Titanium dioxide (TiO_2) and silver/titanium dioxide (Ag/TiO_2) thin films with self-cleaning properties

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Abstract

In this work, TiO_2 and Ag/TiO_2 thin films were synthesized on glass by combination of sol-gel method and dip-coating deposition technique. Thermal treatment in temperatures ranging from 100 °C to 500 °C was used to evaluate changes in structure, morphology and texture of these materials. Adherent and microcrack-free films were obtained. The structural and morphological evolution with temperature was studied by X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM). Average particle size and roughness were determined by atomic force microscopy (AFM). The films were tested for wettability by measuring the contact angle between a drop of distilled water and the material surface. Results of hydrophobic/hydrophilic tests using UV-C irradiation showed that the films change their hydrophobic character to hydrophilic reaching even the superhydrophilic character which indicates their potential application as self-cleaning coatings.

Keywords: Thin films, titanium dioxide, silver, sol-gel, self-cleaning.

Introduction

Several current technologies are moving towards the nanoscale, allowing the discovery of a wide range of properties and applications for nanomaterials as titanium dioxide (TiO_2) **[1]**. TiO_2 is a multifunctional semiconductor that can be found as different polymorphs: anatase, rutile and brookite and also in different structural design as irregular nanoparticles, nanospheres, fibers, nanotubes, nanosheets and thin films **[2**, **3]**. The variability of morphology, shape, size, crystallographic phase and surface properties shown by TiO_2 enables its application in photocatalysis **[3-5]**, dye-sensitized solar cells **[6]**, gas sensors **[7]** and as a self-cleaning material **[8**, **9]**.

In recent years, the development of TiO_2-based self-cleaning materials has received considerable interest and the understanding of their structure-function relationship has enabled the application in various fields of technology as window glasses **[10]**, fabrics **[11]**, building materials **[12]** and solar panels **[13]**. In the case of TiO_2 thin films, two mechanisms are responsible for the self-cleaning property: (i) the hydrophilic mechanism in which the material absorbs sunlight leading to the degradation of the pollutants and (ii) the hydrophobic mechanism which causes the water drops roll off the surface, removing the contaminants from the surface **[14]**. In a hydrophilic surface, the semiconductor can absorb photons with equal or greater energy than its band gap value promoting the electron-hole pair formation, which involves the issuance of an electron (e^-) from the valence band to the conduction band, generating a hole (h^+). The formed pairs can recombine within a few nanoseconds, releasing the energy as heat or, otherwise, the positive and negative sites can react with water and oxygen molecules that are acceptor or electron donors, which are adsorbed on the surface of the semiconductor material **[15]**.

Some studies have demonstrated the application of TiO_2 thin films as a self-cleaning coating, but correlated studies involving textural, morphological and structural properties are required to make the technology more feasible. Wang F. *et al.* **[16]** have prepared anatase-TiO_2 nanosheets array on the glass substrates using a combination of sol-gel process and thermal treatment in autoclave. The TiO_2 films obtained show good wettability and photocatalytic activity to rhodamine B. Meher S.R. *et al.* **[17]** have used the sol-gel spin-coating method to prepare TiO_2 thin films with photocatalytic and electrochromic properties to application in self-cleaning smart windows. The authors did not check the hydrophilic/hydrophobic behavior of the films. Hydrothermal method has been used by Saif M. and coworkers **[18]** to produce nanocrystalline TiO_2 thin films in anatase phase with high self-cleaning activity and photochemical degradation property to remazol red RB-133.

The limitation related to the recombination time of electron-hole pairs in TiO_2 semiconductor has opened a research field to studies involving TiO_2 doping with various molecules or non-metal and metal nanoparticles, which enable to extend the light absorption range, also functioning as an electron trap and increasing the efficient of the photocatalyst **[19]**. Weng K-W. *et al.* **[20]** have used the physical vapor deposition (PVD) and metal plasma ion implantation to prepare anatase-TiO_2 thin films doped with Fe, Cr and V. Measurements of contact angle have shown that the Fe increased the hydrophilicity of TiO_2 film under UV irradiation and the doping process also increased the sunlight absorption with the addition of all three elements. In some studies, metallic silver nanoparticles have been used to doping TiO_2, increasing the recombination time of the electron-hole pairs and enhancing the photocatalytic activity of this semiconductor **[21**, **22]**. Navabpour P. *et al.* **[23]** have demonstrated the improvement of self-cleaning property and antimicrobial potential of the Ag/TiO_2 compared to TiO_2 thin films in mixed anatase/rutile phases prepared using reactive closed field unbalanced magnetron sputtering. Several researchers have used the sol-gel process to prepare thin films due to advantages as: its "green" coating technology with low impurities and waste-free, besides its processing at room temperature and low cost **[24]**.

In the present work, TiO_2 and Ag/TiO_2 thin films were prepared by sol-gel route using precursors as titanium (IV) isopropoxide and silver nitrate in isopropyl alcohol solution to deposition on glass substrates by dip-coating method. Heat treatments are used to obtain a desired crystal structure and to control the porosity and morphology of the coatings. Finally the films were characterized and tested for its hydrophobic/hydrophilic behavior to check the possibility of application as self-cleaning coatings.

Experimental

Synthesis of TiO_2 and Ag/TiO_2 thin films

The sol-gel solution was prepared using titanium (IV) isopropoxide 97% (Sigma-Aldrich) in isopropyl alcohol PA (Merck) as precursor of TiO_2 and silver nitrate (Sigma-Aldrich) as precursor of silver nanoparticles. Physical-chemistry properties of the precursor solutions as pH, density and viscosity were controlled to allow the tailoring of particle size and morphology in the thin films. The solutions were kept under magnetic stirring for 1 hour and subsequently acetic acid was added until they reach a pH between 2 and 4. The Ag:Ti molar ratio of the solution used as precursor of Ag/TiO_2 films preparation was 1:45. This solution was submitted to irradiation by ultraviolet C (UV-C) for 2 hours using a fluorescent mercury lamp Girardi RSE20B, power 15 W and $\lambda = 254$ nm. The glass substrates used were pre-cleaned in an ultrasonic bath with distilled water, acetone and isopropyl alcohol and then dried at 70 °C. The substrates were coated with 1 up to 5 layers by dip-coating method and the films deposited were heat treated from 100 °C to 500 °C during 10 min. Since the method dip-coating is used for the deposition of thin films, this step of the process should be carried out at a controlled withdrawal speed and free from vibration or external interference in order to allow the deposition of a homogeneous film with controlled thickness **[25]**.

Characterization techniques

To evaluate the textural properties of the films, topographical and 3D images were obtained by AFM in a microscope Asylum Research® - model MFP3D where Van der Waals interaction forces were monitored. To determine the crystalline phases, XRD was used in a Shimadzu XRD-7000 diffractometer using Cu tube, K_α ($\lambda = 1.54056$ Å) at 40.0 kV, current of 30 mA and scanning speed of 2° min^{-1} in a range of $20° < 2\theta < 60°$. Microstructure was analyzed by HRTEM in a microscope FEI Tecnai G2-20 with tungsten filament at 200 kV equipped with electron diffraction. The coatings were scraped off and deposited on 200 mesh copper grid Holey Carbon type.

Wettability tests

The wettability of the material was studied from measuring the contact angles of a drop of distilled water with controlled volume in the surface of the TiO_2 and Ag/TiO_2 thin films. The films were photographed with a digital camera SONY DSC-S930 model with a resolution of 10.2 megapixels. The contact angles were determined in three situations: before and after the samples were irradiated by UV-C and after remaining in the dark for 7 days **[8]**.

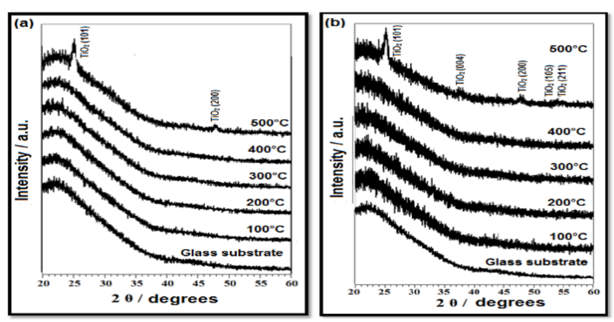

Fig. 1. The XRD patterns of (a) TiO_2 and (b) Ag/TiO_2 thin films with 5 layers treated at temperatures showed.

Results and discussion

The precursor solutions obtained by sol-gel method exhibited appropriate viscosities at the range of 2cP to 5 cP for the preparation of homogeneous, adherent and free of microcracks TiO_2 and Ag/TiO_2 thin films. According to XRD patterns shown in **Fig. 1**, only the films heated at

500 °C showed indexed peaks characteristic of crystalline anatase phase. The diffractograms for the other heated samples was typical of an amorphous structure even at 400 °C, temperature at which the thermodynamic stability of the anatase phase is expected, as shown elsewhere **[26]**. According to resolution of the diffractometer used, the rapid heating was not providing the necessary energy to promote the complete crystallization of the sample heated at 400 °C. No evidence of metallic silver crystallization was observed in the diffractograms.

The AFM images in **Fig. 2** shows homogeneity in deposition of the TiO_2 thin films heated at 300 °C and 500 °C. The amorphous film treated at 300 °C showed a root mean square (RMS) roughness value of 0.33 nm and no definition in particle shape as shown in **Fig. 2a**. Crystalline nanoparticles with average particle size of 30 nm are visualized to the thin film treated at 500 °C, which showed 1.1 nm in RMS roughness.

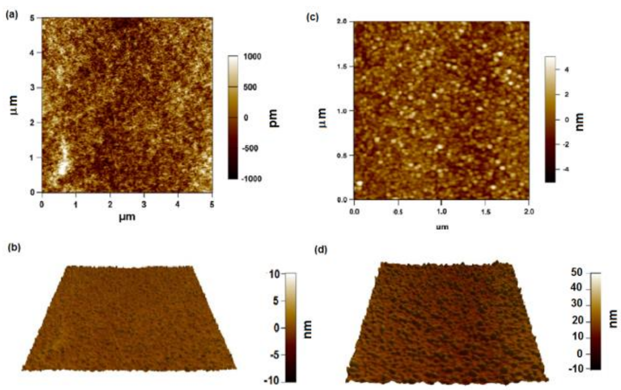

Fig. 2. AFM topography and 3D images of TiO_2 thin films treated at (a and b) 300 °C and (c and d) 500 °C.

The surface profiles in **Fig. 3** of Ag/TiO_2 thin films reveal that both samples treated at 300 °C and 500 °C have greater roughness values compared to TiO_2 thin films. The presence of silver submicrocrystals on the surface of the films influenced the RMS roughness values that are 25 nm and 12 nm to the nanocomposite films treated at 300 °C and 500 °C, respectively. As observed to TiO_2 films, only the sample treated at 500 °C **(Fig. 3b)** showed well-defined TiO_2 crystalline nanoparticles with average particle size of 40 nm.

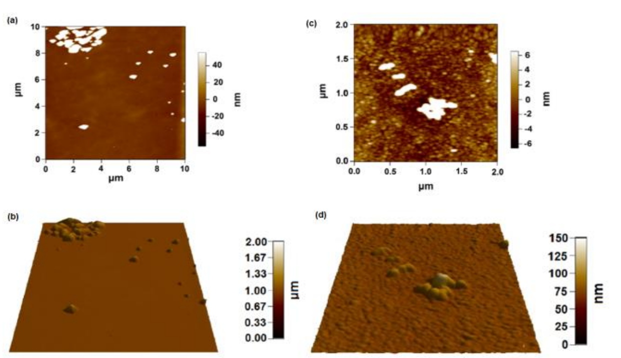

Fig. 3. AFM topography and 3D images of Ag/TiO_2 thin films treated at (a and b) 300 °C and (c and d) 500 °C.

According to literature, TiO_2 thin films with greater roughness and crystal sizes have shown higher hydrophilicity and photocatalytic performance [**27**].

HRTEM was used to investigate the unexpected amorphous character observed by XRD technique to TiO_2 and Ag/TiO_2 thin films treated at 400 °C. According to TEM image and electron diffraction shown in **Fig. 4**, nanoscale crystallite traces of anatase phase were observed, demonstrating the partial crystallization of this TiO_2 film. **Fig. 4b** depicted from **Fig. 4a** showed a 7-nanometer crystallite with an interplanar spacing of 0.351 nm corresponding to anatase crystalline plane (101) and **Fig. 4c** showed an electron diffraction pattern characteristic of a polycrystalline film. Due to its high resolution, HRTEM enabled overcome the limited resolution of the XRD technique in the identification of a partial crystallinity of the samples. The results obtained by HRTEM, corroborated by electron diffraction shown in **Fig. 4d and e**, confirmed the amorphous character of Ag/TiO_2 film treated at 400 °C.

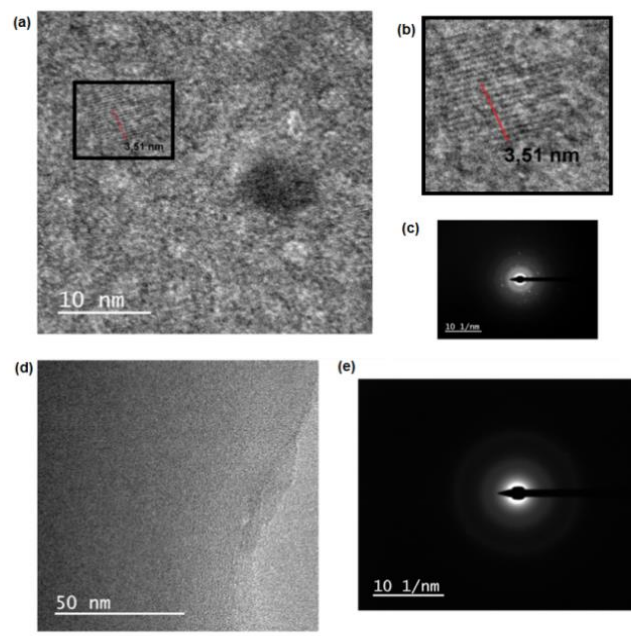

Fig. 4. HRTEM images and electron diffraction of (a, b and c) TiO_2 thin films and (d) and (e) Ag/TiO_2 treated at 400 °C.

Fig. 5 shows the values of the contact angles of the water drop on the surface of 1-layer thin films measured before and after UV-C irradiation and after left in the dark for 7 days. In general, it is observed that crystalline and rougher thin films have proved more hydrophobics. The films diminish their contact angles systematically after irradiation becoming more hydrophilics. **Fig. 5h** showed a contact angle of 0° to Ag/TiO_2 film treated at 500 °C, showing its superhydrophilic character. Sakai and coworkers **[28]** have shown by X-ray photoelectron spectroscopy (XPS) that the ultraviolet irradiation in air promotes the hydroxyl groups (-OH) formation on the TiO_2 surface, surface reducing the hydroxyl amounts attached directly to oxygen vacancies on the surface. The surface reconstruction takes place spontaneously in the dark, restoring the original angles as shown in **Fig. 5c**, **f and i**. Since the films showed hydrophilic/ hydrophobic behavior or even superhydrophilic as discussed above, TiO_2-based coatings have potential for application as a self-cleaning material.

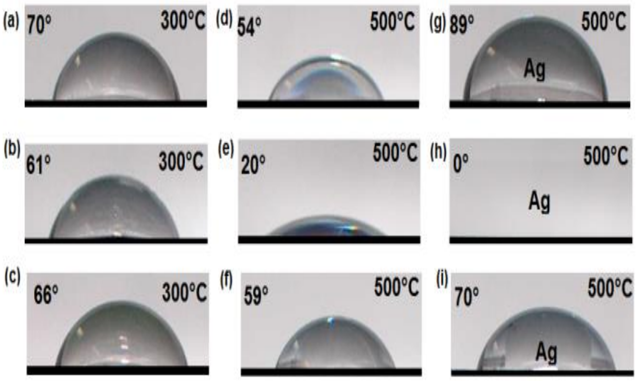

Fig. 5. Contact angles of a water drop on the surface of the TiO_2 and Ag/TiO_2 thin films where (a, d and g) represent the films before UV-C irradiation, (b, e and h) represent the films irradiated and (c, f and i) represent the films left 7 days in the dark. Images (a to f) and (g to i) represent the TiO_2 and Ag/TiO_2 thin films, respectively.

Conclusion

In this work, TiO_2 and Ag/TiO_2 thin films deposited on glass substrates have been prepared from sol-gel method using $AgNO_3$ as a precursor for metallic silver. The films treated at 500 °C crystallinity demonstrated by XRD and the HRTEM technique associated to electron diffraction. It was determined the presence of anatase nanocrystallites embedded in TiO_2 matrix, which formed the structure of the TiO_2 thin film treated at 400 °C. AFM images confirmed the homogeneity of the TiO_2 thin films heat treated at 300 °C and 500 °C and enabled the measure of average nanoparticles sizes of both TiO_2 and Ag/TiO_2 thin films, besides the submicrometric sizes of silver on the surface of the nanocomposite film. The Ag/TiO_2 thin film treated at 500 °C showed change of its hydrophobic character for superhydrophilic when submitted to UV-C radiation and all thin films prepared had surfaces with reversible hydrophobic/hydrophilic characteristics.

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Author's contributions

Conceived the plan: A.F.R.S., N. D. S. M., M. M. V.. Performed the experiments: A.F.R.S., M.M.V. Data analysis: A.F.R.S., N. D. S. M., M. M. V. Wrote the paper: A.F.R.S., N. D. S. M., M. M. V. Authors have no competing financial interests.

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