COMMUNICATION

ChemComm
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Nickel-loaded $La_2Ti_2O_7$ as a bifunctional photocatalyst

Jindo Kim, Dong Won Hwang, Hyun-Gyu Kim, Sang Won Bae, Sang Min Ji and Jae Sung Lee*
Department of Chemical Engineering and School of Environmental Science & Engineering, Pohang University of Science and Technology, San 31 Hyoja-dong, Pohang 790-784, Korea.
E-mail: jlee@postech.ac.kr; Fax: 81-54-279-5528; Tel: 82-54-279-2266

Received (in Cambridge, UK) 19th August 2002, Accepted 26th September 2002
First published as an Advance Article on the web 8th October 2002

Nickel-loaded $La_2Ti_2O_7$, one of the highly donor-doped (110) layered perovskite materials, has been found to be an efficient photocatalyst for simultaneous H_2 production from water splitting and decomposition of tetramethylammonium hydroxide (TMAH) under UV irradiation.

The photocatalytic water splitting reaction has received much attention as a method for solar energy conversion into chemical energy because of its potential to directly obtain clean hydrogen energy. Various perovskite-type materials have been studied for production of H_2 from photocatalytic water splitting.[1–3] Recently, 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 unprecedented high quantum yields. This has been attributed to their unique electronic structure in which either A or B atom has a cation valency greater by + 1 (‘highly donor-doped’) compared with other perovskite compounds! In nickel-loaded perovskite or perovskite type-oxide, NiO appears to act as the reduction site of H^+ ion, whereas host perovskite oxide acts as the oxidation site of OH^- ion.[4] Furthermore, when methanol was added to pure water, the H_2 evolution rate increased about 3 times, although O_2 was not generated. In this case, holes are photogenerated by absorbing UV irradiation and are utilized predominantly for the oxidation of CH_3OH, instead of OH^- ion, since the oxidation potential of CH_3OH is lower (more negative) than that of OH^-. Although TiO_2 has shown a good photocatalytic activity in decomposition of various toxic compounds such as organophosphorus pesticides and 4-chlorophenol,[5–6] nickel-loaded $La_2Ti_2O_7$ was also found to have comparable photocatalytic activity with TiO_2 P25 in CH_3Cl degradation in the presence of O_2.[7] Thus, this material is thought to have a proper photocatalytic property such as band edge position for photocatalytic degradation of toxic compound as well as water splitting reaction. Therefore, if we can find a proper toxic compound that can play a role as hole scavenger like CH_3OH, it is possible to combine these two functions and produce H_2 more economically since H_2 could be obtained while performing destruction of toxic compounds. Tetramethylammonium hydroxide (TMAH; $(CH_3)_4NOH$) is an important and troublesome waste compound generated during the production of semiconductors and thin film transistors for liquid crystal displays. Biodegradation after dilution has been used commonly for most factories. However, the biological treatment of this material has several disadvantages such as requirements of huge systems and highly restrictive treatment conditions.[8] In addition, this process also generates N_2O, which contributes to the greenhouse effect.[9]

Here, we report a novel photocatalytic application of highly donor-doped (110) layered perovskite, $La_2Ti_2O_7$, as a bifunctional photocatalyst, over which both destruction of toxic organic compounds and production of H_2 from water splitting occur simultaneously. TMAH was chosen as a model compound for testing the bifunctional property of highly donor-doped layered oxides. For the preparation of the $La_2Ti_2O_7$ photocatalysts, a stoichiometric mixture of La_2O_3 (Aldrich 99.999%) and anatase-TiO_2 (Aldrich 99.99%) was mixed and ground in a mortar in the presence of ethanol and dried in an oven. Pelletized powders were calcined at 1323 K for 10 h in static air. Calcined samples were converted to the active photocatalysts (NiO/Ni/Perovskite) by loading 1.0 wt % of Ni metal from nickel nitrate solution by incipient-wetness impregnation method.[4] The photocatalytic decomposition of water was carried out at room temperature and atmospheric pressure in a closed gas circulation system containing air using a high pressure Hg lamp (450 W) placed in an inner irradiation-type quartz reaction cell. The catalyst (0.2 g) was suspended in distilled water (500 mL) containing 500 ppm of TMAH by magnetic stirring. The amount of H_2 and O_2 were determined by a gas chromatograph equipped with TCD (molecular sieve 5 Å column). The products were analyzed by a gas chromatograph equipped with a quadrupole mass spectrometer (HP 5972).

The solution containing 500 ppm of TMAH was strongly basic (pH ~ 12). As the reaction proceeded, H_2 was evolved steadily with a rate of 5328 μmol/gcat.h and the amount of O_2 was decreased steadily with a rate of −6107 μmol/gcat.h. However, solution pH dropped to about 9.5 after 6 h of reaction time. In addition, any noticeable deactivation of catalyst was not observed and there was no change in X-ray diffraction (XRD) pattern after photocatalytic reaction. In the absence of TMAH, the rate of H_2 evolution was 1376 μmol/gcat.h, which was about one third of that in the presence of TMAH and the amount of O_2 also increased with a stoichiometric ratio of water splitting (670 μmol/gcat.h). In this case, the solution pH of 7 did not change with reaction time. Decrease in solution pH in the presence of TMAH might result from accumulation of CO_2 in the solution as TMAH was decomposed completely. We also observed CO_2 as the final product by the mass spectrometer. Although CO_2 is only a very weak Lewis acid, at higher pH the strong base OH^- coordinates the C atom, forming the hydrogencarbonate ion, HCO_3^-, which could reduce the solution pH. The photocatalytic oxidative decomposition of TMAH can be depicted as eqn. (1).

$$\mathrm{TMAH} + O_2 \xrightarrow{h\nu} CO_2 + H_2O + N_2 \qquad (1)$$

Therefore, the rate of TMAH decomposition is considered to be proportional to that of O_2 consumption in the photocatalytic decomposition and thus the conversion of TMAH decomposition could be monitored by the extent of O_2 consumption. In Table 1, the rate of TMAH decomposition (O_2 consumption) is summarized as well as the rate of H_2 evolution for nickel-loaded $La_2Ti_2O_7$. The result of TiO_2 P25 was also shown for comparison of relative photocatalytic activity since this has

Table 1 Photocatalytic activity of TiO_2 P25 and nickel-loaded $La_2Ti_2O_7$

Catalyst	Reactant	Hydrogen evolution (μmol/gcat.h)	Oxygen consumption (μmol/gcat.h)
TiO_2 P25	H_2O[a]	5	—
TiO_2 P25	H_2O + TMAH[b]	23	6323
$La_2Ti_2O_7$	H_2O	1376	—
$La_2Ti_2O_7$	H_2O +TMAH	5328	6107

[a] Reaction conditions: water 500 ml H_2O. [b] Concentration of TMAH was 500 ppm.

DOI: 10.1039/b208092c

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been known to be very active in photocatalytic degradation of many organic compounds. TiO_2 P25 also showed some activity of H_2 production in pure water (5 μmol H_2/gcat.h) but this activity was nearly negligible compared with nickel-loaded $La_2Ti_2O_7$. In the presence of TMAH, the rate of H_2 evolution increased a little (23 μmol H_2/gcat.h) and the rate of O_2 consumption (6323 μmol/gcat.h) for TiO_2 P25 was comparable with that for nickel-loaded $La_2Ti_2O_7$ (6107 μmol/gcat.h). Interestingly, the increase of H_2 evolution rate by addition of TMAH was similar for both catalysts by factors of 3.4 for TiO_2 P25 and 3.3 for nickel-loaded $La_2Ti_2O_7$. When 1.0 wt% of nickel was loaded on TiO_2 P25, the H_2 evolution rate did not change much irrespective of the existence of TMAH. The increase of the H_2 evolution rate in the presence of TMAH resulted from more efficient utilization of photogenerated electrons while TMAH adsorbed on the photocatalyst surface was removing photogenerated holes. The latter is possible because the oxidation potential of TMAH is more negative (lower in absolute energy scale) than that of OH^-. The difference of H_2 evolution rate between TiO_2 P25 and $La_2Ti_2O_7$ might be ascribed to the difference in their electronic property. The conduction and valence band edge of TiO_2 P25 and $La_2Ti_2O_7$ could be considered to be similar since the valence band for both catalysts consists mainly of an O2p orbital and the conduction band consists of an Ti3d orbital although an La4f orbital is localized in the middle of the conduction band of $La_2Ti_2O_7$ and the bandgap energies of both catalysts are also similar (3.2 *vs*. 3.1 eV). The highly donor-doped property of a layered slab composed of TiO_6 octahedra might play an important role in photocatalytic reduction of H^+ ion by more efficient utilization of photogenerated electrons. It is noteworthy that H_2 evolution rate over nickel-loaded $La_2Ti_2O_7$ could be increased by destruction of toxic compounds (TMAH in the present study) that is considered to be very difficult to treat with the conventional catalytic oxidation method.[8] Although TiO_2 could also be applied only for destruction of TMAH, only a little hydrogen could be obtained even by using expensive UV irradiation.

The schematic diagram of more efficient H_2 evolution in the presence of TMAH is depicted in Fig. 1. When photocatalyst is illuminated with light of energy larger than its bandgap energy, an excited electron-hole pair is generated. However, the main portion of these charge carriers would be recombined if proper reactants do not exist. Photocatalytic overall water splitting could take place over nickel-loaded $La_2Ti_2O_7$ with a high photon yield of 12% in pure water due to the efficient electron-hole separation by the electric field present in the depletion region. Yet, the H_2 evolution rate could be increased further by removing photogenerated holes using the proper hole scavenger whose oxidation potential is lower than that of OH^-. In this novel application of photocatalysis for both H_2 production and toxic waste abatement, TMAH is a good candidate because, as shown in Fig. 1, the oxidation potential of TMAH is lower than that of OH^-. In the presence of TMAH, an excited hole generated by absorbing the bandgap energy (3.2 eV) is trapped by TMAH adsorbed on the $La_2Ti_2O_7$ surface through path (2) rather than path (1) of Fig. 1 since the oxidation of TMAH is easier to perform thermodynamically. The remaining electron can be transported to the H^+ reduction site, NiO, more easily, which results in an increase of H_2 evolution rate in the presence of TMAH.

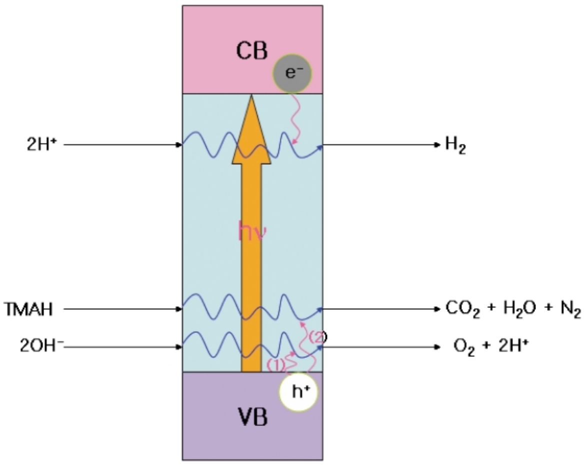

Fig. 1 Schematic diagram of simultaneous H_2 evolution and TMAH.

TiO_2 itself also converted TMAH into less toxic compounds with a similar conversion rate. However the H_2 evolution rate was very low compared with nickel-loaded $La_2Ti_2O_7$. Therefore, it is concluded that only nickel-loaded $La_2Ti_2O_7$ can be utilized as a bifunctional photocatalyst that can produce H_2 from water and decompose toxic compounds like TMAH simultaneously without any catalyst deactivation. Although we tested only TMAH for bifunctional property of nickel-loaded $La_2Ti_2O_7$, other toxic compounds containing CN^- conld also be applied for this purpose if they have a proper oxidation potential. This work has been supported by KOSEF and BK-21 program of Korea Ministry of Education.

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