

Visible-light driven photocatalytic hydrogen generation on Eosin Y-sensitized Pt-loaded nanotube $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$

Qiuye Li^{a,b}, Gongxuan Lu^{a,*}

^a State Key Laboratory for Oxo Synthesis and Selective Oxidation Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences and Graduate School of the Chinese Academy of Sciences, Lanzhou 730000, China

^b Key Laboratory of Special Functional Materials, KaiFeng 475001, China

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Abstract

A novel and highly efficient photocatalyst, Eosin Y-sensitized Pt-loaded nanotube $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$ (NTS), was found to be very active for hydrogen generation in triethanolamine (TEA) solution under visible-light irradiation ($\lambda \geq 420$ nm). The catalyst was prepared by impregnation photo-deposition method, and characterized by transmission electron microscope (TEM), powder X-ray diffraction (XRD), and solid-state diffusion reflectance UV–vis spectra (UV–vis DRS) techniques. The catalyst showed a long-term stability for photocatalytic H_2 generation over 100 h after consecutive 10 runs, up to 14.97% of quantum yield was achieved under visible-light irradiation. The effect of loading amounts of platinum, pH value, the mass ratio of Eosin Y to NTS (E/N), the wavelength of incident light on photocatalytic activity for hydrogen generation, and the reaction mechanism were investigated in detail.

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1. Introduction

Photocatalytic splitting water into H_2 has attracted extensive attention due to its potential to obtain clean and highly efficient hydrogen energy from abundant H_2O . Since the discovery of photocatalytic water splitting on TiO_2 single crystal electrodes by Fujishima and Honda [1], a lot of work has been reported that some semiconductor catalysts show reasonable activities for water splitting into hydrogen under UV light irradiation, such as TiO_2 [2], ZrO_2 [3], SrTiO_3 [4], Ta_2O_5 [5], $\text{Sr}_2\text{M}_2\text{O}_7$ ($M = \text{Nb}, \text{Ta}$) [6,7], ATaO_3 ($A = \text{Li}, \text{Na}$ and K) [8], and so on. While ultraviolet light occupies only 5% among the solar light, in order to utilize the full spectrum of solar light, modifications must be applied to develop a catalyst that will work under visible light. A series of noble metals-loaded perovskite photocatalysts [9,10] and a new kind of solid solution catalysts [11,12] was synthesized and successfully used for H_2 generation under visible-light irradiation. Dye-sensitized solar cell is also a good

idea to harvest visible light, where the Grätzel cell is the most successful [13,14]. And dye-sensitized semiconductor catalysts are also developed for hydrogen production [15]. Although many researchers have explored extensive studies, the catalysts with satisfied properties of sensitizing to visible light, high solar conversion efficiency and good stability are still seldom devised.

Nanotube $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$ (NTS) is a kind of one-dimensional material, which belongs to the orthorhombic system structure and has a large Brunauer–Emmett–Teller (BET) surface [16,17]. This new material is often used as a catalyst or support in the catalytic reactions. To the best of our knowledge, there is no report applying this material to photocatalytic hydrogen generation. In the current study, a novel and highly efficient catalyst, Eosin Y-sensitized Pt-loaded nanotube $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$ is prepared using the impregnation photo-deposition method, which can reduce H_2O into H_2 in the presence of TEA solution as an electron donor under visible-light irradiation ($\lambda \geq 420$ nm). This catalyst shows a good stability for photocatalytic H_2 production over 100 h after 10 runs, up to 14.97% of quantum yield is achieved.

* Corresponding author. Tel.: +86 931 4968178; fax: +86 931 4968178.
E-mail address: gxlu@lzb.ac.cn (G. Lu).

2. Experimental

2.1. Chemical reagents

Eosin Y dye (bisodium salt), namely, 2',4',5',7'-tetrabromofluorescein, was used as the photosensitizer of the catalysts. The chemicals used in our experiments were of analytical grade and used without any further purification.

2.2. Preparation of Eosin Y-sensitized Pt-loaded NTS catalyst

Nanotube $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$ was prepared using the hydrothermal synthesis method, which was a typical procedure described in literature previously [18]. Eosin Y-sensitized NTS was prepared by the impregnation method with water as a solvent. In order to improve the photocatalytic activity of H_2 generation, Pt nanoparticles were deposited by in situ photo-deposition method with an aqueous solution of H_2PtCl_6 .

2.3. Photocatalytic evaluation

Photocatalytic reactions were carried out in a Pyrex flask of 140 ml with a flat window (an efficient irradiation area of 10 cm^2). Typically, 40 mg Eosin Y-sensitized NTS and appropriate H_2PtCl_6 aqueous were suspended in TEA- H_2O mixture (80 ml, 15 vol% aqueous solution), and the magnetic stirring was always conducted in the reaction process. A 300 W tungsten halogen lamp, equipped with a 420 nm cut-off filter (Toshiba, SY44.2), was used as the light source. Prior to irradiation, the suspension of the catalysts was dispersed in an ultrasonic bath for 1 min, and then Ar gas was bubbled through the reaction mixture for 40 min to remove oxygen. The photocatalytic activity was estimated by measuring the amount of hydrogen evolution using a gas chromatography (TCD, molecular sieve 13X column, Ar as gas carrier). pH values of the reaction solution were adjusted by addition of hydrochloric acid or sodium hydroxide using a Markson 6200 model pH meter.

2.4. Characterization

Transmission electron microscopic (TEM) patterns were taken on a JEM-2010 electron microscope. X-ray diffraction (XRD) patterns of the samples were recorded on a Rigaku B/Max-RB diffractometer with a nickel filtered $\text{Cu K}\alpha$ radiation. Solid-state diffuse reflectance UV-vis spectra (UV-vis DRS) of the samples were recorded with a U-3010 UV-vis spectrometer equipped with an integrating sphere diffuse reflectance accessory, using BaSO_4 as a reference.

3. Results and discussion

3.1. Characterization of the catalysts

Four different loading content of Pt (0, 0.5, 1, 2%) were selected to investigate the effect of loading amount on the photocatalytic activity for H_2 generation (Fig. 1), the results showed

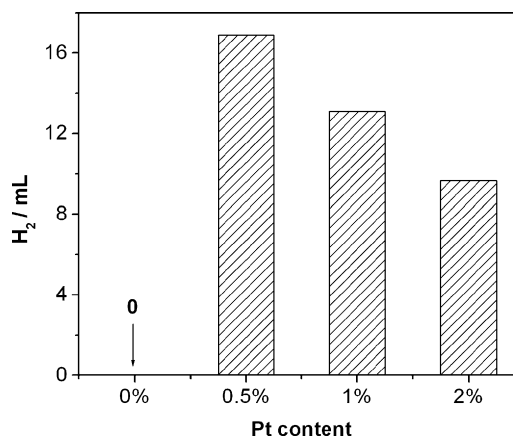


Fig. 1. Dependence of photocatalytic activity for H_2 generation on different Pt loading content. Reaction conditions: E/N = 1/1, 80 ml TEA solution, pH 7. The symbol "0" means that there is no hydrogen generation when no Pt is added.

that there was no hydrogen generation when no Pt was added, and the best activity was obtained when the loading content of Pt was 0.5%. The surface morphology of Eosin Y-sensitized Pt (0.5 wt%)-loaded NTS was shown in Fig. 2. As can be seen from the figure, Pt nanoparticles are successfully deposited on the surface of the NTS, whose size distribution is rather uniform, the average size of Pt nanoparticles is 5–6 nm. Pt nanoparticles are generally believed as the active sites for hydrogen generation and have small overpotential of water reduction. So, Pt is often used as the loading metal on the photocatalysts to improve the photocatalytic activity for hydrogen production.

Nanotube $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$ (NTS) is a semiconductor, which can only be excited by ultraviolet light. In order to well utilize the solar light, a modification must be applied. Dye sensitization to NTS is a good method to expand its absorbance range. The visible-light absorption ability increased remarkably after being sensitized by Eosin Y dye molecule, while the typical orthorhombic structure of NTS was not changed (Fig. 3). The solid-state diffuse reflectance UV-vis spectra (UV-vis DRS) of the catalysts were shown in Fig. 4. As can be seen from the figure, the onset absorption band of NTS is about 390 nm, that is to say, the band energy of NTS is 3.18 eV, which indicated that NTS can only be excited by ultraviolet light. After the surface sensitization with Eosin Y dye, a new band edge at

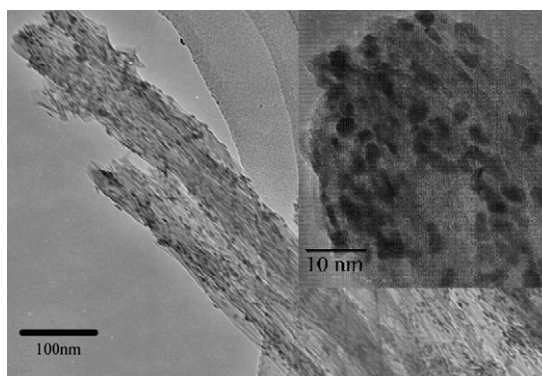


Fig. 2. TEM and HRTEM (insert) images of Eosin Y-sensitized Pt (0.5 wt%)-loaded NTS.

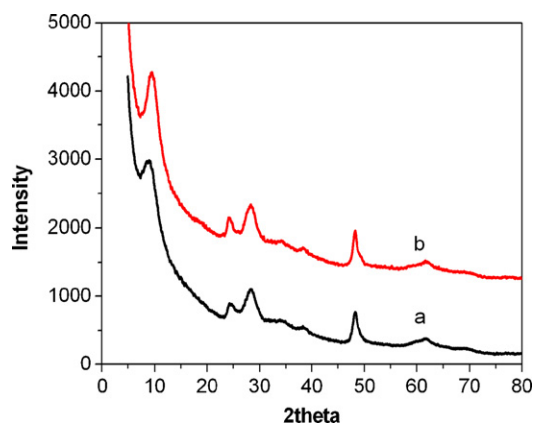


Fig. 3. XRD pattern of NTS (a) and Eosin Y-sensitized NTS (b).

670 nm emerges. The red shift of the UV–vis absorbance of NTS is due to the surface-modification of the dye molecule, which will benefit the samples to absorb visible light.

3.2. Effect of pH on the photocatalytic activity for hydrogen generation

In the dye-sensitized reaction system, the adsorption of dye molecule to catalyst surface is required because the association of the dye with catalyst serves as the path of the electrons from the dye to the catalyst surface. According to the plane and three-dimensional structure of Eosin Y molecular, the dye molecule can fix on the NTS surface by the interaction between carboxylate groups, phenolate oxygen of Eosin Y and surface hydroxyl, Ti species of NTS. The linkage mode between the Eosin Y dye and NTS are some like the form of LB films and can adsorb more dye molecule on NTS surface. The combination between carboxylate groups of dye and surface hydroxyl of NTS is ester-like linkage in TEA solution. The similar case has been reported in literature [19]. pH value has a large effect on the adsorption ability of dye molecule to the surface of a catalyst, and then influences the photocatalytic reaction activity. So it is essential to study the effect of pH value on the photocatalytic activity for H₂ production and the results show in Fig. 5. As can be seen

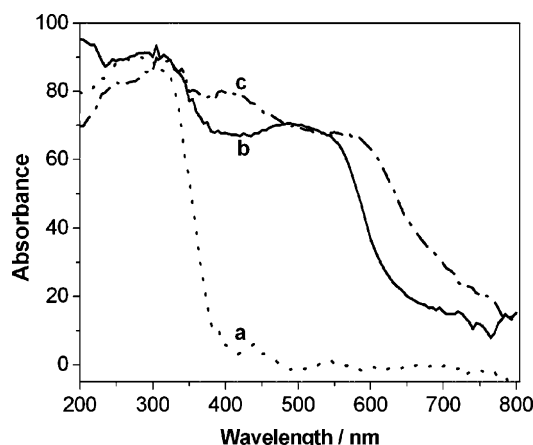


Fig. 4. UV–vis spectra of NTS (a), Eosin Y-sensitized NTS (b) and Eosin Y (c).

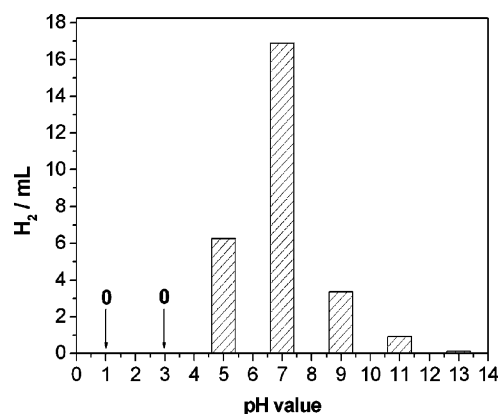


Fig. 5. Dependence of photocatalytic activity for H₂ generation on pH value. Reaction conditions: E/N = 1:1, 0.5% Pt loading, 80 ml TEA solution. The symbol “0” means that there is no hydrogen generation when pH value of TEA solution is 1 or 3.

from the figure, the neutral and weak acidic or basic environment are favourable for H₂ generation, and the photocatalytic activity reaches the maximum at pH 7, while the strong basic and acidic environment is disadvantageous to H₂ production. In the strong basic solution, a part of hydroxyl groups on the surface of NTS first react with hydrogen ion, and then leave a basic group with negative charge. Because of the electrostatic repulsion force, carboxyl groups of Eosin Y are difficult to adsorb on the surface of NTS, which prevents the excited electron of the dye from transferring to the Ti active species of NTS, so the photocatalytic activity for H₂ production is very low. While in the strong acidic solution, the ester-like linkages are difficult to form because of protonation of hydroxyl groups of the Eosin Y molecular. In addition, in the strong basic and acidic environment, the ester-like linkage between the Eosin Y dye and NTS is easy to hydrolyse. Therefore, the better result of photocatalytic activity for H₂ generation obtained in closely neutral solution is reasonable.

3.3. Effect of the mass ratio of Eosin Y to NTS (E/N) on the photocatalytic activity for H₂ generation

In our reaction system, the Eosin Y dye molecule adsorbs on the surface of NTS. Under visible-light irradiation, the Eosin Y dye molecule absorbs visible light and the electrons of the dye are excited from the HOMO to the LUMO state. The excited electrons are transferred to the conduction band of NTS, and then to the surface of the Pt nanoparticles, or the excited electrons are injected to the Pt nanoparticles directly, and then participates in the photocatalytic hydrogen generation. The concentration of Eosin Y plays a role in the number of the excited electrons and is important to the photocatalytic activity. So, it is vital to investigate the effect of E/N on the photocatalytic activity and the results are shown in Fig. 6. As can be seen from the figure, there is no hydrogen generation when no Eosin Y dye is added, which indicates the key role of dye to the reaction system. The photocatalytic activity for hydrogen generation increases with the increase of E/N, and reaches the maximum at E/N = 1, and then decreases with the continuous increase of

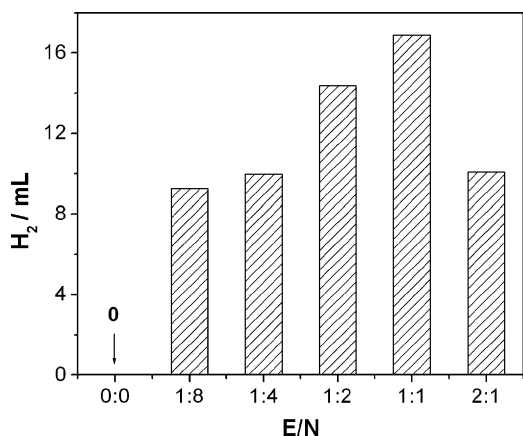


Fig. 6. Dependence of photocatalytic activity for H₂ generation on E/N. Reaction conditions: 0.5% Pt loading, 80 ml TEA solution, pH 7. The symbol “0” means that there is no hydrogen generation when no Eosin Y dye is added.

E/N. As the increase of E/N, the adsorption amount of Eosin Y dye on the surface of NTS increases, and then the number of excited electrons of dye molecule increases under visible-light irradiation, so the photocatalytic activity increases. When the adsorption amount approaches to saturation, the photocatalytic activity reaches the maximum. If E/N increases continuously, the activity will decrease, because the dissociative dye molecule will increase. However, the dissociative dye molecule cannot participate in electron transferring, while absorbs a part of incident light at the same time, resulting in the loss of part of the incident light, so the visible light in participating photocatalytic H₂ production reduces, and therefore the photocatalytic activity declines accordingly.

3.4. Stability of the Eosin Y-sensitized Pt-loaded NTS for H₂ generation

Stability is one of the important properties of a catalyst. The stability of photocatalytic activity for H₂ generation over Eosin Y-sensitized Pt-loaded NTS is listed in Fig. 7. In order

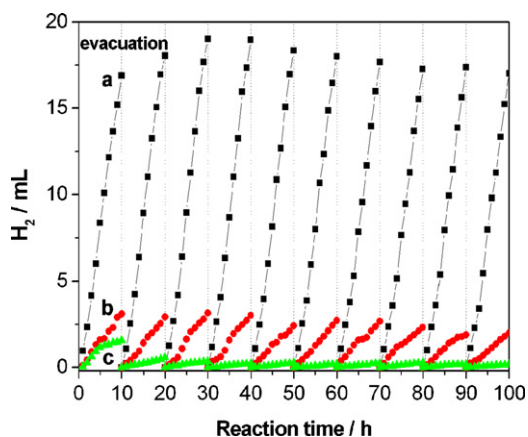


Fig. 7. Dependence of photocatalytic activity for H₂ generation on reaction time. (a) Eosin Y-sensitized Pt-loaded NTS; (b) Eosin Y-sensitized Pt-loaded TiO₂; (c) Eosin Y-sensitized Pt deposition. Reaction conditions: E/N = 1:1, 0.5% Pt loading, 80 ml TEA solution, pH 7.

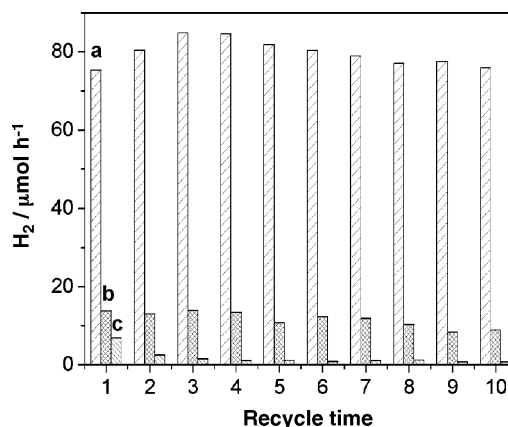


Fig. 8. Relationship between the rate of photocatalytic hydrogen generation and recycle time. (a) Eosin Y-sensitized Pt-loaded NTS; (b) Eosin Y-sensitized Pt-loaded TiO₂; (c) Eosin Y-sensitized Pt deposition. Reaction conditions: E/N = 1:1, 0.5% Pt loading, 80 ml TEA solution, pH 7.

to comparing, the results of Eosin Y-sensitized Pt-loaded TiO₂ and Eosin Y-sensitized Pt deposition under similar conditions are also shown simultaneously. As can be seen, the photocatalytic activity for hydrogen generation of Eosin Y-sensitized Pt-loaded NTS is much higher than that of Eosin Y-sensitized Pt-loaded TiO₂. The BET surface of NTS is about 400 m² g⁻¹, which is much larger than that of TiO₂ (55 m² g⁻¹), so NTS can provide more active sites for Pt deposition and dye adsorption. And the one-dimensional structure of NTS is favourable for electrons transferring, which can reduce the recombination of electron–hole pairs. Therefore, the activity for hydrogen generation of Eosin Y-sensitized Pt-loaded NTS is much higher than that of other two catalysts. In order to observe clearly, the relationship between the rates of photocatalytic hydrogen generation and recycle time was listed in Fig. 8. The rate of hydrogen generation is 75.45 μmol h⁻¹ in the first run, and reaches the maximum in the third run, and declines slightly in the consecutive runs. Pt nanoparticles are loaded by in situ photo-deposition method, so in the fore two runs Pt is possibly not reduced completely, therefore, the rate is a little lower than that in the third run. The slight decrease of the photocatalytic activity of Eosin Y-sensitized Pt-loaded NTS in the consecutive runs is probably caused by the consumption of electron donor (TEA) and the part decomposition of Eosin Y dye molecule. Catalyst c (Eosin Y-sensitized Pt deposition) also has some degree of activity, which indicates that the excited electrons from Eosin Y molecular can transfer to Pt nanoparticle directly. According to the calculation method of quantum yield in literature [20], up to 14.97% of quantum yield is achieved on Eosin Y-sensitized Pt-loaded NTS catalyst under visible-light irradiation.

3.5. Effect of the wavelength of incident light on the photocatalytic activity

The wavelength of incident light is important to a photocatalytic reaction. In the present paper, we conducted the experiments above using the cut-off filter with wavelength longer than 420 nm. In addition, two other cut-off filters (460 and

550 nm) are selected to investigate the effect of the wavelength of incident light on the photocatalytic activity. The quantum yield using the other two filters is 10.86 and 2.08%, respectively. The character absorption peak of Eosin Y in TEA solution is 518 nm, the transmission light can barely excite Eosin Y dye molecule using the 550 nm cut-off filter, so the apparent quantum yield is much lower than others.

3.6. Photocatalytic reaction mechanism for H₂ generation

Photocatalytic reaction mechanism of hydrogen generation over Eosin Y-sensitized Pt-loaded NTS is speculated as follows. Under visible-light irradiation, the Eosin Y dye molecule absorbs visible light and electrons of the dye are excited from the HOMO to the LUMO state. The excited electrons transfer to the conduction band of NTS, and then to the Pt nanoparticles, or the excited electrons transfers to Pt nanoparticles directly. Pt nanoparticles are the hydrogen active sites, the electrons concentrated on Pt nanoparticles participate in photocatalytic water reduction into hydrogen. The dye molecule would regenerate in the electron donor solution.

4. Conclusions

A novel photocatalyst, Eosin Y-sensitized Pt-loaded NTS was found to be highly efficient for photocatalytic hydrogen generation in TEA solution under visible-light irradiation ($\lambda \geq 420$ nm). TEM and HRTEM results showed that Pt nanoparticles were successfully deposited on the surface of NTS and the average size of Pt was rather uniform (5–6 nm). UV–vis spectra indicated that the visible-light absorption ability of NTS was remarkably increased after sensitized by Eosin Y dye, while the typical orthorhombic structure of NTS was not changed.

The photocatalytic activity of Eosin Y-sensitized Pt-loaded NTS for hydrogen generation was largely influenced by pH value of reaction solution, and the best results were obtained under the near neuter environment. The mass ratio of E/N also

had a large effect on the photocatalytic activity and the best ratio was 1:1. Under the optimum conditions, where pH = 7, E/N = 1 and 0.5% Pt loadings, up to 14.97% of quantum yield was achieved for photocatalytic hydrogen generation on this new catalyst under visible-light irradiation ($\lambda \geq 420$ nm), whose stability were remained over 100 h after consecutive 10 runs.

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