ABSTRACT: The efficacy of LaNaTaO3 perovskites decoration RuO2 at diverse contents for the photocatalytic H2 generation has been explored in this study. The photocatalytic performance of RuO2 co-catalyst onto mesoporous LaNaTaO3 was evaluated for H2 under UV illumination. 3%RuO2/LaNaTaO3 perovskite photocatalyst revealed the highest photocatalytic H2 generation performance, indicating that RuO2 nanoparticles could promote the photocatalytic efficiency of LaNaTaO3 perovskite significantly. The H2 evolution rate of 3%RuO2/LaNaTaO3 perovskite is 11.6 and 1.3 times greater than that of bare LaNaTaO3 perovskite employing either 10% CH3OH or pure H2O, respectively. Interestingly, the photonic efficiency of 3%RuO2/LaNaTaO3 perovskite was enhanced 10 times than LaNaTaO3 perovskite in the presence of aqueous CH3OH solutions as a hole sacrificial agent. The high separation of charge carriers is interpreted by the efficient hole capture using CH3OH, hence leading to greater H2 generation over RuO2/LaNaTaO3 perovskites. This is attributed to an adjustment position between recombination electron−hole pairs and also the reduction of potential conduction alignment as a result of RuO2 incorporation. The suggested mechanisms of RuO2/LaNaTaO3 perovskites for H2 generation employing either CH3OH or pure H2O were discussed. The photocatalytic performances of the perovskite photocatalyst were elucidated according to the PL intensity and the photocurrent response investigations.

INTRODUCTION

With the growth of the industrial and scientific community, the photocatalyst as a favorable semiconductor material is considered as a promising and hot theme of research studies owing to its wide implementations in considerable fields, particularly for energy saving and environmental protection. Photocatalytic production of molecular hydrogen through semiconductor materials as efficient photocatalysts is considered as a promising avenue to produce sustainable and clean energy, and promoting semiconductor materials under visible light with a high photonic efficiency for the conversion of solar energy to molecular hydrogen is ultimately desired for potential applications. Recently, water splitting to generate molecular hydrogen employing perovskite oxide materials (ABO3) has attracted increasing attention with a high photonic efficiency. Among ABO3 perovskite oxide materials, the NaTaO3 photocatalyst has been realized for hydrogen generation from H2O using UV irradiation. The band gap of NaTaO3 is 4.0 eV, and it can be synthesized by diverse approaches, for instance, solid-state, molten salt, sol−gel, and hydrothermal methods.

To promote the photocatalytic activity of NaTaO3 particles, numerous scientists have made great effort to employ other synthetic avenues to obtain NaTaO3 nanoparticles as efficient photocatalysts. NaTaO3 as a colloidal array was synthesized using carbon mesopores as a direct structure agent for casting that was reproduced using silica nanosphere configuration. The mesoporous carbon matrix was eliminated by calcination, and then NaTaO3 nanoparticles as a colloidal array were obtained with a 34 m2 g−1 surface area and a 20 nm particle size. The obtained NaTaO3 prepared by this approach exhibited a 3 times higher photocatalytic efficiency than that prepared from the traditional hydrothermal synthesis for overall water splitting. NaTaO3 nanoparticles with ~25 nm crystallite size, synthesized by an exo-template method, exhibited an ~20 times higher hydrogen production rate than those synthesized using the solid-state approach. The recombination of photogenerated holes and electrons of large NaTaO3 nanoparticles was faster than those in smaller NaTaO3 nanoparticles with high crystallinity. On the other hand, much effort was made to perform a greater photonic efficiency of lanthanide-doped NaTaO3. The photocatalytic performances of the perovskite photocatalyst were elucidated according to the PL intensity and the photocurrent response investigations.
The photocatalytic efficiency of NaTaO$_3$ is greatly promoted by employing a co-catalyst such as Ru, NiO, Pt, or Rh, loaded on the NaTaO$_3$ surface. In general, loading of co-catalysts at different contents onto the photocatalyst surface led to a significant boost of molecular H$_2$ production compared with pure photocatalysts. A co-catalyst serves as a trapping agent of electrons, which produces a prolonged lifetime of photo-induced charge carriers, reducing their recombination rate. In terms of the co-catalyst-loaded semiconductor photocatalyst preparation, it is concluded that the crystalline structure of the prepared photocatalysts is very susceptible to synthetic approaches such as solid-state, solvothermal, sol–gel, hydrothermal, alkalide reduction, and electrospinning methods. NaTaO$_3$-based photocatalysts were synthesized via the traditional solid-state and sol–gel approaches. The conventional solid-state approach needs elevated annealing temperatures to produce NaTaO$_3$ with orthorhombic structure, whereas the sol–gel avenue requires low temperatures during the preparation to obtain NaTaO$_3$ with a monoclinic structure. Also, NaTaO$_3$-based photocatalysts could be prepared by the hydrothermal process. Efficient separation and inhibition recombination of charge carriers are paramount for H$_2$O splitting to create molecular H$_2$. In addition, separation and fabrication of active sites for H$_2$ generation are indispensable. Obviously, incorporation of RuO$_2$ co-catalysts onto NaTaO$_3$ perovskite surface is substantial for boosting their photonic efficiency for the production of molecular hydrogen. The photonic efficiency of NaTaO$_3$-based photocatalysts could be considerably calculated by doping foreign ions in the NaTaO$_3$ lattice.

Therefore, in the present proposal, synthesis of mesoporous RuO$_2$/LaNaTaO$_3$ perovskites at different RuO$_2$ contents for molecular H$_2$ generation was investigated employing the CH$_3$OH/H$_2$O system. The H$_2$ evolution rate of 3%RuO$_2$/LaNaTaO$_3$ perovskite is 11.6 and 1.3 times greater than that of the LaNaTaO$_3$ perovskite employing 1% methanol pure H$_2$O, respectively. Interestingly, the photonic efficiency of 3%RuO$_2$/LaNaTaO$_3$ perovskite was enhanced 10 times compared to LaNaTaO$_3$ perovskite in the presence of aqueous CH$_3$OH solutions. The suggested mechanisms of RuO$_2$/LaNaTaO$_3$ perovskites for H$_2$ evolution employing aqueous CH$_3$OH solutions and pure H$_2$O were discussed. The photocatalytic performances of perovskite photocatalyst were evaluated according to the PL intensity and the photocurrent response investigations.

## RESULTS AND DISCUSSION

**Perovskite Investigations.** X-ray diffraction patterns of LaNaTaO$_3$ and RuO$_2$/LaNaTaO$_3$ perovskites at different RuO$_2$ contents were investigated, as shown in Figure 1. The XRD pattern of LaNaTaO$_3$ perovskite was assigned as the monoclinic structure of the synthesized LaNaTaO$_3$ perovskite. The peaks at 22.91, 32.36, 40.04, 46.71, 52.61, 58.17, 68.08, 72.9, and 77.4° (Figure 1a) have corresponded to the planes of (100), (101), (110), (200), (102), and (121) (JCPDS no. 74-2478). After addition of RuO$_2$ at different contents of 0.5, 1, 3, and 5%, the intensity of the mean peak is gradually decreased with increasing RuO$_2$ content (Figure 1b–d). It is documented that the ionic radii of La$^{3+}$ (1.36 Å) and Na$^+$ (1.39 Å) ions are equivalent. In addition, the ionic radius of the Ta$^{5+}$ ion (0.64 Å) is notably smaller than that of the La$^{3+}$ ion (1.03 Å). If Ta$^{5+}$ ions were replaced with La$^{3+}$ ions at the B site position in the perovskite structure, a considerable shift should be recognized. Interestingly, there was no crystalline phase involving RuO$_2$ at different RuO$_2$ concentrations of 0.5–5% that could be detected, indicating that RuO$_2$ nanoparticles are highly contributed over the mesoporous La$_{0.02}$Na$_{0.98}$TaO$_3$ network with a small particle size. This is attributed to the adsorption of the Ru(III)–acetylacetonate complex onto the La$_{0.02}$Na$_{0.98}$TaO$_3$ surface, and then the adsorbed Ru(III)–acetylacetonate complex was decomposed to RuO$_2$ nanoparticles onto the surface of the LaNaTaO$_3$ perovskite network and inside the walls of the pores. The possibility of interaction (substitution of Ru$^{4+}$ for Ta$^{5+}$) between equivalent ionic radii materials Ru$^{4+}$ (0.62 Å) and Ta$^{5+}$ (0.64 Å) could partly explain this observation.

![Figure 1. X-ray diffraction peaks around 32.5° of (a) LaNaTaO$_3$ and LaNaTaO$_3$ doped with RuO$_2$: (b) 1%, (c) 3%, and (d) 5%.

Figure 2 shows SEM images of (a) bare LaNaTaO$_3$ perovskite and RuO$_2$/LaNaTaO$_3$ at 0.5% (b), 1% (c), 3% (d), and 5% (e) loadings. The ordered surface nanostructure of the LaNaTaO$_3$ perovskite was self-constructed as shown in Figure 2a. The particle sizes of the LaNaTaO$_3$ perovskite were enlarged on increasing the RuO$_2$ content from 0.5 to 5% (Figure 2b–e). These characteristics are advantageous in terms of small particle size and high crystallinity for the enhanced photocatalytic efficiency of perovskite photocatalysts. EDS analysis showed the presence of Ru, La, Na, and O and proved that the RuO$_2$/LaNaTaO$_3$ perovskite consisted of the precursor ratios employed in the starting mixtures. The EDS quantitative analysis of 1%RuO$_2$/LaNaTaO$_3$ shows that the weight percents of Ru, La, Na, and O are 0.08, 0.42, 16.91, 18.90, and 63.68, respectively. Figure 3 displays the TEM images of the structure and morphology of mesoporous LaNaTaO$_3$ and 3%RuO$_2$/LaNaTaO$_3$ perovskite. The LaNaTaO$_3$ perovskite particles were highly dispersed with uniform shape and size (~10 nm) as clearly displayed in Figure 3a. The morphology of the 3%RuO$_2$/LaNaTaO$_3$ NPs is similar to the bare LaNaTaO$_3$ perovskite in terms of shape and size (Figure 3b). The atomic planes of RuO$_2$ and NaTaO$_3$ NPs were estimated at 3.2 and 3.80 Å, respectively, which matches to the lattice spacing of (110) and (111), as obviously depicted in Figure 3c, and the NaTaO$_3$ and RuO$_2$ NPs are connected, along with the well matching of selected area electron diffraction of NaTaO$_3$ perovskite with the orthorhombic...
crystal (Figure 3d). The high crystallinity of the synthesized RuO₂/LaNaTaO₃ perovskite was confirmed by clear lattice spacing of atomic planes (Figure 3d).

Nitrogen adsorption isotherms of the bare LaNaTaO₃ and 3%RuO₂/LaNaTaO₃ perovskites are depicted in Figure 4. The adsorption isotherms of both LaNaTaO₃ and 3%RuO₂/LaNaTaO₃ perovskites are of typical reversible type IV. The inflection sharpness was obtained at relative pressures in the capillary condensation range of 0.45–0.7, resulting in mesostructured materials. The mesopores were formed as a result of interparticle voids between prepared nanoparticles. The mesoporosity can be explained by the formation of irregular voids between LaNaTaO₃ particles. In addition, the existence of voids among LaNaTaO₃ NPs participates in boosting the surface area of the prepared LaNaTaO₃ photocatalyst. The BET surface area of 3%RuO₂/LaNaTaO₃ perovskite was calculated to be 34 m² g⁻¹.

XPS spectroscopy was used to examine the states and composition of the 1%RuO₂/LaNaTaO₃ photocatalyst as displayed in Figure 5. Figure 5a shows two peaks located at...
Photocatalytic Performance. Photocatalytic tests were conducted on mesoporous RuO$_2$/LaNaTaO$_3$ perovskites for H$_2$ generation from either CH$_3$OH or pure H$_2$O. The RuO$_2$ loading LaNaTaO$_3$ perovskite at different contents (0–5%) was assessed for H$_2$ generation from either pure H$_2$O or CH$_3$OH (10 vol %). The illumination time of the photocatalytic H$_2$ evolution was conducted over the obtained photocatalysts employing pure H$_2$O and CH$_3$OH, as illustrated in Figure 7a,b. The findings exhibited that the H$_2$ evolution immediately started as the UV lamp was turned on. H$_2$ evolution rates were reached to steady state within 30 min. At this stage, the photocatalytic reaction was illuminated for 6 h to detect and determine the H$_2$ evolution rate. Finally, the UV lamp was turned off, and the H$_2$ evolution abruptly declined to reach the baseline (Figure 7a,b). The H$_2$ evolution rates were calculated by subtracting the baseline and average of the values obtained from the curve with almost steady rates of H$_2$ evolution, as shown in Figure 7. The findings indicated that there was no H$_2$ evolution without using the photocatalysts. It can be seen that the mesoporous LaNaTaO$_3$ perovskite photocatalyst exhibits the minimum photocatalytic performance. The H$_2$ evolution ultimately increased when RuO$_2$ was grafted onto LaNaTaO$_3$ perovskite surface. In addition, the photocatalytic efficiency of the LaNaTaO$_3$ perovskite was enhanced with the increment of the RuO$_2$ content, achieving the highest H$_2$ evolution at 3% RuO$_2$.

Figure 8a exhibits H$_2$ evolution rates evolution over LaNaTaO$_3$ perovskite loading different RuO$_2$ contents (0, 0.5, 1, 3, and 5%), from pure H$_2$O and from 10% CH$_3$OH. The H$_2$ evolution rate was increased from 0 to 1.29 $\mu$mol h$^{-1}$ when pure H$_2$O was used with the increase of RuO$_2$ content from 0 to 5%. However, in the case of 10% methanol, the H$_2$ evolution rate was improved from 0.99 to 11.54 $\mu$mol h$^{-1}$ with the increase of RuO$_2$ content from 0 to 5%. Interestingly, the H$_2$ evolution rate of 3%RuO$_2$/LaNaTaO$_3$ perovskite is the fastest among all of the synthesized photocatalysts. Besides, the H$_2$ evolution rate of 3%RuO$_2$/LaNaTaO$_3$ perovskite is 11.6 times greater than that of LaNaTaO$_3$ employing 10% methanol; however, in the case of pure H$_2$O, the H$_2$ evolution rate of 3% RuO$_2$/LaNaTaO$_3$ perovskite was enhanced 1.3 times than LaNaTaO$_3$. Also, the H$_2$ evolution rate of 3%RuO$_2$/LaNaTaO$_3$ employing 10% methanol is 9 times higher than employing pure H$_2$O. Figure 8b shows the photonic efficiency of RuO$_2$/LaNaTaO$_3$ perovskite at different RuO$_2$ contents (0.5, 1, 3, and 5%), from pure water and 10% methanol. The results revealed that the photonic efficiency was increased from 0.9 to 1.5 with the increase of the RuO$_2$ content from 0 to 5% employing pure water; however, the photonic efficiency was increased from 0.2 to 2% with increasing the RuO$_2$ content from 0 to 3%; then, it was decreased to 1.7% at 5%RuO$_2$ using 10% methanol. Interestingly, the photonic efficiency of 3% RuO$_2$/LaNaTaO$_3$ perovskite was enhanced 10 times than bare LaNaTaO$_3$ perovskite. Table 2 summarizes the comparison between the synthesized photocatalysts and other samples for photocatalytic H$_2$ generation.

It is supposed that the high RuO$_2$ content can cover LaNaTaO$_3$ perovskite surface, suggesting reduction of the photoexciting capability of the LaNaTaO$_3$ perovskite photocatalyst. In addition, it could be caused by the agglomeration and growth of RuO$_2$ onto mesoporous LaNaTaO$_3$ perovskite surface and hence weakened the role of the co-catalyst. The 3%RuO$_2$/LaNaTaO$_3$ perovskite revealed the maximum photocatalytic performance among all of the synthesized photocatalysts.
photocatalysts, indicating that the incorporation of RuO$_2$ could promote the photocatalytic activity of LaNaTaO$_3$ perovskite significantly. The improved photocatalytic performance of the RuO$_2$/LaNaTaO$_3$ perovskite photocatalyst was explained by the effective separation of charge carriers in the present RuO$_2$/LaNaTaO$_3$ perovskite that is accomplished by exciting the electrons from the VB to the CB of LaNaTaO$_3$. Then, the photogenerated electrons migrate to RuO$_2$ NPs (Scheme 1). The addition of RuO$_2$ nanoparticles onto the LaNaTaO$_3$ perovskite leads to prepared materials possessing Brønsted acids with the distinguishing interaction of the Ru–O···H bond, However, the acid strength onto the surface of RuO$_2$ attributes to its capability to eliminate a proton. It is documented that RuO$_2$ possesses the highest electronegativity, small particle size, and the highest oxidation state (IV). Therefore, RuO$_2$ has the strongest Brønsted acid and shows the maximum photocatalytic performances for H$_2$ evolution in both CH$_3$OH solution and pure H$_2$O due to the prohibition of...
To confirm the reason for the promotion of the photocatalytic activity of RuO\(_2\)/LaNaTaO\(_3\) perovskites, photocurrent response and photoluminescence (PL) were measured. The photocurrent response over LaNaTaO\(_3\) and RuO\(_2\)/LaNaTaO\(_3\) perovskites is depicted in Figure 9a in the dark and under illumination. In the dark, there was no response current; however, upon illumination, bare LaNaTaO\(_3\) perovskite revealed the lowest photoresponse. With the increase of RuO\(_2\) from 1 to 3%, the photocurrent intensity was increased gradually decreased at 5%RuO\(_2\)/LaNaTaO\(_3\) perovskite, implying the high tendency upon illumination to facilitate the separation of photo-created electrons and holes. This result is consistent and explained the photocatalytic H\(_2\) generation. The PL of bare LaNaTaO\(_3\) and RuO\(_2\)/LaNaTaO\(_3\) perovskites at diverse RuO\(_2\) percentages is displayed in Figure 9b. The PL peak of bare LaNaTaO\(_3\) perovskite was assigned at \(\lambda \sim 469.34\) nm with a higher PL intensity. However, the PL intensity of the RuO\(_2\)/LaNaTaO\(_3\) perovskites revealed a lower intensity than bare LaNaTaO\(_3\) perovskite. The RuO\(_2\)/LaNaTaO\(_3\) perovskites exhibited a low exciton emission owing to the expedient of charge carrier separation. Interestingly, the PL intensity of RuO\(_2\)/LaNaTaO\(_3\) perovskites decreased with the increase of RuO\(_2\) content, presenting photoinduced electron transfer from the CB of LaNaTaO\(_3\) perovskites to the close contact RuO\(_2\) NPs.

The mechanism of highly effective H\(_2\) evolution over RuO\(_2\)/LaNaTaO\(_3\) photocatalysts in pure H\(_2\)O and CH\(_3\)OH was demonstrated in Scheme 1. After UV illumination, the generated electrons and holes move in a prolonged space to reach the active sites of the RuO\(_2\) surface. As the RuO\(_2\) nanoparticle is decreased in terms of size, the probability of the surface reaction of the generated electrons and holes with adsorbed methanol and water molecules is boosted compared to that of the bulk recombination of charge carriers. At the conduction band of LaNaTaO\(_3\) perovskite, the adsorbed H\(_2\)O molecules can be effectively reduced to molecular H\(_2\) onto RuO\(_2\) nanoparticles. The ordered surface RuO\(_2\)/LaNaTaO\(_3\)
perovskite with a small particle size has promoted the suppression of carrier recombination and of active site separation to prohibit the backward reaction of O2 with H2, indicating the highly effective H2O splitting. In the case of CH3OH as a sacrificial agent, the mechanism is not clear because it is not determined whether the movement of electrons from the reduction of CH2OH radical or conduction band of LaNaTaO3 perovskite is the rate-limiting step or if the photocatalytic activity might be determined by transporting hole to the CH3OH.44,46

CONCLUSIONS

Synthesis of mesoporous RuO2/LaNaTaO3 perovskites at different RuO2 contents for the generation of molecular H2 was investigated employing the CH3OH/H2O system. The XRD findings show that mesoporous LaNaTaO3 perovskite was formed as the monoclinic structure. The adsorption isotherms of LaNaTaO3 perovskite type IV result in a mesopores structure. The H2 evolution rate in the case of pure H2O was increased from 0 to 1.29 μmol h−1 with the increase of RuO2 content from 0 to 5%. However, in the case of 10% methanol, the H2 evolution rate was increased from 0.99 to 11.54 μmol h−1 with the increase of the RuO2 content from 0 to 5%. The H2 evolution rate of 3%RuO2/LaNaTaO3 is the fastest among all of the synthesized photocatalysts. The H2 evolution rate of the 3%RuO2/LaNaTaO3 perovskite is 11.6 times higher than that of LaNaTaO3 employing 10% methanol; however, in the case of pure H2O, the H2 evolution rate of the 3%RuO2/LaNaTaO3 perovskite was enhanced 1.3 times than LaNaTaO3. The H2 evolution rate of the 3%RuO2/LaNaTaO3 perovskite employing 10% methanol is 9 times higher than employing pure H2O. The photonic efficiency of the 3%RuO2/LaNaTaO3 perovskite was enhanced 10 times than LaNaTaO3.

EXPERIMENTAL SECTION

Materials. Ruthenium((III) acetylacetonate, Ru(acac)3, sodium acetate CH3COONa, CH3COOH, Ti(OC(CH3)3)4 (TBOT), lanthanum nitrate, La(NO3)3·xH2O, tantalum(V) chloride, TaCl5, HCl, CH3OH, F-127 pluronic (EO106-PO75EO106, MW 12 600 g mol−1), and C2H5OH were procured from Sigma-Aldrich.

Preparation of Mesoporous RuO2/LaNaTaO3 Perovskites. Mesoporous La2Na1−xTaO3 (x = 0.02) perovskites were synthesized via a wet chemical approach employing F127 copolymer as a proper template. La and Na nanoparticles were homogeneously distributed into the tantalum oxide framework.
Characterization of Mesoporous RuO$_2$/LaNaTaO$_3$ Perovskites. The detailed physicochemical characterization of the developed RuO$_2$/LaNaTaO$_3$ photocatalyst was performed to have a better understanding of composition, structure, and surface morphology of the perovskite photocatalysts. The X-ray diffraction pattern was measured through Cu K$_{α1,α2}$, $λ_{α1} = 154.060$ pm, $λ_{α2} = 154.439$ pm radiation using a Bruker AXS D4 Endeavour X diffractometer. Field emission secondary electron microscopy (FE-SEM) was conducted with an FE scanning electron microanalyzer (JEOL-6300F, 5 kV). The N$_2$ isotherm of the RuO$_2$/LaNaTaO$_3$ perovskites was performed at 77 K by analyzing adsorption isotherms with a Micromeritics ASAP 2010 volumetric adsorption unit. UV−vis diffuse reflectance spectra (DRS) of the RuO$_2$/LaNaTaO$_3$ perovskites were recorded on a UV−vis spectrophotometer (UV-2600, Shimadzu) at $λ = 200−800$ nm. A VG Escalab 200R electron spectrometer was applied to examine X-ray photoelectron spectra (XPS) for RuO$_2$/LaNaTaO$_3$ perovskites equipped with a Mg Kα X-ray source powered at 100 W. The C 1s peak at 284.8 eV was employed as calibration to estimate the binding energies (BE) of 1%RuO$_2$/LaNaTaO$_3$ perovskite.

H$_2$ Generation Experiments. Hydrogen generation was conducted in a continuous flow setup containing gas supply with a mass flow controller and a 100 cm$^3$ photoreactor quartz glass with a double jacket connecting a quadrupole mass spectrometer (QMS) for H$_2$ and O$_2$ detection. The QMS sampling rate is 1 cm$^3$ min$^{-1}$, facilitating a speedy H$_2$ and O$_2$ detection. Furthermore, this experimental setup provides an online recording of the whole course of the photocatalytic hydrogen generation with the utility of the simultaneous monitoring of the formation of H$_2$ and O$_2$ gases through the photocatalytic reaction. In the experimental series, 0.05 g of the synthesized LaNaTaO$_3$ photocatalyst was mixed in 50 mL of pure H$_2$O or 10 vol % CH$_3$OH aqueous solution and was sonicated to disperse the photocatalyst. Afterward, the photoreactor was locked and connected to the QMS through the stainless steel valves. An Ar gas flux was employed to eliminate the dissolved oxygen from the reactor with the 50 cm$^3$ min$^{-1}$ flow rate for 10 min through the reactor to ensure there was O$_2$ or H$_2$ by the QMS. QMS was calibrated using standard H$_2$ and O$_2$ diluted in Ar. The flow rate of Ar gas at 10 cm$^3$ min$^{-1}$ was fixed throughout the photocatalytic system at 25 °C. Before turning on illumination, the photocatalytic reactions with magnetic stirring were kept for 40 min for stabilizing the background of photocatalytic reactions and the baseline was recorded by QMS. Afterward, the suspension was illuminated for 3 h employing an Osram XBO 1000 W Xe arc lamp as a UV source, and it stood inside a Muller LAX parallel photoreactor. During illumination, the obtained H$_2$ or O$_2$ gases were monitored under steady-state conditions. After 3 h illumination, the 1000 W Xe arc was turned off permitting the photocatalytic system to get the baseline again.

![Figure 9](image-url)

**Figure 9.** (A) Photocurrent density response of (a) LaNaTaO$_3$ and LaNaTaO$_3$ doped with RuO$_2$: (b) 1%, (c) 3%, and (d) 5%. (B) PL spectra of (a) LaNaTaO$_3$ and LaNaTaO$_3$ doped with RuO$_2$: (b) 1%, (c) 3%, and (d) 5%.

utilizing the assembly approach. To reduce possible changeability, the molar ratio of Ta$^{5+}$:F127:C$_2$H$_5$OH:HCl:CH$_3$COOH was maintained at 1:0.02:50:2.25:3.75. F-127 polymer surfactant (1.6 g) is added to 30 mL of C$_2$H$_5$OH using a magnetic stirrer at room temperature for 60 min; afterward, 0.74 mL of HCl and 2.3 mL of CH$_3$COOH were added to the clear solution F127 in ethanol, and then 1.82 g of TaCl$_5$ and 0.047 g of La(NO$_3$)$_3$·xH$_2$O were added to the above mixture. Afterward, 3.5 g of CH$_3$COONa was added with stirring for 60 min to obtain LaNaTaO$_3$ perovskite. The mesophase was put in a Petri dish for drying at 110 °C for 24 h. The as-made mesophase was annealed at 450 °C for 4 h and then 650 °C for 4 h and annealed at 900 °C for 8 h in the air to obtain mesoporous LaNaTaO$_3$ perovskite. The synthesized LaNaTaO$_3$ perovskite (1 g) was suspended in 100 mL of ethanol, and a desired amount of ruthenium(III) acetylacetonate solutions containing the equivalent amount of Ru$^{3+}$ was added to the suspension solution with sonication for 10 min to get 0.5, 1, 3, and 5% RuO$_2$/LaNaTaO$_3$ perovskites. The mixture was agitated magnetically for 3 h. The obtained samples were dried at 110 °C for 12 h and then annealed for 3 h at 450 °C to obtain mesoporous 0.5, 1, 3, and 5% RuO$_2$/LaNaTaO$_3$ perovskites.

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The authors declare no competing financial interest.

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### REFERENCES

1. Akhundi, A.; Habibi-Yangjeh, A.; Abitorabi, M.; Pouran, S. R. Review on photocatalytic conversion of carbon dioxide to value-added compounds and renewable fuels by graphic carbon nitride-based photocatalysts. Catal. Rev. 2019, 61, 595–628.

2. Ismail, A. A.; Bahnemann, D. W. Photochemical splitting of water for hydrogen production by photocatalysis: A review. Sol. Energy Mater. Sol. Cells 2014, 128, 85–101.

3. Kadi, M. W.; Mohamed, R. M.; Ismail, A. A.; Bahnemann, D. W. Decoration of mesoporous graphite-like C3N4 nanosheets by NiS nanoparticle-driven visible light for hydrogen evolution. Appl. Nanosci. 2018, 8, 1587–1596.

4. Osterloh, F. E. Inorganic materials as catalysts for photochemical splitting of water. Chem. Mater. 2008, 20, 35–54.

5. Castelli, I. E.; Landis, D. I.; Thygesen, K. S.; Dahl, S.; Chorkendorff, I.; Jaramillo, T. F.; Jacobsen, K. W. New cubic perovskites for one- and two-photon water splitting using the computational materials repository. Energy Environ. Sci. 2012, 5, 9034–9043.

6. Vojvodic, A.; Norskov, J. K. Optimizing perovskites for the water-splitting reaction. Science 2011, 334, 1355–1356.

7. Zhang, G.; Liu, G.; Wang, L.; Irvine, I. T. Inorganic perovskite photocatalysts for solar energy utilization. Chem. Soc. Rev. 2016, 45, 5951–5984.

8. Kato, H.; Kudo, A. Water splitting into H2 and O2 on alkali tantalate photocatalysts ATaO3 (=Li, Na, and K). J. Phys. Chem. B 2001, 105, 4285–4292.

9. Kato, H.; Kudo, A. Photocatalytic water splitting into H2 and O2 over various tantalate photocatalysts. Catal. Today 2003, 78, 561–569.

10. Liu, J. W.; Chen, G.; Li, Z. H.; Zhang, Z. G. Hydrothermal synthesis and photocatalytic properties of ATaO3 and ANbO3 (A= Na and K). Int. J. Hydrogen Energy 2007, 32, 2269–2272.

11. Hu, C. C.; Tsai, C. C.; Teng, H. Structure characterization and tuning of perovskite-like NaTaO3 for applications in photoluminescence and photocatalysis. J. Am. Ceram. Soc. 2009, 92, 460–466.

12. Li, X.; Zang, J. Facile hydrothermal synthesis of sodium tantalate (NaTaO3) nanocubes and high photocatalytic properties. J. Phys. Chem. C 2009, 113, 19411–19418.

13. Fu, X.; Wang, X.; Leung, D. Y.; Xue, W.; Ding, Z.; Huang, H.; Fu, X. Photocatalytic reforming of glucose over La doped alkali tantalate photocatalysts for H2 production. Catal. Commun. 2010, 12, 184−187.

14. Yokoi, T.; Sakuma, J.; Maeda, K.; Domen, K.; Tatsunami, T.; Kondo, J. N. Preparation of a colloidal array of NaTaO3 nanoparticles via a confined space synthesis route and its photocatalytic application. Phys. Chem. Chem. Phys. 2011, 13, 2563–2570.

15. Shi, J.; Liu, G.; Wang, N.; Li, C. Microwave-assisted hydrothermal synthesis of perovskite NaTaO3 nanocrystals and their photocatalytic properties. J. Mater. Chem. 2012, 22, 18808–18813.

16. Meyer, T.; Priebe, J. B.; da Silva, R. O.; Peppel, T.; Junge, H.; Beller, M.; Brückner, A.; Wohlrab, S. Advanced charge utilization from NaTaO3 photocatalysts by multilayer reduced graphene oxide. Chem. Mater. 2014, 26, 4705–4711.

17. Li, Y.; Gou, H.; Lu, J.; Wang, C. A two-step synthesis of NaTaO3 microspheres for photocatalytic water splitting. Int. J. Hydrogen Energy 2014, 39, 13481–13485.

18. Poroh, D. G.; Maggard, P. A. Flux syntheses of La-doped NaTaO3 and its photocatalytic activity. J. Solid State Chem. 2006, 179, 1727–1732.

19. Yan, S. C.; Wang, Z. Q.; Li, Z. S.; Zou, Z. G. Photocatalytic activities for water splitting of La-doped NaTaO3 fabricated by microwave synthesis. Solid State Ionics 2009, 180, 1539–1542.

20. Husin, H.; Chen, H. M.; Su, W. N.; Pan, C. J.; Chang, W. T.; Sheu, H. S.; Hwang, B. J. Green fabrication of La-doped NaTaO3 via H2O2 assisted sol–gel route for photocatalytic hydrogen production. Appl. Catal., B 2011, 102, 343–351.

21. Li, X.; Zang, J. Hydrothermal synthesis and characterization of Lanthanum-doped NaTaO3 with high photocatalytic activity. Catal. Commun. 2011, 12, 1380–1383.

22. Iwase, A.; Kato, H.; Kudo, A. The effect of Au cocatalyst loaded on La-doped NaTaO3 on photocatalytic water splitting and O2 photoreduction. Appl. Catal., B 2013, 136–137, 89–93.

23. Husin, H.; Su, W. N.; Chen, H. M.; Pan, C. J.; Chang, S. H.; Rick, J.; Chiang, W. T.; Sheu, H. S.; Hwang, B. J. Photocatalytic hydrogen production on nickel-loaded La,NaTaO3 prepared by hydrogen peroxide-water based process. Green Chem. 2011, 13, 1745–1754.

24. Mohamed, R. M.; Ismail, A. A.; Basaleh, A. S. ir, H. A. Photodeposition of Ag nanoparticles on mesoporous LaNaTaO3 nanocomposites for promotion H2 evolution. Mater. Res. Bull. 2020, 131, No. 110962.

25. Mohamed, R. M.; Ismail, A. A. Mesoporous Pt/La0.5Na0.5TaO3 nanocomposites as efficient photocatalyst for hydrogen evolution. Mol. Catal. 2020, 486, No. 110885.

26. Mohamed, R. M.; Ismail, A. A.; Basaleh, A. S.; Bawazir, H. A. Construction of highly dispersed Nd2O3 nanoparticles onto mesoporous LaNaTaO3 nanocomposites for H2 evolution. J. Photochem. Photobiol., A 2020, 400, No. 112723.

27. Mohamed, R. M.; Ismail, A. A.; Basaleh, A. S.; Bawazir, H. A. Facile fabrication of mesoporous In2O3/LaNaTaO3 nanocomposites for photocatalytic H2 evolution. Int. J. Hydrogen Energy 2020, 45, 19214–19225.

28. Sudrajat, H.; Babel, S.; Thushari, I.; Laohhasuyaratin, K. Stability of La dopants in NaTaO3 photocatalysts. J. Alloys Compd. 2019, 775, 1277–1285.

29. Iwase, A.; Teramura, K.; Hosokawa, S.; Tanaka, T. A ZnTa2O6 photocatalyst synthesized via solid state reaction for conversion of CO2 into CO in water. Catal. Sci. Technol. 2016, 6, 4978–4985.

30. Qin, R.; Song, H.; Pan, G.; Bai, X.; Dong, B.; Xie, S.; Liu, L.; Dai, Q.; Qa, X.; Ren, X.; Zhao, H. Polyol-mediated synthesis of hexagonal LaF3 nanoplates using NaNO3 as a mineralizer. Cryst. Growth Des. 2009, 9, 1750–1756.

31. Lee, J.; Watanabe, T.; Takata, T.; Hara, M.; Yoshimura, M.; Domen, K. Hydrothermal synthesis of fine NaTaO3 powder as a highly efficient photocatalyst for overall water splitting. Bull. Chem. Soc. Jpn. 2007, 80, 423–428.

32. Nelson, J. A.; Wagner, M. J. Synthesis of sodium tantalate nanorods by alkaline reduction. J. Am. Chem. Soc. 2003, 125, 332–333.

33. Lee, S.; Teshima, K.; Mizuno, Y.; Yubuta, K.; Shishido, T.; Endo, M.; Oishi, S. Growth of well-developed sodium tantalate crystals from a sodium chloride flux. CrystEngComm 2010, 12, 2871–2877.
(34) Yi, X.; Li, J. Synthesis and optical property of NaTaO₃ nanofibers prepared by electrospinning. *J. Sol-Gel Sci. Technol.* **2010**, *53*, 480–484.

(35) Lin, W. H.; Cheng, C.; Hu, C. C.; Teng, H. NaTaO₃ photocatalysts of different crystalline structures for water splitting into H₂ and O₂. *Appl. Phys. Lett.* **2006**, *89*, No. 211904.

(36) Liu, C.; Zou, B.; Rondinone, A. J.; Zhang, Z. J. Sol–gel synthesis of free-standing ferroelectric lead zirconate titanate nanoparticles. *J. Am. Chem. Soc.* **2001**, *123*, 4344–4345.

(37) Liu, J. W.; Chen, G.; Li, Z. H.; Zhang, Z. G. Hydrothermal synthesis and photocatalytic properties of ATaO₃ and ANbO₃ (A= Na and K). *Int. J. Hydrogen Energy* **2007**, *32*, 2269–2272.

(38) Fu, H.; Zhang, S.; Zhang, L.; Zhu, Y. Visible-light-driven NaTaO₃₋ₓNₓ catalyst prepared by a hydrothermal process. *Mater. Res. Bull.* **2008**, *43*, 864–872.

(39) Shannon, R. D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.*, Sect. A **1976**, *32*, 751–767.

(40) Ai, Z.; Ho, W.; Lee, S.; Zhang, L. Efficient photocatalytic removal of NO in indoor air with hierarchical bismuth oxybromide nanoplate microspheres under visible light. *Environ. Sci. Technol.* **2009**, *43*, 4143–4150.

(41) Gonçalves, R. V.; Wender, H.; Migowski, P.; Feil, A. F.; Eberhardt, D.; Boita, J.; Khan, S.; Machado, G.; Dupont, J.; Teixeira, S. R. Photochemical hydrogen production of Ta₂O₅ nanotubes decorated with NiO nanoparticles by modified sputtering deposition. *J. Phys. Chem. C* **2017**, *121*, 5855–5863.

(42) Sreethawong, T.; Ngamsinlapasathian, S.; Suzuki, Y.; Yoshikawa, S. Nanocrystalline mesoporous Ta₂O₅-based photocatalysts prepared by surfactant-assisted templating sol–gel process for photocatalytic H₂ evolution. *J. Mol. Catal. A: Chem.* **2005**, *235*, 1–11.

(43) Noda, Y.; Lee, B.; Domen, K.; Kondo, J. N. Synthesis of crystallized mesoporous tantalum oxide and its photocatalytic activity for overall water splitting under ultraviolet light irradiation. *Chem. Mater.* **2008**, *20*, 5361–5367.

(44) Ivanova, I.; Kandiel, T. A.; Cho, Y. J.; Choi, W. J.; Bahnemann, D. Mechanisms of photocatalytic molecular hydrogen and molecular oxygen evolution over La-doped NaTaO₃ particles: Effect of different cocatalysts and their specific activity. *ACS Catal.* **2018**, *8*, 2313–2325.

(45) Linsebigler, A. L.; Lu, G.; Yates, J. T., Jr. Photocatalysis on TiO₂ surfaces: principles, mechanisms, and selected results. *Chem. Rev.* **1995**, *95*, 735–758.

(46) Schneider, J.; Bahnemann, D. W. Undesired role of sacrificial reagents in photocatalysis. *J. Phys. Chem. Lett.* **2013**, *4*, 3479–3483.