Photocatalytic Activity for Water Decomposition using Two-Dimensional Oxide Materials

Kenji Toda, Sun-Woog Kim, Hironori Ishikawa, Tadashi Ishigaki, Shinnosuke Kamei, Kazuyoshi Uematsu, Mineo Sato, Takaki Masaki, and Dae-HoYoon

***Abstract*—**We synthesized double layered indium perovskite, $La_2BaIn_2O_7$, and measured their photocatalytic activity for water decomposition. Two-dimensional layered perovskite, $La_2BaIn_2O_7$ has high photocatalytic activity for the decomposition in pure water under UV light irradiation without co-catalyst.

***Keywords*—**Water splitting, Photocatalytic activity, Layered perovskite structure, Indate

I. Introduction

THE decomposition of water into H_2 and O_2 using semiconductor photocatalysts has been intensively investigated for solar energy conversion and storage [1]. Many d^0 electron configuration titanates and tantalates such as $NaTaO_3$: La were well-known to show high photocatalytic activity for the water decomposition under UV light irradiation [2-4]. However, the UV light occupies only ca. 5% of the whole solar energy, while the visible light accounting for ca. 40% is open to utilization. Since the tantalates and titanates have a wide bandgap, such oxide photocatalysts cannot absorb long wavelength sunlight efficiently. The response to visible light is required for the photocatalytic water splitting from the view point of efficient solar energy conversion. Although many visible-light-driven photocatalysts have been proposed as potential candidates for overall water splitting, a satisfactory material has yet to be reported. Recently, p-block metal ions with d^{10} electron configuration such as Ga^{3+}, In^{3+}, Sn^{4+} and Sb^{5+} became a core element to be photocatalytic activity in pure water decomposition [5]. Although many indates have a moderate bandgap, few reports are available on photocatalytic activity for the water decomposition. In this study, we investigated the photocatalytic activity of layered perovskite $La_2BaIn_2O_7$ with d^{10} electron configuration [6].

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II. Experimental

$La_2BaIn_2O_7$ powders were successfully synthesized by a conventional solid state reaction. Stoichiometric amounts of powdered carbonates or oxides ($BaCO_3$, La_2O_3 and In_2O_3) were mixed together and fired at 1573 K for 12 h in air. The crystal structure of the obtained sample was characterized by X-ray powder diffraction (MAC Science; MX Labo) with Cu Kα radiation (40 kV, 25 mA) at room temperature. Diffuse reflectance spectra were measured with UV–Vis spectrometer (Jasco; V-550). The optical band-gap energy was calculated from onset of absorption edges.

The photocatalytic decomposition of water was performed with a gas-closed circulating system (Figure 1). Catalysts (0.5 g) were suspended in distilled water (200 ml). A 400 W, high-pressure mercury lamp (Riko-Kagaku Sangyo Co., UVL - 400HA) was employed as light source. The lamp high-pressure mercury irradiated most strongly at 365 nm within the range of 312–577 nm. Before the reaction, the mixture was degassed completely and then Ar (ca. 15 kPa) was introduced. The evolved gases were collected to the sampler (3 ml), directly connected to the closed gas circulation system to avoid any contamination from air and analyzed by gas chromatograph (Hitachi, TCD, molecular sieve 5A column and Ar carrier).

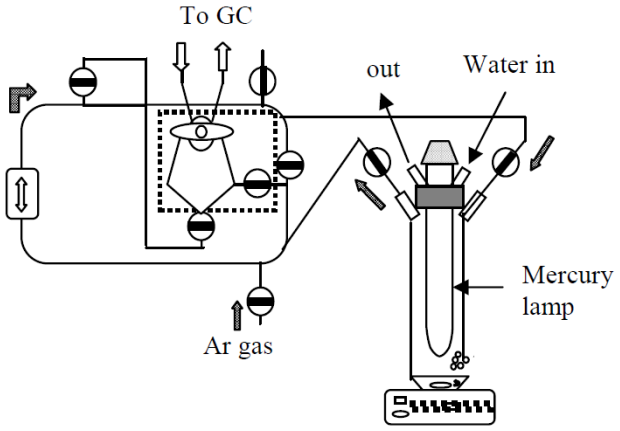

Fig. 1 Schematic diagram of gas evolution measurement system for the water decomposition by the photocatalytic reaction.

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III. Result and Discussion

As shown in Figure 2, XRD pattern confirmed that the sample of layered perovskite $La_2BaIn_2O_7$ is a single phase [6]. The crystal structure of layered perovskite $La_2BaIn_2O_7$ is shown in Figure 3. $La_2BaIn_2O_7$ belong to the Ruddlesden - Popper (RP) family with a general formula, $A_2[A'_{n-1}B_nO_{3n+1}]$ (A, A' = alkali, alkaline earth, or rare earths; B = transition metal) [7]. The A' cations with 12 coordination number are located in the perovskite layer. The A cations have 9 coordination number, and is located at the interlayer with a rock salt structure. These compounds have attracted considerable attention due to their unique properties, for example, optical properties, and electrical transport properties and especially its excellent photocatalytic activity [8].

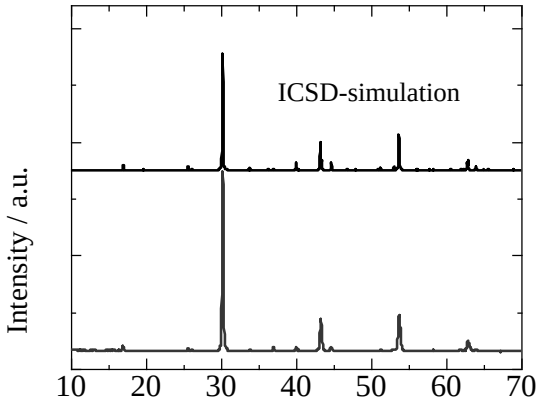

Fig. 2 Powder XRD patterns of $La_2BaIn_2O_7$.

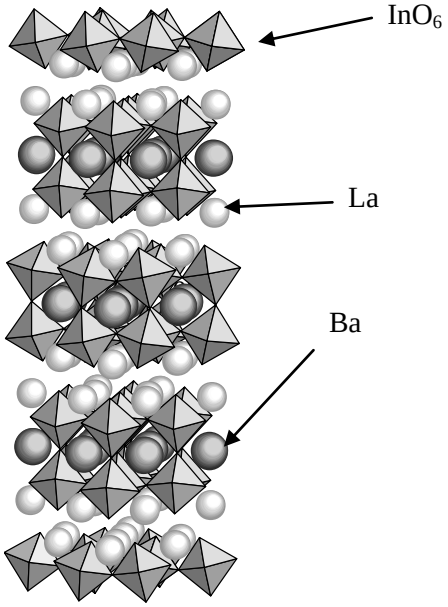

Fig. 3 Crystal structure of $La_2BaIn_2O_7$.

The UV-Vis diffuse reflectance spectra of $La_2BaIn_2O_7$ are shown in Figure 4. $La_2BaIn_2O_7$ show yellow bodycolor because of absorption of blue color region (400 – 500 nm). Since the single phase $La_2BaIn_2O_7$ showed obvious absorption in visible light region up to 500 nm, the indate photocatalyst has the ability to respond to visible light.

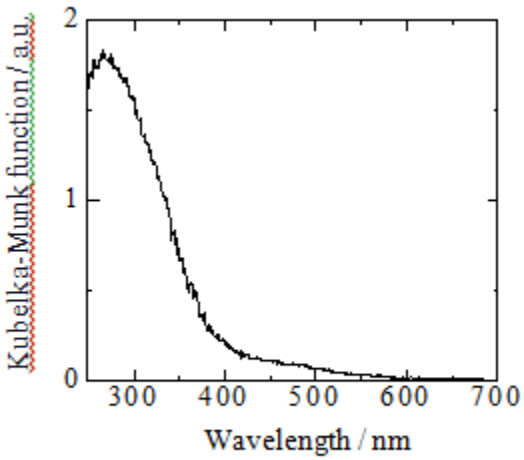

Fig. 4 UV-Vis diffuse reflectance spectra of $La_2BaIn_2O_7$.

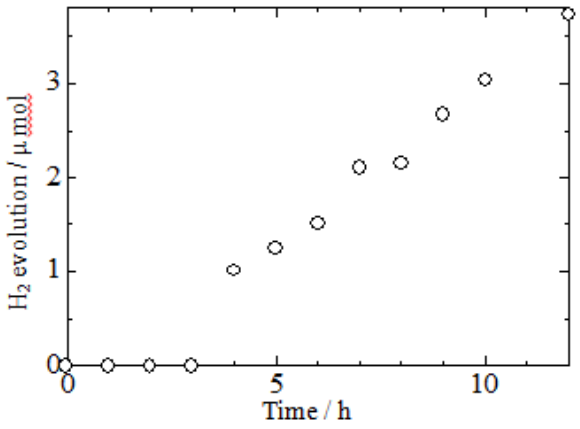

Fig. 5 Photocatalytic activity of $La_2BaIn_2O_7$.

Figure 5 show the photocatalytic activity of $La_2BaIn_2O_7$. It shows the photocatalytic H_2 evolution from pure water under UV light irradiation over the $La_2BaIn_2O_7$ photocatalyst. The amount of gas evolved increased with the progress of reaction time without deactivation. H_2 evolution rates are estimated to be 0.3 μ mol h^{-1} for $La_2BaIn_2O_7$. The influence of the UV light irradiation was also investigated by light on/off shutter studies over $La_2BaIn_2O_7$. Photocatalytic water splitting activity (H_2 evolution) for $La_2BaIn_2O_7$ without loading of the co-catalysts was identified.

As described above, p-block metal oxides including indates, zinc gallate and strontium stannate were found to be photocatalysts for water decomposition under UV illumination. The overall photocatalytic water splitting reaction involves three steps: (1) absorption of light to generate electron-hole pairs, (2) charge separation and migration to the surface of photocatalyst, and (3) water reduction and oxidation reaction

on the surface. The cocatalysts loaded on the photocatalysts can serve as the reaction site and promote the charge separation. Therefore, most of photocatalysts support an expensive co-catalyst such as Pt, NiO and RuO_2. Several reports have demonstrated that layered oxides $K_4Nb_6O_{17}$ and $K_2La_2Ti_3O_{10}$ show a much higher activity for water splitting than the bulk-type catalysts [9,10]. These facts suggest that physical separation of the electron and hole pairs generated by photoabsorption can suppress the electron-hole recombination process. In the view of this point, we hypothesized that low-dimensional structures could retard the electron-hole recombination, creating structures that show high activity for water splitting.

Therefore, we focused our research on a low-dimensional structure photocatalyst with d^{10} electron configuration. As a result, we could obtained novel photocatalyst, $La_2BaIn_2O_7$ with the layered perovskite structure. To the best of our knowledge, this is the first report of photocatalytic activity in the two-dimensional indate without a cocatalyst for water splitting under UV irradiation.

IV. Conclusion

Layered perovskite $La_2BaIn_2O_7$ showed the photocatalytic hydrogen production without loading co-catalysts. The UV−vis spectra showed that $La_2BaIn_2O_7$ absorbed visible light and that the band gap energy of $La_2BaIn_2O_7$ was smaller than that for the conventional layered perovskite photocatalyst with d^0 electron configuration, suggesting that the $La_2BaIn_2O_7$ may show photocatalytic activity under visible light.

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