Mesoporous Structure of Doped and Undoped PEG on Ag/TiO₂ Thin Film

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Abstract. In this research, photocatalyst silver titanium dioxide was doped and modified by Polyethylene Glycol (PEG). The purpose of the present study was to analyse the synthesized Ag/TiO₂ thin film doped and undoped PEG. Ag/TiO₂ thin films on silicon wafer have been prepared by sol–gel spin coating. The samples were characterized by Grazing Incidence X-ray diffraction (GIXRD), Field Emission Scanning Electron Microscopy (FESEM) and Atomic Force Microscope (AFM). The doped and undoped PEG Ag/TiO₂ thin films showed a mesoporous TiO₂ matrix which includes TiO₂ crystallites of 10-20 nm in size and small Ag nanoparticles (white spots) with various sizes ranging from 10 to 30 nm. However, doped PEG Ag/TiO₂ thin film showed the Ag nanoparticles became agglomerates but still remained roughly uniform on the surface.

1. Introduction

Thin films of titania (TiO₂) composed of nanosized particles in the anatase form show a very high photocatalytic activity due to their large internal surface. Both the optical properties and the photocatalytic activity of TiO₂ coatings depend on the crystalite size, the phase, and porosity of the coatings. Hence, the micro- or nanostructure of the TiO₂ films and their strict control through the preparation methodology of paramount importance. Recently, significant effort has been directed towards the low-temperature transformation of TiO₂ by using the sol-gel process. In a previous work, they have found that nanostructured anatase phase TiO₂ thin films can be fabricated by a sol-gel method at temperatures as low as 100 °C. These films, with nanometric (5 nm) grain size, were obtained by using a structure-directing agent such as poly(ethylene glycol) (PEG) [9].

Main advantages of this photocatalyst reside in its strong resistance to a wide variety of chemicals, as well as to the photocorrosion, besides its low cost. However, a drawback to this material is that it has a forbidden band value (band gap) in the range of the ultraviolet light (3.2 eV), which within the solar spectrum extents to only 4%. Therefore, its activity is negligible under visible light irradiation and consequently its application is limited [1]. For this reason, studies have been conducted to reduce the bandwidth of TiO₂ into the visible light range through its doping. So far, there is an important
amount of literature related to Ag doped TiO$_2$ for the decomposition of organic molecules [2,3]. However, reports about Ag doped TiO$_2$ for water splitting hydrogen production under visible light are scarce [4,5]. Recently, researchers have concentrated in modifying TiO$_2$ with Ag to achieve a high-efficiency electron-hole separation by forming a Schottky barrier at the Ag-TiO$_2$, thus enhancing its photocatalytic activity [6,7]. Therefore, metal Ag, which is cheaper than other precious noble metals like Pt, Au and Pd, present a greater opportunity to modify TiO$_2$ [8].

Porous films have been obtained by using PEG as a chelating agent. Some researchers used PEG in order to control the porosity of Fe$^{3+}$ doped TiO$_2$ films starting with Ti(OC$_2$H$_5$)$_4$ as TiO$_2$ precursor and PEG with molecular weight of 600. The porosity increases with the PEG amount introduced in the film. Other researchers prepared TiO$_2$ films starting with Ti(OC$_3$H$_7$)$_4$ and PEG with different molecular weights and amounts. The amount of PEG used in the papers mentioned above varied between 1 and 9% [9].

In the present work, we prepared porous Ag/TiO$_2$ thin films by a sol-gel spin-coating process using titanium alkoxide with and without organic or polymer compound additives. The phase analysis was done using GIXRD. The morphology of the sample were observed using FESEM and the surface topography and roughness of the thin films were characterized and analyzed with atomic force microscopy (AFM).

2. Methodology

All the chemicals used in the study were of analytical reagent grade, or the highest purity available from several suppliers and were used as received. Titanium tetraisopropoxide (TTIP) was purchased from Acros, Silver Nitrate (AgNO$_3$) from Bendosen, and Acetic Acid (37%) were from J. T. Baker. Other reagents used were ethanol and 2-propanol from Qrec. The additive agent used in this experiment is Polyethylene Glycol 2000 (PEG 2000), from Merck, Germany. When precursors with strong reactivity towards water (like titanium alkoxides) are used, the hydrolysis reaction can result in precipitation. The problem can be overcome using non-aqueous sol-gel techniques with titanium chloride or titanium alkoxides as a precursor. In case of the reactions using TiCl$_4$ as a precursor, TiO$_2$ forms under release of a large amount of HCl gas. Because HCl gas is toxic and chlorine impurities often remain in the final oxide material, we preferred titanium isopropoxide as precursor. In order to increase the stability of the solutions from titanium alkoxide precursors, it is not sufficient to switch to a non-aqueous sol-gel route. Indeed a chelating agent is still needed in a non-aqueous sol-gel route to obtain highly stable sols [10].

Procedures of solution preparation can be referred to our previous study [11] For the doped PEG Ag/TiO$_2$ sols, 0.3g of PEG 2000 was added and the solution were kept stirring until it was completely dissolved.

The PEG doped and undoped Ag/TiO$_2$ thin films were characterised structurally through GIXRD, morphologically by FESEM and AFM. The phase composition of the synthesized thin film were determined by using an Grazing Incident X-ray diffraction (XRD) over a 20 range 10°-80° using Cu K$_\alpha$ ($\lambda=1.5046$). Analysis of the XRD pattern will be carried out using Diffrac Eva Software. Systematic information on the thin film morphology was obtained by (FESEM). The topographical 2D and 3D AFM images were taken over area of 5 x 5μm, for displaying purpose and subsequent statistical data analysis.

3. Results and Discussion

3.1 Phase Analysis

Measurements were performed in the 10-80° range using for the PEG doped and undoped Ag/TiO$_2$ thin films as shown in Figure 1. The undoped Ag/TiO$_2$ thin film shows a sharp and intense peak in spectra are indication of the presence of highly crystalline films. The observed diffraction peaks matched the characteristic peaks for the crystal structure of anatase coincide with the JCPDS Card No: 01-078-2486. The diffraction peaks shows the 20 at 25.31°, 35.57°, 48.04°, 55.07° and 62.69° which
were corresponding to (101), (112), (200), (211) and (204) plane, respectively. However, the X-ray pattern for the doped PEG Ag/TiO$_2$ thin film showed a shape and intensity of the diffraction lines is not representative for well-crystallized, but for nanosized, poorly crystallized materials. The addition of the PEG 2000 in the Ag/TiO$_2$ influenced on the unit cell parameters of anatase [10]. Both doped and undoped PEG 2000 Ag/TiO$_2$ thin films shows the presence of Ag nanoparticles with the characteristic peak at 37.04˚ with the plane of (101).

![Figure 1: XRD patterns of doped and undoped PEG Ag/TiO$_2$ thin films.](image)

3.2 Morphology and Topography Observations

Field Emission Scanning Electron Microscope (FESEM) was utilized to observe the surface morphology of doped and undoped PEG on Ag/TiO$_2$ thin film. As shown in Figure 2 (a), the undoped Ag/TiO$_2$ thin film exhibit the forming of wormlike TiO$_2$ grains with white spots uniformly distributed throughout the samples. Considering that heavy elements (e.g. Ag) backscatter electrons more strongly than light elements (e.g. O, Ti), the metallic silver appears brighter in the image. Instead of having a smooth surface, the Ag/TiO$_2$ composite films displayed a rough surface morphology. The addition of silver salt results in a more mesoporous TiO$_2$ matrix, which includes TiO$_2$ crystallites of 10–20 nm in size and small Ag nanoparticles (white spots) with various sizes ranging from 10 to 30 nm. For the doped PEG Ag/TiO$_2$ thin film, it can be detected that the Ag nanoparticles became gradually aggregated but still remained roughly uniform on the surface, as shown in Figure 2 (b).

Although the size of the silver particles is smaller with diameter around 10 nm, there are more nano-pores detected in the thin film. It is reported that heating promotes aggregation of Ag atoms. As radius of Ag$^+$ ions (ca. 126 pm) is much larger than that of Ti$^{4+}$ (ca. 68 pm), the Ag$^+$ ions introduced by the sol–gel process would not enter into the lattice of the TiO$_2$ anatase phase. When the samples were heat-treated to a certain temperature, the reduction of Ag$^+$ to Ag$^0$ took place as the AgNO$_3$ decomposed. During the annealing process, these uniformly dispersed Ag$^+$ ions would gradually migrate along with the anatase grain boundaries to the surface of the TiO$_2$ film, while TiO$_2$ anatase grains would grow at the same time. Finally, the Ag$+$ ions probably exist on the surface of the anatase grains by forming Ag–O–Ti bonds. In literature study, the movement of the resulting nanoparticles in the TiO$_2$ matrix could also be restricted by tuning the molar ratio of water to Ti when adding the Ag$^+$ preparing sol, and hence particle aggregation is controlled. The anatase grain growth is thereby depressed and the specific surface area increases. The porous feature of the film indicates that it should have a rough surface [12].
AFM has been demonstrated to be a very versatile and powerful tool for surface imaging at the submicrometer level and the revelation of the surface characteristics of the films. AFM was used to characterize the morphology and surface roughness of the samples. The darkest and brightest regions of all AFM images in this paper correspond to those regions with the largest height gradients. The brightness of a region corresponds directly to its height. Figure 3 shows the representative top view images and angle view images of the surface morphology of a scan area 5 $\mu$m x 5 $\mu$m of the doped and undoped PEG Ag/TiO$_2$ composite films on silicon wafers by three spin-coating cycles. It was observed that the surface morphology and roughness of the nanocrystalline thin films reveal a significant difference between doped and undoped PEG Ag/TiO$_2$. The film prepared without PEG is covered with homogenously dispersed silver particles and has a surface roughness of 3.020 nm and statistical mean roughness 7.700 nm. The particle size and average roughness of the film decreased with the addition of PEG into the sol, which is 2.300 nm and statistical mean roughness is 5.238 nm. The Ag particles were dispersed uniformly, throughout the samples (white dot), but in the doped PEG Ag/TiO$_2$, there were more larger size of Ag particles, shows that the Ag particles are agglomerates, in agreement with FESEM results. The PEG present in Ag/TiO$_2$ leads to the agglomeration of Ag particles, hence the TiO$_2$ matrix with less Ag particles distribution become smooth, and the surface roughness value is lower than Ag/TiO$_2$ particles without PEG.
Figure 3: AFM micrograph of (a) undoped Ag/TiO$_2$ thin film (b) doped PEG Ag/TiO$_2$ thin film

4. Conclusions
This work observes the effect of doped and undoped PEG on the growth of Ag/TiO$_2$ thin films synthesized via sol-gel spin coating method. X-Ray diffraction shows both samples, doped and undoped PEG Ag/TiO$_2$ exhibit peaks of anatase TiO$_2$ and Ag particles. FESEM observation shows some agglomeration of Ag particles on the sample of doped PEG Ag/TiO$_2$. As for the topography analysis, the surface roughness of the sample decreased for the doped PEG Ag/TiO$_2$.

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