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Enhancing the photocatalytic activity under visible light of chromium doped TiO_2 thin film prepared by sol-gel method

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Abstract: The pure TiO_2 and Cr doped TiO_2 (TiO_2:Cr) photocatalyst thin films were prepared by solgel method using chromium (III) chloride and tetra butyl orthotitanate with doping levels of 1 to 7 at. %. The structure of TiO_2:Cr thin films was determined through XRD diffraction. Surface morphology and grain size were estimated by SEM images. Doped concentrations of chromium in the films were determined by EDX spectrum. The visible light photocatalytic activity of the samples was quantified by measuring the rate of degradation of methylene blue (MB) under visible light irradiation. The results show that all films possess the anatase structures and the crystalsizes of them are about 18 nm. The 5 at.% Cr doped TiO_2 film shows the highest visible light photocatalytic activity. It can nearly decompose about 50% MB solution and get super wet state after 150 minutes under visible light irradiation. The TiO_2:Cr films have the better photocatalytic activity under visible light than that of pure TiO_2 films.

Key words: Photocatalyst, solgel, Cr doped TiO_2, degradation, visible light irradiation.

1. Introduction

TiO_2 is a well-known photocatalyst for the decomposition of environmental pollutants, because it is cheap, nontoxic, and chemically stable. However with large band gap (about 3.2 eV for anatase phase), TiO_2 can only absorb the ultraviolet light, a small fraction of solar light. On the other hand, the recombination rate of the photoelectron - hole pairs of TiO_2 is high, so it reduces photocatalytic efficiency. Thus, in order to improve the photocatalytic activity of TiO_2, it is necessary to extend the photoresponse of TiO_2 to the visible spectrum as well as to prevent the photoelectron hole recombination [1].

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Doping TiO_2 with transition metals is one of the effective ways for shifting the TiO_2 absorption from the ultraviolet to the visible region. The substitution of transition metal ions for Ti^{4+} changes the electronic properties of TiO_2, which reduces the band gap to absorb visible light [2, 3]. Among these transition metal ions, Cr^{3+} has received much attention because its introduction can excellently extend the visible light absorption [4].

Although various physical and chemical methods have been reported for synthesis of TiO_2:Cr catalyst materials, most of these studies focus on fabricating TiO_2:Cr powder. There are still rare in studies related to synthesis of TiO_2:Cr thin film.

In this study, we carry out the fabrication of Cr doped TiO_2 thin films on glass substrates at different concentrations of Cr by sol-gel method to enhance the photocatalytic activity under visible region.

2. Experimental proceduce

Pure and TiO_2:Cr thin films were synthesized by sol-gel method. Figure 1 shows the sol-gel procedure of TiO_2:Cr thin films. Chromium III chlorine ($CrCl_3$) (99.98%) was completely dissloved in ethanol (solution I). Solution II was prepared by using tetra butyl orthotitanate ($Ti(OBu)_4$) (99.99%) dissolved in the mixture solution of diethanolamine ($HN(C_2H_4OH)_2$) (99.99%) and ethanol (C_2H_5OH) (99.99%) with stirring for 1 hour. Then water was added dropwise under continuous stirring at room temperature for 2 hours until the transparent sol was obtained. The molar ratio of tetra butyl orthotitanate, diethanolamine, water and ethanol was 1:1:1:17.. A various amounts of solution II, according to the required Cr dopant amount (1%, 3%, 5% and 7% molar fraction), were slowly dropped into the solution I with constant stirring.

The TiO_2:Cr with dopant concentrations of 1%, 3%, 5% and 7% were named Cr1, Cr3, Cr5 and Cr7, respectively. All the resultant solutions were stirred for an hour at room temperature to increase its homogeneity before dip coating. Both glass and silicon substrates were dipped into the resultant sols to obtain thin films which were further baked at 80^0C for 15 minutes. Then, the samples were thermally treated in the air at 500^0C for 2 hours. Undoped TiO_2 was also prepared with same procedure without solution II.

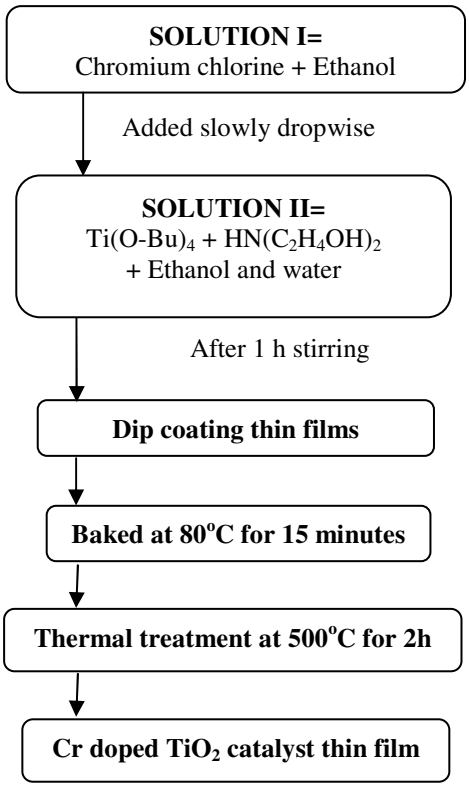

Fig. 1: Procedure of TiO_2:Cr catalyst thin films by solgel method.

The surface morphology of films were characterized by JEOL 7510 Scanning electron microscopy (SEM). Crystal structure of films were examined by D8 Advance XRD spectrometer (Brucker) with CuKα line 0.1541 nm. The concentration of chromium in film were determined by EDX spectrum. The optical absorption spectra of films were measured at room temperature in air using a Halo RB-10 spectrophotometer in the wavelength range from 200 to 1100 nm.

The photocatalytic activity of the Cr doped TiO_2 films was evaluated by measuring the degradation rate of MB on the film under 20W compact lamp as the light source having wavelength in visible range. In each experiment, a film of 25x25mm^2 was settled on the bottom of a 10 ml beaker, which contained 10 ppm aqueous MB solution. Then the absorption of solutions was measured at a wavelength of 662 nm at different irradiation times to evaluate the MB concentration changes during the experiment. The Lambert–Beer's law has been employed to calculate the concentration of the MB solution at different irradiation times.

3. Results and discussion

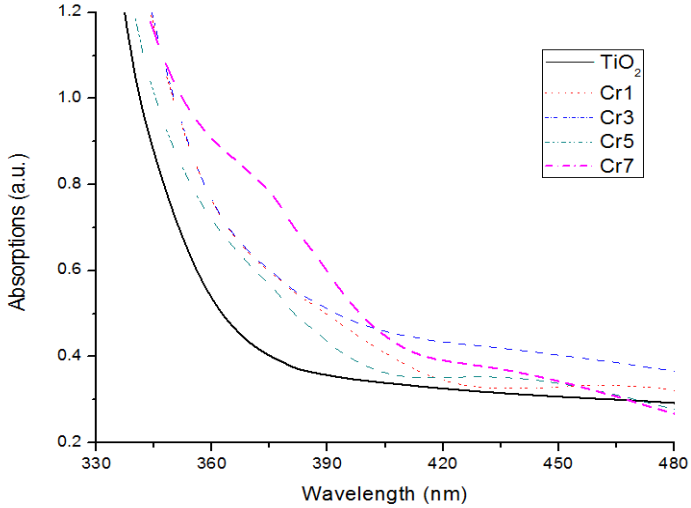

Fig. 2: UV-Visible absorption spectra of TiO_2 and TiO_2:Cr with different concentrations thin films.

The optical properties of the undoped and TiO_2:Cr were studied by measuring the absorption spectra. The results are presented in figure 2. It clearly shows a shift in the absorption band edge towards longer wavelength as the concentration of Cr in the TiO_2 films increase. This extended absorbance indicates that the photocatalytic activity of TiO_2:Cr thin films is possibly enhanced under visible light irradiation.

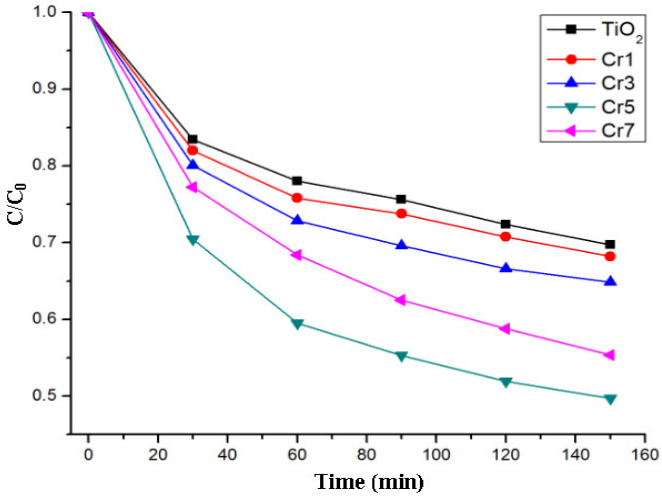

Fig. 3: Photocatalytic degradation of MB over TiO_2 and TiO_2:Cr with different concentrations thin films under compact light irradation

The photocatalytic activity of TiO_2 and TiO_2:Cr thin films were evaluated by using methylene blue (MB) as the target pollutant. Figure 3 shows the degradation curves of MB over TiO_2 film and TiO_2:Cr films under the compact light irradiation as the visible light, (C and C_0 stand for the remnants and initial concentration of MB, respectively). Comparing to the pure TiO_2, All TiO_2:Cr thin films exhibits a significant increase in the MB photodegradation rate. It is found that the photocatalytic activity of TiO_2:Cr thin films increase with increasing of Cr doping with 1-5% content. At 5% content Cr-doped TiO_2 thin film exhibits the best photocatalytic activity among all samples with MB photodegradation rate about 50%, implying that this film has more absorption in visible range and Cr can create the intermediate level in the band gap of TiO_2. This leads to the separation between the charged particles and constrains the recombination between electron and hole.

However, when Cr content is more than 5%, the photocatalytic activity of Cr-doped TiO_2 thin films decrease. It is indicated that the introduction of appropriate amounts of Cr ions into TiO_2 lattice might effectively restrains the recombination rate of photogenerated electron–hole pairs, so it enhances the photocatalytic activity of doped TiO_2 [7].

Figure 4 shows the XRD pattern of pure TiO_2 and TiO_2:Cr thin films. Only the anatase TiO_2 (101) is formed. No chromium oxide impurity phase is detected. It is can be ascribed to the lower doping content that is not strong enough to affect the growth of anatase crystals and Cr atoms substitute Ti atoms in TiO_2 lattices to form the impurities energy levels in bandgap. In fact, Cr^{3+} ions can be easily incorporated into the TiO_2 lattice via displacing Ti^{4+} sites due to their close ionic radius of Ti^{4+} (0.68A°) and Cr^{3+} (0.64A°) [5]. The average crystalline size calculated by the Scherrer equation is about 18 nm. Similar results have been reported previously [6].

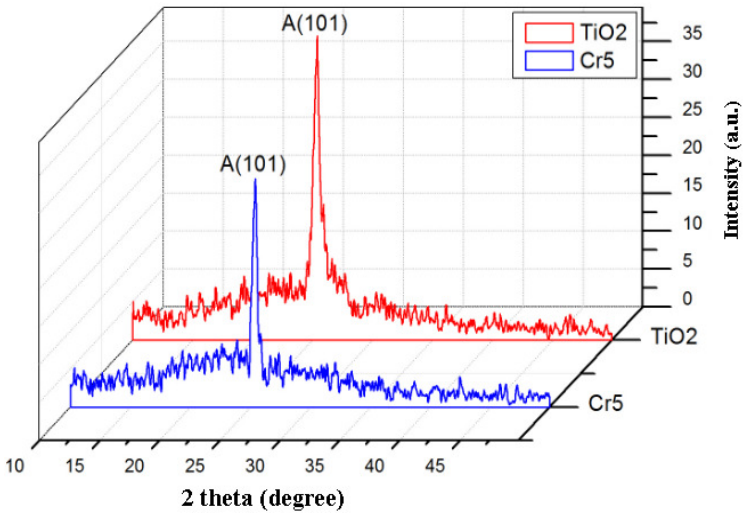

Figure 4: XRD pattern of TiO_2:Cr thin films.

Typical scanning electron microscopy (SEM) image of the best sample is observed in figure 5. It shows that the surface morphology of this film is uniform. The porosity of film is high.

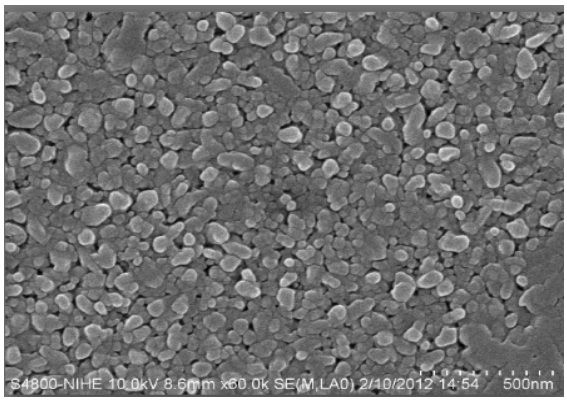

Fig 5: SEM image of 5% Cr doped TiO_2 film.

In addition, the concentration of Cr in film created in optimal condition was determined by EDX spectrum in the figure 6:

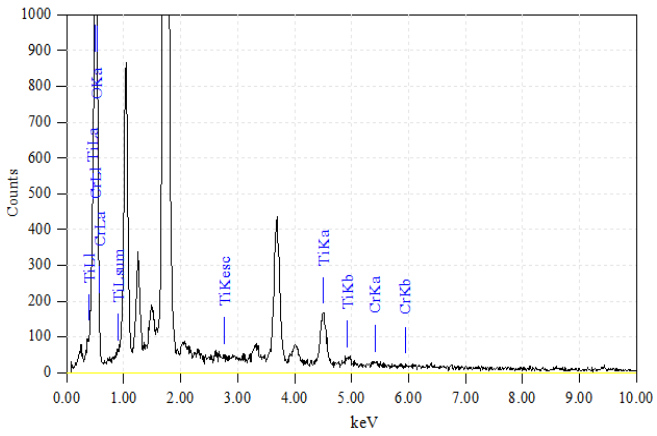

Fig 6: EDX pattern of 5% Cr doped TiO_2 film

The concentration of chromium in the best film was 1.03%.

4. Conclusion.

The TiO_2:Cr thin films have been successfully prepared by sol-gel method. The structure of films have only anatase phase. The results show that the doping of Cr ions has significant influence on the band gap energy of TiO_2 films. Cr ions have been inserted into films and have played the important role in creating the intermediate level in the band-gap of TiO_2. This leads to the separation between the charged particles, constrains recombination between electron and hole, and improves the photocatalytic properties of TiO_2:Cr films. The TiO_2:Cr 5% thin film exhibits the best

photocatalytic activity under visible light irradiation with MB photodegradation rate about 50% and concentration of Cr in the film is 1.03%.

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