Photoluminescent and photocatalytic properties of layered caesium titanates, $Cs_2Ti_nO_{2n+1}$ ($n=2, 5, 6$)

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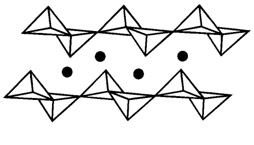
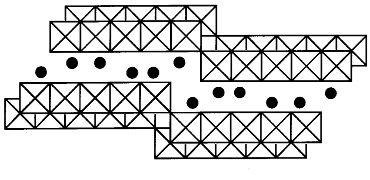
Photoluminescence and photocatalytic H_2 evolution reactions of layered caesium titanates, $Cs_2Ti_nO_{2n+1}$ ($n=2,5,6$), have been studied to evaluate the photoactivity of these materials. $Cs_2Ti_2O_5$ showed a broad emission around 420 nm upon excitation at 270 nm at 77 K, while both $Cs_2Ti_5O_{11}$ and $Cs_2Ti_6O_{13}$ showed an emission around 490 nm upon excitation at 290 nm. $Cs_2Ti_2O_5$ showed a blue emission even at 300 K. The Raman spectrum of $Cs_2Ti_2O_5$ was similar to that of the well characterized $K_2Ti_2O_5$. The results of the luminescence and the Raman spectrum suggested that $Cs_2Ti_2O_5$ consists of a layered structure with TiO_5 units, as observed in $K_2Ti_2O_5$. $Cs_2Ti_2O_5$ with the five-coordinate structure showed higher photocatalytic activity for H_2 evolution from aqueous methanol solutions than $Cs_2Ti_5O_{11}$ and $Cs_2Ti_6O_{13}$ with ordinary six-coordinate structures.

Titanium dioxide and many white titanates are known to work as efficient photocatalysts and semiconductor electrodes.[1,2] Among the titanates, layered titanates ($M_2Ti_nO_{2n+1}$) consisting of titanium oxide layers and interlayer cations are unique materials which can be modified by ion-exchange reactions.[3–5] One of the authors has reported that $K_2Ti_2O_5$, $Na_2Ti_3O_7$ and $K_2Ti_4O_9$ ($n=2$, 3 and 4) showed photoluminescence[6] and activities for a photocatalytic H_2 evolution reaction even without Pt co-catalysts.[7] Of these materials, $K_2Ti_2O_5$ showed the highest activity and photoluminescence even at room temperature. Inoue *et al.* reported the photocatalytic activities for water splitting of $M_2Ti_nO_{2n+1}$ with layered and tunnel structures.[8] In general, titanates consist of octahedral TiO_6 units. In contrast, $K_2Ti_2O_5$ has a layered structure with TiO_5 units as shown in Fig. 1(a).[9]

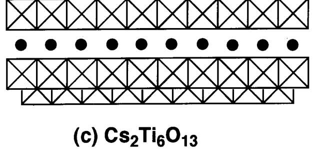
Some layered titanates have been employed as hosts of methyl viologen and ruthenium complexes for photochemical research.[10,11] Therefore, the photochemical properties of other layered titanates are also of interest. Grey *et al.*[12] and Bursill *et al.*[13] have synthesized layered caesium titanates ($Cs_2Ti_5O_{11}$ and $Cs_2Ti_6O_{13}$) with $n=5$ and 6. As shown in Fig. 1, $Cs_2Ti_5O_{11}$ has a layered structure periodically stepped to give five-octahedra wide, corner-linked ribbons, while the layers in $Cs_2Ti_6O_{13}$ are continuous in two dimensions. Sasaki *et al.* have reported the ion-exchange reaction of $Cs_2Ti_5O_{11}$.[14] However, the photochemical properties of these compounds have not been reported. On the other hand, $Cs_2Ti_2O_5$ has been synthesized[15] and its photoactivity is also interesting in comparison with that of $K_2Ti_2O_5$ with the same stoichiometric composition.



(a) $K_2Ti_2O_5$ ($Cs_2Ti_2O_5$)



(b) $Cs_2Ti_5O_{11}$



(c) $Cs_2Ti_6O_{13}$

Fig. 1 Structures of layered titanates

In the present study, the photoluminescent and photocatalytic properties of layered $Cs_2Ti_2O_5$, $Cs_2Ti_5O_{11}$ and $Cs_2Ti_6O_{13}$ materials have been investigated for evaluation of their photoactivities. The relationship between their properties and structures is also discussed.

Experimental

Layered caesium titanates were prepared by melting or calcining mixtures of TiO_2 (Kanto Chemical, 99%) and Cs_2CO_3 (Kanto Chemical, reagent grade) at 1270 K (2 h), 1270 K (20 h) and 1070 K (20 h) for $Cs_2Ti_2O_5$, $Cs_2Ti_5O_{11}$ and $Cs_2Ti_6O_{13}$, respectively, in air using a platinum crucible.[12–15] An excess of Cs_2CO_3 (10 mol%) was added to compensate for losses due to volatilization. The structures of the synthesized powders were confirmed by X-ray diffraction (Rigaku, RINT-1400). H^+-exchange reactions for $Cs_2Ti_2O_5$ were carried out by suspending the powder in an aqueous HCl solution (0.035 mol dm^{-3}). The degree of H^+ exchange was determined by an EDX instrument (Kevex, DeltaPlus) equipped with an SEM (Hitachi, S-5000). An FTIR spectrometer (JEOL, JIR-7000) equipped with a Raman unit (RS-RSU200) was used for Raman measurements. The Raman spectra were obtained using radiation of 1064 nm from a Nd-YAG laser. Diffuse reflectance spectra were measured using a UV–VIS–NIR spectrometer (JASCO, Ubest V-570). The spectra were treated with the Kubelka–Munk method. Powdered samples were used for luminescence measurements using a quartz cell and a fluorometer (Spex, Fluoromax, light source 150 W Xe lamp, photomultiplier tube R928P).

Photocatalytic reactions were carried out in a gas-closed circulation system after deaeration. A reaction cell made of quartz and a 450 W high-pressure mercury lamp were employed. The H_2 and O_2 evolved were determined by GC (Ohkura GC-802, MS5A column, Ar carrier). Methanol, ethanol, propanol and butanol (Kanto Chemical, reagent grade) were used as hole scavengers for photocatalytic H_2 evolution reactions. Photochemical reduction of H_2PtCl_6 in the reaction solutions was employed for Pt addition.

Results and Discussion

SEM, XRD and Raman characterization

Layered structures were observed for $Cs_2Ti_2O_5$, $Cs_2Ti_5O_{11}$ and $Cs_2Ti_6O_{13}$ by scanning electron microscopy. The SE micrographs showed that the shape of $Cs_2Ti_2O_5$ was rectangular and those of $Cs_2Ti_5O_{11}$ and $Cs_2Ti_6O_{13}$ were fibrous as reported.[13] The dimensions were several μm by several tens of μm.

Fig. 2 shows XRD patterns of the layered titanates. All patterns agreed with the reported patterns.[12,15] The pattern of $Cs_2Ti_5O_{11}$ was of the hydrated form $[Cs_2Ti_5O_{11}\cdot(1+x)H_2O]$. The pattern of $Cs_2Ti_2O_5$ between 25 and 40° was similar to that of $K_2Ti_2O_5$, although there were some differences. The partial similarity of the patterns might reflect the titanate layer structure. Next, Raman spectra were measured to obtain information on the coordination states of local structures as shown in Fig. 3. The Raman spectrum of $Cs_2Ti_2O_5$ was very similar to that of five-coordinate $K_2Ti_2O_5$ but was different from those of six-coordinate $Cs_2Ti_5O_{11}$ and $Cs_2Ti_6O_{13}$. These results indicate that $Cs_2Ti_2O_5$ has a layered structure consisting of TiO_5 units, like $K_2Ti_2O_5$ as shown in Fig. 1(a). This is also supported by the similarity of the photoluminescent properties of these two compounds, as mentioned below. Here, the sharp and intense Raman peaks at 850–950 cm^{-1} were assigned to the stretching modes of extremely short Ti—O bonds which stick out into the interlayer spaces.[9]

Photoluminescence

Fig. 4 and 5 show the excitation and emission spectra of $Cs_2Ti_2O_5$, $Cs_2Ti_5O_{11}$ and $Cs_2Ti_6O_{13}$ at 77 K. All of these compounds showed photoluminescence. Although many studies have been carried out on titanate luminescence,[16,17] the number of reports on the luminescence of two-dimensional layered titanates is small.[6,18,19] Most luminescent layered titanates reported are quaternary oxides and have layered perovskite structures. It should be noted that ion-exchangeable layered titanates of ternary oxides show luminescence. Excitation spectra with onsets at 330 nm and emission spectra with maximums around 490 nm were obtained for $Cs_2Ti_5O_{11}$ and $Cs_2Ti_6O_{13}$. This result indicates that the energy structures of photoexcitation and relaxation for these layered caesium titanates are similar, in spite of the different layered structures shown in Fig. 1. Structures were observed in their excitation spectra. Shoulders in the excitation spectra are often observed by the formation of extrinsic luminescent centres owing to defects.[17,20] The wavelength of the extrinsic luminescence is usually longer than that of the intrinsic one. The excitation processes of $Cs_2Ti_5O_{11}$ and $Cs_2Ti_6O_{13}$ were found to be intrinsic because the emission spectra were not shifted greatly by changing the excitation wavelength. For $Cs_2Ti_2O_5$, excitation with an onset at 285 nm and emission spectra around 420 nm were obtained. The blue intrinsic emission was observed even at 300 K. This behaviour is noteworthy because most titanates do not show luminescence at room temperature.[16–18] These luminescent properties of $Cs_2Ti_2O_5$ are the same as those of $K_2Ti_2O_5$,[6] supporting the structural similarity between $Cs_2Ti_2O_5$ and $K_2Ti_2O_5$.

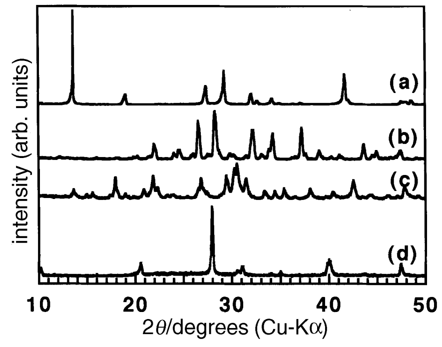


Fig. 2 XRD patterns of layered titanates: (a) $K_2Ti_2O_5$, (b) $Cs_2Ti_2O_5$, (c) $Cs_2Ti_5O_{11}$, (d) $Cs_2Ti_6O_{13}$

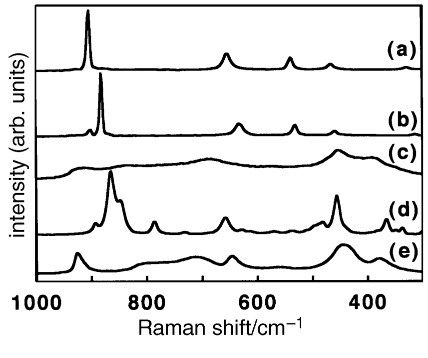


Fig. 3 Raman spectra of layered caesium titanates: (a) $K_2Ti_2O_5$, (b) $Cs_2Ti_2O_5$, (c) water-treated $Cs_2Ti_2O_5$, (d) $Cs_2Ti_5O_{11}$, (e) $Cs_2Ti_6O_{13}$

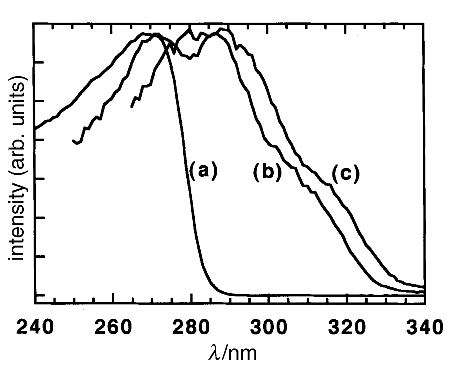


Fig. 4 Excitation spectra of layered caesium titanates at 77 K: (a) $Cs_2Ti_2O_5$, (b) $Cs_2Ti_5O_{11}$, (c) $Cs_2Ti_6O_{13}$

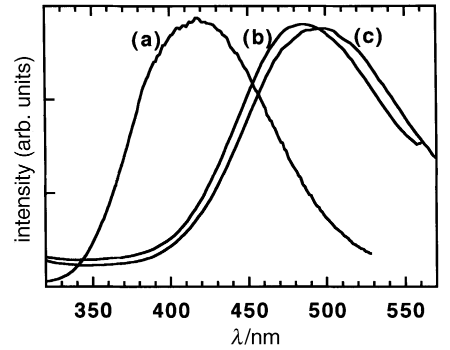


Fig. 5 Emission spectra of layered caesium titanates at 77 K: (a) $Cs_2Ti_2O_5$, (b) $Cs_2Ti_5O_{11}$, (c) $Cs_2Ti_6O_{13}$

In general, the luminescence of transition-metal oxoacids such as titanates and tungstates had been thought to be due to the charge transfer transition between metal and oxygen ions. Recently, it was pointed out by Blasse that the charge transfer was incorrect.[17] However, it is clear from the experimental results reported[6,16–18] that the luminescent properties depend on the characteristics of the Ti—O bond although the transition mechanism is complicated. Therefore, the extremely short Ti—O bonds as seen in $K_2Ti_2O_5$[9] play an important role in the luminescent properties of $Cs_2Ti_2O_5$. The importance of the coordination states in the luminescent properties has been discussed in detail for other titanates.[17] It is reasonable that the blue and room-temperature luminescence of $Cs_2Ti_2O_5$

Table 1 Photocatalytic activity for H_2 evolution over layered caesium titanates[a]

catalyst	rate of H_2 evolution/μmol h^{-1}
$Cs_2Ti_2O_5$	500
$H_2Ti_2O_5$[b]	852
Pt(1 mass%)/$H_2Ti_2O_5$[b]	2512
$Cs_2Ti_5O_{11}$	90
$Cs_2Ti_6O_{13}$	38

[a]Catalyst 1 g, reaction solution H_2O (350 ml)+CH_3OH (10 ml), light source 450 W high-pressure mercury lamp, reaction cell quartz. [b]Degree of H^+ exchange >95%.

which is not observed in the cases of $Cs_2Ti_5O_{11}$ and $Cs_2Ti_6O_{13}$ is due to the five-coordinate state because the low coordination state causes the formation of the short Ti—O bond.

Photocatalytic reactions

Table 1 shows activities for the photocatalytic H_2 evolution reaction from an aqueous methanol solution over $Cs_2Ti_2O_5$, $Cs_2Ti_5O_{11}$ and $Cs_2Ti_6O_{13}$. They showed activity without any added Pt, which usually works as hydrogen evolution sites. Of these materials, $Cs_2Ti_2O_5$ showed the highest activity. The H_2 evolution activities of layered titanate photocatalysts are often increased by exchanging interlayer cations with H^+.[7,21,22] The photocatalytic activity of $Cs_2Ti_2O_5$ was also increased by H^+ exchange. The reasons for the increase in activity by the H^+ exchange are thought to be: (i) formation of H_2 evolution sites, (ii) hydration of interlayers,[4] and (iii) a change in excitation energy of the titanate layers.[11] Protons can easily capture electrons at the sites in which H^+ is exchanged resulting in H_2 evolution [for (i)]. The mass transfer can be achieved readily under hydration of interlayers [for (ii)]. Absorption edges of some layered titanates and niobates are red-shifted by H^+ exchange and, therefore, the number of available photons will be increased [for (iii)]. The absorption edge of the diffuse reflectance spectrum of water-treated $Cs_2Ti_2O_5$ in which some of the Cs^+ was exchanged with H^+ (as mentioned below) was also red-shifted (*ca.* 70 nm) compared with the excitation spectrum of $Cs_2Ti_2O_5$. High activity, 2512 μmol h^{-1}, was obtained by the addition of Pt catalysts to H^+-exchanged $Cs_2Ti_2O_5$ ($H_2Ti_2O_5$). However, the increase in activity upon Pt addition was only three times, whereas the activities of conventional TiO_2 photocatalysts were increased drastically by the procedure.[1] This means that $H_2Ti_2O_5$ has sufficient active sites for H_2 evolution and that Pt catalysts can work only at the external surface of layered structures. On the other hand, the rate of photocatalytic O_2 evolution from an aqueous solution in which $AgNO_3$ was dissolved as an electron scavenger (0.05 mol l^{-1}) was 155 μmol h^{-1} over $Cs_2Ti_2O_5$. Thus, $Cs_2Ti_2O_5$ was found to have the potential for H_2 and O_2 evolution from water under the existence of sacrificial reagents. However, in distilled water, only small amounts of H_2 were evolved (7, 7 and 6 μmol h^{-1} for $Cs_2Ti_2O_5$, $Cs_2Ti_5O_{11}$ and $Cs_2Ti_6O_{13}$, respectively) but O_2 evolution was not observed.

As mentioned above, $Cs_2Ti_2O_5$ showed the highest activity. $Cs_2Ti_2O_5$ was hygroscopic, like $K_2Ti_2O_5$. Therefore, it is questionable if the structure changes during photocatalytic reactions in aqueous solutions. Anderson and Wadsley suggested that five-coordinate $K_2Ti_2O_5$ was rearranged into a six-coordinate perovskite structure by reactions with water.[9]

$$K_2Ti_2O_5 + H_2O \rightarrow 2KHTiO_3 \qquad (1)$$

In contrast, Fujiki and co-workers concluded that about 50% of K^+ in $K_2Ti_2O_5$ was ion-exchanged with H^+ by the reaction with water and that the five-coordinate structure was maintained after the ion-exchange judging from Raman measurements.[4]

$$K_2Ti_2O_5 + (n+1)H_2O \rightarrow KHTi_2O_5 \cdot nH_2O + K^+ + OH^- \qquad (2)$$

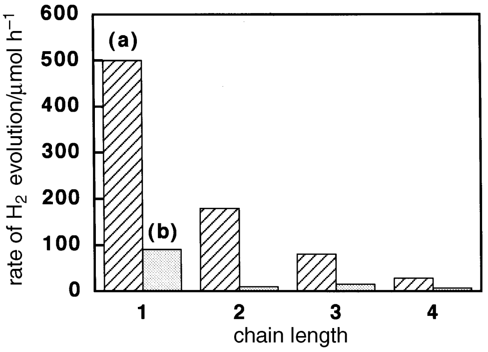


Fig. 6 Dependence of the carbon chain length of the alcohol on photocatalytic hydrogen evolution activity: (a) $Cs_2Ti_2O_5$, (b) $Cs_2Ti_5O_{11}$

The Raman spectrum of $Cs_2Ti_2O_5$ after the reaction with water was obtained [Fig. 3(c)]. The degree of H^+ exchange for this sample was 65%. The peak at 900 cm^{-1} almost disappeared and the Raman peak intensities were decreased. The Raman spectrum was the same as that of $K_2Ti_2O_5$ after water treatment.[4]

Anpo and co-workers have shown that unsaturated coordination sites work as the active sites of catalytic reactions and photoluminescence in highly dispersed metal oxide photocatalysts (V_2O_5, MoO_3, TiO_2, *etc.*).[23] In general, titanium oxides consist of octahedral units. The five-coordinate structure in $Cs_2Ti_2O_5$ is regarded as an unsaturated coordination state for titanates. It is noteworthy that unsaturated active sites which are normally observed on the oxide surface or in highly dispersed oxides regularly exist with a high density in layered oxides and contribute to the photoactivity. Although the detailed structure of the H^+-exchanged $Cs_2Ti_2O_5$ is not clear at the present, the five-coordinate structure, or the structure derived from the five-coordination by the H^+ exchange, *e.g.* hydrated structure, seems to contribute to the high photocatalytic activity of $Cs_2Ti_2O_5$ in addition to the effect of H^+ exchange.

Fig. 6 shows the photocatalytic activities for H_2 evolution in some aqueous alcohol solutions. The highest activity was obtained when methanol was employed as a sacrificial reagent. The activity was very low in an aqueous butanol solution. Such a dependence of the activity on the alcohol was observed for a layered $HCa_2Nb_3O_{10}$ photocatalyst.[22] This behaviour indicates the shape selectivity that small alcohols are advantageous for intercalation, showing that the photocatalytic reaction proceeds at interlayers. As mentioned above, the interlayer of $Cs_2Ti_2O_5$ is very easily hydrated resulting in high activity even in an aqueous ethanol solution. The interlayers of $Cs_2Ti_5O_{11}$ are more readily hydrated than those of $Cs_2Ti_6O_{13}$.[12] This must be the reason why $Cs_2Ti_5O_{11}$ showed higher activity than $Cs_2Ti_6O_{13}$ as shown in Table 1.

Summary

It was found for the first time that $Cs_2Ti_2O_5$, $Cs_2Ti_5O_{11}$ and $Cs_2Ti_6O_{13}$ with layered structures showed photocatalytic activities for H_2 and O_2 evolution from aqueous solutions and photoluminescence. In particular, $Cs_2Ti_2O_5$ showed blue luminescence at 300 K. These materials are new photoactive materials with two-dimensional structures.

$Cs_2Ti_2O_5$ with the five-coordinate structure was more active for photocatalytic reactions and luminescence than $Cs_2Ti_5O_{11}$ and $Cs_2Ti_6O_{13}$ with six-coordinate structures.

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