

# Influence of Cr<sup>3+</sup> Doping on Photocatalytic Hydrogen Production Performance of TiO<sub>2</sub> Film Growing in Situ on the Surface of Ti Plate

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**Abstract:** The Cr<sup>3+</sup> doped TiO<sub>2</sub> films (Cr@TiO<sub>2</sub>) were prepared by in-situ growing on the pure Ti plate substrate in the electrolyte solution of Na<sub>3</sub>PO<sub>4</sub> containing a certain amount of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> using micro-arc oxidation (MAO) technique. The Cr@TiO<sub>2</sub> were characterized by SEM, XPS, XRD and DRS. The influence of Cr<sup>3+</sup> doping amount on the morphology, structure and photocatalytic hydrogen production performance of Cr@TiO<sub>2</sub> was studied. The characterization results showed that Cr<sup>3+</sup> doping into TiO<sub>2</sub> film not only affects the crystallinity of TiO<sub>2</sub>, but also affects the composition of crystal phase, and the maximum absorption edge of Cr@TiO<sub>2</sub> reflects an obvious redshift, reaching around 650 nm of visible light with the increase of Cr<sup>3+</sup> content. The Cr<sup>3+</sup> doping was good for the improvement of photocatalytic performance. The Cr@TiO<sub>2</sub> prepared under the condition of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> adding amount of 0.29 g/L exhibited the highest rate of 0.378 mol/cm<sup>2</sup>·h.

## 1. Introduction

Since the photocatalytic splitting of water on TiO<sub>2</sub> electrodes was found by Fujishima and Honda in 1972<sup>[1]</sup>, a great many research have been carried out in theory and application of the photocatalytic reaction. At present, the environmental pollution has become an obstacle to sustainable development. Hydrogen as a clean fuel is the best way to solve environmental pollution<sup>[2]</sup>.

The powdered TiO<sub>2</sub> exhibits excellent mass transfer performance, but low efficiency of light utilization and difficult cycle use of catalysts for suspension system has limited its application. The TiO<sub>2</sub> film can better solve the above problems and is beneficial to industrialization<sup>[3]</sup>.

The production methods of TiO<sub>2</sub> film include the CVD technology<sup>[4]</sup>, sol-gel method<sup>[5]</sup>, sputtering and electrochemical method<sup>[6]</sup>. The micro-arc oxidation (MAO) technique allows the in-situ growing of ceramic-like film with excellent chemical durability and bonding strength on the surface of metals in electrolyte solutions<sup>[7-8]</sup>. Metal-doped TiO<sub>2</sub> film on Ti surface can be prepared by adding metallic and nonmetallic elements to the electrolyte solution<sup>[9]</sup>.

In this research, MAO technique was used to prepare the Cr<sup>3+</sup> doped TiO<sub>2</sub> film (Cr@TiO<sub>2</sub>) by using the pure Ti plate as substrate. The effect of Cr<sup>3+</sup> doping amount on the morphology, structure and photocatalytic



hydrogen evolution performance of TiO<sub>2</sub> film was investigated.

## 2. Experimental

### 2.1. Preparation of Cr@TiO<sub>2</sub> film

All chemicals used are chemically pure. Commercial pure Ti plate as the substrate needs to be cleaned by a mixed solution of HNO<sub>3</sub>/HF/H<sub>2</sub>O. The MAO treatment of Ti plate was carried out in 0.11 mol/L Na<sub>3</sub>PO<sub>4</sub> electrolyte solution containing a certain amount of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> using HG-I device as power source with current density of 4 A/cm<sup>2</sup> for oxidation time of 9 min. The final Cr<sup>3+</sup> doped TiO<sub>2</sub> film (Cr@TiO<sub>2</sub>) was obtained by washing and drying.

### 2.2. Characterization of Cr@TiO<sub>2</sub> film

The X-ray diffraction spectra (XRD) were obtained on a Bruker D8 Advance X-ray diffractometer using Cu K $\alpha$  irradiation. The patterns were recorded from 10° to 70° (2 $\theta$ ). The UV-Vis diffuse reflectance spectra (DRS) were completed on Shimadzu UV-2450 spectrophotometer in the scanning range from 250 to 700 nm. The experimental data were obtained by transferring from reflection to absorption by Kubelka-Munk method. The scanning electron microscopy (SEM) was characterized on a HITACHI S-4800 instrument operated at 20 kV. The X-ray photoelectron spectroscopy analysis (XPS) was completed on a Thermo Electron instrument.

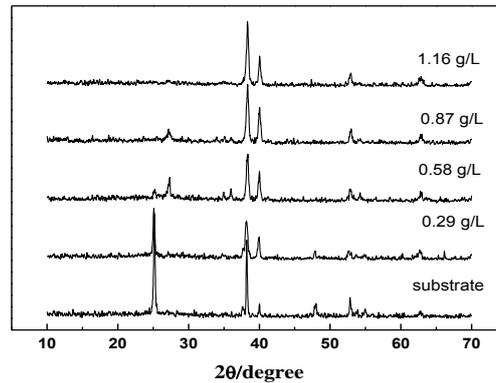
### 2.3. Evaluation of photocatalytic hydrogen production performance

Photocatalytic experiments were carried out in an inner-irradiation quartz reactor. A 250 W high-pressure lamp was used as light source. In order to get visible light, 1 M NaNO<sub>2</sub> solution was added into an inner circulating system to remove the UV part of the light with a wavelength less than 400 nm. The above-prepared Cr@TiO<sub>2</sub> films were added into aqueous mixed solution of 0.25 M Na<sub>2</sub>SO<sub>3</sub> and 0.35 M Na<sub>2</sub>S. Before opening light source, N<sub>2</sub> was purged through as-above prepared solution to remove oxygen. The photocatalytic reaction temperature was controlled at 30 ± 5°C. Photocatalytic hydrogen production performance was evaluated by collecting the amount of hydrogen evolution by drainage extraction method. Hydrogen purity analysis was conducted on GC with thermal conductivity detector.

## 3. Results and discussion

### 3.1. Structure

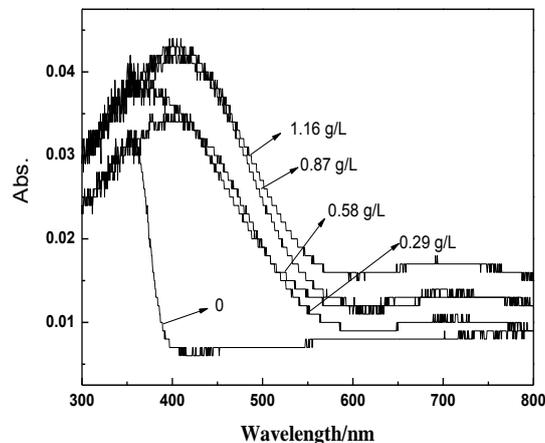
Figure 1 showed XRD patterns of Cr@TiO<sub>2</sub> with different Cr<sup>3+</sup> doping amount. It was shown in Figure 1 that with the increase of the addition amount of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in the electrolyte, the characteristic peak strength of anatase located in 2 $\theta$ =25.28° gradually weakens and shifts towards a small angle. When the addition amount of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> exceeds 0.58g/L, the characteristic diffraction peaks of rutile phase (110) crystal plane located at 2 $\theta$ =27.45° and rutile phase (101) crystal plane at 2 $\theta$ =36.09° can be found in the XRD patterns, indicating that the addition of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> not only affects the crystallinity of TiO<sub>2</sub>, but also affects the composition of crystal phase. When the addition amount of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> exceeded 0.87g/L, the characteristic peak of anatase disappeared, indicating that the addition of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> hindered the growth of anatase TiO<sub>2</sub> in the system and affected the crystallinity of TiO<sub>2</sub>. When the addition of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> exceeded 1.16 g/L, no other peaks were found except the basal peak. The color of prepared TiO<sub>2</sub> film changed from grey to golden, but the color of the film did not change significantly with the addition amount of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. When the addition amount of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> exceeded 1.45g/L, micro-arc discharge could not be generated, and the generated golden yellow film was broken off on the surface of the substrate, exposing the substrate. TiO<sub>2</sub> thin film prepared under such conditions could not be used for photocatalytic evaluation.



**Figure 1.** XRD patterns of Cr@TiO<sub>2</sub> films prepared at different concentrations of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>

### 3.2. Optical Properties

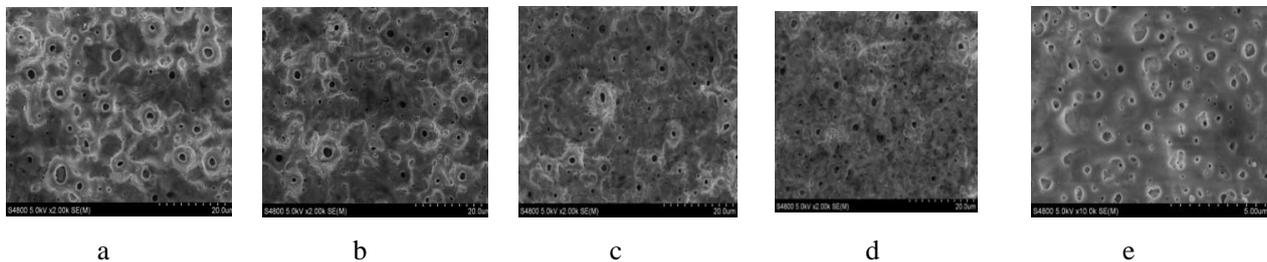
Figure 2 showed the DRS spectra of Cr@TiO<sub>2</sub> with different Cr<sup>3+</sup> doping amount. With the increasing of the addition amount of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> into the electrolyte, the maximum absorption edge of Cr@TiO<sub>2</sub> showed an obvious red shift, reaching around 650 nm of visible light. The reason for this phenomenon is due to the formation of impure energy levels by the Cr<sup>3+</sup> doping in the forbidden band, reducing band gaps to enhance utilization of visible-light. However, when the addition amount of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> exceeds 0.87 g/L, anatase phase TiO<sub>2</sub> no longer exists in the film layer, and rutile phase TiO<sub>2</sub> plays the role of light absorption in the film layer. Since no EDTA complexant was added to the electrolyte during Cr<sup>3+</sup> doping, the color of the solution did not change after the reaction. It indicated that Cr<sup>3+</sup> was not deposited on the surface of film, but was doped into the lattice of TiO<sub>2</sub>.



**Figure 2.** UV-Vis absorption spectra of Cr@TiO<sub>2</sub> films prepared at different concentrations of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>

### 3.3. Morphology

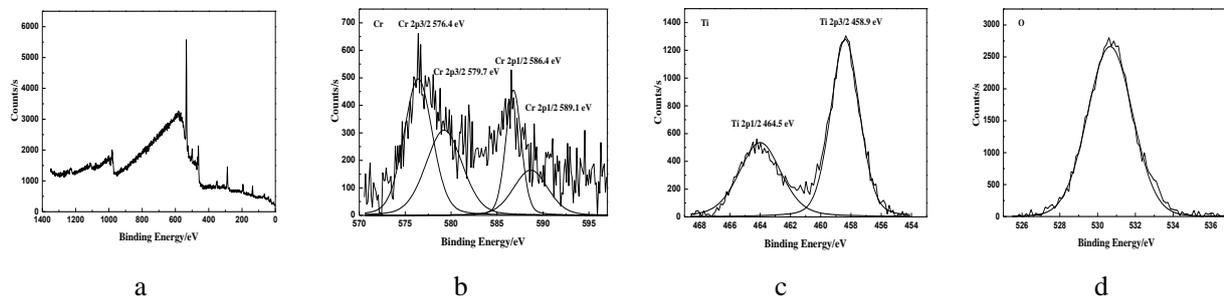
Figure 3 showed that SEM images of Cr@TiO<sub>2</sub> with different Cr<sup>3+</sup> doping amount. It was seen from Figure 3 that with the addition amount of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> into electrolyte, the corrosion degree of TiO<sub>2</sub> film surface increases, indicating that K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> will cause corrosion of the film during the process of Cr<sup>3+</sup> doping. When K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> addition amount is less than 0.58 g/L, there are a lot of holes with the diameter of 2~4 μm on the film surface due to the electric breakdown. Damage on the film surface morphology caused by corrosion is seen at the adding amount of more than 0.58 g/L. When the amount of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> continues to increase more than 1.45 g/L, the voltage to 100 V or so will stop growing, micro-arc discharge cannot occur. No oxidized film can be formed on the surface of the substrate, leaving only tiny discharge channels.



**Figure 3.** SEM images of Cr-TiO<sub>2</sub> films prepared at different concentrations of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (a)0.29 g/L(b) 0.58 g/L (c)0.87 g/L (d)1.16 g/L (e) 1.45 g/L

### 3.4. Surface State Analysis

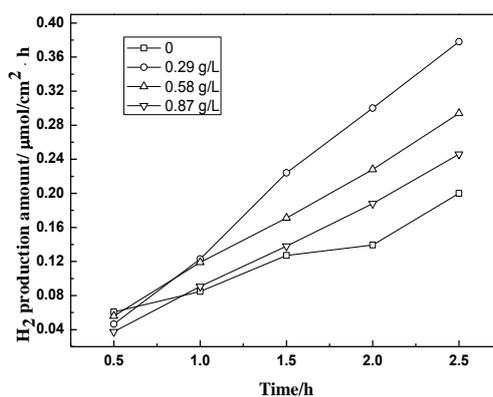
Figure 4 (a-d) showed that XPS analysis of Cr@TiO<sub>2</sub> films with different Cr<sup>3+</sup> doping amount. The characteristic peaks of survey spectrum are seen in Figure 4 (a). The P2p diffraction peak at 134.7 eV was also found in the XPS spectra. As shown in the Cr2p spectra of Figure 4(b), there are two peaks at 576.4 eV and 586.4 eV corresponding to the Cr2p<sub>1/2</sub> and Cr2p<sub>3/2</sub>, indicating Cr<sup>3+</sup> doping into the film layer, and two peaks at 579.7 eV and 589.1 eV corresponding to the Cr2p<sub>3/2</sub> and Cr2p<sub>1/2</sub>, indicating that Cr<sup>6+</sup> is contained in the film layer. The diffraction peaks at 458.8 eV and 464.5 eV in Figure 4(c) correspond to Ti2p<sub>3/2</sub> and Ti2p<sub>1/2</sub> respectively, indicating that the valence of Ti is 4+. The binding energy of O in Figure 4(d) indicates that only lattice oxygen exists in the film, and no chemisorption oxygen exists.



**Figure4.** XPS spectra of Cr@TiO<sub>2</sub> films prepared at different concentrations of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (a) Survey spectrum, (b) Cr, (c) Ti (d) O

### 3.5. Photocatalytic Hydrogen Production Performance

Figure 5 showed the photocatalytic hydrogen evolution rate of with different Cr<sup>3+</sup> doping amount. H<sub>2</sub> production rate showed a trend of increasing first and then decreasing with the increasing of Cr<sup>3+</sup> doping amount. The Cr@TiO<sub>2</sub> with the addition of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> of 0.29 g/L exhibited the highest rate of 0.378 mol/ cm<sup>2</sup>·h. This was because the increase of the concentration of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in the electrolyte hindered the growth of anatase phase TiO<sub>2</sub>, and seriously corroded the film layer, causing the generated film to break away from the substrate, which directly affected the photocatalytic activity.



**Figure 5.** H<sub>2</sub> production rate over the Cr@TiO<sub>2</sub> films prepared at different concentrations of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>

#### 4. Conclusions

The Cr<sup>3+</sup> doped TiO<sub>2</sub> film on the pure Ti plate have been prepared by micro-arc oxidation process (MAO). The addition of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> not only affects the crystallinity of TiO<sub>2</sub>, but also affects the composition of crystal phase. The Cr<sup>3+</sup> doping into TiO<sub>2</sub> film results in the formation of impure energy levels in the forbidden band, reducing band gaps to enhance utilization of visible-light. The maximum absorption edge of Cr@TiO<sub>2</sub> reflects an obvious red shift, reaching around 650 nm of visible light with the increase of Cr<sup>3+</sup> content. The Cr<sup>3+</sup> doping was good for the improvement of photocatalytic performance. The Cr@TiO<sub>2</sub> with the addition amount of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> of 0.29 g/L exhibited the highest rate of 0.378 mol/ cm<sup>2</sup>·h.

#### 5. References

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