

Research Article

H₂ Evolution on Lanthanum and Carbon Co-doped NaTaO₃ Photocatalyst

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Abstract

We report a carbon-modify lanthanum doped sodium tantalum oxide powders (La-C-NaTaO₃) by sol-gel process. The resultant materials are characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The X-ray diffraction of La-C-NaTaO₃ show a single phases with a good crystallinity and without any impurity. The sample is exactly indexed as NaTaO₃ monoclinic structure with the space group P2/m. The SEM measurements give a smaller particle size of doped NaTaO₃ than pure NaTaO₃. The effect of dopant on the photocatalytic activity of La-C-NaTaO₃ in the photocatalytic of hydrogen generation is studied and compared with pure NaTaO₃. The results show that the rate of hydrogen evolution over La-C-NaTaO₃ is higher as compared to that of pure NaTaO₃. The enhancement of photocatalytic activity of La-C-NaTaO₃ nanocrystalline is mainly due to their capability for reducing the electron hole pair recombination. The La-C-dopant is believed to play a key role in the enhancement of photocatalytic properties of La-C-NaTaO₃ crystalline. © 2014 BCREC UNDIP. All rights reserved

Keywords: Photocatalyst; La-C-doped; sodium tantalum oxide; hydrogen generation

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1. Introduction

Hydrogen has emerged as a potential energy carrier in various low greenhouse gas energy applications due to its renewability and environmentally friendly [1-4]. Photocatalytic water splitting into hydrogen using solar energy, as one of the most promising ways to obtain hydrogen and has attracted great scientific interest [5-6]. Much attention has been paid to find-

ing ways to produce hydrogen from renewable energy sources such as the sun and wind [7]. Hydrogen production from water by using semiconductors as photocatalysts provides a potential way to obtain hydrogen efficiently, due to its clean, low-cost and environmentally friendly production process by utilizing solar energy.

Sodium tantalum oxide has been proved to be a promising photocatalyst material for applications in hydrogen production. Doping rare-earth or other metal oxides into the perovskite type alkali tantalates can increase their capability of trapping and transferring electron/hole

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pairs, which improves their photocatalytic activities [8-9]. Husin *et al.* [10] observed that the water-splitting reaction of NaTaO₃ could be improved by lanthanum doping, because the La-doped NaTaO₃ powders have a small particle size with high crystallinity. But this photocatalyst works only under UV-light irradiation.

Zhou *et al.* reported that Fe-doped NaTaO₃ was red-shifted to the visible region, which potentially could be active for overall water splitting under visible light irradiation [11]. Recently, Fu *et al.* synthesized N-doped NaTaO₃ photocatalysts, which showed high photo activity for formaldehyde photo-degradation under visible-light irradiation [12]. However, in their studies, they did not use this photocatalyst to split water. In semiconductor doping technology, co-doping can overcome some limitations of single ion doping, such as poor thermal stability and more recombination centres for electron-hole pairs. Thus, we attempt to dope carbon at La-NaTaO₃ to modify its performance. To our knowledge, studies on carbon doping at La-doped NaTaO₃ and its photocatalytic performance have not been reported so far.

In this work, a La-C co-doped NaTaO₃ photocatalyst was synthesized by the sol-gel reaction method. The samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The hydrogen evolution was used to evaluate the photocatalytic properties of the photocatalyst. The effect of various carbon contain will be report in the future work.

2. Materials and Methods

2.1. Materials

All reagents were of analytical grade and were used without further purification. Commercially available tantalum chloride (TaCl₅) (Acros, 99.9%), ethanol (Acros, 99.5%), La(NO₃)₃.6H₂O (Merck, purity: 98.0%), NaOH (Acros, ACS grade), methanol (Acros, 99.9% HPLC grade), and sucrose (Fisher scientific), citric acid (across, 99.0%), NH₃ (35% Fisher Scientific) were used as received. Tantalum was prepared using ethanol. Other solutions were dissolved using high purity deionized water.

2.2 Catalyst Preparation

La-C-doped NaTaO₃ was synthesized by means of sol-gel procedure using ethanol as solvent system. All chemicals were analytical grade reagents and used without further purification. In a typical procedure, a TaCl₅ was firstly dissolved in ethanol solution and then

NaOH dissolved in deionized water. La(NO₃)₃.6H₂O was dissolved in deionized water and then added into the solution. The mixture was mixed with C₁₂H₂₂O₁₁ solution for 2 h under magnetic stirring. Citric acid solution was employed as a chelating agent in the developed process. Under vigorous stirring, 50 ml of citric acid solution was slowly dropped into the above solution to produce sol solution. The pH was adjusted to 4 with NH₃ solution. Then, a La-C-doped NaTaO₃ compound was obtained by heating the mixture at constant temperature of 80 °C until a white gels formed. The obtained gel was dried in oven at 100 °C. The resulting powder precursor was sintered at 400 °C and continuous heating at 800 °C for 8 h under air flow. The sample was cooled to room temperature and underwent characterization. In this work, we also prepared the NaTaO₃ sample without doping for comparison.

2.2. Catalyst Characterization

To investigate the morphology of the structure, a scanning electron microscope (SEM) images of the final nanosized of the La-C-NaTaO₃ was recorded by a (SEM, Philips XL-30) apparatus. The transmission electron microscope (TEM) images of the nanosized NaTaO₃ were recorded by a Philips/FEI Tecnai 20G2 S-Twin TEM apparatus. The samples were characterized by X-ray powder diffraction (XRD). The XRD measurements were performed on a XRD-7000 with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The operation voltage and current were maintained at 40 kV and 40 mA, respectively.

2.3. Catalyst Testing for Photocatalytic Water Splitting

Photocatalytic hydrogen evolution reactions were carried out in an inner irradiation quartz reactor. Typically, 1 g of the catalyst was suspended in an aqueous solution of 400 ml (H₂O and 10 vol.% of methanol). The suspension was degassed for 30 minute with high-purity argon prior to light irradiation in order to eliminate dissolved oxygen. The amount of H₂ produced was measured by gas chromatography (Shimadzu 8A) equipped with a molecular sieve column and a TCD detector with Helium carrier gas.

3. Results and Discussion

3.1. XRD Measurements

The XRD patterns of the NaTaO₃ without doping and La-C co-doped NaTaO₃ are given in

Figure 1. The patterns of NaTaO_3 show a single phase with a narrow diffraction peak indicated a high crystallinity of the sample.

The X-ray diffraction patterns of La-C- NaTaO_3 powders (La: 1 mol %, C: 2 mol %) are shown in Figure 1b. It can be observed that the XRD analysis of the La-C- NaTaO_3 and non-doped NaTaO_3 have a similar crystal structure. Compare to the data documented in the powder diffraction files of the JCPDS, the La-C co-doped NaTaO_3 sample should be respectively assigned to the monoclinic symmetry perovskite-type of NaTaO_3 , in agreement with the JCPDS card no 74-2478 (P2/m with $a = 3.8936 \text{ \AA}$, $b = 3.8905 \text{ \AA}$ and $c = 3.8936 \text{ \AA}$).

A similar phenomenon was also observed by Hu *et al.* [13] who synthesized NaTaO_3 powder with monoclinic phase from the sol-gel methods. The powder X-ray diffraction patterns of La-C co-doped NaTaO_3 shows all diffraction peaks can be readily assigned to a pure phase and no diffraction peaks from impurity phase were observed.

These behaviours confirm that the well-defined structure, high purity and good crystallinity were achieved by doping substitution. From the XRD pattern, we can see that the relative intensity of the peaks sample decrease

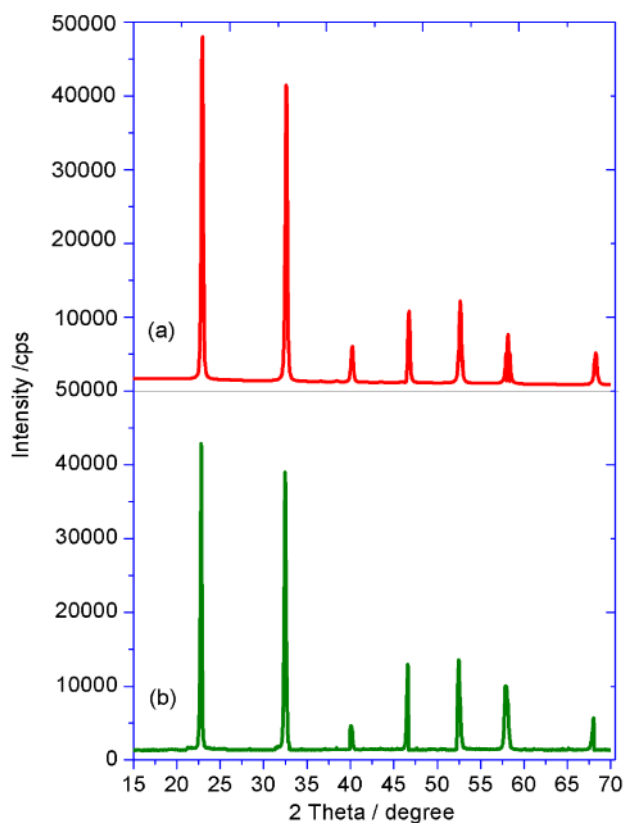


Figure 1. Powder X-ray diffraction pattern of (a) non-doped NaTaO_3 and (b) La-C-co-doped NaTaO_3 photocatalyst

after doping lanthanum and carbon as co-doped suggesting that the existence of doping can suppress the crystal growth of NaTaO_3 .

In this report, the average crystallite sizes of the catalysts was calculated from XRD diffraction peaks using Scherrer formula with the full-width at half plane (100) of NaTaO_3 and La-C- NaTaO_3 peaks. Data for the average crystallite sizes of both samples are listed in Table 1.

The crystallite size of the non-doped NaTaO_3 is demonstrated of 37.3 nm. The size of the samples is greatly improved after doping lanthanum and carbon (46.0 nm), where intensive diffraction peaks of La-C- NaTaO_3 phase can be observed at 2θ of 22.799° , as depicted in Figure 1b. The XRD was known to be crystallite size sensitive where the larger crystallite size within the samples would produce the narrower and stronger diffraction peaks [14].

3.2. SEM and TEM Images

Scanning electron microscopy (SEM) micrograph of the non-doped and La-C-doped NaTaO_3 photocatalysts are shown in Figure 2 and 3. As demonstrated in Figure 2, the non-doped NaTaO_3 grew into irregular shapes with the particle sizes of the powders were approximately 50-400 nm.

For La-C- NaTaO_3 powders prepared under the same conditions, the doped photocatalysts are uniform, had a very regular shape, demonstrates the stabilizing effect of the La-C dopants on the samples. Since the substitution of the NaTaO_3 lattice by dopant species could protect the NaTaO_3 nanoparticles from agglomeration during calcinations [14].

The particle sizes of La-C- NaTaO_3 powders were around 30-200 nm as depicted in Figure 3, which is much smaller than the pure NaTaO_3 particles.

The regular shape and smaller particle sizes of doped NaTaO_3 describing the enhancement in crystalline quality and stability of the samples. The inset of Figure 3 shows a magnification of monoclinic La-C-co-doped NaTaO_3 photocatalyst.

Table 1. Crystallite size of photocatalyst samples.

Sample	Crystal sizes (nm) ^a
Non-doped NaTaO_3	37.3
La-C- NaTaO_3	46.0

^aEstimated by using the Scherrer equation

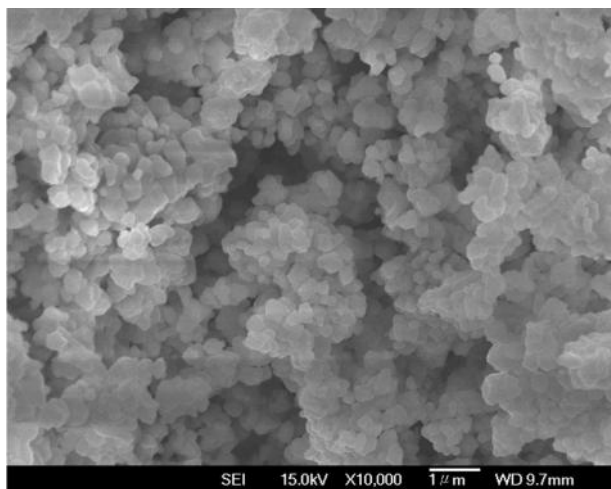


Figure 2. Scanning electron microscopy (SEM) micrograph of the NaTaO₃ without doping.

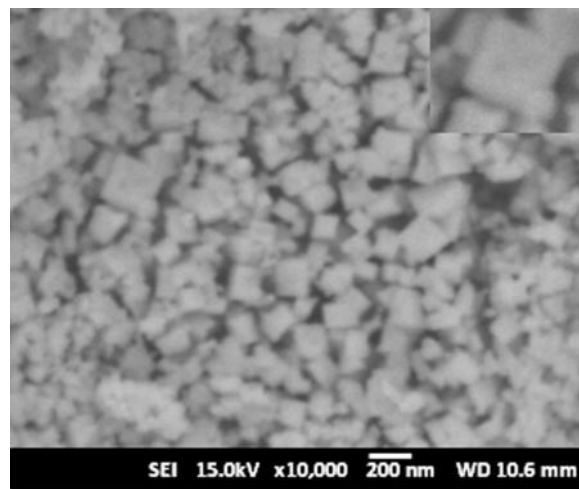


Figure 3. Scanning electron microscopy (SEM) images of the La-C-NaTaO₃

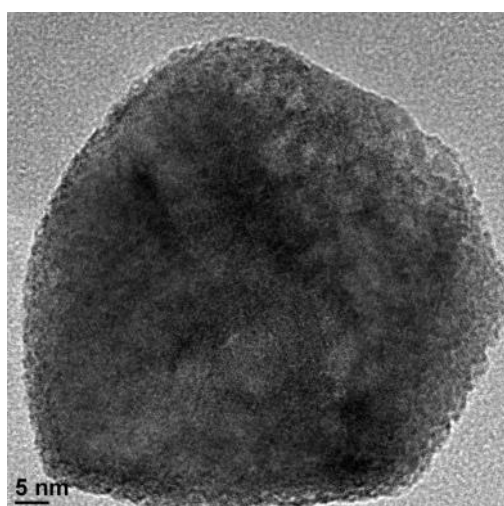


Figure 4. Transmission electron microscopy (TEM) images of pure NaTaO₃.

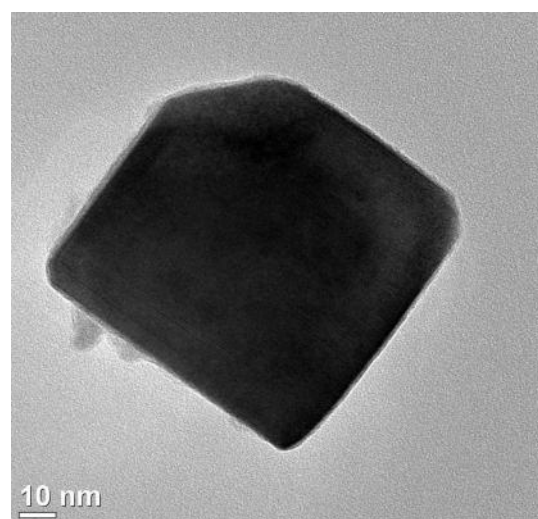


Figure 5. Transmission electron microscopy (TEM) images of La-C-NaTaO₃

The regular shape and smaller particle sizes of doped NaTaO₃ describing the enhancement in crystalline quality and stability of the samples. The inset of Figure 3 shows a magnification of monoclinic La-C-co-doped NaTaO₃ photocatalyst.

Figure 4 and 5 show the TEM morphologies of the La-C co-doped NaTaO₃ samples obtained via sol-gel method. The La-C-NaTaO₃ shows smaller particle sizes than either the undoped NaTaO₃, indicating that dopant can prevent agglomeration. The results are also consistent with the XRD results. The La-C-NaTaO₃ nanocrystal with high crystallinity is expected to have high photocatalytic activity. The picture shows a clear surface, suggesting the good crystal character of the as-synthesized La-C-NaTaO₃.

This crystal La-C-NaTaO₃ has an advantage over the crystalline particles as photocatalyst because the smooth surface interfaces in crystal particles can effectively reduce the recombination probability of the photogenerated holes and electrons [15].

3.3. Photocatalytic Activity

The photocatalytic activity of La-C-NaTaO₃ was evaluated by hydrogen evolution from aqueous methanol-solution in a closed reactor circulations system. In order to investigate the effect of doping on NaTaO₃ precursor on the photocatalytic activity, the experiment was performed by comparing the non-doped and doped La-C-NaTaO₃.

Figure 6 shows the photocatalytic activities

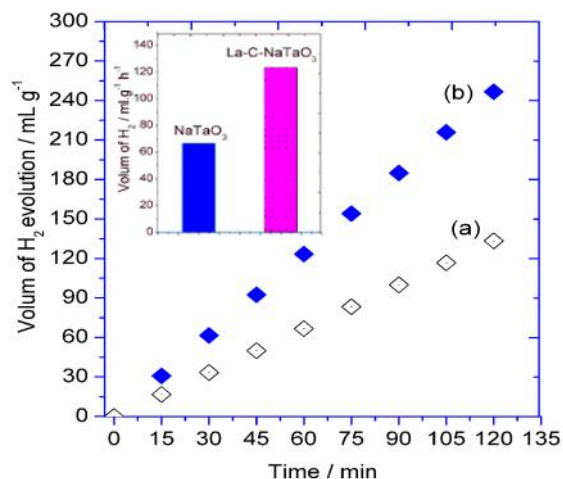


Figure 6. Photocatalytic hydrogen evolution from (a) non-doped NaTaO₃ and (b) La-C co-doped NaTaO₃; insert picture: the average of hydrogen evolution

of pure NaTaO₃ and La-C-NaTaO₃ from methanol aqueous solution. As can be seen in Figure 6, the photocatalytic of hydrogen production on non-doped NaTaO₃ achieve of 66.7 (ml g⁻¹ h⁻¹). The photocatalytic activity of La-C-NaTaO₃ is increases remarkably (123.333 ml g⁻¹ h⁻¹ or 1.85 times) after doping of lanthanum and carbon. It is clear that the La-C-doped NaTaO₃ exhibited higher photocatalytic activities than that of pure NaTaO₃. There are many important parameters taken into account to explain the obtained results. As can be seen from the XRD investigation (Figure 1, Table 1), that the La-C-NaTaO₃ shows higher crystallinity than the non-doped sample. The reason is due to the fact that the high crystallinity of the samples could suppress recombination between photogenerated electron (e⁻) and hole (h⁺) pairs, in order to perform the desired redox reactions, which may lead to high photocatalytic activity and stability.

The dopant makes a more uniform crystalline phase and helps to increase the crystal growth, prevent agglomeration, and smaller particle sizes of NaTaO₃ photocatalyst [10], as depicted from SEM images. The particle sizes of La-C-NaTaO₃ (Figure 3), was smaller than that of non-doped NaTaO₃ (Figure 2). Generally speaking, higher crystallinity, stability, and smaller particle size can improve the photocatalytic activity of a La-C-NaTaO₃ catalyst, associated with the distance electron-hole pairs must travel through the bulk of the catalyst particle to reach the active sites [16]. This arises from the efficient separation of photo-generated carriers at the photocatalyst inter-

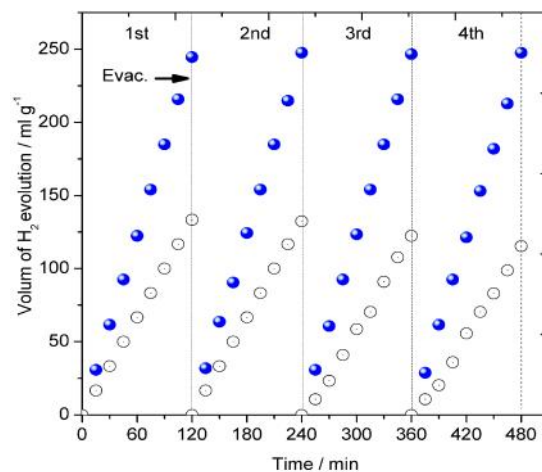


Figure 7. Time course of hydrogen evolution on the doped La-C-NaTaO₃ (close circle) and pure NaTaO₃ (open circle). The reaction was continued for 8 h irradiation, with evacuation every 2 h.

faces and/or the promotion of catalytic performance.

This is attributed to the short distance from the bulk to surface, which is derived from small particle, so that photogenerated electrons and holes efficiently migrate onto the surface with less opportunity for recombination [17]. In addition, in general catalysis, the surface area of sample plays significant role in determining the reaction activity due to the capability of adsorbing reactants on surface active sites for undertaking reaction [18].

The La-C-NaTaO₃ was quite stable for repeated cycles of hydrogen production, as demonstrated in Figure 7, while the deactivation was started at the third run on the pure NaTaO₃ can be observed. The TEM images show the clear difference between La-C-NaTaO₃ and the pure NaTaO₃ catalysts. The La-C-NaTaO₃ particles (see Figure 5), shows regular cubic-shape morphology and a clear surface. Therefore, the electron transfer on La-C-NaTaO₃ is well defined with enhanced and efficient charge separation.

4. Conclusions

Nanocrystalline La-C-NaTaO₃ photocatalyst with smaller particle size was successful synthesized by a sol-gel technique. From XRD result, the La-C co-doped NaTaO₃ sample should be respectively assigned to the monoclinic symmetry perovskite-type of NaTaO₃. The SEM measurements give a particle size of pure and doped NaTaO₃ are around 50-400 nm and 30-200 nm, respectively. The resulting La-C-NaTaO₃ photocatalysts was systematically

evaluated their performance via the photocatalytic H₂ evolution in comparison with pure NaTaO₃. The La-C-NaTaO₃ photocatalyst provided higher photocatalytic activities than that of pure NaTaO₃. Dopant La-C makes the photocatalyst possess small particle sizes with a high crystallinity, which may lead to high photocatalytic activity and stability. Thus the La-C codoped NaTaO₃ photocatalyst shows high activity of H₂ evolution from aqueous methanol solution.

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