

Highly donor-doped (110) layered perovskite materials as novel photocatalysts for overall water splitting

Hyun G. Kim, Dong W. Hwang, Jindo Kim, Young G. Kim and Jae S. Lee*

Department of Chemical Engineering and School of Environmental Engineering, Pohang University of Science and Technology, San 31 Hyoja-dong, Pohang, 790-784, Korea. E-mail: jlee@postech.ac.kr

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Highly donor-doped (110) layered perovskite materials with a generic composition of $A_mB_mO_{3m+2}$ ($m = 4, 5$; $A = Ca, Sr, La$; $B = Nb, Ti$) loaded with nickel have been found to be efficient photocatalysts for overall water splitting with quantum yields as high as 23% under UV irradiation.

Among various methods of solar energy conversion, photocatalytic splitting of water into H_2 and O_2 has received most attention because of its potential to obtain directly clean and high-energy containing H_2 from abundant H_2O . Since its discovery in 1972,¹ water splitting with semiconductor photocatalysts under ultraviolet (UV) irradiation has become the subject of extensive studies.^{2–4} However, quantum yields (% of absorbed photons that have been actually used to generate a photoreaction product) for well known photocatalysts such as TiO_2 and $SrTiO_3$ are very low (*ca.* <1%). Recently, (100) layered perovskite materials such as $K_4Nb_6O_{17}$ and $A_4Ta_xNb_{6-x}O_{17}$ ($A = K, Rb$) were found by Domen and coworkers to be much more efficient, showing quantum yields of *ca.* 5%.^{5,6} This greatly improved quantum yield has been attributed to the use of their interlayer spaces as reaction sites. Inoue *et al.*⁷ have reported an efficient water splitting over RuO_2 – $BaTi_4O_9$ with a tunnel structure. However, it is desirable to find photocatalytic materials with even higher quantum yields in order for the water splitting to become a viable method to solve both energy and environmental problems in the future.

Here, we report a group of novel photocatalysts for overall water splitting with photon yields as high as 23% under UV irradiation. The materials are a series of homologous structures based on perovskite-type slabs with a generic composition of $A_mB_mO_{3m+2}$ ($m = 4, 5$; $A = Ca, Sr, La$; $B = Nb, Ti$) loaded with nickel. Unlike the (100) layered perovskite-type materials reported by the Domen group, our materials have the perovskite slabs parallel to (110) relative to the perovskite structure and are highly donor-doped. These structural and electronic characteristics are believed to be responsible for the much improved quantum yields.

For the preparation of the photocatalysts, *ca.* 10 g of commercial powders of metal carbonates and oxides were mixed in a desired composition and pressed in the form of a pellet. Pellets were calcined at 1123–1173 K for 6 h in an electric furnace and sintered at 1273–1623 K for 5 h. The presence of the (110) perovskite phase in the sintered ceramics was confirmed by X-ray diffraction (XRD) analysis using $Cu-K\alpha$ radiation. Particle sizes of 0.5–8 μm were obtained by pulverizing the sintered pellets in a mortar. In order to obtain photocatalysts exhibiting high activities for water splitting, it was essential to load a transition metal on our perovskite materials and nickel was found to be the most effective. Thus, perovskite powders were impregnated with an aqueous $Ni(NO_3)_2$ solution to give a Ni loading of 1 wt% which was determined to be the optimum loading that gave the highest rate of water splitting. Ni-loaded $A_mB_mO_{3m+2}$ ($m = 4, 5$) catalysts were reduced with dihydrogen at 973 K, and then oxidized with oxygen at 473 K. This reduction–oxidation procedure was found to be an effective method to obtain active photocatalysts based on (100) layered perovskite materials.^{5,6}

The photocatalytic decomposition of water was carried out at room temperature in a closed gas circulation system using a high pressure Hg lamp (450 W) placed in an inner irradiation-type quartz reaction cell. The catalyst (1.0 g) was suspended in distilled water (350 mL) by magnetic stirring. The rates of H_2 and O_2 evolution were determined by a gas chromatograph.

Fig. 1 shows a typical time course of H_2 and O_2 gas evolution for the photocatalytic decomposition of water over $Ni/Sr_2Nb_2O_7$. Note that $Sr_2Nb_2O_7$ is the reduced formula of $Sr_4Nb_4O_{14}$, the first member of the series $A_mB_mO_{3m+2}$ with $m = 4$. The catalyst produces H_2 (402 $\mu mol h^{-1}$) and O_2 (198 $\mu mol h^{-1}$) in a stoichiometric ratio ($H_2 : O_2 = 2 : 1$). In early studies of water splitting, the simultaneous evolution of O_2 and H_2 (overall water splitting) had been a challenge due to the difficulty of O_2 formation and the rapid reverse reaction between the two products. Furthermore, the reaction proceeds at steady rates with no indication of catalyst deactivation for 20 h during which the mol of H_2 produced are greater than the mol of the catalyst by factors of *ca.* 50 for Ni and *ca.* 2 for Nb contained in the whole catalyst. Since two electrons are needed to produce a molecule of H_2 from water, the latter corresponds to the turnover number of 4 if all Nb atoms have participated in the water splitting. This demonstrates that overall water splitting on this material proceeds *catalytically*.

Table 1 summarizes results of water decomposition and catalyst characterization for a number of photocatalysts. Our (110) layered perovskite catalysts ($Ca_2Nb_2O_7$, $Sr_2Nb_2O_7$, $La_2Ti_2O_7$ and $La_4CaTi_5O_{17}$) are compared with previously known (100) layered perovskite catalysts ($K_4Nb_6O_{17}$ and $K_4Ba_2Ta_3O_{10}$) and bulk-type TiO_2 catalyst (Degussa P-25), all under the same reaction conditions. $La_4CaTi_5O_{17}$ is the second member of $A_mB_mO_{3m+2}$ with $m = 5$. All perovskite-type catalysts were loaded with Ni, while Pt was loaded onto TiO_2 because Pt is known to be the best modifier for TiO_2 . The BET surface areas of all perovskite-type photocatalysts fabricated by sintering at 1250 °C for 5 h are 4–5 $m^2 g^{-1}$. The band gap energies estimated from UV–VIS diffuse reflectance spectra of all catalysts are in the UV energy region of 3.1–4.3 eV. A

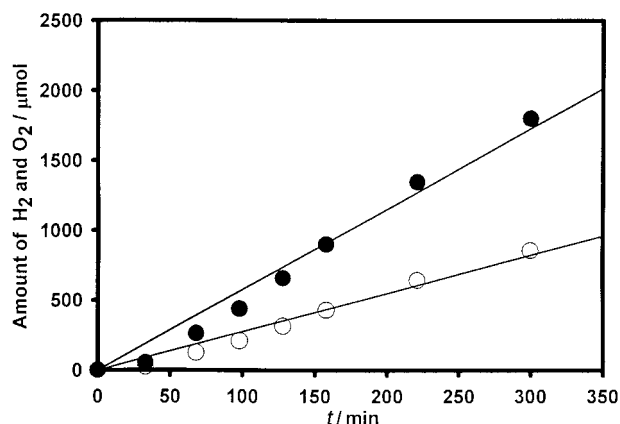


Fig. 1 Time courses of H_2 (●) and O_2 (○) evolution from distilled water over Ni (1.0 wt%)/ $Sr_2Nb_2O_7$.

Table 1 Physical properties, H₂ evolution rates and quantum yields for various photocatalysts

Catalyst ^a	BET surface area/m ² g ⁻¹	Band gap/eV	Second harmonic generation	Rate of H ₂ evolution/μmol h ⁻¹	Quantum yield (%)
Ca ₂ Nb ₂ O ₇	4.2	4.3	Yes	101	7 (< 288 nm)
Sr ₂ Nb ₂ O ₇	5.1	4.1	Yes	402	23 (< 300 nm)
La ₂ Ti ₂ O ₇	5.2	3.2	No	441	12 (< 360 nm)
La ₄ CaTi ₅ O ₁₇	4.9	3.8	No	499	20 (< 320 nm)
TiO ₂	50.0	3.1	—	0.3	< 1 (< 360 nm)
K ₄ Nb ₆ O ₁₇	4.5	3.3	No	210	5 (< 360 nm)
KBa ₂ Ta ₃ O ₁₀	4.2	3.5	No	150	8 (< 350 nm)

^a All perovskite-type catalysts were loaded with Ni [1.0 wt% for (110) layered materials and 0.1 wt% for (100) layered materials] while 1.0 wt% Pt was loaded onto TiO₂.

second harmonic generation (SHG) in Ca₂Nb₂O₇, La₂Ti₂O₇ and K₄Nb₆O₁₇ ceramics was checked by using a fundamental wave of a pulsed Nd³⁺:YAG laser at wavelength of 1064 nm as the incident light since Sr₂Nb₂O₇ is a known non-linear optical material showing SHG.⁸ Although a SHG was clearly observed in Ca₂Nb₂O₇, La₂Ti₂O₇ and K₄Nb₆O₁₇ ceramics exhibited no SHG.

It is clear that (110) layered perovskite catalysts are, as a group, much more active than previously known (100) layered perovskite or bulk-type TiO₂ for the photocatalytic decomposition of water into H₂ and O₂ under UV irradiation. The rate of H₂ evolution over Pt/TiO₂ was a mere 0.3 μmol h⁻¹. Dramatic improvement is observed for Ni-doped (100) layered perovskites and still further for (110) layered perovskites. The quantum yield of H₂ evolution over photocatalysts was estimated by using the chemical actinometer ferrioxalate⁹ [Fe(C₂O₄)₃³⁻] based on known photon absorbance during the reduction of Fe³⁺ to Fe²⁺. The quantum yield is the more meaningful parameter than the rate of H₂ evolution itself to gauge the performance of a photocatalyst because the rate is normalized against the absorbed photons. The photon flux from the UV lamp varies depending on the wavelength and, hence, the quantum yield is not necessarily proportional to the rate of H₂ production when semiconductors of different band gaps are used as catalysts. Yet, it is again clear that (110) layered perovskite materials are superior to previously known photocatalysts also in terms of the quantum yield. In fact, to the best of our knowledge, the quantum yield of 23% is the highest among reported semiconductor photocatalysts for overall water splitting. The quantum yield of 5% for K₄Nb₆O₁₇ is in agreement with the previous reports for the same material.^{5,6}

Examination of quantum yields listed in Table 1 reveals that the superior performance of A_mB_mO_{3m+2} (m = 4,5) is general and not limited to one specific composition. Probably, their structure is important for photocatalytic activity. Compounds with structures that are composed of slabs with distorted perovskite-type atomic configurations are classified into two groups according to the geometrical relations of the slabs to the perovskite structure.¹⁰ The slabs in (100) layered perovskites^{11,12} are obtained by cutting the perovskite structure parallel to (100) and those in (110) layered perovskites¹³ are parallel to (110).

As mentioned, (100) layered perovskites^{5,6} or tunnel structures⁷ have received attention recently since they are much more active than the generally used TiO₂ or SrTiO₃ for photocatalytic water splitting. The high activity of these materials has been attributed to effective utilization of interlayer space as reaction sites. We have discovered that the (110) layered perovskites of A_mB_mO_{3m+2} (m = 3, 4; A = Ca, Sr, La; B = Nb, Ti) are still more active with unprecedentedly high quantum yields. These novel photocatalysts are of a layered structure and hence the contribution of interlayer space as reaction sites is expected as in (100) layered perovskite materials. Yet, we have to consider other factors to account for the further increased quantum yields.

If the TiO₂ component of CaTiO₃ or SrTiO₃ with the ideal perovskite structure is completely replaced by Nb₂O₅, the product is Ca₂Nb₂O₇ or Sr₂Nb₂O₇. The replacement of Ti⁴⁺ by Nb⁵⁺ results in excess electrons and slabs of a distorted perovskite structure of m unit cells thick in order to accommodate excess oxygen.¹³ This also occurs when Ca²⁺ or Sr²⁺ is replaced by La³⁺ as in La₂Ti₂O₇. This structural substitution gives highly donor-doped (110) layered perovskite materials A₄B₄O₁₄, commonly denoted as A₂B₂O₇. When a part of the oxygen is lost, the next structure A₅B₅O₁₇ in the series is obtained as in La₄CaTi₅O₁₇. In the photocatalytic water splitting over a semiconductor, excited electron-hole pairs are generated when the catalyst is illuminated with light having energy equal to or greater than the band gap. The principal challenge is how to suppress the energy-wasteful recombination of the formed electron-hole pairs. Recombination is usually much more facile than the subsequent steps needed for water cleavage. In a semiconductor-liquid interface, the electron-hole pairs are separated by the electric field present in the depletion layer. It is expected that the highly donor-doped (110) perovskite would create a narrower depletion layer than undoped perovskite as is observed for metal-ion doped TiO₂.¹⁴ Band bending would then take place on a depletion layer with a narrower width or become more drastic.¹⁵ Finally, the increased band bending would allow more efficient charge separation and enhance the overall quantum yield of water splitting.

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