Hydrophobic properties of high Fe$^{3+}$ ion containing Fe$_2$O$_3$-TiO$_2$ coatings

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Abstract. The treatment of environmental pollution using semiconductor photo catalysis converts contaminants to innocuous products, such as CO$_2$ and H$_2$O. The most promising semiconductor photo catalysts are titania based materials. However, the main drawback of titania anatase polymorph is the large band gap which limits the spectrum of photons that can create electron–hole pairs to participate in oxidation or reduction. In this study Fe$_2$O$_3$–TiO$_2$ coatings were successfully prepared on soda-lime silicate glass slide substrates using sol–gel method. Coating surface and morphology has been studied using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM). Coatings were obtained using dip-coating method. The present research is devoted to the studies of aging time and heat treatment effects on films hydrophobicity. The purpose of this contribution was the development of iron oxide rich Fe$_2$O$_3$–TiO$_2$ hydrophobic thin films depending on different preparation parameters. SEM and AFM investigation revealed the formation of two layered, porous coating microstructure consisting of rough flattened areas which formed the backbone for irregularly shaped particles.

1. Introduction

In recent years, environmental clean-up and water splitting applications have been one of the most active areas in heterogeneous photocatalysis. [1,2]. Titanium dioxide (TiO$_2$) offers various advantages such as low cost, no secondary pollution, photoreaction occurring at room temperature and atmospheric pressure [3], optical and electronic properties, chemical stability, non-toxicity [4–6].

TiO$_2$ as a semiconductor photocatalyst has been widely used in the degradation of various organic compounds into harmless CO$_2$ and H$_2$O [7,8]. Photocatalytic performance is essentially determined by the radicals (e.g. O$_2$‘, h', OH') generated during irradiation [9]. When TiO$_2$ is irradiated by UV rays, electron-hole pairs are created. The holes react with water molecules or with the hydroxyl ions and hydroxyl radicals are formed, which are strong oxidants of the organic molecules. It has been shown that the photocatalytic activity of TiO$_2$ is influenced by the crystal structure (anatase and rutile), surface area, size distribution, porosity, surface hydroxyl group density, etc. These properties have an influence on the production of electron–hole pairs on the surface adsorption and desorption processes as well as the redox process [5].

However, TiO$_2$ requires UV light photoactivation, a disadvantage when the applications are focused on solar sunlight, only accounting with 5% of UV irradiation at sea level [10,11]. Transition metal ions (iron, copper, zinc, cobalt and nickel), have been used as dopants for TiO$_2$ photosensitization to harvest maximum energy of the sunlight [5, 12–14].
Among various transition metal ions, most researchers found that the incorporation of Fe$^{3+}$ can enhance the photocatalytic activity of TiO$_2$ [15]. Several studies reported that iron-doped titanium oxides show catalytic activity in several catalytic reactions such as the oxidation of cyclohexane, acrylic acid, methylene blue dye and 4-chlorophenol degradation $\alpha$-pinene oxide isomerization, O-cresol photo-degradation and methanol oxidation [3,12,16–18]. Catalytic activity of Fe/Ti oxide coatings and powders should largely depend on the preparation methods, iron content, sintering temperature, coating thickness [19], particle size and phase composition [20].

The development of superhydrophobic surfaces is of special interest, because properties such as anti-sticking, anti-contamination, and self-cleaning are expected [21]. One unique property of the sol–gel process is the ability to go all the way from the molecular precursor to the product, allowing a better control of the whole process and the synthesis of tailor made materials (monolithic gels, fibbers, films and powders) for various applications [5]. Thus, it was expected that by tailoring the preparation procedures of sol-gel thin film hydrophobic surfaces could be developed.

2. Experimental

High Fe$^{3+}$ ion amount (65 mol% Fe$_2$O$_3$, 35 mol% TiO$_2$) containing Fe$_2$O$_3$–TiO$_2$ sols were prepared using titanium (IV) tetraisopropoxide with a purity of 97% (MERCK), iron (III) chloride hexahydrate (FeCl$_3$ × 6H$_2$O) with a purity of 99% (Aldrich), ethylene glycol (99%, Aldrich), acetic acid (99%, Lach-ner), and isopropanol (99.5% Aldrich). In the first step of the sol synthesis, 80.8g of FeCl$_3$ × 6H$_2$O was dissolved in 100 mL of ethylene glycol preparing solution A. The solution A was stirred for 4h at 40 °C. In the second step, 0.6 mL acetic acid which was used as a chelating agent [22] and 6.43 mL of titanium (IV) tetraisopropoxide were mixed and then 29.36 mL of isopropanol (99.5% Aldrich) was added to the solution while stirring. Predetermined amount of solution A (65 mol% Fe$_2$O$_3$) then was added to a mixture B dropwise while stirring and then 0.4 mL of glycerol (98%, Fluka) as a drying process controlling chemical additive [23] was added obtaining sol solution. Finally obtained sol was treated by ultrasound for 5 minutes. The total volume of the prepared sol was 50 mL. The Fe$_2$O$_3$–TiO$_2$ system coatings were prepared by dip-coating method as described in a previous work [24]. Schematic flow chart of sol-gel synthesis is shown in Figure 1.

![Flow chart of sol-gel processing for Fe$_2$O$_3$-TiO$_2$ films.](image)

Soda-lime silicate glass slides (Menzel) with dimensions of 25x75x1 mm were used as substrates for thin films deposition. Dishwashing liquid, distilled water, 1M HNO$_3$ and ethanol were used to clean and prepare glass slides for further experiments as shown (Fig. 2).
Figure 2. Glass slide preparation for dip coating process.

One and two layers of film was deposited by dip-coating process as it has been shown that different dip-coating techniques reasonably could affect the properties of thin films [25]. Substrates dipped/withdrawn with 60 mm/min speed and held in the sol for 30 seconds. The optimized heat treatment was used as follows. The films were dried at room temperature for 15 min, annealed at 500 °C, with temperature increase regime 5 °C/min starting from room temperature and held at 500 °C for 1-5 h in air. TiO₂-Fe₂O₃ powders were prepared by drying each sol at 60 °C for 72 h in air. Honey like mass then was placed in a crucible and were thermally processed in the same way as the films.

Crystalline phases were determined using X-ray diffraction analysis (Rigaku Ultima+) with CuKα radiation from 20 to 60 2θ degrees. The morphology and topography of coatings was analysed using field emission scanning electron (FEI Nova NanoSEM 650) and atomic force microscopes (CP II VEECO Scanning Probe Microscope), respectively. UV/VIS spectrophotometer (Shimadzu SolidSpec – 3700 and Genesys 10S UV-VIS) were used to determine the optical properties of coatings. The surface wettability was evaluated by measuring the contact angle of water droplets deposited on the film surface under ambient conditions by the use of Attension Theta Optical Tensiometer - Biolin Scientific.

3. Results and discussion

Figure 3 a-d shows the coating surface morphology and topography revealed by FESEM and AFM studies. Comparing FESEM micrographs it was observed that both 1 h, and 5 h annealed coating (Fig. 3 a and d respectively) morphology could be described as containing pores and irregularly shaped particles with the size of 50-200 nm. The remarkable difference is the presence of rough flattened areas which forms the backbone for irregular particles (Fig.3 a). Particle and pore size increased while rough flattened areas disappeared increasing the time of the heat treatment. This was confirmed by the AFM measurements. It was determined that the approximate height of particles, which size/length and proportions increased by increasing the heat treatment time from an average of 77 nm to 103 nm (during 1-5 h period). As can be seen, that the average calculated particle height increased by 33%, which confirms the fact that decline of the contact angle is associated with the increase in the average surface roughness. The XRD pattern of the Fe₂O₃-TiO₂ coating and xerogel is shown in Fig. 4a and 4b. 14 glass slide substrates with coatings were mechanically scraped off to find out crystalline phase formation on the surface of the sample. The pattern shows diffraction peaks related to α-Fe₂O₃ (hematite) and TiO₂ phases (anatase) for coatings (Fig. 4a.) and as well brookite and rutile for calcined xerogel (Fig. 4b.). Coated sample XRD peaks showed formation of sodium chloride crystalline phases. We assume, that sodium ions come out of the soda lime glass slide surface and reacts with chloride ions formed during calcination process. That is why xerogel did not showed this crystalline phase formation. No considerable peaks related to Fe–Ti composition phases were observed in the pattern, may be due to weak intensity of such peaks and/or formation of small amounts of such phases. It can be seen that the peaks at 20 of 25.28, 38.08 and 47.92 are assigned to (1 0 1), (0 0 4) and (2 0 0) lattice planes of TiO₂ [26]. Additional peaks assigned to rutile, brookite and hematite were found as well [27,28].
Figure 3. FESEM and AFM images of coatings heat treated at 500 °C during 1h (a and b) and 5h (c and d). The inset of the figure shows the 3D topography of AFM images.

Figure 4. XRD of Fe$_2$O$_3$-TiO$_2$ heat-treated samples: a) coating scraped off from 14 coated glass substrates; b) heat-treated xerogel powder.
From light absorption spectra shown in Figure 5a, it follows that the maximum coating light absorbance is observed in the range below 300-400 nm. This decrease is due to the fundamental absorption of light caused by the excitation of electrons from the valence band to the conduction band of TiO\textsubscript{2}. High iron content shifts (red shift in the region 400 to 550 nm) light transmittance and absorption edge towards longer wavelengths [29]. In hematite crystal case, the low transmittance (or absorption (1−T))/ high absorption at 400–600 nm wavelength region can be assigned to the pair excitation (electron and an electron hole formation/interaction), possibly overlapped by the charge-transfer band tail [19]. Moreover, the low absorption/higher transmittance at wavelength region of 600–750 nm is assigned to the charge-transfer transition at about 640 nm [19,30]. By increasing the heat treatment time of the TiO\textsubscript{2}-Fe\textsubscript{2}O\textsubscript{3} thin films, the transmission of the film (at wavelengths > 400 nm) decreased due to film thickness increase [19] and particle growth, which can be seen by AFM and SEM measurements. Looking at the specular light reflection spectra (Fig. 5b) shows that samples minimally reflect light waves below 500 nm range. This shows that the obtained samples absorb light also in the visible light spectral range.

![Figure 5. Sample optical properties after heat treatment 1-5 hours: a) UV/VIS light transmittance; b) light reflectance spectra.](image)

Table 1 data shows that the coating drying, deposition and heat treatment affected properties of contact angle changes. Four coating preparation methods were used. According to the method A, single layer coating was deposited immediately after sol preparation, then dried at ambient atmosphere for 15 min, and calcined in the furnace. Method B: two coating layers were deposited and cured instantly after the preparation of sol. The 1st layer of coating was treated at 200 °C for 5 minutes, then cooled down to the room temperature, and then coated with the 2nd layer of sol and dried at ambient atmosphere for 15 minutes. Final thermal treatment was done at 500 °C. Method C: single coating deposited and cured after aging of sol during 24 h, then calcined at 500 °C. The method D differs in that two layers were deposited and cured after 24h aging of sol. The first layer was dried in the air after the deposition during 15 min, then the second layer was deposited, dried in air for 15 min and finally calcined at 500 °C. All coatings prepared according methods A-D were cured in a muffle furnace keeping the temperature regime mentioned before. Prolonged heat treatment time caused a decrease of contact angle. As shown in previous research the coating preparation, deposition speed and heat treatment time affects the surface and the properties of coating, including contact angle. The contact angle of calcined coatings was under 30°. The formation of hydrophobic surface observed after storing the coated samples at laboratory ambient conditions for 1 week. The change of contact angle after storing of samples could be caused by the interaction of moisture and CO\textsubscript{2} with the surface of coatings.
Table 1. Contact angle of coatings depending on the methods of coating preparation.

| The method of sample preparation | Contact angle of coatings after one week storage at ambient atmosphere and temperature depending on heat treatment time at 500 °C |
|---------------------------------|-------------------------------------------------------------------------------------------------------------------|
|                                 | After 1 hour<sup>a</sup> | After 2 hours<sup>a</sup> | After 3 hours<sup>a</sup> | After 4 hours<sup>a</sup> | After 5 hours<sup>a</sup> |
| Method A                        | 139,0-141,1°              | 128,9-124,5°              | 113,2-106,3°              | 84,9-81,9°                 | 75,5-60,3°                |
|                                 | 139,5-137,6°              | 122,0-117,7°              | 108,8-100,8°              | 88,7-84,5°                 | 79,4-68,2°                |
| Method B                        | 113,1-110,0°              | 112,1-106,4°              | 113,6-111,6°              | 104,7-102,3°               | 94,7-83,5°                |
|                                 | 108,7-107,2°              | 107,5-98,8°               | 100,7-92,3°               | 103,4-96,9°                | 89,5-85,2°                |
| Method C                        | 142,3-140,0°              | 133,9-128,2°              | 94,9-92,5°                | 98,1-91,1°                 | 58,0-48,8°                |
|                                 | 140,2-137,5°              | 124,9-119,8°              | 102,6-96,6°               | 97,8-90,6°                 | 52,6-46,4°                |
| Method D                        | 137,3-137,6°              | 138,4-133,9°              | 128,5-120,5°              | 113,7-105,0°               | 83,2-77,2°                |
|                                 | 139,2-139,1°              | 137,4-132,9°              | 124,7-119,0°              | 122,0-116,2°               | 96,7-85,5°                |

<sup>a</sup> Each row under the photograph of water droplet contains the data of contact angle of two measurements on different places of the sample. The first data point in each row corresponds to the measurement of contact angle done as soon as the drop of water sticks to the sample, and the other one - after 10 seconds. The Attension Theta Optical Tensiometer gave contact angle measurement results starting from the moment when water droplet reached the surface of the coating to 10 sec. The volume of water droplet was 3-10 µL.

4. Conclusions

Crack free and homogeneous, sol-gel derived hydrophobic TiO$_2$-Fe$_2$O$_3$ thin films attaining water contact angle up to 140° were obtained onto soda-lime silicate glass slides. Morphology and topography studies of hydrophobic coatings performed by FESEM and AFM analysis showed the formation of two layered, porous coating microstructure consisting of rough flattened areas which formed the backbone for irregularly shaped particles with the size of 50-200 nm. The increase of calcination time of deposited sol-gel layers caused the decrease of contact angle. Prolonged calcination time resulted in the decrease of particle size onto surface of coatings and contact angle due to the formation of larger crystallites. During prolonged calcination time of coatings, the increase of absorption in the visible region spectra was observed.

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