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Article

Ultrafine metal nanoparticles loaded on TiO₂ nanorods: Synthesis strategy and photocatalytic activity

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ABSTRACT

Ultrafine noble metal nanoparticles (Pt, Pd, or Au) co-catalyst loaded on the surface of rutile and brookite TiO₂ were prepared via a simple photo-deposition strategy under high vacuum conditions. The properties of the prepared samples were determined by different characterization techniques, including X-ray diffraction, transmission electron microscopy, diffuse reflectance ultraviolet–visible spectroscopy, and photoluminescence spectroscopy. The photocatalytic performance of the samples was evaluated by monitoring the reforming of methanol. Co-catalyst loading greatly improved the photocatalytic activity of TiO₂. Specifically, Pt-TiO₂ displayed the highest photocatalytic activity among all samples studied, followed by Pd-TiO₂ and then Au-TiO₂. Furthermore, this photocatalytic behavior was not influenced by the intrinsic nature of the TiO₂ semiconductor photocatalyst. Similar photocatalytic activity trends were achieved with both sets of noble metal-loaded photocatalysts prepared using rutile and brookite TiO₂ as supports. By examining the physicochemical and photocatalytic properties, the factors controlling the photocatalytic activity of the noble metal-loaded TiO₂ samples were discussed in detail.

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1. Introduction

Over the past decades, semiconductor photocatalysis has attracted considerable attention owing to its wide applications especially in solar energy conversion, environmental remediation, and organic synthesis [1–4]. Among the many semiconductor materials examined, TiO₂ has been regarded as a promising candidate for application in solar energy conversion because of its high chemical stability, high abundance, non-toxicity, and low cost [5,6]. However, the low quantum efficiency generated during solar energy conversion and limited

utilization of visible light or sunlight, which respectively result from the high rate of electron-hole recombination under irradiation and the relatively wide band gap of TiO₂, greatly hinder the application of TiO₂ [7,8].

To overcome these drawbacks, some strategies have been explored to improve the photocatalytic efficiency of TiO₂ such as surface modification and element doping [9–17]. Regarding element doping into TiO₂, a suitable dopant and suitable level of doping are required because the defects induced by the dopant unavoidably introduce new charge carrier traps and recombination centers that could be detrimental to the photo-

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catalytic performance of the resulting TiO₂ material. In contrast, surface modification of TiO₂ with metals, especially noble metals, possesses unique advantages such as its simplicity in operation and ability in significantly enhancing the efficiency of the photocatalytic process. Noble metals, such as Pt and Au, deposited on TiO₂ nanoparticles have been proved to feature high Schottky barriers. Furthermore, the noble metals can act as electron traps to enhance charge separation at the interface between the metal particles and TiO₂, thus retarding the recombination of photo-excited electron and holes, consequently prolonging the lifetime of the carriers for efficient photocatalysis [18–21]. Pt, which features the largest work function and lowest overpotential for hydrogen production, has been demonstrated to be the best candidate for TiO₂ surface modification for photocatalytic hydrogen production [19].

In the absence of a co-catalyst, TiO₂ shows very low activity toward hydrogen production from water splitting. Thus, in addition to the light-harvesting ability of the semiconductor, the photocatalytic reaction highly depends on the nature of the co-catalyst [20,22]. A comprehensive investigation of such catalytic system will be helpful for achieving highly efficient production of hydrogen from water or other derivatives, as well as contributing to the fundamental understanding of the photocatalytic process. However, to date, systematic studies on the photocatalytic performance of such noble metal-loaded TiO₂ nanocomposites are limited and several fundamental issues remain unresolved. A primary issue is how the type of noble metal affects the photocatalytic activity of TiO₂ under irradiation. Furthermore, TiO₂ exists in three crystal forms i.e., anatase, rutile, and brookite. Among these crystal forms, rutile and anatase have attracted considerable attention, and thus many extensive studies relating to their photocatalytic activity feature in the literature. In contrast, very limited research studies on brookite are available [23,24].

Herein, a series of noble metal-loaded TiO₂, M-TiO₂ (M = Pt, Au, Pd; TiO₂ = Anatase, Rutile), samples with ultrafine metal clusters were prepared and examined as photocatalysts for water splitting with methanol (methanol photo-reforming). As the properties of the co-catalysts may be influenced by the preparation method, photo-deposition, a simple, but popular method, was employed in the present study. Rutile and brookite TiO₂ were employed as the semiconductors. The effects of noble metal surface deposition on the photocatalytic activity of TiO₂ toward hydrogen production were examined.

2. Experimental

2.1. Preparation of photocatalysts

All chemical reagents (analytical grade) were purchased from Alfa Aesar Chemical Co. and used as received without further purification. Rutile and brookite TiO₂ nanorods were prepared according to previous literature reports [25,26]. The obtained fresh TiO₂ powder was calcined at 400 °C for 4 h in flowing air before further use. To obtain the noble metal-loaded TiO₂ samples, a modified photo-assisted loading process was developed. The process was conducted under high vacuum

conditions for minimizing the heterogeneous nucleation rate of the loaded metals. Typically, a known amount of metal precursor solution (H₂PtCl₆, PdCl₂, or HAuCl₄) was added to a TiO₂ methanolic aqueous solution (10 mL methanol and 90 mL H₂O; 0.5 g TiO₂) under stirring without pH adjustment. Then, the entire closed reaction system was evacuated for 10 min, then irradiated using a 200 W Xe lamp (wavelength: 320–780 nm) for 6 h. The resulting precipitates were filtered and washed thoroughly with methanol and deionized water, and then dried under ambient conditions.

2.2. Characterization

X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8 ADVANCE powder diffractometer using Cu K α radiation (λ = 0.1542 nm) at a scanning rate of 4°/min in the region of 2θ = 20°–60°.

The metal contents of the samples were determined by inductively coupled plasma–atomic emission spectroscopy (ICP-AES; IRIS Advantage). The specific Brunauer-Emmett-Teller (BET) surface areas (S_{BET}) of the samples were determined from N₂ adsorption-desorption isotherms collected on a Quantachrome iQ-MP gas adsorption analyzer. Prior to measurement, the samples were dehydrated at 300 °C for 2 h.

Transmission electron microscopy (TEM) images were taken on a Philips Tecnai G² 20 S-TWIN electron microscope, operating at an acceleration voltage of 200 kV. A few drops of alcohol suspension containing the sample were placed on a carbon-coated copper grid, followed by evaporation at ambient temperature.

Diffuse reflectance ultraviolet-visible (UV-Vis) absorption spectra of the samples were recorded on a Varian Cary 300 UV-Vis spectrometer using BaSO₄ as reference.

The photoluminescence (PL) spectra of the samples were recorded on a Spex FL201 fluorescence spectrophotometer. The samples were dry-pressed into self-supporting wafers and then illuminated using a 325-nm He-Cd laser as an excitation source at ambient temperature.

2.3. Photocatalytic evaluation

The photocatalytic reforming of methanol (also known as photocatalytic water splitting with methanol (as the sacrificial agent)) was performed in a top-irradiation-type Pyrex reaction cell connected to a closed gas circulation and evacuation system under irradiation of a Xe lamp fitted with a filter (wavelength: 320–400 nm). In a typical experiment, about 100 mg catalyst sample was added to 100 mL methanol aqueous solution (10%) in the reaction cell. After evacuation for 30 min, the reactor cell was irradiated by the Xe lamp at 200 W under stirring. The evolved gas product H₂ was analyzed using an online gas chromatograph (Varian CP-3800) equipped with a thermal conductivity detector.

3. Results and discussion

3.1. Physicochemical properties of the photocatalysts

The XRD patterns of the prepared TiO_2 materials are shown in Fig. 1. The diffraction pattern of the prepared rutile TiO_2 (Rutile) sample (Fig. 1(a)) agreed with that of rutile (JCPDF#21-1276), whereas the prepared brookite TiO_2 (Brookite) (Fig. 1(b)) displayed a pattern typical of brookite (JCPDF#29-1360). No other crystalline phases were detected in either sample, thereby indicating the phase (rutile or brookite) purity of the prepared materials. After metal loading, no diffraction peaks corresponding to Pt, Pd, or Au species could be observed in the M-Rutile and M-Brookite samples. This result was attributed to the low loading of the metal species (~ 1.0 wt%) and the formation of ultrafine clusters (1.0–2.0 nm), as discussed later.

Diffuse reflectance UV-Vis spectroscopy was performed to study the optical properties of the prepared TiO_2 materials, and the results are shown in Fig. 2. All TiO_2 samples displayed a typical UV absorption band at ~ 250 – 400 nm, which can be

primarily ascribed to electron promotion in TiO_2 from the valence band (VB) to the conduction band (CB) [20]. Compared with the bare rutile and brookite samples, a slight red shift in the absorption edge was observed for the M- TiO_2 samples, thereby indicating that noble metal deposition can slightly extend the absorption of light of TiO_2 to the visible region. Both sets of M-Rutile and M-Brookite samples displayed similar shifts. This can further be confirmed by calculating the band gap values of the samples according to the plot in Fig. 2(c, d), obtained via transformation based on the Kubelka-Munk function. The estimated band gap values of Pd-Rutile, Pt-Rutile, and Au-Rutile nanocomposites were 2.80, 2.91, and 2.96 eV, respectively. These band gap values were smaller than that of pristine rutile (3.04 eV). Furthermore, the estimated band gap values of Pd-Brookite, Pt-Brookite, and Au-Brookite nanocomposites were 3.33, 3.30, and 3.25 eV, respectively, which are likewise lower than that of pristine brookite (3.37 eV). Therefore, it can

Fig. 1. XRD patterns of the prepared rutile TiO_2 and M-Rutile (a) and brookite TiO_2 and M-Brookite (b) samples.

Fig. 2. UV-Vis spectra of the TiO_2 samples. (a, c) Rutile; (b, d) Brookite.

be concluded that deposition of the noble metals studied herein induced very mild effects on the optical properties of the M-TiO₂ nanocomposites. Furthermore, an additional wide absorption band at ca. 580 nm was observed for the Au-loaded rutile and brookite samples, revealing the formation of plasmonic Au nanoparticles on TiO₂ surface [27,28]. This observation illustrates the presence of surface plasmon resonance effect in the synthesized Au-TiO₂ samples.

The morphologies of the prepared M-TiO₂ samples were studied by TEM to analyze the distribution and size of Au, Pd, and Pt. Fig. 3 shows that the ultra small uniform Au, Pd, and Pt nanoparticles were evenly distributed on the surface of rutile and brookite. Specifically, the M-Rutile samples featured uniform Au, Pd and Pt nanoparticles with average sizes of 1.3–1.5

nm. In contrast, the M-Brookite samples featured slightly larger metal particles with average sizes of 1.9–2.1 nm. It should be noted that no agglomerated particles were observed, indicating that the photo-deposition method, which does not require a calcination step, employed in the present study can effectively avoid aggregation of noble metal nanoparticles. Accordingly, the formation of uniform ultrafine nanoparticles with a narrow size distribution could be achieved on the surface of TiO₂. For direct comparison, some relevant physicochemical properties of the prepared M-TiO₂ samples are summarized in Table 1.

3.2. Photocatalytic performance of the TiO₂ samples

The photocatalytic activities of TiO₂ and M-TiO₂ samples

Fig. 3. TEM images of the M-TiO₂ samples and associated size distribution histograms of the metal nanoparticles loaded on rutile or brookite TiO₂.

Table 1Physicochemical properties of the prepared M-TiO₂ samples.

Sample	Size of M particles ^a (nm)	Loading of M particles ^b (wt%)	<i>S</i> _{BET} (m ² /g)
Rutile	—	—	58.2
Au-Rutile	1.4	0.96	56.4
Pd-Rutile	1.5	0.94	57.3
Pt-Rutile	1.5	0.93	56.8
Brookite	—	—	53.4
Au-Brookite	2.1	0.95	52.7
Pd-Brookite	2.0	0.96	51.8
Pt-Brookite	1.9	0.92	52.3

^a Estimated by TEM observations; ^b Determined by ICP-AES.

were investigated through photocatalytic reforming of methanol, and the results are shown in Fig. 4. As observed, both bare rutile and brookite TiO₂ samples displayed some level of activity toward hydrogen production from photocatalytic reforming of methanol; however, the yield of hydrogen was relatively low within the time-on-stream (TOS) of 5 h studied. After co-catalyst loading, the photocatalytic activity of TiO₂ greatly improved. Pt-TiO₂ displayed the highest photocatalytic activity among all samples studied, followed by Pd-TiO₂ and then Au-TiO₂. This trend was consistent with results of previous reports [20,29]. The enhanced photocatalytic activity was attributed to the presence of the noble metal particles that can act as traps for the photogenerated electrons and reduce the extent of recombination between the electrons and holes. It is well known that Pt is an excellent co-catalyst for water splitting, exhibiting a lower overpotential and better activity than Pd and Au toward hydrogen evolution. Furthermore, for the same type of noble metal deposition, similar photocatalytic activity trends were observed over the rutile and brookite supports.

3.3. Stability of Pt-TiO₂ samples

The stability of a catalyst is a very important issue for practical application in photocatalytic hydrogen production from water splitting. Thus, the recyclability of the most active samples, i.e., Pt-Rutile and Pt-Brookite, was investigated; three

successive runs (5 h per run) were conducted. The results are shown in Fig. 5. After each run, the produced hydrogen was removed by evacuation. As observed, Pt-TiO₂ displayed good recyclability, and no significant decrease in the photocatalytic activity after three cycles was observed. Furthermore, the TEM observations (not shown here) confirmed that the morphology of the Pt clusters on TiO₂ remained unchanged following the successive catalytic runs. Thus, the experimental results demonstrate that the prepared Pt-TiO₂ samples exhibit a stable activity toward photocatalytic hydrogen production.

3.4. Factors controlling the photocatalytic activity of the TiO₂ samples

Hydrogen production from photocatalytic reforming of methanol not only depends on the light-harvesting properties of photocatalysts, but also relies highly on the properties of the co-catalyst. In the present study, rutile and brookite were used as the intrinsic photocatalysts, and Pt, Pd, or Au was used as co-catalysts. For the same intrinsic photocatalyst, the morphologies and nature of the co-catalyst would directly influence hydrogen production. Considering that the average particle sizes, particle distribution, and surface areas were comparable across the samples studied (for a given semiconductor support) (Table 1), the properties of the co-catalyst, e.g., work function and hydrogen overvoltage, are thought to be the key factors controlling the photocatalytic activity.

Generally, photo-induced holes (h⁺) and electrons (e⁻) would rapidly recombine in excited bare TiO₂, consequently resulting in a low quantum yield and poor efficiency of the photocatalytic reactions [22]. As the work functions of the co-catalysts (Pt 5.7 eV, Pd 5.1 eV, Au 5.1 eV) are larger than that of TiO₂ (4.2 eV) [19,30,31], the photo-induced e⁻ will transit from the TiO₂ matrix to the co-catalyst until their Fermi levels are aligned. This phenomenon can effectively suppress the recombination of e⁻ and h⁺ owing to the formation of Schottky barriers at the M/TiO₂ interface, and promote the evolution of H₂. Among the co-catalysts examined in the present study, Pt exerted the greatest effect on hydrogen evolution, followed by Pd and Au. The obtained photocatalytic activity can be further

Fig. 4. Photocatalytic activity of hydrogen production over the different TiO₂ samples. (a) Rutile and M-Rutile; (b) Brookite and M-Brookite.

Fig. 5. Recycling of Pt-TiO₂ catalysts in the hydrogen production process. (a) Pt-Rutile; (b) Pt-Brookite.

explained by determining the hydrogen overvoltage (HOV) values of the electrodes composed of the different metals studied herein, as shown in Table 2. An inverse correlation between the hydrogen formation rates and HOV values is expected. In other words, the higher the HOV, the more difficult is the reduction of protons (H⁺) by electrons. Therefore, Pt which features the lowest HOV value, can effectively reduce H⁺ by electrons, and thus exhibits the best photocatalytic activity, which is in agreement with previous reports. These results indicate that the co-catalyst loaded on TiO₂ acted as sites for H⁺ reduction (hydrogen formation). Furthermore, this phenomenon was not influenced by the nature of the semiconductor photocatalyst, i.e. similar photocatalytic activity trends were achieved over rutile and brookite.

The separation and transfer of electron-hole pairs under irradiation are illustrated in Scheme 1. Under UV light irradiation, the TiO₂ matrix is excited, and the excited electrons transit from the VB of TiO₂ to the CB, of TiO₂ forming e⁻-h⁺ pairs. Generally, the e⁻ and h⁺ will recombine quickly, and only a small fraction of e⁻ and h⁺ participate in the photocatalytic reaction, resulting in low photocatalytic efficiencies. In the presence of co-catalysts, the photogenerated electrons can transit to the metal nanoparticles to participate in the reduction reaction. According to a previous study, extremely small noble metal particles with sizes of less than 1.0 nm have higher energy band separation owing to quantum confinement, thereby preventing electron transfer from the CB of TiO₂ to metal [32]. As the particle sizes of the co-catalysts prepared in the present study are in the range of 1.3–2.1 nm, and the new Fermi energy levels of the M-TiO₂ samples are lower than that of the energy level of the bottom of the CB of TiO₂, the photo-excited electrons could effectively transit from the TiO₂ matrix to the metal nanoparticles driven by the above potential energy. At the metal-semiconductor interface, Schottky barriers can form and serve as efficient electron traps, thereby retarding photogener-

ated electron-hole recombination and increasing the photocatalytic activity of the M-TiO₂ samples.

To investigate the efficiency of charge carrier trapping, migration, and transfer in the TiO₂ samples, room temperature emission PL spectra of the samples were recorded, and the results are shown in Fig. 6. As observed, after co-catalysts loading, the PL intensities decreased distinctly. And the changes in the intensity of the PL signals correlated well with the observed photocatalytic activity (i.e., a lower PL signal intensity corresponds to a higher photocatalytic activity). These results indicate that the loaded co-catalyst can act as a trapping site, capturing photogenerated electrons from the CB and effectively inhibiting the recombination of the photogenerated electron-hole pairs [25]. Furthermore, the peak positions of the M-TiO₂ samples and pure TiO₂ were comparable, thus indicating that co-catalysts loading did not lead to new light-emitting phenomena, however, only affected the intensity of the PL signals.

4. Conclusions

Ultrafine noble metal (Pt, Pd, Au) nanoparticles with sizes of ~1.0–2.0 nm were successfully loaded on rutile and brookite TiO₂ surface through a simple photo-deposition strategy under high vacuum conditions. Compared with bare rutile and brookite TiO₂, the prepared M-TiO₂ photocatalysts exhibited remarkable photocatalytic activity toward hydrogen evolution. This enhancement greatly related to the work function and HOV of the co-catalysts. Higher co-catalyst work functions enabled effective transfer of the photo-induced e⁻ from the TiO₂ matrix

Table 2

Work function and hydrogen overvoltage of the metals studied herein.

Metal	Work function (eV) [30]	Hydrogen overvoltage (eV) [31]
Pt	5.7	0.01–0.09
Pd	5.1	0.04
Au	5.1	0.18

Scheme 1. Schematic diagram of H₂ production mechanism over M-TiO₂ samples.

Fig. 6. PL spectra of Rutile (a) and M-Rutile and Brookite and M-Brookite (b) TiO_2 samples recorded at room temperature.

to the co-catalyst and suppression of the recombination of the e^- and h^+ owing to the formation of Schottky barriers at the M/ TiO_2 interface. In contrast, the co-catalysts in the M- TiO_2 samples acted as sites for H^+ reduction, and the hydrogen formation rates inversely correlated to the HOV values. Furthermore, for the same type of noble metal deposition, similar photocatalytic activity trends were observed over rutile and brookite.

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Graphical Abstract

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Ultrafine metal nanoparticles loaded on TiO_2 nanorods: Synthesis strategy and photocatalytic activity

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Ultrafine metal nanoparticles (co-catalysts) on TiO_2 nanorods were prepared via a simple photo-deposition strategy under high vacuum conditions. The co-catalysts acted as major active sites for H^+ reduction in the photocatalytic hydrogen production process.

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超细金属纳米粒子修饰的二氧化钛纳米棒:合成策略和光催化活性

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摘要:作为一种新兴技术, 半导体催化在太阳能转化、环境净化以及有机合成等多种领域中具有重要的用途, 因而近年来引起了研究者的广泛关注. 在众多半导体材料中, TiO_2 具有价廉, 无毒, 来源广泛和光化学稳定等优点, 被认为是太阳能转化领域最有潜力的催化剂. 然而, 由于其相对较宽的禁带宽度和激发条件下较快的光生电子和空穴的复合率, 导致 TiO_2 在太阳能转化过程中具有较低的量子效率. 为了克服以上缺陷, 研究者尝试了多种方法来提高 TiO_2 的量子效率, 如 TiO_2 的表面修饰以及元素掺杂等. 其中, 过渡金属尤其是贵金属(如Au, Pd和Pt等)的掺杂能有效提高其催化效率, 主要原因在于大多数贵金属的费米能级低于 TiO_2 半导体催化剂, 因此, 光生电子迁移到催化剂表面的同时, 会被贵金属捕获, 进而有效地防止电子与空穴的复合, 提高其催化效率. 在众多贵金属助催化剂中, Pt因具有较大的功函数和较低氢过电势而被认为是 TiO_2 在光解水反应中最好的表面修饰剂. 然而, 有关贵金属负载的 TiO_2 在光解水反应中的系列性的对比研究还相对较少, 一些基础的问题还有待解决. 如在相同激发条件下, 不同贵金属如何影响 TiO_2 的光催化活性? TiO_2 的晶体结构对其光催化活性是否有影响? 在 TiO_2 的三种晶体结构中, 金红石和锐钛矿的光催化活性得到了较多的研究, 而有关板钛矿的研究却较少. 基于此, 本文首先采用水热法合成纳米棒状的锐钛矿和板钛矿 TiO_2 , 随后利用光沉积法在上述 TiO_2 载体上负载不同的贵金属(Pt, Pd和Au)助催化剂, 利用透射电镜(TEM), 紫外可见光谱(UV-Vis), 荧光光谱(PL)等手段对比研究了贵金属助催化剂和晶体结构对其催化光解水制氢反应的影响.

射线衍射(XRD)结果表明, 负载贵金属后的锐钛矿和板钛矿晶型保持完好, 且未出现贵金属物种的衍射峰. UV-Vis结果表明, 负载贵金属后的锐钛矿和板钛矿样品的紫外光吸收均略有红移, 并且紫外光谱的变化趋势相同, 说明 TiO_2 的晶型对其紫外光吸收性质影响不大. 此外, TEM结果发现, 贵金属纳米颗粒在 TiO_2 表面分散均匀, 并且颗粒规整, 没有出现团聚的现象, 在锐钛矿和板钛矿表面的颗粒大小分别为1.3–1.5和1.9–2.1 nm, 与XRD结果吻合. 最后, 利用紫外光激发下的甲醇水蒸气重整制氢反应考察了不同样品的催化性能. 结果表明, 在无贵金属助催化剂存在的条件下, 锐钛矿和板钛矿样品上的光催化活性均较低. 负载贵金属后, Pt- TiO_2 的光催化活性最高, Pd- TiO_2 次之, Au- TiO_2 最差, 与文献结果类似. 结合表征结果推测, 造成上述样品活性差异的主要原因在于助催化剂的本征性质, 如功函数和氢过电势等.

Pt, Pd和Au共催化剂的功函数分别为5.7, 5.1和5.1 eV, 均高于 TiO_2 (4.2 eV). 在紫外光激发下, 光生电子可以有效地从 TiO_2 载体传递到贵金属助催化剂上, 并在 TiO_2 载体表面形成肖特基势垒, 进而有效地阻止光生电子和空穴的复合, 提高其光催化活性. 因此, 负载Pt, Pd和Au后的 TiO_2 样品上产氢效率均高于 TiO_2 载体. 不同样品的PL结果也与其催化活性数据相吻合, 说明贵金属助催化剂的负载能有效地捕获光生电子, 进而阻止光生电子与空穴的复合, 提高其催化活性. 此外, 氢过电势也是影响贵金属助催化剂活性差异的主要原因: 氢过电势越高, 其还原质子的能力越弱, 在产氢反应中的产氢效率越低. 因此, 三种金属中, 具有最低氢过电势的Pt产氢效率最高. 此外, 同种贵金属负载的锐钛矿和板钛矿上的催化活性相似, 表明负载型贵金属催化剂载体对其催化活性的影响较低.

关键词: 光催化剂; 产氢; 锐钛矿; 板钛矿; 共催化剂

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