Promotion effect of nanosized Pt, RuO$_2$ and NiO$_x$ loading on visible light-driven photocatalysts K$_4$Ce$_2$M$_{10}$O$_{30}$ (M = Ta, Nb) for hydrogen evolution from water decomposition

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Abstract

Metal oxide photocatalysts K$_4$Ce$_2$M$_{10}$O$_{30}$ (M = Ta, Nb) capable of responding to visible light were synthesized by conventional high temperature solid-state reaction. The photocatalysts have an appropriate band gap energy ca. 1.8–2.3 eV and excellent chemical potential level to evolve H$_2$ from aqueous solutions containing a sacrificial electron donor (Na$_2$SO$_3$) under visible light irradiation ($\lambda > 420$ nm) without any co-catalyst. When they were loading with Pt, RuO$_2$ and NiO$_x$, the activities for evolving H$_2$ were prompted markedly. By SEM and TEM investigations, it can be seen that these loading metal and metal oxides are dispersed on the surface of photocatalysts K$_4$Ce$_2$M$_{10}$O$_{30}$ (M = Ta, Nb) in diameter of about 10–30 nm particles, especially the NiO$_x$ loading even formed double layered structure with metal nickel (Ni) and metal oxide (NiO). The reasons for the increasing activities after these loading may be attributable to facilitate electron migrating from the conduction band of K$_4$Ce$_2$M$_{10}$O$_{30}$ (M = Ta, Nb) to the Pt, RuO$_2$ and NiO$_x$ nanoparticles, which function as H$_2$ production sites on the surface of catalysts. The same phenomenon appears on the solid solution K$_4$Ce$_2$Ta$_{10-x}$Nb$_x$O$_{30}$ ($x = 0–10$) with loading RuO$_2$.

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1. Introduction

The development of H$_2$ as a renewable energy is well believed to be a potential way to solve the current energy and environmental problems. At present, hydrogen is mainly produced by steam reforming of hydrocarbons such as methane in industry, but from a long and ideal run, it must be produced from water using a renewable energy source such as solar energy when takes the cost and environmental issues into consideration. Using semiconductor photocatalysts to decompose water into H$_2$ under irradiation is one of the most promising ways to develop H$_2$ energy. The most important work in photocatalytically decomposing water into H$_2$ process is to develop semiconductor photocatalysts capable of responding to visible light and possessing high quantum yield. Based on this, series of semiconductor compounds were investigated and different modified ways were intensively studied to prompt their activities. Among these, loading of noble metal or metal oxide such as Pt, RuO$_2$ and NiO$_x$ to prompt H$_2$ evolution activities have been intensively practiced [1–7].

In the present paper, metal oxide photocatalysts K$_4$Ce$_2$M$_{10}$O$_{30}$ (M = Ta, Nb) capable of responding to visible light were presented. The photocatalysts have an appropriate band gap energy ca. 1.8–2.3 eV, corresponding to absorption edge of 540–690 nm, and excellent chemical potential level for utilization of solar energy to evolve H$_2$ from aqueous solutions containing a sacrificial electron donor (Na$_2$SO$_3$) under visible light irradiation ($\lambda > 420$ nm) without any co-catalyst. When they were loading with Pt, RuO$_2$ and NiO$_x$, the activities of
evolving H₂ were prompted markedly. The solid solution K₄Ce₂Ta₄₀–ₓNb₂O₃₀ (x = 0–10) showed photocatalytic activities consistent with their photophysical properties and also the remarkable promotion effect with loading RuO₂.

2. Experimental

2.1. Preparation and characterization of materials

K₄Ce₂M₁₀O₃₀ (M = Ta, Nb) were synthesized from high purity K₂CO₃·3H₂O, Ce(NO₃)₃·6H₂O, Ta₂O₅ (or Nb₂O₅) through conventional high-temperature solid-state reactions, first at 800 °C for 5 h then 1100 °C for 12 h, with a regrinding process in between. Excess K₂CO₃·3H₂O (ca. 20%) was used to compensate for the loss caused by volatilization during calcination. After the reaction, the product was washed with distilled water and dried. The solid solution compounds of Ta and Nb phases, denoted as K₄Ce₂Ta₄₀–ₓNb₂O₃₀ (x = 0–10), followed the same procedures above with corresponding ratio between Ta₂O₅ and Nb₂O₅.

Pt of 0.3 wt% was in situ photodeposited on the K₄Ce₂M₁₀O₃₀ catalysts from precursor of H₂PtCl₆·6H₂O, and RuO₂ was loaded by impregnation of RuCl₃·3H₂O and then calcinated at 500 °C for 2 h in atmosphere, as reported [8]. The 1.0 wt% NiO-loaded photocatalysts were obtained through calcination at 350 °C for 1 h in air after drying the mixture of powder samples with aqueous Ni(NO₃)₂ solution at 80 °C. As-prepared photocatalysts loaded with NiO were further reduced in H₂ atmosphere at 500 °C for 2 h, then, treated in air atmosphere at 200 °C for 1 h. The samples followed with this reduction–oxidation procedure were denoted as NiOₓ loading [6].

The resulting samples were identified by X-ray diffraction on Bruker-AXS D8 Advance with Cu-Kα radiation (λ = 1.540562 Å). UV–Vis diffuse reflectance spectra were measured using TU-1901 spectrophotometer. The reflectivity spectrum was transformed to absorbance intensity through Kubelka–Munk method. The BET surface areas of the K₄Ce₂M₁₀O₃₀ (M = Ta, Nb) powders were determined from N₂ adsorption–desorption isotherm on Quantachrome NOVA 1000-TS. The SEM was recorded on FEI SIRION 200 and TEM on JEM1200EX with accelerating voltage of 80 kV.

2.2. Measurement of photocatalytic activity

The photocatalytic reaction was carried out in a photoreactor, which was provided with an entry window of optical flat quartz glass of ca. 64.0 cm². Photocatalyst powder of 0.1 g was dispersed and suspended in 20 mL of aqueous solution in the reactor under the vertical irradiation with 300 W Xe lamp. Visible light irradiation condition was carried out through a glass cut-off filter (λ > 420 nm) to remove UV light. H₂ and O₂ evolutions were measured by gas chromatography (QC-9101) with thermal conductivity detector (TCD) and high-purity Ar as carrier gas.

3. Results and discussions

3.1. Light absorbance properties and electronic structure of K₄Ce₂M₁₀O₃₀ (M = Ta, Nb)

The resulting powders of K₄Ce₂M₁₀O₃₀ (M = Ta, Nb) had an X-ray diffraction pattern consistent with the tetragonal tungsten bronze structured [9], being in parallelepiped morphological structure. The UV–Vis diffuse reflectance spectra of K₄Ce₂M₁₀O₃₀ (M = Ta, Nb) are shown in Fig. 1. The absorption edge of K₄Ce₂Ta₁₀O₃₀ is at about 540 nm, corresponding to band gap energy of 2.3 eV; and the absorption edge of K₄Ce₂Nb₁₀O₃₀ is at about 690 nm, corresponding to band gap energy of 1.8 eV. Their absorbance properties are consistent with their appearance colors (golden yellow for K₄Ce₂Ta₁₀O₃₀, while K₄Ce₂Nb₁₀O₃₀ appeared deep brown). The as-prepared K₄Ce₂M₁₀O₃₀ (M = Ta, Nb) catalysts present a band gap energy near 2.0 eV, which is regarded as a very appropriate level for photocatalytic water splitting [2].

It is well known that electronic structure is an important factor dominating materials’ properties and the study of it is necessary to bridge their relationship between structure and properties. Quantum mechanical calculations provide a means to understand and to predict the interactions between atoms and molecules and to model chemical reactions on a microscopic scale. Atomistic computational technologies (computational quantum mechanics, molecular simulations and molecular mechanics) are an effective way to bridge the gap between fundamental materials science and materials engineering [10]. First-principle calculation based on density functional theory (DFT) has been extensively used to study the electronic structures of materials. By first-principle calculation based on DFT within general gradient approximation (GGA) and...
plane-wave pseudopotential (PWP) method [11], the obvious results obtained firstly are that the band gap of K$_4$Ce$_2$M$_{10}$O$_{30}$ is 1.6 eV for M = Ta and 1.1 eV for M = Nb. The band gap calculated by DFT was smaller than that obtained experimentally, which is frequently pointed out as a common feature of DFT calculations for the discontinuity in the exchange-correlation potential is not taken into account within the framework of density functional theory [12]. From the close investigations of the band structure and the partial density of states, it can be proposed that their valence bands are composed of hybridization with O2p + Ta5d (or Nb4d) and occupied Ce4f orbitals, the conduction bands of these photocatalysts K$_4$Ce$_2$M$_{10}$O$_{30}$ (M = Ta, Nb) are mainly attributable to the Ta5d (or Nb4d) orbitals. Although the unoccupied Ce4f orbitals have overlap in the bottom of conduction band, they are less effective in transferring electrons and photocatalytic activities for their highly localized nature. The contribution of these orbitals to the energy bands affects the electronic structure of both the photocatalysts and gives rise to their differences in light absorption and photocatalytic activities [13].

3.2. Photocatalytic H$_2$ evolution on K$_4$Ce$_2$M$_{10}$O$_{30}$ (M = Ta, Nb) loading with Pt, RuO$_2$ and NiO$_x$

H$_2$ evolution on K$_4$Ce$_2$M$_{10}$O$_{30}$ (M = Ta, Nb) without any loading and with loading of Pt, RuO$_2$ and NiO$_x$ in aqueous Na$_2$SO$_3$ solution under visible light ($\lambda$ > 420 nm) were shown in Fig. 2. As shown in Fig. 2, the activities for H$_2$ evolution on photocatalysts loading with Pt, RuO$_2$ and NiO$_x$ were prompted markedly compared with those without any loading. The amount of H$_2$ evolution in Na$_2$SO$_3$ solution under visible light irradiation ($\lambda$ > 420 nm) for 4 h on NiO$_x$ loading K$_4$Ce$_2$M$_{10}$O$_{30}$ reached 135 $\mu$mol (M = Ta) and 51 $\mu$mol (M = Nb), respectively, which is about 4–7 times of that loading with Pt or RuO$_2$, and 10–15 times of that without any loading.

The SEM images of photocatalysts K$_4$Ce$_2$M$_{10}$O$_{30}$ (M = Ta, Nb) without loading, with loading Pt, RuO$_2$ and NiO$_x$ are shown in Fig. 3. In SEM recording, it can be seen that these loading metal or metal oxide are dispersed on the surface of photocatalysts K$_4$Ce$_2$M$_{10}$O$_{30}$ (M = Ta, Nb) with diameter of 10–30 nm particles. Especially, following the reduction–oxidation procedure denoted as NiO$_x$ loading, it formed the metal Ni and metal oxide NiO double layer structure loading in order, as shown in the TEM images in Fig. 4. The reasons for the increasing activities after these loading may be attributable to the facilitation of electron migration from the conduction band of K$_4$Ce$_2$M$_{10}$O$_{30}$ (M = Ta, Nb) to the Pt, RuO$_2$ and NiO$_x$ nanoparticles, which function as H$_2$ production sites on the surface of catalysts [14]. The parallelepiped (tunnel) surface structure of K$_4$Ce$_2$M$_{10}$O$_{30}$ (M = Ta, Nb) is beneficial to the formation of “nest”, where nanoparticles of Pt, RuO$_2$ and NiO$_x$ are strongly associated, improving the photocatalytic activity greatly [15]. Furthermore, since the surface NiO works as a H$_2$ evolution site, electrons photogenerated in photocatalysts have to cross the interface between photocatalysts and loaded co-catalyst to reach the surface for reducing water. In this case, the barrier for the electron crossing the interface between heat-treated Ni metal and oxide photocatalysts seems to be lower than that at the interface between NiO and oxide photocatalysts. Thus, the double-layered structure of nickel formed by the treatment of reduction–oxidation is easier to assist the electron transfer from photocatalysts to co-catalysts and retention of the back reaction of H$_2$ and O$_2$ on surface [16], therefore, this loading showed the highest activities for H$_2$ evolution compared with other current loadings. It is worth noting that the activities for H$_2$ evolution on K$_4$Ce$_2$Ta$_{10}$O$_{30}$ are more excellent than that on K$_4$Ce$_2$Nb$_{10}$O$_{30}$ (as seen in Fig. 2), although the band gap of K$_4$Ce$_2$Nb$_{10}$O$_{30}$ (1.8 eV) is narrower than that of K$_4$Ce$_2$Ta$_{10}$O$_{30}$ (2.3 eV) and the BET surface area of M = Ta (1.67 m$^2$/g) is smaller than that of M = Nb (2.65 m$^2$/g). From previous study, there is suggestion that the difference in the photocatalytic properties between isostructure tantalates and niobates is mainly due to the difference in their band structure rather than their difference in light absorption and surface properties [13]. It is well known that Ta5d level is higher than that of Nb4d. The higher the level of conduction band edge, the higher reduction ability it possesses, therefore, resulting in the driving force for H$_2$ evolution on K$_4$Ce$_2$Ta$_{10}$O$_{30}$ is more powerful than that on K$_4$Ce$_2$Nb$_{10}$O$_{30}$, and so do those with loading of Pt, RuO$_2$ and NiO$_x$.

In general, the effect for the H$_2$ evolution on the interaction between these widely used co-catalysts (Pt, RuO$_2$, NiO$_x$) and conventional electron donors (Na$_2$SO$_3$, CH$_3$OH) is little taken into consideration. In order to check the effect of these co-catalysts with Na$_2$SO$_3$ aqueous solution on H$_2$ evolution in the absence of as-prepared
photocatalysts $\text{K}_4\text{Ce}_2\text{M}_{10}\text{O}_{30}$ ($\text{M} = \text{Ta}, \text{Nb}$) under visible light irradiation, Pt (0.3 wt%), RuO$_2$ (1.0 wt%), and NiO$_x$ (1.0 wt%) were loaded, respectively, by the same procedures on TiO$_2$ (P25), which is only active under UV light. Photocatalytic reactions were carried out in Na$_2$SO$_3$ aqueous solution under the visible light irradiation.
(λ > 420 nm). Hardly any evolved H2 was examined for long time. Therefore, it can be confirmed that the H2 evolution on K4Ce2M10O30 (M = Ta, Nb) loading with Pt, RuO2, NiO (NiOx) in Na2SO3 solution under visible light irradiation is ascribed to the photocatalytic reaction.

4. Photocatalytic activity of solid solution K4Ce2Ta10−xNb2O30 (x = 0−10)

Usually, tantalates and niobates form isostructure compounds for the similar properties of atom Ta and Nb, especially the diameter of their cations (0.68 Å for Ta5+ and 0.69 Å for Nb5+). There is no exception in the current system K4Ce2M10O30 (M = Ta, Nb), being in the same tetragonal tungsten bronze structure. Their solid solution compounds K4Ce2Ta10−xNb2O30, the values of x ranging from 0 to 10, also posed the same tetragonal tungsten bronze [9], as their XRD patterns shown in Fig. 5. The UV–Vis diffuse reflectance spectra of these solid solution compounds are shown in Fig. 6. From the UV–Vis spectra, it is demonstrated that with increased amount of Nb, the absorbance edges shift to red zone, correspondingly, and they show the band transition absorption properties. Furthermore, the UV–Vis spectrum of physical mixture of powder samples of pure Ta and Nb phases is also shown in Fig. 6. The physical mixture displayed obvious two absorption edges belonging to pure phase of M = Ta and M = Nb, respectively, which further confirmed the formation of single phase solid solution.

Fig. 4. The TEM images of photocatalysts K4Ce2M10O30 (M = Ta, Nb) with NiO and NiOx anchoring on. (a) and (b) represent NiO and NiOx anchoring on M = Ta phase; while (c) and (d) are for M = Nb phase with NiO and NiOx anchoring, respectively.

Fig. 5. XRD patterns of K4Ce2Ta10−xNb2O30 (x = 0−10).
compounds of Ta and Nb through high-temperature solid-state reaction. Their photocatalytic activities for H2 evolution on without loading and loading with RuO2 under visible light irradiation in the presence of sacrificial electron acceptor Na2SO3 aqueous solution are shown in Fig. 7. On these without any loading, their activities for H2 evolution decreased with the increase of Nb amount in K4Ce2Ta10−xNb6O30 (x = 0–10), and the activities of these solid solution compounds are between these of single-phase Ta and Nb. The reason for this phenomenon may be ascribed to their differences in conduction bands. As the results of the electronic structures analysis shown in our previous work [13], the higher photocatalytic activity of K4Ce2Ta10O30 than that of K4Ce2Nb10O30 is due to the higher chemical potential of Ta5d than that of Nb4d, which is proposed to the configuration of their conduction bands, respectively. The higher the conduction band is, the higher the ability to reduce H+ to H2 it has. Moreover, the UV–Vis diffuse reflectance spectra of these solid solution compounds indicate their absorbance edges shift to the red region with increased amount of Nb in K4Ce2Ta10−xNb6O30, correspondingly, resulting in the lower band edges and the lower ability to reduce water to H2, so there showed decreased activities with increased amount of Nb. The same trend appears on those loaded with RuO2, and the remarkable promotion effect on their photocatalytic activities are also attributed to the electron migration from the conduction band of K4Ce2Ta10−xNb6O30 (x = 0–10) to the RuO2 nanoparticles, which function as H2 production sites on the surface of catalyst.

5. Conclusion

Metal oxide photocatalysts K4Ce2M10O30 (M = Ta, Nb) capable of responding to visible light were presented. The photocatalysts have an appropriate band gap energy ca. 1.8–2.3 eV and excellent chemistry potential level for utilization of solar energy to evolve H2 from aqueous solutions containing a sacrificial electron donor (Na2SO3) under visible light irradiation (λ > 420 nm) without any co-catalyst. When they were loading with Pt, RuO2 and NiOx, which disperse on the surface of the host catalyst with diameter of 10–30 nm particles and function as H2 production sites, the activities of evolving H2 were prompted markedly, especially following with partial reduction–oxidation procedures denoted as NiOx loading. The same remarkable promotion effect appears on solid solution K4Ce2Ta10−xNb6O30 (x = 0–10) with RuO2 loading. It can be concluded that loading with noble metal or metal oxide such as Pt, RuO2 and NiOx etc. is an efficient way to prompt photocatalytic activities.
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