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Development of solar-light-driven photocatalyst for energy and environmental application

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Abstract. Efficient utilization of solar energy could relieve many energy and environmental problems. Overall photocatalytic water-splitting using solar energy has received enormous attention for production of renewable hydrogen from water. Recently, a novel Ag₃PO₄ photocatalyst with band gap of 2.43 eV, possessing remarkable photocatalytic ability for organic dye degradation has been reported. In this work a highly efficient photocatalyst P/Ag/Ag₂O/Ag₃PO₄/TiO₂ has been synthesized and characterized by SEM, TEM, XRD, EDS, XPS, UV-vis and PL respectively. The results suggest that a highly efficient photocatalyst P/Ag/Ag₂O/Ag₃PO₄/TiO₂ has been synthesized successfully and performed strong absorption band in visible-light region, high separation efficiency of photo excited electron-hole pairs and small band gap (approximately 2.2 eV). On the other hand, Rodamine B (RhB) and methanol are representative organic compounds that can be used as sacrificial reagent for increasing water-splitting efficiency. For the purpose of identifying the possibility of generating oxygen and hydrogen by the as-prepared P/Ag/Ag₂O/Ag₃PO₄/TiO₂ under simulated solar irradiation, the accumulated amount of oxygen and hydrogen was evaluated. The results showed that the optimal conditions of water-splitting process by using the mixture of RhB and methanol under solar light is 20% of methanol, 1.0 ppm of RhB and 0.100 g/L of catalyst dosage. In summary, as-prepared $P/Ag/Ag_2O/Ag_3PO_4/TiO_2$ composite has the potential for environmental and energy application under solar light.

1. Introduction

Photocatalytic water splitting has received enormous attention for production of renewable hydrogen from water since the discovery of Honda-Fujishima effect in 1970s [1]. In the past decades, one of the most prominent photocatalysts that have been used is TiO_2 . Although TiO_2 has excellent characteristics as a photocatalyst, the wide band gap of pure TiO_2 (3.2 eV) limits its utilization in the visible light region [2]. As such, regarding the development of photocatalysts that work not only under UV light but also under visible-light illumination to more efficiently utilize solar energy, a highly efficient photocatalyst P/Ag/Ag₂O/Ag₃PO₄/TiO₂ has been synthesized successfully in our previous reports and it performed strong absorption band in visible-light region, high separation efficiency of photo excited electron-hole pairs and small band gap (approximately 2.2 eV) [3]. It has been demonstrated with remarkable photocatalytic efficiency in decomposing the organic matters and sterilization of bacteria [4]. However, regarding its photocatalytic water-splitting ability, there is no research being conducted. It's predicted that P/Ag/Ag₂O/Ag₃PO₄/TiO₂ should also have high ability for photocatalytic watersplitting process under solar light irradiation.

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Usually, the direct splitting of water into H_2 and O_2 has a very low efficiency due to its uphill reaction along with rapidly recombination of photo excited electrons and holes as well as rapid reverse reaction [5]. To provoke water-splitting process for hydrogen production by modified TiO₂ photocatalyst from distilled water, adding sacrificial reagent (electron donors), such as dyes or alcohols, to react with the photo-excited holes in the valence band can inhibit the photo-excited electron-hole pair recombination. Rodamine B (RhB), as a representative dye that can be an indicator of organic pollution, has been reported efficient for increasing gas generation as sacrificial agent in photocatalytic water-splitting process [6]. Considering the solar energy utilization and environment decontamination, production of hydrogen by photocatalytic water splitting from dye wastewater appears to be an exciting idea. On the other hand, using methanol as a sacrificial agent was reported efficient in provoking overall water-splitting process [7]. In addition, it is reported that initial concentration of sacrificial agent, mass of photocatalyst and pH of the reaction solution can significantly affect the efficiency of photocatalytic water-splitting process [2].

Hence, the main purpose of this study is to identify the possibility of generating gas by $P/Ag/Ag_2O/Ag_3PO_4/TiO_2$ under simulated solar light irradiation within the sacrificial reagent existed, such as RhB and Methanol, and then optimize the H₂ and O₂ generation by identifying the optimal reaction conditions.

2. Materials and methods

2.1. Preparation of P/Ag/Ag₂O/Ag₃PO₄/TiO₂ photocatalyst

At first, the transparent $P/Ag/Ag_2O/Ag_3PO_4/TiO_2$ sol was prepared according to our previous study [3]. Then, the solution was transferred into a Teflon-lined autoclave and heated in an oven at a certain temperature. After heat treatment, the resulting precipitates were separated from the rest of solution by 3 times centrifuge (9800 rpm) and dried at 60°C for 12 h. Finally, the $P/Ag/Ag_2O/Ag_3PO_4/TiO_2$ photocatalyst powder was successfully synthesized and stored in desiccator. All the agents used during this study were purchased from FUJIFILM Wako Pure Chemical Corporation, Japan.

2.2. Preparation of photocatalytic water-splitting reactant

Firstly, a certain amount of $P/Ag/Ag_2O/Ag_3PO_4/TiO_2$ powder and sacrificial reagent (RhB (40 mg/L) or methanol) were added into the water-splitting reactor and mixed with distilled water to achieve 150 mL reaction solution. After that, the reactor containing 150 mL reactant was agitated with a magnetic stirrer in dark for 30 min and then purged with N₂ gas for 3 times. After the purge step was completed and the photo reaction will be started under a simulated solar lamp (XC-100, SERIC., Ltd.) irradiation (550 W/m²) for 3.0 h. During the RhB-H₂O reaction system, the effects of initial RhB concentration (0.5, 1.0 and 2.0 ppm), catalyst dosage (0.050, 0.100, 0.200 g/L) and pH (3.0, 7.0 and 11.0) on the photoccatalytic activity were systematically investigated. As for methanol-H₂O reaction system, the effects of methanol percentage (10%, 20% and 30%) and catalyst dosage (0.025, 0.050 and 0.100 g/L) were evaluated.

2.3. Water-splitting activity investigation and evaluation

During the water-splitting test, gas and liquid samples were taken out every 30 min. The gas sample was directly examined by Gas Chromatography (GC-8A, SHIMAZU, Japan) to measure the amount of accumulated oxygen and hydrogen, while, for the liquid sample, firstly the photocatalyst powder was separated from the mixed reactant by centrifugation (8000 rpm), and then the optical absorption of the clarified solution was analyzed to calculate the pseudo-first-order kinetic apparent rate constant of RhB degradation by using a spectrophotometer (UV-1600, Shimadzu) at a wavelength of 554 nm which corresponds to the maximum absorption wavelength of RhB molecules.

3. Results and Discussion

3.1. Optimization of O_2 generation in RhB solution

In order to identify the possibility of generating O_2 by $P/Ag/Ag_2O/Ag_3PO_4/TiO_2$ photocatalyst, water splitting experiment was conducted under simulated solar light irradiation. As results shown in Figure 1 (a), O_2 evolution could be detected both in distilled water and RhB aqueous solution. And when adding sacrificial reagent RhB into distilled water, the ability of generating O_2 had been significantly enhanced which implied that RhB is an efficient sacrificial reagent.

To investigate the optimal experiment conditions for photocatalytic O_2 generation by $P/Ag/Ag_2O/Ag_3PO_4/TiO_2$ in RhB solution, the influence of initial RhB concentration, catalyst dosage and reaction pH were taken into consideration (Figure 1 (b-d)). From Figure 1 (b) we can conclude the initial RhB concentration had obviously effects on generating O_2 and the highest O_2 evolution was obtained when initial RhB concentration was 1.0 ppm. Ultimately, the accumulated O_2 achieved 164.00 µmol after 3.0 h reaction which was higher than that of 0.5 ppm and 2.0 ppm RhB concentration. Figure 1 (c) shows the dependence of photocatalytic O_2 generation on the dosage of photocatalyst. It can be found that at first with increasing the catalyst dosage, the amount of evolved O_2 also increased. Then the accumulated O_2 reached maximum at 0.100 g/L of dosage, while it largely decreased with further increasing the dosage to 0.200 g/L, indicating 0.100 g/L was the optimal dosage for the RhB-H₂O reaction system. Besides, the photocatalytic O_2 production was also affected by reactant pH (Figure 1 (d)). When the experiment was conducted at pH 7.0, the highest amount of accumulated O_2 (259.66 µmol) was achieved in comparison with pH at 3.0 or 11.0, suggesting the generation of O_2 by the P/Ag/Ag₂O/Ag₃PO₄/TiO₂ photocatalyst was more favourable under natural condition.



Figure 1. Accumulated O_2 by $P/Ag/Ag_2O/Ag_3PO_4/TiO_2$ (a) in pure water and Rh B solution under different (b) Rh B concentration, (c) catalyst dosage and (d) pH after 3.0 h solar light irradiation.

In addition, through all the experiments, the RhB degradation was also achieved along with the water-splitting and the pseudo-first-order kinetic parameters was calculated according to the RhB degradation efficiency, which is summarized in Table 1. The variation of RhB degradation rate under different conditions showed a similar tendency with O_2 evolution and the faster decomposition of RhB is, the more O_2 produced. The *k* value reached maximum (0.1410) under the same optimal conditions with the accumulated O_2 results. Thus, the optimal conditions for both O_2 production and RhB

degradation by $P/Ag/Ag_2O/Ag_3PO_4/TiO_2$ photocatalyst during RhB-H₂O reaction system was the initial RhB concentration at 1.0 ppm, catalyst dosage at 0.100 g/L and pH at 7.0.

Factors	Values	Other conditions	$k (\min^{-1})$
Initial RhB	0.5	Catalyst dosage: 0.200 g/L	0.0788
concentration (ppm)	1.0	Initial pH: 7.0	0.0808
	2.0	-	0.0424
Catalyst dosage (g/L)	0.050	Initial RhB concentration: 1.0 ppm	0.0839
	0.100	Initial pH: 7.0	0.1410
	0.200	-	0.0808
Initial pH	3.0	Initial RhB concentration: 1.0 ppm	0.0504
	7.0	Catalyst dosage: 0.100 g/L	0.1410
	11.0	-	0.0739

Table 1. First order kinetic results of RhB degradation under different experiment conditions.

3.2. Optimization of O_2 and H_2 generation in methanol solution

In previous study, the optimal conditions of generation O_2 has been confirmed. However, the overall water-splitting process was not achieved. For the purpose of identifying the possibility of overall water-splitting process and increasing the production of O_2 and H_2 generation by $P/Ag/Ag_2O/Ag_3PO_4/TiO_2$ under simulated solar irradiation, the accumulated amount of O_2 and H_2 evolution was investigated in methanol solution. From Figure 2, it was confirmed that the overall water-splitting was realized in a methanol- H_2O system by using the as-prepared composite. Both O_2 and H_2 were successfully detected and the amount of accumulated O_2 and H_2 gradually increased with time profile under solar light irradiation.



Figure 2. O_2 (a) and H_2 (b) evolution by $P/Ag/Ag_2O/Ag_3PO_4/TiO_2$ under solar light irradiation in methanol solution (Dosage: 0.050 g/L, pH=7.0, 20% Methanol).

To further enhance the overall water-splitting efficiency, the percentage of methanol in reaction solution was optimized (Figure 3 (a)). Compared to 10% and 30% of methanol, using methanol percentage of 20%, ultimately the highest amount of accumulated O_2 and H_2 achieved after 3.0 h reaction which were 424.55 µmol and 18.77 µmol, respectively. This result was also better than the optimal O_2 generation using RhB as sacrificial reagent that achieved 259.66 µmol of O_2 . Figure 3 (b) exhibited the influence of P/Ag/Ag₂O/Ag₃PO₄/TiO₂ dosage on O_2 and H_2 evolution in methanol solution. It indicated that the dosage of catalyst had obviously effects of generating O_2 and H_2 . The best performance occurred when catalyst loading was 0.050 g/L. This result is not same with the optimal production of O_2 generation in RhB-H₂O system which the optimal dosage of catalyst was 0.100 g/L. Thus, both of the optimal dosage of P/Ag/Ag₂O/Ag₃PO₄/TiO₂ (0.050 g/L and 0.100 g/L)

should be investigated when use the mixture of RhB and methanol as sacrificial reagents. As shown in Figure 3 (c), when the RhB and methanol were involved in the reaction system simultaneously, more O_2 and H_2 was observed at the 0.100 g/L of catalyst dosage. Under this condition, the amount of accumulated O_2 and H_2 reached to 524.99 and 26.49 µmol after 3.0 h, respectively, which achieved the highest production through this study. Therefore, the optimal conditions of overall water-splitting process by using P/Ag/Ag₂O/Ag₃PO₄/TiO₂ under solar light irradiation was 0.100 g/L of catalyst dosage with the mixture of 1.0 ppm of RhB and 20% of methanol.



Figure 3. Influence of (a) methanol percentages, (b) catalyst dosage and (c) sacrificial reagent with the best dosage of $P/Ag/Ag_2O/Ag_3PO_4/TiO_2$ on O_2 and H_2 generation after 3.0 h (a: 20% methanol + 0.050 g/L, b: 20% methanol + 1.0 ppm Rh B + 0.050 g/L, c: 20% methanol + 1.0 ppm Rh B + 0.100 g/L and d: 1.0 ppm Rh B + 0.100 g/L)

3.3. Overall water-splitting process in long-time reaction under optimal conditions

The long-time photocatalytic water-splitting experiment was finally carried out to verify the stability and durability of the as-prepared composite under the optimal conditions. As displayed in Figure 4, there is no obvious loss of photocatalytic activity even after 36 h, implying the outstanding stability of the composite in the long-time photocatalytic reaction. Only a slight decrease of generation rate was observed after 12 h which was mainly caused by the consumption up of the RhB sacrificial reagent. To further compare with other photocatalysts as shown in Table 2, the O₂ and H₂ yield rates of the asprepared photocatalyst was much higher than reported values. Therefore, the above results substantiate that the P/Ag/Ag₂O/Ag₃PO₄/TiO₂ composite is an effective photocatalytic water-splitting material with reasonable stability.



Figure 4. (a) H₂ and (b) O₂ evolution with RhB degradation by P/Ag/Ag₂O/Ag₃PO₄/TiO₂ under solar light irradiation in mixed solution after 36 h (Dosage: 0.100 g/L, 20% Methanol and 1.0 ppm RhB). **Table 2.** Photocatalysts comparison for H₂ and O₂ evolution from aqueous solutions.

Photocatalyst	Light source	Activity (µmol/h/g)		Reference
		H_2	O_2	
TiO ₂ NiOx	Hg-P	6	2	[8]
CaTiO ₃ NiO _x	Hg-Q	30	17	[9]
SrTiO ₃ Rh	Xe-P	27	14	[10]
P/Ag/Ag ₂ O/Ag ₃ PO ₄ /TiO ₂	Simulated solar light	589	11667	This research

4. Conclusion

In summary, the $P/Ag/Ag_2O/Ag_3PO_4/TiO_2$ photocatalyst exhibited remarkable photocatalytic watersplitting activity under solar light irradiation. The generation of O₂ from RhB solution showed better performance than that from pure water and further the overall water-splitting process was achieved by using methanol as sacrificial reagent. The optimal conditions of overall water-splitting process by using the mixture of RhB and methanol under solar light irradiation is 20% of methanol, 1.0 ppm of RhB and 0.100 g/L of catalyst dosage. By taking the advantages of dye waste decontamination and H₂ generation, the as-prepared solar-light-driven $P/Ag/Ag_2O/Ag_3PO_4/TiO_2$ composite has great potential for environmental and energy application.

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