Ni Underlayer Effect for the Structure Development and Visible Light Photocatalytic Efficiency of Carbon-Doped TiO₂ Film

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Abstract – Photocatalytic treatment of contaminated aqueous solutions makes use of the specific interaction between photocatalysts and ultra-violet or visible light irradiation. This method belongs to the wider class of Advanced Oxidation Processes that generates reactive oxygen species (peroxides, superoxide, hydroxyl radical, singlet oxygen, etc.) and uses them for the non-selective oxidation of various organic and inorganic compounds. In THE current study magnetron sputtering technique was used to deposit carbon-doped TiO₂ films which are known to have significant photocatalytic activity in the visible light spectra and can be used for the neutralisation of contaminated solutions. Structural properties of the as-deposited films were analysed by XRD, XPS and AFM techniques, whereas their visible light photocatalytic activity was estimated by analysing Rhodamine B solution bleaching kinetics. When carbon-doped TiO₂ photocatalysts were formed on borosilicate glass XRD analysis showed that they consisted of mixed phase (rutile-anatase) TiO₂ where both phases contributed by similar parts. However, when the same deposition procedure was used to deposit carbon-doped TiO₂ films on glass covered by Ni layer, formation of metastable anatase phase was enhanced. Estimation of visible light photocatalytic activity of the films revealed that Ni underlayer had positive effect for the efficiency of Rhodamine B solution bleaching and it could be beneficial for the practical wastewater treatment systems. It was suggested that observed improvement was mainly achieved due to the structural changes of TiO₂ crystal phase, but other mechanisms like prevention of impurity diffusion from the glass substrate to the carbon-doped TiO₂ film, or positive Ni doping effect could not be excluded completely.

Keywords – Carbon-doped TiO₂; crystal structure; magnetron sputtering; visible light photocatalysis; water cleaning

Nomenclature

AOPs	Advanced Oxidation Processes	–
ITO	Indium Tin Oxide	–
DC	Direct current	–
MFC	Mass Flow Controller	–
XRD	X-ray Diffraction	–
XPS	X-ray photoelectron spectrometry	–
AFM	Atomic Force Microscope	–

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RhB	Rhodamine B	—
at. %	atomic percentage	%
Ra	Arithmetic average roughness	nm

1. INTRODUCTION

During the last century viewpoints and official policies on environment issues have undergone several remarkable changes [1]. During the first half of the 20th century society, politics, and industry were mostly focused on solving economic and social problems which were intensified by the two World Wars. In that context environmental pollution issue was hardly recognised by the public, almost unaccepted by the policy makers and ignored by the industry. In 1950s and 1960s people experienced several deadly smog episodes in Donora Pennsylvania (1948), London (1952, 1956), New York (1953), Los Angeles (1954) [2], started to observe fearful outcomes of the nuclear tests [3], and began to realise the potential toxicity of the globally used pesticides [4]. By witnessing these occurrences general public became aware of the environmental pollution issues and foundations for larger changes were laid up. It took few more decades to step up from the recognition of the problem to the delivery of the early significant responses, but at the end of the 20th century ‘stopping and prevention of environment pollution’ became words of the daily political agenda [5], [6].

Unfortunately, more recent environment and climate change studies revealed that recognition of the problem and reaction to it was too slow and in general too weak. Accordingly, scientific community reasons that it is not enough only to limit or prevent the pollution but it is equally important to develop new methods to neutralise pollutants which are already present in the environment [7]. This ultimate change in the paradigm of the environment sustainability has made environment and climate research much more multidisciplinary with the significant emphasis on rising of public awareness [8], development and applications of new highly efficient technologies [9] and functional materials. For instance, catalysts make up the class of functional materials that are used to enable or favour the formation of the desired products and/or to suppress the formation of undesirable by-products. Traditionally their usage was basically limited to the industrial processes with a single purpose to make production feasible and economical [10]. But the change of environment sustainability paradigm introduced catalyst into various end-user products (for example vehicles with diesel engines) where catalyst sole role is to make product usage environmentally friendlier. Moreover, some specific catalysts help to create technologies and products that are purposefully designed to reduce energy consumption or to provide pollution cleaning solutions [11].

Advanced Oxidation Processes (AOPs) generates reactive oxygen species (peroxides, superoxide, hydroxyl radical, singlet oxygen, etc.) and uses them for the non-selective oxidation of various organic and inorganic compounds. Photocatalytic purification of waste water [12], disinfection of liquids (or environmental surfaces) [13] and self-cleaning windows [14] are just a few examples of sustainable environment oriented AOPs [15] which thrust the development of TiO₂ based photocatalysts research [16]. Up to now TiO₂ synthesis has been realised by the countless number of methods based on sol-gel [17], microemulsion-mediated processes [18], electrodeposition [19], hydro/solvothermal processes [20], anodisation [21], sonochemical [22] and microwave-assisted techniques [23], chemical vapour deposition [24], physical vapour deposition [25], spray pyrolysis [19], etc. Most of the early studies synthesised TiO₂ by wet chemical methods and produced it in powder form. In addition to some trivial necessities like large surface area, comprehensive analysis of TiO₂

powder brought out the importance of its crystallinity and phase composition (namely anatase/rutile ratio) [26], [27]. Moreover, it became clear that in order to increase TiO_2 photocatalytic efficiency and to functionalise it in visible light spectra native band gap of approximately 3.2 eV has to be reduced by doping [28], dye sensitisation [29], creating composites with semiconductors [30] or by using other techniques [31].

Various forms of TiO_2 nanopowder can have exceptionally large specific surface area reaching more than $1400 \text{ m}^2/\text{g}$ [32]. Naturally, their intrinsic photocatalytic activity is high but their practical applications are often limited by other factors. First, after TiO_2 powder are used for the photocatalytic ‘cleaning’ of contaminated solutions it is difficult to collect them back. Second, similarly to some other nanomaterials, although macroscopic forms of TiO_2 are proven to be inert and not toxic [33] their nanopowder forms potentially can be harmful for the environment and living organisms [34], [35]. Accordingly, moving towards practical applications TiO_2 based photocatalysts are immobilised on solid substrates.

Self-cleaning windows represent one of the potential TiO_2 application areas and conventional soda lime glass was amongst early substrates which were used to support active TiO_2 coatings [36]. Unfortunately, soon it was realised that sodium and calcium diffuse from the soda lime glass to the TiO_2 matrix and reduce its photocatalytic efficiency significantly [37]. On the other hand, much more expensive fused silica glass (amorphous silica without added impurities) substrate was stable and no interdiffusion between SiO_2 - TiO_2 was observed [37]. Ensuing studies involved more substrate types including ceramics [38], [39], metals [40], [41], polymers [42], [43] and other. Some of them (for example ITO glass or crown glass coated with a SiO_2 layer [44]) provided relatively similar result to the fused silica glass, whereas others (for example glazed ceramic tiles and 6061 Al alloy [45]) decreased the photocatalytic efficiency of TiO_2 coatings.

In current study we further analysed how support affects the photocatalytic activity of TiO_2 based photocatalyst. More specifically we used magnetron sputtering process to deposit carbon doped TiO_2 films on bare borosilicate glass and the same glass pre-covered by nickel layer. Changes in crystal structure, surface roughness and efficiency of photocatalytic Rhodamine B dye degradation under visible light irradiation are presented.

2. METHODS AND METHODOLOGY

2.1. Carbon-Doped TiO_2 Film Deposition

Borosilicate discs made from D263 glass (*SCHOTT*) with diameter of 30 mm were selected as film substrates. In comparison to traditional soda lime glass, D263 glass contains significantly lower amounts of various additive elements, maintains higher stability at elevated temperatures and has high chemical resistance. Most importantly, it has already been successfully used with TiO_2 based films in our previous studies [46], [47].

Film deposition process was implemented in the custom modified physical vapor deposition system equipped with rotary and cryogenic vacuum pumps (PVD-75, *Kurt J. Lesker Company*). Base vacuum level before each experiment was not worse when 1×10^{-7} mbar. Prior to film deposition, borosilicate glass substrate was cleaned by supplying 600 V DC bias to the sample holder and initiating oxygen plasma (1×10^{-1} mbar pressure) for 10 min.

Fig. 1. Experimental set-up scheme during carbon-doped TiO₂ formation.

Carbon-doped TiO₂ films were deposited using unbalanced magnetron sputtering technique. 99.99 % purity Ti disc (76 mm diameter) was used as a cathode for *Torrus 3* magnetron (*Kurt J. Lesker Company*). For the in-situ TiO₂ film doping four graphite pieces were placed on Ti cathode as shown in Fig. 1. The size of carbon-covered area on Ti cathode was approximately one cm² for each graphite piece. The selected amount of carbon was predetermined experimentally finding optimal conditions for the formation of carbon-doped TiO₂ films. Each deposition process was started at room temperature and no auxiliary heat treatment was used during or after the deposition. During carbon-doped TiO₂ film deposition total Ar-O₂ gas mixture (MFC flow ratio 5:1) pressure was kept constant at 6×10^{-3} mbar. The distance between the sample holder and Ti cathode was fixed at 4 cm. As samples were placed directly above the magnetron, sample size was significantly smaller than the cathode diameter and there were no indications of films inhomogeneity therefore deposition of TiO₂ films was performed without any additional rotation of the substrate. During experiments magnetron sputtering was performed for 180 min with pulsed DC power supply operating at 300 W power. When Ni layer was used, it was pre-deposited at pure argon atmosphere (6×10^{-3} mbar) using DC powered magnetron (170 W) with 99.99 % purity Ni disc. The approximate thickness of the carbon-doped TiO₂ and Ni layers was 1300 nm and 200 nm respectively. All used deposition parameters were preselected experimentally during pilot studies not reported here.

2.2. Structural Characterization of the Films

Phase structure of the deposited carbon-doped TiO₂ films was identified by X-Ray diffractometer (XRD, *Bruker D8*) operating with Cu K α radiation. Crystallite sizes were evaluated by *Topas* software with Lorentzian convolution. Chemical state and elemental composition of the films was analysed by X-ray photoelectron spectrometer (XPS, *PHI Versaprobe 5000*) using monochromated 1486.6 eV Al radiation, 25 W beam power, 100 μ m beam size and 45° measurement angle. Sample charging was compensated using dual neutralization system consisting of low energy electron beam and ion beam. The thickness of as-deposited carbon-doped TiO₂ films was measured using stylus profiler (*Ambios XP-200*). Surface morphology and roughness was evaluated by an atomic force microscope (AFM, *Microtestmachines NT-206*). Arithmetic average roughness parameter (Ra) values were

calculated by measuring 3 to 5 different areas ($23 \times 23 \mu\text{m}$ size) of the samples and calculating their mean value.

2.3. Photocatalytic Efficiency of the Films

Photocatalytic bleaching of aqueous Methylene Blue, Rhodamine B (RhB) and other dye solutions is one of the most widely adopted ways to assess the potential of the photocatalyst to be used for the neutralisation (oxidation) of the harmful compounds and/or microorganisms (bacteria, viruses) [48]. Accordingly, in current study photocatalytic properties of carbon-doped TiO_2 films were assessed by the photocatalytic bleaching of RhB. Daylight (DL) LED lamp (*Solis-3C*, 5700 K, Thorlabs) was used as the light irradiation source. The sample was positioned 230 mm below the DL lamp. Irradiation intensity at the surface of the sample was approximately 65 mW/cm^2 (measured with *Thorlabs PM16-401* Power meter). The samples were placed into the quartz glass petri dish with the diameter of 45 mm. 10 mL of 10 mg/L concentration aqueous RhB solution was syringed above the sample. In order to minimize evaporation of RhB solution, the top of the petri dish was covered by $500 \mu\text{m}$ thick fused silica disc. The magnetic stirrer was used to ensure mixing of solution with 500 rpm. Prior to the illumination experiment the samples with mentioned conditions were kept in the dark for 1 hour to ensure the adsorption equilibrium. During the experiment, the petri dish with sample was mounted on the Peltier element, which maintained the solution temperature at 20°C .

Photocatalytic degradation of RhB solution was evaluated by measuring its concentration changes (UV-VIS spectrophotometer, *Jasco V-650*). The strongest peak at 554.5 nm wavelength was used for actual value measurement. All the measurements were performed with 30 minutes interval using 1.5 mL of RhB solution. After the measurement, which took less than 2 minutes, the solution was syringed back to the petri dish for further degradation. Photolysis measurement (treatment of RhB solution with bare glass substrate irradiated by the same light source) was used as the control sample.

3. RESULTS AND DISCUSSION

3.1. Structural Properties of the Carbon-Doped TiO_2 Films

XPS surface analysis (Fig. 2) of Carbon-doped TiO_2 film has confirmed that at the surface there were only three expected elements: Ti, O and C (part of the carbon is detected due to the adventitious contamination from atmosphere). Ti 2p spectra had Ti 2p_{3/2} peak located at 458.7 eV and Ti 2p peak at 464.4 eV. Peak positions and their separation (5.7 eV) correspond to the binding energies of corresponding values for Ti(IV) oxide [49]. Other oxidative states of Ti were not observed by XPS. O 1s peaks at approximately 530.0 and 531.6 eV were assigned to the Ti-O bonds in the TiO_2 lattice and to the hydroxyl groups or water moisture adsorbed from the atmosphere. Unfortunately, sputtering by Ar ions disturbs titanium spectra severely and it loses chemical information. Accordingly, it was not possible to confirm that in the bulk titanium remains in the same chemical state as on the surface, but elemental analysis of sputtered points confirmed that it still maintains small fraction of carbon impurities (approximately 2 at. %), while Ti and O concentrations were approximately 31–32 and 65–67 at. %, respectively.

Fig. 2. Survey and high resolution elemental XPS spectra of the as deposited carbon-doped TiO_2 films.

XRD crystal structure analysis of magnetron sputter deposited carbon-doped TiO_2 films (Fig. 3) showed that films consisted of preferentially oriented anatase (metastable phase) and rutile (the most stable TiO_2 form) phase mixture.

Fig. 3. XRD patterns of as deposited films: a) carbon-doped TiO_2 film deposited directly on borosilicate glass substrate; b) carbon-doped TiO_2 film deposited on Ni underlayer.

Rietveld refinement revealed that Ni underlayer effect for the crystallite size of anatase and rutile phases is not significant, but its effect on phase ratio is more pronounced (Table 1). Later fact has important practical meaning because different TiO_2 phases differ by their photocatalytic response: rutile has the widest band gap and the lowest photocatalytic response; anatase photocatalytic efficiency is considerably higher; but the highest efficiency is reached for the anatase mixture with a small share of rutile (up to few tenths of percent)

[27], [50], [51]. Previously it was observed that during magnetron sputtering process carbon-doped TiO_2 films initially has the tendency to form a phase mixture with a larger share of rutile phase which shifts towards anatase as film thickness increases [52]. It could be assumed that in the case of thicker films internal microstrains acts as the main factor which stabilizes anatase formation. Whereas in current study carbon-doped TiO_2 thickness is equal for the two films and is low in comparison [52] study. Therefore, anatase stabilization factor is different and it probably can be ascribed to the Ni underlayer.

TABLE 1. STRUCTURAL PARAMETERS OF AS-DEPOSITED CARBON-DOPED TiO_2 FILMS

Substrate	Thickness	Anatase crystallite size	Rutile crystallite size	Anatase fraction	Rutile fraction	Arithmetic average roughness, Ra
Borosilicate glass	1300 nm	61 nm	10 nm	56 %	44 %	2.1 nm
Borosilicate glass coated by Ni	1500 nm	55 nm	9 nm	85 %	15 %	6.1 nm

Despite relatively large 1300 nm film thickness and 55–60 nm anatase phase crystallite size surface roughness of the as-deposited films was low (Fig. 4). Arithmetic average roughness (Ra) values for carbon-doped films deposited directly on the glass and on Ni underlayer were only 2.1 nm and 6.1 nm, respectively. Also, it can be noticed, that carbon-doped TiO_2 film on Ni underlayer had significant long-range waviness, whereas films deposited directly on borosilicate glass retain flatter surface with repetition of approximately 500 nm diameter nanostructures. The observed morphological surface characteristics did not differ substantially, but subtle changes indicate possibility of slightly different film growth modes. Surface features of the film deposited directly on borosilicate glass can be considered as the result Frank–van der Merwe (layer-by-layer) film growth mode, whereas film deposition on Ni underlayer has some characteristics which are more typical for the Stranski–Krastanov (layer-plus-island) growth mode. Such differences in growth modes can be explained by the stronger affinity between titanium oxide and borosilicate glass which mainly consists of silicon dioxide and boron trioxide. At the same time, this subtle change in growth mode correlates with the stabilization of metastable anatase phase which was discussed above.

Fig. 4. 3D AFM surface images: a) uncovered borosilicate glass; b) Ni film on borosilicate glass; c) carbon-doped TiO_2 film deposited directly on borosilicate glass substrate; d) carbon-doped TiO_2 film deposited on Ni underlayer.

Results of the photocatalytic RhB solution bleaching by the carbon-doped TiO₂ films irradiated by the visible light are presented in Fig. 5. The rate constant of RhB photocatalytic degradation (first-order reaction constants, k values) under visible light without photocatalyst was approximately $4 \times 10^{-4} \text{ min}^{-1}$. With photocatalyst corresponding rate constants increased several times and reached $22 \times 10^{-4} \text{ min}^{-1}$ and $27 \times 10^{-4} \text{ min}^{-1}$ for carbon-doped TiO₂ film deposited directly on glass and Ni underlayer respectively. The positive effect by caused by Ni underlayer can have several explanations. First, it presumably alters the growth mode of the film and shifts anatase:rutile ratio to the anatase side. Higher efficiency of anatase phase TiO₂ has been proven by photocatalytic bacteria treatment in urban waste water [53] as well as by theoretical and experimental studies using non-organic compounds [50], [51]. Second, although borosilicate glass is chemically more stable than traditional soda lime glass, it still contains a fraction of harmful elements [37] which potentially can diffuse from the glass to the film. In this respect Ni layer serves as a blocking element in preventing semiconductive photocatalyst from poisoning. Third, it is known that decorating TiO₂ catalyst by some of the noble metals has positive effect for the photocatalytic disinfection of bacteria [54]. Similarly, TiO₂ films coated on stainless steel [55] and foam nickel [56] substrates, also showed stronger antibacterial effect and photocatalytic activity than using glass substrate. Finally, in this particular study nickel impurities were not observed directly (by XPS) neither at the surface nor in the subsurface layers of the carbon-doped TiO₂ film. But due to the relatively large thickness of the film our XPS sputtering was not performed throughout all of the coating, therefore it cannot be excluded that some Ni impurities are not diffusing to the carbon-doped TiO₂ structure. Positive effect of titanium doping by Ni was reported at [56], but how nickel would affect the electronic structure of carbon-doped TiO₂ remains unknown. If in fact Ni would diffuse, this factor potentially could add new electronic levels between the valence and conduction bands of TiO₂ and enhance its activation by visible light adsorption caused by electrons moving between these intermediate levels.

Fig. 5. RhB solution bleaching by the visible light activated carbon-doped TiO₂ films.

4. CONCLUSIONS

Carbon-doped TiO₂ films were successfully deposited by magnetron sputtering technique. When films were formed on borosilicate glass XRD analysis showed that they consisted of

mixed phase (rutile-anatase) TiO₂ where both phases contributed by similar parts. However, when the same deposition procedure was used to deposit carbon-doped TiO₂ films on glass covered by Ni layer, formation of the metastable anatase phase was enhanced. Estimation of visible light photocatalytic activity of the films revealed that Ni underlayer had positive effect for the efficiency of RhB solution bleaching. Earlier reports have demonstrated that anatase phase TiO₂ had stronger antibacterial effect and larger photocatalytic activity. Accordingly, it was suggested that observed improvement of RhB solution bleaching was mainly achieved due to the structural changes of TiO₂ crystal phase, but other mechanisms like prevention of impurity diffusion from the glass substrate to the carbon-doped TiO₂ film, or positive Ni doping effect could not be excluded completely. More detailed examination of the latter two possibilities will be one the objects of our wider study of substrate effects for the TiO₂ and ZnO based photocatalysts.

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