



## Photocatalytic and photoelectrocatalytic performance of 1% Pt doped TiO<sub>2</sub> for the detoxification of water

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### Abstract

The degradation of formic acid (HCOOH), FA (a surrogate contaminant) using titanium dioxide (TiO<sub>2</sub>) and 1% Pt doped TiO<sub>2</sub> electrodes, prepared by sol-gel methods, was investigated in a photoelectrocatalytic (PEC) system in order to determine the effect of Pt doping on the oxidation potential of TiO<sub>2</sub>. Pt doping shifts the position of band edge and therefore the direct and indirect oxidation potentials of TiO<sub>2</sub> in PEC systems. As a result, the degradation of formic acid via the generation of hydrogen peroxide production on 1%Pt-TiO<sub>2</sub> electrodes was much better than that on non-doped electrodes. The degradation of HCOOH was also examined with respect to the faradaic efficiency of this process. It was found that the 1%Pt-TiO<sub>2</sub> photoanode had a 30% higher efficiency than that of non-doped TiO<sub>2</sub> photoanodes.

### 1. Introduction

In general, solids having band gap energies less than 3.5 eV are known to be semiconductors. Since the energy crises of the early 1970s, there have been many studies using some of these materials for solar energy conversion. Many different semiconductors have been tried for conversion of solar light into electric energy by producing H<sub>2</sub> via the splitting of water [1–3]. Amongst the many kinds of semiconductor tried, TiO<sub>2</sub> with a band gap energy of 3.0 eV was thought to be the most promising due to its low cost, chemical and physical stability and the close relationship between its band edges and the oxidation/reduction for hydrogen and oxygen production from water. Unfortunately, the quantum efficiency of this process proved to be quite low and research efforts shifted to using particles and immobilized semiconductor to mineralize toxic organic compound [4–9].

Photocatalysis in PEC systems and doping of TiO<sub>2</sub> with metals are the most used methods to increase the quantum efficiency of the TiO<sub>2</sub>. PEC system consists of biasing a TiO<sub>2</sub> coated photoanode against a working cathode. Photogenerated electrons are withdrawn to the cathode while holes remain at the anode surface.

Anderson and coworkers have demonstrated that by applying such a biasing potential one decreases the recombination of electrons ( $e_{CB}^-$ ) and holes ( $h_{VB}^+$ ), thereby improving the photocatalytic activity of TiO<sub>2</sub> [10]. Later, the PEC treatment methods were applied for degrading organic pollutants such as chlorophenol [11], phenol [12], 4-chlorocatechol [13], oxalic acid [14], lignin [15], humic acid [16] and azo dyes [17]. More recently, some authors have applied TiO<sub>2</sub> coated photoelectrodes in the PEC system for the disinfection of water [18–20]. All these studies reported that the treatment efficiencies in PEC systems are found to be more favourable than photocatalysis alone. On the other hand, loading a semiconductor with metals creates new energy levels. As result of improved charge separation, a concomitant increase in the overall photocatalytic activity of TiO<sub>2</sub> is observed [21]. Of all of the metals tried, Pt has been known to be the most effective with respect to transferring photogenerated electrons to reducible species at the surface of the catalyst [22].

In this study, we have investigated the effect of doping the TiO<sub>2</sub> thin-film photoanode with 1%Pt for the oxidation of formic acid in water. PEC experiments were performed as a function of applied potential.

Photocurrents as well as the direct and indirect oxidation of formic acid were compared in both doped and undoped TiO<sub>2</sub> systems.

## 2. Materials and methods

### 2.1. Chemicals

Nitric acid (ACS reagent grade), titanium(IV) Isopropoxide (Aldrich) and hydrogen hexachloroplatinate(IV) (Aldrich) were used to prepare doped and undoped suspensions of titanium. NaClO<sub>4</sub> (Aldrich) was employed as an electrolyte due to the high stability of ClO<sub>4</sub><sup>-</sup> under electrochemical reactions. Formic acid (HCOOH, Fisher Scientific, 88% certified ASC) (hereafter referred to as FA) was used as the target organic contaminant. All solutions were made with ultrapure deionized water.

### 2.2. Organic carbon analysis

The test solution of  $1.0 \times 10^{-2}$  M NaClO<sub>4</sub> and 2.1 mM (TOC = 28 mg l<sup>-1</sup>) FA was employed in all experiments. A total organic carbon (TOC) analyser (Shimadzu Instruments, Model TOC 5000) was used to monitor formic acid degradation.

### 2.3. Thin-film photoelectrodes

Titanium(IV) isopropoxide (Aldrich) was used as a precursor for preparing TiO<sub>2</sub> colloidal suspensions. After adding 20 ml of titanium isopropoxide to a nitric acid solution, the required volume of hydrogen hexachloroplatinate(IV) was added keeping the ratio Ti/Pt/H<sup>+</sup>/H<sub>2</sub>O at 1/0.01/0.5/200. The resulting precipitate was continuously stirred until completely peptized to form a stable colloidal suspension. This suspension was dialysed against milli-Q water to pH 3.2 by using a Micro-pore 3500 MW cut-off membrane [23]. Photoelectrodes (20 cm × 14 cm, 0.5 mm thick, TiO<sub>2</sub> foil, Goodfellow Cambridge) were prepared using a sequential procedure of dipping, drying and firing at 300 °C for 3 h. Further details are available in the literature [24]. One of the TiO<sub>2</sub> electrodes was used as a counter electrode in all experiments. Another TiO<sub>2</sub> electrode was used as a working electrode to determine the effect of Pt doping on the PEC efficiency of TiO<sub>2</sub>.

### 2.4. Reactor design and experimental procedures

All PEC experiments were performed using a 100 ml test solution (Figure 1) with a three-electrode configuration: counter TiO<sub>2</sub> and working TiO<sub>2</sub> or 1%Pt–TiO<sub>2</sub> photoanode electrodes were used and a saturated calomel electrode (SCE) was employed as the reference. A Princeton Applied Research (PAR) potentiostat, model 6310 was employed to measure photocurrent and biasing potentials applied to the working electrode. The photoactive area of the anode was 20 cm<sup>2</sup> and this

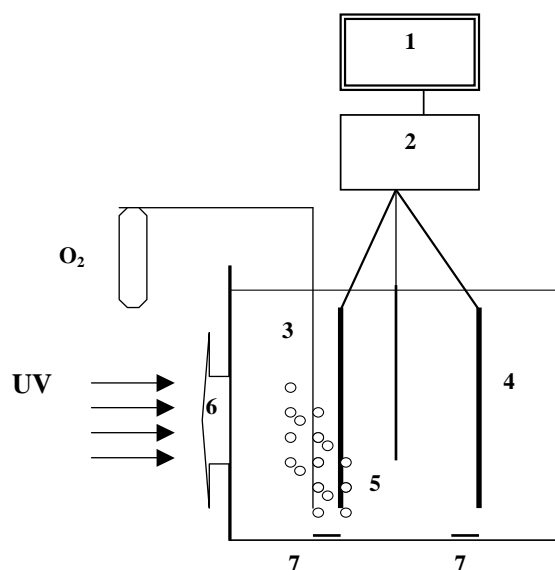


Fig. 1. Diagram for the reactor system used in the PEC reactions: (1) computer; (2) potentiostat; (3) working photoelectrode (TiO<sub>2</sub> or 1%Pt doped electrode); (4) counter electrode (TiO<sub>2</sub> coated TiO<sub>2</sub> foil); (5) reference electrode (SCE); (6) kuars glass; (7) stirring bar.

electrode was illuminated by a 450 W Xe–Hg arc lamp Oriol, model 6262 u.v. light source. The light intensity impinging on the electrode surface, 7 mW cm<sup>-2</sup>, was measured with a photometer (International Light Inc., model IL 1400A). Pure oxygen was bubbled into the solution during all experiments. The pH of the solution was measured with a double-junction combination electrode (Orion model 81-72BN) connected to a pH meter (Fisher Scientific Accumet 50). All experiments were performed at room temperature (around 20 ± 3 °C). Dissolved oxygen (DO) was measured by DO meter (Great Lakes Instruments, model 867). The dissolved oxygen concentration was around 31 ppm when oxygen was supplied.

## 3. Results

### 3.1. Blank experiments

Some experiments were performed to determine FA losses from the test solution ( $1.0 \times 10^{-2}$  M NaClO<sub>4</sub> and 2.1 mM FA at pH 3.2) by simple photolysis or electrolysis. Test solutions were illuminated under u.v. light to determine photolysis of FA. No photolysis of FA was discernable with our limits of detection in the experiments during a typical 3 h experiment. The electrochemical experiment was performed using the test solution with the 1%Pt–TiO<sub>2</sub> anode and a TiO<sub>2</sub> cathode under 1 V external potential but without u.v. illumination. No electrochemical FA degradation was measurable during a similar 3 h reaction period.

### 3.2. Photocurrents

Comparative experiments were performed to compare TiO<sub>2</sub> and 1%Pt–TiO<sub>2</sub> thin film electrodes with respect to

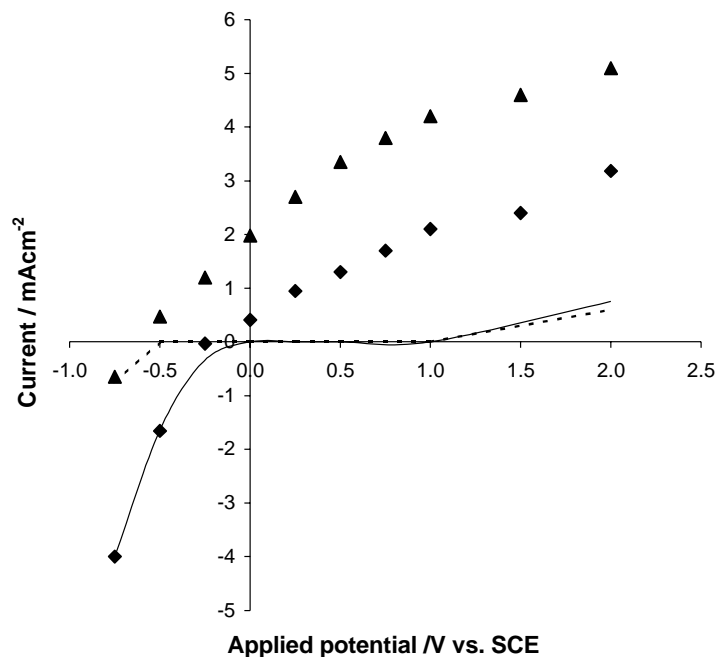


Fig. 2. Change of current during 1%Pt-TiO<sub>2</sub> PEC formic acid degradation at different applied external potentials: 2.1 mM formic acid,  $1.0 \times 10^{-2}$  M NaClO<sub>4</sub>, pH 3.2.

the photocurrent. Figure 2 shows the dark current as well as the photocurrent under u.v. illumination using the test solution of 2.1 mM FA and  $1.0 \times 10^{-2}$  M NaClO<sub>4</sub> at pH 3.2. The electrochemical behaviour of the 1%Pt-TiO<sub>2</sub> and the TiO<sub>2</sub> electrodes were almost the same under positive potentials. We could not detect any current between 0.0 and 1.0 V potential. A slight current was detected and increased at potentials positive of 1.0 V but this increase was very low, about  $0.6 \text{ mA cm}^{-2}$  at 2 V. On the other hand, the electrochemical performance of the 1%Pt-TiO<sub>2</sub> and TiO<sub>2</sub> electrodes are significantly different under a negative applied potential. Negative current was noticeable at potentials  $< -0.5$  V when using the TiO<sub>2</sub> electrode while it was observed at potentials lower than 0 V when using the 1%Pt-TiO<sub>2</sub> electrode.

Photoanodic current measurement under u.v. light illumination were performed at different positive potentials (between 0.0 and 2.0 V) in the test solution containing 2.1 mM FA and  $1.0 \times 10^{-2}$  M NaClO<sub>4</sub> at pH 3.2. When the 1%Pt-TiO<sub>2</sub> photoelectrode was illuminated with u.v. light at positive potentials, a photocurrent appeared and increased with applied potential. As seen in Figure 2, the photocurrent in the 1%Pt-TiO<sub>2</sub> photoanodic experiments was lower than that in TiO<sub>2</sub> experiments ( $0.6$  and  $3.2 \text{ mA cm}^{-2}$  photocurrents occurred by biasing with 0.0 and 2.0 V potential in the 1%Pt-TiO<sub>2</sub> PEC experiments while higher photocurrents, 1.98 and  $5.1 \text{ mA cm}^{-2}$  were observed at the same potentials, respectively, in the TiO<sub>2</sub> PEC experiments).

Under negative potentials (0.0–0.75 V), negative currents (between 0.0 and  $-4.0 \text{ mA cm}^{-2}$ ) in 1%Pt-TiO<sub>2</sub> experiments were much higher than that in TiO<sub>2</sub>

experiments (between 0.0 and  $-0.75 \text{ mA cm}^{-2}$ ). Also, negative currents in the TiO<sub>2</sub> and 1%Pt-TiO<sub>2</sub> experiments were observed at different potentials, at  $-0.25$  V in Pt-TiO<sub>2</sub> PEC experiments and at  $-0.5$  V in TiO<sub>2</sub> experiments (Figure 2). The negative current was not a function of illumination. In fact, the current remained almost constant in both the 1%Pt-TiO<sub>2</sub> and TiO<sub>2</sub> experiments upon illumination with u.v. light.

### 3.3. Photocurrent stability

Figure 3 shows the stability of the current during the 1%Pt-TiO<sub>2</sub> experiments conducted at three different potentials (0.5, 1 and 2 V). In these experiments,

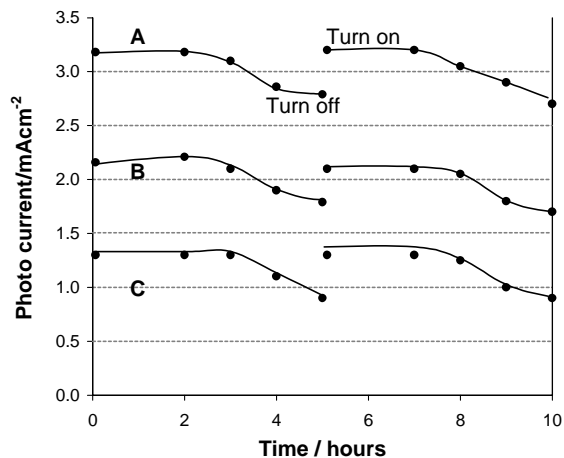
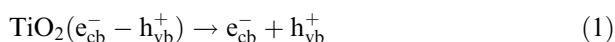


Fig. 3. Stability of the photocurrent in 1%Pt-TiO<sub>2</sub> PEC experiments: 2.1 mM formic acid,  $1.0 \times 10^{-2}$  M NaClO<sub>4</sub>, pH 3.2. Key: (A) 0.5 V; (B) 1 V and (C) 2 V.

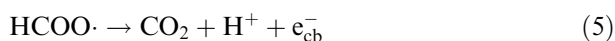
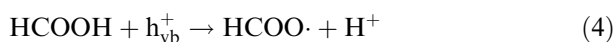
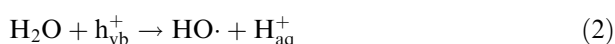
photocurrent was observed during an initial 5 h reaction period. Initial photocurrent decreased over time but when the new solution was used, the photocurrent regained its initial state. After five hours, the system was turned off and a new test solution applied. The PEC reactions were then repeated for another 5 h period of time. In the PEC system, photocurrent is a function of the concentration of both oxidizable species and u.v. intensity [20] and photocurrent can decrease in the PEC system according to the varying concentration of oxidizable organics [25–27]. Thus, the photocurrent decrease during the 5 h time period can likely be attributed to the decrease in FA concentration. Consequently, it was concluded that the photocurrent efficiency of %Pt–TiO<sub>2</sub> electrode was almost same during 10 h reaction period of time.

### 3.4. Formic acid oxidation

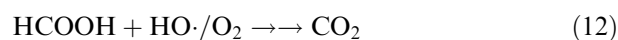
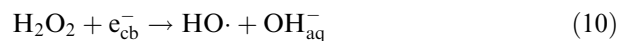
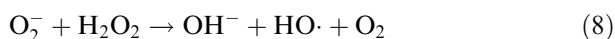
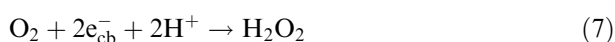
In the PEC processes, when the TiO<sub>2</sub> photoelectrode is illuminated by ultraviolet light (energy greater than TiO<sub>2</sub> band gap), electrons (e<sub>cb</sub><sup>-</sup>) are excited to the conduction band leaving holes (h<sub>vb</sub><sup>+</sup>) remaining in the valance band as defined with Equation 1:



By applying a positive potential to the photoelectrodes under illumination in PEC systems, photogenerated holes are produced that react with water leading to oxygen evolution and hydroxyl radical (HO·) formation. This, in turn, results in the oxidation of organics, such as formic acid, to CO<sub>2</sub> in the following hole reactions [24, 25]:



On the other hand, it is well known that hydrogen peroxide formation can occur via electron reactions and under u.v. illumination and therefore it may also play an important role in the indirect oxidation of organics in aqueous solution. This is illustrated with the following types of reactions given in Equations 6–12 [25, 28].



In order to determine the effect of 1% Pt loading on the oxidation performance of TiO<sub>2</sub> with respect to generating reactive hole reactions in these PEC systems, experiments were performed under different positive potentials for the oxidation of formic acid at pH 3.2. As can be seen in Figure 4, reactions involving holes in the 1%Pt–TiO<sub>2</sub> PEC experiments begin at 0 V while that in the TiO<sub>2</sub> PEC experiment started at –0.5 V. The optimum potential for the FA degradation was 1 V in 1%Pt–TiO<sub>2</sub> experiments and 0.5 V for the plain TiO<sub>2</sub> photoanode. The oxidation performances of the 1%Pt–TiO<sub>2</sub> and undoped TiO<sub>2</sub> were almost the same at 1.0 V and further increases in potential did not cause a subsequent increase in the degradation rate on either of these electrodes.

As can be seen in Figure 5, the electron reactions start at 0.0 V potential on the 1%Pt–TiO<sub>2</sub> photoelectrode. However, when the TiO<sub>2</sub> electrode is employed, these reactions start at –0.5 V. The formation of hydrogen peroxide in electron reactions under negative potentials does not result from the illumination with u.v. light, but can be obtained by the reduction of the oxygen in the dark under a suitable biasing potential between –0.9 and –0.3 V [11, 29–31]. On the other hand, a few studies have speculated that Pt loading increase the adsorption of O<sub>2</sub> on TiO<sub>2</sub> thereby resulting in the formation of peroxo species such as H<sub>2</sub>O<sub>2</sub> on the TiO<sub>2</sub> surface [8, 32, 33]. From a different perspective, this study agrees with the literature in that Pt doping shifts the band edge position of TiO<sub>2</sub> to more positive potentials. Thus, hole or electron reaction potentials of TiO<sub>2</sub> in PEC systems change and this improves the indirect oxidation of FA under negative potentials.

### 3.5. Faradaic efficiency

Both current and photocurrent curves were different in TiO<sub>2</sub> and 1%Pt–TiO<sub>2</sub> PEC experiments under the same conditions. In photoelectrochemistry, faradaic efficiency (FE) is used to explain the electron efficiency for degrading formic acid. In this study, the percentage FE ( $\eta$ ) is calculated as follows:

$$\eta = \frac{2 \times \text{moles of FA degraded}}{\text{the moles of electrons passing through electrode} \times 100}$$

As seen in Figure 5, FE at –0.5 external potential was 80% using the 1%Pt–TiO<sub>2</sub> electrode and only 48% with that of the TiO<sub>2</sub>. The improvement in FE in the 1%Pt–TiO<sub>2</sub> experiment was almost the same (30%) under both

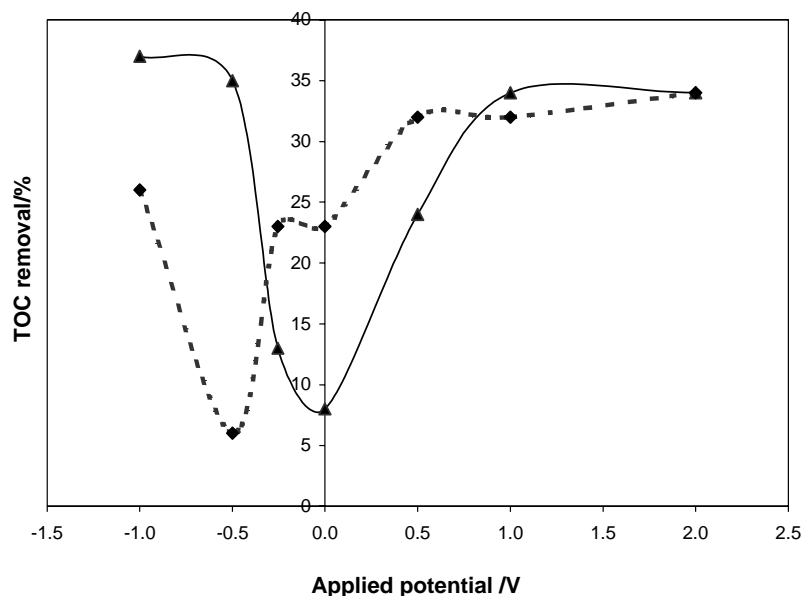


Fig. 4. Effect of 1%Pt doping on the oxidation of formic acid in hole and electron reactions. 2.1 mM formic acid,  $1.0 \times 10^{-2}$  M NaClO<sub>4</sub>,  $t = 90$  min and pH 3.2. Key: (▲), 1%Pt-TiO<sub>2</sub> and (◆), TiO<sub>2</sub>.

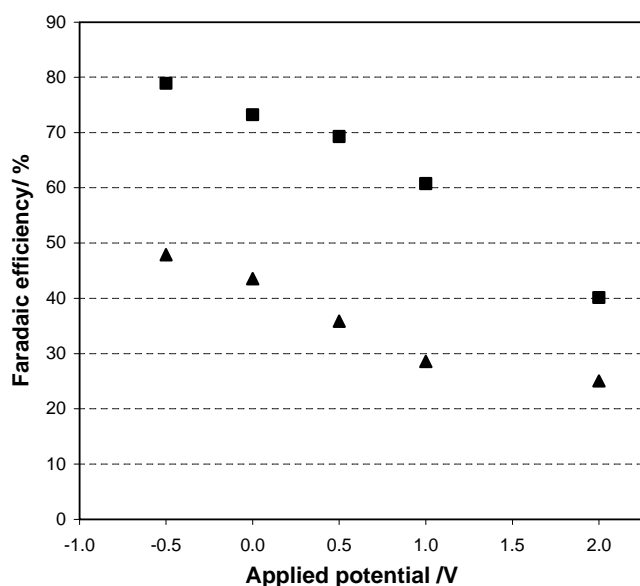


Fig. 5. Comparison of the FE of TiO<sub>2</sub> and 1%Pt-TiO<sub>2</sub> electrodes as a function of applied potential; 2.1 mM formic acid,  $1.0 \times 10^{-2}$  M NaClO<sub>4</sub>,  $t = 90$  min, pH 3.2. Key: (▲), 1%Pt-TiO<sub>2</sub> and (◆), TiO<sub>2</sub>.

negative and positive potentials. This reflects the fact that Pt improves the conductive properties of the pure TiO<sub>2</sub> and electrons move faster, which may increase both direct and indirect oxidation of organics in aqueous solution.

#### 4. Conclusions

The following conclusions can be drawn:

- (i) TiO<sub>2</sub> and 1%Pt-TiO<sub>2</sub> thin film electrodes have been compared in the PEC process with respect to photocurrents. It is observed that a 1%Pt doping

decreased the photocurrent efficiency of TiO<sub>2</sub> under positive potentials.

- (ii) 1%Pt-TiO<sub>2</sub> electrodes were used in the PEC systems under different external potentials during a 10 h period of reaction and with changes in the test solution of 2.1 mM formic acid in  $1.0 \times 10^{-2}$  M NaClO<sub>4</sub> at pH = 3.2 after 5 h. When compared 5 h time periods, it is observed that photocurrent trends were stable over 10 h.
- (iii) The photocurrent in the 1%Pt-TiO<sub>2</sub> PEC experiment was lower than that in the TiO<sub>2</sub> PEC experiments. Almost the same rate of FA degradation occurred in both the 1%Pt doped and undoped TiO<sub>2</sub> experiments at 1.0 V under u.v. illumination.
- (iv) 1%Pt doping shifts the band edge position of TiO<sub>2</sub> to more positive potentials. As a result, the oxidation and reduction potentials of TiO<sub>2</sub> in the PEC system changed. Thus, favourable indirect oxidation of formic acid under negative potentials were observed in 1%Pt-TiO<sub>2</sub> experiments.
- (v) A 1% Pt doping increases the FE by about 30%. This suggests that Pt doping also improves the use of photogenerated holes or electrons for the oxidation of organic contaminants.

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