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Pt doped TiO_2 (Pt-TiO_2) sol gel thin films

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Pt was supported on a TiO_2 surface using different methods. Pt doped TiO_2 (Pt-TiO_2) sol gel thin films were successfully produced by reducing chloroplatinc acid (H_2PtCl_6). The structures of the prepared composites were investigated using X-ray diffraction (XRD). The physical morphologies of the composites were examined using transmission electron microscope (TEM). After annealing the grain size of the Pt-TiO_2 thin film was also measured by an atomic force microscope (AFM).

Keywords: TiO_2, Pt annealing, Pt-TiO_2 sol gel film.

INTRODUCTION

Recently, extensive research of titanium dioxide (TiO2) has been carried out in efforts to develop a variety of applications including capacitors for photovoltaic cells [1], sensors [2], antireflection films [3], white pigments [4], optical coatings [5] and high density dynamic random access memory devices [6]. TiO_2 has three different crystal phases, such as anatase, rutile and brookite [7]. Rutile is the most common natural form of TiO_2. The brookite phase crystallizes in the orthorhombic system and does not exhibit any photocatalytic activity. Anatase TiO_2 has an excellent photocatalytic activity, physical and chemical stability and antimicrobial activity [8-11].

Earlier studies have revealed that the photocatalytic activity of TiO_2 can be improved significantly by doping with noble metals such as Pt, Au and Ag [12,13]. It is well known that the coverage of TiO_2 with platinum often shows a high photocatalytic activity. The doping of TiO2 with platinum can form a Schottky diode barrier between the metal and the electronic potential barrier at the metal-semiconductor heterojunction and the TiO_2 covered with platinum traps the photogenerated electrons efficiently [14]. The deposition of Pt on the TiO_2 surface has been widely reported to improve the photocatalytic performance of the split water and the degradation of different harmful compounds [15].

In this paper, we report characteristic properties of the TiO_2 and Pt composite including the UV-visible spectra, transmission electron microscope (TEM) images, X-ray diffraction (XRD) patterns and atomic force microscope (AFM) images.

EXPERIMENTAL DETAILS

Titanium oxide was used as a sol-gel precursor. The metal alkoxide was mixed with ethanol. The resulting solution became a milky color and white precipitation was observed. Hydrochloric acid was slowly added to the solution with vigorous stirring until the solution become transparent. Various amounts of chloroplatinc acid (H_2PtCl_6) (8 wt. % in water) was added to the TiO_2 sol-gel solution. Sodium borohydride ($NaBH_4$) was dispersed in ethanol and slowly added to the H_2PtCl_6/TiO_2 solution to reduce the $[PtCl_6]^{2-}$ to zero Pt. The aged sol was spin coated on to the glass and the silicon substrate by spin-coating at 2000 RPM and heated at 200 ^oC for 5 minutes. UV-visible spectra were obtained with a diode array spectrophotometer (Hewlett-Packard 8452 A). The sol-gel was diluted to ethanol and dropped on to the copper TEM grid. Using this copper grid sample, TEM images were obtained with a CM200 (Philips) microscope. The TiO_2 thin films coated on to a silicon wafer were annealed in a gas environment tube furnace (EM Tech). The annealing process started from room temperature up to 750 ^oC in steps of 5 ^oC/min and then maintained the temperature for 1 h. The films naturally cooled down to room temperature. The TiO_2 thin films doped with Pt were subject to XRD analysis with an X'Pert MPD Pro diffractometer (Philips). The surface of the film was also analyzed with a NanoScope 3D (Veeco) microscope.

RESULTS AND DISCUSSION

UV-visible spectra of bare TiO_2 and Pt-TiO_2 prepared with different Pt concentrations are shown in Figure 1. The single broad intense absorption peak of Pt-TiO_2 between 300 – 350 nm can be attributed to the charge-transfer from the valence

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band to the conduction band. The UV-visible absorption peaks also show a red shift due to the modification of TiO_2 with Pt [16].

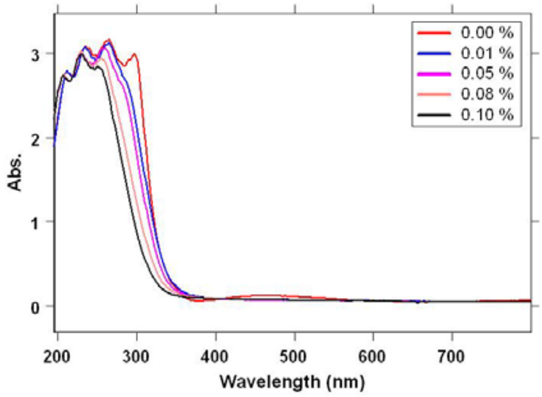

Fig. 1. UV-Visible spectra of a bare TiO2 and Pt-TiO2 sol-gel thin film after annealing.

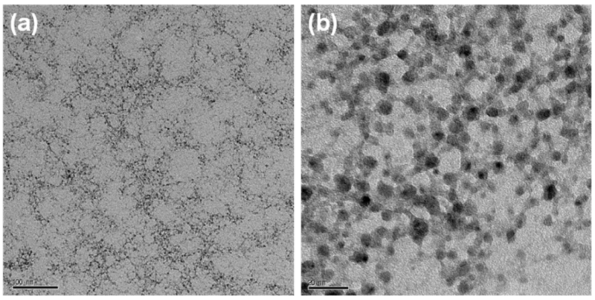

Fig. 2. TEM image of TiO2-Pt with 0.1% Pt.

The UV-visible spectra show the possible uniform distribution of Pt-nanoparticles throughout the sol-gel films. To obtain the particle size and distribution, a TEM was employed. Figure 2 (a) shows the TEM image for the film of 0.1 % Pt-TiO_2 with a scale bar size of 100. The aggregated area was further focused and the image obtained with a scale bar size of 20 nm is shown in Figure 2 (b). Pt-nanoparticles do not have big aggregates, distribute relatively uniformly and have particle sizes between 4–8 nm.

Figure 3 (a) shows the XRD patterns for Pt-TiO_2 films prepared by the sol-gel method with various amounts of Pt. All these samples show typical TiO_2 diffraction peaks in the form of anatase. As observed these almost coincide with the pure TiO_2 diffraction peaks and show no diffraction peaks due to the doped Pt. It can be assumed that the amount of Pt doped particles was very low, which resulted in the non-appearance of Pt crystalline peaks [17,18]. However, the diffraction intensity increased with the increase of Pt concentration. The crystalline size of the Pt-TiO_2 samples after annealing was estimated from line broadening using the Scherrer equation based on the (101) peak of anatase TiO_2 [19].

$$D = 0.9\lambda / \beta \cos\theta$$

where λ is the X-ray wavelength of Copper Kα radiation, θ is the Bragg's angle and β is the pure full width of the diffraction line at half of the maximum intensity (Figure 3(b)). The calculated grain sizes are 15 nm (0.01%), 20 nm (0.05%), 35 nm (0.08%) and 40 nm (0.1%), respectively. The results refer to Pt doping and also retard the grain growth of the TiO_2 thin film.

AFM images of the Pt-TiO_2 surface were used to monitor the grain size of the sol-gel thin film that depends on the Pt concentration. 1 µm × 1 µm scans revealed it is clear that the grain size of Pt-TiO_2 gradually increased with Pt loading.

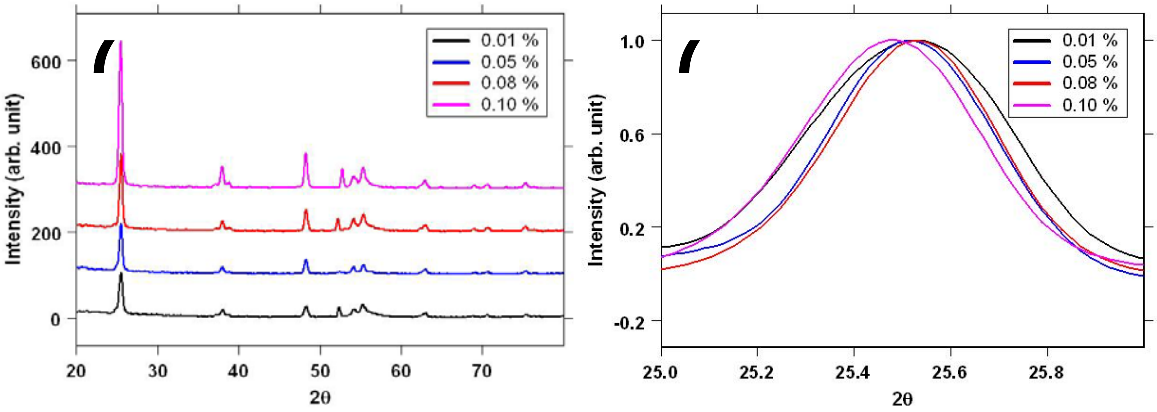

Fig. 3. XRD pattern of the TiO_2-Pt thin film depending on the Pt concentration.

CONCLUSIONS

Metallic doping is one factor for the TiO_2 anatase phase grain growth. The intensity of the main anatase diffraction peak increased with increasing Pt concentration. The grain sizes estimated from the anatase XRD major diffraction peaks were 15, 20, 35 and 40 nm for the sample with Pt concentrations of 0.01%, 0.05%, 0.085 and 0.1%, respectively. The measured grain sizes using AFM images also increased depending on the Pt concentration. The governing factor to determine the grain size of the TiO_2 thin films is Pt doping.

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ТЪНКИ ФИЛМИ ОТ TiO_2, ПОЛУЧЕНИ ПО ЗОЛ-ГЕЛ МЕТОДА И ДОТИРАНИ С ПЛАТИНА (Pt-TiO_2)

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(Резюме)

Платината е фиксирана върху повърхността от TiO_2 с помощта на различни методи. Дотирането с платина на зол-гел тънки филми TiO_2 (Pt-TiO_2) става успешно чрез редуциране на хлороплатинова киселина (H_2PtCl_6). Структурата на приготвените композити е изследвана чрез рентгено-структурен анализ (XRD). Физичната морфология на композитите е изследвана с трансмисиона електронна микроскопия (TEM). След закаляване дебелината на филмите е определяна атомен силов микроскоп (AFM).