Black TiO$_2$ nanotube arrays decorated with Ag nanoparticles for enhanced visible-light photocatalytic oxidation of salicylic acid

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ABSTRACT: Novel form of black TiO$_2$ nanotubes-based photocatalysts for water purification were prepared. Two features were combined: decoration of TiO$_2$ nanotube arrays with Ag nanoparticles (sample TiO$_2$-NT's@Ag) and further hydrogenation of this material (TiO$_2$-NT's@Ag-HA). Obtained photocatalysts show high efficiency for degradation of salicylic acid, a typical water-borne pollutant. The photocatalysts considerably exceed the photocatalytic properties of TiO$_2$ nanotubes and commercial TiO$_2$ P25 taken as a reference for modelling of the photocatalytic process. The comparison of photocatalytic activities between novel photocatalyst was based on a numerical approach supported by the complex kinetic model. This model allowed a separate study of different contributions on overall degradation rate. Contributions include: salicylic acid photolysis, photocatalysis in UVB,

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UVA and in the visible part of applied simulated solar irradiation. The superior photocatalytic performance of the photocatalyst TiO_2-NT's@Ag-HA, particularly under visible irradiation, was explained by the combined effect of a local surface plasmon resonance (LSPR) due to Ag nanoparticles and creation of additional energy levels in band-gap of TiO_2 due to Ti^{3+} states at nanotube surfaces. The presence of Ag also positively influenced on charge separation of created electron-holes pairs. The synergy of several effects was quantified by a complex kinetic model through the factor of synergy, f_{Syn}. Stability testing indicated that the catalysts were stable for at least 20 hours. The novel design of catalysts, attached on Ti foils, presents a solid base for the development of more efficient photocatalytic reactors for large-scale with a long-term activity.

KEYWORDS black TiO_2 nanotubes arrays, Ag decoration, salicylic acid photodegradation, solar irradiation, kinetic model

1. INTRODUCTION

The TiO_2 based materials are one of the most studied materials in the last 40 years. They found applications in many fields such as: solar cells [1], photocatalysis [2], water splitting [3], batteries [4], for bone and dental implants due to biocompatibility [5], gas sensing due to change in electrical and optical properties [6]. On the other hand, TiO_2 nanotubes are widely investigated material from its beginnings in 2001, when Grimes and co-workers for the first time synthesized TiO_2 nanotube arrays by electrochemical oxidation of Ti-foil [7]. It is a relatively simple process and it is possible to apply the same procedure on the large scale to growth uniform array of TiO_2 nanotubes. Advantages of obtained TiO_2 nanotubes are temperature and chemical stability, relatively low cost of production, film flexibility, and high specific surface area [8]. The anodization process enables to precisely control the morphological parameters of thin film growth: film thickness, nanotubes diameter, wall thickness, surface roughness [8]. Those parameters can be controlled by variation of: applied DC voltage, type of electrolyte, the concentration of water and fluoride ions, reaction time [8]. The anodization parameters also influence the adhesion of the TiO_2 nanotube arrays to Ti substrate, so the adhesion can be enhanced by two-step anodization process described by Yu et al. [9]. Advantages of TiO_2 nanotube arrays compared to other TiO_2 morphologies are a high specific area (many reaction centers at the nanotube surface), good carrier mobility due to the wire like morphology, and environmental stability [10]. The photocatalytic activity of pure TiO_2 nanotubes is limited due to the relatively large band gap of 3.2 eV for anatase and 3.02 eV for rutile (bulk materials) [11]. In order to increase activity, it is essentially to modify the surface; to dope or decorate the nanotubes with the aim to tune band gap in the desired range of solar irradiation absorption (visible and near infrared, NIR) [12].

In the last 30 years there were many different approaches and attempts to increase photo catalytic activity of TiO_2 by doping with non-metal and metal atoms [13-23], depositing or decorating the surface of TiO_2 nanostructure (nanoparticles, nanowire, nanotubes, nanobelts) by noble metal nanoparticles (Pt, Pd, Au, Ag) or metal oxide nanoparticles (WO_3, Cu_2O, CeO_2, Fe_2O_3) [23-33]. The electron trapping in the junction between noble metal nanoparticles and TiO_2 is determined by the work function of the metal, which is usually larger than in TiO_2. The electron-hole pair can be formed by photon absorption at the surface of TiO_2, formed electron would be transferred from conduction band (CB) of TiO_2 to metal nanoparticles. Schottky barrier, which is formed at the junction, leads to efficient charge separation due to the existence of an internal electric field between TiO_2 and metal nanoparticles and acts as a trap for the generated charge carriers.

The photocatalytic materials decorated by noble metals are classified as plasmonic photocatalyst [34]. The noble metal nanoparticles can be uniformly deposited (Au, Ag, Pd, Pt) by one of the chemical methods with the particles size in the range of a few nanometers up to several 100 nm. The aim of deposit nanoparticles at the surface of the nanotubes is to increase UV and visible light absorption, to ensure better charge carrier separation, an increase of local electric field and localized surface plasmon resonance (LSPR). By the variation of the nanoparticles size, it is possible to tune the wavelength of absorption maximum [34]. The embedding of the noble metal nanoparticles at the surface of the semiconductor provide several beneficial effects. In the plasmonic photocatalysis, there are two distinct features which contribute to better performances of the plasmonic photocatalysts in comparison to conventional ones. Those are: (i) Schottky junction and (ii) localized surface plasmon resonance (LSPR). There is forced electron-hole separation close to the interface and fast lane charge transfer due to the first feature. While LSPR induced several more effects: visible light response, enhanced UV-vis absorption, reduced electron-hole diffusion

length, enhanced local electric field, LSPR electron-hole generation, local heating effects and molecule polarization effect [34]. Yu et al. [35] prepared a new metal–semiconductor nanocomposite plasmonic photocatalyst by depositing AgCl nanoparticles into the self-organized TiO_2 nanotubes, followed by partial reduction of Ag^+ ions in the surface region of AgCl particles. Such photocatalyst showed a high visible-light photocatalytic activity for the photocatalytic degradation of methyl orange. Different authors studied the influence of the particle size of noble-metal elements (Ag, Au) that decorate the TiO_2 nanostructures on the intensity and red shift of the absorbance in the visible region [36, 37].

The ''black'' TiO_2 nanostructures obtained by annealing in the reductive atmospheres (H_2, Ar/H_2, CO, NO) has drawn a lot of attention recently. Reduced TiO_2 nanostructures have better properties for applications in DSSC cells, water splitting and photocatalysis compared to non-reduced TiO_2 [38, 39]. One of the reasons is narrowed band gap (< 3 eV), which allows the photocatalytic activity of TiO_2 in the visible range of solar irradiation. The narrower band gap could result in a higher efficiency in the photocatalytic reactions [40]. Recent studies gave an explanation in terms of creation of Ti^{3+} states during thermal treatment of TiO_2 nanotubes in the reductive atmosphere [41, 42]. High-temperature annealing in the inert oxygen-free atmosphere, in a vacuum or reductive atmosphere lead to the release of O_2 molecules and formation of Ti^{3+} ions, usually at the nanotubes surfaces. Reduced nanotubes showed absorption in the visible part of solar spectra and better conductivity. These effects can be explained through the appearance of the high density of localized donor states which are created in forbidden gap of TiO_2 due to the formation of Ti^{3+}, which actually represents electron donor state closely to the bottom of the conduction band of TiO_2. The high-pressure H_2 treatment of TiO_2 nanotubes lead to anatase-like "black titania", showing a high open-circuit photocatalytic hydrogen production rate without the presence of a co-catalyst. Through these processes, it is possible to create the most of 1% Ti^{3+} from Ti^{4+}, before crystal structure

collapsed. This process is reversible till some point, because exposure to air or O_2 atmosphere leads to oxidation. Similar as Ti^{3+}, the oxygen vacancies also increase absorption in the visible part of solar spectra. Chen and co-workers firstly reported on the synthesis of ''black'' TiO_2 nanoparticles by annealing in the reductive atmosphere (H_2 atmosphere at 200 °C for 5 days and pressure 20 Bar) [38]. The nanoparticles had a core-shell structure with crystalline TiO_2 inner part of nanoparticles and outer amorphous shell. Naldoni et al. synthesized TiO_2 nanocomposites with core-shell structure, with crystalline core and amorphous 2 nm thick shell [43]. They explained narrowing of the bandgap by the existence of defects such as Ti^{3+} and oxygen vacancies which create energy states inside the bandgap. These states allowed the absorption and intraband transition in the energy region smaller than 3.2 eV. Tao et al. applied a different approach to obtain narrowed bandgap of 2.1 eV. They obtained TiO_2 phase forms on the surface of rutile TiO_2 (011) by oxidation of bulk titanium interstitials [44], which resulted in the similar photocatalytic activity due to TiO_2 self-doping with Ti^{3+} during annealing process in a reductive atmosphere of CO or NO [45]. Wang et al. proposed that H-doped amorphous shell plays the same role as Ag or Pt loading on TiO_2 nanocrystals, which induces the localized surface plasmon resonance and black coloration, resulting in enhanced photocatalytic activity [46]. Wu et al.   [47] applied the electrochemical hydrogenation doping for the introduction of interstitial hydrogen ions and oxygen vacancies. Similar process was used by Zhao et al. [48] to reduce Ti^{4+} to Tn^{3+}, that is approved by XPS measurements. In our previous work [49], powder of titanate ($H_2Ti_3O_7$) nanotubes decorated by Ag was studied for photocatalytic properties. We have shown that annealing of the protonated type of titanate nanotubes in Ar/H_2 induce a transition to TiO_2 anatase phase nanoparticles can be used as efficient powder catalyst. Moreover, $H_2Ti_3O_7$ nanotubes decorated with Ag nanoparticles after annealing in the reductive atmosphere (Ar/H_2) had two times higher photocatalytic activity than those which were annealed in Ar/H_2 but not decorated with Ag.

With the aim to prepare the efficient easy-handling photocatalyst for purification of waste water from the industry, we studied the modification and decoration of titanium oxide nanotube arrays (TiO$_2$-NT's) that are completely attached on titanium foil. In that manner, there are no nanoparticles left in purified water as in the case of the use of suspended powder catalyst (e.g. P25 TiO$_2$). To increase the efficiency of the TiO$_2$-NT's photocatalyst caused by LSPR, titanium oxide nanotubes arrays were decorated by Ag nanoparticles (sample TiO$_2$-NT's@Ag) and subsequently reduced by annealing in hydrogen (TiO2-NT's@Ag-HA) with the aim to narrow band gap of titania. The photocatalysts were evaluated by photodegradation of salicylic acid (SA) in aqueous solution. SA was chosen as a model pollutant due to its widespread use in dyestuff, resins and aspirin production, which results in its release to the environment through various waste streams. SA was listed as a pollutant in precipitation,

surface waters (approx. 0.1 μg L^{-1}) and as a constituent of humic material in drinking waters. It may be released to the aquatic environment in wastewater discharges from industry and even sewage treatment facilities [50].

The TiO$_2$-NT's arrays were modified by Ag using similar procedures as in our previous research [49]. In this work it was shown that TiO$_2$ nanotubes formed by anodization process on Ti foil decorated with Ag nanoparticles after annealing in the reductive atmosphere (TiO$_2$@Ag-HA) have the best overall photocatalytic performance, even 1.53 times larger than commercial P25. The increase in the efficiency is explained by the combined effect of localized surface plasmon resonance (LSPR) of the silver nanoparticles and the increased absorption of visible light and NIR due to the reduction of TiO$_2$ in hydrogen and formation of defects such as Ti^{3+} and oxygen vacancies. These defects create energy states inside the bandgap that allow an interband transition in the energy region smaller than 3.2 eV that can be achieved by visible light.