

Research Letter

Pt/TiO₂ Coupled with Water-Splitting Catalyst for Organic Pollutant Photodegradation: Insight into the Primary Reaction Mechanism

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A composited system was fabricated by coupling Pt/TiO₂ with water-splitting catalyst for photooxidation of organic pollutants in aqueous solutions. The new composited system exhibits more efficient photocatalytic activity than pure Pt/TiO₂ does under UV light irradiation. The promoting effect is dependent on the photo-produced H₂ over the composited system. The active oxygen species, hydroxyl radical ($\cdot\text{OH}$) and hydrogen peroxide (H₂O₂), are measured by fluorescence spectroscopy and photometric method, respectively. The results reveal that the produced H₂ by photocatalytic water splitting over NiO/NaTaO₃:La transfers to Pt particle of TiO₂ surface, then reacts with introducing O₂ to generate in situ intermediate H₂O₂, and finally translates into $\cdot\text{OH}$ radical to accelerate the photooxidation of organic pollutants.

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1. INTRODUCTION

Photoinduced charge transfer occurring on semiconductor materials can achieve direct conversion of photo energy to chemical energy, and thus it can be used for elimination of organic pollutants and splitting water into hydrogen. However, the utility of semiconductor-based photocatalytic process is controlled to a large extent by the separation efficiency of the initially formed excited states ($h_{\nu_b}^+$ and $e_{\nu_b}^-$) [1]. A variety of approaches was made to enhance electron-accepting or electron-donating ability of the material surface to favor the interfacial charge separation and consequently increase the photocatalytic efficiency. One approach involves addition of surface adsorbed redox species capable of scavenging selectively either of the excited states to the photoreaction system [2, 3]. Another promising approach concerns modification of TiO₂ with noble metals, other semiconductors, and coloring matters to improve the separation of the excited states [4–6].

Deposition of platinum on TiO₂ has been reported to enhance extremely the photocatalytic efficiency for organic

pollutant elimination due to its high electron-trapping effect [7], although an excessive number of platinum particles per grain of TiO₂ can be detrimental to the performance of the reaction system [8]. We have recently demonstrated that trace amount of H₂ can efficiently improve the activity of benzene photooxidation over Pt/TiO₂ [9, 10]. However, the mechanisms have not been fully understood, and a practical approach for the environmental application has not yet to be achieved, due to the difficulties in realizing the integration of H₂ gas and photocatalysis into a practical system.

Herein, an alternative system was fabricated by coupling Pt/TiO₂ with water-splitting catalyst NiO/NaTaO₃:La to supply the in situ H₂ to enhance photocatalytic oxidation organic pollutants in an aqueous solution, where the obtained composited system is quite different from the classic coupled semiconductor system. The data show that the high photocatalytic efficiency of the composited system is attributed to the formation of more $\cdot\text{OH}$ which is dependent on the generation of in situ H₂O₂ from the combination between the photo-produced H₂ by the NiO/NaTaO₃:La and bubbled O₂ on Pt/TiO₂ surface.

TABLE 1: Rate constants for SA photodegradation with different composited catalysts. Catalyst: 0.0500 g, the rate of NiO/NaTaO₃:La to Pt/TiO₂ (or TiO₂) is 25 wt%. reactant solution: 120 mL SA (5×10^{-4} mol L⁻¹), with two 254 nm UV lamps irradiation.

Photocatalyst	k (min ⁻¹)
Pt/TiO ₂	0.00308
NiO/NaTaO ₃ :La-Pt/TiO ₂	0.00429
TiO ₂	0.00289
NiO/NaTaO ₃ :La-TiO ₂	0.00286
NiO/Ta ₂ O ₅ -Pt/TiO ₂	0.00267
NiO/Sr ₂ Ta ₂ O ₇ -Pt/TiO ₂	0.00415

2. EXPERIMENTAL

2.1. Sample preparation

Titanium dioxide (TiO₂) particles were prepared by a sol-gel technique. Titanium isopropoxide (0.1 mol) was first added dropwise to 100 mL of nitric acid aqueous solution. The suspension was stirred to clear and then dialyzed to pH of ca. 4 to obtain the TiO₂ sol. The sol was dried at 333 K in an oven for 3 days. The resulting solid powders were ground to fine powders and finally calcined at 623 K for 3 hours.

NaTaO₃:La was prepared by the solid state reaction according to the literature [11]. In typical, 0.02 mol Ta₂O₅, 0.0206 mol Na₂CO₃, and 0.0004 mol La₂O₃ were mixed and then calcined in air at 1173 K for 1 hour and 1423 K for 10 hour.

Platinum supported catalyst was prepared by the incipient wetness impregnation method. The calcined TiO₂ was impregnated with a 5.22×10^{-2} M aqueous solution of H₂PtCl₆. The impregnated sample was dried at 393 K for 6 hours and subsequently reduced with an NaBH₄ solution (0.1 M). After reduction, the solid sample was washed with deionized water to remove residual ion, and finally dried in air at 333 K (denoted as Pt/TiO₂). The initial ratio of Pt to TiO₂ was fixed at 1 wt%.

NiO loaded catalysts were prepared by an impregnation method from a 2.36×10^{-2} M aqueous solution of Ni(NO₃)₂ and then dried at 383 K for 2–5 hours. The sample thus obtained was subsequently calcined at 543 K for 1 hour in air using a muffle furnace. The initial ratio of NiO to NaTaO₃:La was fixed at 0.2 wt%.

2.2. Photocatalytic reactions and methods

The photocatalytic reaction was performed at room temperature in a quartz tubal reactor surrounded with 254 nm UV lamps (Philips TUV, 4 W, Holland). The photocatalyst-powders were dispersed in the salicylic acid (SA) solution bubbled with oxygen (10 mL min⁻¹). The concentration of SA was analyzed by a high-performance liquid chromatograph (HPLC Waters) equipped with a reverse phase column (Merk, LiChrospher RP-18e, 5 μ m) and a UV detector with detection wavelength of 297 nm. The mobile phase consisted of 30 mmol L⁻¹ acetate (pH = 4.9) and the flow rate was 1.0 mL min⁻¹. The evolved CO₂ during the reaction was

collected with a Ba(OH)₂ solution and then determined by a titrate with an oxalic acid (H₂C₂O₄) solution (0.02 mol L⁻¹). The evolved H₂ during the reaction was monitored by a hydrogen sensor (Dräger Pac III).

Hydroxyl radical ·OH was captured by terephthalic acid to form fluorescent 2-hydroxyterephthalic acid [12] and then determined with fluorescence spectroscopy (FS/FL920, excitation wavelength: 312 nm, and fluorescence peak: 426 nm). Hydrogen peroxide was analyzed photometrically by the POD (horseradish peroxidase) catalyzed oxidation product of DPD (*N,N*-diethyl-*p*-phenylenediamine) at 551 nm [13].

3. RESULTS AND DISCUSSION

Table 1 lists the rate constants of salicylic acid (SA) photodegradation with different catalysts under UV light irradiation in the presence of O₂. The results show that NiO/NaTaO₃:La has distinct effect on TiO₂ and Pt/TiO₂ for SA photodegradation. NiO/NaTaO₃:La enhances the rate of the SA photodegradation in Pt/TiO₂ reaction system, and yet has no effect on the SA photodegradation over TiO₂. Two controlled experiments are carried out, respectively, under UV irradiation without catalyst and with NiO/NaTaO₃:La. The results show that NiO/NaTaO₃:La is photocatalytically inactive for SA degradation despite it was reported to be highly active for photocatalytic splitting water into H₂ even without sacrificial agent. Therefore, it can be deduced that the NiO/NaTaO₃:La plays a promoting role for Pt/TiO₂ photocatalytic degradation of SA, and the existence of Pt is indispensable for the promoting effect of NiO/NaTaO₃:La.

The conduction band level of the NaTaO₃ and TiO₂ is -1.03 eV and -0.52 eV, respectively, while the valence band level of the NaTaO₃ and TiO₂ is 2.97 eV and 2.64 eV, respectively, [14, 15]. It is obvious that both the valence and conduction band of TiO₂ are sandwiched between the corresponding bands of NaTaO₃. Thus in the NiO/NaTaO₃:La-Pt/TiO₂ composited system, the promoting effect of NiO/NaTaO₃:La is unexpected from the viewpoint of coupled semiconductors [5]. It is verified by the fact that NiO/NaTaO₃:La has no effect on TiO₂ for SA photodegradation (Table 1). Furthermore, simple mechanical addition NiO/NaTaO₃:La to Pt/TiO₂ suspensions cannot make them intimate contact which was necessary to form coupled semiconductors for an acceleration in photocatalytic reaction rate [16]. Therefore, The results provide a clear conclusion that there are other reasons attributing to NiO/NaTaO₃:La promoting effect. NiO/NaTaO₃:La was well documented to be a highly efficient photocatalyst for water splitting into H₂ under UV light irradiation [11]. In our previous work, the trace amount of H₂ was found to significantly increase the activity of Pt/TiO₂ for photocatalytic oxidation of volatile organic compounds (VOC's). Therefore, the promoting effect may be attributed to the trace amount of H₂ produced from photocatalytic water splitting by NiO/NaTaO₃:La to enhance the activity of Pt/TiO₂ for SA photodegradation.

In order to check the effect of NiO/NaTaO₃:La, the following comparative experiments were carried out under the same conditions. It is experimentally verified that NiO/Ta₂O₅ is photocatalytically inert for both the SA degradation

and water splitting (data not shown here) [17], but has the same band energy level as the NaTaO_3 [18]. Adding $\text{NiO}/\text{Ta}_2\text{O}_5$ instead of $\text{NiO}/\text{NaTaO}_3:\text{La}$ into the Pt/TiO_2 suspension, the photodegradation rate of SA shows no change (Table 1). In contrast, replacing $\text{NiO}/\text{NaTaO}_3:\text{La}$ with another efficient water-decomposing photocatalyst NiO (0.15 wt.%) / $\text{Sr}_2\text{Ta}_2\text{O}_7$ [19], SA photodegradation can also be markedly accelerated (Table 1). The above results confirm that the promoting effect is dependent on the water-splitting function of $\text{NiO}/\text{NaTaO}_3:\text{La}$. Furthermore, we examine the photodegradation of other organic contaminations such as phenol with the $\text{NiO}/\text{NaTaO}_3:\text{La}-\text{Pt}/\text{TiO}_2$ suspensions under 125 W high-pressure mercury lamp irradiation for 55 minutes, showing that both the degradation and mineralization of phenol can be enhanced significantly from 63% to 97% and from 54% to 84%, respectively. These results demonstrate that coupling of Pt/TiO_2 with a splitting-water photocatalyst is more efficient for the photocatalytic elimination of organic pollutants in aqueous solution than pure Pt/TiO_2 does.

To understand the origin of the promoting effect of $\text{NiO}/\text{NaTaO}_3:\text{La}$, the variety of evolved H_2 in the reaction process was monitored. Figure 1 shows the change in H_2 yield and SA photodegradation in the composited system with reaction time under O_2 bubbling. As H_2 evolution reaches a steady state, injecting SA into the system results in a notable decrease of H_2 evolution along with quick degradation of SA. However, as the SA is completely decomposed, the production of H_2 progressively comes after its former steady state (Figure 1). This indicates that the produced H_2 is partly consumed to accelerate the SA photodegradation over Pt/TiO_2 . This is supported by the result that introducing H_2 from an outer bottle instead of $\text{NiO}/\text{NaTaO}_3:\text{La}$ into the Pt/TiO_2 reaction system, the rate of SA photodegradation was enhanced and comparable. In combination with the results of the SA degradation (Table 1), it is deduced that the promoting effect of $\text{NiO}/\text{NaTaO}_3:\text{La}$ to accelerate Pt/TiO_2 for SA photodegradation is correlated to the produced H_2 consumed by Pt particle on TiO_2 in the presence of O_2 .

Photocatalytic degradation of SA and phenol is initial from the attack of $\cdot\text{OH}$ radical [20]. Figure 2 shows the plots of increase in fluorescence intensity at 426 nm against illumination time for the reaction system. The linear increase in fluorescence intensity for $\text{NiO}/\text{NaTaO}_3:\text{La}-\text{Pt}/\text{TiO}_2$ system is higher than that for pure Pt/TiO_2 system, suggesting that a larger amount of $\cdot\text{OH}$ radical was produced in $\text{NiO}/\text{NaTaO}_3:\text{La}-\text{Pt}/\text{TiO}_2$ composited system. Thus we conclude that the consumed H_2 is converted to a larger amount of active oxidative species $\cdot\text{OH}$ to induce quicker degradation of SA and phenol.

In the presence of H_2 and O_2 , Au supported Ti-based catalysts were reported to selective vapor-phase epoxidation of propylene. The reaction is likely due to the in situ preparation of H_2O_2 from H_2 and O_2 at perimeter interface of the catalyst [21]. Thus it is possible that in the $\text{NiO}/\text{NaTaO}_3:\text{La}-\text{Pt}/\text{TiO}_2$ system, the produced H_2 by photocatalytic water splitting and bubbled O_2 are primarily combined to form H_2O_2 on Pt/TiO_2 . Figure 3 shows the absorbance (at 551 nm) of the produced H_2O_2 against illumination time for the

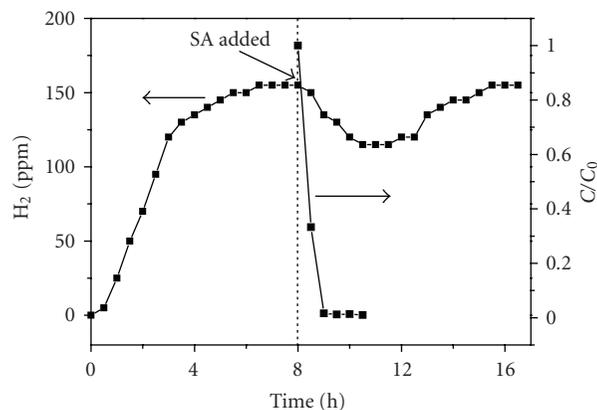


FIGURE 1: Hydrogen evolution and SA degradation over $\text{NiO}/\text{NaTaO}_3:\text{La}-\text{Pt}/\text{TiO}_2$ with oxygen bubbling under UV light illumination.

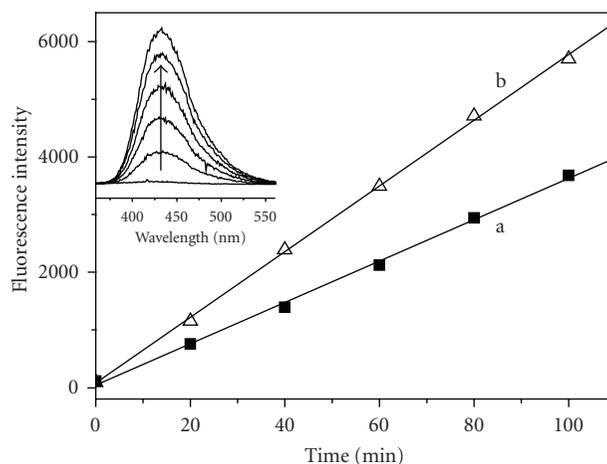


FIGURE 2: Fluorescence spectra (insert) and induced fluorescence intensity (426 nm) against illumination time for terephthalic acid solution on (a) Pt/TiO_2 and (b) $\text{NiO}/\text{NaTaO}_3:\text{La}-\text{Pt}/\text{TiO}_2$ samples under UV irradiation.

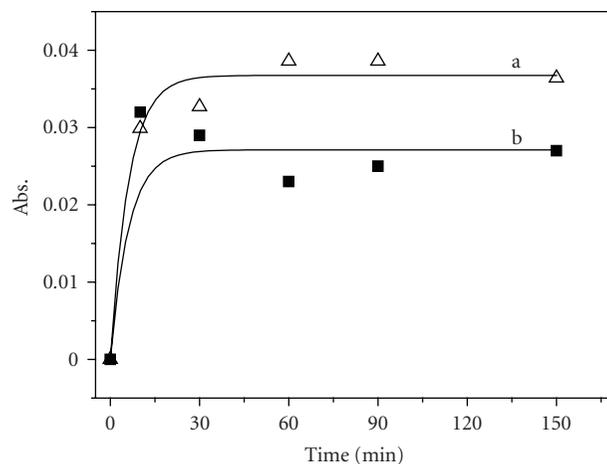


FIGURE 3: Absorption intensity (551 nm) of DPD/POD reagent after reaction with H_2O_2 against illumination time in the aqueous solution of (a) $\text{NiO}/\text{NaTaO}_3:\text{La}-\text{Pt}/\text{TiO}_2$ and (b) Pt/TiO_2 .

reaction system. It is obvious that a larger amount of H_2O_2 was produced on $\text{NiO}/\text{NaTaO}_3:\text{La}-\text{Pt}/\text{TiO}_2$ reaction system than that on Pt/TiO_2 reaction system. The produced H_2 and bubbled O_2 can be responsive to the generation of more amount of H_2O_2 for the composited system. It is confirmed by the result that as the Pt/TiO_2 solutions were bubbled both with H_2 and O_2 in the dark, some amount of H_2O_2 was detected. The effect of H_2O_2 on the photocatalytic activity was investigated earlier. Shiraishi and Kawanishi [22] have declared that the photocatalytic activity is closely related to the formation of H_2O_2 . Additional dosage of H_2O_2 into the TiO_2 suspension was often used and found to efficiently enhance the degradation of organic compounds due to the generation of $\cdot\text{OH}$ radical by the direct photolysis or the photoinduced electron reduction of H_2O_2 [23]. Thereby, in the composited reaction system, the produced H_2 and introducing O_2 directly combine to form in situ H_2O_2 on Pt particle of TiO_2 firstly, and then the H_2O_2 traps the photoinduced electron on Pt particle surface or is photocleaved to form $\cdot\text{OH}$ radical. Moreover, the larger amount of H_2O_2 is produced by the composited reaction system not only simply, but also practicably, and it may be useful for photocatalytic selective oxidation reaction by in situ H_2O_2 via the $\text{NiO}/\text{NaTaO}_3:\text{La}$ and Pt/TiO_2 co-deposition on suitable support.

4. CONCLUSIONS

This work opens up a new efficient composited system for improving the efficiency of the photocatalytic process. Coupled with the water-splitting catalyst, $\text{NiO}/\text{NaTaO}_3:\text{La}$ can efficiently promote the photocatalytic performance of Pt/TiO_2 for organic pollutant elimination in aqueous solutions. It is shown that the in situ H_2O_2 is not only simply, but also practicably formed in the composited system by directly combining H_2 produced by photocatalytic water splitting with introducing O_2 on Pt particle of TiO_2 , and then the in situ H_2O_2 is photocleaved or reduced by photogenerated electron to produce $\cdot\text{OH}$ radical to accelerate photooxidation reaction. This work is clearly very useful to explore a new efficient and practical route for photocatalytic elimination of organic contaminations.

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