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EDGE ARTICLE

Sensitization of Wide Band Gap Photocatalysts to Visible Light by a Molten CuCl treatment[†]

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Cu(I)-substituted metal oxide photocatalysts were prepared by a molten CuCl treatment to wide band gap photocatalysts. The Cu(I)-substituted metal oxide photocatalysts possessed a new absorption band in the visible light region and showed photocatalytic activities for the hydrogen evolution from an aqueous solution containing sulfur sacrificial reagents under visible light irradiation. Especially, Cu(I)-K₂La₂Ti₃O₁₀ and Cu(I)-NaTaO₃ photocatalysts showed relatively high activities for the hydrogen evolution and gave 0.18% of apparent quantum yields at 420 nm. These photocatalysts responded up to 620 nm. Thus, the Cu(I)-substitution by a molten CuCl treatment was an effective strategy for sensitizing a metal oxide photocatalyst with a wide band gap to visible light.

Introduction

Solar water splitting using a photocatalyst is a candidate for an ultimately clean technology for hydrogen production to address the energy and environmental issues. In order to achieve highly efficient solar water splitting, we have to develop photocatalysts which can utilize wide range of visible light. Metal oxide photocatalysts generally possess wide band gaps, because O 2p orbitals form a deep valence band. Forming a new valence band is one of the strategies for development of visible-light-driven photocatalysts.¹ Ag(I),² Sn(II)³ and Bi(III)⁴ are useful components to give visible light responses to oxide photocatalysts with wide band gaps, because they form new valence bands at more negative level than that consisting of O 2p orbitals. The fact that Cu(I) forms shallower valence band than O 2p has been recently proven by the linear muffin-tin orbital (LMTO) method⁵ and the plane-wave density functional theory package CASTEP.⁶⁻⁸ Moreover, Cu(I) is a component to form a new valence band which locates at more negative level than that formed by Ag(I).^{9,10} Visible-light-driven photocatalysts containing Cu(I) are recently realized by forming a solid solution.^{8,11} LiNb₃O₈-CuNb₃O₈ and Cu₃Ta₇O₁₉-LaTa₇O₁₉ solid solutions show photocatalytic activity for the hydrogen evolution from an aqueous methanol solution under visible light irradiation. Moreover, Cu(I)-containing oxide electrode gives cathodic photocurrent by water splitting under visible light irradiation.⁷ The Cu(I) is a promising key component to develop a visible-light-driven photocatalyst, while it possesses problems with chemical and crystallographical stabilities. Cu(I) is easily oxidized to Cu(II), when a Cu(I)-containing oxide is prepared in air by a solid-state reaction. Moreover, Cu⁺ favors 2-coordination in a crystal structure of oxides.¹² Therefore, only limited crystal structures

are reported as a Cu(I)-containing oxide. In other words, the development of new Cu(I)-containing oxides is a challenging topic. Ion exchange by a molten salt treatment is a useful technique to develop new oxide materials.¹³ We have developed a new material of AgLi_{1/3}Ti_{2/3}O₂ with delafossite structure by a silver nitrate molten treatment to Li₂TiO₃.¹⁴ Cu(I)-containing oxides are also expected to be prepared by a molten CuCl treatment. In this study, we prepared Cu(I)-containing metal oxide photocatalysts with not only layered but also bulky ilmenite and perovskite structures by a molten CuCl treatment. Their photocatalytic activities for the hydrogen evolution were also evaluated under visible light irradiation.

Experimental

Material synthesis

K₄Nb₆O₁₇,¹⁵ KLaNb₂O₇,¹⁶ RbCa₂Ta₃O₁₀,¹⁷ LiTaO₃,¹⁸ NaTaO₃¹⁸ and KTaO₃¹⁸ were prepared by a solid-state reaction, as previously reported. Starting materials used were as follows: Li₂CO₃ (Wako Pure Chemical; 99.0%), Na₂CO₃ (Kanto Chemical; 99.0%), K₂CO₃ (Kanto Chemical; 99.5%), Rb₂CO₃ (Kojundo Chemical; 99%), CaCO₃ (Kanto Chemical; 99.5%), La₂O₃ (Kanto Chemical; 99.99%), Nb₂O₅ (Kojundo Chemical; 99.95%) and Ta₂O₅ (Rare Metallic; 99.99%). K₂La₂Ti₃O₁₀¹⁹ was prepared by a polymerized complex method. The precursor was obtained from K₂CO₃ (Kanto Chemical; 99.5%), Ti(OC₄H₉)₄ (Kanto Chemical; 97%), La(NO₃)₃ (Kanto Chemical; 99.99%), ethylene glycol (Kanto Chemical; 99.5%) and citric acid (Sigma Aldrich; 99.5%) by pyrolysis and was calcined at 1173 K for 2 h in air using an alumina crucible. CuCl was freshly prepared by reduction of CuCl₂ (Wako Pure Chemical; 99.0%) with metallic Cu in boiling dilute

hydrochloric acid. A molten CuCl treatment was carried out by immersing prepared photocatalysts in molten CuCl at 773 K for 10 h in a quartz ampoule tube under vacuum. After a molten salt treatment, the excess CuCl was removed by an aqueous NH₃ solution.

Physical characterization

Crystal structures of synthesized metal oxides were confirmed by powder X-ray diffraction (Rigaku; Mini Flex). Raman spectra were recorded with a Raman spectrometer (JASCO; RMP-5300). A Green laser (532 nm) was used as an excitation source. Diffuse reflectance spectra were measured using a UV-vis-NIR spectrometer with an integrating sphere (JASCO; UbestV-570) and were converted from reflection to absorbance mode by Kubelka-Munk method. The bulk composition analysis of photocatalysts was investigated by an X-ray fluorescence (PANalytical; Epsilon5) and Inductively Coupled Plasma Atomic Emission Spectrometry (HITACHI; P-4010). Since the K₂La₂Ti₃O₁₀ with and without a molten CuCl treatment can be dissolved in an aqua regia, ICP-AES was employed for these samples. Compositions of other samples were analyzed by XRF. Detail of the experimental procedures is described in Supplementary Information. XPS and Auger spectra were obtained using an X-ray photoelectron microscopy

(JEOL; JPS-9010MC) to see the surface chemical states and composition of photocatalysts.

Photocatalytic reaction

The photocatalytic hydrogen evolution from an aqueous potassium sulfite (0.5 mol L⁻¹) and sodium sulfide (0.1 mol L⁻¹) solution and the oxygen evolution from an aqueous silver nitrate solution (0.02 mol L⁻¹) were carried out in a top-irradiation cell with a Pyrex window connected in a gas-closed-system. Photocatalyst powder (0.1 – 0.2 g) was dispersed in the reactant solution (120 mL). Ru cocatalyst (0.3 wt%) was loaded *in-situ* by a photodeposition method using an aqueous RuCl₃ solution. A 300 W Xe arc lamp (Perkin-Elmer; Cermax-PE300BF, a monochromatic light intensity at 420 nm: ca. 5.3 mW cm⁻²) was employed as a light source. A cold mirror and cutoff filters (HOYA) were used to cut off IR and UV light, respectively. The amounts of evolved hydrogen and oxygen were determined using an online gas chromatograph (Shimadzu; GC-8A, MS-5A column, TCD, Ar carrier). Apparent quantum yields were measured using a 100 W Xe arc lamp (Asahi Spectra; LAX-102) with bandpass filters (Asahi Spectra), and a photodiode head (OPHIRA PD300-UV) and a NOVA power monitor, according to the following eqn (1):

Apparent quantum yield %

$$= \frac{[\text{The number of reacted electrons or holes}]}{[\text{The number of incident photons}]} \times 100 \quad (1)$$

Results and discussion

Preparation and characterization of the Cu(I)-substituted layered photocatalysts

We examined the effect of a molten CuCl treatment on physical properties of UV light-driven photocatalysts with layered structure that showed activities for water splitting. Figure 1A shows diffuse reflectance spectra of K₂La₂Ti₃O₁₀, K₄Nb₆O₁₇, KLaNb₂O₇ and RbCa₂Ta₃O₁₀ with and without a molten CuCl treatment. The treated samples are denoted as Cu(I)-K₂La₂Ti₃O₁₀, Cu(I)-K₄Nb₆O₁₇, Cu(I)-KLaNb₂O₇ and Cu(I)-RbCa₂Ta₃O₁₀. Upon treating by a molten CuCl, the absorption edges of all photocatalysts red-shifted into a visible light region. The energy gaps of the photocatalysts with a molten CuCl treatment were 1.1–1.5 eV narrower than the band gaps of non-treated photocatalysts. The new absorption bands in visible light region were assigned to be electronic transition from valence bands and/or electron donor levels consisting of substituted Cu(I) to conduction bands of the host materials, since their absorption profiles were different from those of Cu₂O, CuO, CuCl and CuCl₂ that might exist as impurities.

The ratio and valency of exchanged Cu were analyzed by XPS and Auger spectra as shown in Figure 2. A K 2s peak and no Cu peaks were observed for non-treated K₂La₂Ti₃O₁₀. In contrast, the Cu 2p_{3/2} peaks including Cu(II) with a satellite peak appeared and the K 2s peak vanished after the molten CuCl treatment. An Auger LMM peak for Cu(I) was observed

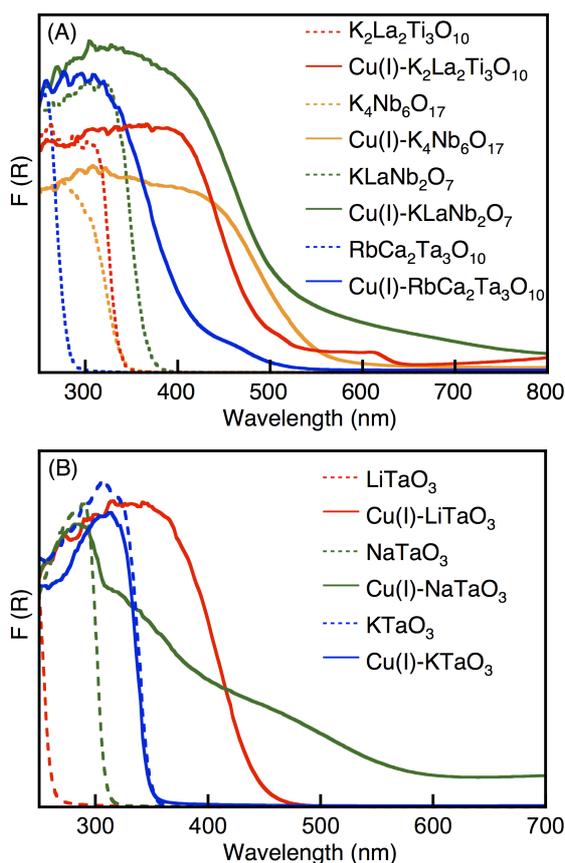


Figure 1. Diffuse reflectance spectra of K₂La₂Ti₃O₁₀, K₄Nb₆O₁₇, KLaNb₂O₇ and RbCa₂Ta₃O₁₀ of (A) layered oxides, and LiTaO₃, NaTaO₃ and KTaO₃ of (B) bulk oxides before and after CuCl-treatment.

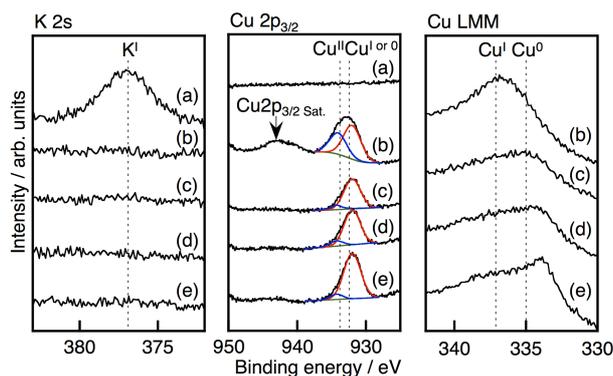
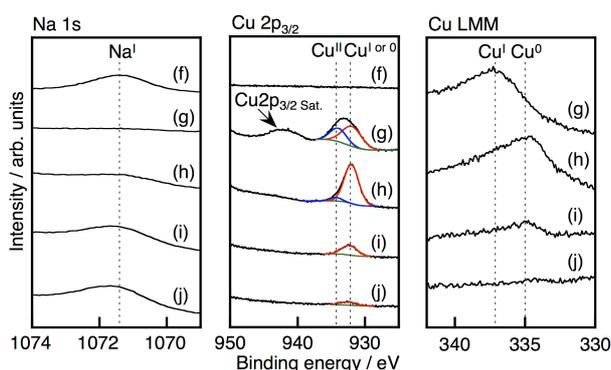
K₂La₂Ti₃O₁₀ and Cu(I)-K₂La₂Ti₃O₁₀NaTaO₃ and Cu(I)-NaTaO₃

Figure 2. X-ray photoelectron and Auger spectra of (a) K₂La₂Ti₃O₁₀, (b–e) Cu(I)-K₂La₂Ti₃O₁₀ (f) NaTaO₃, (g–j) Cu(I)-NaTaO₃. Ar etching time: (b, g) 0 s, (c, h) 5 s, (d, i) 30 s, (j) 60 s and (e) 300 s. Assigned by ref. 20.

for the Cu(I)-K₂La₂Ti₃O₁₀. These results indicate that the Cu species at the surface of the Cu(I)-K₂La₂Ti₃O₁₀ were the mixture of Cu(I) and Cu(II). The surface Cu(II) species probably formed when the treated sample was exposed in air. Cu 2p, Auger LMM and no K 2s peaks were observed even after Ar etching, while the Cu(II) species almost disappeared after Ar etching indicating that all K⁺ ions in interlayers were

exchanged for Cu⁺. The Auger LMM spectrum for Cu(0) became large with the etching time. This is due to the reduction of Cu(I) during the Ar etching. No absorption spectrum due to metallic Cu was not observed in Figure 1A. Therefore, it is concluded that the main Cu species inside of Cu(I)-K₂La₂Ti₃O₁₀ is Cu(I).

The diffraction peak at around 10° based on their layered structures of K₂La₂Ti₃O₁₀, K₄Nb₆O₁₇, KLaNb₂O₇ and RbCa₂Ta₃O₁₀ shifted to higher degree, when they were treated by molten CuCl (Figure S1). These shifts indicate that K⁺ and Rb⁺ ions in the interlayers were exchanged for smaller Cu⁺ ions with keeping the layered structure, judging from the ionic radii (Cu⁺: 0.46 Å for 2 coordination, K⁺: 1.51 and 1.55 Å for 8 and 9 coordination, Rb⁺: 1.61 Å for 8 coordination).

Table 1 shows the Cu(I)-exchange ratio calculated from XRF and ICP results for these layered photocatalysts. More than half of K⁺ and Rb⁺ in K₂La₂Ti₃O₁₀, K₄Nb₆O₁₇, KLaNb₂O₇ and RbCa₂Ta₃O₁₀ were exchanged for Cu⁺.

Raman measurement also supported the Cu(I)-exchange (Figure S2). The band observed at 875 cm⁻¹ on the Raman spectra of K₂La₂Ti₃O₁₀ is assigned to the large stretching motion of the double bond like Ti-O which projects into the interlayer.²¹ The band shifted toward low wavenumber by the molten CuCl treatment, because the bond order of Ti-O bonds of Cu(I)-K₂La₂Ti₃O₁₀ were lower than that of K₂La₂Ti₃O₁₀. In general, the bond order of Ti-O bonds should decrease due to formation of a covalent bond with Cu⁺ in the interlayer. Therefore, the band shift by the molten CuCl treatment was due to the exchange of K⁺ in the interlayer for Cu⁺.

Preparation and characterization of the Cu(I)-substituted bulky photocatalysts

We have also examined the Cu(I)-substitution on the wide band gap photocatalysts of LiTaO₃, NaTaO₃ and KTaO₃ with bulky ilmenite and perovskite structures by a molten CuCl treatment. The treated samples are denoted as Cu(I)-LiTaO₃, Cu(I)-NaTaO₃ and Cu(I)-KTaO₃. The amounts of substituted Cu(I) were estimated by XRF measurement as shown in Table 1.

Table 1 | Photocatalytic hydrogen evolution from an aqueous K₂SO₃ and Na₂S solution under visible light irradiation over photocatalysts with and without a molten CuCl treatment

Photocatalyst	Cu(I)-exchange ratio %	EG(BG)/eV		Sacrificial reagent ^(c)	H ₂ -evolution /μmol h ⁻¹
		Before	after CuCl-treatment		
Cu(I)-K ₂ La ₂ Ti ₃ O ₁₀	100 ^(a)	3.5	2.0	Yes	12
Cu(I)-K ₂ La ₂ Ti ₃ O ₁₀	100 ^(a)	3.5	2.0	No	None
K ₂ La ₂ Ti ₃ O ₁₀	0 ^(a)	3.5	–	Yes	0.6
Cu(I)-K ₄ Nb ₆ O ₁₇	69 ^(b)	3.3	2.2	Yes	0.25
Cu(I)-KLaNb ₂ O ₇	65 ^(b)	3.2	2.3	Yes	0.04
Cu(I)-RbCa ₂ Ta ₃ O ₁₀	90 ^(b)	4.5	2.8	Yes	0.72
Cu(I)-LiTaO ₃	2 ^(b)	4.8	2.8	Yes	0.18
Cu(I)-NaTaO ₃	9 ^(b)	4.0	2.0	Yes	18
Cu(I)-NaTaO ₃	9 ^(b)	4.0	2.0	No	None
NaTaO ₃	0 ^(b)	4.0	–	Yes	0.03
None	–	–	–	Yes	None

Catalyst: 0.1 - 0.2 g, cocatalyst: Ru (0.3 wt%), light source: 300 W Xe lamp (λ > 420 nm), top irradiation cell with Pyrex window. a) Determined by ICP, b) determined by XRF, c) sacrificial reagent: 0.5 mol L⁻¹ K₂SO_{3(aq)} + 0.1 mol L⁻¹ Na₂S (120 mL).

Cu(I)-LiTaO₃ and Cu(I)-NaTaO₃ contained a small number of Cu(I), while no Cu(I) existed in the Cu(I)-KTaO₃.

Diffuse reflectance spectra shown in Figure 1B also indicated the presence of Cu(I). Each absorption edge of Cu(I)-LiTaO₃ and Cu(I)-NaTaO₃ red-shifted into a visible light region, while that of Cu(I)-KTaO₃ was not so.

The XRD patterns of Cu(I)-LiTaO₃ and Cu(I)-NaTaO₃ were the same as those of LiTaO₃ and NaTaO₃ with no shifts, respectively (Figure S1). Since the ionic radii of Li⁺ (0.76 Å for 6 coordination) is quite similar to that of Cu⁺ (0.77 Å for 6 coordination), the shift in XRD patterns between LiTaO₃ and Cu(I)-LiTaO₃ should not be observed. The positions of XRD peaks of Cu(I)-NaTaO₃ was also the same as those of NaTaO₃ regardless of the much smaller ionic radii of Cu⁺ than Na⁺. This implies that the Na⁺ ions were substituted with Cu⁺ ions not in the bulk, but at and/or near the surface of the particles.

The depth profile of the composition of the Cu(I)-NaTaO₃ was studied by XPS. Cu 2p and no Na 1s peaks were observed for Cu(I)-NaTaO₃ as shown in Figure 2. When the Cu(I)-NaTaO₃ was etched with Ar, the Na 1s peak appeared. The intensity of Na 1s gradually increased with the etching time accompanied with the decrease in the Cu 2p peaks. Additionally, the Cl 2p peak was not observed, indicating no existence of CuCl and/or CuCl₂ on the surface. Thus, the XPS

and XRD measurements revealed that the Na⁺ ions were substituted with Cu⁺ ions at and/or near the surface of the particles. The similar gradient of Cu⁺ concentration was observed for Cu(I)-LiTaO₃ (Figure S3). It is noteworthy that the substituted Cu⁺ at and/or near the surface forms an electron donor level and contributes to visible light absorption as shown in Figure 1B. A couple of visible light absorption bands as seen for Cu(I)-NaTaO₃ would be due to Cu(I) in different environment.

Photocatalytic activities of the Cu(I)-substituted materials

The photocatalytic activities for hydrogen and oxygen evolution in the presence of sacrificial reagents were evaluated. Ru cocatalyst that was a stable and effective cocatalyst in the aqueous K₂SO₃ and Na₂S solution¹⁰ rather than Pt was loaded on the photocatalysts by an *in-situ* photodeposition method for the sacrificial hydrogen evolution. Although non-treated K₂La₂Ti₃O₁₀ and NaTaO₃ were active photocatalyst under UV light irradiation, they showed negligible activity for the hydrogen evolution under visible light irradiation due to no absorption in the visible light region. All Cu(I)-substituted photocatalysts produced hydrogen under visible light irradiation as shown in Table 1. Especially, Ru-loaded Cu(I)-K₂La₂Ti₃O₁₀ and Cu(I)-NaTaO₃ showed relatively high activities. Any Cu(I)-substituted samples did not produce hydrogen and/or oxygen from pure water under visible light irradiation, indicating that the substituted Cu⁺ ions were not oxidized and/or reduced by photogenerated electrons and holes. In other words, the substituted Cu⁺ ions in these samples can remain as Cu⁺ even in water and photoirradiation. Figure 3 shows the time courses of hydrogen evolution from an aqueous solution containing sulfur compounds of sacrificial reagents under visible light irradiation over Ru-loaded Cu(I)-K₂La₂Ti₃O₁₀ and Cu(I)-NaTaO₃ with the typical layered and bulk structures, respectively. These photocatalysts steadily evolved hydrogen after a few hours of an induction period when Ru-cocatalyst was loaded on these photocatalysts. Turnover numbers of electrons reacted for the hydrogen evolution over Cu(I)-K₂La₂Ti₃O₁₀ and Cu(I)-NaTaO₃ to the number of substituted Cu⁺ were 1.7 at 20 h and 13 at 40 h, respectively. The turnover number larger than the unity indicates that the hydrogen evolution photocatalytically proceeds with negligible oxidation of Cu(I). Apparent quantum yields of the hydrogen evolution over Ru/Cu(I)-K₂La₂Ti₃O₁₀ and Ru/Cu(I)-NaTaO₃ from an aqueous solution containing sulfur sacrificial reagents under monochromatic light irradiation at 420 nm were both 0.18%. All Cu(I)-substituted photocatalysts hardly showed activities for oxygen evolution from an aqueous silver nitrate solution, because the potential of valence band maxima of these Cu(I)-substituted photocatalysts are similar or more negative than that of water oxidation to oxygen. Figure 4 shows the wavelength dependence of the hydrogen evolution over Ru/Cu(I)-K₂La₂Ti₃O₁₀ and Ru/Cu(I)-NaTaO₃. The incident wavelength was controlled with cutoff filters. These photocatalysts responded to visible light up to 620 nm. The higher base lines

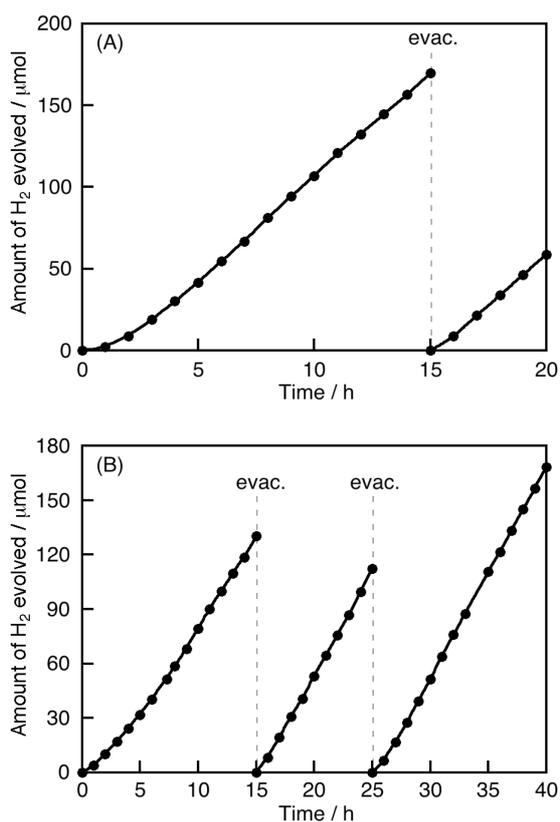


Figure 3. Photocatalytic hydrogen evolution from an aqueous 0.5 mol L⁻¹ K₂SO₃ + 0.1 mol L⁻¹ Na₂S solution (120 mL) under visible light irradiation over (A) Ru(0.3 wt%)/Cu(I)-K₂La₂Ti₃O₁₀ (0.1 g) and (B) Ru(0.3 wt%)/Cu(I)-NaTaO₃ (0.2 g). Conditions: light source, 300 W Xe lamp ($\lambda > 420$ nm), top-irradiation cell with a Pyrex glass window.

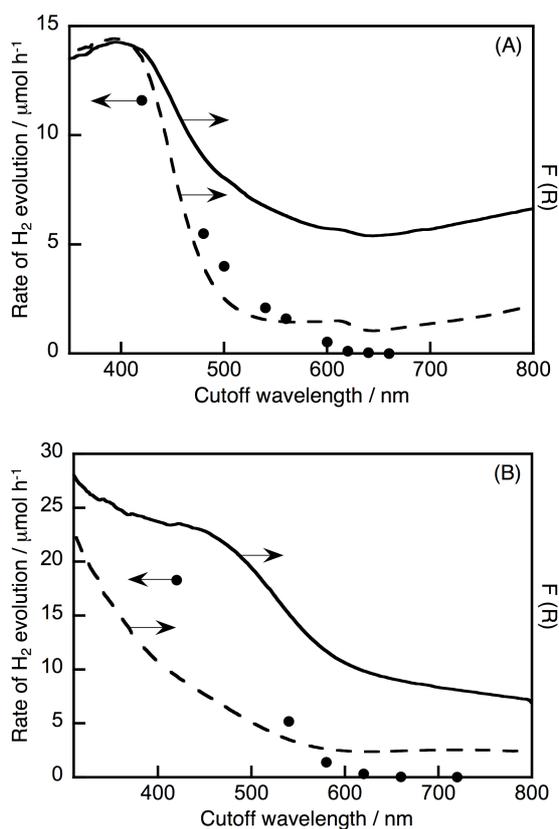


Figure 4. Wavelength dependence of the hydrogen evolution (closed circles) from an aqueous 0.5 mol L⁻¹ K₂SO₃ + 0.1 mol L⁻¹ Na₂S solution (120 mL) and diffuse reflectance spectra of Ru(0.3 wt%) loaded (A) Cu(I)-K₂La₂Ti₃O₁₀ and (B) Cu(I)-NaTaO₃ photocatalysts (solid line) and non-loaded photocatalysts (dashed line). Conditions: light source, 100 W Xe lamp, top-irradiation cell with a Pyrex glass window.

of diffuse reflectance spectra were due to loaded Ru-cocatalyst. The onsets of the wavelength dependencies of the hydrogen evolution agreed with those of the diffuse reflectance spectra of Ru/Cu(I)-K₂La₂Ti₃O₁₀ and Ru/Cu(I)-NaTaO₃. This result indicates that the hydrogen evolution over these photocatalysts proceeded by photoexcitation from valence bands consisting of Cu(I) to the conduction bands. The band gaps and energy gaps were determined from diffuse reflectance spectra and the wavelength dependencies of the photocatalytic reaction.

Conclusions

We have successfully given visible light responses to oxide photocatalysts with wide band gap by a molten CuCl treatment. A molten CuCl treatment is useful for visible-light-responded metal oxide photocatalyst because Cu(I)-substituted photocatalysts can not be prepared by a solid-state reaction. In a layered material of K₂La₂Ti₃O₁₀, Cu⁺ ions were substituted by a molten CuCl treatment to layered photocatalysts for alkali ions at the interlayer, resulting in band gap narrowing from 3.5 eV to 2.0 eV. In a bulky material of NaTaO₃, Cu⁺ ions were substituted by a molten CuCl treatment to bulky photocatalysts for alkali ions near or just the surface. The substituted Cu⁺ at and/or near the surface contributed to

visible light absorption, resulting in that the Cu(I)-substituted NaTaO₃ possessed 2.0 eV of energy gap. The Cu(I)-substituted K₂La₂Ti₃O₁₀ and NaTaO₃ photocatalysts produced hydrogen steadily by utilizing visible light up to 620 nm, accompanied with photoexcitation from valence bands consisting of Cu(I) to the conduction bands. This band engineering by the Cu⁺ ion substitution will be a promising guideline for design of a visible-light-driven photocatalyst.

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Notes and references

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