

Research Article

Photocatalytic H₂ or O₂ Evolution over A-Site Deficient Perovskite-Type Compounds La_{1/3}MO₃ (M = Nb, Ta) from Aqueous Solutions

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Two compounds La_{1/3}MO₃ (M = Nb, Ta) with A-site deficient perovskite-type structure were synthesized by the solid state reaction method. The photocatalytic properties of these compounds were characterized by H₂ evolution with Pt cocatalyst from CH₃OH/H₂O solution and by O₂ evolution from AgNO₃ aqueous solution under UV light irradiation. The results showed that the average rate of H₂ evolution was about 61.07 μmol h⁻¹ for La_{1/3}NbO₃ and 95.79 μmol h⁻¹ for La_{1/3}TaO₃ after 24 hours of reaction time, while the initial rate of O₂ evolution was 26.31 μmol h⁻¹ for La_{1/3}NbO₃ and 16.21 μmol h⁻¹ for La_{1/3}TaO₃, respectively. H₂ evolution was also observed over La_{1/3}MO₃ (M = Nb, Ta) with NiO cocatalyst from pure water under UV light irradiation.

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1. INTRODUCTION

Photocatalytic reactions for H₂ and/or O₂ evolution from aqueous solutions over metal oxides have received much attention from a viewpoint of the photon energy conversion and environmental issues [1, 2]. In the past three decades, research efforts have been mainly focused on TiO₂, because it exhibits high photocatalytic activity with long-term stability against photo and chemical corrosion; it is also inexpensive and nontoxic [2–4]. To better understand the fundamental processes and enhance the photocatalytic efficiency [5, 6], much attentions have been paid to investigating the mechanisms of photocatalysis. Kudo et al. have developed many new photocatalysts. Some metal oxides, such as ATaO₃ (A = Li, Na, K) [7–9], K₂La₂Ti₃O₁₀ [10], Sr₂M₂O₇ (M = Nb and Ta) [11], PbBi₂Nb₂O₉ [12], Zn₂GeO₄ [13], and so forth, have been reported to possess reasonable activities for splitting water into H₂ and O₂ under light irradiation. Moreover, La-doped NaTaO₃ with NiO cocatalyst gives the most photocatalytic activity and an apparent quantum yield of 56% for water splitting up to date [8]. The perovskite structure seems to favor the photocatalytic reaction of water splitting. Machida et al. [14] have studied the effect of A-site lanthanide (Ln = La, Ce, Pr, Nd, and Sm) on the photocatalytic activities of perovskite-related oxide photocatalysts LnTaO₄, of which the

highest photocatalytic activity was found over LaTaO₄ due to its special crystal structure and electronic structure, and the photocatalytic activity of LnTaO₄ was strongly dependent on lanthanide. Recently, A-site deficient perovskite type oxides with lithium insertion sites, for example, La_{1/3}NbO₃ [15], La_{1/3}TaO₃ [16], and Gd_{1/3}TaO₃ [17], are of interest for commercial application as well as model compounds for the basic study of solid-state electrochemical reactions, but their photocatalytic properties have never been reported. La_{1/3}NbO₃ is crystallized in orthorhombic symmetry with space group *Pmmm* and lattice parameters *a* = 3.909 Å, *b* = 3.917 Å, *c* = 7.910 Å [18], but La_{1/3}TaO₃ exhibits a tetragonal lattice with space group *P4/mmm* and lattice parameters *a* = 3.921 Å, *b* = 3.921 Å, *c* = 7.902 Å [16]. It is known that oxygen vacancies in photocatalysts would work as recombination centers between photogenerated electrons and holes [19, 20]. To better understand the function of crystal deficiency, here we report the photocatalytic properties of the compounds La_{1/3}NbO₃ and La_{1/3}TaO₃ for water splitting.

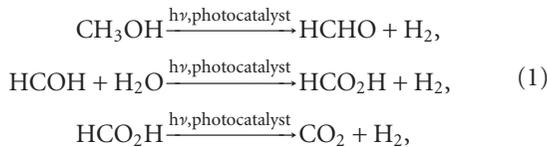
2. EXPERIMENTAL

Polycrystalline powders of La_{1/3}NbO₃ and La_{1/3}TaO₃ were synthesized by the solid state reaction method using La₂O₃ (99.99%), Nb₂O₅ (99.99%), and Ta₂O₅ (99.99%) as the

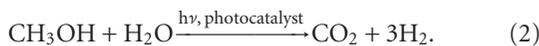
starting materials. The precursors were initially preheated at 600°C for 12 hours. The predried powders were then mixed thoroughly in chemical stoichiometry in an ethanol solution. $\text{La}_{1/3}\text{NbO}_3$ sample was calcined at 1320°C in air for 10 hours, while $\text{La}_{1/3}\text{TaO}_3$ sample was sintered at 1520°C in air for 8 hours.

The crystal structure of the compounds was determined by a powder X-ray diffraction (XRD) method using a Rigaku (D/MAX Ultima III) X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). UV-Vis diffuse reflectance spectra were collected at room temperature with a UV-Vis spectrophotometer (Shimadzu, UV-2550) using BaSO_4 as a reference, and were converted from reflection to absorbance by the Kubella-Munk method. The surface area of the powder samples were measured by N_2 adsorption and desorption at 77 K using BET surface area measurement (Shimadzu, Micromeritics Tristar 3000) after pretreatment at 473 K for 4 hours. The photoluminescence (PL) spectra of the compounds were detected at 77 K with a spectrofluorometer (Cary Eclipse, Varian).

The photocatalytic H_2 or O_2 evolution from aqueous solutions was conducted in an inner irradiation quartz cell, which was connected to a closed gas-circulating system. A 400 W high-pressure Hg lamp (RIKO, UVL-400HA) was taken as the light source with a quartz jacket to keep the temperature constant, and the measured photon flux was about 120.46 W. 0.5 g powder sample was dispersed by a magnetic stirrer in aqueous solutions in the reaction cell for every experiment. To evaluate the photocatalytic properties of the compounds, three kinds of photocatalytic reactions were performed. Namly, the photocatalytic H_2 evolution was firstly carried out in an aqueous solution of $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (0.5 g powder sample, cocatalyst Pt 0.5 wt%, 50 ml CH_3OH , 350 ml H_2O) by taking the sacrificial reagent methanol as electron donor, and methanol is oxidized to CO_2 [21]:



and the total reaction [22] is



The Pt cocatalyst as active sites for H_2 evolution was loaded on the surface of the powder samples by an in situ photodeposition method using an aqueous $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ solution. The PtCl_6^{2-} anion was reduced by photogenerated electrons, and highlydispersed metal particles were deposited on the surface of the compound. Pt cocatalyst could significantly accelerate H_2 production from water in the presence of a sacrificial electron donor such as methanol [23]. Secondly, the photocatalytic O_2 evolution was observed in an aqueous solution of 2 mmol AgNO_3 (400 ml H_2O) using the sacrificial reagent silver nitrate as electron acceptor according to these reactions represented by following equations [24]:

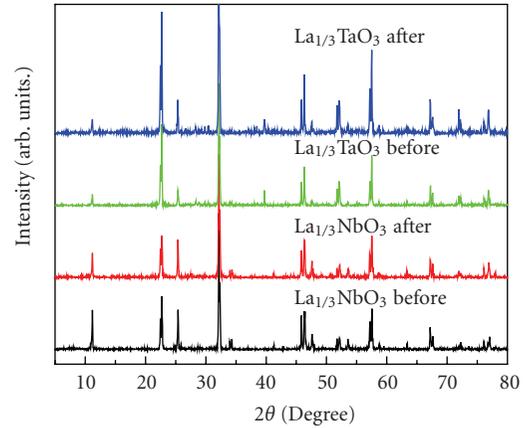
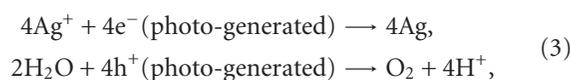
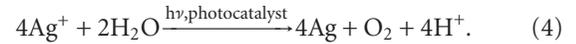


FIGURE 1: Powder X-ray diffraction patterns of the $\text{La}_{1/3}\text{MO}_3$ ($M = \text{Nb, Ta}$) powders before and after photocatalytic reaction of H_2 evolution from aqueous methanol solution dispersed with the 0.5 wt% Pt-loaded $\text{La}_{1/3}\text{MO}_3$ ($M = \text{Nb, Ta}$) powder (0.5 g) catalysts under UV light irradiation. Light source: a 400 W high-pressure Hg lamp.

and the total reaction [22] is



Finally, the photocatalytic splitting of pure water was conducted in distilled water using NiO-loaded catalysts (0.5 g powder sample, 0.8 wt% NiO cocatalyst, 400 ml H_2O). The NiO-loaded catalysts were prepared by impregnation of as-synthesized powders with an aqueous solution of $\text{Ni}(\text{NO}_3)_2$. Thus, the powder samples were carefully mixed with an equivalent molar amount of an aqueous $\text{Ni}(\text{NO}_3)_2$ solution in a porcelain crucible on a water bath at 90°C and then the mixture was calcined at 380°C for 2 hours to get the NiO cocatalyst on the surface of the powder samples. Prior to the reaction, the closed gas circulation system and the reaction cell were well deaerated by evacuation to remove O_2 and N_2 dissolved in water and about 30 Torr argon gas was introduced. The H_2 or O_2 gas evolved was determined on an on-line gas chromatograph (Shimadzu, GC-8AIT, molecular sieve 5 A column, TCD, Ar carrier) connected with the circulation system.

3. RESULTS AND DISCUSSION

The crystal structures of the $\text{La}_{1/3}\text{MO}_3$ ($M = \text{Nb, Ta}$) compounds were determined by powder X-ray diffraction (XRD). Figure 1 gives the X-ray diffraction patterns of the synthesized samples. The indexed results are in agreement with that previously reported in the JCPDS database card (no. 72-2080, $\text{La}_{1/3}\text{NbO}_3$, and no. 72-2029, $\text{La}_{1/3}\text{TaO}_3$) [16, 18], indicating that all of the synthesized powders are of single phase. The BET measurement showed that the synthesized samples had a low surface area: 0.68 m^2/g for $\text{La}_{1/3}\text{NbO}_3$ and 0.53 m^2/g for $\text{La}_{1/3}\text{TaO}_3$, respectively.

With the data of atomic positions listed in the literatures [18], the crystal structures of the compounds are constructed by corner-shared MO_6 ($M = \text{Nb, Ta}$) in three-space direction

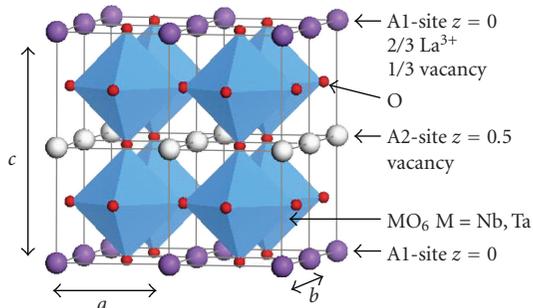


FIGURE 2: Crystal structure model of $\text{La}_{1/3}\text{MO}_3$ ($M = \text{Nb, Ta}$).

with alternative arrangement of La ions along c -axis, and the Materials Studio package (Accelrys Inc., USA) was employed. As shown in Figure 2, the unit cell of the compounds contains two MO_6 ($M = \text{Nb, Ta}$) octahedra with the La ions located in A-site in every second layer, leaving the other layers of A-sites remain vacant. La ions and vacancies at A-site are ordered within alternate (001) planes. According to this structure, the c -parameter of the primitive perovskite-type cell is doubled. In this structure, La^{3+} ions randomly locate at A1 site with 2/3 occupancy, but A2 site is not occupied. That is to say, there is enough room to insert extra cations. Consequently, this distribution leads to twice the c -parameter of the cubic perovskite-type cell, and the tetragonal symmetry could be expected. In the case of $\text{La}_{1/3}\text{NbO}_3$, the crystal structure has orthorhombic symmetry because a small orthorhombic distortion occurs. In the past years, a variety of niobium- or tantalum-based photocatalysts containing NbO_6 or TaO_6 octahedra, which were interconnected in the one-, two-, or three-dimensional manner, showed high photocatalytic activities in splitting water into H_2 and O_2 under UV light irradiation [7–9, 11, 25]. It was thought that the formed NbO_6 or TaO_6 octahedral chains or layers favor a possible delocalization of charge carriers [25, 26]. So, it could be speculated that photocatalytic water splitting over the compounds $\text{La}_{1/3}\text{MO}_3$ ($M = \text{Nb, Ta}$) might be observed.

Diffuse reflection spectra of the $\text{La}_{1/3}\text{MO}_3$ ($M = \text{Nb, Ta}$) powders synthesized by the solid state reaction method are shown in Figure 3. Both of the compounds had an intense absorption band with a steep edge in the ultraviolet (UV) light region, which was indicative of a band gap transition, and their shapes were similar to each other. Compared with the compound $\text{La}_{1/3}\text{TaO}_3$, the absorption edge of the compound $\text{La}_{1/3}\text{NbO}_3$ was red-shifted to longer wavelength, suggesting that $\text{La}_{1/3}\text{NbO}_3$ could be responsive to the incident photons with less energy. The band gaps of niobates are usually narrower than those of tantalates because the levels of the conduction bands consisting of Nb 4d are more positive than those of Ta 5d. Niobates can therefore show absorption in longer wavelength region under light irradiation. The absorption band gap E_g of the compounds $\text{La}_{1/3}\text{MO}_3$ ($M = \text{Nb, Ta}$) can be determined according to the relation [27]

$$(\alpha h\nu)^n = A(h\nu - E_g), \quad (5)$$

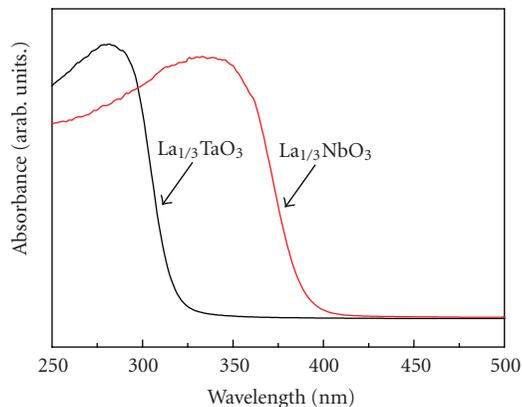


FIGURE 3: UV-Vis diffuse reflection spectra of $\text{La}_{1/3}\text{MO}_3$ ($M = \text{Nb, Ta}$).

where E_g is the band gap energy of the semiconductors, $h\nu$ is the incident photo energy, α is the absorption coefficient, A is a proportionality constant relative to the material, respectively. The value of the index n depends on the type of electronic transition, and is equal to 2 for a direct transition material, whereas $n = 1/2$ for an indirect band gap material. On the basis of the absorption spectra for the compounds $\text{La}_{1/3}\text{MO}_3$ ($M = \text{Nb, Ta}$), the plots of $(\alpha h\nu)^n$ versus $h\nu$ were obtained for $n = 1/2$ and 2, respectively. The results exhibited the linear dependence of $(\alpha h\nu)^n$ versus $h\nu$ when n was fixed at 1/2, suggesting that the synthesized $\text{La}_{1/3}\text{MO}_3$ ($M = \text{Nb, Ta}$) powder samples were semiconducting with indirect transitions, that is, the fundamental electronic transition were all indirectly allowed and involved phonons. The $(\alpha h\nu)^{1/2}$ versus $h\nu$ curves for the $\text{La}_{1/3}\text{MO}_3$ ($M = \text{Nb, Ta}$) compounds are plotted in Figure 4. Accordingly, the values of the band gaps E_g for the two compounds were evaluated to be 3.08 eV for $\text{La}_{1/3}\text{NbO}_3$ and 3.78 eV for $\text{La}_{1/3}\text{TaO}_3$ when the relevant linear region of $(\alpha h\nu)^{1/2}$ versus $h\nu$ was extrapolated to zero ordinate.

Figure 5 represents the excitation and emission spectra of the synthesized $\text{La}_{1/3}\text{MO}_3$ ($M = \text{Nb, Ta}$) at room temperature. The excitation spectrum agreed well with the diffuse reflection spectrum, suggesting these emissions were derived from band gap excitation. The PL spectra of oxide semiconductors are useful to disclose the information of the photogenerated electron-hole pairs, such as migration, transfer, and recombination of the charge carrier. Niobate or tantalate photocatalysts exhibiting photoluminescence were reported to be capable of splitting water [11, 28, 29]. Therefore, photocatalytic activities of the $\text{La}_{1/3}\text{MO}_3$ ($M = \text{Nb, Ta}$) compounds for water splitting were possibly observed.

The light-induced production of the charge carriers is the prerequisite for the application of semiconductors in photocatalysis. It is believed that the process of photocatalytic water splitting with a semiconductor includes several reactions: (i) the photoinduced generation of electron-hole pairs by the absorption of band gap photons in the semiconductor, (ii) the separation and migration of the charge carriers (electron-hole pairs), resulting in the formation of electrons

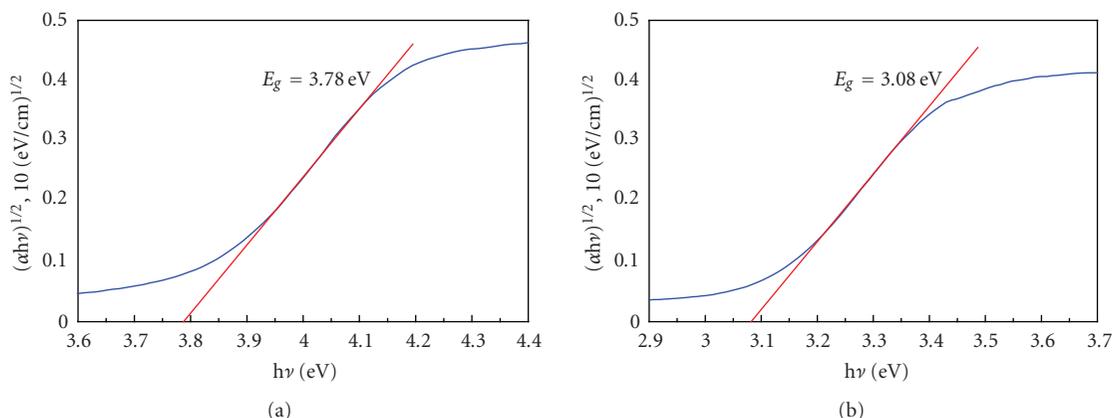


FIGURE 4: $(\alpha h\nu)^{1/2}$ versus $h\nu$ curves for the $\text{La}_{1/3}\text{MO}_3$ ($M = \text{Nb, Ta}$) compounds: (a) $\text{La}_{1/3}\text{NbO}_3$; (b) $\text{La}_{1/3}\text{TaO}_3$.

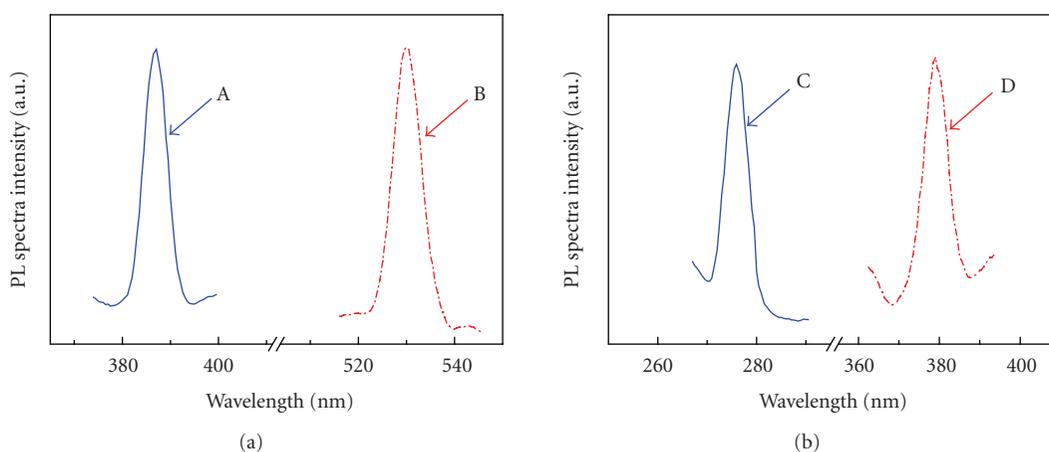
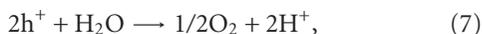


FIGURE 5: Photoluminescence (PL) spectra of the synthesized $\text{La}_{1/3}\text{MO}_3$ ($M = \text{Nb, Ta}$) powders at 77 K: (a) A: an excitation spectrum of $\text{La}_{1/3}\text{NbO}_3$ monitored at 530 nm, B: an emission spectrum of $\text{La}_{1/3}\text{NbO}_3$ excited at 387 nm; (b) C: an excitation spectrum of $\text{La}_{1/3}\text{TaO}_3$ monitored at 379 nm, D: an emission spectrum of $\text{La}_{1/3}\text{TaO}_3$ excited at 275 nm.

in the conduction band (CB) and holes in the valence band (VB) represented by (6):



and (iii) the redox reaction on the surface of the semiconductor, for example, oxidization of water by holes at the valence band:



and reduction of hydrogen ions by electrons at the conduction band:



Therefore, the crystal structure and related electronic structure of the semiconductor plays a dominant role in its photocatalytic properties.

To evaluate the photocatalytic activity of the $\text{La}_{1/3}\text{MO}_3$ ($M = \text{Nb, Ta}$) compounds, The evolution rate of H_2 gas was firstly observed from $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ with cocatalyst Pt

(0.5 wt%) using CH_3OH as sacrificial reagent under UV light irradiation, and the experimental results were depicted in Figure 6. It shows the amount of evolved H_2 gas increased linearly with progress of irradiation time using these compounds. After every about 12 hours of reaction time for H_2 evolution, the dark test was conducted. Clearly, the H_2 evolution rate was zero when the light was turned off and the reaction cell was reevacuated. The average rates of H_2 evolution in the third run (after about 24 hours of reaction time) were about $61.07 \mu\text{mol h}^{-1}$ for $\text{La}_{1/3}\text{NbO}_3$ and $95.79 \mu\text{mol h}^{-1}$ for $\text{La}_{1/3}\text{TaO}_3$. The turnover number (TN), which can be adopted in photocatalytic reactions as the ratio of total amount of hydrogen atom in H_2 gas evolved to the catalyst used ($2671 \mu\text{mol La}_{1/3}\text{NbO}_3$ and $1817 \mu\text{mol La}_{1/3}\text{TaO}_3$ in the present experiment), exceeded 1.92 for $\text{La}_{1/3}\text{NbO}_3$ and 3.57 for $\text{La}_{1/3}\text{TaO}_3$, respectively, after about 36 hours of reaction time. The crystal structure of the residue of the compounds after H_2 evolution reaction was confirmed again by XRD as shown in Figure 1. It demonstrates that X-ray diffraction patterns of the $\text{La}_{1/3}\text{MO}_3$ ($M = \text{Nb, Ta}$) powders were unchanged after photocatalytic reaction of H_2 evolution, indicating that

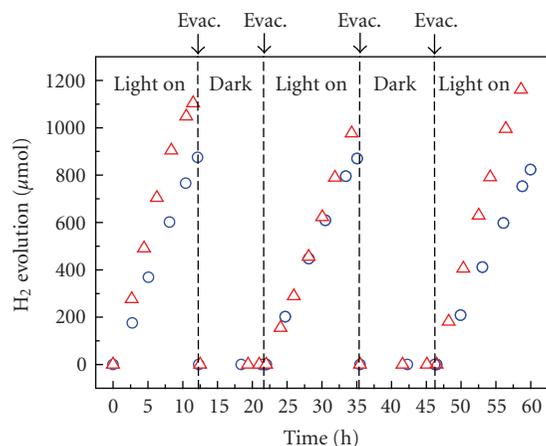


FIGURE 6: Photocatalytic H₂ evolution from the aqueous methanol solution (50 ml CH₃OH, 350 ml H₂O) dispersed with the 0.5 wt% Pt-loaded La_{1/3}MO₃ (M = Nb, Ta) powder samples (0.5 g) under UV light irradiation. Light source: a 400 W high-pressure Hg lamp ○ : La_{1/3}NbO₃; △: La_{1/3}TaO₃.

the synthesized samples were stable under UV light irradiation. Accordingly, all the aforementioned results proved that the reaction for H₂ evolution was photocatalysis, but not a photocorrosion. From the crystal structure as shown in Figure 2, the bond angles of Nb–O–Nb were calculated to be 180°, 165.73°, 166.66° in the three directions in La_{1/3}NbO₃ perpendicular to each other, respectively; while those of Ta–O–Ta existed as 180°, 174.92° in La_{1/3}TaO₃. Energy delocalization for oxide semiconductors depends largely on the bond angle. The closer the M–O–M bond angle is to 180°, the more the excitation energy is delocalized [9], that is, the photogenerated electron pairs can migrate relatively easily to the surface of the photocatalyst, which was beneficial to the photocatalytic reactions. This means that the bond angle of M–O–M in MO₆ octahedra is one of the important factors that affect the photophysical and photocatalytic properties of semiconductors. Thereby, the bond angle of Ta–O–Ta in La_{1/3}TaO₃, which is closer to ideal 180°, might facilitate the migration of photogenerated electron-hole pairs and eliminate the recombination of electron-hole pairs, and finally increase the photocatalytic activity. As a results, the La_{1/3}TaO₃ compound showed higher photocatalytic activity for H₂ evolution despite of poorer adsorption of incident photons compared with La_{1/3}NbO₃.

Figure 7 represents the time courses of the evolution rates of O₂ evolution from aqueous solution (0.5 g photocatalyst, 2 mmol AgNO₃, 400 ml H₂O) without any cocatalyst under UV light irradiation for the La_{1/3}MO₃ (M = Nb, Ta) photocatalysts. The initial rates of O₂ evolution were calculated to be 26.31 μmol h⁻¹ for La_{1/3}NbO₃ and 16.21 μmol h⁻¹ for La_{1/3}TaO₃. With an increase in the reaction time, the evolution amount of O₂ gas over La_{1/3}NbO₃ increased steadily, whereas the O₂ evolution rate over La_{1/3}TaO₃ decreased drastically. After about 3 hours, the activity of La_{1/3}TaO₃ almost reached a plateau, indicating that the photocatalyst was deactivated. One reason for this deactivation was possibly that

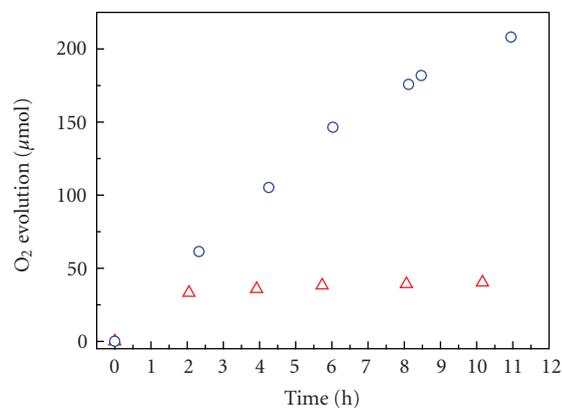


FIGURE 7: Photocatalytic O₂ evolution from aqueous solution (0.5 g photocatalyst, 2 mmol AgNO₃, 400 ml H₂O) without any cocatalyst under UV light irradiation. Light source: a 400 W high-pressure Hg lamp ○ : La_{1/3}NbO₃; △: La_{1/3}TaO₃.

the metallic Ag deposited on the surface of the La_{1/3}TaO₃ photocatalyst from the AgNO₃ sacrificial reagent shielded the incident light and minimized the surface active sites of the photocatalyst [30]. The crystal structure of the La_{1/3}TaO₃ photocatalyst was also checked by XRD after photocatalytic O₂ evolution. It was indicative of the metallic Ag peak. On the other hand, Scaife had examined that the valence band should be assumed by the O 2p levels in MO₆ and the conduction band assumed by d levels in MO₆ when an oxide semiconductor contains MO₆ octahedron [31]. The potential levels of valence band of the La_{1/3}MO₃ (M = Nb, Ta) consisting of O 2p levels could be reasonably speculated at the same level. Therefore, La_{1/3}NbO₃ with narrower band gap would absorb more incident photons than La_{1/3}TaO₃ under the UV light irradiation with the identical light source, and the more photogenerated holes in the valence band of La_{1/3}NbO₃ resulted in a larger amount of O₂ evolution. The photocatalytic O₂ evolution from AgNO₃ aqueous solution is also associated with the surface characterization of the photocatalyst [32]. Thereby, the property of the La_{1/3}TaO₃ surface was not compatible with the oxygen evolution being lack of the active site.

For a semiconductor, the conduction band is separated from the valence band by a band gap E_g . The excitation of an electron from valence band to conduction band is initiated by the absorption of a photon with energy equal to or greater than the band gap energy of the semiconductor. Thus, if the conduction band potential level is more negative than the redox potential of H⁺/H₂ and the valence band potential level is more positive than the redox potential of O₂/H₂O, the photogenerated electrons and holes will move to the surface of the photocatalysts and cause redox reactions. Namely, decomposition of water by semiconductor is possible even without applying electric power [1]. With the results of H₂ or O₂ evolution described above, it can be concluded that the band structures of La_{1/3}MO₃ (M = Nb, Ta) meet the electrochemical requirements for splitting water. Hence, there exists a possibility for the photocatalytic decomposition of pure water over the photocatalysts.

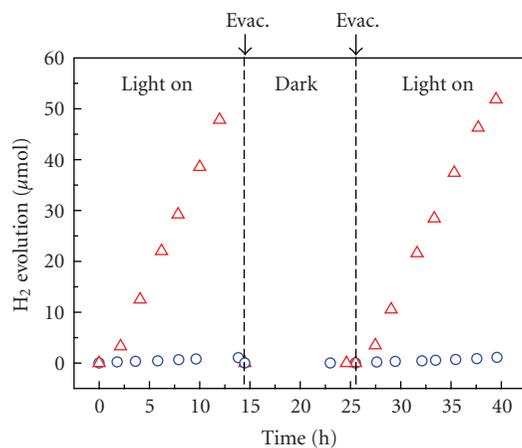


FIGURE 8: Photocatalytic water splitting from pure H₂O on NiO/La_{1/3}MO₃ (M = Nb, Ta) photocatalysts (0.8 wt% NiO, 0.5 g photocatalyst, 400 ml H₂O) under UV light irradiation. Light source: a 400 W high-pressure Hg lamp. ○: La_{1/3}NbO₃; △: La_{1/3}TaO₃.

It has been reported that NiO was a cocatalyst with high efficiency for photocatalytic water splitting [7, 8]. Figure 8 shows the photocatalytic water splitting on NiO loaded La_{1/3}MO₃ (M = Nb, Ta) photocatalysts (0.8 wt% NiO, 0.5 g photocatalyst, 400 ml H₂O) in pure water. Apparently, H₂ evolution could be detected over the NiO loaded La_{1/3}TaO₃ (NiO/La_{1/3}TaO₃) photocatalyst under UV light irradiation. In contrast, the activity of the NiO loaded La_{1/3}NbO₃ (NiO/La_{1/3}NbO₃) photocatalyst was remarkably smaller. The average rates of H₂ formation were about 0.08 μmol h⁻¹ for NiO/La_{1/3}NbO₃ and 3.71 μmol h⁻¹ for NiO/La_{1/3}TaO₃, respectively, after 20 hours of induction period.

Generally, the electronic structure of the transition-metal oxide with perovskite structure is consisted by the d level of the transition metal and the 2p level of the ligand O atom [31]. The potential level of valence band of the La_{1/3}MO₃ (M = Nb, Ta) consisting of O 2p levels should be at the same level, and the potential level of conduction band of the semiconductor could be estimated by the following equation [31]:

$$V_{fb} = 2.94 - E_g \quad (9)$$

Kato and Kudo had illustrated the correlation between the photocatalytic activity and the position of the conduction band of some tantalate photocatalysts relative to that of NiO (-0.96 eV versus NHE) in details [7, 33]. In the same way, the potential levels of conduction band of the La_{1/3}MO₃ (M = Nb, Ta) photocatalysts were calculated to be -0.14 eV for La_{1/3}NbO₃ and -0.84 eV for La_{1/3}TaO₃ according to this equation. It means that the potential level of La_{1/3}NbO₃ was more positive than that of NiO. Therefore, the photogenerated electrons in the conduction band of the La_{1/3}NbO₃ photocatalyst were difficult to transfer to the conduction band of the NiO cocatalyst as an active site on the surface for H₂ evolution, resulting in low efficiency of the charge separation. By contrast, the conduction band of the La_{1/3}TaO₃ photocatalyst

was approximately at the same level to that of the NiO cocatalyst. Thereby, the relatively higher activity was obtained over La_{1/3}TaO₃ due to its conduction band level, which was suitable for the transfer of generated electrons to NiO particles on the surface.

However, no sign of O₂ evolution was observed in these experiments with NiO/La_{1/3}MO₃ (M = Nb, Ta) photocatalysts, which should be accompanied by H₂ evolution in a stoichiometric ratio (H₂ : O₂ = 2 : 1). The same phenomenon has arisen over AgInW₂O₈ [34], TiO₂ [35], and so forth. It was proposed that there were both physisorbed and chemisorbed O₂ molecules on the surface of TiO₂ through low-energy photon irradiation [35], where the physisorbed O₂ is produced through the neutralization of chemisorbed O₂⁻ species by photogenerated holes. Moreover, the redox potential for photogenerated holes is much different for oxide semiconductors. Depending upon the exact conditions, O₂ and some intermediates, such as ·OH radicals, O₂⁻, H₂O₂, may appear in photocatalytic reactions [4]. In addition, the intraparticle and interparticle charge excitation, separation and transportation are rather complicated and the detailed mechanisms should be further clarified.

4. CONCLUSIONS

The perovskite-type compounds La_{1/3}MO₃ (M = Nb, Ta) with A-site deficiency were synthesized by the solid state reaction method. Both of these compounds could function as a photocatalyst for H₂ evolution from an aqueous methanol solution and for O₂ evolution from AgNO₃ aqueous solution, respectively, under UV light irradiation. But only H₂ evolution was observed over NiO/La_{1/3}MO₃ (M = Nb, Ta) from pure water without an accompanying evolution of O₂ gas. Compared with La_{1/3}NbO₃, La_{1/3}TaO₃ showed relatively higher photocatalytic activity for H₂ evolution. This can be mainly attributed to the differences in their crystal structures and band gap structures. In summary, the A-site deficient perovskite-type oxides, La_{1/3}MO₃ (M = Nb, Ta), could function as photocatalyst for water splitting under light irradiation.

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