doi:10.1246/cl.2011.108

Photocatalytic Overall Water Splitting over $ALi_2Ti_6O_{14}$ (A: 2Na and Sr) with Tunneling Structure

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(Received October 26, 2010; CL-100909; E-mail: r.amal@unsw.edu.au)

RuO_2-cocatalyst-loaded $ALi_2Ti_6O_{14}$ (A: 2Na and Sr) with a unique tunneling structure shows photocatalytic activity for water splitting into H_2 and O_2 in stoichiometric amounts under UV irradiation. The addition of LiOH in the reactant solution, to replenish Li^+ defects within the tunneling structure, improved the photocatalytic activities of $ALi_2Ti_6O_{14}$ (A: 2Na and Sr) by approximately 10 and four times, respectively.

Exploration of new photocatalysts for water splitting into H_2 and O_2 has been extensively researched with the aim of realizing a hydrogen-energy society. In particular, metal oxides with d^0 and d^{10} cation electron configurations are some of the most promising water splitting photocatalysts under UV irradiation.[1–3] Among them, some of the photocatalyst materials are characterized by unique crystal structures such as the layered structures of $K_4Nb_6O_{17}$,[4] $K_2La_2Ti_3O_{10}$,[5] $Sr_2M_2O_7$ (M: Nb and Ta),[6] La–Ti–oxides,[7] and $Ba_5M_4O_{15}$ (M: Nb and Ta);[8,9] the pillared structure of $K_3Ta_3M'_2O_{13}$ (M′: B and Si);[10,11] and tunneling structures of $Na_2Ti_6O_{13}$[12] and $BaTi_4O_9$.[13] These unique structures have a desirable effect on the photocatalytic performance compared to bulk structures. For example, the interlayer may function as an H_2 and/or O_2 evolution site, promoting charge separation,[4,5] although the exact mechanism is not yet fully understood. Quite recently, $ALi_2Ti_6O_{14}$ (A: 2Na and Sr) has been reported to possess a similar tunneling structure to $Na_2Ti_6O_{13}$ and $BaTi_4O_9$, as shown in Figure 1.[14,15] The framework of $ALi_2Ti_6O_{14}$ (A: 2Na and Sr) consists of corner- and edge-shared TiO_6 octahedra with lithium cations existing in the tunnel. Such a unique crystal structure further motivates us to investigate its photocatalytic activity in overall water splitting. Insights into the relationship between the photocatalytic activity and the presence of Li^+ ions in the tunnels are also discussed in this work.

Powders of $ALi_2Ti_6O_{14}$ (A: 2Na and Sr) were synthesized by a solid-state reaction. Starting materials of Na_2CO_3 (Ajax Finchem; 99.8%), $SrCO_3$ (Alfa Aesar; 99%), $LiOH{\cdot}H_2O$ (Aldrich; 98%), and TiO_2 (Aldrich; 99.9%) were mixed in a ratio of Na:Li:Ti = 1.05:2.2:6 for $Na_2Li_2Ti_6O_{14}$ and Sr:Li:Ti = 1:2.2:6 for $SrLi_2Ti_6O_{14}$. The excess amounts of Na and Li were added to the starting mixture to compensate for volatilization during synthesis. The mixtures were calcined in air at 1223 K for 10 h in an alumina crucible. The excess alkali metal ions were removed by rinsing with excess water after the calcination. RuO_2 cocatalyst was loaded by impregnation with an aqueous solution of $RuCl_3{\cdot}nH_2O$ (Sigma-Aldrich; 38–40% as Ru). The photocatalyst powder and desired amount of aqueous $RuCl_3$ solution were placed in a porcelain crucible and dried on a hot plate. The impregnated powder was calcined in air at 773 K for 1–2 h.

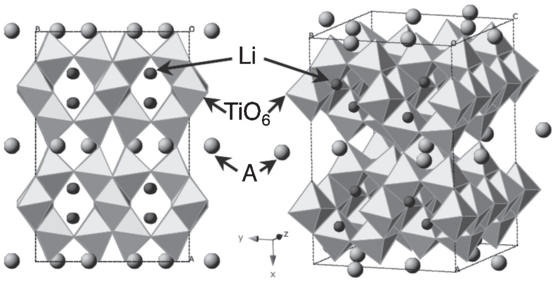

Figure 1. Crystal structure of $ALi_2Ti_6O_{14}$ (A: 2Na and Sr).[14,15]

The crystal phase of the prepared powder was analyzed on an X-ray diffractometer (Philips, X'pert Multipurpose X-ray Diffraction) with Cu $K\alpha$ radiation. The crystal structure of $ALi_2Ti_6O_{14}$ based on $SrLi_2Ti_6O_{14}$ (PDF 95908) was created using CrystalMaker (CrystalMaker Software Ltd.). Diffuse reflectance spectra were obtained by a UV–vis–NIR spectrometer (Varian, Cary 300) equipped with an integrating sphere and were converted to absorbance by the Kubelka–Munk method. The specific surface area of the sample was determined by N_2 adsorption using the Brunauer–Emmett–Teller (BET) method (Micromeritics, TriStar 3000). Morphology and particle size of the photocatalyst powder were observed using a scanning electron microscope (Hitachi, S4500).

Photocatalytic water splitting was carried out in a gas-closed circulation system with a catalyst powder (0.2–0.3 g) dispersed in 230 mL of water (Millipore, Milli-Q) or 0.01 mol L^{-1} aqueous solutions of AOH (A: Li, Na, or K). A quartz cell with internal irradiation (100-W high-pressure Hg lamp, SEN HL100CH-4) was employed. The amounts of H_2 and O_2 evolved were determined by a gas chromatography unit (Shimadzu GC 8A, TCD detector, molecular sieve 5A packed column, Ar carrier gas).

Figure 2 shows the XRD patterns of $ALi_2Ti_6O_{14}$ (A: 2Na and Sr) powders prepared by the solid-state reaction. A single phase of $Na_2Li_2Ti_6O_{14}$ was obtained, while a small amount of TiO_2 (rutile) was observed for $SrLi_2Ti_6O_{14}$. The band gaps of $ALi_2Ti_6O_{14}$ (A: 2Na and Sr) were estimated to be 3.7 and 3.8 eV respectively from the onsets of absorption of the diffuse reflectance spectra (334 and 327 nm). The specific surface area of $Na_2Li_2Ti_6O_{14}$ (0.5 $m^2\,g^{-1}$) was found to be smaller than that of $SrLi_2Ti_6O_{14}$ (1.2 $m^2\,g^{-1}$) due to the presence of excess Na_2CO_3 (starting material) that promoted the crystal growth of $Na_2Li_2Ti_6O_{14}$ by working with Li as a flux reagent during calcination.

Table 1 shows the photocatalytic water splitting activities of $ALi_2Ti_6O_{14}$ (A: 2Na and Sr) under UV irradiation. In the absence of RuO_2 cocatalyst, both samples were inactive for overall water splitting (Entries 1 and 6). In contrast, upon loading with RuO_2 cocatalyst, the overall water splitting proceeded for both samples (Entries 2 and 7). Although, as mentioned earlier that TiO_2 was present as impurity phase in the

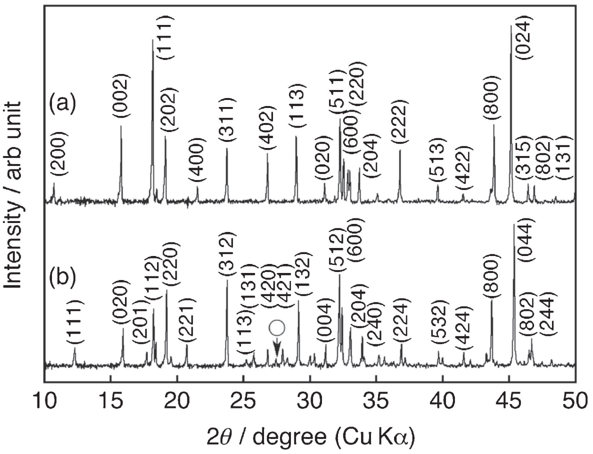

Figure 2. XRD patterns of (a) $Na_2Li_2Ti_6O_{14}$ and (b) $SrLi_2Ti_6O_{14}$. Open circle corresponds to TiO_2 (rutile).

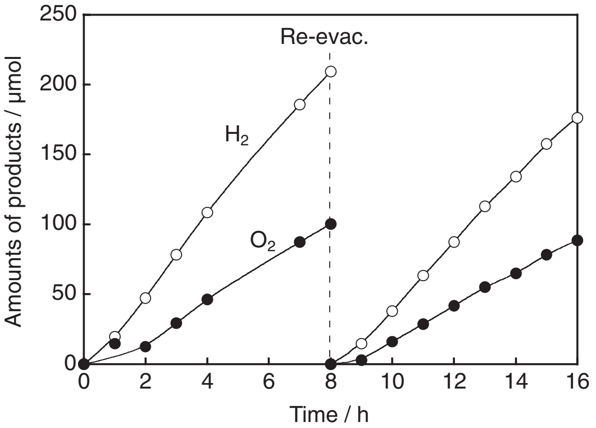

Figure 3. Photocatalytic overall water splitting over RuO_2 (0.5 wt %)-loaded $Na_2Li_2Ti_6O_{14}$. Catalyst: 0.2 g, reactant solution: 0.01 mol L^{-1} LiOH aq. 230 mL, reaction cell: inner irradiation cell made of quartz, light source: 100-W high-pressure mercury lamp.

Table 1. Photocatalytic water splitting into H_2 and O_2 over $ALi_2Ti_6O_{14}$ (A: 2Na and Sr) under UV irradiation[a]

Entry	Photocatalyst	BG/eV	SA/m^2 g^{-1}	RuO_2/wt %	Reactant solution	Activity/μmol h^{-1}	
						H_2	O_2
1	$Na_2Li_2Ti_6O_{14}$	3.7	0.5	None	Water	1.0	0
2	$Na_2Li_2Ti_6O_{14}$	3.7	0.5	0.5	Water	2.9	1.4
3	$Na_2Li_2Ti_6O_{14}$	3.7	0.5	0.5	LiOH[b]	27	14
4	$Na_2Li_2Ti_6O_{14}$	3.7	0.5	0.5	NaOH[b]	6.9	3.5
5	$Na_2Li_2Ti_6O_{14}$	3.7	0.5	0.5	KOH[b]	6.8	3.1
6	$SrLi_2Ti_6O_{14}$	3.8	1.2	None	Water	1.3	0
7	$SrLi_2Ti_6O_{14}$	3.8	1.2	0.5	Water	3.6	1.5
8	$SrLi_2Ti_6O_{14}$	3.8	1.2	0.5	LiOH[b]	13	6.8

[a] Catalyst: 0.2–0.3 g, reactant solution: 230 mL, light source: 100-W high-pressure Hg lamp, cell: inner irradiation cell made of quartz.
[b] 0.01 mol L^{-1} aqueous solution.

$SrLi_2Ti_6O_{14}$ sample, individual RuO_2-loaded TiO_2 did not show any activity for overall water splitting under the present experimental conditions (unlike Rh- or NiO_x-loaded TiO_2[16,17]). In other words, the photocatalytic water splitting activity can be attributed to the RuO_2-loaded $SrLi_2Ti_6O_{14}$ alone.

Further significant enhancement in photocatalytic activities was achieved for both RuO_2-loaded $Na_2Li_2Ti_6O_{14}$ and $SrLi_2Ti_6O_{14}$ in the presence of LiOH (Entries 3 and 8, respectively); activity was enhanced 10- and fourfold, respectively, in comparison to water splitting in pure water. While the addition of NaOH and KOH also improved the photocatalytic activities (Entries 4 and 5, respectively), enhancement was much lower than that of LiOH. The key factor lies in the location of Li^+ ions in the tunneling structure (Figure 1). It is possible that the small ionic radii of Li^+ permits mobility in the tunneling structure and can be easily removed by washing with water during preparation as well as during the water splitting reaction. This can result in the formation of Li^+ defects, which in turn act as the charge recombination center. Therefore, the addition of LiOH can make up for the Li^+ defects and drastically enhance the photocatalytic activity of $Na_2Li_2Ti_6O_{14}$. Similar enhancement in photocatalytic activity by adding cations in the reactant solution to replenish defect sites was also reported previously for the $Ba(OH)_2$–$BaTa_2O_6$ system.[18] Some photocatalysts exhibited higher activity for water splitting from the addition of AOH (A: Na, K, Rb, and Cs) as a means of controlling pH of the reactant solution.[19,20] Therefore, the enhancement observed in the presence of NaOH and KOH is attributed to OH^- ion, since Na^+ and K^+ ions are too large to accommodate in the tunnel structure.

Figure 3 shows the time courses of H_2 and O_2 evolution over RuO_2-loaded $Na_2Li_2Ti_6O_{14}$ in the presence of LiOH. Again, the stoichiometric amounts of H_2 (27 μmol h^{-1}) and O_2 (14 μmol h^{-1}) evolved steadily with calculated turnover number i.e., ratio of reacted electrons to the molar quantity photocatalyst, of 2.2 at 16 h. Although not shown, analysis of the used photocatalyst confirms the preservation and stability of the crystallite structure over the course of the reaction. The results also reaffirm that the overall water splitting had proceeded photocatalytically and not by the sacrificial degradation of the photocatalysts.

In conclusion, we discovered RuO_2-loaded $ALi_2Ti_6O_{14}$ (A: 2Na and Sr) photocatalysts with a tunneling structure capable of overall water splitting under UV irradiation. The activity is dependent on the presence of both Li^+ and OH^- ions. In particular, the stability of Li^+ ions in the tunneling structure is crucial to the photocatalytic performance of the catalysts.

We thank the Australian Research Council for its financial support.

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