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Effect of Precursors on the Morphology and the Photocatalytic Water-Splitting Activity of Layered Perovskite $La_2Ti_2O_7$

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Abstract−A [110] layered perovskite, $La_2Ti_2O_7$, was a good photocatalyst under ultraviolet light in water splitting reaction. The material was synthesized with La_2O_3 and TiO_2 as precursors by solid-state transformation. The morphology and photocatalytic activity of $La_2Ti_2O_7$ depended on the preparation methods, as well as purity and morphology of the precursors. Wet-grinding of precursors in ethanol gave a product with higher crystallinity and phase purity, and thus higher photocatalytic activity, than dry-grinding without solvent. It was important to reduce the particle size of La_2O_3, as it usually had larger initial particle sizes than TiO_2. Thus, the particle size of La_2O_3 had a strong effect on the crystallinity and surface area of the product $La_2Ti_2O_7$. On the other hand, a severe chemical purity control was required for TiO_2, while the effect of morphology was relatively small. In all cases, a high degree of crystallinity and purity of the prepared $La_2Ti_2O_7$ was critical to show a high photocatalytic water-splitting activity.

Key words: Layered Perovskite, Photocatalyst, Water Splitting, $La_2Ti_2O_7$, Precursor

INTRODUCTION

Photocatalytic water splitting directly produces clean and high energy-containing H_2 in a CO_2-neutral manner from abundant H_2O using solar energy. If successfully developed with economic viability, this could be the ultimate technology that could solve future energy and environmental problems. The possibility of solar energy harvesting using semiconductor-based photoelectrodes was demonstrated in the 1950s [Williams, 1960]. TiO_2 electrode was first studied for water splitting under ultraviolet (UV) light [Boddy, 1968; Fujishima and Honda, 1971; Fujishima and Honda, 1972].

Splitting a water molecule requires that photocatalysts have band gaps larger than at least the theoretical dissociation energy of water (1.23 eV) and band edges must also be positioned appropriately with respect to the redox potential of the water splitting reaction. As the conduction band edge position of TiO_2 is almost the same as the reduction potential of water, some external bias is indispensable. With $SrTiO_3$ of appropriate band edge position, Wagner et al. [Wagner and Somorjai, 1980] could split water without external bias with about a quantum yield of 5% under UV light. The quantum yield is defined as the number of hydrogen atoms produced divided by the number of photons absorbed by the photocatalyst. Later, some researchers performed a water-splitting reaction using colloidal platinized TiO_2 and $SrTiO_3$ systems [Damme and Hall, 1979].

Recently, $K_4Nb_6O_{17}$ and $A_4Ta_xNb_{6-x}O_{17}$ (A=K, Rb) with (100) layered structure showed much improved quantum yields of *ca.* 10% [Domen et al., 1986]. These layered materials use their interlayer space as reaction sites, where electron-hole recombination process could be retarded by physical separation of electron and hole pairs generated by photo-absorption. The present investigators also found novel photocatalysts, (110) layered perovskite materials [Schmalle et al., 1993; Ishizawa et al., 1982; Balachandran and Eror, 1989], which showed much-improved photon yields as high as 23% [Kim et al., 1999]. The materials are a series of homologous structures with a generic composition of $A_mB_mO_{3m+2}$ (m=4, 5; A=Ca, Sr, La; B=Nb, Ti). Fig. 1 shows the schematic feature of the layered structure of $La_2Ti_2O_7$ [Williams et al., 1991], a member of (110) layered perovskite materials with m=4. The layers are parallel to (110) planes of perovskite structure. At the moment, photon yields as high as 30% under UV light have been reported for this type of semiconductor photocatalyst.

During our study of these materials, it has been observed that performance of the photocatalysts varies widely with the catalyst

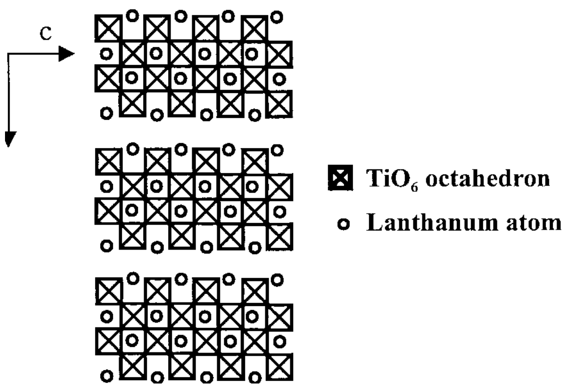

Fig. 1. Layered structure of $La_2Ti_2O_7$.

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‡This paper is dedicated to Professor Wha Young Lee in honor of his retirement from Seoul National University.

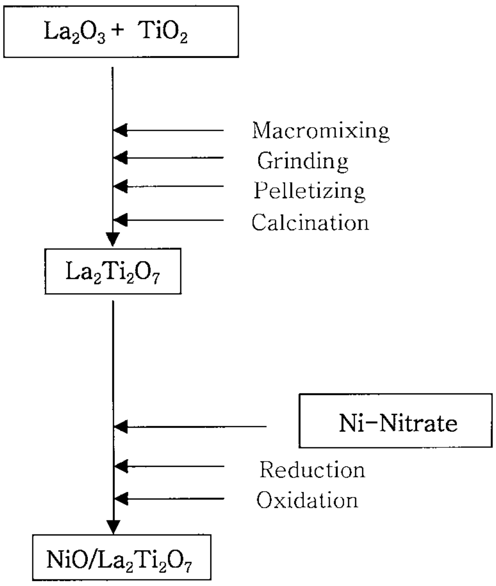

Fig. 2. A procedure to prepare of layered perovskites and nickel-loaded photocatalyst.

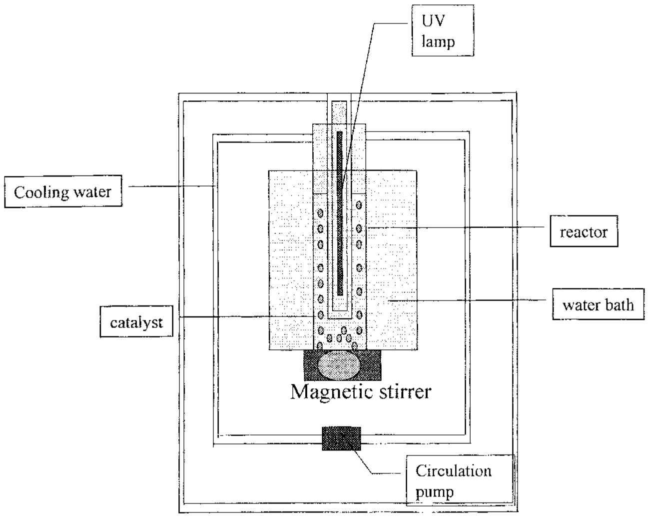

Fig. 3. A closed circulation reaction system for photocatalytic water splitting.

preparation conditions. This might also be the source of some discrepancies in reports from different laboratories [Hwang et al., 2000; Kudo et al., 2000]. These mixed oxides are usually prepared by a solid-state transformation, which involves mixing and grinding of each precursor oxide powders followed by calcining at high temperatures. This solid transformation is a very slow process [Zhong et al., 1995] and governed by a number of factors [Shin et al., 1993] including morphology, particle size, and purity of the precursors and the grinding methods. In this study, we investigated the effects of these preparation variables on the structure and photocatalytic water-splitting activity of resulting perovskite oxides. We chose $La_2Ti_2O_7$ as a representative of (110) layered perovskite materials, which can be synthesized from La_2O_3 and TiO_2 as precursors [Marzullo and Bunting, 1958; MacChesney and Sauer, 1962].

EXPERIMENTAL

1. Synthesis of Layered Perovskite $La_2Ti_2O_7$

Layered perovskites used in this research were prepared by the typical solid-state transformation with the dry grinding method or slurry grinding method. The typical material preparation procedure is shown in Fig. 2. In the dry-grinding method, a mixture of precursor oxides or carbonates in the stoichiometric ratio was ground directly in dried powder state, or in the slurry grinding method it was ground in slurry state with ethanol and dried in an oven.

In the preparation of $La_2Ti_2O_7$, we used La_2O_3 (Aldrich, 99.99%), $La(OH)_3$ (Aldrich, 99.9%) and $La_2(CO)_3$ (Aldrich, 99.9%) as La sources and several anatase-TiO_2 (Aldrich, 99.99%; MTA-500, 99.9%; Hombikat, 99.9%; P25, 99.99%) and rutile-TiO_2 (Aldrich, 99.999%) as Ti sources. Some of La precursors, $La(OH)_3$ and La_2

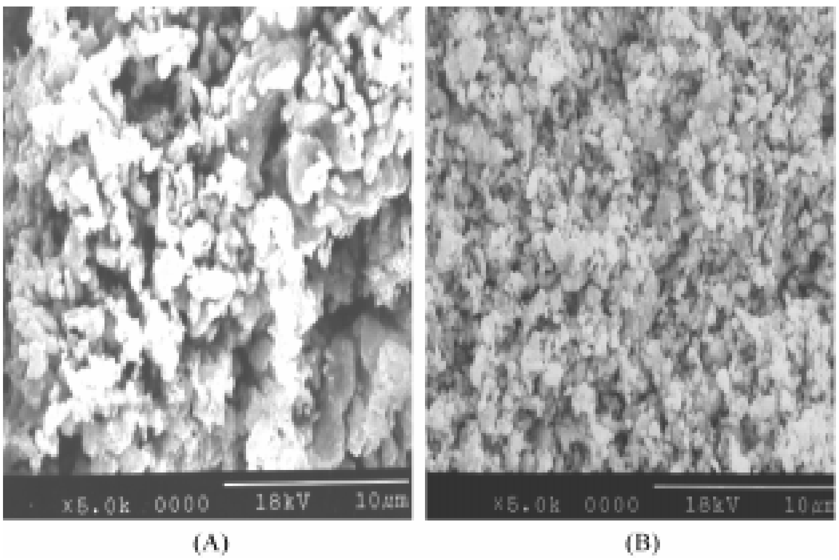

Fig. 4. Scanning electron microscope of $La_2Ti_2O_7$ prepared with different grinding methods.
(A) Dry grinding method, (B) Wet grinding method

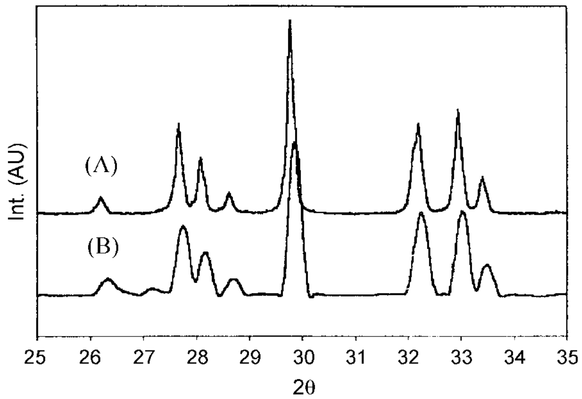

Fig. 5. XRD patterns of $La_2Ti_2O_7$ prepared with different grinding methods.
(A) Wet grinding method, (B) Dry grinding method

$(CO_3)_3$, were precalcined at 823 K to obtain La_2O_3 first. The precursors of La_2O_3 and TiO_2 were roughly mixed in a mortar (macro-mixing), ground manually, and then calcined at 1,273 K for 10 h in static air. Prepared $La_2Ti_2O_7$ samples were converted to active photocatalysts as $NiO/La_2Ti_2O_7$ by loading 1 wt% of Ni by an incipient impregnation method [Sakata and Kawai, 1983]. Thus, a determined amount of aqueous nickel nitrate solution was added to the weighed perovskite material, dried in an oven at 373 K, and calcined at 573 K in air for 1 h. The Ni-loaded perovskites were then reduced by flowing H_2 in a Pyrex cell at 773 K for 2 h and oxidized by air at 473 K for 1 h.

2. Characterization

Powder X-ray diffraction (XRD) patterns of the prepared layered perovskites were obtained on a Mac Science M18XHF diffractometer using Cu Kα radiation (40 kV, 200 mA). The BET surface area was determined by N_2 adsorption at 77 K in a constant volume adsorption apparatus (Micrometrics Accusorb 2100E). The morphology of the samples was observed by SEM on a Hitachi S-2460N electron microscope. For SEM analysis, calcined pellets were examined directly without post grinding.

3. Photocatalytic Water-Splitting Reaction

The photocatalytic activity of the water splitting reaction was measured at room temperature in a closed, circulating reactors shown in Fig. 3. A high-pressure Hg lamp (Ace glass Inc, 450 W) was used as a UV source. An aliquot of 0.3 g catalyst was suspended in distilled water (500 ml) by magnetic stirring and the concentrations of generated H_2 and O_2 were analyzed by GC (HP6890) with TCD (Molecular Sieve 5 Å, Ar Carrier).

RESULTS AND DISCUSSION

1. Effects of Grinding Methods of the Precursor Mixture

Our photocatalyst $La_2Ti_2O_7$ was synthesized from La_2O_3 and TiO_2

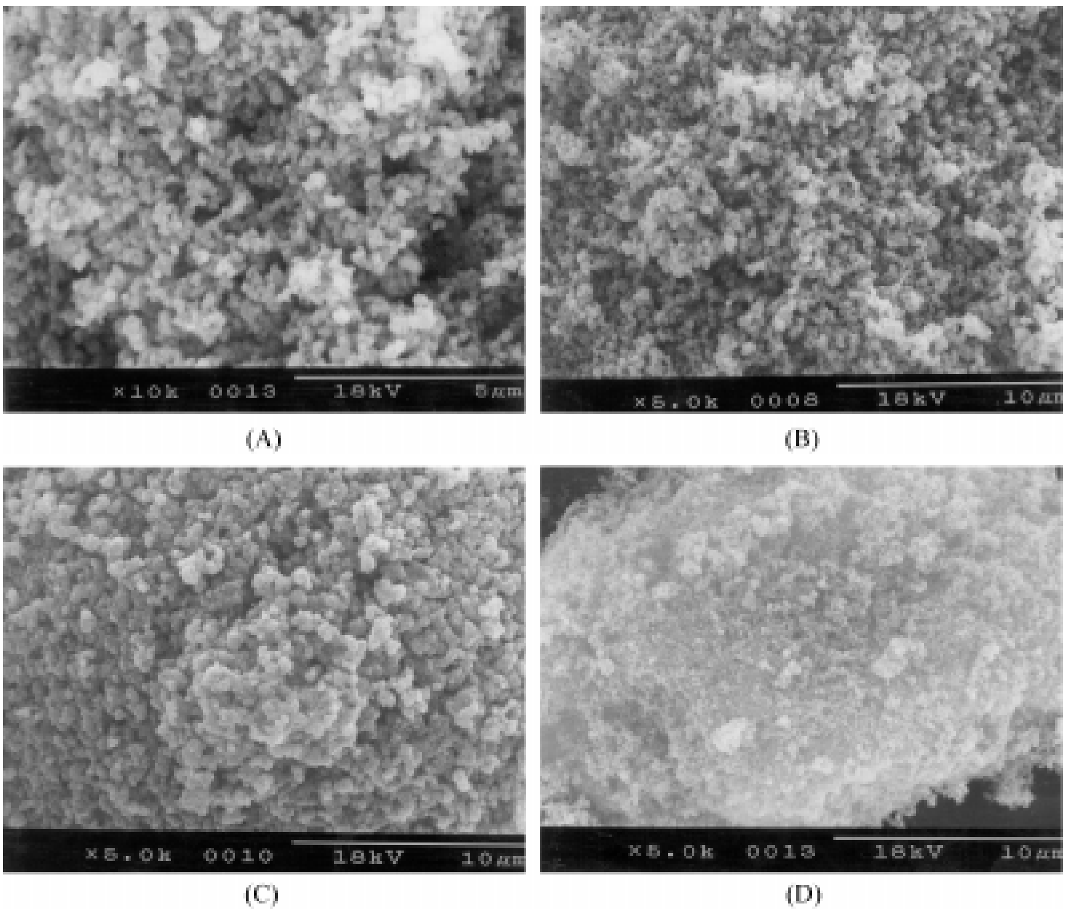

Fig. 6. Scanning electron microscope of several TiO_2 precursors used as Ti precursor for the synthesis of $La_2Ti_2O_7$.
(A) Antase-TiO_2 (Aldrich), (B) TiO_2-MTA, (C) TiO_2-Hombikat, (D) TiO_2-P25

as precursors by solid-state transformation. Each precursor oxide was mixed and ground together prior to calcinations in static air at 1,173-1,273 K. We found that photocatalytic water splitting activity of $La_2Ti_2O_7$ was highly dependent on the grinding method for the precursor La_2O_3-TiO_2 mixture. The "wet grinding" was done for the precursor mixture-ethanol slurry, while "dry grinding" was done for dry powders without any solvent. Both catalysts were calcined at 1,273 K for 10 h after grinding and loaded with 1 wt% nickel. After reduction/oxidation treatment, NiO/$La_2Ti_2O_7$ catalysts prepared from wet-ground precursor mixtures showed much higher water-splitting activity than those prepared from dry-ground precursor mixtures. In one case, it was 473 μmol/h of H_2 generation vs. 150 μmol/h under otherwise the same preparation and reaction conditions.

The two $La_2Ti_2O_7$ catalysts from differently ground precursors were characterized by SEM and XRD. As shown in Fig. 4, wet-grinding gives $La_2Ti_2O_7$ with rather uniform particle sizes of 1-2 μm, while dry-grinding gives particles with non-uniform shapes and sizes of 1-5 μm. XRD patterns shown in Fig. 5 indicate that $La_2Ti_2O_7$ prepared from wet-ground precursors has a higher crystallinity. Furthermore, the catalyst prepared from dry-ground precursors contained an impurity phase derived from unreacted La_2O_3. Thus it appears that dry-grinding is not efficient for obtaining uniform and small precursor particles that would facilitate slow solid-state transformation. Higher crystallinity and phase purity of $La_2Ti_2O_7$ prepared from wet-ground precursors appear to be responsible for its higher photocatalytic water-splitting activity. Hereafter, all the catalysts studied in this paper were prepared by employing the wet-grinding method.

2. Effect of TiO_2 Precursor

In order to study the effect of TiO_2 precursors, commercial TiO_2 samples obtained from different sources have been examined as precursors to $La_2Ti_2O_7$ with the source of La_2O_3 fixed (Aldrich). As shown in Fig. 6 morphologies of these precursors were widely different. Although these precursors were ground in the same manner (wet grinding) before calcination, it was found that the nature of these precursors had a great effect on the produced $La_2Ti_2O_7$ as shown in Figs. 7-8. Photocataytic activities of $La_2Ti_2O_7$ prepared from different TiO_2 samples are compared in Table 1 together with surface areas of $La_2Ti_2O_7$ and of precursors. From these data, it would be

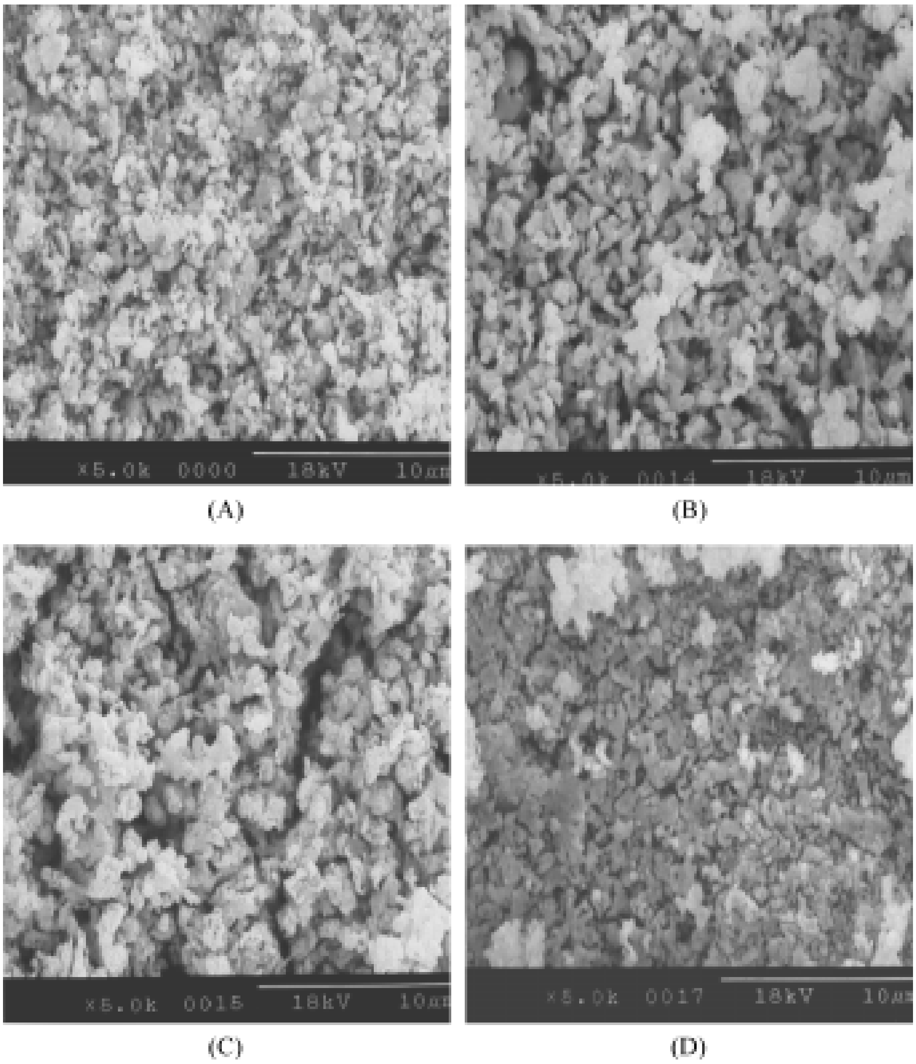

Fig. 7. Scanning electron microscope of several $La_2Ti_2O_7$ prepared with several TiO_2 precursors.
(A) Antase-TiO_2 (Aldrich), (B) TiO_2-MTA, (C) TiO_2-Hombikat, (D) TiO_2-P25

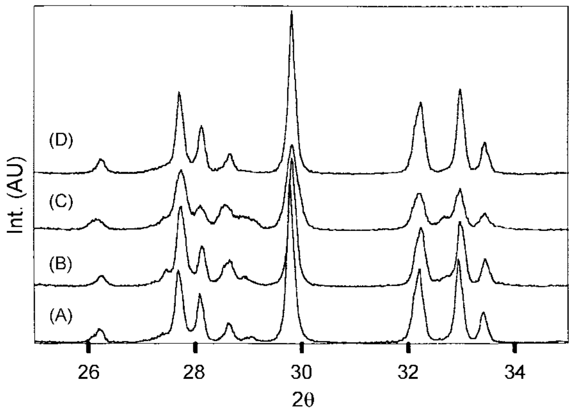

Fig. 8. XRD patterns of $La_2Ti_2O_7$ from various Ti precursors.
(A) Antase-TiO_2 (Aldrich), (B) TiO_2-MTA, (C) TiO_2-Hombikat, (D) TiO_2-P25

Table 1. Physical properties and photocatalytic activities of several $La_2Ti_2O_7$ samples prepared from different TiO_2 precursors with a fixed La precursor of La_2O_3 (Aldrich)

Run	Ti precursor	BET area of TiO_2 (m^2/g)	BET area of $La_2Ti_2O_7$ (m^2/g)	Photocatalytic activity (μmolH_2/gcat·hr)
1	Anatase-TiO_2 (Ald)	8.6	2.9	631
2	Rutile-TiO_2 (Ald)	1.3	2.4	428
3	TiO_2-MTA	98	3.5	331
4	TiO_2-Hombikat	280	3.4	512
5	TiO_2 P25	55	2.3	788

generally stated that the nature of precursors is very important for the structure and photocatalytic water-splitting activity of produced $La_2Ti_2O_7$.

Despite quite different morphologies of TiO_2 precursors as shown in Fig. 6, the difference in morphology among prepared $La_2Ti_2O_7$ catalysts in Fig. 7 was not that great. Rather, the morphology of $La_2Ti_2O_7$ catalysts was similar to that of ground La_2O_3 (not shown). In general, grain sizes of La_2O_3 precursors shown later in Fig. 9 were larger than those of TiO_2 precursors in Fig. 6. Thus, during the processes of grinding and calcination, the morphology of the product appears to be determined mostly by that of La_2O_3 precursor.

The $La_2Ti_2O_7$ photocatalyst with the highest activity was the one prepared from TiO_2 P25. As shown in Fig. 6D, it showed large chunks that looked fluffy and consisted of very fine primary particles. The size of the primary particle of P25 was far smaller than 0.5 μm, the size that cannot be fractured further by the usual mechanical grinding. Further, this particle size of P25 was the smallest among those tested TiO_2 precursors. The solid-state reaction between TiO_2 and La_2O_3 must have been facilitated by the small size of TiO_2 P25 in the formation of final $La_2Ti_2O_7$ phase due to increased interfacial area between two solid precursors. Indeed, the crystallinity of the P25-derived $La_2Ti_2O_7$ phase as well as its phase purity was better than other $La_2Ti_2O_7$ as shown in Fig. 8. It appears these factors have contributed to the highest photocatalytic activity of the P25-derived $La_2Ti_2O_7$ catalyst. It has the smallest surface areas, although the difference is not that great. The effect of the small surface area of the P25-derived $La_2Ti_2O_7$ catalyst seemed fully compensated by the good crystallinity.

Anatase-TiO_2 (Aldrich) produces a $La_2Ti_2O_7$ catalyst with even smaller BET surface area. Yet the $La_2Ti_2O_7$ catalyst showed again high crystallinity and phase purity, and also was very active in photocatalytic water-splitting. Another anatase-MTA-500 produced the $La_2Ti_2O_7$ catalyst with its particle morphology similar to that of anatase-TiO_2 (Aldrich), but with a larger BET surface area. Anatase-Hombikat had the largest BET surface area among tried TiO_2 precursors and has plate-like morphology different from other Ti precursors. However, $La_2Ti_2O_7$ prepared from it showed the particle morphology similar to that from anatase-TiO_2 (Aldrich). Rutile-TiO_2 of Aldrich has the smallest surface area among the tested Ti precursors, but $La_2Ti_2O_7$ prepared from it showed a surface area similar to others. It had morphology (not shown) very similar to that of anatase-TiO_2 (Aldrich). These catalysts showed lower photocatalytic activities, which were correlated with their lower crystallinity and phase purity as shown in Fig. 8.

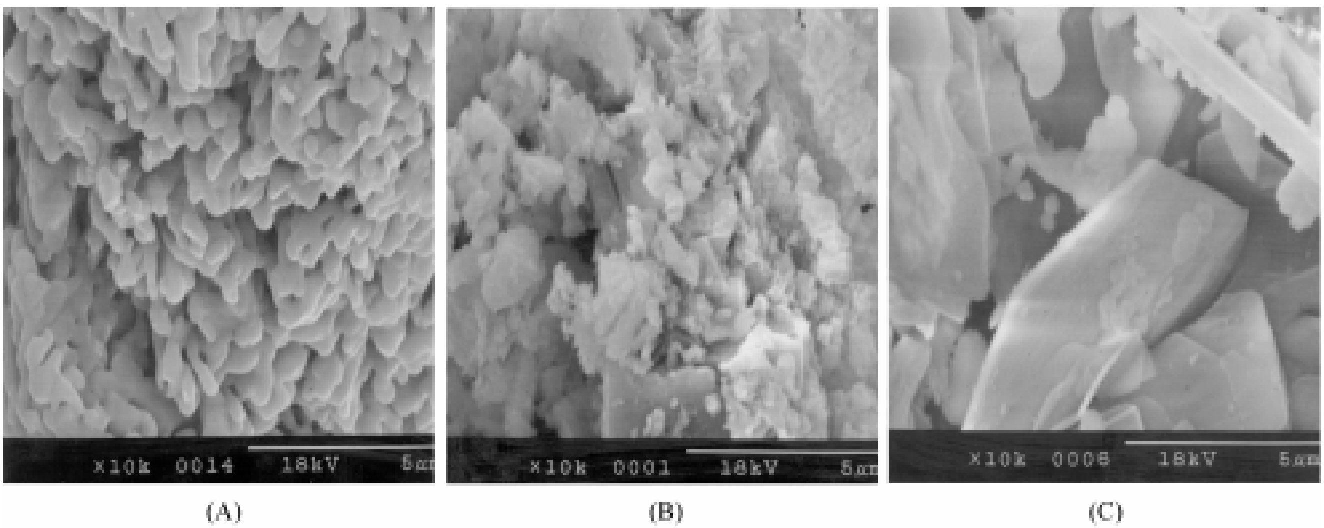

Fig. 9. Scanning electron microscope of several La_2O_3 used as La precursor for the synthesis of $La_2Ti_2O_7$.
(A) La_2O_3, (B) La_2O_3 from $La(OH)_3$, (C) La_2O_3 from $La_2(CO_3)_3$

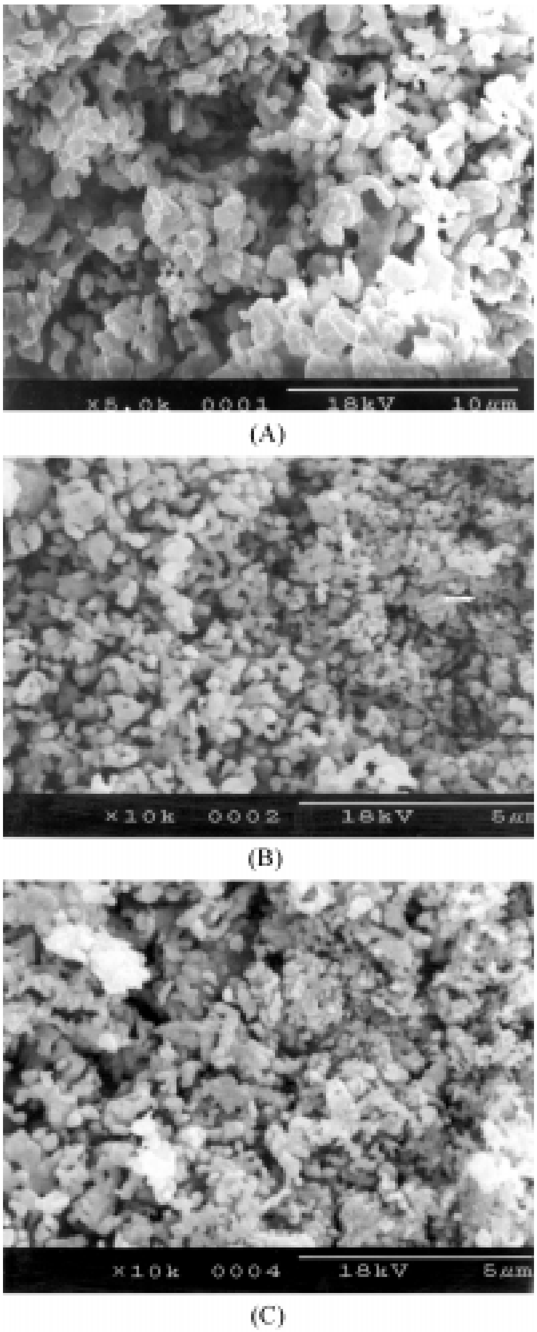

Fig. 10. Scanning electron microscope of several $La_2Ti_2O_7$ prepared with several La_2O_3 precursors.
(A) La_2O_3, (B) La_2O_3 from $La(OH)_3$, (C) La_2O_3 from $La_2(CO_3)_3$

One more important variable in TiO_2 precursors was in the level of contained impurity, especially iron compounds. Among the precursors, anatase-MTA-500 and anatase-Hombikat contained relatively higher amounts of iron compounds as impurities that originated from the manufacturing processes of TiO_2 (A process scheme to produce TiO_2 for figment, *Korea Titanium Co. Ltd*). The final $La_2Ti_2O_7$ catalyst prepared from these precursors showed lower photocatalytic activities in spite of their higher surface area. It is known that these transition metal impurities left in the final product $La_2Ti_2O_7$ provide photoelectron-hole pair recombination sites and reduce the quantum yields.

3. Effect of La_2O_3 Precursor

To study the effects of La_2O_3 precursors, we employed La_2O_3 derive from three sources with fixed TiO_2 source of P-25: La_2O_3, La $(OH)_3$, and $La_2(CO_3)_3$, all from Aldrich. As shown in Fig. 9, La_2O_3 powders have two kinds of sizes: i.e., many 0.5 μm primary particles agglomerated into 5-10 μm secondary particles. By grinding, the secondary structure was crushed, but further grinding did not fracture the primary particles. The La_2O_3 obtained from calcining $La(OH)_3$ at 823 K had coarser morphology and could be crushed easily. Compared to these two La precursors, La_2O_3 from $La_2(CO_3)_3$ has more ordered structure with a large cluster type morphology, which is hard to crush by solid grinding. As shown in Fig. 10, the morphology of $La_2Ti_2O_7$ derived from La_2O_3 and $La(OH)_3$-based La_2O_3 was more homogeneous and finer than La_2O_3 derived from $La_2(CO_3)_3$. It could be seen from XRD in Fig. 11 that there were some impurity phases in $La_2Ti_2O_7$ prepared from $La_2(CO_3)_3$. As summarized in Table 2, the photocatalytic activity was the highest for $La_2Ti_2O_7$ derived from La_2O_3 in spite of its lowest surface area. Thus, again, crystallinity and phase purity appear to be the main factors determining the photocatalytic activity of the final $La_2Ti_2O_7$ phase in the water-splitting reaction.

As mentioned, crushing the agglomerated structure of La_2O_3 was critical to synthesizing homogeneous and fine $La_2Ti_2O_7$ particles because La_2O_3 precursor had far larger and coarser particle morphology than TiO_2 precursors. In some cases, unreacted La_2O_3 particles remained in synthesized $La_2Ti_2O_7$ and lowered activity of the

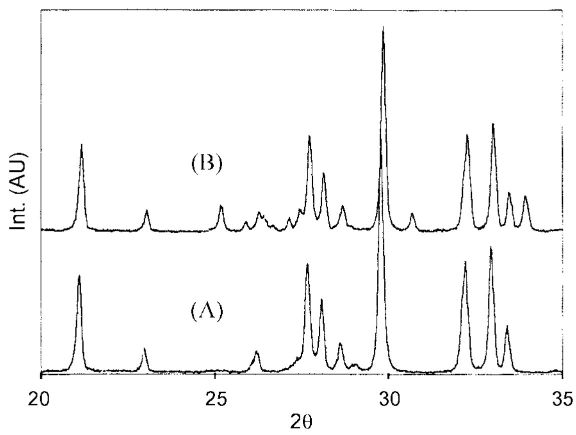

Fig. 11. XRD patterns of $La_2Ti_2O_7$ from different La precursors.
(A) La_2O_3, (B) La_2O_3 from $La_2(CO_3)_3$

Table 2. Physical properties and photocatalytic activities of several $La_2Ti_2O_7$ samples prepared from different La precursors with a fixed Ti precursor of TiO_2-P25

Run	La precursor	BET area of La_2O_3 (m^2/g)	BET area of $La_2Ti_2O_7$ (m^2/g)	Photocatalytic activity (μmolH_2/gcat·hr)
1	La_2O_3 (Aldrich)	0.832	2.3	788
2	La_2O_3-2 (Aldrich)	10.37	3.7	534
3	La_2O_3-3 (Aldrich)	6.98	3.4	329

*La_2O_3-2 (Aldrich); $La(OH)_3$ (Aldrich) calcined at 823 K, 5 hrs
La_2O_3-3 (Aldrich); $La_2(CO_3)_3$ (Aldrich) calcined at 823 K, 5 hrs

photocatalyst.

CONCLUSIONS

In the preparation of $La_2Ti_2O_7$, as photocatalyst, purities and morphologies of the precursors have great effects on the morphology and photocatalytic activity of the prepared $La_2Ti_2O_7$. It is important to reduce the particle size of La_2O_3 precursor, since it usually has larger particle size and coarser morphology than TiO_2 precursors. As a precursor to photocatalyst, TiO_2 should have a high level of purity and fine morphology. A high degree of crystallinity and purity of the prepared $La_2Ti_2O_7$ was critical for its high photocatalytic water-splitting activity.

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