TiO_2/Au Nanomaterial for Photocatalytic Degradation of hormones

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Abstract

Photocatalyst based on TiO_2 nanotubes doped with Au nanoparticles was prepared and characterised. Raman spectroscopy was used for the basic characterization of the nanostructures which confirmed the anatas crystal phase of TiO_2 photocatalyst and presence of Au on the surface. The morphology of the surface on the nanoscale and chemical composition of the samples were examined with a field emission gun scanning electron microscopy (FEG-SEM) equipped with an energy dispersive spectroscopy (EDS) system with which the preparation of TiO_2NT/Au was established. The photolytic and photocatalytic degradation of estrogenic hormone 17 β-Estradiol (E2) over a wide range of wavelengths of input radiation (300-1100 nm) indicate the ability of the newly synthesized catalyst to absorb radiation of the visible part of the spectrum and pronounced photocatalytic activity.

Key words: nanostructured TiO_2, Au nanoparticles, photocatalysis, hormones

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Introduction

The manipulation of matter on a nanometre scale to produce new materials and devices has received considerable attention in the last twenty years[1,2]. Unique physicochemical properties of nanomaterials substantially deviate from characteristics of bulk materials[3]. As a result, we can employ nanomaterials in various fields, such as energy conversion and storage[4], rechargeable lithium batteries[5], sensors[6], etc.

Widely studied nanostructured TiO_2 with its versatile properties has proved to be a very promising material for application in dye-sensitized solar cells[7,8], sensors[9], photocatalysis[10], optical coatings[11], biomedical coatings[12] and so forth. A number of techniques are currently used for nanostructured TiO_2 preparation including chemical (template) synthesis[13], hydrothermal synthesis[14,15] and electrochemical anodization[16-19]. Back in 1999, Zwilling et al[20] demonstrated the formation of a self-ordering TiO_2 nanoporous structure by anodization in fluoride containing chromic acid. They stressed that small amount of fluoride ions in the electrolyte is crucial for the formation of self-ordering TiO_2 nanoporous structures. Following this study, many research groups have worked to optimize anodization parameters in order to develop self-ordering nanotubular arrays[21-28]. Electrochemical anodization of titanium is a straightforward, inexpensive and direct approach of synthesising TiO_2 nanostructures. Variation of the anodization parameters can affect the diameter, shape and density of the nanostructures[29-31]. TiO_2 exists in amorphous form and three crystal structures, rutile, anatase and brookite. As-prepared nanoporous material has an amorphous structure, therefore thermal annealing is necessary to obtain a well-defined nanocrystalline phase[32] showing better photocatalytic properties. In conventional photolytic wastewater treatment processes, TiO_2 in the form of nanoparticles is already used due to its chemical and biological inertness, significant photocatalytic activity in the UV range and reasonable prices[33]. In order to extend photocatalytic activity to the visible part of the spectrum (VIS) and thus exploit more energy, the doping of TiO_2 with precious metals[34] such as gold (Au) has been investigated.

Rapid industrial development has led to a significant rise in the concentration of pollutants in the environment. Pollutants are different types of substances that pose a threat to the ecosystem. In Directive 2013/39/EU[35] of the European Parliament and of the Council 17 β-Estradiol (E2, Figure 1), one type of steroidal estrogen was added to the list of substances that pose a threat to human health. E2 belongs to a group of endocrine-disrupting chemicals and can be found in environmental water samples and thus enter the human food chain. As E2 concentrations increase each year, monitoring and removal of quantities exceeding the maximum permitted values is required.

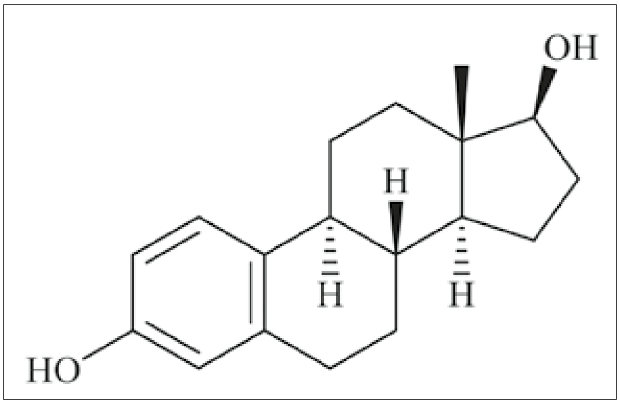

Figure 1. **Chemical structure of 17 β-Estradiol (E2).**

In November 2013, the European Parliament and the Council of the European Union adopted the current, seventh action program that promotes sustainable development and innovation while respecting Earth's natural resources and protecting the health and well-being of its inhabitants. The program lists nine priority objectives[36] and employment of renewable energy sources (sunlight) is one of them. Photocatalysis is one of the most important wastewater treatment techniques that uses a renewable energy source. It belongs to the so-called advanced oxidation processes (AOP). In these processes, highly reactive hydroxyl radicals (OH•) are formed with the help of light, which decompose organic compounds into CO_2 and H_2O with little or no secondary waste.

Adequate means to use natural resources responsibly and sustainably include improvement of existing processes and the design of new materials relevant to renewable energy. The main purpose of this study was to prepare and characterize a catalyst based on TiO_2 in the form of nanotubes (TiO_2NT) modified with Au nanoparticles (TiO_2NT/Au) and its ability to oxidize the model E2 molecule.

Materials and methods

Chemicals and solutions

Ethylene glycol (EG), ammonium fluoride (NH_4F), acetone, isopropanol, hydrogen tetrachloroaurate solution ($HAuCl_4$), 17 β-Estradiol (E2), formic acid and acetonitrile were obtained from Merck (Germany). All the chemicals were of analytical grade. Ultrapure water with conductivity of 0.055 µS/cm used for electrolyte preparation was from SG Reinstwassersystem (Austria). Titanium foil of 0.25 mm thickness was from Merck (Germany).

Preparation of TiO_2NT/Au

Nanostructured TiO_2NT was prepared by anodizing Ti foil. Prior to anodizing, the Ti foil was cleansed using a 3-step procedure: (i) acetone, (ii) isopropanol, and (iii) demineralized water. The anodization was carried out at room temperature in a conventional two-electrode cell using a direct current (DC) power supply (Figure 2). Ti foil (working electrode) was connected as an anode, and platinum (Pt) electrode (counter electrode) was connected as a cathode. Ti foil was pressed with the o-ring in the electrochemical cell and the area exposed to the electrolyte was 1 cm^2. The anodization was performed in an electrolyte of mass composition 1.2% NH_4F, 2% demineralized water in EG at 30 V, for 30 min. Details of chemical reactions and phenomena that occur during the process have already been explained[37]. After anodization, the samples were immediately washed with ultrapure water and dried in nitrogen stream. As-prepared TiO_2 films were amorphous. Stable anatase phase was obtained by thermal annealing. Annealing was carried out in a tube furnace for 2 h at 500 °C using a ramp rate of 1 °C/min. Decoration of nanostructured TiO_2NT with Au nanoparticles was performed by photoreduction. The prepared TiO_2NT samples were immersed in 0.05 M hydrogen tetrachloroaurate solution ($HAuCl_4$) and, with constant stirring at 500 rpm, illuminated with UV light for 4 h. After 4 h, samples 1 and 2 were washed with ethanol and deionized water. Samples TiO_2NT/Au 1 and TiO_2NT/Au 2 were prepared.

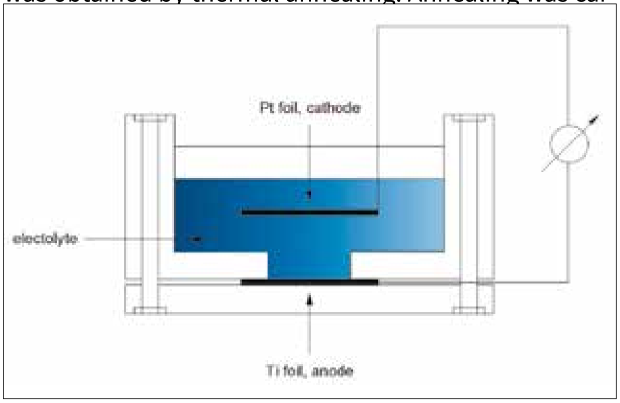

Figure 2. **Conventional two-electrode cell.**

Instrumentation

Anodization was done with the device DC power supply DF 1731 SBO (V&A Instrument, China). Raman spectroscopy (RS) measurements were performed using a Horiba/Jobin-Yvon T64000 spectrometer (Villeneuve D'Ascq, France) with a Coherent Innova 400 (Santa Clara, CA, USA) argon-ion laser operating at 514.5 nm for the excitation. The Raman data were collected with a multi-channel CCD detector. The morphology of the surface and chemical composition of the samples were examined with a field emission gun scanning electron microscopy (FEG-SEM) device JEOL model 7000F equipped with an energy dispersive spectroscopy (EDS) system.

Photocatalytic experiments were performed in a flow cell (d = 4.5 cm, h = 2 cm) connected to a peristaltic pump (q = 67 mL min^{-1}). Photocatalytic film foils were placed on the bottom of the cell so that the photocatalyst stood perpendicular to the light radiation[38]. Prior to the experiments, solution E2 (c_0(E2) = 0.3 mmol dm^{-3}) was recirculated through a system in the dark to achieve adsorption balance of the analyte on the photocatalyst (lamps are lit at t = 0 min). The radiation sources were: (i) a full-spectrum fluorescent lamp simulating solar radiation (Exo Terra, 20W) and (ii) an incandescent lamp emitting only visible light (Osram daylight, 100 W). The change in E2 concentration over time from both sources was monitored on the two photocatalysts prepared in the same manner, using the LC analyses. The LC analysis was done using Knauer HPLC system with fluorescence (FLD) detector and C18 column (150 mm×4.60 mm, particle size 4 **µm**). The analysis was done using eluent A (0.01% formic acid in MilliQ water) and eluent B (acetonitrile) in gradient elution mode which started with a 4 min linear gradient from 70% A to 60% B, followed by a 3 min linear gradient to 95% B which was maintained for 6 min and then a 0.1 min linear gradient back to 70% of A; the flow rate was 0.5 mL/min. Detection of E2 in all samples was accomplished at an excitation wavelength of 280 nm and an emission of 310 nm. Fluorescence detector wavelengths were selected based upon literature[39].

Results and discussion

Charac terisation

Raman spectra of TiO$_2$NT and TiO$_2$NT/Au (Figure 3) shows characteristic lines related to the anatas crystal phase40. We notice the loss of some spectral lines (designated with arrows), which indicates that the modification of TiO$_2$NT with Au nanoparticles was successful.

The surface of the TiO$_2$NT sample is displayed at the magnification of 33,000, 75,000 and 200,000 times respectivly (Figures 4, 5 and 6). We observed neat morphology and orderly arrangement of nanotubes. The approximate size of nanotube diameter was determined to be 0.125 µm. Figure 7 shows colloidal solution of Au nanoparticles. Approximate nanoparticle diameter was 51 nm, which indicates that particles of this size are easily positioned within TiO$_2$NT. Figure 8 illustrates the surface of the TiO$_2$NT/Au sample at the magnification of 100,000 times, where Au nanoparticles are clearly seen. The presence of Au nanoparticles was also confirmed with EDS analysis. Figure 9 demonstrates elementary analysis which established the existence of Ti, O and Au atoms on the sample, which is further evidence of the preparation of TiO$_2$NT/Au.

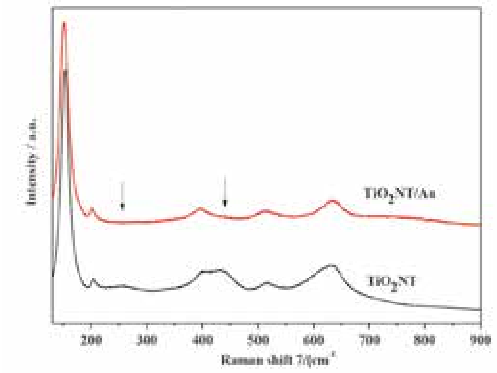

Figure 3. **Raman spectra of TiO$_2$NT and TiO$_2$NT/Au.**

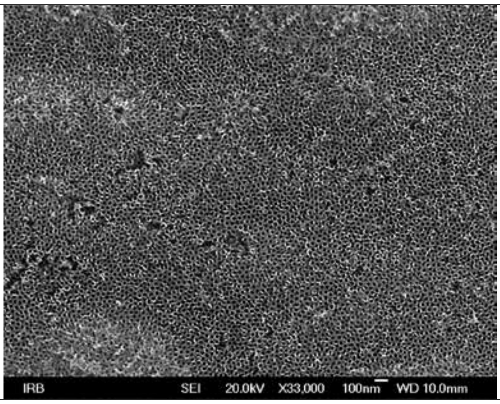

Figure 4. **The surface of the photocatalyst TiO$_2$NT at a magnification of 33.000 times.**

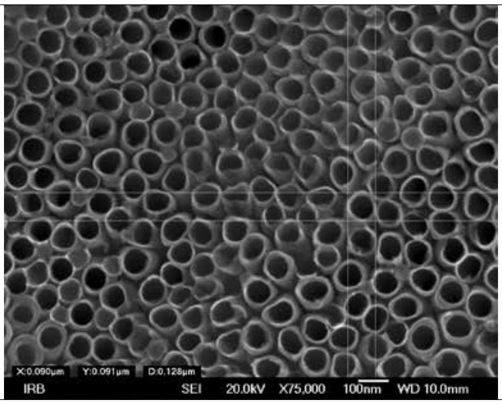

Figure 5. **The surface of the photocatalyst TiO$_2$NT at a magnification of 75.000 times and the approximate size of the nanotube.**

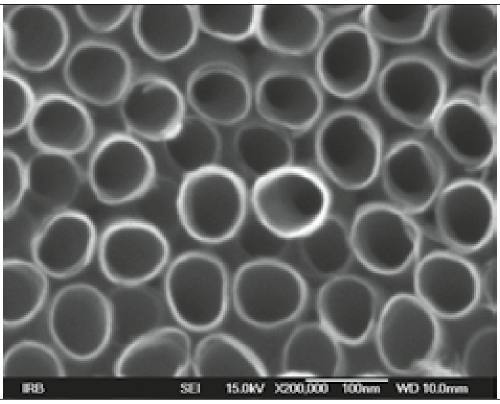

Figure 6. **The surface of the photocatalyst TiO$_2$NT at a magnification of 200.000 times.**

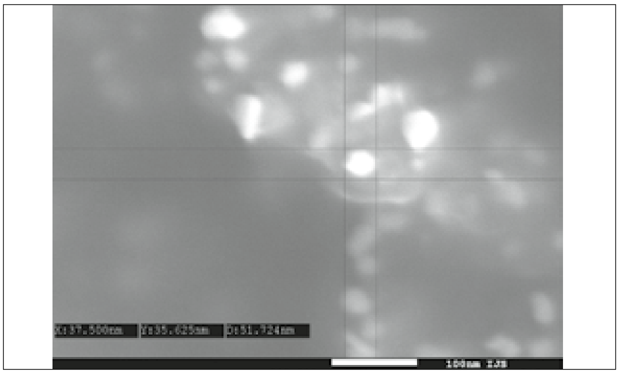

Figure 7. **Colloidal solution of Au nanoparticles.**

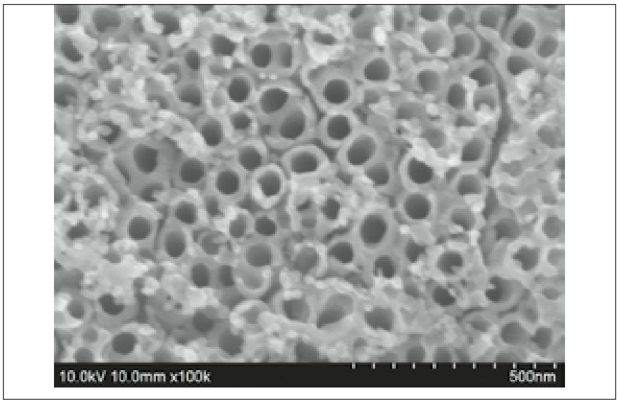

Figure 8. **The surface of the photocatalyst TiO_2NT/Au at a magnification of 100.000 times.**

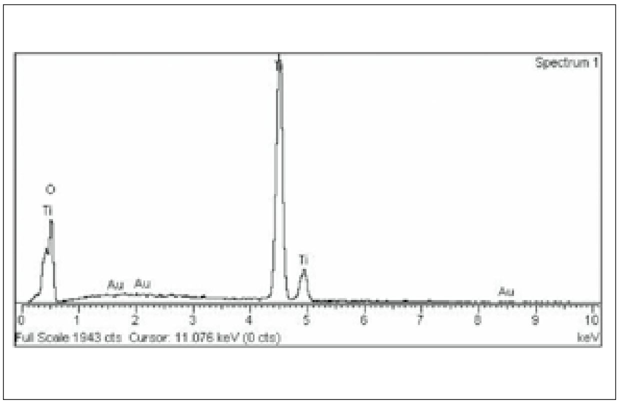

Figure 9. **Elemental analysis (EDS) of photocatalyst TiO_2NT/Au.**

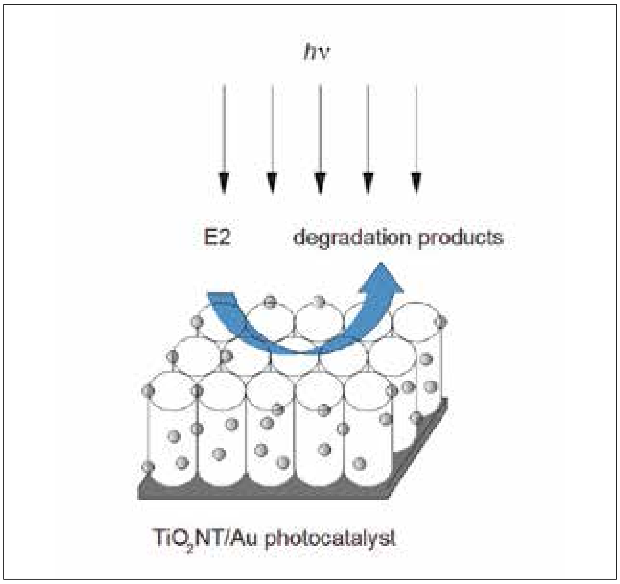

Figure 10. **Schematic representation of photocatalytic degradation of E2.**

Photocatalysis

Schematic representation of photocatalytic degradation of E2 onto TiO_2NT/Au is shown in Figure 10. The kinetics of photocatalytic degradation of E2 under the simulated full spectrum of solar radiation and visible light are shown in Figures 11 and 12 respectively. Photochemical degradation of E2 was observed during simulated solar radiation, which was expected because E2 contains chromophores that make it sensitive to photolysis. However, the photocatalytic degradation of E2 is significantly faster with TiO_2NT/Au with both radiation sources. Kinetic parameters, reaction rate constant (*k*) for photolysis (decomposition without catalyst) and photocatalytic degradation on TiO_2NT, TiO_2NT/Au 1 and 2 are given in Table 1 for both radiation sources.

The results of E2 degradation show that photolytic degradation due to UV absorption (λ_{max} ~ 280 nm) is evident at the full spectrum of solar radiation. At the full spectrum, there is a slightly smaller difference between the E2 degradation rate constants without and with catalysts. Sample 2 proved to be the best photocatalyst, which achieved about 1.8 times faster degradation of E2 than photolysis. In visible radiation (with a very low content of UVA part of the radiation) photolysis is almost negligible and the decomposition can be attributed to thermal decomposition rather than photolytic. In this case, sample 1 proved to be better, with which degradation of E2 was about 2.9 times faster than by photolysis. The differences in photocatalyst samples behaviour can be attributed to different absorption of irradiation at photocatalysts surface, where Sample 1 exhibited higher absorption in the visible region of applied irradiation.

Table 1. **E2 degradation rate constantsin a flow cell with TiO$_2$NT and TiO$_2$NT/Au.**

full spectrum of solar radiation		visible light	
sample	k x 10^{-2}, min^{-1}	sample	k x 10^{-3}, min^{-1}
-*	2.60	-*	2.41
TiO$_2$NT	3.81	TiO$_2$NT	4.19
TiO$_2$NT/Au 1	3.70	TiO$_2$NT/Au 1	7.02
TiO$_2$NT/Au 2	4.79	TiO$_2$NT/Au 2	6.66

*only photolysis of E2 due to radiation absorption was observed in the experiment

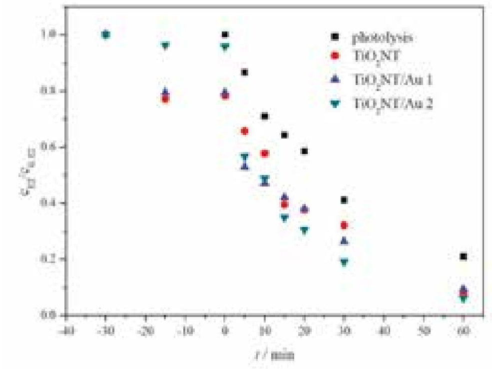

Figure 11. **Kinetics of photolysis and photocatalytic degradation of E2 with the full spectrum of solar radiation.**

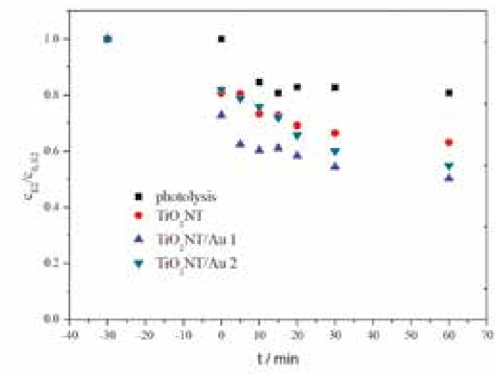

Figure 3. **Raman spectra of TiO$_2$NT and TiO$_2$NT/Au.**

Conclusion

The prepared photocatalyst TiO$_2$NT/Au was characterized and its photocatalytic activity in model E2 solution was tested. The results indicate the ability of the catalyst to absorb radiation of the visible part of the spectrum and pronounced photocatalytic activity. TiO$_2$NT/Au presents a promising platform for future research in wastewater treatment since it enables employment of renewable energy sources.

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Nanomaterijal TiO_2/Au za fotokatalitičku razgradnju hormona

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Sažetak

Pripremljen je fotokatalizator na bazi nanocjevčica TiO_2 dopiranih nanočesticama Au. Za osnovnu karakterizaciju nanostruktura primijenjena je Ramanova spektroskopija, koja je potvrdila anatas kristalnu fazu fotokatalizatora TiO_2 i prisutnost Au na površini. Morfologija površine na nanoskali i kemijski sastav uzoraka ispitani su skenirajućom elektronskom mikroskopijom (FEG-SEM) opremljenom sustavom energetske disperzivne spektroskopije (EDS), što je potvrdilo pripremu TiO_2NT/Au. Fotolitička i fotokatalitička degradacija estrogenskog hormona 17-beta-estradiola (E2) u širokom rasponu valnih duljina ulaznog zračenja (300 do 1100 nm) ukazuju na sposobnost novosintetiziranog katalizatora da apsorbira zračenje vidljivog dijela spektra i izraženu fotokatalitičku aktivnost.

Ključne riječi: nanostrukturirani TiO_2, nanočestice Au, fotokataliza, hormoni