Au Modified F-TiO₂ for Efficient Photocatalytic Synthesis of Hydrogen Peroxide

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Abstract: In this work, Au-modified F-TiO₂ is developed as a simple and efficient photocatalyst for H₂O₂ production under ultraviolet light. The Au/F-TiO₂ photocatalyst avoids the necessity of adding fluoride into the reaction medium for enhancing H₂O₂ synthesis, as in a pure TiO₂ reaction system. The F⁻ modification inhibits the H₂O₂ decomposition through the formation of the ≡Ti–F complex. Au is an active cocatalyst for photocatalytic H₂O₂ production. We compared the activity of TiO₂ with F⁻ modification and without F⁻ modification in the presence of Au, and found that the H₂O₂ production rate over Au/F-TiO₂ reaches four times that of Au/TiO₂. In situ electron spin resonance studies have shown that H₂O₂ is produced by stepwise single-electron oxygen reduction on the Au/F-TiO₂ photocatalyst.

Keywords: photocatalysis; hydrogen peroxide; fluorination; TiO₂

1. Introduction

Hydrogen peroxide (H₂O₂) is widely used as a clean oxidant in environmental purification and organic synthesis [1,2]. It is widely used in pulp bleaching, wastewater treatment, and disinfection of industrial and household wastes with only water as the by-product [3]. At present, most H₂O₂ in industry is prepared by the anthraquinone method with H₂ and O₂ [4]. This method requires a lot of energy and organic solvents with complicated reaction steps and high risk of explosion. Therefore, finding a simple and direct method for H₂O₂ synthesis has become the focus of research. H₂O₂ can be effectively produced through photo-electrocatalysis [5] and photocatalysis. In recent years, the photocatalytic synthesis of H₂O₂ with oxygen and sunlight as the input energy has attracted great attention. At present, many semiconductor materials with UV and visible light activities, such as ZnO [6,7], C₃N₄ [8–10], BiVO₄ [11], and TiO₂ [12–18] have demonstrated the potential for direct synthesis of H₂O₂. Especially when these semiconductors are loaded with appropriate cocatalysts, the photocatalytic activity of the catalysts could be greatly improved. Au has been proved to be a very effective cocatalyst for promoting H₂O₂ production.

As a classic photocatalyst, TiO₂ is one of the most frequent and promising semiconductors because of its low cost and high stability. Under UV irradiation, H₂O₂ can be directly produced in aqueous solution in the presence of O₂ without hydrogen over TiO₂. An important feature of photocatalytic H₂O₂ synthesis is that the formation of H₂O₂ from the oxygen reduction reaction (ORR) is accompanied by the decomposition process. Zhao et al. [19] reported that adsorption of H₂O₂ on TiO₂ will readily form surface peroxide complexes in the form of ≡Ti–OOH, which can be easily photodegraded with a
zero-order kinetic process, even with the irradiation of visible light, thus leading to the decrease in H$_2$O$_2$ production. Maurino et al. [20] also reported that the production of H$_2$O$_2$ increased remarkably after adding fluoride into the reaction suspension of TiO$_2$. These studies showed the competition of the F$^-$ with superoxide/peroxide species for the surface sites of TiO$_2$. The ≡Ti–F formation decreases the amount of ≡Ti–OOH and thus, inhibits H$_2$O$_2$ degradation. This method is interesting but it will cause fluoride pollution to the reaction medium and the difficulty of H$_2$O$_2$ purification. In order to solve these problems, we developed F$^-$-modified TiO$_2$ by a hydrothermal method instead of adding NaF in the photocatalytic reaction medium and used Au as the cocatalyst of F-TiO$_2$. The anchored F$^-$ on the TiO$_2$ surface will compete with the formation of peroxide species to suppress the decomposition of H$_2$O$_2$ and increase the H$_2$O$_2$ production rate. F-TiO$_2$ avoided adding fluoride into the reaction medium as used in a pure TiO$_2$ reaction system and thus, simplified the reaction procedure. In situ ESR reveals that the H$_2$O$_2$ is efficiently formed through a stepwise single-electron ORR process on the Au/F-TiO$_2$ photocatalyst.

2. Materials and Methods

2.1. Experimental Materials Preparation

To produce the F-TiO$_2$ photocatalyst, 1 g commercial anatase TiO$_2$ and 0.42 g NaF (n$_{\text{F}}$:n$_{\text{Ti}}$ = 0.5:1) were mixed with 25 mL absolute ethanol and 15 mL water for hydrothermal treatment. The powder mixtures were maintained at 180 °C for 4 h in a homogeneous reactor. Then, the mixtures were transferred into the deionized water for centrifugation, washing and drying. By changing the amount of NaF and TiO$_2$ with different molar ratios of F/Ti, we prepared a series of F-TiO$_2$ photocatalysts. The photocatalysts loaded with 0.1 wt% Au were obtained by the deposition–precipitation method reported previously [21].

2.2. Material Characterization

UV–Vis spectra were recorded with a Spectrum Lambda 750 S (Perkin-Elmer, Waltham, MA, USA). High-resolution transmission electron microscopy (TEM) characterization was performed with an 8000EX microscope (JEOL, Tokyo, Japan) operating at 200 kV. The S-4800 scanning electron microscope (SEM) from Hitachi Instruments was used to observe the morphology of the photocatalyst.

2.3. Photocatalytic Activity Test

A reaction kettle (200 mL) was used as a photocatalytic reactor; 0.2 g Au/F-TiO$_2$ was added into the reaction solution of alcohol (4 wt%) and deionized water. F$^-$ was directly modified on the surface of the TiO$_2$ by the hydrothermal method without adding F$^-$ into the reaction solution. The suspension was treated by ultrasonication for 2–3 min; then, oxygen was bubbled for 30 min before turning on the light. A 300 W Xe arc lamp (PLS-SXE300, Perfectlight Technology Co., Ltd., Beijing, China) was used as a light source. The reaction was carried out under magnetic stirring water cooling. The concentrations of H$_2$O$_2$ generated were determined by using the DMP (2, 9-dimethyl-1, 10-phenanthroline) method [22].

2.4. Quantification of H$_2$O$_2$ (DMP Method)

One milliliter of DMP (0.1 g/L), 1 mL of copper (II) sulfate (0.1 M), 1 mL of phosphate buffer (Ph 7.0) solution, and 1 mL of reaction solution were added to a 10 mL volumetric flask and mixed; then, deionized water was added to the volumetric flask to the tick mark. After mixing, the absorbance of the sample at 454 nm was measured. The blank solution was prepared in the same manner but without H$_2$O$_2$.

The concentrations of H$_2$O$_2$ were calculated by the following formula:

$$A_{454} = \zeta [H_2O_2] \times 1/10$$

where $A_{454}$ is the difference of the absorbance between the sample and blank solutions at 454 nm, $\zeta$ is the slope of the calibration curve, and [H$_2$O$_2$] is the H$_2$O$_2$ concentration (µM).
2.5. In Situ ESR Test

Using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as spin trapping reagent, the reduction pathways of O2 on different catalysts were determined by in situ electron spin resonance (ESR) analysis. An ESP 300E spectrometer (Bruker, Switzerland) was used to detect the ESR signals of radicals trapped by DMPO. Generally, the catalyst (1 mg) was put into a mixture containing 1 mL alcohol/water (4 wt%) and 0.125 mmol DMPO. After passing the O2 for 3 min, the sample was irradiated under UV light for 5 min before testing.

3. Results and Discussion

Au/TiO2 and TiO2 have similar XRD test spectra (Figure S1). The diffraction peak of Au was not observed. It is presumed that the content of Au is too low and it is highly dispersed in the catalyst, which makes it impossible to form obvious characteristic diffraction peaks. In order to explore the existence and state of F− in the catalyst, the XPS of Au/TiO2 and Au/F-TiO2 was tested (Figure S2). Compared with the full spectrum of Au/TiO2, the full spectrum of Au/F-TiO2 has a peak corresponding to F1s between 600 eV and 700 eV, which can preliminarily prove that F− has been successfully introduced into the catalyst. From the peak fitting results of the high-resolution XPS spectrum of F1s (Figure 1), it is found that the F1s is mainly composed of two peaks. The low binding energy peak at 683.4 eV is the signal peak of the formation of complex ≡Ti-F due to the chemical adsorption of F− on the surface of TiO2. The small peak with high binding energy near 684.5 eV is attributed to the signal peak of the doped F atom in TiO2; that is, the F atom substituting for the oxygen site in TiO2 lattice.

![Figure 1. High-resolution XPS spectrum of F1s.](image)

From the TEM image of TiO2 and F-TiO2 (Figure 2), it is found that the morphology of F-TiO2 prepared by the hydrothermal method has a very obvious change compared with that of TiO2. TiO2 has an irregular shape, while F-TiO2 is almost spherical. This is because F− has an etching effect on TiO2 during hydrothermal treatment [23]. The F− has a strong complexation ability with Ti on the surface of TiO2, which corrodes the edges and corners of TiO2 particles and changes the irregular TiO2 into a spherical shape [24].
The SEM and energy dispersive spectroscopy (EDS) of 0.1% Au/F-TiO$_2$ (Figure S3) show that there are F and Au elements on the surface of the catalyst. This also proved that the F$^-$ modification and Au loading on TiO$_2$ were successfully realized in the sample preparation. The element mapping of Au/F-TiO$_2$ ($n_F:n_{Ti}=2.5$) in Figure 3 shows that both F and Au are evenly distributed on the surface of TiO$_2$, which is consistent with the element types shown in the EDS result (Figure S3).

**Figure 2.** TEM images of (a) TiO$_2$ and (b) F-TiO$_2$. 

**Figure 3.** (a) SEM and mapping images of (b) Ti, (c) F and (d) Au elements on Au/F-TiO$_2$ ($n_F:n_{Ti}=2.5$).
Figure 4a shows the UV–Vis spectrum of F-TiO₂, 0.1% Au/F-TiO₂ and pure TiO₂. Besides the characteristic absorption bands of TiO₂ at lower than 370 nm, the absorption bands caused by the loading of Au nanoparticles are located between 500 nm and 650 nm, which is a typical Au surface plasma band [25]. According to the calculation, the band gap of TiO₂ is about 3.2 eV and F-TiO₂ is about 3.1 eV (Figure 4b).

The photocatalytic activity of H₂O₂ synthesis on Au/F-TiO₂ hybrids was tested under UV light and the concentration of H₂O₂ was quantified by spectrophotometry with copper ions and 2,9-dimethyl-1,10-phenanthroline (DMP). The standard curve showed that there was a good linear relationship between the absorbance and concentration of H₂O₂; the R squared value was 0.9996 (Figure S3). Figure 5 shows the photocatalytic synthesis of H₂O₂ over Au-loaded F-TiO₂ catalysts. Compared with the unmodified catalyst, the photocatalytic activity increased with the increase in F content, and the photocatalytic activity reached its highest when the F/Ti molar ratio increased to 2.5. The F⁻ on the surface of TiO₂ will compete with superoxide/peroxide species for the surface sites of TiO₂ and inhibit the adsorption of peroxy radicals, thus suppressing the decomposition of H₂O₂. With the continuous increase in F content, when the F/Ti molar ratio is 3, the activity of the catalyst decreases. Excessive F⁻ caused serious defects on the surface of TiO₂ and destroyed the crystallinity of TiO₂, thus decreasing the photocatalytic activity of the catalyst.

![Figure 4](image1.png)

**Figure 4.** (a) UV–Vis absorbance from Kubelka–Munk function of diffuse–reflectance spectra of TiO₂, F-TiO₂ and 0.1% Au/F-TiO₂; (b) Tauc plot from (a).

![Figure 5](image2.png)

**Figure 5.** Photocatalytic H₂O₂ production over 0.1% Au/F-TiO₂ prepared with different F/Ti ratios.
In general, H₂O₂ from 2 e⁻ ORR by CB electrons can be produced through stepwise coupled electrons and proton transfers (Equations (1)–(3)) [26]. In order to further study the mechanism of photocatalytic ORR for H₂O₂ synthesis over Au/F-TiO₂, DMPO was used as a trapping agent of free radical in situ ESR tests for different samples. In situ ESR spectra of Au/F-TiO₂, Au/TiO₂ and pure TiO₂ under UV irradiation are shown in Figure 6. The results clearly show the signal of •OOH formed via equation (2) over various TiO₂ photocatalysts [27]. The DMPO-•OOH radical signal could be detected in both Au-loaded samples except pure TiO₂. The superoxide radical is formed by the first combination of O₂ in the photocatalytic reaction medium with electrons and protons. The generated HO₂• will continue to react with one electron and a proton and finally, generate H₂O₂. Therefore, the H₂O₂ is formed by a stepwise single-electron ORR over Au/F-TiO₂. In addition, compared with TiO₂, Au/TiO₂ and Au/F-TiO₂ produced a more obvious HO₂• signal, which implied that Au and F⁻ promoted the formation of HO₂•, and both of them promoted the photocatalytic synthesis of H₂O₂.

\[
\text{Semiconductor} \rightarrow e^- + h^+ \tag{1}
\]
\[
e^- + O_2 + H^+ \rightarrow •OOH \tag{2}
\]
\[
•OOH + H^+ + e^- \rightarrow H_2O_2 \tag{3}
\]

Figure 6. In situ ESR spectra of 0.1% Au/TiO₂ prepared with different F/Ti ratios and pure TiO₂.

4. Conclusions

In this work, we have designed Au/F-TiO₂ as an efficient photocatalyst for the production of H₂O₂ in aqueous solution. The Au/F-TiO₂ makes it possible to obtain a high H₂O₂ yield in fluoride-free reaction medium. The H₂O₂ production rate reached four times that of Au/TiO₂. The in situ ESR test showed that the synthesis mechanism of H₂O₂ was not changed by F⁻ modification. The H₂O₂ was synthesized over Au/F-TiO₂ through a stepwise single-electron ORR.

Supplementary Materials: The following are available online. Figure S1: XRD spectra of Au/TiO₂ and TiO₂. Figure S2: XPS spectra of (a) Au/TiO₂, (b) Au/F-TiO₂. Figure S3: (a) SEM image of 0.1%Au/F-TiO₂, (b) EDS spectrum of 0.1%Au/F-TiO₂. Figure S4: Standard curve: linear relationship between absorbance at 454 nm and H₂O₂ concentration.
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