REVIEW ARTICLE

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Layered alkali titanates $(A_2Ti_nO_{2n+1})$: possible uses for energy/environment issues

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Abstract Uses of layered alkali titanates ($A_2Ti_nO_{2n+1}$; Na2Ti3O7, K2Ti4O9, and Cs2Ti5O11) for energy and environmental issues are summarized. Layered alkali titanates of various structural types and compositions are regarded as a class of nanostructured materials based on titanium oxide frameworks. If compared with commonly known titanium dioxides (anatase and rutile), materials design based on layered alkali titanates is quite versatile due to the unique structure (nanosheet) and morphological characters (anisotropic particle shape). Recent development of various synthetic methods (solid-state reaction, flux method, and hydrothermal reaction) for controlling the particle shape and size of layered alkali titanates are discussed. The ion exchange ability of layered alkali titanate is used for the collection of metal ions from water as well as a way of their functionalization. These possible materials design made layered alkali titanates promising for energy (including catalysis, photocatalysts, and battery) and environmental (metal ion concentration from aqueous environments) applications.

Keywords layered alkali titanates, photocatalysis, hydrogen evdution, metal ions collection

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1 Introduction

Layered alkali titanates is a class of layered solids composed of titania/titanic acid nanosheets and charge neutralizing alkali cations, which can be exchanged with various inorganic and organic cations, in the interlayer space [1]. Due to the unique nanostructures and the chemical characteristics associated with the structures, layered alkali titanates are regarded as a unique type of nanostructured titania. From the nanostructures, the large surface area can be used for the reactions and, in order to take benefits of this aspect, exposure of the surface of nanosheets has been reported by the exfoliation and pillaring [1,2]. The particle morphology (from platy particles to whisker and nanotubes) determined from the nanostructures and the variation of the synthetic methods is another characteristics of layered alkali titanates, which is not easily available for common titania (anatase and rutile).

Taking the advantage of the characteristic features mentioned above, layered alkali titanates/titanic acids have been used in applications such as battery [3], solar cell [4], ion exchange/adsorption/separation [5], catalysis [6], and other functional materials. Layered alkali titanates have been expected as candidates for photocatalytic applications including decomposition of toxic organic pollutants, water splitting, CO₂ reduction, and chemical syntheses, because of the large surface area based on the nanosheets and possible spatial separation of active sites (distinct charge separation). To design the performances of the materials and to find new functions, the preparation of layered alkali titanates and the hybridization with a variety of guest species have been extensively investigated [2,7,8]. Layered alkali titanates have been converted to protonated forms by treating them with an acidic solution [9]. The collection of metal and organic cations from aqueous environments by ion exchange reactions has been reported using pristine layered alkali titanates and their protonated forms. In addition to the cation exchange of layered alkali titanates, the functionalization has been examined by the

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intercalation [10,11], the exfoliation and subsequent restacking [12,13], and the pillaring [14]. Titanate nanosheets have been obtained by the exfoliation of layered alkali titanates through the ion exchange with appropriate organoammonium ions, which is a colloidal form of the titanates and can be processed by layer-bylayer assembly to obtain films. Porous heterostructured particles were obtained by re-stacking the exfoliated nanosheets with guest species to be connected [15]. The adsorbed metal ions have been converted to compound particles such as oxide [14] and sulfide [16,17]. A variety of nanostructured titanium oxides and their hybrids have been constructed from layered alkali titanates as shown in Fig. 1. Nanostructures of the hybrids have been designed by the selection of host and guest as well as the synthetic methods to control the functions (Fig. 2). There are several layered alkali titanates, whose structures and properties have been examined and, depending on the structure, the ion exchange, optical, electronic, and colloidal properties are known to vary. If compared with lepidocrocite-type layered titanates [7], $A_2Ti_nO_{2n+1}$ -type layered alkali titanates (Na2Ti3O7, K2Ti4O9, and Cs2Ti5O11) possess a higher cation exchange capacity, which makes them promising as adsorbents and solid electrolytes for possible large adsorption/storage capacity. In addition, the titanate sheet of Na₂Ti₃O₇, K₂Ti₄O₉, and Cs₂Ti₅O₁₁ is not molecularly flat due to TiO₆ octahedra blocks being stepped every three, four, and five, respectively. In the present review, the attention will be focused on the three layered alkali titanates, Na2Ti3O7, K2Ti4O9, and

 $Cs_2Ti_5O_{11}$, because of the useful structural characteristics, the morphology of the particles, and chemical reactivities, for the application in energy and environmental issues with a special emphasis on adsorption and photocatalysis. Recent developments of layered alkali titanates and their hybrids on the synthesis, modification, structure/morphology, and applications are summarized.

2 Structures of layered alkali titanates

Layered alkali titanates with a general formula of $A_2Ti_nO_{2n+1}$ are composed of nanosheets consisting of TiO₆ octahedral units connected by corners and edges sharing, and the interlayer alkali ion for compensating the negative charge of the titanate sheets. K₂Ti₂O₅ and Cs₂Ti₂O₅ are composed of sheets of TiO₅ unit connected by corners sharing, and interlayer alkali ion. The crystal structure of K₂Ti₂O₅, Na₂Ti₃O₇, K₂Ti₄O₉, Cs₂Ti₅O₁₁, Na₂Ti₆O₁₃, and K₂Ti₆O₁₃ are shown in Fig. 3. The crystal structures of layered alkali titanates are monoclinic, and belong to space groups $P2_1/m$ for $Na_2Ti_3O_7$ [18] and C_2/m for $K_2Ti_2O_5$ [19], $K_2Ti_4O_9$ [10], $Cs_2Ti_5O_{11}$ [20], Na₂Ti₆O₁₃ [21], and K₂Ti₆O₁₃ [22]. The titanate sheets form zigzag ribbons extend in the direction of the b axis of layered alkali titanates. The ribbons are connected by sharing corners of octahedra to form staggered sheets. The titanate sheets stack in the direction of the *a* axis and the stacking is different in layered alkali titanates (Na₂Ti₃O₇, $K_2Ti_4O_9$, and $Cs_2Ti_5O_{11}$). The sequence of the titanate



Fig. 1 Functionalization of layered alkali titanates and titania.



Fig. 2 Illustration for diverse applications of hybrids based on layered alkali titanates.

sheets is AAA for Na₂Ti₃O₇ and ABA for K₂Ti₄O₉ and Cs₂Ti₅O₁₁ [23,24]. For ABA stacking in K₂Ti₄O₉, the neighboring layers shift relative to each other titanate sheets in the b axis, so that there are two kinds of interlayer spacings. The potassium ions (K(I)) are accommodated in the interlayer space of the titanate sheets $[(Ti_4O_9)^{2-}]$. Half of K(I) in K₂Ti₄O₉ are located at the level of y = 1/4 in one interlayer region and the rest are at y = 3/4 in the other interlayer region. In the case of Na₂Ti₃O₇, sodium ions (Na(I)) are located at the levels of y = 1/4 and 3/4 in the same interlayer space. For Na2Ti6O13 and K2Ti6O13, the titanate sheets are connected in the direction of a axis by sharing the corners between the titanate sheets to form interstitial tunnels, which are filled by alkali ions (Figs. 3 (b) and 3(c)). The interlayer cations of layered alkali titanates have been exchanged with various metal ions and cationic molecules to from intercalation compounds.

3 Preparation

The preparation of layered alkali titanates has been done by the solid-state reaction [18–20,23,25,26], the flux method [27,28], and the hydrothermal reaction [29–35]. The layered alkali titanates (Na₂Ti₃O₇ [18], Tl₂Ti₄O₉ [10], K₂Ti₄O₉ [23] and Cs₂Ti₅O₁₁ [20]) were prepared by solidstate reactions in 1980. The starting materials for the solidstate reaction were stable phases such as anatase TiO₂, K₂CO₃, Na₂CO₃, and Cs₂CO₃ for mixing under ambient conditions. The mixture of the starting materials was activated by heating to obtain thermodynamically stable phases (target phase). Excess alkali metal may be necessary to compensate the evaporation of alkali metal during heating. For example, Na₂Ti₃O₇ was prepared by the solid-state reaction between Na₂CO₃ and anatase TiO₂ at a molar ratio of 1:2 at 1000°C, where large excess Na from stoichiometry was used [18]. Yang et al. [36] investigated the effect of the particle size of the starting materials on the formation of Na₂Ti₃O₇ as summarized in Table 1. Single phase Na₂Ti₃O₇ was obtained by heating at 800°C in air for 8 h, when anatase TiO₂ with a particle size of 20 nm was used as the Ti source. On the other hand, anatase TiO₂ with a size of $> 1 \mu m$ gave the single phase Na₂Ti₃O₇ with larger particle size after the solid-state reaction with Na₂CO₃ at 800°C for 40 h as shown in Fig. 4. The preparation of layered alkali titanate was also examined by using starting materials with a higher chemical reactivity. Bao et al. [37,38] prepared $K_2Ti_4O_9$ by heating the mixture of K_2CO_3 and $TiO_2 \cdot nH_2O$, which was obtained by the hydrolysis of titanyl sulfate in hot water, at the molar ratio of K₂O and TiO₂ of 1:3 at 920°C for 10 h.

One dimensionally anisotropic particles were seen irrespective of the synthetic methods, while the size of layered alkali titanates depends on the methods of the preparation. The layered alkali titanates with fibrous and elongated rectangular shape with the particle length of submicrometer to micrometer scale were obtained by the solid-state reaction and the flux method [18,20,23,27,28]. On the other hand, the hydrothermal synthesis of layered



 $\label{eq:Fig.3} \begin{array}{c} Fig. \ 3 \ \ Crystal \ structures. \\ (a) \ K_2 Ti_2 O_5; \ (b) \ Na_2 Ti_6 O_{13}; \ (c) \ K_2 Ti_6 O_{13}; \ (d) \ Na_2 Ti_3 O_7; \ (e) \ K_2 Ti_4 O_9; \ (f) \ Cs_2 Ti_5 O_{11}. \end{array}$

Table 1Summary of the products obtained by the solid-state reaction of the mixture of Na_2CO_3 and anatase TiO_2 at a molar ratio of 1:3 at different
temperatures and times [36]

Reaction condition	Average particle size of the starting anatase TiO_2						
	20 nm	200 nm	> 1 µm				
750°C, 2.5 h	$TiO_2 + Na_2Ti_6O_{13}$	$TiO_2 + Na_2Ti_6O_{13}$	TiO ₂				
750°C, 5 h	Na ₂ Ti ₆ O ₁₃	Na ₂ Ti ₆ O ₁₃	TiO ₂ Na ₂ Ti ₆ O ₁₃				
750°C, 26 h	$Na_2Ti_6O_{13} + Na_2Ti_3O_7$ (major)	$Na_2Ti_6O_{13} + Na_2Ti_3O_7$ (major)	$\mathrm{Na_2Ti_6O_{13}+Na_2Ti_3O_7}$				
800°C, 8 h	Na ₂ Ti ₃ O ₇	$Na_2Ti_6O_{13} \text{ (minor)} + Na_2Ti_3O_7$	$Na_{2}Ti_{6}O_{13} + Na_{2}Ti_{3}O_{7}$ (minor)				
800°C, 16 h	_	Na ₂ Ti ₃ O ₇	$Na_2Ti_6O_{13}$ (minor) + $Na_2Ti_3O_7$				
800°C, 40 h	-	-	Na ₂ Ti ₃ O ₇				



Fig. 4 TEM images of $Na_2Ti_3O_7$ obtained by the solid-state reaction of the mixture of Na_2CO_3 and the anatase TiO_2 with different average particle sizes by heating at 800°C (adapted with permission from Ref. [36]). (a) 20 nm; (b) 200 nm; (c) > 1 μ m

alkali titanates gave tubular shaped particles with the diameter of a few tens of nanometer and micrometer scale in the length [29,33,34]. The particle morphology of $K_2Ti_4O_9$ is whisker with a diameter of 1.0–2.0 µm and a length of 10–50 µm as shown in Fig. 5. Fibrous particles

were obtained for $Cs_2Ti_5O_{11}$, which was prepared by heating the mixture of Cs_2CO_3 and anatase TiO_2 at a molar ratio of 1:4 at 1000°C for 20 h [20,25].

Flux materials (such as V_2O_5 , PbO, Bi_2O_3 and K_2MoO_4) were used to induce the melting/dissolution of the starting



Fig. 5 SEM image of $K_2Ti_4O_9$ prepared by heating the mixture of K_2CO_3 and $TiO_2 \cdot nH_2O$ at 920°C for 10 h (adapted with permission from Ref. [38]).

materials. Subsequent crystallization during cooling process was done to control the phase as well as the particle size/shape of the product. For example, the $K_2Ti_6O_{13}$ fiber was prepared by using K_2CO_3 - V_2O_5 flux at different molar ratios as summarized in Table 2 [27]. The shape and length of the $K_2Ti_6O_{13}$ particles obtained by the flux method were significantly affected by the fraction of flux as shown in Fig. 6 [27]. The $K_2Ti_6O_{13}$ needle was formed from the flux at the weight ratio of $Bi_2O_3/K_2Ti_6O_{13} = 0.7$ to 1.5 and PbO/ $K_2Ti_6O_{13} = 0.7$ to 2 [27]. Impurity (or minor phase) phases were also formed depending on the cooling rate. $K_2Ti_6O_{13}$ co-existed with $K_2Ti_4O_9$ when the melt was quenched from 1150°C to room temperature, while $K_2Ti_4O_9$ and $K_2Ti_2O_5$ were formed by slow cooling at the cooling rate of 16°C/h from 1150°C to 950°C and then quenched to room temperature [26–28]. The crystals of Na₂Ti₃O₇ with the length of 0.1–0.3 mm were obtained by the crystallization from the melt of Na₂CO₃, TiO₂, and GeO₂ at 950°C (Fig. 7) [39]. $K_2Ti_4O_9$ and $K_2Ti_6O_{13}$ were obtained from the mixture of (K_2O)_{1/4}·TiO₂ and K_2MoO_4 at a molar ratio of 30:70 [40]. The fraction of $K_2Ti_4O_9$ and $K_2Ti_6O_{13}$ depended on the reaction temperature. The mixture of 50% $K_2Ti_4O_9$ and 50% $K_2Ti_6O_{13}$ formed by heating at 1100°C for 60 min, while $K_2Ti_4O_9$ was obtained as single phase by heating at 950°C for 60 min. The mixed phases of the layered alkali titanates have been reported by the flux method [26–28,39,40].

The TiO₂ (anatase) powder is usually used as the starting material for the syntheses of layered alkali titanates by the hydrothermal method [32,41–43]. The starting mixtures were dissolved at autogenous pressure [29–31]. The fibrous particles of Na₂Ti₃O₇ with a particle length of 20–100 μ m and a width smaller than 1 μ m were obtained by the hydrothermal reaction of TiO₂ and aqueous solution of NaOH at a concentration lower than 3 mol/L, at a temperature above 400°C, and a pressure above 17 MPa [29]. Parameters such as pH of the starting solution and the composition are known to determine the product, while the composition of the product is difficult to be precisely controlled [30]. The temperature for the syntheses affected

Table 2 Particle shape and the length of K₂Ti₆O₁₃ fiber obtained from K₂CO₃-V₂O₃ flux under different conditions [27]

K ₂ CO ₃ :V ₂ O ₃	Weight ratio flux/K ₂ Ti ₆ O ₁₃	Temperature/°C	Particle shape	Maximum length/mm
40:60	1.5	1200 to 900	Rutile, needle-like	4
48:52	2	1250 to 700	Needle-like crystals	4
	1.5	1250 to 700	Needle-like crystals	5
	1	1250 to 700	Needle-like crystals	4
53:47	2	1200 to 900	Needle-like crystals	5
	1.5	1200 to 900	Needle-like crystals	5
	1	1200 to 900	Needle-like crystals	4



Fig. 6 TEM images of $K_2 Ti_6 O_{13}$ fiber obtained by flux method using $K_2 CO_3: V_2 O_5$ flux at different molar ratios (adapted with permission from Ref. [27]).



Fig. 7 SEM image of the crystal of $Na_2Ti_3O_7$ obtained by the crystallization from the melt of Na_2CO_3 , TiO_2 and GeO_2 at 950°C (adapted with permission from Ref. [39]).

the aggregation of the titanate nanotubes in addition to the structure of the titanate [33,34]. Titanate nanotubes were obtained by heating rutile TiO₂ with NaOH at a concentration of 10 mol/L and a temperature of 150°C, while the titanate nanorods was formed at 180°C for 48 h as shown by the TEM images (Fig. 8). A bundle of titanate nanotube was observed when the preparation was done at 180°C for 5 h. After prolonged to the reaction for 30 h, the bundle turned into a rod with nanotubes attached on the outer surface as shown in Fig. 9 [33]. Flower-like layered sodium titanate was prepared by hydrothermal method in a weakly alkaline medium, where NaCl was claimed to act as a morphology directing agent [44]. The formation of flower-like layered sodium titanate depended on NaCl concentration, as shown in Fig. 10. Layered alkali titanates with fibrous or tubular particle morphology were prepared by utilizing the hydrothermal method and the particle size of a micrometer in length and a few tens to hundreds of nanometers in width was obtained [29-35].

In general, one dimensionally anisotropic shaped particles of the layered alkali titanates were obtained while the particle size and shape largely depend on the methods of preparation. The layered alkali titanates particles with fibrous/whisker and elongated rectangular shapes of submicrometer to micrometer scale in size were



Fig. 8 $H_2Ti_3O_7$ nanotubes and nanorods obtained by treating rutile at a NaOH concentration of 10 mol/L for 48 h (adapted with permission from Ref. [33]). (a) 150°C; (b) 180°C.



Fig. 9 TEM images of $H_2Ti_3O_7$ synthesized by heating rutile at a NaOH concentration of 10 mol/L and a temperature of 180°C (adapted with permission from Ref. [33]). (a) 5 h; (b) 30 h.



Fig. 10 SEM images of flower-like layered sodium titanate obtained by hydrothermal reaction in the presence of NaCl at different concentrations (adapted with permission from Ref. [44]). (a) 0 mol/L; (b) 2.0 mol/L; (c) 3.0 mol/L; (d) 4.0 mol/L.

obtained by the solid-state reaction and flux method [18–20,23,25–28], while the hydrothermal synthesis of the layered alkali titanates gave tubular shape in nanometer size [29–34]. A comparison of the preparation methods is given in Table 3.

4 Characteristics of layered titanates

Adsorptive and (photo)catalytic properties of layered titanate have been modified by the functionalization through cation exchange and nanoparticle immobilization, which are introduced in Section 4 as cation exchange, complexation with metallic nanoparticles, and hybridization with semiconductor nanoparticles.

	Solid-state reaction	Flux method	Hydrothermal method
Operation	★ Relatively high temperature processing $\sqrt{1}$ Atmospheric pressure	𝔅 Relatively high temperature processing √ Atmospheric pressure	$\sqrt{\text{Relatively low temperature processing}}$ X Pressurized
			✗ Requires concentrated and hot alkali solutions
Shape	Rectangular shaped (fibrous/whisker)	Elongated rectangular shaped (needle)	Nanotubes, nanofibers, nanorods
Size	Length: submicrometer to micrometer Width: submicrometer	Length: micrometer to submillimeter Width: submicrometer	Length: submicrometer to submillimeter Diameter: nanometer

 Table 3
 Methods for preparation of layered alkali titanate

4.1 Cation exchange

The ion exchange of metal ions on layered alkali titanates has been examined in order to take advantage of the high cation exchange capacity (CEC) of some layered alkali titanates. The theoretical cation exchange capacity of Na₂Ti₃O₇, K₂Ti₄O₉, and Cs₂Ti₅O₁₁ calculated from the chemical formula are 6.63, 4.83, and 2.94 meq/g, which are quite high compared with layered silicates such as smectites (0.6–1.2 meq/g), magadiite (2.0 meq/g) [2]. The high cation exchange capacity is an advantageous aspect for the application on the concentration of novel and toxic metal ions from aqueous environments and the materials design based on the layered titanates.

The ion exchange of the layered alkali titanates with several metal ions such as Ag(I), Cu(II), Sr(II), Br(II), Pb (II), Cd(II), Eu(III), Cr(III), and Ce(III) has been reported [45–52]. The quantitative ion exchange of $Na_2Ti_3O_7$ with mono, di and trivalent ions (proton, NH_4^+ , Mg(II), Ni(II), Co(II), and Al(III)) was studied by Ikenaga et al. [53]. The preferential adsorption of proton from acidic aqueous solution containing Ni(II) and Al(III) was reported compared with Ni(II) and Al(III), while the ion exchange between Na₂Ti₃O₇ and the monovalent ions (proton and NH_4^+) gave $H_2Ti_3O_7$ and $(NH_4)_2Ti_3O_7$, respectively. The intercalation was examined by XRD to observe the change of basal spacing (Fig. 11) [53]. The adsorption of metal from aqueous solution has been investigated and the adsorption isotherms have been used to understand the interaction. Liu et al. reported the efficient concentration of



Fig. 11 XRD patterns (adapted with permission from Ref. [53]). (a) Na₂Ti₃O₇; (b) H₂Ti₃O₇; (c) (NH₄)₂Ti₃O₇.



Fig. 12 Adsorption isotherm of Hg(II) on $Na_2Ti_3O_7$ nanoflowers (adapted with permission from Ref. [54]).

Hg(II) from aqueous solution on flower-like $Na_2Ti_3O_7$ by the L-type adsorption isotherm shown in Fig. 12 [54].

Proton exchange of Na₂Ti₃O₇, K₂Ti₄O₉, and Cs₂Ti₅O₁₁ was done by treating the titanates in the HCl solution to obtain H₂Ti₃O₇, H₂Ti₄O₉·H₂O, and H₂Ti₅O₁₁·3H₂O [9,23,55–58]. The ion exchange of the protonic forms of layered alkali titanates with cations such as Li(I), Na(I), K(I), Rb(I), Cs(I), Ag(I), Ba(II), Co(II), Cu(II), Fe(II), Ni(II), Cd(II), Zn(II), Co(II), Pb(II), Sr(II), Br(II), Ca(II), Mg(II), Mn(III), La(III), Gd(III), Eu(III), Tb(III), Lu(III), NH_4^+ , and alkylammonium has been reported [11,23,45,55,57–69]. The ion exchange of protonic forms of titanates with alkali ions was influenced by the pH and ionic radii of alkali metals [55,56]. The ion exchange of $H_2Ti_3O_7$ with Na(I) required a pH higher than 11 as shown in Fig. 13. The ion exchange of H₂Ti₃O₇ with Li(I), Na(I), and K(I) was about 63%, 43%, and 11% of CEC of $H_2Ti_3O_7$ (7.76 meg/g) after the reaction for 3 days at room temperature (Fig. 14). The degree of ion exchange decreased when the ionic radii of alkali metals was larger [55]. The ionic radii of Li(I), Na(I), and K(I) are 0.74, 1.02, and 1.38 Å, respectively [70].

Wang et al. examined the competitive adsorption of Pb(II), Cd(II), and Cr(III) on Na₂Ti₃O₇ nanotubes to find the ion selectivity as Pb(II) > Cd(II) > Cr(III) [49]. The selective and irreversible adsorption of Hg(II) from aqueous solution on a flower-like Na₂Ti₃O₇ was investi-



Fig. 13 Effect of pH value on cation exchange of $H_2Ti_3O_7$ with Na(I) (adapted with permission from Ref. [55]).



Fig. 14 Ion exchange of $H_2Ti_3O_7$ with Li(I), Na(I), and K(I) using the aqueous solution of LiOH, NaOH, and KOH at a concentration of 0.1 mol/L (adapted with permission from Ref. [55]).

gated to show the high selectivity of Hg(II) in the presence of Mg(II) and Ca(II) [54]. The competitive ion exchange of Mn(II) and Gd(III) on H₂Ti₃O₇ was examined to show the selectivity order of Gd(III) > Mn(II) [60]. Recently, the ion exchange of layered alkali titanates with several alkali metal halides has been obtained by solid-state reaction at room temperature [71]. The adsorbed amount of metal ions and the understanding of the sequence of the ion exchange from aqueous solution on layered titanates are still worth further investigation.

The intercalation of a cationic dye into the interlayer space of layered titanates has been reported for the purposes of photosensitization and photofunctional materials design [72]. The dimethylviologen cation was intercalated into the interlayer space of $K_2Ti_4O_9$ to show photoinduced charge transfer, which is demonstrated by the color change from colorless to blue (photochromism) by the UV irradiation to the powder sample [73]. Some cationic cyanine dyes were intercalated into Na₂Ti₃O₇ and $Cs_{0.7}Ti_{1.98} \square 0.02O_4$ (\square represents vacancy) by cation exchange reactions using the alkylammonium-exchanged forms as the intermediates [74,75]. The alkylammonium exchanged forms were used as the precursor of organic derivates of the layered titanates [76,77]. On the other hand, macrocyclic compounds were used to accelerate the ion exchange of $K_2Ti_4O_9$ [78,79].

4.2 Complexation with metallic nanoparticles

Nanoparticles of Pt and Pd have been synthesized from the adsorbed metal ions in/on the layered alkali titanates [62,80]. Pt nanoparticles have been prepared by the ion exchange of the alkali ions of the layered titanates $(A_2Ti_3O_7, A = Li(I), Na(I) and K(I))$ with Pt complexes $([Pt(NH_3)_2]^{2+})$ and the subsequent reduction of the adsorbed $[Pt(NH_3)_2]^{2+}$ by the heat treatment under H₂. The Pt nanoparticles located on the internal and external surfaces of the titanate nanotube (Fig. 15(a)) [80]. The particle size of the Pt nanoparticles was around 0.5-1.5 nm as shown in Fig. 15(b). The deposition of Pd nanoparticles on H₂Ti₃O₇ nanotubes was done by the ion exchange of Pd(II) in acidic solution at room temperature and subsequent reduction [62]. The particle size distribution of the spheroidal particle of Pd was in the range of 1.9-4.8 nm. Spatial distribution of Pd nanoparticles depended on the Pd (II) loading as shown in Fig. 16. The nonuniform deposition of Pd nanoparticles was seen at the Pd(II) loading of 4.75% (mass fraction), while the distribution of Pd nanoparticles was more uniform at the Pd(II) loading of 6.97 and 8.86% (mass fraction).

4.3 Hybridization with semiconductor nanoparticles

The metal ions adsorbed on layered titanates have been converted to semiconductor particle such as oxides and sulfides. Margues et al. reported the intercalation of Ce(IV) and Ce(III) on Na₂Ti₃O₇ by the ion exchange with aqueous solution of $(NH_4)_2Ce(NO_3)_6$ and the subsequent formation of CeO₂ particles on the external surface of the titanate nanotube [81]. The amount of CeO_2 nanoparticles on the surface of the titanate nanotube increased as the Ce concentration of the starting solution increased, and the relation is summarized in Fig. 17. SiO₂- and Al₂O₃-pillared Ti_4O_9 were prepared by the ion exchange of $K_2Ti_4O_9$ with alkylammonium cation and subsequent reactions with tetraethyl orthosilicate (TEOS) and aqueous solution of aluminum hydroxide oligomers [Al₁₃O₄(OH)₂₄(H₂O)₁₂]⁷⁺, respectively, followed by the calcination at 500°C under O₂ [82,83]. The pillaring of K₂Ti₄O₉ with TiO₂ particles was examined by the reaction alkylammonium-Ti₄O₉ with TiO₂



Fig. 15 Pt nanoparticles dispersed on Na₂Ti₃O₇ nanotubes (adapted with permission from Ref. [80]).
(a) TEM image; (b) particle size distribution of Pt nanoparticles.



Fig. 16 TEM image of H₂Ti₃O₇ after ion exchange with Pd(II) at different Pd(II) loading (adapted with permission from Ref. [62]). (a) 4.75% (mass fraction); (b) 6.97% (mass fraction); (c) 8.86% (mass fraction).

sol and subsequent decomposition of alkylammonium ions by UV irradiation in water [84]. The RuO₂ supported Na₂Ti₃O₇ was prepared by the impregnation of dodecacarbonyltriruthenium (Ru₃(CO)₁₂) from tetahydrofuran followed by the reduction at 400°C under H₂ and the subsequent oxidation in air at 400°C [85]. The TEM images (Fig. 18) indicated that the immobilized RuO₂ particle had spherical shape with the size of 2–3 nm.

Nanoparticles of γ -Fe₂O₃ was incorporated in H₂Ti₃O₇ nanotubes by the self-assembly of γ -Fe₂O₃ nanoparticles and H₂Ti₃O₇ nanotubes in water at pH 6.5 [86]. The γ -Fe₂O₃ nanoparticles were attached on H₂Ti₃O₇ bundles at both ends of the nanotubes and the free γ -Fe₂O₃ nanoparticles were presented when the fraction of γ -Fe₂O₃ nanoparticles increased to 25% (mass fraction) as shown by the TEM images (Fig. 19). Lin et al. prepared CdS-pillared H₂Ti₃O₇ by the self-assembly of exfoliated titanate nanosheets and CdS sol through the electrostatic interactions [87]. The CdS-pillared H₂Ti₃O₇ showed a microporous structure as characterized by the XRD patterns (with the basal spacing of 2.60 nm, corresponded to the interlayer space of 1.82 nm) and the N₂ adsorption/ desorption isotherms (Fig. 20). The CdS-pillared $H_2Ti_3O_7$ at a CdS:Ti₃O₇²⁻ molar ratio of 1:1, 1:2, and 1:3 exhibited a bimodal pore size distribution at 2.3 and 4.6 nm, corresponding to the interlayer space of the CdS pillared titanate and the interparticle space between the nanohybrids [87].

The dehydration/dehydroxylation of the proton exchanged forms, H₂Ti₃O₇, H₂Ti₄O₉, and H₂Ti₅O₁₁, resulting in the formation of a metastable form of titania, $TiO_2(B)$, which was transformed to anatase and then rutile by further thermal treatment at higher temperatures [23,56,88,89]. The dehydration of the titanic acids was claimed to proceed through the following three steps: condensation of layered titanate nanosheets as the layers join together through corner-sharing TiO₆ octahedra (endothermic reaction), formation of TiO₂(B) intermediate (exothermic reaction), and low energy transformation of $TiO_2(B)$ [88]. The formation of $TiO_2(B)$ depended on the original structure of the layered titanates while the crystallinity of the $TiO_2(B)$ depended on the length of the connection of TiO₆ octahedra and the temperature of dehydration [88].



Fig. 17 TEM images of $Na_2Ti_3O_7$ nanotube before and after the ion exchange with aqueous solution of $(NH_4)_2Ce(NO_3)_6$ of a Ce concentration of 0.05, 0.5, 1.0, 5.0, 10, 20, 30 and 40 mmol/L (adapted with permission from Ref. [81]).



Fig. 18 TEM image of RuO_2 supported $Na_2Ti_3O_7$ (adapted with permission from Ref. [85]).

5 Applications of layered alkali titanates and their hybrids

The applications of layered alkali titanate and their hybrids related to environment and energy issues are discussed in this section. The application includes adsorbent of metal ions, photocatalysts for water treatment and artificial photosyntheses (H₂ and/or O₂ production and CO₂ reduction) as summarized in Table 4.

5.1 Adsorbents

The adsorption of target metal ions from water for the



Fig. 19 TEM images of γ -Fe₂O₃ incorporated H₂Ti₃O₇ with varied γ -Fe₂O₃ contents (adapted with permission from Ref. [86]). (a) 0% (mass fraction); (b) 5% (mass fraction); (c) 10% (mass fraction); (d) 15% (mass fraction).

water purification and collection of useful metal ions has been reported using layered alkali titanates. Zou et al. prepared Zr-doped Na₂Ti₃O₇ with a porous core of an ultrafine nanofiber for the removal of multiple heavy metal ions such as Pb(II), Cd(II), Cu(II), and Sr(II) [90]. The adsorption isotherms with the Langmuir model and the adsorption kinetic curves of Pb(II), Cd(II), Cu(II), and Sr(II) on Zr-doped Na₂Ti₃O₇ are shown in Fig. 21. The adsorbed amounts of Pb(II), Cu(II), and Cd(II) were 2.91, 2.56, and 2.10 mmol/g, which corresponded to the removal efficiency of 100% within 20, 10 and 20 min, respectively. The removal efficiency of Sr(II) was 77% within 60 min (1.59 mmol/g). The layered titanates $(H_rNa_{2-r}Ti_3O_7)$ prepared by the hydrothermal reaction were used to concentrate Cu(II) and Cd(II) from aqueous solutions [50]. The maximum adsorbed amounts of Cu(II) and Cd(II) were 120 mg/g and 210 mg/g, respectively. $Cs_2Ti_5O_{11}$ and Na₂Ti₃O₇ were used to concentrate Cd(II) from aqueous solution [91]. Cd(II) was collected by the ion-exchange for Cs₂Ti₅O₁₁ and the formation of CdCO₃ accompanied with the proton-Na(I) exchange for Na₂Ti₃O₇. The maximum collected Cd(II) amounts were 1.28 mmol/g Cs₂Ti₅O₁₁ and 1.16 mmol/g $Na_2Ti_3O_7$. The collection of In(III) in aqueous solution was also possible by using $Na_2Ti_3O_7$ [92] and the collected In(III) existed as In(OH)₃ on the surface of the layered titanate. The maximum collected In(III) amount for $Na_2Ti_3O_7$ was 2.0 mmol/g, which is quite high if compared with those achieved by common ion exchangers.

The Na₂Ti₃O₇ nanofibers were used to remove divalent radioactive and heavy metal ions such as Sr(II) (0.63 mmol/g), Ba(II) (0.95 mmol/g), and Pb(II) (1.35 mmol/g) from wastewater [46]. The selective adsorption of Sr(II), Ba(II), and Pb(II) over Na by the Na₂Ti₃O₇ nanofibers was achieved in the presence of excess of Na(I).

5.2 Photocatalyst

5.2.1 Pristine layered alkali titanates and their protonated forms

Some layered alkali titanates are useful photocatalysts for water splitting and the oxidation of organic molecules in water under UV irradiation [93–98]. Shibata et al.



Fig. 20 XRD patterns, N₂ adsorption/desorption isotherms and the pore size distribution of CdS-pillared H₂Ti₃O₇ at varied molar ratios of CdS:Ti₃O₇²⁻ (adapted with permission from Ref. [87]).



Fig. 21 Adsorption behavior of Pb(II), Cd(II), Cu(II), and Sr(II) on Zr-doped Na₂Ti₃O₇ (adapted with permission from Ref. [90]). (a) Adsorption isotherms; (b) adsorption kinetic curve.

 Table 4
 Summary of layered alkali titanate-based photocatalysts for H₂ evolution and CO₂ reduction reactions

 Photocatalytic H₂ evolution reaction

Layered alkali titanates or its derivative	Starting materials	Synthetic method	Photocatalytic conditions	Light source	Co-catalysts	Efficiency $/(\mu mol \cdot (h \cdot g)^{-1})$	Ref.
Na ₂ Ti ₃ O ₇	_	Solid-state reaction	Methanol-water (20%, volume fraction)	500 W Xe	– Pt	5.8 38	[93]
$H_2 Ti_3 O_7$	Na ₂ Ti ₃ O ₇	Proton exchange reaction	Methanol-water	500 W Xe	_	3.8	
			fraction)		Pt	11	
K ₂ Ti ₂ O ₅	-	Solid-state reaction	Methanol-water (20%, volume	500 W Xe	– Pt	41.6 69.4	
H ₂ Ti ₂ O ₅	K ₂ Ti ₂ O ₅	Proton exchange reaction	Methanol-water	500 W Xe	-	66.8	
			fraction)		Pt	83.8	
K ₂ Ti ₄ O ₉	-	Solid-state reaction	Methanol-water (20%, volume	500 W Xe	– Pt	7 9.6	
UTO	K T: O	Durten andrenen undien	fraction)	500 W V-		<i>C</i> A	
$H_2 H_4 O_9$	K ₂ 11 ₄ O ₉	Proton exchange reaction	(20%, volume fraction)	500 W Xe	– Pt	6.4 27.6	
K ₂ Ti ₆ O ₁₃	_	Solid-state reaction	Methanol-water	500 W Xe	_	8.4	
			(20%, volume fraction)		Pt	121	
$\mathrm{H}_{2}\mathrm{Ti}_{6}\mathrm{O}_{13}$	$K_2 Ti_6 O_{13}$	Proton exchange reaction	Methanol-water	500 W Xe	-	30.2	
			(20%, volume fraction)		Pt	166	
Cs ₂ Ti ₂ O ₅	-	Solid-state reaction	Methanol-water (3%, volume fraction)	400 W high-pressure Hg	_	500	[94]
$H_2 Ti_2 O_5$	$Cs_2Ti_2O_5$	Proton exchange reaction	Methanol-water	400 W	_	852	
			(3%, volume fraction)	high-pressure Hg	Pt	2510	
$Cs_2Ti_5O_{11}$	_	Solid-state reaction	Methanol-water (3%, volume fraction)	400 W high-pressure Hg	_	90	
$Cs_2Ti_6O_{13}$	-	Solid-state reaction	Methanol-water (3%, volume fraction)	400 W high-pressure Hg	_	38	
K ₂ Ti ₄ O ₉	_	Solid-state reaction	Methanol-water	300 W Xe	_	40	[13]
			(20%, volume fraction)		Pt	2210	
$H_2 Ti_4 O_9$	_	Proton exchange reaction	Methanol-water	300 W Xe	_	290	
			(20%, volume fraction)		Pt	2520	
TBA2-Ti4O9	$H_2Ti_4O_9$	Exfoliation	Methanol-water	300 W Xe	—	140	
			(20%, volume fraction)		Pt	4050	
Sn(II)-K ₂ Ti ₄ O ₉	K ₂ Ti ₄ O ₉	Ion exchange reaction	Methanol-water (10%, volume fraction)	300 W Xe	Pt	115	[96]
Sn(II)-K ₂ Ti ₂ O ₅	K ₂ Ti ₂ O ₅	Ion exchange reaction	Methanol-water (10%, volume fraction)	300 W Xe	Pt	25	
Sn(II)-Cs ₂ Ti ₆ O ₁₃	$Cs_2Ti_6O_{13}$	Ion exchange reaction	Methanol-water (10%, volume fraction)	300 W Xe	Pt	35	

						(Cont	tinued)
Photocatalytic H ₂ evo	olution reaction						
Layered alkali titanates or its derivative	Starting materials	Synthetic method	Photocatalytic conditions	Light source	Co-catalysts	Efficiency /(μ mol·(h·g) ⁻¹)	Ref.
Sn(II)-K ₂ Ti ₆ O ₁₃	K ₂ Ti ₆ O ₁₃	Ion exchange reaction	Methanol-water (19%, volume fraction)	300 W Xe	Pt	250	[122]
Li_{2-x} H _x Ti ₃ O ₇	_	Alkaline hydrothermal and ion exchange reaction	Methanol	30 W UV	Pt	2910	[97]
Na _{2-x} H _x Ti ₃ O ₇	_	Alkaline hydrothermal and ion exchange reaction	Methanol	30 W UV	Pt	2700	
$K_{2 \rightarrow x} H_x Ti_3 O_7$	_	Alkaline hydrothermal and ion exchange reaction	Methanol	30 W UV	Pt	3630	
Cs_{2-x} H _x Ti ₃ O ₇	_	Alkaline hydrothermal and ion exchange reaction	Methanol	30 W UV	Pt	2280	
K ₂ Ti ₆ O ₁₃ fibers	_	Flux synthesis and heat treatment	Methanol-water (2%, volume fraction)	250 W Hg	_	298	[100]
K ₂ Ti ₆ O ₁₃ fibers	-	Flux synthesis	Water vapor	300 W Xe	Rh	18	[101]
$[Ti_{3-x}Rh_xO_7]^{2^-}$ nanosheets	_	Solid-state reaction and exfoliation	Triethylamine- water (pH 11)	500 W Xe (>220 nm)	_	1040	[102]
				500 W Xe (>340 nm)	_	302	
$\left[Ti_{3}O_{7}\right]^{2^{-}}nanosheets$				500 W Xe (>220 nm)	Rh	1970	
$H_2Y_xTi_{2-x}O_5 \cdot H_2O$	_	 Microwave-assisted alkaline hydrothermal method in the presence of Y salt and proton exchange reaction 	Methanol-water	Hg-Xe lamp	-	72	[103]
/anatase/rutile					Ni	6660	
					Cu	11660	
					Co	5280	
Anatase TiO ₂ / K ₂ Ti ₄ O ₉	K ₂ Ti ₄ O ₉	Hydrothermal treatment in TBA, NH ₄ F solution	Methanol-water (5%, volume fraction)	150 W Xe (>450 nm)	Ni	0.12	[123]
$WO_3/H_2Ti_3O_7$	$H_2Ti_3O_7$	₂ Ti ₃ O ₇ Microwave-assisted hydrothermal method	2-propanol-water (50%, volume	UV LED (365 nm)	Rh	4680	[113]
			fraction)	Vis LED (450 nm)	Rh	1740	
Cr ₂ O ₃ /titanate nanosheets	$H_2Ti_3O_7$	Alkaline hydrothermal treatment in the presence of Cr source and proton exchange reaction	Triethanolamine- water (10%, volume fraction)	300 W Xe (>420 nm)	Pt	473	[124]
$H_2 Ti_2 O_4 (OH)_2$	-	Alkaline hydrothermal treatment	Na ₂ S/Na ₃ SO ₃ - water	300 W Xe	-	195	[125]
GQDs /H ₂ Ti ₂ O ₄ (OH) ₂	H ₂ Ti ₂ O ₄ (OH) ₂ nanotubes	Solvothermal treatment of H ₂ Ti ₂ O ₄ (OH) ₂ with citric acid in DMF			_	290	
CdS/GQDs/ H ₂ Ti ₂ O ₄ (OH) ₂	GQDs/ H ₂ Ti ₂ O ₄ (OH) ₂	Ion exchange with Cd(II) followed by sulfurization			_	530	
H ₂ Ti ₃ O ₇ nanobelts	Na ₂ Ti ₃ O ₇	Alkaline hydrothermal treatment and proton exchange reaction	Methanol-water (18%, volume fraction)	Solar simula- tor (AM 1.5 G, > 300 nm)	Pt	n/d	[109]
Mesoporous TiO ₂ -B	H ₂ Ti ₃ O ₇	Heat treatment in air			Pt	9375	

Pt

4030

nanobelts Anatase TiO₂

nanobelts

 $\mathrm{H}_{2}\mathrm{Ti}_{3}\mathrm{O}_{7}$

Heat treatment in air

643

(Continued)

Photocatalytic H ₂ ev	olution reaction					×	,
Layered alkali titanates or its derivative	Starting materials	Synthetic method	Photocatalytic conditions	Light source	Co-catalysts	Efficiency $/(\mu mol \cdot (h \cdot g)^{-1})$	Ref.
Octahedral Anatase Particles (OAPs)	K ₂ Ti ₈ O ₁₇	Hydrothermal treatment of $K_2 Ti_8 O_{17}$	Methanol-water (50%, volume fraction)	400 W High pressure Hg	Pt	4320	[121]
Anatase TiO ₂ nanorods	H ₂ Ti ₃ O ₇ nanotubes	Heat treatment in air	Ethanol-water (10%, volume fraction)	100 W UV LED (365 nm)	Au	14400	[126]
			Glycerol-water (10%, volume fraction)			29200	
Anatase TiO ₂	H ₂ Ti ₃ O ₇	Heat treatment	Ethanol-water	100 W UV	Pd	30000	[110]
nanorods	nanotubes		(10%, volume fraction)	LED (365 nm)	Au	8700	
			naction)		Pd-Au	39000	
N-doped defected-anatase TiO ₂	$H_2Ti_2O_5 \cdot H_2O$	Heat treatment of DMF $/H_2Ti_2O_5 \cdot H_2O$ in air	50%, volume fraction methanol-water	Solar simulator	_	1035	[105]
Rutile TiO ₂ nanobundles	$H_2Ti_5O_{11}\cdot 3H_2O$	HNO ₃ treatment of layered titanic acid under reflux	Triethanolamine- water	300 W Xe arc (0.38 W/cm ²)	Pt	8048 (3.1 times over Degussa P25)	[127]
Ni(0)-Anatase TiO ₂ /Titanate	H ₂ Ti ₄ O ₉ ·H ₂ O	Precipitation of Ni(OH) ₂ onto H ₂ Ti ₄ O ₉ ·H ₂ O and thermalreduction in innert atmosphere	2-propanol-water (1%, volume fraction	100 W Hg)	_	1040	[128]
NiTiO ₃ /Anatase TiO ₂ nanotube	$H_2Ti_nO_{2n+1}$ nanotubes	Adsorption of Ni(II) and heat treatment in air	Methanol-water (10%, volume fraction)	300 W Xe	_	680	[129]
Cu(OH) ₂ -Ni(OH) ₂ / Anatase TiO ₂ nanorods	H ₂ Ti ₃ O ₇ nanotubes	Heat treatment of H ₂ Ti ₃ O ₇ and co-deposition of copper and nickel hydroxides	Ethanol-water (20%, volume fraction)	100 W UV LED (365 nm)	_	26600	[130]
Anatase TiO ₂ microspheres	H ₂ Ti ₄ O ₉ nanotube	Hydrothermal treatment of H ₂ Ti ₄ O ₉ in HF/urea solution	Tri-ammonium phosphate-water	1000 W Hg	-	31250 (2.5 fold greater than $H_2Ti_4O_9$ nanotube)	[117]
Anatase/ K_{2-x} H_x Ti _n O _{2n+1} , n = 6, 8	-	Alkaline hydrothermal and proton exchange reaction	0.3 mol/L NH ₃ BH ₃ / H ₂ O + 40°C	100 W UV LED (365 nm)	_	10000	[116]
rGO/Na2Ti3O7	-	Alkaline hydrothermal treatment in the presence of rGO	Ammonia borane-water	Xe lamp (220 mW/cm ²)	_	131 mL/(g _{cat} ⋅min) (2.7 times higher than Na ₂ Ti ₃ O ₇)	[119]
Fe-Co exchanged titanate nanotubes	Na ₂ Ti ₃ O ₇	Ion exchange reaction with Fe and Co cations	Triammonium phosphate-water	Sun light (Egypt, latitude 29° N)	-	$\begin{array}{l} 348200 \; \mu mol / \\ (h \cdot g_{salt} \cdot g_{cat}) \end{array}$	[118]
Photocatalytic CO ₂ r	reduction						
Layered alkali titanates or its derivative	Starting materials	Synthetic method	Photocatalytic conditions	Light source	Co-catalysts	Efficiency	Ref.
Titanate- (Zr)UiO-66	H ₂ Ti ₂ O ₅ ·H ₂ O	Microwave-assisted solvothermal treatment in the presence of Zr and 2-aminoteraphtalic acid	CO ₂ -H ₂ -Water	150 W Xe arc (>325 nm)	_	0.45 (μmol CO/(h·g))	[131]
Anatase- (Zr)UiO-66		Heat treatment and microwave-assisted solvothermal treatment	CO ₂ -H ₂ -Water		-	0.85 (μmol CO/(h·g))	

						(*******	
Photocatalytic CO ₂ re	eduction						
Layered alkali titanates or its derivative	Starting materials	Synthetic method	Photocatalytic conditions	Light source	Co-catalysts	Efficiency	Ref.
CdS/(Cu(0)- Na _x H _{2-x} Ti ₃ O ₇)	Na _x H _{2-x} Ti ₃ O ₇	Adsorption of Cu(II) and heat treatment in inert atmosphere (H ₂ /N ₂), Adsorption of Cd(II), hydrothermal treatment in Na ₂ S aqueous solution for sulfurization, and heat treatment in inert atmosphere	CO ₂ -water	450 W Xe (>420 nm)	_	27.5(μL CH ₄ / (h·g)), 17(μL C ₂ H ₆ / (h·g)), 10(μL C ₃ H ₈ / (h·g))	[120]
Octahedral Anatase Particles (OAPs)	$K_2 Ti_8 O_{17}$	Hydrothermal treatment of $K_2 Ti_8 O_{17}$	Acetic acid-water (5%, volume fraction)	400 W High pressure Hg	Pt	1130 (µmol $CO_2/(h \cdot g)$)	[121]

examined the H₂ production from the aqueous methanol solution using Na₂Ti₃O₇, K_2 Ti₂O₅, K_2 Ti₄O₉, K_2 Ti₆O₁₃ and proton exchange forms of the layered alkali titanates with and without the Pt deposition as photocatalysts [93]. The layered alkali titanates were synthesized by solid-state reactions and the proton exchanged forms were prepared by treating the layered alkali titanates with the aqueous solution of H₂SO₄. The K₂Ti₂O₅ and the proton exchanged form (H₂Ti₂O₅) exhibited a high activity of H₂ production for the samples with and without Pt deposition. The photocatalytic H₂ production of layered cesium titanates $(Cs_2Ti_2O_5, Cs_2Ti_5O_{11}, and Cs_2Ti_6O_{13})$ was examined by Kudo and Kondo [94]. The Cs₂Ti₂O₅ composed of TiO₅ units showed a higher photocatalytic H₂ production activity from aqueous methanol solution than those from Cs₂Ti₅O₁₁ and Cs₂Ti₆O₁₁, which are composed of TiO₆ units. In addition to the break-down approach [95], a small sized layered titanate was obtained by lowering reaction temperature of the solid-state reaction [99]. Ogawa et al. [99] reported improved dispersion and photocatalytic activity of the small sized titanate (0.2 μ m) obtained by lower temperature synthesis (600°C), if compared with that (30 µm) prepared by reported synthetic conditions (800°C–1000°C), leading to the reduced light scattering and the larger surface area for the substance. K₂Ti₆O₁₃ fibers, which were prepared by flux synthesis, showed a photocatalytic active by UV irradiation for H₂ production from aqueous methanol solution [100]. The H₂ production rate of 298 μ mol/(h·g) was reported for K₂Ti₆O₁₃ fibers without co-catalyst. K₂Ti₆O₁₃ after Rh loading as cocatalyst was able to catalyze water vapor into H2 by the UV irradiation at the rate of 18 μ mol/(h \cdot g) [101].

5.2.2 Metal-doped titanates nanosheets

Rh-doped titanate nanosheets ($[Ti_{3-x}Rh_xO_7]^{2-}$) were synthesized by solid-state reaction between Na₂CO₃, anatase TiO₂, and Rh₂O₃ mixture followed by the exfoliation through acid-base reaction [102]. The shift in the absorption edge to a longer wavelength was found on the Rh-doped titanate nanosheets if compared with pristine titanate, corresponding to the role of 4d level of Rh³⁺ or Rh⁴⁺, which are thought to be doped in the titanate framework (Fig. 22). Figure 22 shows the H₂ evolution from the Rh-doped titanate nanosheets. In the presence of triethylamine (TEA), the Rh-doped titanate nanosheet (Rh: Ti = 1%(mole fraction)) exhibited the H₂ evolution at the rates of 1040 and 302 µmol/(h·g) by UV irradiation (>220 nm) and near UV irradiation (>340 nm), respectively, which were approximately 25 and 7.5 times greater than those by undoped titanate nanosheets.

Microwave-assisted hydrothermal treatment of TiO₂ precursor in the presence of yttrium nitrate solution from highly alkaline media and subsequent proton exchange reaction was done to obtain Y-doped titanic acid nanotubes $(H_2Y_xTi_{2-x}O_5 \cdot H_2O)$. As a result, the band gap narrowing by about 0.28 eV and inducing anatase/rutile phase to form $H_2Y_xTi_{2-x}O_5 \cdot H_2O$ /anatase/rutile heterostructure were observed [103]. By the 1% (mass fraction) Y-doping, H₂ production from aqueous methanol solution by the UVvisible light irradiation for 7 h was higher by a factor of 5.5 compared to $H_2Ti_2O_5 \cdot H_2O$, which was attributed to the enhanced light harvesting (smaller band gap) and effective charge separation. The rates were increased from 72 µmol/ (h·g) (H₂Y_xTi_{2-x}O₅·H₂O/anatase/rutile) to 6660, 11660, and 5280 μ mol/(h \cdot g) after the loading of Ni, Cu, and Co by the in situ photoreduction method, respectively.

5.2.3 Titania derived from protonated layered titanates

Phase transformation of protonated layered titanates $(H_2Ti_nO_{2n+1})$ to crystalline titania (anatase, rutile, $TiO_2(B)$, brookite) occurs by the heat treatment and the product phases depended on the type of the protonated layered titanates, impurities and heat treatment conditions. The photocatalytic activity of $H_2Ti_2O_5$ depended on the heat treatment temperature of $H_2Ti_2O_5$, where the $H_2Ti_2O_5$ heated at 350°C showed the highest H_2 production activity,

(Continued)



Fig. 22 Time course of H_2 production over Rh-doped and undoped titanate nanosheets from aqueous solution of triethylamine under UV (>220 nm) and near UV irradiation (>340 nm) (adapted with permission from Ref. [102]). (The inset shows proposed energy band structure of Rh-doped titanate nanosheets.)

which was explained as a result of the transformation of the layered titanate to anatase [93]. Layered structure of titanates also favored the homogeneous substitution of oxygen by nitrogen, led to a band-to-band visible-light excitation [104]. N-doped anatase TiO_2 with oxygen vacancies was prepared by the heat treatment of H₂Ti₂O₅·H₂O mesoporous assembly containing N,Ndimethylformamide (DMF) in air [105]. The N-doped anatase thus prepared showed a photocatalytic activity for the H₂ production at the rate of 1035 μ mol/(h·g) from methanol-water solution under solar light irradiation (solar simulator). The action spectrum for the H_2 evolution on the photocatalyst exhibited the negligible visible light response photocatalysis (>400 nm) and thus, suggested that the inducing of oxygen vacancies mediated by the N doping played the role in the enhanced charge separation and photocatalytic efficiency. Depending on the heat treatment temperature, mesoporous TiO₂(B) nanobelts were obtained by the heat treatment of H₂Ti₃O₇ nanotubes in air at 450°C, while anatase nanobelts were obtained by annealing at 750°C [106]. Mesoporous TiO₂(B) nanobelts after Pt loading exhibited a H₂ evolution capability from aqueous methanol solution with the rate of 9375 µmol/ $(h \cdot g)$, which was higher than that of anatase TiO₂ nanobelts (4030 μ mol/(h·g)) by solar light irradiation. Calcination of H₂Ti₃O₇ nanotubes in air under various conditions (temperature and time) was investigated to prepare a series of anatase TiO₂ nanorods. Reduction of specific surface area of anatase nanorods, irrespective of the crystallinity (crystallite size derived by Scherrer's equation), was observed as a result of sintering at a higher temperature and/or longer time. Anatase nanorods calcined at 600°C (optimal condition) exhibited the H₂ evolution rates of 8700, 30000, 39000 µmol/(h·g) from ethanolwater solution by UV irradiation after loading with Au, Pd, and Pd-Au, respectively [107]. The calcination of protonated-trititanate nanosheets and nanotubes (obtained by hydrothermal reaction) at 450°C-550°C has been reported

to obtain anatase/TiO₂(B) heterostructures [108–110]. The anatase/TiO₂(B) heterostructures prepared by heating protonated-trititanate nanotubes at 550°C, exhibited a H₂ production activity of 21.72 mmol/g after 2 h of solar light irradiation (about 1.16 and 10 times over P25 and that heated at 350°C). The efficient H₂ production was claimed to be due to the synergistic effect of the high surface area and the promoted electron-hole separation between anatase and TiO₂(B) interface, which were supported by the specific surface area, photoluminescence, and decay time from transient photovoltage spectra [109].

5.2.4 Metal-exchanged titanates

The layered alkali titanates have been functionalized by the ion exchange for visible light responsive photocatalyst. The Sn(II) ion exchanged forms of $K_2Ti_2O_5$ and $K_2Ti_4O_9$ were active photocatalyst for H₂ production from aqueous methanol solutions by visible light irradiation [96]. The visible light absorption of Sn(II) intercalated K₂Ti₂O₅ and K₂Ti₄O₉ was explained as the electronic transition from an electron donor level consisting of Sn 5s orbitals to the conduction band consisting of Ti 3d orbitals. Mesoporous Co(II) intercalated layered titanate formed by the selfassembly of Co(II) and titanate nanosheets ([Ti₄O₉]²⁻) was active photocatalyst for the decomposition of MB by visible light irradiation [111]. The Co(II) gave visible light response due to the electronic transition from the valence band consisting of O 2p orbitals to the electron acceptor level consisting of Co 3d and Ti d orbitals.

5.2.5 Nanoparticles immobilized titanates

Layered titanates have been functionalized by the hybridization with nanoparticles of metals and metal oxides such as Pt and RuO_2 which are expected to act as co-catalysts for H_2 and O_2 production, respectively. H_2

production from water by K₂Ti₄O₉, H₂Ti₄O₉, and the titanate nanosheets (designated as TBA₂Ti₄O₉), which were obtained by using tetrabutylammonium ion for the exfoliation of H₂Ti₄O₉, has been reported by UV irradiation in the presence of methanol [13]. The H₂ production activity of K₂Ti₄O₉, H₂Ti₄O₉, and TBA₂Ti₄O₉ increased after Pt deposition. The layered titanates after Pt deposition were active for the O_2 production from aqueous AgNO₃ solution, and the results are shown in Fig. 23 [13]. The photocatalytic water splitting by RuO₂/Na₂Ti₃O₇ was active under UV irradiation, while the smaller particle size of RuO₂/Na₂Ti₃O₇ exhibited a higher activity than that by larger sized RuO₂ particle as shown in Fig. 24 [85]. Pt nanoparticles were deposited on the layered titanate nanotubes (M_{2-x}H_xTi₃O₇, M is Li(I), Na(I), K(I), and Cs(I) by impregnation for photocatalytic H₂ production from neat alcohol [97]. The electron transfer between the layered titanates nanotube and Pt nanoparticles was accelerated and the particle size of Pt nanoparticles were larger for the layered titanate nanotubes with larger alkali metal ions. The electron density on Pt nanoparticles affected the reduction of proton and the rate of H_2 production, while the larger particle size of Pt nanoparticles, which had excessive accumulation of the electron, led to the increase of the electron-hole recombination and reduced H_2 production.

SiO₂-pillared H₂Ti₄O₉ prepared by the intercalation of organosilanes into the interlayer space of $K_2Ti_4O_9$ followed by the calcination was applied for the photo-degradation of methylene blue (MB) under UV irradiation [83]. The SiO₂-pilared H₂Ti₄O₉ showed a higher MB adsorbed amount compared with H₂Ti₄O₉ and K₂Ti₄O₉ due to the higher surface area, which was shown by N₂ adsorption desorption isotherms (Fig. 25), and the degradation of MB by using SiO₂-pilared H₂Ti₄O₉ and K₂Ti₄O₉ was also faster than those by H₂Ti₄O₉ and K₂Ti₄O₉. TiO₂



Fig. 23 H_2 and O_2 production from aqueous solution of sacrificial electron donors (methanol) and acceptors (AgNO₃) under UV irradiation (adapted with permission from Ref. [13]).



Fig. 24 Photocatalytic activity and the SEM images of $RuO_2/Na_2Ti_3O_7$ (L) and $RuO_2/Na_2Ti_3O_7$ (S) ($RuO_2/Na_2Ti_3O_7$ (L) and $RuO_2/Na_2Ti_3O_7$ (S) represent the samples with larger and smaller particle size of RuO_2 .) (adapted with permission from Ref. [85]).

intercalated $Pt/H_2Ti_4O_9$ was capable of splitting water into H_2 and O_2 by UV irradiation at 60°C, producing 0.3 mmol of H_2 over 5 h [84].

 $Cd_{1-x}Zn_xS/K_2Ti_4O_9$ was used for the decomposition of Rhodamine B (abbreviated as RhB) by visible light irradiation [112]. The photocatalytic activity depended on Zn content and the loading amount of Cd_{0.8}Zn_{0.2}S. $Cd_{0.8}Zn_{0.2}S/K_2Ti_4O_9$ with a 30% (mass fraction) Cd_{0.8}Zn_{0.2}S exhibited the highest photocatalytic activity as shown in Fig. 26. WO3 and Rh nanoparticles were deposited on a protonated titanate nanotube $(H_2Ti_3O_7)$ to prepare a ternary photocatalyst by microwave-assisted hydrothermal method. The ternary photocatalyst was active for H₂ evolution from water using 2-propanol as sacrificial donor under UV light and visible light [113]. Combining Rh and WO₃ on titanate nanotubes (with the optimal content of 0.5% (mass fraction) Rh: 3% (mass fraction) WO₃: H₂Ti₃O₇), enhanced H₂ production and stability during repeated cycles were achieved if compared with those for Rh supported- or WO₃ supported-titanate nanotubes. The deposition of Rh nanoparticles onto WO_3 /titanate significantly improved H₂ production to

achieve a rate of 4680 and 1740 μ mol/(h·g) by UV (365 nm) and visible light (450 nm) irradiation, respectively, which were higher than those (1320 and 260 μ mol/(h·g)) from WO₃/titanate. WO₃ was explained to act as a stabilizer to prevent the collapsing of titanate nanostructure during the repeated uses.

Extracting H₂ from hydrogen-rich chemical substances (such as ammonia borane and ammonium phosphates) is a useful means of hydrogen storage due to its high hydrogen content (up to 19% (mass fraction), 148.2 kg/m³ in the case of ammonia borane). H₂ is released from the compounds by thermolysis in solid state, from aqueous solution in the presence of appropriate catalysts, for thermohydrolysis and photocatalytic hydrolysis. H₂ evolution by light irradiation was reported using titania- and titanate-based materials for photocatalytic hydrolysis of ammonia borane [114–116] and ammonium phosphates [117,118]. The photocatalytic hydrolysis of ammonia borane on reduced graphene oxide coupled with Na₂Ti₃O₇ microspheres (rGO/Na₂Ti₃O₇) by visible light irradiation was improved compared to those by pristine rGO and Na₂Ti₃O₇, suggesting a possible synergistic effect of the hybridization between rGO and



Fig. 25 Increase in porosity and photocatalytic activity of $K_2Ti_4O_9$ by pillaring with SiO₂. (a) N₂ adsorption/desorption isotherms; (b) change in the concentration of MB by UV irradiation (adapted with permission from Ref [83].).



Fig. 26 Photodegradation of RhB on a series of $Cd_{1,x}Zn_xS/K_2Ti_4O_9$ by visible light irradiation (adapted with permission from Ref. [112]). (a) $Cd_{1,x}Zn_xS/K_2Ti_4O_9$; (b) $Cd_{0,8}Zn_{0,2}S/K_2Ti_4O_9$ with different loading amount of $Cd_{0,8}Zn_{0,2}S$.

 $Na_2Ti_3O_7$. The suppression of the charge recombination by rGO and the photothermal effect of rGO can contribute to the accelerated H₂ release by the rGO/Na₂Ti₃O₇ microspheres (Fig. 27) [119]. The ion exchange of Na₂Ti₃O₇ nanotubes with Fe and Co ions was done using the solution mixture of ferrous sulfate and cobalt sulfate to obtain FeCo-exchanged Ti₃O₇. A superior photocatalytic activity was observed for FeCo-exchanged Ti₃O₇ (Fe:Co weight ratio of 3:7) toward tri-ammonium phosphate hydrolysis by sun light for an hour to give the H₂ production of 348200 μ mol/(h · g_{salt} · g_{cat}) (salt means the dry tri-ammonium phosphate) if compared with those for pristine TiO₂ (80200 μ mol/(h \cdot g_{salt} \cdot g_{cat}), Fe-exchanged Ti₃O₇ (223200 μ mol/(h·g_{salt}·g_{cat})), and co-exchanged Ti₃O₇ (196400 μ mol/(h · g_{salt} · g_{cat})) [118]. The enhancement was explained by the extension of the absorption to visible light region by the incorporation of Fe and Co ions.

A ternary photocatalyst (CdS/(Cu-TNTs)) obtained by sequential deposition of metallic copper (Cu(0)) and CdS quantum dots onto sodium trititanate nanotubes $(Na_xH_{2-x}Ti_3O_7)$ was reported to convert CO₂ and water into C1-C3 hydrocarbons (e.g., CH₄, C₂H₆, C₃H₈, C₂H₄, and C_3H_6) upon visible light irradiation (>420 nm) as shown in Fig. 28 [120]. It was explained that, by visible light irradiation, photogenerated electrons in CdS were transported to metallic Cu through the titanate nanotube as a solid mediator and reduced CO₂ to C1-C3 hydrocarbons, on the contrary, holes oxidized water (Fig. 28(a)). In addition, the role of remaining Na in the interlayer space of the titanate was also discussed (Fig. 28(b)), where the increment of interlayer Na(I) promoted C2-C3 production due to specific surface area increasing as well as some impact on the formation of surface-bound carbonate as confirmed by DRIFT.

Wei et al. reported a morphology-dependent photocatalytic activity of octahedral anatase particles (OAPs) obtained by hydrothermal treatment of $K_2Ti_8O_{17}$ nanowires for oxidative decomposition of acetic acid from water by UV irradiation. The photocatalytic activity was enhanced for the sample with a higher OAP content, correlated to slower time-resolved microwave conductivity (TRMC) signal decay, i.e., slower recombination of charge carriers (e^{-/h^+}) probably due to lower content of deep electron traps (Fig. 29) [121].

5.3 Other applications

Lavered titanates have been considered as a negative electrode material. The Li(I) insertion behavior of H₂Ti₃O₇ nanotubes was reported. The H₂Ti₃O₇ nanotube exhibited a large capacity at an initial capacity of 282.2 mAh/g over a potential range of 2.5–1.0 V [132]. Li₂Ti₃O₇ was prepared by the ion exchange of Na₂Ti₃O₇ in molten LiNO₃/LiCl [133]. The reversible Li(I) intercalation and deintercalations was in a voltage range of 1.5–2.0 V (versus Li/Li(I)) and the initial Li(I) intercalation capacity of Li₂Ti₃O₇ was 147 mAh/g. The capacity of Li₂Ti₃O₇ decreased from 147 to 70 mAh/g during the initial 10 cycles (Fig. 30). Na₂Ti₃O₇ was reported as an effective low voltage material for Na(I) battery because its reversed ability uptakes 2 Na (I) per formula unit with a capacity of 200 mAh/g at an average potential of 0.3 V versus Na(I)/Na(0) [134]. The intensity of the XRD patterns of the Na₂Ti₃O₇ trended to decrease when the diffraction patterns of Na₄Ti₃O₇ were found after the reduction, and the intensity of Na₂Ti₃O₇ increased by the reversed process as shown in Fig. 31.

6 Conclusions and future perspectives

The preparation, characterization, and function/functionalization of layered alkali titanates were summarized with the special emphasis on $Na_2Ti_3O_7$, $K_2Ti_4O_9$, and $Cs_2Ti_5O_{11}$. The cation exchange of the interlayer cations has been used to concentrate various metal cations from water, where very large capacity has been expected and



Fig. 27 Photothermal and photocatalytic properties of $rGO/Na_2Ti_3O_7$ microspheres (adapted with permission from Ref. [119]). (a) Infrared photographs of $rGO/Na_2Ti_3O_7$ microspheres, $Na_2Ti_3O_7$ microspheres, and rGO sheets at different times of illumination; (b) change of reaction temperature during illumination; (c) time course of H₂ production from ammonia borane using rGO/Na₂Ti₃O₇ microspheres at different rGO contents under visible light irradiation.

achieved to some extent. Combining the advantages of the nanostructure (nanosheet based structure, with potentially large surface area), materials design on $Na_2Ti_3O_7$, $K_2Ti_4O_9$, and $Cs_2Ti_5O_{11}$ has been done for applications such as electrode and adsorbent. A wide range of morphological variation (achieved by the synthetic methods and conditions as well as by the post synthetic treatments) with anisotropic particles from nanometer to micrometer scales and their suspension and films made application as photocatalysts is one of the important

directions and morphological variation and the hybridization achieved by the chemical reactivities of the layered titanates has been reported. New, simple, and eco-friendly hybridization methods of layered titanates-based materials are worth developing to control the structure of the hybrids, which may not be available by other reported methods, as well as to obtain improved/new functions. Comprehensive understanding to describe the synthesisstructure and the structure-property relationships is also required. Further systematic studies on the effects of the compositional, morphological variation, and the hybridi-



Fig. 28 Photocatalytic CO₂ conversion over a series of CdS/(Cu-Na_xH_{2-x} Ti₃O₇) photocatalysts (The Na/Ti ratios were 0.093 (low), 0.143 (medium), and 0.507 (high).) (adapted with permission from Ref. [120]).

(a) Proposed reaction pathways of photocatalytic CO_2 conversion into Hydrocarbons; (b) gas evolution rates of C1-C3 hydrocarbons on CdS/(Cu-TNTs) as a function of the intercalated Na(I) amount (Na_xH_{2-x}Ti₃O₇) and the specific surface area.



Fig. 29 Influence of OAP content on photocatalytic properties and electron-hole recombination behavior (adapted with permission from Ref. [121]).

(a) Photocatalytic activity of acetic acid decomposition and dehydrogenation of methanol by UV irradiation; (b) time course of TRMC signals of OAPs.



Fig. 30 Cycling performance of Li(I) intercalation and deintercalation reaction of $Li_2Ti_3O_7$ (adapted with permission from Ref. [133]).



Fig. 31 In situ XRD patterns of $Na_2Ti_3O_7/Na$ cell cycled between 2.5 and 0.01 V at C/50 rate (*n* is mole of Na(I) reacted per mole $Na_2Ti_3O_7$.) (adapted with permission from Ref. [134]).

zation are worth conducting, in order to establish the potential of the layered alkali titanates and other related layered transition metal oxides.

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