



# Investigation of the photodecomposition process of thin layers of arachidic acid on titanium dioxide coatings modified by silver nanoparticles observed *in situ* by atomic force microscopy



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## ABSTRACT

The photocatalytic process of arachidic acid decomposition on titanium dioxide in the form of polycrystalline anatase and on titanium dioxide modified by silver nanoparticles (AgNPs/TiO<sub>2</sub>) was observed using atomic force microscopy (AFM) and Fourier transform infrared spectroscopy (FT-IR). Arachidic acid (AA) was chosen as a model pollutant because its molecules have an ability to organize in the form of Langmuir – Blodgett monolayers on a water/air interface and, subsequently, may be transferred onto the surface of TiO<sub>2</sub> and AgNPs/TiO<sub>2</sub> coatings. Such a system is easily observable by AFM technique. As expected, titanium dioxide coatings induced the photocatalytic degradation of AA under UV illumination, however, in the presence of AgNPs this process ran either more rapidly or slower. The decomposition of AA proceeded through the continuous disappearance of AA layers while preserving the layer thickness. The received results allowed us to reach a conclusion about the mechanism which occurred during AA photodegradation on both types of coatings. It was suggested that the process was initiated in active surface sites and subsequently propagated until the whole amount of AA was decomposed. The linear dependence of the surface coverage vs. the time of illumination showing the degradation rate of AA layers indicates a zero kinetics order of reaction.

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## 1. Introduction

Titanium dioxide is one of the most widely known and intensively investigated photocatalyst, mainly because of its low cost, nontoxicity and ability to decompose hazardous substances in both air and liquid [1,2]. It was reported that titanium dioxide has an ability to decompose organic molecules, such as fatty acids, deposited on its surface under UV illumination [3–8]. Yadav et al. found that doping anatase nanoparticles by metals causes an exhibition of absorption in visible light range in comparison with pure TiO<sub>2</sub> [9,10]. The presence of noble metals such as platinum [11], palladium [12] and silver nanoparticles [13] induced a higher efficiency of the photodegradation process due to the better separation of electron (e<sup>-</sup>) – hole (h<sup>+</sup>) pairs [14]. Since the work function of silver (−4.26 eV) is below the conduction level of titanium dioxide, which is −4.2 eV, the recombination of photo-generated electrons with holes is slowed down, making the

photoactivity of the AgNPs/TiO<sub>2</sub> system more efficient. This property was used to improve the efficiency of the degradation of fatty acids in air as an example of the decomposition of solid pollutants adsorbed on the surface of the photocatalyst.

Today's literature provides examples of such investigations. Photodegradation of a Langmuir – Blodgett film of stearic acid was investigated *in situ* and reported for the first time by Sawunyama et al. in 1997 [4]. Monolayers of stearic acid were deposited on the surface of polycrystalline anatase and the decomposition process under UV illumination was observed using atomic force microscopy and FT-IR. After 10 min of illumination, 50% of stearic acid was decomposed. After 60 min of UV illumination, a complete disappearance of the adsorbed compound was observed, which was confirmed by FT-IR investigations.

In another paper devoted to the photocatalytic decomposition of stearic acid, Sawunyama et al. investigated the photodegradation of stearic acid completely or partially covering the TiO<sub>2</sub> rutile single crystal (110) surface [15]. The organic compound created round, island-like structures of various sizes, which had not been presented in other papers. According to the authors, these domains were formed already at the water – air interface, before deposition

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on the  $\text{TiO}_2$  surface. These structures are thermodynamically more favorable due to the reduction in interfacial length and curvature, which results in a minimalization of the surface energy. The average thickness of the layers was 2.13 nm. The reactivity of round domains at the edges of the island was comparable to the reactivity in their interior. The photodegradation process was initiated in active sites, which were randomly distributed on the surface of titanium dioxide. Subsequently, the photodegradation process was propagated by the constant growth of photodegraded areas around the active sites and the creation of new ones. In all likelihood, at the same time there is a competitive process of passivation of active sites by the products of photocatalysis, which may inhibit the reaction. The authors suggest two possible routes of degradation: oxidation initiated by holes ( $h^+$ ) and radical oxidation of molecules nearby active sites.

Similar research was conducted by Zaleska et al. [16], who described the photodecomposition process on the surface of monocrystalline rutile and anatase. Lauric acid was used as a model pollutant and deposited using a spin – coating method. It was observed that lauric acid decomposed under UV illumination without changing the thickness of the layer while the domain surface decreased. Expanding fissures and pinholes were noticeable at the beginning of photodecomposition, while isolated domains were observed during further illumination. The surface areas of these domain structures decreased linearly while retaining a constant thickness [16]. It was also reported that the degradation of organic contaminants is enhanced in the presence of  $\text{SiO}_2$  layer between  $\text{TiO}_2$  layer and the substrate [17].

Besides AFM studies, spectroscopic investigations on the decomposition process of fatty acid were also performed.

An FT-IR survey of the decomposition of stearic acid multilayers deposited on a commercial self – cleaning Bioclean glass containing anatase under UV light was investigated [18]. The authors concluded that the molecule of stearic acid could be arranged in two ways: perpendicularly or at an angle of  $30^\circ$ . The thickness of the monolayer was calculated as 2.5 nm and 2.16 nm, respectively. The amount of adsorbed acid decreased linearly with

a constant decomposition rate, which indicated a zero kinetic order of reaction, caused by the high concentration of reactants.

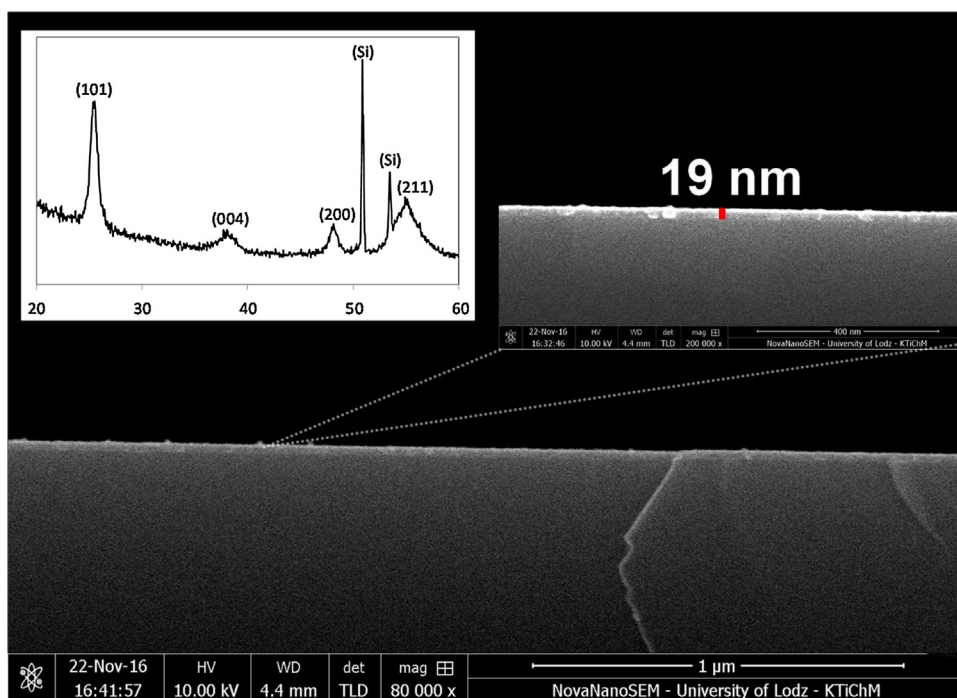
Although, these investigations were focused on describing the photodegradation process of model contamination on  $\text{TiO}_2$  *in situ*, to our knowledge, there are no reports about similar research on  $\text{TiO}_2$  coatings modified with silver nanoparticles ( $\text{AgNPs}/\text{TiO}_2$ ). Therefore, with the aim of elucidating the effect of  $\text{AgNPs}$  on the decomposition of fatty acids deposited on sol-gel  $\text{TiO}_2$  coatings, additional experiments showing the differences in the decomposition of AA between  $\text{TiO}_2$  and  $\text{AgNPs}/\text{TiO}_2$  were performed. In the present study, the photocatalytic properties of  $\text{TiO}_2$  and  $\text{AgNPs}/\text{TiO}_2$  was observed with the use of atomic force microscopy (AFM) and arachidic acid as a model contamination.

## 2. Experimental

Silicon wafers (100) were purchased from the Institute of Electronic Materials Technology, Warsaw, Poland. Analytical grade isopropanol (Aldrich Chemistry) was used as a solvent in a solution of tetraisopropoxide (Aldrich Chemistry).  $\text{AgNO}_3$  and arachidic acid (AA) were both purchased from Sigma-Aldrich (99% and 99.8% pure, respectively) and used without further purification. AA was dissolved in analytical grade chloroform, provided by Chempur.

### 2.1. Preparation of $\text{TiO}_2$ and $\text{AgNPs}/\text{TiO}_2$ coatings

Titanium dioxide coatings were deposited on silicon substrate using the sol – gel method described in our previous studies [19,20]. In brief, the acidic solution of titanium tetraisopropoxide and isopropanol was stirred for 20 min by magnetic stirrer and subsequently transferred onto a purified silicon substrate using a dip-coating method at the velocity of  $25 \text{ mm min}^{-1}$ . The coatings were annealed at  $100^\circ\text{C}$  and calcined at  $500^\circ\text{C}$  (for 2 h at both temperatures) in order to obtain an anatase structure which is known to exhibit the highest efficiency in photocatalysis among all  $\text{TiO}_2$  structures.



**Fig. 1.** Crosssectional view of  $\text{TiO}_2$  coating having the average thickness of 19 nm deposited on Si wafer. Inset: XRD pattern of  $\text{TiO}_2$  coatings on Si wafer showing reflections typical for anatase structure.

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