Hydrogen evolution from water splitting on nanocomposite photocatalysts

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Abstract

The photocatalytic production of H₂ in one step is potentially one of the most promising ways for the conversion and storage of solar energy. The paper overviews our recent studies on the photocatalysts splitting water into hydrogen under irradiation. The attention was mainly focused on the promotion effects of nanosized modifications in the interlayer and surface of photocatalysts for hydrogen evolution with visible light. The photocatalytic activity depended significantly on modification techniques, such as loading, proton exchange, and intercalation. The formation of a “nest” on the particle surface promoted a uniform distribution and strong combination of the nanosized particles on the surface of catalysts. By the methods of intercalation and pillaring as well as by selecting both host and guest, a large variety of molecular designed host–guest systems were obtained. Cadmium sulfide (CdS)-intercalated composites showed higher activity and stability. This activity of K₄Ce₂M₁₀O₃₀ (M = Ta, Nb) evolving H₂ under visible light irradiation was enhanced by the incorporation of Pt, RuO₂ and NiO as co-catalysts. Especially, the nanosized NiOₙ (Ni–NiO double-layer structure) greatly prompted the photocatalytic H₂ evolution significantly.

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1. Introduction

The production of renewable and non-polluting fuels by the direct conversion of solar energy into chemical energy remains a fascinating challenge for this 21st century. Among various interesting reactions, the cleavage of water into hydrogen and oxygen by sunlight is potentially one of the most promising ways for the photochemical conversion and storage of solar energy. Since the evolution of hydrogen and oxygen on TiO₂ and Pt counterelectrodes under the irradiation of ultraviolet (UV) light was reported by Fujishima and Honda in 1972 [1], photocatalysis has been received much attention and widely studied with the aim of efficiently converting solar energy into clean hydrogen energy. Up to now, these compounds locating in d block possessing d⁰ electronic configuration [2–5] such as SrTiO₃, KₓNbₓO₇₋ₓ, ATaO₃ (A = Li, Na, K), A₂Ta₂O₆ (A = Ca, Sr, Ba) and Cs₂Nb₂O₁₁, and these locating in p block possessing d¹⁰ electronic configuration [6,7], such as Mn₂O₄ (M = Ca, Sr), Sr₂SnO₄, NaSbO₃, and Zn₂GeO₄ were intensively studied. Most of them showed high stability and activities. However, these photocatalysts are only active under UV light, which accounts for only about 3–5% of the solar spectrum at the earth’s surface. Therefore, the development of photocatalysts responding visible light and with high efficient conversion for water splitting is currently attracting much attention as a potentially efficient utilization of solar energy.

The main processes in a photocatalytic reaction include absorption of photons, charge separation and migration, and the surface chemical reactions (active sites) and quantity (surface area) [8]. The processes in photocatalytic hydrogen evolution are shown in Fig. 1. While the absorption edge of light is governed by the band gap, the conversion efficiency (quantum yield) is mainly dependent on the charge separation and migration, as well as the catalyst surface chemical reactions. Our recent studies are mainly focused on the promotion effects of nanosized modifications in the interlayer and surface of...
photocatalysts for high conversion efficiency and visible light adsorption in hydrogen evolution.

2. Nanostructured “nest” surfaces and loading

Some compounds with tunnel structures and layered structures have highly photocatalytic activity. Loading of Pt and RuO₂ also increases photocatalytic activity. To compare the effect of surface structures and loading Pt and RuO₂ on the photocatalytic decomposition of water, we prepared various mixed metal oxides with layer or tunnel structures by calcining carbonates, acetates, nitrates, and simple oxides at about 800–1200 °C [9].

Comparing various catalysts (Fig. 2), it is noted that while KCa₂Nb₃O₁₀ and KTiNbO₅ are comparable to M₂Ti₆O₁₃ and BaTi₄O₉ with respect to the photocatalytic activity, loading of Pt or RuO₂ more significantly increases the activity of the latter two. It seems that the higher activity of these catalysts (such as Pt/M₂Ti₆O₁₃, RuO₂/M₂Ti₆O₁₃, RuO₂/BaTi₄O₉) is attributed to the formation of a “nest” on the particle surface that promotes a uniform distribution of the small particles. This “nest” prevents the loaded particles (Pt, RuO₂) from aggregating to grow into larger size, which results in the formation of an ordered nanostructure in the photocatalyst surface. The nanostructured particles loaded uniformly in the “nest” are strongly associated, which acts as photocatalytic active sites to promote the photocatalytic decomposition of water [9,10].

Nanosized Pt and RuO₂ are usually loaded to introduce active sites for H₂ evolution on photocatalysts because the conduction band levels of many oxide photocatalysts are not high enough to reduce H₂O to produce H₂ without catalytic assistance. The promotion effect of nano-co-catalysts was also found in the Pt/TiO₂ films [11].

3. Nanostructured layered metal oxides

The successful methods of preparation for intercalated materials which were first developed from intercalating clays and clay materials led to many attempts to prepare new classes of porous materials [12]. But the intercalation
and pillaring procedures developed for smectite clays are not generally applicable to layered metal oxides due to their high charge densities on the frameworks. One of most important characteristics of transition metal oxides is the semiconducting property of the host layers. Therefore, transition metal oxides are generally promising candidates used as intercalation hosts for photocatalysts. Recently, preparations of some pillared metal oxides by pillaring alumina or silica have been reported. In our study, the interlayer structures of some layered metal oxides (such as KTiNbO₅, K[Ca₂Na₃–₃Nb₃O₉₃+1]) were modified by ion-exchange and interlayer reaction, in which alkylammonium and tetraethylorthosilicate (TEOS), were used as an interlayer exchange guest and a pillar precursor (Fig. 3) [13–16].

The intercalation reactions and synthesis for pillared products concern a series of complexed processes. The characteristics (surface area, interlayer structure, thickness, etc.) of the pillared compounds are depended not only on preparation conditions but also on the constituent metal cations and the structures of host. The layer height of intercalated compounds is remarkably dependent on the sort of alkylamine, and increases with increasing the number of carbons [14]. We previously synthesized a silicapillared layered titanium niobium oxide (SiO₂–TiNbO₅), but the surface area was lower than that expected [13]. It might result from the weak Bronsted acidity of HTiNbO₅ and a large amount of silica incorporated into the interlayers. Silica clusters-pillared Ca₂Nb₂.₉Cr₀.₁O₁₀ layers produced the surface area of 239 m²/g and an interlayer-free gallery no less than 1 nm high [14]. TEM image (Fig. 3e) reveals that the nanolaminated structure is clearly visible and has a plate-like-free gallery.

Experimental results indicated [16] that the proton-exchanged and silica-pillared compounds facilitated the adsorption and combination of Pt on the surface, hence the activity increased. Band gap excitation produces an electron–hole pair in the semiconductor particle by adsorption of light. The electron is subsequently channelled to Pt sites where hydrogen evolution occurs. The combination between Pt and the semiconductor particle promotes the electron transference and the hydrogen evolution. The proposal mechanism for the activity promotion of pillared layer compounds is shown in Fig. 4.

4. CdS-intercalated layered nanocomposites

Cadmium sulfide (CdS) has a band-gap energy (E_g) of 2.4 eV that suits very well with the solar spectrum. However, it is not stable in aqueous solutions under irradiation due to electrochemical dissolution. In order to improve the photocatalytic properties, we prepared CdS-intercalated metal oxides via direct Cd²⁺ exchange, which in followed by a sulfurization process [17,18].

As shown in Table 1, CdS-intercalated compounds were superior to simple CdS and the physical mixture of CdS and metal oxides with respect to photocatalytic hydrogen evolution. The promotion effect was maybe attributed to the formation of the CdS nanoparticles incorporated in the interlayer, as well as the nanoheterojunctions between the host layer and the CdS. The incorporation of CdS nanoparticles into the interlayer of these layered metal oxides could suppress the particle growth. The band gap of CdS-intercalated composites is larger than that of the neat CdS. The blue shift of the absorption shows a quantum size effect, and the formation of CdS nanoparticles [19]. Photogenerated electrons could quickly be transferred through the nanostructure, and the recombination between the photoinduced charge carriers (electron and hole) was effectively depressed. Consequently, the photocatalytic evolution of hydrogen was enhanced.

It was found that the activity of CdS-intercalated compounds was dependent on host layer. In order to investigate the effect, the analysis of luminescence spectra was carried out. As known, the luminescence property is due to electron–hole recombination processes within the
semiconductor. The analysis of luminescence spectra suggested that the order of the photogenerated electron–hole recombination was as follows: CdS/K2Ti3.9Nb0.1O9 < CdS/K2Ti4O9 < CdS/K2Ti3.9Nb0.1O9. The substitution of Nb for partial Ti brought the quick transference of the electrons photogenerated in CdS through the host layer into the surface of photocatalysts. Thus, the electron–hole recombination was suppressed, and the hydrogen evolution increased.

Moreover, a further improvement of the photocatalytic activity was obtained in this case by loading Pt on the surface of the layered composite incorporating CdS in the interlayer space. The deposition of Pt acts as an electron-transfer catalyst on the surface of the host layers and the CdS microcrystals incorporated in the interlayer, while S2-/CO32- ions in the solution act as hole scavengers. The photocatalytic process is suggested as shown in Fig. 5. The photocatalytic hydrogen production under visible light was confirmed by the fact that H2 was detected when UV light was removed.

5. Nanoloading on K4Ce2M10O30 (M = Ta, Nb)

Recently, some metal nitrides and oxynitrides such as TaON [20], Ta3N5 [21], and Y2Ta2O3N2 [22] have been developed as visible light sensitive photocatalysts. There may be a concern for the stability of substituted anions under reaction conditions for the compounds, so the most promising candidates for photocatalysts under visible light are single-phase metal oxides. In order to develop new photocatalysts, some compounds including rare earth elements have been received great attention. In our laboratory, a series of single-phase metal oxide photocatalysts K4Ce2M10O30 (M = Ta, Nb) having an appropriate band gap energy ca. 1.8–2.3 eV (corresponding to absorption edge of 540–690 nm) were prepared [23]. Density function theory (DFT) calculation indicated that while their valence bands are composed of hybridization with O 2p+Ta 5d (or Nb 4d) and occupied Ce 4f orbitals, the conduction bands of these photocatalysts K4Ce2M10O30 (M = Ta, Nb) are mainly attributable to the Ta 5d (or Nb 4d) orbitals (Fig. 6). The contribution of these orbitals to the energy bands affects the electronic structure of the both photocatalysts and gives rise to their differences in light absorption and photocatalytic activities. It is noted that K4Ce2M10O30 (M = Ta, Nb) have parallelepiped (tunnel) surface structure. This is beneficial to the formation of “nest”, where nanoparticles of Pt, RuO2 and NiOx are strongly associated, improving the photocatalytic activity greatly. Fig. 7 shows the TEM images of the catalysts loaded with NiOx with uniform distribution.

As shown in Fig. 8, the activity was further increased by doping both Pt and RuO2 on the catalysts. NiOx loading is superior to NiO loading with respective to promote the activity, while both the loading enhanced the hydrogen evolution under visible irradiation. The amount of H2 evolution for 4 h on NiOx-loaded K4Ce2Ta10O30 reached 135 μmol, which is about 4 times of that co-loaded with Pt and RuO2, and 5 times of that loaded with NiO. It is seen that NiOx derived from partial reduction and oxidation procedure formed the double-layer particles including metallic Ni and NiO, while NiO formed the uniform particles anchoring on the surface of K4Ce2M10O30.

### Table 1

| Sample                  | Bandgap (eV) | CdS content (wt%) | Specific surface area (m² g⁻¹) | Evolved H₂ (mmol m⁻² h⁻¹) |
|-------------------------|--------------|-------------------|-------------------------------|---------------------------|
| CdSb                    | 2.4          | /                 | 20.5                          | 3.24                      |
| CdS/KTiNbO₅             | 2.6          | 6.5               | 10.3                          | 3.68                      |
| CdS/K₂Ti₄O₉             | 2.6          | 10.2              | 12.4                          | 3.80                      |
| CdS/K₂Ti₃.9Nb₀.1O₉     | 2.5          | 19.5              | 19.3                          | 4.70                      |
| CdS + K₂Ti₃.9Nb₀.1O₉    | /            | /                 | /                             | /                         |

*aThe rate of H2 evolution under xenon lamp (300 W) in the aqueous solution of Na2S (0.1 M, 20 ml).

*bA neat CdS powder.

*cThe physical mixture of 20 wt% CdS + 80 wt% K2Ti3.9Nb0.1O9.
The loaded NiO and NiO\textsubscript{x} particles facilitate the transfer of photoinduced electron to these sites, restraining the recombination of photoinduced charges. Since the surface NiO works as a H\textsubscript{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. Thus, 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 [24].

6. Conclusions

The acticity for photocatalytic hydrogen production could be increased by nanostructural modification on the surface and in the interlayer of catalysts. Tunnel surfaces provide the nano “nest” structure, in which there is stronger combination between the catalyst surface and co-catalyst. Pillared layer compounds have larger surface area and stronger intercalation of co-catalyst on the surface. The activity of CdS-intercalated compounds was dependent on layer structures and hole scavengers. The substitution of Nb for partial Ti brought the quick transference of the electrons in CdS pillars through the host layer into the surface of photocatalysts. Ni–NiO double-layer loading prompted significantly the photocatalytic H\textsubscript{2} evolution on K\textsubscript{4}Ce\textsubscript{2}M\textsubscript{10}O\textsubscript{30} (M = Ta, Nb), which is novel metal oxide photocatalysts with an appropriate band gap (1.8–2.3 eV) and chemical potential level for utilization of solar energy.

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