



Synthesis, photocatalytic properties and morphology of various TiO_2 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

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Abstract. TiO_2 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 TiO_2 activation as those can decrease band gap of anatase and increase photocatalytic activity significantly. Also the morphology of TiO_2 plays an important role in photocatalytic activity. In this research self-organized TiO_2 nanotube and nanopore layers were prepared by electrochemical anodization and plasma electrolytic oxidation (PEO) of titanium foil. TiO_2 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 TiO_2 nanostructures.

Key words: photocatalysis, TiO_2 , 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. TiO_2 nanopowders can be transformed into TiO_2 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. TiO_2 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 TiO_2 nanoparticles can be increased by doping with precious metals as Pt, Pd and especially Au. TiO_2 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 TiO_2 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 TiO_2 nanostructures modified with Au under UV and VIS irradiation under the same experimental conditions.

2. METHODS

2.1. Preparation of TiO_2 nanotubes

Coating of self organized TiO_2 nanotube layers was prepared by electrochemical anodization of titanium foil in 200 mL 0.2 M $(\text{NH}_4)_2\text{SO}_4$ electrolyte with 1 wt% HF for 45 min at 20 V DC. Teflon reaction vessel was used for this process.

2.2. Preparation of TiO_2 nanopores

Coating of self organized TiO_2 nanopore layers was prepared by using plasma electrolytic oxidation (PEO) of titania foil in 0.1 M H_2SO_4 electrolyte, using Pt foil as counter electrode. The current was 160 V DC and experimental process was 5 min long.

2.3. Preparation of TiO_2 nanofibres

3 g of TiO_2 anatase nanopowder (Sigma–Aldrich, $\geq 99.7\%$, < 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 TiO_2 particles were left to precipitate. After this procedure, KOH solution was decanted from vessel and obtained TiO_2 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 TiO_2 suspensison 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 TiO_2 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 TiO_2 nanofibres surface.

2.4. Modification of TiO_2 nanostructures with Au

Prepared nanostructures were modified with Au nanoparticles by using chemical deposition method. AuCl_3 solution was used as Au source. TiO_2 substrates containing 0.1, 0.5 and 1 wt% of Au were prepared. AuCl_3 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 TiO_2 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 Torndo 23 W halogen lamp as visible light source. Degradation process of MB solution was controlled by spectrophotometer (Janwey 6300). Absorption of MB solution was measured at wave lenght of 664 nm. 0.1000 g TiO_2 nanofibre powder and 1 cm^2 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 TiO_2 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), TiO_2 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-

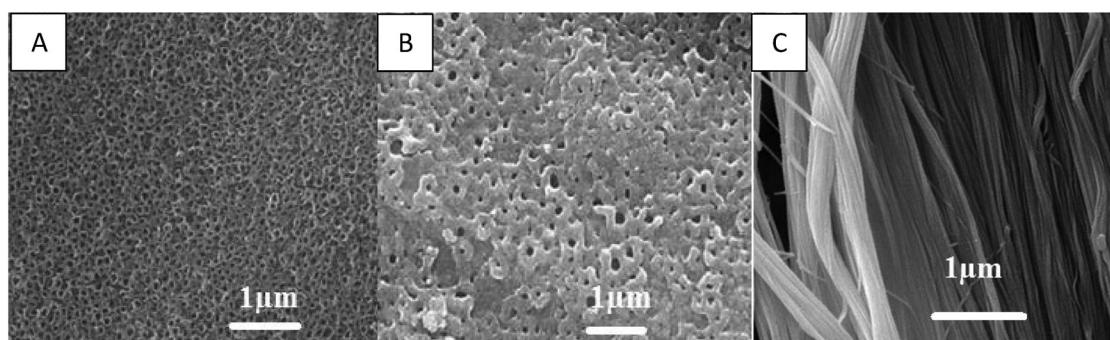


Fig. 1. SEM micrographs of pure substrates: (A) TiO_2 nanotubes; (B) TiO_2 nanopores; (C) TiO_2 nanofibres.

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 TiO_2 nanofibres had extremely large specific surface area of $158.5\text{ m}^2/\text{g}$. Modified with Au

nanoparticles TiO_2 nanofibres had specific surface area in the range of $73.5\text{--}80.1\text{ m}^2/\text{g}$ 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

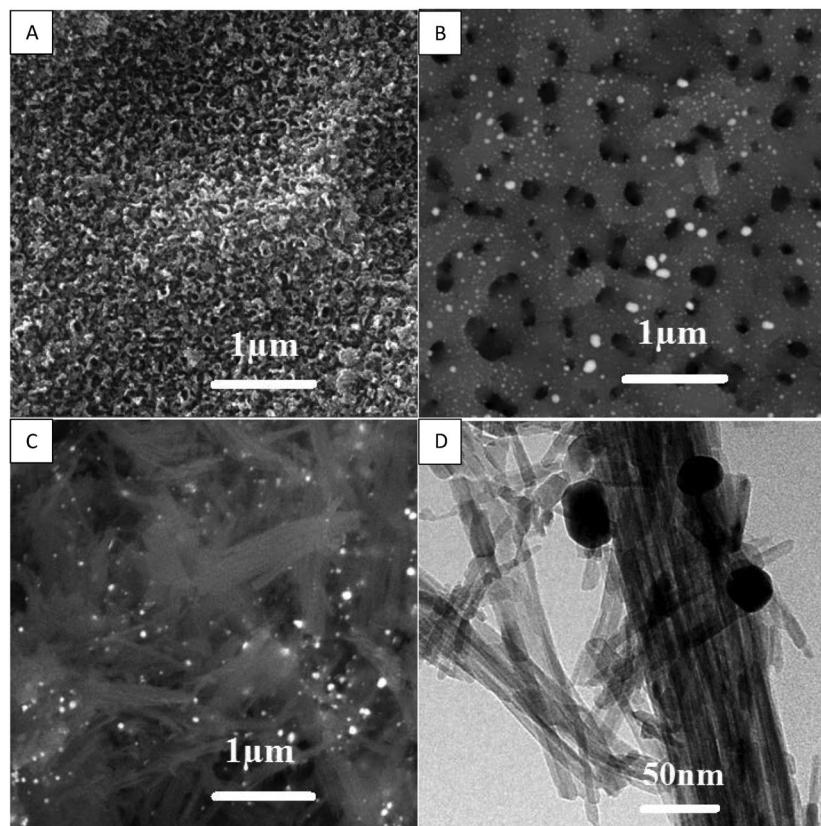


Fig. 2. SEM micrographs of 1% Au modified TiO_2 : (A) nanotubes; (B) nanopores; (C) nanofibres; (D) TEM micrograph of 1% Au modified TiO_2 individual nanofibres. For (B) and (C) backscattered detector was used. Gold nanoparticles are highlighted with white color.

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 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

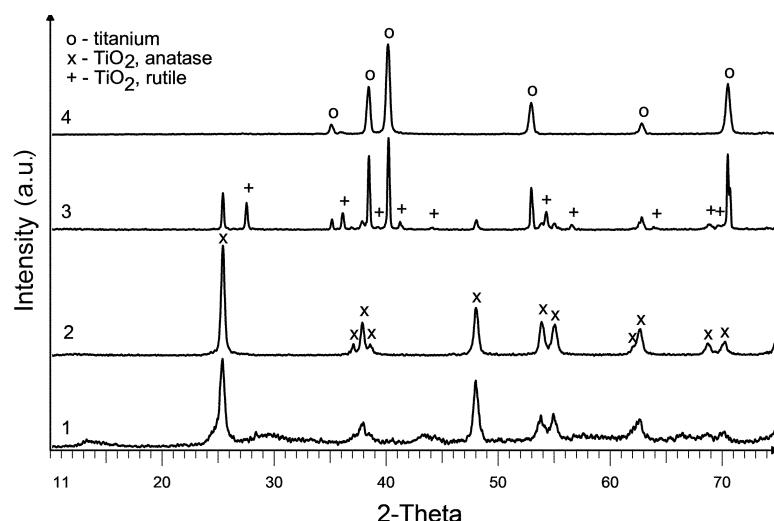


Fig. 3. Phase content of TiO₂ substrates (XRD): (1) nanofibres; (2) commercial anatase nanopowder; (3) nanopores; (4) nanotubes.

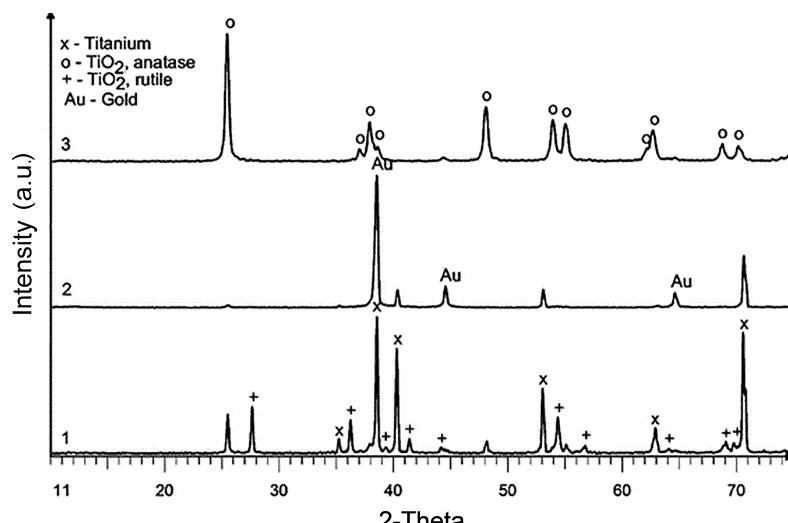


Fig. 4. Phase content of 1% Au modified TiO₂ nanostructures (XRD): (1) nanopores; (2) nanotubes; (3) nanofibres.

TiO_2 nanoparticles didn't make any notable changes to the TiO_2 crystal structures and lattice parameters. This could be explained by the fact that Au nanoparticles were located on the surface of TiO_2 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.

TiO_2 nanostructures modified with gold nanoparticles show much higher photocatalytic activity compared to the pure TiO_2 nanostructures under UV radiation. By increasing amount of gold in the sample the photocatalytic activity increases (Figs 5–7). TiO_2 photocatalysts modified under UV irradiation had up to 45% higher activity with respect to the pure TiO_2 nanostructures.

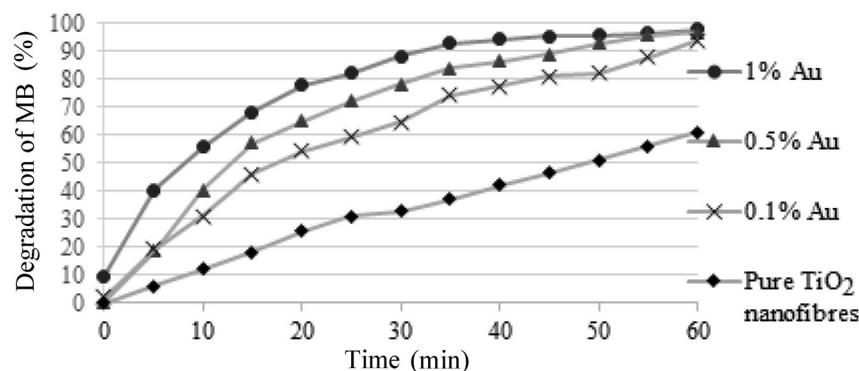


Fig. 5. Degradation of MB under UV irradiation: TiO_2 nanofibres modified with 0.1; 0.5 and 1% Au and pure TiO_2 nanofibres.

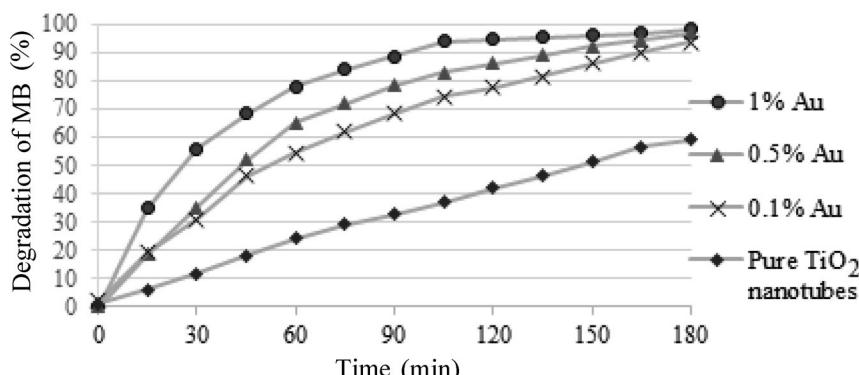


Fig. 6. Degradation of MB under UV irradiation: TiO_2 nanotubes modified with 0.1; 0.5 and 1% Au and pure TiO_2 nanotubes.

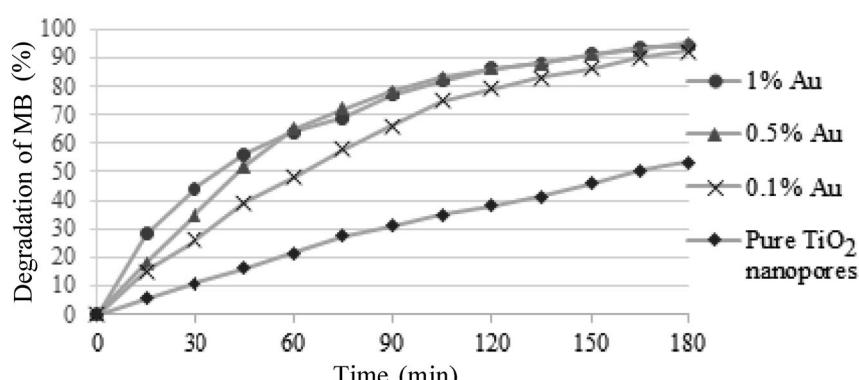


Fig. 7. Degradation of MB under UV irradiation: TiO_2 nanopores modified with 0.1; 0.5 and 1% Au and pure TiO_2 nanopores.

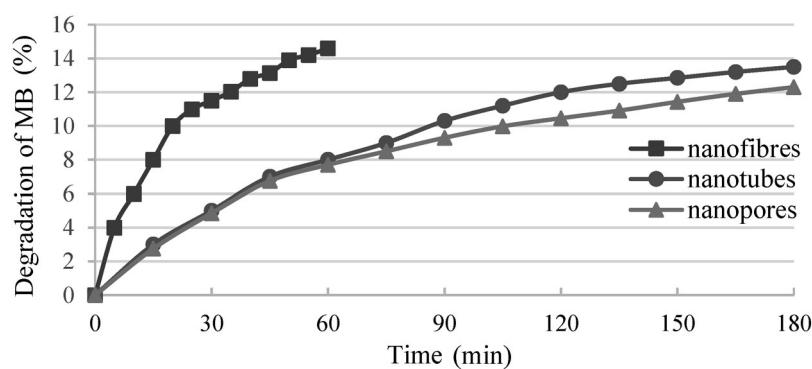


Fig. 8. Degradation of MB under VIS irradiation by using 1% Au modified TiO_2 nanofibres, nanotubes and nanopores.

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 TiO_2 nanofibres, 12.5% in 180 mins for nanopores and 13.50% for nanotubes (Fig. 8).

4. CONCLUSIONS

Modified TiO_2 photocatalysts had up to 45% higher activity compared to the pure TiO_2 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 TiO_2 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.

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Kullaga modifitseeritud erineva morfoloogiaga TiO_2 nanostrukturide süntees ja fotokatalüütised omadused

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

TiO_2 on paljutõotav materjal fotokatalüsaatorite valmistamiseks vesiniku tootmiseks veest päikeseenergia abil. Suure keelutsooni laiuse (3,2 eV) tõttu ei suuda anataas päikesevalguse nähtavat spektriosa tõhusalt neelata. Vääris-metallide nanoosakesed on TiO_2 aktiveerimiseks paljulubavad lisandid, kuna need võivad vähendada anataasi keelutsooni laiust ja oluliselt suurenndada fotokatalüütlist aktiivsust. Ka TiO_2 morfoloogial on fotokatalüsaatori aktiivsus oluline tähtsus. Selles uuringus valmistati TiO_2 nanotorude ja nanopoorsed iseorganiseeruvad kihid titaanfooliumi elektrokeemilise anoodimise ning plasma elektroliüütilise oksüdatsiooni abil. TiO_2 nanofibrite kihid valmistati mikrolainetega assisteeritud sünteesi abil. Saadud kilede modifitseerimiseks kulla nanoosakestega kasutati keemilist sadestamist. Kõik kullaga modifitseeritud proovid näitasid puhta TiO_2 nanostrukturidega vörreldes kõrgemat fotokatalüütlist aktiivsust.