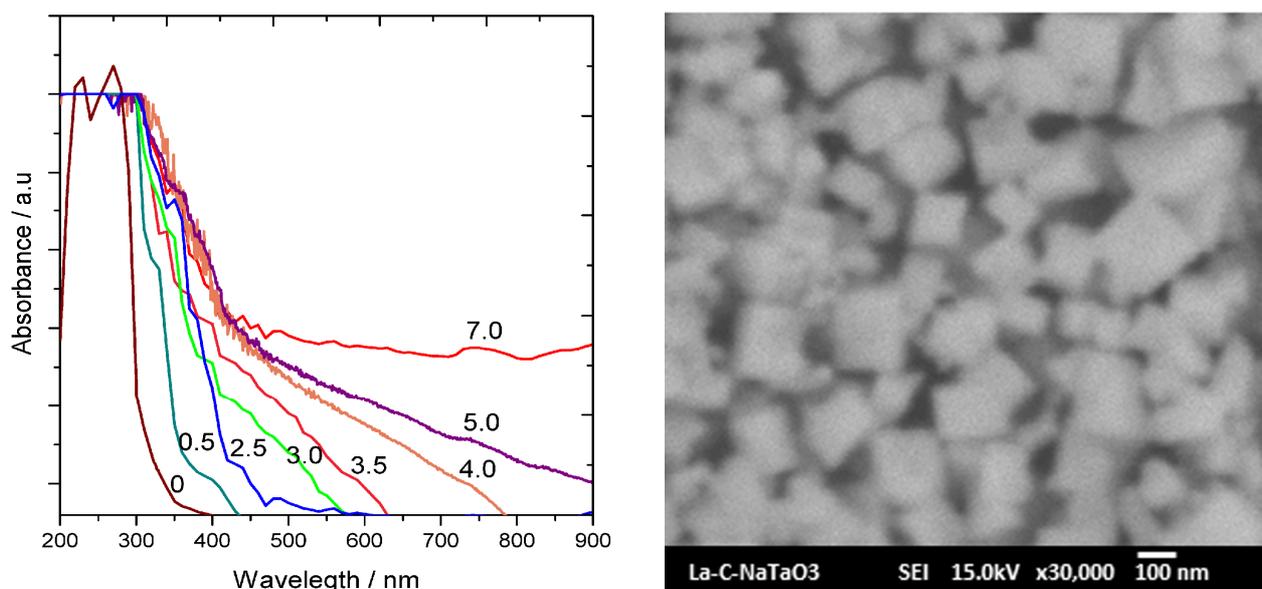


Fig. 2. Diffuse reflectance spectra of La-C-co-doped  $\text{NaTaO}_3$  samples at various amounts of carbon co-doping levels (left side), SEM images of the as-prepared La-C-co-doped  $\text{NaTaO}_3$ , with carbon content of 2.5 mol % (right side)

The SEM morphologies of the La-C-co-doped  $\text{NaTaO}_3$  samples obtained via sol-gel method is presented in Fig. 2 (right side). The La-C-co-doped  $\text{NaTaO}_3$  shows homogeneous particle distribution, indicating that the La-C-co-doped could effectively inhibit the agglomeration of the  $\text{NaTaO}_3$  nanoparticles. The sample structure shows to have an orthorhombic-shaped morphology with particle size of about 40-300 nm, suggesting high crystallinity of La-C-co-doped  $\text{NaTaO}_3$  can be observed.

**Photocatalytic Hydrogen Production.** The photocatalytic performance of the samples was evaluated by hydrogen evolution in the presence of methanol as sacrificial reagent under visible light. The effect of varying amount of carbon doping on the photocatalytic hydrogen evolution from 0.5% - 5.0 mol % of carbon are listed in Table 1.

Table 1.  $\text{H}_2$  evolution from methanol aqueous solution on La-C-co-doped  $\text{NaTaO}_3$  photocatalyst

Amount of C doped [mol %]	$\text{H}_2$ evolution [ $\mu\text{mol h}^{-1}$ ]
0,0	0
0,5	0
1,5	9,05
2,5	40,2
3,5	24,9
5,0	12,6

As can be seen in Table 1, the pristine  $\text{NaTaO}_3$  and 0.5 amount of carbon content do not show any photocatalytic activity under visible light irradiation, due to their wide band gaps. It clearly demonstrates that the photocatalytic activity of La-C- $\text{NaTaO}_3$  depends strongly on the doping content of carbon, and the La-C- $\text{NaTaO}_3$  prepared samples show the highest photocatalytic activity in hydrogen evolution. Among all samples examined, the La-C- $\text{NaTaO}_3$  at 2.5 mol % carbon content was found to exhibit the best photocatalytic activity. The La-C-co-doped  $\text{NaTaO}_3$  photocatalyst with a high crystallinity is responsible for superior photocatalytic activity under visible light. Photocatalysis is a complex process of which many factors such as surface area, particle size, crystallinity, pore and phase structures, and band gap values of photocatalysts may affect the photocatalytic activities of water splitting [19]. As shown from XRD investigation (Figure

1), the La-C-NaTaO<sub>3</sub> shows higher crystallinity. The reason is due to the fact that the high crystallinity of the samples could suppress recombination between photogenerated electron (e<sup>-</sup>) and hole (h<sup>+</sup>) pairs, in order to perform the desired redox reactions. Such process eventually may lead to high photocatalytic activity and stability. The higher crystalline but smaller particle size leads to an effective utilization of charge carriers since the photo-generated carriers diffuse fast to the surface and reacts rapidly with the adsorbed water molecules [7]. It is presumed that the incorporation of the La and C lead to diminish the electron-hole recombination that improves the photocatalytic activity under simulated solar light.

### Summary

Photocatalyst of La-C-co-doped NaTaO<sub>3</sub> crystalline has been successfully synthesized by means of sol-gel technique. The carbon can be incorporated into the NaTaO<sub>3</sub> lattice, which leads to the enhanced photocatalytic activity in La-C-co-doped NaTaO<sub>3</sub> samples. It is concluded that the photocatalytic reactivity of La-C-co-doped NaTaO<sub>3</sub> under visible light irradiation is mainly due to the presence of localized occupied states caused by interstitial carbon and the electron/hole pairs generated under visible light irradiation. The photocatalyst La-C-co-doped NaTaO<sub>3</sub> prepared with 2.5 mol % carbon shows the highest photocatalytic activity in the water-methanol solutions. This La-C-co-doped NaTaO<sub>3</sub> provides an effective visible-light-responsive photocatalyst for future industrial applications in green energy.

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