Tetragonal tungsten bronze-type nanorod photocatalysts with tunnel structures: Ta substitution for Nb and overall water splitting

Ping Wang, Larissa Schwertmann, Roland Marschall and Michael Wark

Tetragonal tungsten bronze-type tantalum (Ta) substituted Sr₂KNb₅O₁₅ nanorod photocatalysts with tunnel structures were prepared by a facile and low-cost molten salt method using potassium chloride (KCl) at 850 °C for only 2 h. Although all native photocatalysts did not possess any detectable activity in pure water splitting, after deposition of NiOₓ (double-layered Ni/NiO) as co-catalysts, samples of Sr₂KNb₅O₁₅ and Sr₂KTa₅O₁₅ can split pure water into H₂ and O₂ in a stoichiometric amount (≈2:1), which can be ascribed to the improved charge carrier separation and transfer in the presence of NiOₓ. Furthermore, Ta substitution effects on the photocatalytic behaviour were systematically investigated for hydrogen production by aqueous methanol reforming. The average H₂ formation rates of Sr₂KTa₅₋ₓNbxO₁₅ first decrease with tantalum substitution for x < 2.5, presumably due to a decreased amount of absorbed photons and an obvious reduction of their exposed surface areas, whereas the activity is significantly improved for samples containing more Ta (x > 2.5) and especially the fully substituted Sr₂KTa₅O₁₅. This can be explained by a stronger driving force for photogenerated conduction band electrons to reduce water.

Introduction

Photocatalytic water splitting and hydrogen production by semiconductor photocatalysis for converting solar energy into chemical energy has drawn ever-growing interest in both science and engineering fields. During the past few years, several types of semiconductor photocatalysts such as bulk-type simple oxides (TiO₂, Nb₂O₅, Ta₂O₅, ZnO and ZrO₂, etc.) as well as perovskite-type oxides (SrTiO₃, K₂NbO₇, NaTaO₃, and A₂La₂Ti₃O₁₀ (A = Na, K and Rb), etc.) have been widely studied. It is well known that the superior photocatalytic ability of layered oxides can be attributed to the unique structure, compared to the above-mentioned bulk-type oxides. The past two decades have also witnessed great efforts on the synthesis of tunnel-structured oxides, such as BaTi₄O₉ and A₂Ti₃O₁₁ (A = Na, K, Rb), etc. The deficient perovskite tetragonal tungsten bronze-type (TTB) niobates (A₁)ₓ(A₂)₁₋ₓ(A₃)ₓNb₁₀O₃₀, consisting of corner-sharing NbO₆ octahedra arrays and three different tunnels (A₁, A₂ and A₃) for cation filling, have been widely investigated as ferroelectric and piezoelectric materials in view of their large spontaneous polarization and high dielectric constants. They also exhibit dominant electron-hole separation and transport via static electric fields between structure-induced dipole moments in distorted metal-oxygen polyhedra. Therefore, a slight structural modification by altering the cation-site occupancy has a dramatic effect on the charge mobility. However, to our knowledge except the paper by Wu, there have been no reports on photocatalytic properties of the modified tunnel-structure bronze-type niobates.

In principle on all the three cation positions A₁, A₂ and A₃ a cation exchange can be done, but since recent studies in niobate/tantalate systems have shown that the substitution of the Nb site with tantalum (Ta) could considerably improve the photocatalytic activity, we concentrated on this substitution. However, most reports of substitution effects are focused on the photodegradation of organic compounds. It still remains a great challenge to directly split water into H₂ and O₂ and to determine the variation of the Ta substitution induced-structure properties and photocatalytic behaviour. In the present work, by employment of a simple and cost-effective molten salt technique, the Sr₂KNb₅₋ₓTaₓO₁₅ nanorod photocatalysts with different Nb/Ta substitution ratios were synthesized. The Ta substitution effect on the photocatalytic behaviour for photocatalytic hydrogen production from methanol reforming was systematically investigated.
Experimental

Photocatalysts preparation

Powders of Sr$_x$K Nb$_{3-x}$Ta$_2$O$_{15}$ with $x = 0, 1, 2.5, 4$ and $5$ were prepared by molten salt method.\[^{29}\] SrCO$_3$ (>99.99%, Aldrich), K$_2$CO$_3$ (>99.99%, Alfa Aesar), Nb$_2$O$_5$ (99.99%, Alfa Aesar), and Ta$_2$O$_5$ (99.85%, Alfa Aesar) were used as starting materials. The desired stoichiometric molar ratios of the starting materials were ground together with potassium chloride (KCI: 99.3%, Honeywell Riedel-de Haén) at a weight ratio of 1 : 2. The well-mixed powders were heated at different calcination temperatures for 2 h in air using a corundum crucible. After cooling down to room temperature, the mixture was intensively washed with distilled water in order to remove any residual salts and then dried in air at 80 °C. The 1.0 wt% NiO$_x$ loaded samples were prepared by impregnation method.\[^{20,21}\] the respective powders were dispersed in a suitable amount of Ni(NO$_3$)$_2$ (99.9983%, STREM Chemicals) solution and heated under constant stirring until the water was completely evaporated. The resulting powder was dried at 80 °C in air, followed by calcination at 200 °C for 2 h, and further treated by reduction under H$_2$ flow at 300 °C for 2 h and re-oxidation under O$_2$ flow at 200 °C for 1 h.

Characterization

The X-ray diffraction (XRD) patterns of all samples were recorded with a PANalytical MPD diffractometer using Cu-Kz radiation ($\lambda = 0.1541$ nm), and the data were collected from 10° to 60° ($2\theta$). Static N$_2$ physisorption measurements were carried out at −196 °C using an Autosorb-1MP Quantachrome system and samples were degassed at 200 °C for 6 h before the measurements. The UV-Vis diffuse reflectance spectra were measured using MgO as a reference on a UV/Vis Varian Cary 4000 spectrophotometer. Band gap energies were calculated by analysis of the Tauc-plots resulting from Kubelka-Munk transformation of diffuse reflectance spectra. Powder samples were sputter-coated with a thin layer of Au particles and then examined in scanning electron microscopes (SEM) using a LEO (Zeiss) 1530 Gemini field-emission. The transmission electron microscope (TEM) images were recorded by a Philips/FEI Tecnai F20 S-TWIN TEM instrument operating at 200 kV.

Photocatalytic activity for H$_2$ production

Photocatalytic reactions were performed in a typical double-walled inner irradiation-type quartz reactor connected to a closed gas evolution system.\[^{29,22}\] The reaction temperature was maintained at 10 °C to prevent any thermal catalytic effect with a double-walled quartz jacket filled with a flow of cooling water from a thermostat (LAUDA). A 500 W Hg mid-pressure immersion lamp (Peschl UV-Consulting) was used as a light source. High-purity Argon (6.0) was used as carrier gas for the reaction products, of which continuous gas flow was set to 50 mL min$^{-1}$ controlled by a Bronkhorst mass flow controller. The evolved gases were analyzed online using a multi-channel analyzer (Emerson) equipped with a detector for the determination of the concentration of hydrogen (thermal conductivity detector), oxygen (paramagnetism) and carbon dioxide (IR). In a typical run, 0.1 g of photocatalyst powder was suspended in 500 mL distilled water. In case of photocatalytic methanol reforming, an additional 50 mL of methanol was added. Prior to irradiation, the whole system including the photocatalysts was purged with argon to remove air completely.

Results and discussion

Synthesis of materials optical and physical properties

In order to determine the optimum calcination temperature, Sr$_x$K Ta$_2$O$_5$ was prepared under different calcination temperatures from 850 to 1050 °C (higher than the melting point of KCl, 774 °C) and the photocatalytic activity of these samples was probed by photocatalytic methanol reforming for H$_2$ production. As shown in Fig. 1, the diffraction peaks of the Sr$_x$K Ta$_2$O$_5$ (JCPDS 40-0345) become sharper and stronger with increasing temperature, indicating the increase of the average crystallite size and the improvement of the crystallinity of Sr$_x$K Ta$_2$O$_5$ crystals. As shown in Table 1, the sample calcined at 850 °C shows a BET surface area of 8.5 m$^2$ g$^{-1}$, and an increase in calcination temperature resulted in the significantly decreased surface areas of 5.3 and 2.7 m$^2$ g$^{-1}$ for samples calcined at 950 °C and 1050 °C, respectively. Presumably enhanced particle growth results in a loss of active surface sites with increasing temperature, leading to an increasingly detrimental effect on the photoactivity for H$_2$ production. Therefore, we chose for the preparation of the samples with different Nb/Ta ratios Sr$_x$K Nb$_{3-x}$Ta$_2$O$_{15}$ ($x = 0, 1, 2.5, 4$ and $5$) a temperature of 850 °C.

Structural properties

X-ray powder diffraction patterns of Sr$_x$K Nb$_{3-x}$Ta$_2$O$_{15}$ ($x = 0, 1, 2.5, 4$ and $5$) with different molar Nb/Ta ratios prepared at 850 °C for 2 h are shown in Fig. 2. All the powders are well-crystallized and no significant shifts are observed in the diffraction patterns. This indicates that Ta$^{5+}$ has diffused into the tetragonal tungsten bronze (TTB) structure to form a solid solution in which Ta$^{5+}$ occupies the Nb lattice sites, because the effective ionic radii of Nb$^{5+}$ and Ta$^{5+}$ ions in the Sr$_x$K Nb$_{3-x}$Ta$_2$O$_{15}$ are similar.

![Fig. 1 XRD patterns of typical Sr$_x$K Ta$_2$O$_5$ samples synthesized with different calcination temperatures for 2 h.](image-url)
(64 pm), and on the contrary, the effective ionic radius of the Ta$^{5+}$ ion is remarkably smaller than those of the Sr$^{2+}$ ion and the K$^+$ ion.$^{23}$ As shown in Fig. 2a, the pattern of our Sr$_2$KNb$_5$O$_{15}$ can be indexed to a TTB structure on basis of the reported data of bulk Sr$_2$KNb$_5$O$_{15}$ crystals (JCPDS 34-0108, space group $P4_{2}bm$ belonging to the point group 4 mm). However, the most intense reflection is (410), instead of (311, 420), and the intensity of (211) reflection decreases by more than half. This agrees very well with reported results,$^{24-26}$ and can be attributed to the anisotropic growth of the Sr$_2$KNb$_5$O$_{15}$ particles leading to a strong (001) orientation. It is important to note that some unknown impurity (<3%) was observed for Sr$_2$KNb$_5$O$_{15}$, as indicated by the arrows in Fig. 2a. Interestingly, no impurity peaks were detected with increasing $x$ and the phenomenon of the preferred (001) orientation gradually began to be weakened for these solid solutions, indicating that the anisotropic grain growth is inhibited by Ta$^{5+}$ substitution. A complete substitution of Ta$^{5+}$ for Nb$^{5+}$, the Sr$_2$KTa$_5$O$_{15}$ phase was derived according to the JCPDS 40-0345. The diffraction peak at about 46.3° splits into two peaks (Fig. 2b). This suggests that when substituting Nb$^{5+}$ with Ta$^{5+}$, the crystal structure transition to a symmetric center appeared from tetragonal point group 4mm to tetragonal point group 4/mmm, in good agreement with the literature.$^{27,28}$

Representative SEM images of Sr$_2$KNb$_5$O$_{15}$ (a), Sr$_2$KNb$_{2.5}$Ta$_{2.5}$O$_{15}$ (b) and Sr$_2$KTa$_5$O$_{15}$ (c) samples are shown in Fig. 3. The samples display a nanorod-shaped morphology with the diameters in the range of 100–400 nm and the lengths up to a few microns, suggesting that the eutectic KCl salt favors the formation of nanorod morphology. With increasing Ta/Nb ratio most of the nanorods become more uniform in size, but also more agglomerated, and grow shorter in length, implying that the anisotropic grain growth can be to some extent be suppressed by the Ta$^{5+}$ substitution, which is in accordance with the XRD analysis. A similar suppression caused by Ta$^{5+}$ substitution was also found in other ceramic systems like (K$_{0.44}$Na$_{0.52}$Li$_{0.04}$)(Nb$_{0.96-x}$Ta$_x$Sb$_{0.04}$)O$_3$, and Sr$_{0.53}$Ba$_{0.47}$Nb$_{2-x}$Ta$_x$O$_6$.$^{29,30}$

The microstructure, the lattice parameters and growth properties of the Sr$_2$KNb$_5$O$_{15}$ and Sr$_2$KTa$_5$O$_{15}$ nanorod samples were further studied by TEM, high-resolution TEM (HRTEM), and selected area electron diffraction (SAED). Fig. 4a shows a TEM image of a typical Sr$_2$KNb$_5$O$_{15}$ nanorod at low magnification. The HRTEM image of the Sr$_2$KNb$_5$O$_{15}$ sample taken from

<table>
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<th>Temperature (°C)</th>
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<th>Rate of $\text{H}_2$ (mmol h$^{-1}$)</th>
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<td>950</td>
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*Measured by the Brunauer–Emmett–Teller (BET) method. Reaction conditions: 0.1 g of photocatalysts; 50 mL of methanol dissolved in 500 mL of water; 500 W Hg lamp.*

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Fig. 2 (a) XRD patterns of Sr$_2$K$_{2-x}$Ta$_x$O$_{15}$ with $x =$ 0, 1, 2.5, 4 and 5 prepared at 850 °C for 2 h, (b) enlarged XRD patterns of the Sr$_2$K$_{2-x}$Ta$_x$O$_{15}$ ranging from 2θ = 45°–47°.

Fig. 3 Representative SEM images of Sr$_2$K$_{2.5}$Ta$_{2.5}$O$_{15}$ (a) and Sr$_2$KTa$_5$O$_{15}$ nanorods (b) and Sr$_2$KTa$_5$O$_{15}$ nanorods (c), respectively.

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Table 1 Effect of calcination temperature on BET surface area and photocatalytic activity for $\text{H}_2$ production

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the top part of the Sr$_2$KNb$_5$O$_{15}$ nanorod (as marked by a white rectangle in Fig. 4a) and the corresponding SAED pattern are presented in Fig. 4b and c, respectively. The lattice fringes of the Sr$_2$KNb$_5$O$_{15}$ [001] and [400] planes are found to be about 0.39(0) nm and 0.31(2) nm, respectively and the SAED pattern can be assigned to tetragonal Sr$_2$KNb$_5$O$_{15}$ single crystals with the electron beam closely parallel to [010] direction. These observations unambiguously indicate that the Sr$_2$KNb$_5$O$_{15}$ nanorod is a high quality single crystal with tetragonal structure, grown along the [001] direction (marked by a white arrow in Fig. 4b).

A typical Sr$_x$KTa$_{5-x}$O$_{15}$ nanorod can be observed in the low-magnification TEM image of Fig. 5a. The HRTEM image in Fig. 5b, which corresponds to the area marked by a white rectangle in Fig. 5a, shows the same crystal planes and the same growth direction (as indicated by a white arrow) as illustrated in Fig. 4b. Therefore, clear evidence for preferential growth direction of Sr$_2$KNb$_5$O$_{15}$ and Sr$_x$KTa$_{5-x}$O$_{15}$ nanorod samples could be further found and both of them have the same [001] growth direction. Therefore, it is suggested that the use of molten salt as a reaction medium plays a dominant role for the formation of nanorod morphology and their preferential growth, while presumably the growth inhibition caused by Ta substitution in these Ta substituted samples, as observed in above XRD and SEM results, is limited.

Fig. 5c shows a representative TEM image of a typical 1.0 wt % NiO$_x$ loaded Sr$_x$KTa$_{5-x}$O$_{15}$ sample. It can be clearly seen that distinguishable nano-NiO$_x$ co-catalyst particles are anchored on an individual Sr$_2$KTa$_{5-x}$O$_{15}$ nanorod. The nano-NiO$_x$ co-catalyst particles consist of a solid Ni metal core and a brighter NiO outer layer. Furthermore, the inset on the lower right shows a lattice resolved HRTEM image of a nano-NiO$_x$ particle, in which the lattices of the outer layer-cubic NiO can be determined to be the [111] and [200] crystal planes with d-spacings of 0.24 nm and 0.21 nm, respectively. The results demonstrate that the double-layered structure of metallic Ni and metal oxide NiO is created on the surface of the Sr$_x$KTa$_{5-x}$O$_{15}$ nanorods photocatalyst by reduction–reoxidation processes. The formation of a Ni metal at the surface of photocatalyst results in the formation of a Schottky contact at the interface, and thus provides an opportunity to facilitate electron transport to the NiO shell to enhance the photocatalytic activity of the photocatalysts for overall water splitting as will be discussed below.

### Optical and physical properties

The UV-Vis diffuse reflectance spectra of Sr$_x$K$_{1-x}$Nb$_5$O$_{15}$ with $x = 0, 1, 2.5, 4$ and $5$ are shown in Fig. 6a. The absorption edges of Sr$_x$K$_{1-x}$Nb$_5$O$_{15}$ obviously shift to shorter wavelengths with increasing Ta content. On basis of Kubelka–Munk transformation of the diffuse reflectance spectra, the band-gap energies from Tauc plots were larger than the apparent band-gap energies if direct transition is assumed for light absorption by the samples. As indicated in Fig. 6b, the assumption of indirect transition is in good agreement with apparent band gap energies, thus suggesting that the as-prepared oxides are indirect band gap semiconductors. Fig. 6c shows the band gaps of Sr$_x$K$_{1-x}$Nb$_5$O$_{15}$, Sr$_x$K$_{1-x}$Ta$_{5-x}$O$_{15}$, Sr$_x$K$_{1-x}$Ta$_{2.5}$O$_{15}$, Sr$_x$K$_{1-x}$Ta$_{0.5}$O$_{15}$ and Sr$_x$K$_{1-x}$Ta$_{5}$O$_{15}$ being estimated to about 3.19, 3.24, 3.32, 3.51 and 3.89 eV, respectively. The band gap of Sr$_x$K$_{1-x}$Nb$_5$O$_{15}$ is almost consistent with the reported value (3.24 eV). The data indicate that the band gaps do not linearly increase with the Ta substitution; for high Ta contents the band gap widening is more prominent.
On the other hand, the BET surface areas of Sr$_2$KNb$_{5-x}$Ta$_x$O$_{15}$ with $x = 0, 1, 2.5, 4$ and $5$ decrease almost linearly with the substitution of Ta, as shown in Fig. 6c. The surface area of as-prepared Sr$_2$KNb$_5$O$_{15}$ (19.1 m$^2$ g$^{-1}$) was improved by more than 60 times compared with that of the sintered sample (0.31 m$^2$ g$^{-1}$) by the conventional solid state reaction method, which may provide more active sites, recombine the photogenerated electron–hole pairs, and thus greatly enhance photocatalytic efficiency. This can be ascribed to the lower reaction temperature and the shorter reaction times (at 850°C for 2 h) possible due to the intimate contacts in the molten salt moderated reaction.

The band structure of photocatalysts is one of the important factors affecting the photonic efficiency. The valence band (VB) potentials of all Sr$_2$KNb$_{5-x}$Ta$_x$O$_{15}$ solid solutions should be quite similar because of the same crystal structure and the same orbitals (O 2p orbitals) comprising the VB. Thus, the difference of band gap energies is due to the orbitals forming the conduction band (CB). According to the report by Scaife, for oxides containing no partly filled d-levels, the following equation can be used to approximately determine the flat band potential:

$$V_{fb}(\text{NHE}) = 2.94 - E_g$$

where $V_{fb}$ and $E_g$ represent a flat band potential and a band gap, respectively. The band structures of Sr$_2$KNb$_{5-x}$Ta$_x$O$_{15}$ with $x = 0, 1, 2.5, 4$ and $5$ are schematically illustrated in Fig. 7. The CB of Sr$_2$KNb$_5$O$_{15}$ consists of Nb 4d, while that of Sr$_2$KTa$_5$O$_{15}$ is from Ta 5d. The CB formed by the empty Ta 5d orbitals lies at a considerably more negative potential than the Nb 4d orbitals. Thus, with increasing Ta substitution, the larger band gap will lead to the decreased amount of absorbed photons. On the contrary, it also means that the CB potential becomes more negative than the water reduction potential (<0 V vs. NHE at pH 0), suggesting that the driving force of Sr$_2$KNb$_{5-x}$Ta$_x$O$_{15}$ for water reduction by electrons in the CB becomes larger, thus

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**Fig. 5** TEM images of the Sr$_2$KTa$_5$O$_{15}$ sample: (a) low-magnification TEM image of a typical Sr$_2$KTa$_5$O$_{15}$ nanorod, (b) HRTEM taken from the edge of the Sr$_2$KTa$_5$O$_{15}$ nanorod as marked by a white rectangle in (a). The white arrow indicates growth direction of the Sr$_2$KTa$_5$O$_{15}$ nanorod along the [001] facet planes, (c) the TEM image of the 1.0 wt% NiO$_x$ loaded Sr$_2$KTa$_5$O$_{15}$ nanorod with inset of a NiO$_x$ particle.

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**Fig. 6** (a) UV-Vis diffuse reflection spectra of Sr$_2$KNb$_{5-x}$Ta$_x$O$_{15}$ with $x = 0, 1, 2.5, 4$ and $5$, (b) Tauc plots (for indirect band gap transition) calculated from the Kubelka–Munk transformation, and (c) band gap energies and BET surface areas of Sr$_2$KNb$_{5-x}$Ta$_x$O$_{15}$ with $x = 0, 1, 2.5, 4$ and $5$, respectively.
promoting the transfer of photoelectrons. It can be concluded that the Ta substitution molar ratio has a great effect on the band structures and thus plays a crucial role in determining the efficiency of H₂ production. Furthermore, the bottom level of the CB was much more negative than the reduction potential of H⁺/H₂ (0 eV), while the top level of the VB was more positive than the oxidation potential of O₂/H₂O (+1.23 eV). It is therefore reasonable to infer that these photocatalysts might be able to split water into H₂ and O₂ by the appropriate excited energy.

**Effect of Ta substitution on photocatalytic H₂ production by reforming of aqueous methanol solution**

The photocatalytic H₂ production rates over co-catalyst-free Sr₂KnO₁₅ with x = 0, 1, 2.5, 4 and 5 from photocatalytic reforming of methanol are shown in Fig. 8. Note that the activities of photocatalysts with different Ta substitution molar ratio were compared by the average rate of H₂ production in the first 1 h and the same photocatalytic trend can be obtained by at least three repeated measurements. For comparison, commercial TiO₂ nanoparticles (Evonik P25) were also tested for photocatalytic H₂ production under the same conditions. The Sr₂KnTaO₁₅ solid solutions photocatalysts exhibited superior photocatalytic activity than P25. And it is clearly seen that the photocatalytic activity of Sr₂KTaO₁₅ is much higher than that of Sr₂KnO₁₅. With the increased content of Ta substitution, the average formation rates of H₂ decreased first, the lowest activity was observed for the Sr₂KnTaO₁₅, and then began to increase in the case of x > 2.5. It might be possible that the crystal sizes and crystallinity of the solid solutions negligibly influence the photocatalytic activity because their crystal sizes and high crystallinity were not significantly changed by Ta substitution from the XRD results. Therefore, the obvious decrease of H₂ formation rate (x < 2.5) can be related to the decreased number of absorbed photons and lower specific surface areas. With higher Ta substitution (x > 2.5), the increase of H₂ formation rate can be mainly attributed to the stronger driving force and more effective photoelectron transfer from the CB as described above.

**Photocatalytic overall water splitting**

All native photocatalysts did not possess photocatalytic activity in pure water, probably due to the low charge separation and transfer efficiency. While 1.0 wt% NiO was loaded as co-catalyst, the photocatalytic overall water splitting into stoichiometric amounts of H₂ and O₂ can be efficiently promoted over prototypical examples of Sr₂KnO₁₅ and Sr₂KTaO₁₅ photocatalysts. Fig. 9 shows the time course of H₂ and O₂ evolution from pure water over 1.0 wt% NiO/Sr₂KnO₁₅ and 1.0 wt% NiO/Sr₂KTaO₁₅ photocatalysts under UV light irradiation for 5 h. After some short induction period of about 15 minutes of irradiation, the formation of H₂ and O₂ in a stoichiometric ratio (H₂/O₂ ≈ 2/1) was observed and there was no appreciable decrease by on-line monitoring of gas evolution, indicating that the samples are stable under UV light irradiation. Therefore, it is demonstrated that the presence of the double-layered nano-NiO particles as co-catalysts on the surface of photocatalysts can improve the photocatalytic activity for overall water splitting. Based on the above TEM results, the formation of a Ni metal core at the surface of photocatalyst results in the formation of a Schottky contact at the interface, and thus facilitate electron transport to the NiO shell and suppress the backward
reaction of water formation, leading to an enhancement of photocatalytic activity for overall water splitting. Furthermore, the average rates of H2/O2 evolution over Sr2KNb5O15 and Sr2KTa5O15 photocatalysts were estimated to be about 36.2/15.2 and 84.5/46.3 µmol h⁻¹, respectively, thus the latter was more than 2 times higher than the former, in agreement with the above-presented comparison value from photocatalytic H2 production by methanol reforming. These experimental results not only proved the photocatalytical abilities of the tunnel structured photocatalysts for overall water splitting, but also consistently confirmed the above reasonable prediction resulting from the theoretical calculation of the band structures.

Conclusions

The novel Sr2KNb5Ta5-xO15 nanorod photocatalysts with tunnel structure were prepared by molten salt technique for 2 h at 850 °C. The effective improvement of the photocatalytic H2 production activity by Ta substitution has been demonstrated in methanol reforming. Compared to a bulk TiO2 sample, the Sr2KNb5Ta5-xO15 nanorod photocatalysts showed much higher activity. Moreover, by loading of NiOx co-catalyst on prototypical Sr2KNb5O15 and Sr2KTa5O15 photocatalysts, the decomposition of water into H2 and O2 at a stoichiometric amount (≈ 2 : 1) under UV irradiation was observed, which can be attributed to the improved charge separation and transfer in the presence of double-layer structure NiOx co-catalyst. Therefore, it can be concluded that the tunnel structure photocatalysts are a new type of photocatalyst materials for overall water splitting from the viewpoint of the tunable components because it consists of three different tunnels and octahedral arrays. Our ongoing work will continue to study on the different tunnels and octahedral arrays, for extending the photosensitivity of photocatalytic oxides into the visible-light region.

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Notes and references