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Article

Simultaneous hydrogen and peroxide production by photocatalytic water splitting

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ABSTRACT

Photocatalytic oxidation of water is a promising method to realize large-scale H₂O₂ production without a hazardous and energy-intensive process. In this study, we introduce a Pt/TiO₂(anatase) photocatalyst to construct a simple and environmentally friendly system to achieve simultaneous H₂ and H₂O₂ production. Both H₂ and H₂O₂ are high-value chemicals, and their separation is automatic. Even without the assistance of a sacrificial agent, the system can reach an efficiency of 7410 and 5096 μmol g⁻¹ h⁻¹ (first 1 h) for H₂ and H₂O₂, respectively, which is much higher than that of a commercial Pt/TiO₂(anatase) system that has a similar morphology. This exceptional activity is attributed to the more favorable two-electron oxidation of water to H₂O₂, compared with the four-electron oxidation of water to O₂.

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1. Introduction

H₂O₂ is not only a high-value industrial chemical, in growing demand on the global market, but also a potentially attractive energy carrier [1,2]. H₂O₂ is widely used in chemical synthesis, disinfection, wastewater treatment, pulp, etc. [3] Moreover, due to the advantage of a simple membrane-free structure, hydrogen peroxide fuel cells have attracted extensive attention [4,5]. The traditional method for H₂O₂ production has been the anthraquinone process, which is an indirect batch method requiring sequential hydrogenation, oxidation of a 2-alkylanthraquinone, and extraction of H₂O₂ from organic solvents [6]. However, this multistep method is hazardous, energy-intensive, and difficult for in situ H₂O₂ production. Thus,

extensive efforts have been devoted to achieving direct synthesis of H₂O₂ by eco-friendly and low-cost processes [7]. H₂O₂ production by photocatalytic methods, which are powered by clean solar energy, is considered one of the most promising approaches. To date, photocatalysis has been studied in many fields, including hydrogen production, CO₂ reduction, and water treatment [8–24]. However, there is still a great deal of potential for photocatalytic H₂O₂ production. Recently, intense efforts have been made to achieve H₂O₂ production by photocatalytic O₂ reduction [25,26]. However, research concerning simultaneous H₂ and H₂O₂ production during water splitting is scarce. Compared with the traditional four-electron transfer process, converting water to H₂ and H₂O₂ by a two-electron/two-proton oxidation process is considered as the ideal method, in which

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all the products are value-added chemicals [27]. Moreover, the system avoids the problem of separation because H_2 and H_2O_2 exist in gas and liquid phases, respectively, which is a significant advantage over the H_2 and O_2 production system. To date, fewer catalysts are known for the selective two-electron oxidation of water to produce hydrogen peroxide, compared with the four-electron oxidation of water to produce oxygen [28,29]. To the best of our knowledge, two systems, Pt/P25 [30] and Pt/C₃N₄ [31] have been reported for photocatalytic hydrogen and hydrogen peroxide production from pure water. However, the catalytic efficiency is still very low. The H_2 and H_2O_2 evolution rates are 42.75 $\mu\text{mol g}^{-1} \text{h}^{-1}$ (first 30 min) and 34.38 $\mu\text{mol g}^{-1} \text{h}^{-1}$ (average of 2 h), and 10.80 $\mu\text{mol g}^{-1} \text{h}^{-1}$ (average of 25 h) and 13.80 $\mu\text{mol g}^{-1} \text{h}^{-1}$ (average of 25 h), for Pt/P25 and Pt/C₃N₄, respectively.

In this study, we introduce Pt/TiO₂(anatase) as a photocatalyst, which produces hydrogen in the gas phase, and H_2O_2 on the surface of catalyst and in solution. The H_2 and H_2O_2 production efficiencies can reach up to 7410 and 5096 $\mu\text{mol g}^{-1} \text{h}^{-1}$ (first 1 h), respectively, without the assistance of a sacrificial agent. The H_2 production efficiency is 173 and 686 times higher than those of the Pt/P25 and Pt/C₃N₄ systems, respectively. Additionally, the H_2O_2 production efficiency is 148 and 369 times higher than those of the Pt/P25 and Pt/C₃N₄ systems, respectively. Therefore, it is clear that the present system is promising for production of high value-added chemicals by photocatalytic water splitting.

2. Experimental

2.1. Materials

All chemical reagents were analytical grade and used without further purification. Ethylalcohol, methanol, silver nitrate (AgNO₃), ammonia solution and titanium tetrachloride (TiCl₄) were obtained from Beijing Sinopharm Chemical Reagent Co., Ltd. H₂PtCl₆ was obtained from J&K Scientific Ltd.

2.2. Preparation of TiO₂ NPs

A solution of 0.2 mol/L TiCl₄ was slowly dropped into a 0.5 mol/L ammonia solution (50 mL) under vigorous stirring at room temperature until the pH value of the solution reached ~8. A white precipitate was formed and then centrifuged and washed with distilled water until chloride ions were not detectable in the washed water (1.0 wt% AgNO₃ solution). A quarter of the precipitation was dispersed in 50 ml of anhydrous ethylalcohol by ultrasonic treatment for 20 min in an autoclave, and was kept at 150 °C for 5 h. The products were collected and washed with deionized water three times. After that, the samples were dried and calcined at 400 °C for 2 h. The Pt NPs were loaded by an in-situ photo-deposition method using H₂PtCl₆ (Pt 1wt% in the whole sample) as the precursor and MeOH as the electron donor (10%). After 1 h of UV light irradiation, the sample was collected by centrifugation and dried at 80 °C overnight to remove the remaining MeOH and H₂O.

2.3. Photocatalytic reaction

The prepared Pt/TiO₂ hybrid (1 mg) was dispersed in 20 mL deionized water in a quartz reactor and sealed with a rubber septum. After purging with argon flow for 30 min to remove dissolved air, the suspensions were irradiated by a 500 W Hg lamp under magnetic stirring at room temperature. The evolved H_2 in the gas phase was examined by a Techcomp gas chromatograph (GC-7900) with a thermal conductivity detector (TCD), 5 Å molecular sieve columns, and Ar carrier.

2.4. The H₂O₂ test method

The hydrogen peroxide measurement was performed in 2.0 mL reaction suspension. A 0.5 mL volume indicator (1% *o*-tolidine in 0.1 mol/L HCl) was added to the suspension and the mixture was allowed to react for 10 min. The color of the mixture turns to blue. Subsequently, 2.0 mL HCl (1.0 mol/L) was added to the mixture, and the color turns to yellow from blue. Immediately, the mixture was centrifuged and the absorption spectrum of the liquid supernatant was recorded with a UV-vis spectrophotometer. The absorption spectrum of the 2-electron oxidized toluidine has a characteristic maximum at 437 nm.

2.5. Characterization of samples

UV-Vis spectra were measured with a Hitachi U-3900 spectrophotometer. Scanning electron microscopy (SEM) images were taken by using a Zeiss electron microscope. Transmission electron microscopy (TEM) images were obtained by using a 2100F (JEOL) electron microscope at an acceleration voltage of 200 kV. X-ray diffraction (XRD) of the samples was performed with a SmartLab Goniometer with Cu K-beta radiation, operating at 40 kV and 200 mA. X-ray photoelectron spectroscopy (XPS) analysis was carried out on a Thermo Scientific ESCALAB 250Xi spectrometer (all the peaks corrected with reference to the C signal (284.8 eV)). Raman spectrum was recorded on a Renishaw inVia Raman microspectrometer and laser excitation wavelength was 633 nm. The static fluorescence spectral measurements were carried out with an F-4600 (Hitachi) spectrofluorometer. The ESR measurements were conducted by a Bruker ESP-300E spectrometer at 9.8 GHz, X-band, with 100 Hz field modulation.

2.6. Calculation of the valence band of TiO₂

The valence band of titanium oxide was calculated by the theory of elemental electronegativity. The valence band is calculated by using element electronegativity and material's band gap which comes from the UV-vis diffuse reflectance spectra.

$$E_c = -[\chi(A)^a \cdot \chi(B)^b \cdot \chi(C)^c]^{1/(a+b+c)} + 1/2 E_g + E_0$$

$$E_v = E_c + E_g$$

Where $\chi(A)$ is the absolute electronegativity of element A, E_g is the band gap, and E_0 is the reduction potential of water (4.5 eV).

Fig. 1. (a) XRD pattern and (b) SEM images for the TiO₂ NPs; TEM and HRTEM images for the (c, d) pure TiO₂ NPs and (e, f) Pt/TiO₂ hybrid.

3. Results and discussion

The anatase TiO₂ nanoparticles (NPs), with an average diameter of 28.9 ± 3.9 nm, were obtained by an improved hydrothermal strategy, in which TiCl₄ was selected as the Ti precursor [32]. To construct the Pt/TiO₂ hybrid, Pt nanoparticles (NPs) were loaded onto the TiO₂ NPs by in situ pho-

to-deposition [33]. The weight of the Pt NPs was 1.0 wt% compared with the TiO₂ NPs. Both XRD and Raman spectra show a single-phase diffraction pattern assigned to anatase TiO₂ (Fig. 1a) (JCPDS No. 21-1272). Five main diffraction peaks near or at $2\theta = 25.3^\circ, 37.8^\circ, 48.0^\circ, 53.9^\circ$, and 55.1° are observed, corresponding to the (101), (004), (200), (105) and (211) diffraction planes of anatase TiO₂, respectively [34]. The Raman shifts of 397, 516 and 639 cm^{-1} correspond to anatase TiO₂ (Fig. S1) [35]. The morphology of the TiO₂ catalyst was characterized by SEM and TEM (Fig. 1b–f). As shown in Fig. 1b, the TiO₂ NPs display a spherical morphology with an average diameter of 28.9 ± 3.9 nm, from the SEM image statistics. The lattice spacing is 0.35 nm, which is assigned to the (101) crystal plane of anatase TiO₂, from the TEM images (Fig. 1c–d). For the Pt/TiO₂ hybrid (Fig. 1e), the Pt NPs, with a size of 2 nm, are well dispersed onto TiO₂. The *d*-spacings of 0.35 and 0.23 nm correspond to the (101) and (111) planes of TiO₂ and Pt, respectively [36].

The photocatalytic performance of the catalysts was evaluated under Hg lamp irradiation ($\lambda \geq 300$ nm) at room temperature. As shown in Fig. 2a, our system achieved the highly efficient H₂-production activity of $7410 \mu\text{mol g}^{-1} \text{h}^{-1}$ for the first 1 h, in deionized water, without an electron sacrificial agent. The produced H₂O₂ was measured using the peroxide indicator *o*-tolidine, after a period of irradiation, and a typical absorption peak at 437 nm was easily detected using UV-vis spectroscopy [31]. As depicted in Fig. S2, the H₂O₂ production efficiency is $5096 \mu\text{mol g}^{-1} \text{h}^{-1}$. In contrast, the commercial Pt/anatase TiO₂ hybrid only exhibits an efficiency of $3041 \mu\text{mol g}^{-1} \text{h}^{-1}$ and $2644 \mu\text{mol g}^{-1} \text{h}^{-1}$ for H₂ and H₂O₂, respectively (Fig. 2a). It should be noted that the commercial anatase TiO₂ NPs have a similar morphology to our system (Figs. S3–5), and, as shown in Fig. S6, the average pore sizes and Brunauer-Emmett-Teller (BET) surface areas were determined to be 18.2 nm and $46.0 \text{ m}^2/\text{g}$ for the present sample, and 17.8 nm and $53.8 \text{ m}^2/\text{g}$ for the commercial anatase TiO₂ NPs, respectively, by N₂ adsorption. The results indicate that the difference in surface area does not lead to the difference in photocatalytic efficiency. Therefore, compared with the commercial Pt/anatase TiO₂, the present system

Fig. 2. (a) Activity comparisons between the present anatase TiO₂ NPs and commercial anatase TiO₂ NPs with a similar morphology (all photocatalyst samples weighed 1 mg and contained 1.0 wt% Pt NPs); (b) Stability evaluation of Pt/TiO₂ for H₂ and H₂O₂ (inset) production. All the experiments were conducted in 20 mL deionized water with 1 mg Pt (1.0 wt%)/TiO₂ hybrid photocatalyst.

demonstrates significant advantages not only in H_2 evolution, but also in H_2O_2 production. To demonstrate the potential value in practical applications, a photocatalytic stability experiment was carried out. As depicted in Fig. 2b, the photocatalytic hydrogen evolution activity could be sustained for more than 15 h, and more than $61723 \mu\text{mol/g H}_2$ was produced. The amount of H_2O_2 initially increased, and then decreased with an increase in irradiation time. It was proposed that H_2O_2 could decompose to H_2O and O_2 under prolonged irradiation. However, no oxygen was detected during the photocatalytic reaction, and hydrogen peroxide (H_2O_2) was detected as the only oxidative product. The produced O_2 could be easily reduced by the photo-generated electrons, and further mechanistic studies are ongoing. Collectively, these results indicate that the present photocatalytic system is highly efficient and promising for H_2 and H_2O_2 production without separation problems.

For the water splitting reaction ($2\text{H}_2\text{O} \rightarrow \text{H}_2 + \text{H}_2\text{O}_2$), it is widely accepted that H_2 is generated on Pt [37]. For the mechanism of H_2O_2 formation, it has been proposed that H_2O_2 is mainly derived from the recombination of hydroxyl radicals ($\bullet\text{OH}$). During the photocatalytic reaction, $\bullet\text{OH}$ is confirmed as the crucial reactive intermediate. To gain insight into the process, XPS measurements were first used to investigate the surface properties of the TiO_2 NPs (Figs. S7–10). Before irradiation, TiO_2 and Pt/TiO_2 samples show two main peaks, corresponding to surface lattice oxygen (529.7 eV, 529.8 eV) and surface hydroxyls (531.6 eV, 531.9 eV). At the same time, for the Pt/TiO_2 sample, a weak peak near 533.3 eV, associated with physisorbed water is observed. After 1 h of irradiation, there is

a distinct change in the spectrum. The peak at 533.2 eV, associated with physisorbed water, is greatly enhanced, and the hydroxyl peak is significantly increased, compared with the other samples (Fig. 3a) [38,39]. In contrast, Ti atoms demonstrate a similar bonding environment before and after irradiation (Fig. 3b). The binding energies of $\text{Ti } 2p_{3/2}$ and $2p_{1/2}$, 458.6 and 464.4 eV, respectively, are the characteristic peaks of Ti^{4+} in TiO_2 [40]. Therefore, it is proposed that the hydroxyls and adsorbed water have a significant impact on the formation of H_2O_2 . In order to capture the reactive intermediate during the irradiation reaction, electron spin resonance (ESR) and fluorescence labeling measurements were performed. As shown in Fig. 3c, a characteristic quartet of peaks (1:2:2:1, $a_N = a_H = 15.4 \text{ G}$) associated with the 5,5-dimethyl-1-pyrroline-*N*-oxide- OH (DMPO- OH) radical adduct is immediately detected after 60 s of UV light irradiation [41]. Additionally, when terephthalate (TANA) was added to the system, an obvious fluorescence signal at 422 nm, assigned to 2-hydroxyterephthalic acid (TAOH), was detected (Fig. 3d) [42]. The ESR and fluorescence results imply that the generated $\bullet\text{OH}$ radicals play a significant role in the formation of H_2O_2 [30]. The bandgap and valence band for the present anatase TiO_2 are 3.21 and 2.97 eV, respectively, confirmed by diffuse reflectance UV-vis spectroscopy (Fig. 3e). The oxidation potentials $E_{\text{ox}}(\bullet\text{OH}/\text{OH}^-)$ and $E_{\text{ox}}(\bullet\text{OH}_{\text{ads}}/\text{OH}^-_{\text{ads}})$ are 1.89 and 1.5 V versus the NHE, respectively [43,44]. Therefore, the H^+ photogenerated by the anatase TiO_2 has enough oxidation potential to convert $\bullet\text{OH}$ to OH^- and OH^-_{ads} to $\bullet\text{OH}_{\text{ads}}$. Furthermore, compared with the commercial anatase TiO_2 NP sample, the present anatase NPs possess more hydroxyls and adsorbed

Fig. 3. XPS spectra of (a) O 1s and (b) Ti 2p in TiO_2 , Pt/TiO_2 , and Pt/TiO_2 (UV light 1 h), respectively; (c) ESR spectra for $\bullet\text{OH}$ radical detection in the presence of Pt/TiO_2 and DMPO in aqueous solution under UV light irradiation; (d) FI spectra for $\bullet\text{OH}$ radical detection using TAOH as the trapping agent; (e) Diffuse reflectance spectrum of the TiO_2 sample (insert: the transformed Kubelka-Munk function versus band gap); (f) Schematic of the mechanism for photocatalytic water splitting into H_2 and H_2O_2 .

water (Fig. S11). Therefore, it can be concluded that the surface properties, and the quantities of hydroxyls and physisorbed water are related to the catalytic performance. Based on the above analysis, the reaction mechanism is depicted in Fig. 3f. To date, different oxidation products have been reported for photocatalytic water splitting using anatase. No oxygen was detected, or the final ratios of H_2/O_2 were below 2 [28,29,45]. Therefore, water oxidation products other than oxygen play a significant role. In the present Pt/TiO₂ (anatase) system, we detected H₂O₂ as the water oxidation product, and further mechanistic investigation is underway.

4. Conclusions

We have developed a much more valuable and efficient photocatalytic water splitting system by converting water to H₂ and H₂O₂ simultaneously. The stable and easily-prepared Pt/TiO₂(anatase) hybrid is introduced as the catalyst. The H₂ and H₂O₂ production rates can reach up to 7410 and 5096 $\mu\text{mol g}^{-1} \text{h}^{-1}$. More importantly, H₂ and H₂O₂ are separated automatically, avoiding additional separation costs. The excellent activity is attributed to the more favored two-electron oxidation of water to H₂O₂, compared with the four-electron oxidation of water to O₂. Therefore, photocatalytic oxidation of water to H₂O₂ is a promising method to achieve large-scale H₂ and H₂O₂ production without a hazardous and energy-intensive process.

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Graphical Abstract

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Photocatalytic water splitting into hydrogen and peroxide, two value-added chemicals, is achieved over a Pt/TiO₂(anatase) photocatalyst, avoiding separation problems.

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光催化分解水制备氢气和过氧化氢

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摘要: 过氧化氢不仅是一种广泛应用于化学合成、消毒、废水处理及纸浆漂白等领域的高价值化学品, 还是一种具有潜力的能源载体。此外, 过氧化氢燃料电池因其结构简单而受到广泛关注。蒽醌法是工业生产过氧化氢的传统方法, 但是这种方法不仅能耗高, 而且生产过程会造成严重的环境问题。因此, 通过环保并且低成本的工艺直接合成过氧化氢具有重要研究意义。以太阳能动力的光催化法生产过氧化氢被认为是最有前景的方法之一。目前, 光催化已在制氢、二氧化碳还原和水处理等诸多领域取得了重要进展。但是, 利用光催化分解水制备过氧化氢的研究还非常少。尽管通过光催化还原氧气可以制备过氧化氢, 但是通过分解水同时制备高价值过氧化氢和氢气更具有吸引力。

在本项工作中, 我们利用Pt/TiO₂(锐钛矿)光催化剂在没有牺牲剂的条件下实现了高效产氢和过氧化氢, 氢气和过氧化氢的生成速率分别达到7410和5096 μmol g⁻¹ h⁻¹ (第一小时), 远高于市售的Pt/TiO₂ (锐钛矿)体系和文献报道数值。本文采用X射线光电子能谱(XPS)、电子自旋共振(ESR)和荧光标记法等表征手段研究了Pt/TiO₂上同时生成氢气和过氧化氢的催化机理。

XPS测试结果表明, Pt/TiO₂在光照射1 h后, XPS信号发生明显变化。与其他样品相比, 物理吸附水和羟基的峰明显增加。因此, 我们推测羟基和物理吸附水对过氧化氢的生成具有重要影响。进一步采用电子自旋共振(ESR)和荧光标记法对羟基进行了测量。ESR结果显示, 紫外光照60 s即可检测到羟基捕获剂与羟基的结合物5,5-dimethyl-1-pyrroline-N-oxide-OH (DMPO-OH)的特征峰。此外, 在体系中加入荧光标记分子对苯二甲酸(TANa)后也可以迅速检测到2-羟基对苯二甲酸(TAOH)在422 nm处明显的荧光信号。因此, ESR和荧光结果均表明所产生的羟基自由基在过氧化氢形成中起着重要作用。

上述结果表明, 在本体系中氢气和过氧化氢的生成遵循两电子转移过程。与传统全分解水体系生成氢气和氧气相比, 两电子转移过程比四电子过程更容易发生。因此, 光催化水氧化制过氧化氢是实现大规模生产氢气和过氧化氢的一种很有前景的方法。

关键词: 光催化分解水; 氢气; 过氧化氢; 锐钛矿

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