A Multichannel System for Rapid Determination of the Activity for Photocatalytic H_2 Production

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Introduction

Photocatalytic hydrogen production from water under visible light over a semiconductor has attracted increasing attention for its many advantages.[1–4] A large amount of photocatalysts have been found in the past few decades. However, most traditional reactors have been designed to evaluate one photocatalyst in one experiment.[5–7] Due to the lack of rapid screening technologies, photocatalytic activity of most of the newly designed catalysts cannot be exactly evaluated, or actually without being tested, which, thus, greatly hinders the development of new materials for photocatalytic hydrogen production.

Combinatorial methods based on automated synthesis and screening has been investigated.[8] The problem for this method is that all the photocatalyst have to be first prepared in film form. However, the physicochemical properties of the photocatalyst as film are supposed to be much different from its counterpart in powder form.

It has also been agreed that even for a specified powdered photocatalyst, being employed at different reaction conditions could lead to significantly different photocatalytic properties.[9] By involving the changes in solution condition, e.g., the concentration of photocatalyst, sacrificial reagents, there would be a large number of experiments yet to do in the screening process. Consequently, in view of industrial application of photocatalytic hydrogen production technique, a new setup capable of rapid screening of the photocatalytic materials in various reaction conditions in a simple and time-efficient way is desired.

Gasochromic films consist of an electrochromic layer such as WO_3, and a very thin coating of a catalyst was reported to be very sensitive to the existence of H_2, and has been widely investigated for application in windows with a variable transmittance in recent years.[10–12] Based on the unique gasochromic properties of WO_3 film, herein, we report the design of a multichannel system for rapid screening of photocatalytic materials designed for H_2 production. The system contains six channels, allowing for six tests in the same time (the number of channels could be further increased if needed). To demonstrate the reliability of our system, $Zn_xCd_{1-x}S$ solid solution of various x values are prepared. The H_2 evolution rate over these photocatalysts determined by our system was found to correspond well with that determined by traditional gas chromatography (GC). Our system was supposed to provide an alternative approach for rapid screening of photocatalytic materials in various reaction conditions in a simple and time-efficient way.

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Experiment

Preparation of $Cd_xZn_{1-x}S$ photocatalysts

All reagents are in analytical grade. A mixture was prepared by dissolving the appropriate amount of Zn $(NO_3)_2$ and Cd $(NO_3)_2$ in deionized water. $Cd_xZn_{1-x}S$ was coprecipitated by slowly adding aqueous solution of Na_2S to the mixture solutions while keeping stirring during the reaction. The precipitate was washed with deionized water repeatedly and then dried in an oven at 60°C for 10 h. The nominal Zn/Cd ratio for the final samples are 4:1, 2:1, 1:1, 1:2, 1:4, and 0:1, respectively.

Preparation of Pd/WO_3 film

In a typical synthesis, 10 g tungsten powder was added slowly in a 40 mL of aqueous solution containing 30% H_2O_2. After stirring for 6 h at room temperature, tungsten was totally dissolved into white milk-like solution. Subsequently, the solution was heated to 40°C to remove excessive H_2O_2. Ethanol was then added to the solution. The sol was allowed to maintain at 80°C until it was transformed into an orange emulsion. To prepare Pd doped WO_3 sol, certain $PdCl_2$ powder was first dissolved in ethanol and then added to WO_3 sol.

A glass substrate of (58 mm × 78 mm) was treated for 20 min by ultrasonic oscillation in acid, alkali and deionized water, sequentially. Pd/WO_3 film was then coated on glass substrate by spin coating (2,000 rad/s), and then heat-treated at 200°C for 2 min to obtain the final film.

Characterization

The transmittance of the Pd/WO_3 film before and after the reaction was determined by diffuse reflectance UV–vis spectra with Hitachi U-4100. For photocatalytic test, the photocatalyst powder was dispersed in a 50 mL aqueous solution

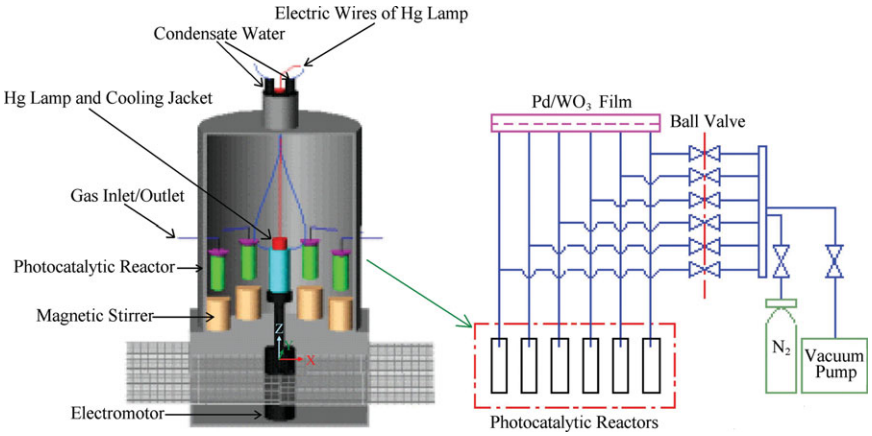

Figure 1. Schematic illustration of multichannel rapid screening system.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

containing Na_2S and Na_2SO_3 as electron donors. The photocatalysts were irradiated by a 300 W Hg lamp and all the reaction times were controlled to 2 h. The amount of H_2 gas was determined using online thermal conductivity detector (TCD) gas chromatography (NaX zeolite column, TCD detector, N_2 carrier). To obtain reliable data, we performed three measurements for each sample and taken the average value to reduce occasional errors.

Results and Discussion

Gasochromic coloration of porous WO_3 films has been found to be similar to the electrochromic reaction.[10] The mechanism for the coloration process is still in dispute and many models have been proposed. Briefly, for a Pd/WO_3 film in wet H_2/N_2 atmosphere, hydrogen is supposed to be first absorbed by noble metal Pt or Pd, and then transferred to WO_3, forming an intermediate state. Shortly, oxygen vacancies as color centers and H_2O are generated, leading to coloration. Quick bleaching will take place when the colored film was exposed to oxygen or air.

Based on the unique properties of Pd/WO_3 film, we designed our evaluation setup as shown in Figure 1. The system mainly includes three units, i.e., the photocatalytic reaction unit, control unit and hydrogen detection unit. Before light irradiation, the cell with reactant solution was evacuated and then purged with N_2 to completely eliminate O_2. The stirring rate, direction of rotation and the temperature of the reaction can be controlled in the process. Circulation water over the Hg lump was used to control its temperature. In the photocatalytic experiment under visible light, $NaNO_2$ solution could be introduced into the water jacket as an internal circulation cooling medium to eliminate light with a wavelength shorter than 400 nm. UV–vis spectrum of the $NaNO_2$ solution showed that it could effectively absorb light with wavelengths below 400 nm and thus act as a cut-off filter.[13] It is easy to find from Figure 1 that more photocatalytic channels (here we take six channels as an example) can be integrated into the system to achieve large-scale screening.

To demonstrate the reliability of our designed setup, we chose the well-studied $Zn_xCd_{1-x}S$ solid solution with various Zn/Cd ratios as photocatalysts for activity evaluation. It is known that the band gap of this solid solution can be continuously adjusted by changing its Zn/Cd ratios, which inevitably leads to varied activities for photocatalytic hydrogen production.[14]

As a blank experiment, we measured by the diffuse reflectance UV–vis spectra the transmittance of Pd/WO_3 glass before photocatalytic reaction, as shown in Figure 2. As is seen, the transmittance of Pd/WO_3 shows a quick increase below a wavelength of 400 nm. The transmittance is about the same beween 400–800 nm and the highest transmittance is around about 75%. The photograph for the glass before reaction showed no visible coloration, as shown in the inset of Figure 2.

For photocatalytic test, equal amounts of various $Zn_xCd_{1-x}S$ photocatalysts were dispersed in six reaction cells, respectively. The six reactions were conducted at same temperature, same stirring rate and the same reaction conditions in general. The photograph for the colored film is shown in the inset of Figure 3. Six round regions on the film corresponded to the six channels. Blue coloration of the film after reaction could be found clearly by visual observation and the extent of coloration for the six sampls were much different. The transmittance of Pd/WO_3 film after reaction was determined again, as shown in Figure 3. It was found that all the glass plates undergone a decrease of transmittance after reaction. The greatest decrease of transmittance was found for

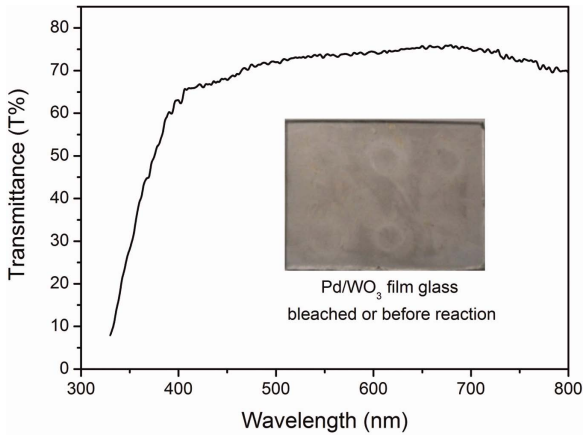

Figure 2. Transmittance and photograph (inset) of the Pd/WO_3 film before photocatalytic reaction.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

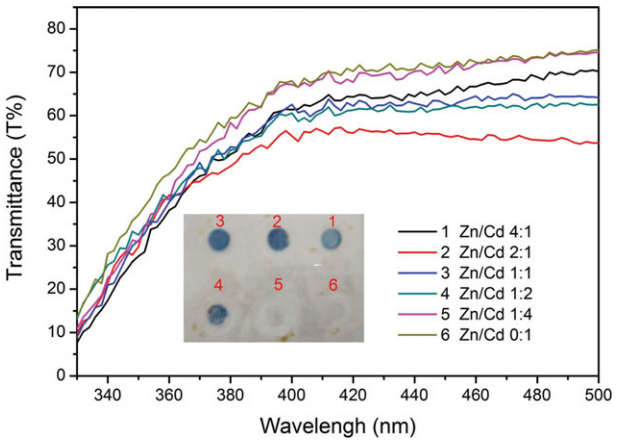

Figure 3. The transmittance of the Pd/WO_3 film after photocatalytic H_2 evolution over $Zn_xCd_{1-x}S$ photocatalysts with various Zn/Cd ratios.

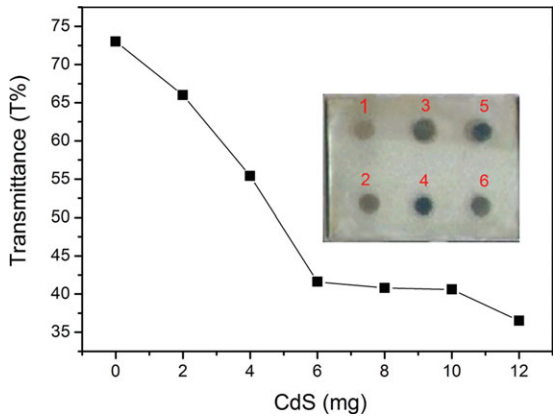

Figure 5. The transmittance of the Pd/WO_3 film after photocatalytic reaction over CdS photocatalysts of various addition amounts, reaction volume 50 mL, Pt wt 2%.

sample 2. For sample 5 and 6, however, only a slight decrease of transmittance could be oberved compared to that before reaction. These results indicated that sample 2 might lead to highest hydrogen evolution rate.

To verify our assumption, we monitored the H_2 evlotion in each channel with a thermal conductivity detector (TCD) of gas chromatography. The results were presented in Figure 4. For easy comparison, the transmittance at 440 nm of the 6 glass plates after reaction were taken from Figure 3 and replotted in Figure 4. As expected, the hydrogen production over sample 2, i.e., Zn/Cd ratio of 2:1,was found to be the largest, corresponding to lowest transmittance at 440 nm. Here, it was found that the sample 5 and especially sample 6 showed only very low activity. The reason could be ascribed to the absence of Pt as cocatalyst for our photocatalysts. It is well-known that the cocatalyst such as Pt is very crucial for CdS to show high activity. However, introduction of Zn to form $Cd_xZn_{1-x}S$ solid solution could remarkably enhance its activity without needing Pt loading.[15]

To simulate the change of reaction conditions, various amounts of pure CdS were empolyed and evaluated in our system. This time, 2 wt % of Pt was deposited on CdS by a photoreduction method, as we reported previously.[16] The results are shown in Figure 5.

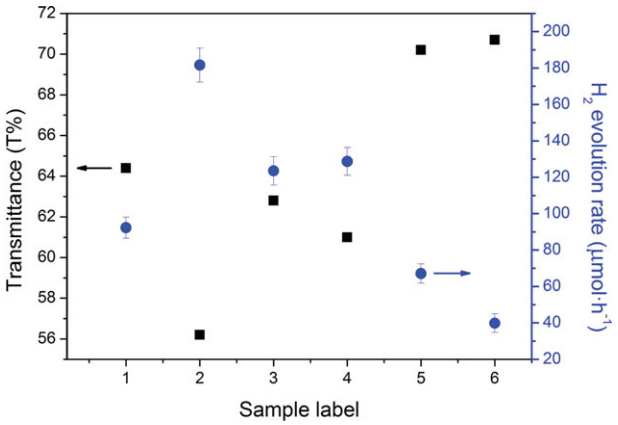

Figure 4. The relationship between the H_2 evolution rate and the corresponding transmittance of the Pd/WO_3 film.

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Basically, for the Pd/WO_3 film, the coloration precedure is dependent on the H_2 concentration, as aforementioned. Higher H_2 pressure in the channel is supposed to lead to faster coloration. We also suppose that the hydrogen evolution rate could be accelarated by increasing CdS addition amount. As shown in Figure 5, when we established the relationship between the H_2 evolution rate and the transmittance of the Pd/WO_3 film, a linear relation of these two parameters could be found with CdS adding amount below 6 mg. Further addition of CdS might result in low transmitannce and strong light scattering in the reaction slurry, which could counteract the benefit of increased CdS concentration. Hence, the transmittance curve deviates from the linear relationship. Our aforementioned results demonstrated that the designed setup can qualitatively reflect the activity of the photocatalyst in various reaction conditions, and enable evaluation of photocatalyst acitivty even by visual observation without needing GC equipment.

It should be noted here that we have treated Pd/WO_3 film at 200°C for 2mins to ensure slower bleaching of the colored film, for the convenience of UV–vis measurement. The slow bleaching, however, also means a slow coloration, considering that coloration of Pd/WO_3 is a reversible process. This is the reason why we have to conduct at least a 2 h photocatalytic reaction in our experiment. Such long experimental time is obviously not satisfactory for a quick screening system. In fact, it has been found that by controlling the preparation conditions, the response time for Pd/WO_3 film could be significantly shortened.[17]

Taken the Pd/WO_3 film without heat treatment as example, we found that it could respond to hydrogen gas within seconds. As shown in Figure 6, the colored film showed rapid bleaching when exposed to air. The film was bleached completely and ready for the second use around 280 s. This indicated that the photocatalyst evaluation process could be completed in much shortened time, if more sensitive Pd/WO_3 film was employed.

Conclusions

Gasochromic coloration of porous WO_3 films has been widely investigated for application in windows with a

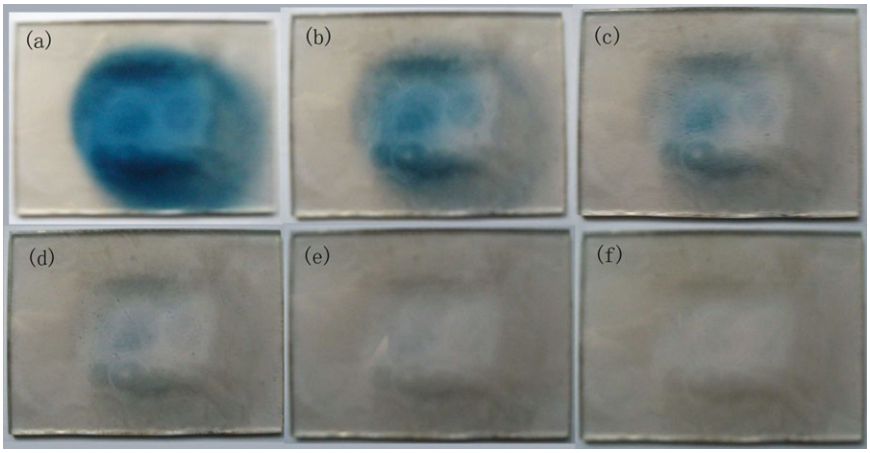

Figure 6. Bleaching of the colored Pd/WO_3 film when exposed to air. (a) 20 s, (b) 50 s, (c) 80 s, (d) 120 s, (e)180 s, and (f) 280 s.

variable transmittance. In this report, based on the gasochromic properties of Pd/WO_3 film, we designed, for the first time, a multichannel system containing hydrogen sensitive gasochromic films for rapid determination of the activity of the photocatalytic materials for H_2 production. The designed system well coupled the photocatalytic reaction with hydrogen sensitive Pd/WO_3 film and could qualitatively reflect the activity of the photocatalyst in various reation conditions. As demonstrated by GC and UV–vis measurement, the system enabled quick evaluation of photocatalyst acitivty even by visual observation As a result, the concept of our system provides an alternative approach for rapid screening of photocatalytic materials in various reaction conditions in a simple and time-efficient way. Moreover, the technique is also supposed to be extended to other hydrogen production reactors. Of course, further improvement of our system is necessary to make it more appropriate for practical applications.

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