



Synthesis, photocatalytic properties and morphology of various TiO₂ nanostructures modified with gold

Reinis Drunka^{*}, Janis Grabis, Dzidra Jankovica, Dzintra-Arija Rasmane, and Aija Krumina

Institute of Inorganic Chemistry, Riga Technical University, Paula Valdena St. 7, LV-1048, Riga, Latvia

Received 25 May 2017, revised 10 October 2017, accepted 13 October 2017, available online 30 November 2017

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Abstract. TiO₂ is promising material for preparing photocatalysts for water splitting and hydrogen production using solar energy. Due to its large band gap 3.2 eV, anatase cannot absorb sun light effectively in visible light (VIS) spectral part. Precious metal nanoparticles are promising dopants for TiO₂ activation as those can decrease band gap of anatase and increase photocatalytic activity significantly. Also the morphology of TiO₂ plays an important role in photocatalytic activity. In this research self-organized TiO₂ nanotube and nanopore layers were prepared by electrochemical anodization and plasma electrolytic oxidation (PEO) of titanium foil. TiO₂ nanofibre layers were prepared by using microwave-assisted synthesis. Chemical deposition method was used to modify obtained substrates with gold nanoparticles. All modified samples showed higher photocatalytic activity than pure TiO₂ nanostructures.

Key words: photocatalysis, TiO₂, nanofibres, coating, nanopores, nanotubes, gold.

1. INTRODUCTION

Titania is promising material for the photocatalytic decomposition of organic compounds, photoelectrochemical (PEC) water splitting and for dye-sensitized solar cells (DSSC), due to the large specific surface area and the relatively simple and cost-effective preparation methods [1–3].

Activity of nanostructural photocatalysts highly depends on their specific surface area, morphology and content of dopants. TiO₂ nanopowders can be transformed into TiO₂ nanofibre coatings with extremely high surface area by using microwave-assisted synthesis method. Short synthesis time is the main advantage for microwave-assisted synthesis method compared to the hydrothermal synthesis method [4, 5].

Also electro-chemical methods as anodization [6, 7] and plasma electrolyte oxidation [8, 9] allow to obtain thin layer nanotube and nanoporous oxide coatings in short time. TiO₂ coatings obtained on metal substrate have better mechanical properties compared to nanopowder photocatalysts and are perspective for solving energy and environmental pollution problems.

However, titania exhibits high photocatalytic activity under ultraviolet (UV) illumination due to wide band-gap (3.2 eV). Only 5% from sunlight is UV radiation, about 45% is visible light. It is determined that photocatalytic activity of TiO₂ nanoparticles can be increased by doping with precious metals as Pt, Pd and especially Au. TiO₂ produces electron-hole pairs under illumination. Precious metals reduce the possibility of electron-hole recombination, causing efficient charge separation and higher photocatalytic reaction rates. Gold can improve electron transfer, leading to higher photocatalytic activity by decreasing the band gap [10, 11, 12].

^{*} Corresponding author, reinis.drunka@rtu.lv

There are many publications about modified TiO₂ nanostructures but it is hard to compare the results. As experimental conditions of photocatalysis measurements differ, the purpose of this research is to compare photocatalytic activity of various TiO₂ nanostructures modified with Au under UV and VIS irradiation under the same experimental conditions.

2. METHODS

2.1. Preparation of TiO₂ nanotubes

Coating of self organized TiO₂ nanotube layers was prepared by electrochemical anodization of titanium foil in 200 mL 0.2 M (NH₄)₂SO₄ electrolyte with 1 wt% HF for 45 min at 20 V DC. Teflon reaction vessel was used for this process.

2.2. Preparation of TiO₂ nanopores

Coating of self organized TiO₂ nanopore layers was prepared by using plasma electrolytic oxidation (PEO) of titania foil in 0.1 M H₂SO₄ electrolyte, using Pt foil as counter electrode. The current was 160 V DC and experimental process was 5 min long.

2.3. Preparation of TiO₂ nanofibres

3 g of TiO₂ anatase nanopowder (Sigma–Aldrich, ≥ 99.7%, < 25 nm particle size) was dissolved in 670 mL of 10 M KOH at room temperature. This aqueous solution was poured into microwave vessel made from teflon. The microwave treatment was performed at 240 °C for 60 min by using Anton Paar Masterwave BTR microwave system. Solution was stirred with speed of 700 rpm during the reaction time. The pressure during holding time was above 20 bar. The obtained solution was then cooled to the room temperature and TiO₂ particles were left to precipitate. After this procedure, KOH solution was decanted from vessel and obtained TiO₂ suspension was diluted with large amount of deionized water to decrease concentration of KOH. Washing and decanting procedures were repeated several times. Finally, a certain amount 1 M HCl was added to TiO₂ suspension to reduce pH to 7.0. Obtained solution was filtered by using 1.0 µm cellulose nitrate membrane filter. Particles were washed on filter several times with deionized water and 96% ethanol. The powder was dried at 110 °C for 24 h. After drying TiO₂ nanofibre powder was stirred in 1 M HCl solution for 24 h to remove titanates. This procedure also allowed to decrease absorption process of methylene blue (MB) on TiO₂ nanofibres surface.

2.4. Modification of TiO₂ nanostructures with Au

Prepared nanostructures were modified with Au nanoparticles by using chemical deposition method. AuCl₃ solution was used as Au source. TiO₂ substrates containing 0.1, 0.5 and 1 wt% of Au were prepared. AuCl₃ solution was reduced with sodium borohydride. All samples were calcined at 500 °C for 2 h.

2.5. Determination of photocatalytic activity

Photocatalytic properties of the obtained TiO₂ nanostructures were tested by using degradation of MB solution under ultraviolet (UV) and visible light (VIS) irradiation. FEK–56, 120 W mercury high pressure UV lamp was used as UV light source and Philips Torndio 23 W halogen lamp as visible light source. Degradation process of MB solution was controlled by spectrophotometer (Janway 6300). Absorption of MB solution was measured at wave length of 664 nm. 0.1000 g TiO₂ nanofibre powder and 1 cm² of nanopore or nanotube coating were used for degradation of 100 mL MB (7.2 mg/L).

2.6. Analysis of physical properties

Characterization of physical properties (morphology, crystallization, element analysis and surface areas) were done by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray fluorescent element analysis (XRF) and surface area analysis methods. Morphology analysis were made with scanning electron microscope system (Tescan Lyra) and transmission electron microscope (FEI Tecnai). Specific surface area was obtained with Brunauer–Emmett–Teller (BET) method and HROM 3 gas analyzer. X-ray diffractometer Bruker AXS D8 Advance was used for phase content analysis of obtained samples.

3. RESULTS

SEM micrographs (Fig. 1) show morphology of prepared TiO₂ substrates. Nanotubes with diameter 30–80 nm and length 7–9 µm, nanopores with diameter 50–500 nm and depth 50 nm–1.2 µm (SEM cross-section), TiO₂ layer thickness 12–16 µm and nanofibres with diameter 5–30 nm (TEM) were obtained. The average crystallite size of nanofibres was 15–20 nm (calculated from XRD patterns). For nanopores the average crystallite size was: 40 nm for anatase phase and 50 nm for rutile phase, respectively (calculated from XRD patterns). SEM and TEM analysis were used to determine gold nano-

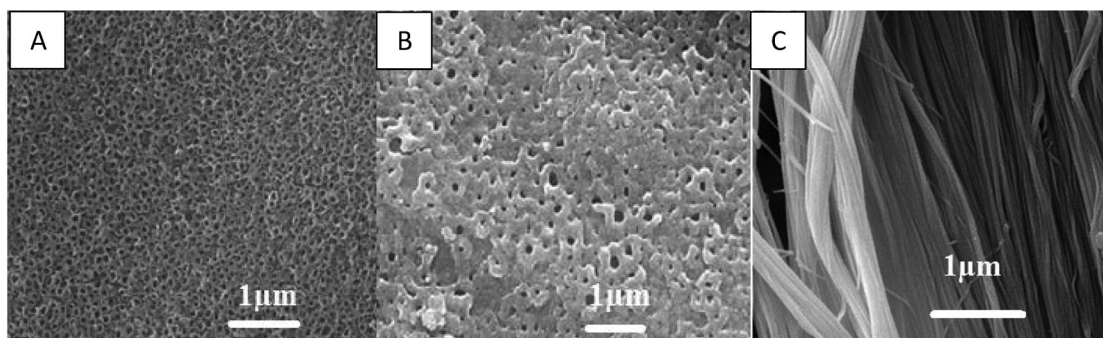


Fig. 1. SEM micrographs of pure substrates: (A) TiO₂ nanotubes; (B) TiO₂ nanopores; (C) TiO₂ nanofibres.

particles on the surfaces of each morphology substrate after modification (Fig 2). The average particle size of gold was 15–20 nm (calculated with Sherrers method).

No changes in morphology were noticed in SEM and TEM figures before and after thermal treatment of modified samples.

Prepared TiO₂ nanofibres had extremely large specific surface area of 158.5 m²/g. Modified with Au

nanoparticles TiO₂ nanofibres had specific surface area in the range of 73.5–80.1 m²/g depending on Au content (Table 1.).

Before calcination, XRD pattern showed only maxima of titanium, but pictures of SEM showed that there was nanotube layer on the surface of Ti foil. After calcination, SEM did not show any changes in the morphology of the sample, but XRD pattern showed some small maxima

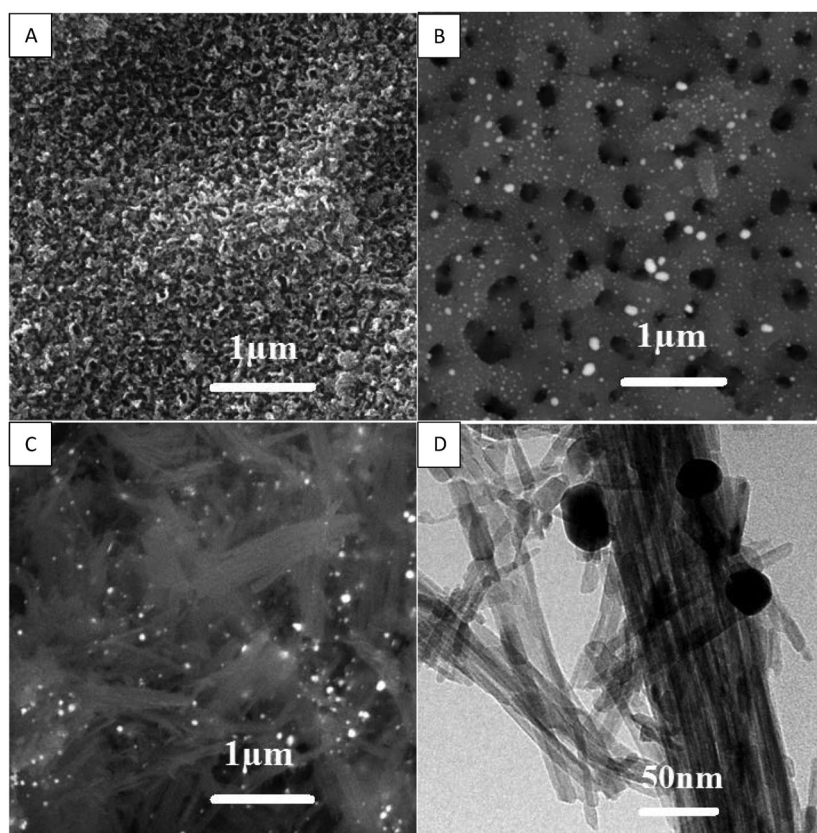


Fig. 2. SEM micrographs of 1% Au modified TiO₂: (A) nanotubes; (B) nanopores; (C) nanofibres; (D) TEM micrograph of 1% Au modified TiO₂ individual nanofibres. For (B) and (C) backscattered detector was used. Gold nanoparticles are highlighted with white color.

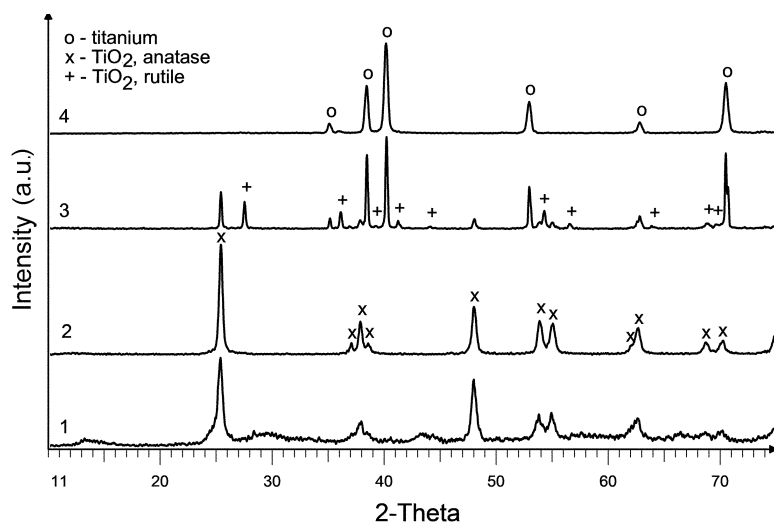
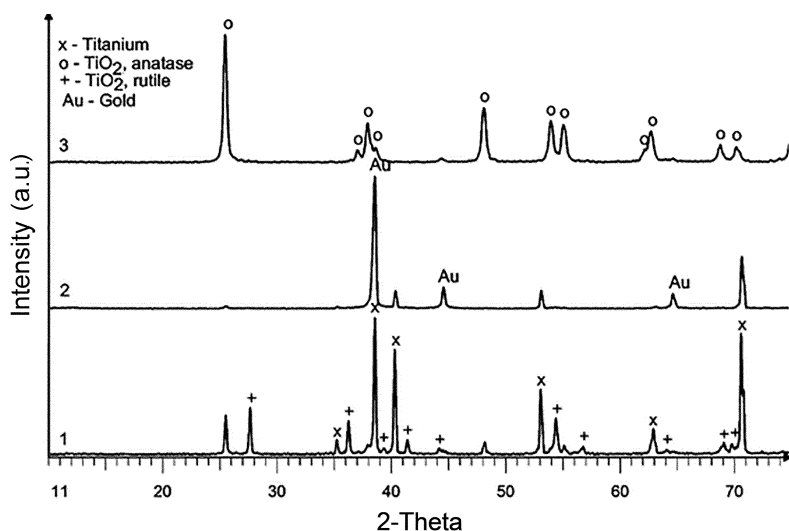
Table 1. Properties of Au modified TiO₂ nanofibres

Sample	Au content, % (XRF)	Specific surface area, m ² /g (BET)
TiO ₂ -Au (0.1%)	0.12	80.5
TiO ₂ -Au (0.5%)	0.50	76.4
TiO ₂ -Au (1%)	0.95	73.1
Pure TiO ₂ nanofibres (without calcination)	–	158.5
Pure TiO ₂ nanofibres (after calcination in at 500 °C for 2 h)	–	85.4
Pure TiO ₂ anatase nanopowder (Sigma Aldrich)	–	43.5

of anatase. This indicates that before thermal heating nanotube layer was X-Ray amorphous. All other samples show strong anatase maxima (Fig. 3). TiO₂ nanotube and nanoporous samples prepared on titanium foil show also strong titanium maxima. Nanoporous samples contain rutile phase as in micro spark discharge process temperature of substrate surface was much higher than

during anodization process. The calcination process of nanofibre samples decreased the content of TiO₂ unnamed mineral phase (monoclinic, base centred). No other phase content changes were noticed.

After modification with Au and thermal treatment at 500 °C for 2 h nanotube samples showed also weak anatase and strong Au maxima (Fig. 4.). Modification with

**Fig. 3.** Phase content of TiO₂ substrates (XRD): (1) nanofibres; (2) commercial anatase nanopowder; (3) nanopores; (4) nanotubes.**Fig. 4.** Phase content of 1% Au modified TiO₂ nanostructures (XRD): (1) nanopores; (2) nanotubes; (3) nanofibres.

Au nanoparticles didn't make any notable changes to the TiO₂ crystal structures and lattice parameters. This could be explained by the fact that Au nanoparticles were located on the surface of TiO₂ nanostructures and only some of the superimposed crystal layers were doped with Au atoms, which in general had small effect on the average values of lattice parameters determined by the XRD.

TiO₂ nanostructures modified with gold nanoparticles show much higher photocatalytic activity compared to the pure TiO₂ nanostructures under UV radiation. By increasing amount of gold in the sample the photocatalytic activity increases (Figs 5–7). TiO₂ photocatalysts modified under UV irradiation had up to 45% higher activity with respect to the pure TiO₂ nanostructures.

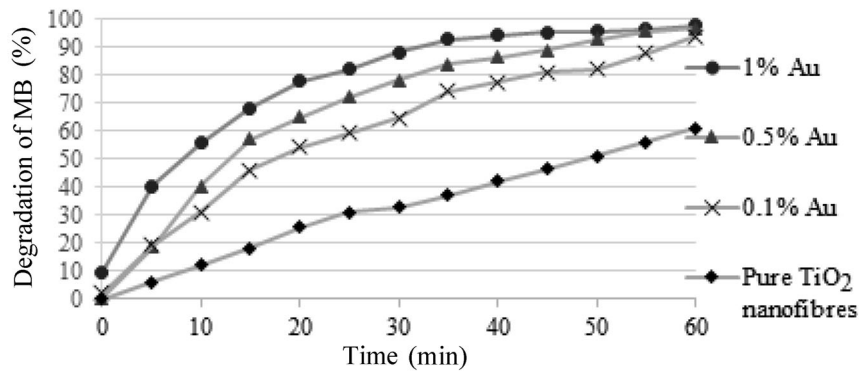


Fig. 5. Degradation of MB under UV irradiation: TiO₂ nanofibres modified with 0.1; 0.5 and 1% Au and pure TiO₂ nanofibres.

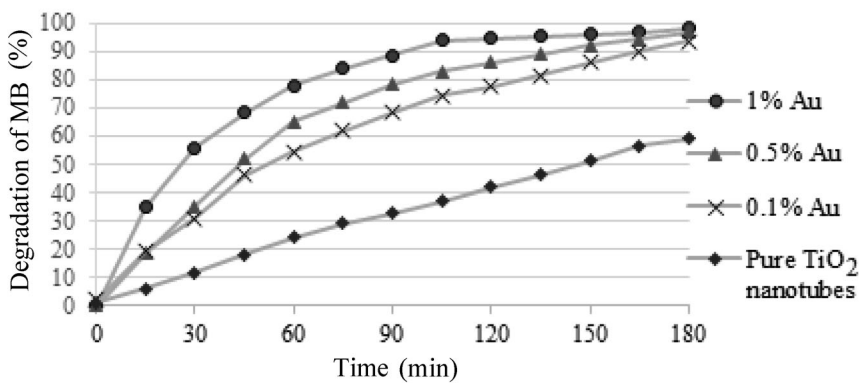


Fig. 6. Degradation of MB under UV irradiation: TiO₂ nanotubes modified with 0.1; 0.5 and 1% Au and pure TiO₂ nanotubes.

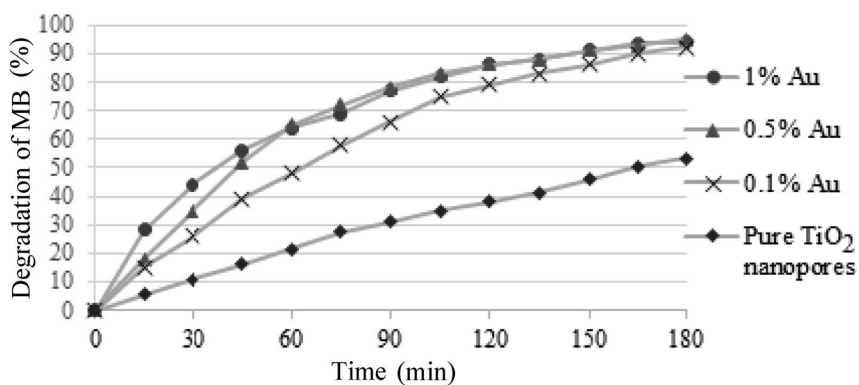


Fig. 7. Degradation of MB under UV irradiation: TiO₂ nanopores modified with 0.1; 0.5 and 1% Au and pure TiO₂ nanopores.

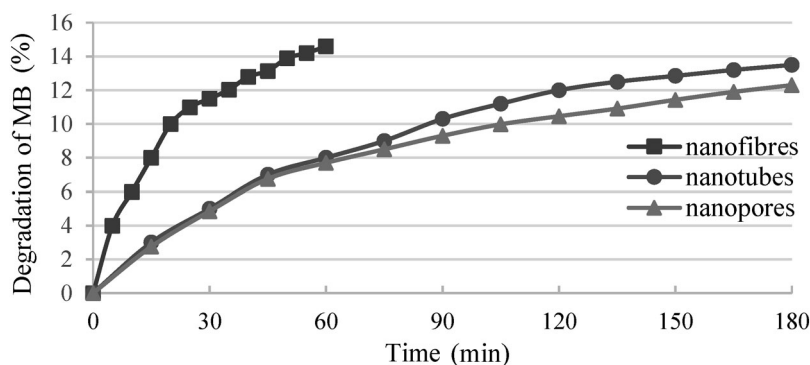


Fig. 8. Degradation of MB under VIS irradiation by using 1% Au modified TiO₂ nanofibres, nanotubes and nanopores.

Nanofibre samples reached MB degradation degree of 95% in 60 min but nanotubes and samples of nanoporous coating reached at the same level in more than 180 min. Nanofibre sample containing 1% Au showed the highest photocatalytic activity under UV and VIS irradiation. Degradation degree of MB under VIS irradiation for samples modified with 1% Au reached 14.6% in 60 min for TiO₂ nanofibres, 12.5% in 180 mins for nanopores and 13.50% for nanotubes (Fig. 8).

4. CONCLUSIONS

Modified TiO₂ photocatalysts had up to 45% higher activity compared to the pure TiO₂ nanostructures under UV irradiation. Nanofibre samples reached MB degradation degree of 95% in about 3 times faster than samples of nanotubes- and nanopores-based coatings. Nanofibre sample containing 1% Au showed the highest photocatalytic activity under UV and VIS irradiation. Degradation degree of MB under VIS irradiation reached 14.6% in 60 min for TiO₂ nanofibres modified with 1% Au. Prepared photocatalysts are perspective for hydrogen generation in water photocatalytic electrolysis process under UV and visible light irradiation and also for degradation of harmful organic compounds in waste water.

ACKNOWLEDGEMENTS

The financial support of National research program project IMIS² is greatly acknowledged. The publication costs of this article were covered by the Estonian Academy of Sciences and the University of Tartu.

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Kullaga modifitseeritud erineva morfoloogiaga TiO₂ nanostruktuuride süntees ja fotokatalüütilised omadused

Reinis Drunka, Janis Grabis, Dzidra Jankovica, Dzintra–Arija Rasmane ja Aija Krumina

TiO₂ on paljutootav materjal fotokatalüsaatorite valmistamiseks vesiniku tootmiseks veest päikeseenergia abil. Suure keelutsooni laiuse (3,2 eV) tõttu ei suuda anataas päikesevalguse nähtavat spektriosa tõhusalt neelata. Väärismetallide nanoosakesed on TiO₂ aktiveerimiseks paljulubavad lisandid, kuna need võivad vähendada anataasi keelutsooni laiust ja oluliselt suurendada fotokatalüütilist aktiivsust. Ka TiO₂ morfoloogial on fotokatalüsaatori aktiivsuses oluline tähtsus. Selles uuringus valmistati TiO₂ nanotorude ja nanoporsed iseorganiseeruvad kihid titaanfooliumi elektrokeemilise anoodimise ning plasma elektrolüütilise oksüdatsiooni abil. TiO₂ nanofiibrite kihid valmistati mikrolainetega assisteeritud sünteesi abil. Saadud kilede modifitseerimiseks kulla nanoosakestega kasutati keemilist sadestamist. Kõik kullaga modifitseeritud proovid näitasid puhta TiO₂ nanostruktuuridega võrreldes kõrgemat fotokatalüütilist aktiivsust.