

Influence of Cr³⁺ Doping on Photocatalytic Hydrogen Production Performance of TiO₂ Film Growing in Situ on the Surface of Ti Plate

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Abstract: The Cr³⁺ doped TiO₂ films (Cr@TiO₂) were prepared by in-situ growing on the pure Ti plate substrate in the electrolyte solution of Na₃PO₄ containing a certain amount of K₂Cr₂O₇ using micro-arc oxidation (MAO) technique. The Cr@TiO₂ were characterized by SEM, XPS, XRD and DRS. The influence of Cr³⁺ doping amount on the morphology, structure and photocatalytic hydrogen production performance of Cr@TiO₂ was studied. The characterization results showed that Cr³⁺ doping into TiO₂ film not only affects the crystallinity of TiO₂, but also affects the composition of crystal phase, and the maximum absorption edge of Cr@TiO₂ reflects an obvious redshift, reaching around 650 nm of visible light with the increase of Cr³⁺ content. The Cr³⁺ doping was good for the improvement of photocatalytic performance. The Cr@TiO₂ prepared under the condition of K₂Cr₂O₇ adding amount of 0.29 g/L exhibited the highest rate of 0.378 mol/ cm²·h.

1. Introduction

Since the photocatalytic splitting of water on TiO₂ electrodes was found by Fujishima and Honda in 1972^[1], 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^[2].

The powdered TiO₂ 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 TiO₂ film can better solve the above problems and is beneficial to industrialization^[3].

The production methods of TiO₂ film include the CVD technology^[4], sol-gel method^[5], sputtering and electrochemical method^[6]. 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^[7-8]. Metal-doped TiO₂ film on Ti surface can be prepared by adding metallic and nonmetallic elements to the electrolyte solution^[9].

In this research, MAO technique was used to prepare the Cr³⁺ doped TiO₂ film (Cr@TiO₂) by using the pure Ti plate as substrate. The effect of Cr³⁺ doping amount on the morphology, structure and photocatalytic



hydrogen evolution performance of TiO₂ film was investigated.

2. Experimental

2.1. Preparation of Cr@TiO₂ film

All chemicals used are chemically pure. Commercial pure Ti plate as the substrate needs to be cleaned by a mixed solution of HNO₃/HF/H₂O. The MAO treatment of Ti plate was carried out in 0.11 mol/L Na₃PO₄ electrolyte solution containing a certain amount of K₂Cr₂O₇ using HG-I device as power source with current density of 4 A/cm² for oxidation time of 9 min. The final Cr³⁺ doped TiO₂ film (Cr@TiO₂) was obtained by washing and drying.

2.2. Characterization of Cr@TiO₂ film

The X-ray diffraction spectra (XRD) were obtained on a Bruker D8 Advance X-ray diffractometer using Cu K α irradiation. The patterns were recorded from 10° to 70° (2 θ). 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 been used as light source. In order to get visible light, 1 M NaNO₂ 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@TiO₂ films were added into aqueous mixed solution of 0.25 M Na₂SO₃ and 0.35 M Na₂S. Before opening light source, N₂ was purged through as-above prepared solution to remove oxygen. The photocatalytic reaction temperature was controlled at 30 \pm 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@TiO₂ with different Cr³⁺ doping amount. It was shown in Figure 1 that with the increase of the addition amount of K₂Cr₂O₇ in the electrolyte, the characteristic peak strength of anatase located in 2 θ =25.28° gradually weakens and shifts towards a small angle. When the addition amount of K₂Cr₂O₇ exceeds 0.58g /L, the characteristic diffraction peaks of rutile phase (110) crystal plane located at 2 θ =27.45 ° and rutile phase (101) crystal plane at 2 θ =36.09 ° can be found in the XRD patterns, indicating that the addition of K₂Cr₂O₇ not only affects the crystallinity of TiO₂, but also affects the composition of crystal phase. When the addition amount of K₂Cr₂O₇ exceeded 0.87g /L, the characteristic peak of anatase disappeared, indicating that the addition of K₂Cr₂O₇ hindered the growth of anatase TiO₂ in the system and affected the crystallinity of TiO₂. When the addition of K₂Cr₂O₇ exceeded 1.16 g/L, no other peaks were found except the basal peak. The color of prepared TiO₂ film changed from grey to golden, but the color of the film did not change significantly with the addition amount of K₂Cr₂O₇. When the addition amount of K₂Cr₂O₇ 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. TiO₂ thin film prepared under such conditions could not be used for photocatalytic evaluation.

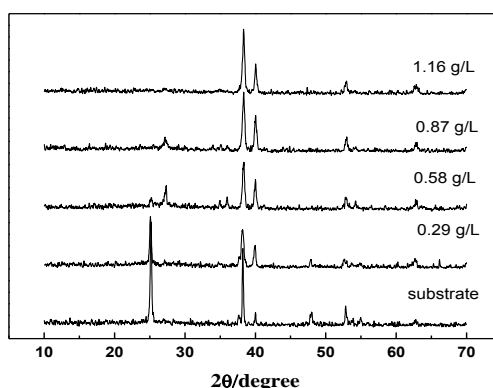


Figure1. XRD patterns of Cr@TiO₂ films prepared at different concentrations of K₂Cr₂O₇

3.2. Optical Properties

Figure2 showed the DRS spectra of Cr@TiO₂ with different Cr³⁺ doping amount. With the increasing of the addition amount of K₂Cr₂O₇ into the electrolyte, the maximum absorption edge of Cr@TiO₂ 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 Cr³⁺ doping in the forbidden band, reducing band gaps to enhance utilization of visible-light. However, when the addition amount of K₂Cr₂O₇ exceeds 0.87g /L, anatase phase TiO₂ no longer exists in the film layer, and rutile phase TiO₂ plays the role of light absorption in the film layer. Since no EDTA complexant was added to the electrolyte during Cr³⁺ doping, the color of the solution did not change after the reaction. It indicated that Cr³⁺ was not deposited on the surface of film, but was doped into the lattice of TiO₂.

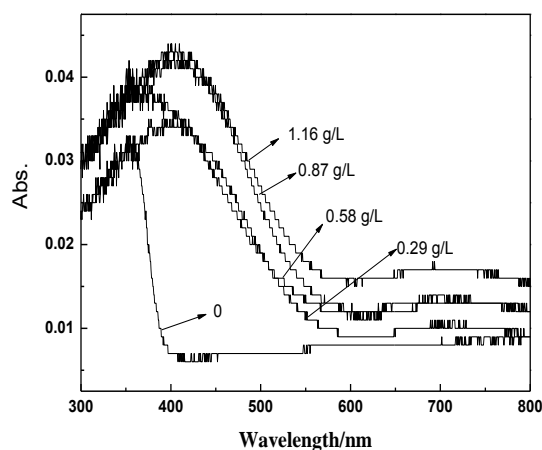


Figure 2.UV-Vis absorption spectra of Cr@TiO₂ films prepared at different concentrations of K₂Cr₂O₇

3.3. Morphology

Figure 3 showed that SEM images of Cr@TiO₂ with different Cr³⁺ doping amount. It was seen from Figure 3 that with the addition amount of K₂Cr₂O₇ into electrolyte, the corrosion degree of TiO₂ film surface increases, indicating that K₂Cr₂O₇ will cause corrosion of the film during the process of Cr³⁺ doping. When K₂Cr₂O₇ 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 K₂Cr₂O₇ 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.

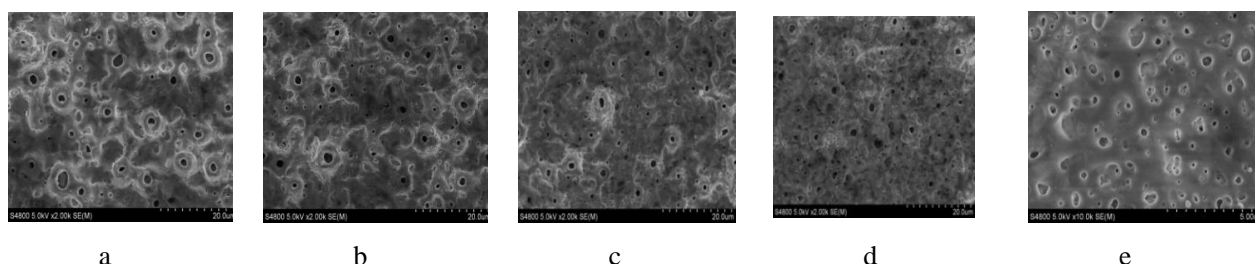


Figure 3. SEM images of Cr-TiO₂ films prepared at different concentrations of K₂Cr₂O₇ (a)0.29 g/L(b) 0.58 g/L (c)0.87 g/L (d)1.16 g/L (e) 1.45 g/L

3.4. Surface State Analysis

Figure 4 (a~d) showed that XPS analysis of Cr@TiO₂ films with different Cr³⁺ 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_{1/2} and Cr2p_{3/2}, indicating Cr³⁺ doping into the film layer, and two peaks at 579.7 eV and 589.1 eV corresponding to the Cr2p_{3/2} and Cr2p_{1/2}, indicating that Cr⁶⁺ is contained in the film layer. The diffraction peaks at 458.8 eV and 464.5 eV in Figure 4(c) correspond to Ti2p_{3/2} and Ti2p_{1/2} 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.

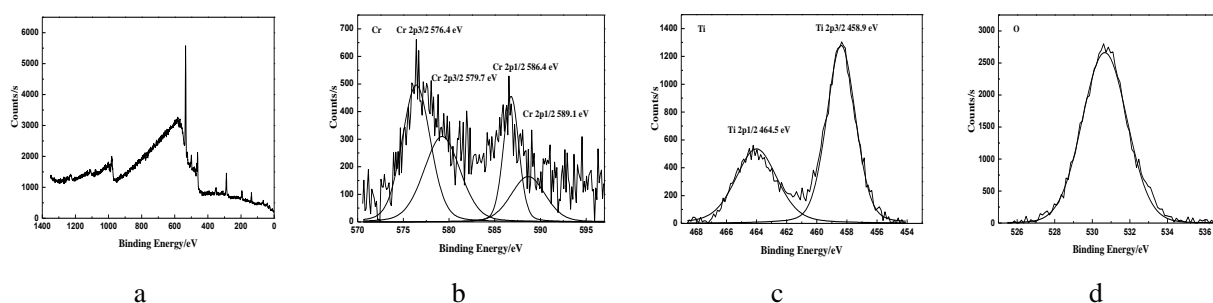


Figure4. XPS spectra of Cr@TiO₂ films prepared at different concentrations of K₂Cr₂O₇ (a) Survey spectrum, (b) Cr, (c) Ti (d) O

3.5. Photocatalytic Hydrogen Production Performance

Figure 5 showed the photocatalytic hydrogen evolution rate of with different Cr³⁺ doping amount. H₂ production rate showed a trend of increasing first and then decreasing with the increasing of Cr³⁺ doping amount. The Cr@TiO₂ with the addition of K₂Cr₂O₇ of 0.29 g/L exhibited the highest rate of 0.378 mol/ cm²•h. This was because the increase of the concentration of K₂Cr₂O₇ in the electrolyte hindered the growth of anatase phase TiO₂, and seriously corroded the film layer, causing the generated film to break away from the substrate, which directly affected the photocatalytic activity.

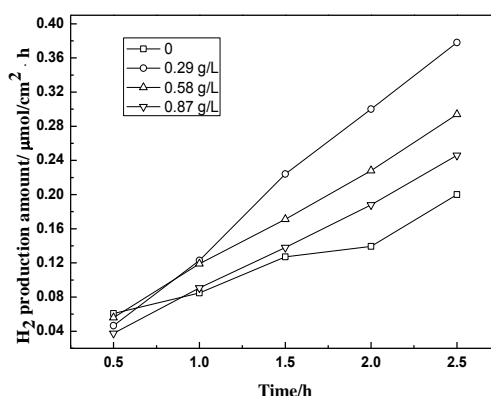


Figure 5. H₂ production rate over the Cr@TiO₂ films prepared at different concentrations of K₂Cr₂O₇

4. Conclusions

The Cr³⁺ doped TiO₂ film on the pure Ti plate have been prepared by micro-arc oxidation process (MAO). The addition of K₂Cr₂O₇ not only affects the crystallinity of TiO₂, but also affects the composition of crystal phase. The Cr³⁺ doping into TiO₂ 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@TiO₂ reflects an obvious red shift, reaching around 650 nm of visible light with the increase of Cr³⁺ content. The Cr³⁺ doping was good for the improvement of photocatalytic performance. The Cr@TiO₂ with the addition amount of K₂Cr₂O₇ of 0.29 g/L exhibited the highest rate of 0.378 mol/ cm²·h.

5. References

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