High-temperature hydrogenation of pure and silver-decorated titanate nanotubes to increase their solar absorbance for photocatalytic applications

Milivoj Plodinec [a], Andreja Gajović [a,*], Gregor Jakša [b], Kristina Žagar [b], Miran Čeh [b]

[a] Ruđer Bošković Institute, Bijenička 54, HR-1002 Zagreb, Croatia
[b] Institute Jožef Stefan, Jamova 39, 1000 Ljubljana, Slovenia

A B S T R A C T

Titanate nanotubes (TiNTs) and silver-decorated titanate nanotubes (TiNTs@Ag) were synthesized using the hydrothermal method. In the decorated nanotubes the silver particles were obtained by the photoreduction of $AgNO_3$ under UV light. Pure and Ag-decorated nanotubes were high-temperature heat treated at 550 °C in a hydrogen atmosphere and the "core–shell"-structured TiO_2 nanoparticles were formed. For the structural characterization of all the titanate nanostructures we used conventional and analytical transmission electron microscopy (TEM) techniques, X-ray diffraction (XRD) and Raman spectroscopy. The Ag-decorated titanate nanostructures were additionally studied by X-ray photo-electron spectroscopy (XPS), with the aim being to investigate the surface chemistry. Using UV–ViS-NIR spectroscopy we studied the photocatalytic activity on caffeine for the TiNT and TiNT@Ag samples that were high-temperature heat treated at 550 °C in a hydrogen atmosphere. We found that hydrogenation at high temperature of the TiNTs and TiNTs@Ag is essential to increase the absorption of light in the visible and near-IR regions. In the case of the hydrogenated TiNTs@Ag the absorption is even stronger in the visible region than in the UV, which was not observed in TiO_2-based nanostructures up until now, to the best of our knowledge. The hydrogenated TiNTs@Ag sample had a two-times higher photodegradation impact on the caffeine than the hydrogenated TiNT samples, which is a consequence of the increased absorption of visible light and the synergetic effects between the silver and the TiO_2 nanoparticles that increase the efficiency of the formation of electron–hole pairs and the charge transfer to the surface of the nanoparticles.

1. Introduction

TiO$_2$-based nanostructures have been extensively investigated materials over the past two decades, because of their promising physical and chemical properties, such as a high specific surface area, the low costs of synthesis, a high photo-activity and environmental stability [1–3]. Because of these properties the titania nanostructures can be used for photocatalysis, in solar cells (DSSC) and sensors, and in the cosmetics industry [3–11]. Typically, during photocatalytic reactions in TiO_2-based materials photo-generated electrons are produced in the conduction band, along with the corresponding positive holes in the valence band due to the absorption of light. The excited electrons form a superoxide radical ion (O_2^-) from the surrounding O_2 while the holes left in the valence band can react with adsorbed water (or OH^-) to form very reactive hydroxyl radicals (·OH), which decompose the adsorbed pollutant molecules [12]. Since TiO_2 has a relatively large bandgap of 3.2 eV for anatase and 3 eV for rutile, both crystal forms are photocatalytically active only under irradiation with UV light. So, one of the key parameters necessary to increase the photocatalytic activity in the visible and near-IR regions is to optimize the bandgap of TiO_2-based materials towards the bandgap of monocrystal silicon, i.e., 1.1 eV. Several papers were published on the subject of doping TiO_2 with different metals and non-metals to decrease the bandgap value [13–17]. However, while the obtained materials have a reduced energy gap, their photocatalytic activity is not increased very much. One of the main reasons for this is the introduction of impurities (dopants) that create additional recombination centers for light-excited electrons in the material.

In the past few years there has been substantial interest from researchers in hydrogen-reduced TiO_2 nanostructures. By comparing the "normal" TiO_2 with a reduced TiO_2, it was clear that the reduced TiO_2 is more attractive for use in dye-sensitized solar cells (DSSCs), for photocatalysis and in hydrogen production [18,19]. This is because the smaller energy gap (smaller than the 3 eV)

allows photocatalytic activity in the visible part of the solar spectrum and thus induces better efficiency [20]. Naldoni et al. [21] synthesized TiO_2 composites with a "core–shell" structure, with the core having point defects (Ti^{3+} and oxygen vacancies) and the shell being amorphous, up to 2 nm thick. Tao et al. [22] also synthesized a new, pure TiO_2 phase formed on the surface plane of rutile TiO_2 by the oxidation of Ti in an interstitial solid TiO_2 sample with an energy gap of only 2.1 eV. Chen et al. [18] synthesized black TiO_2 nanoparticles with an optical gap of ∼1.0 eV. They treated nanocrystalline TiO_2 in a hydrogen atmosphere at 200 °C and at a pressure of 20 bars for 5 days. An increase in the photocatalytic activity in the visible region is also achieved by self-doping the TiO_2 with Ti^{3+} through a process of annealing the TiO_2 in a reducing atmosphere (CO and NO) [23]. Increased photo-activity in the visible range of solar radiation, as well the increased efficiency of TiO_2 as a photocatalyst, were also achieved by doping and decorating TiO_2-based nanostructures with nanoparticles of metal and noble-metal elements (Fe, Pt, Ag, Au) [24–31]. It was shown that the noble-metal nanoparticles have the property of the collective excitations of electrons in the visible region, known as the process of surface plasmon resonance (SPR), so such photocatalysts are called plasmonic photocatalysts. In a plasmonic photocatalyst the excited electrons have enough energy to move directly into the conduction band of the TiO_2. In addition, it is reported that the elements of the noble metals increase the separation of the electrons and the holes, acting as traps for the electrons, thus expanding the photocatalytic properties of TiO_2 nanostructures into the visible region [27–32]. Moreover, Yu et al. [33] prepared a new, metal–semiconductor, nanocomposite, plasmonic photocatalyst by depositing AgCl nanoparticles into the self-organized TiO_2 nanotubes, and then reducing partial Ag^+ ions in the surface region of the AgCl particles. Such a photocatalyst shows a highly visible-light photocatalytic activity for the photocatalytic degradation of methyl orange. Some authors [28,30] also studied the influence of the particle sizes 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.

In this paper we studied how a heat treatment in a reducing atmosphere of hydrothermally synthesized titanate nanotubes (TiNTs) influenced their structure, morphology, phase transitions, UV–ViS-NIR absorbance and photocatalytic activity. For the synthesis of the nanotubes we employed the hydrothermal method. However, since TiNT has a low photo-efficiency because of its wide energy gap (about 3.6–3.8 eV) and the rapid recombination of electron–hole pairs affected by the UV radiation, the use of such nanotubes as efficient photocatalysts is limited. Nevertheless, we observed an increase in the TiNTs' photocatalytic activity after a heat treatment in a reducing atmosphere that also induces the transformation of nanotubes to elongated nanoparticles. With the aim to additionally improve the photocatalytic activity of TiNTs obtained when using the hydrothermal method, we decorated the nanotubes with silver nanoparticles (sample named TiNTs@Ag) prior to the heat treatment in the reducing atmosphere. The increase in the photocatalytic activity of the hydrogenated titanate nanostructures decorated with Ag nanoparticles (TiNTs@Ag-HA) as compared to the hydrogenated titanate nanostructures without Ag nanoparticles (TiNTs-HA) was shown. In the case of TiNTs@Ag-HA the absorption is even stronger in the visible region than in the UV region. Such a result was not observed in TiO_2-based nanostructures up to now, to the best of our knowledge. It can be explained as a synergetic effect of the disordered shell of the "core–shell"-structured TiO_2 nanoparticles, the point defects in its core and the surface plasmon resonance of the Ag nanoparticles. This because silver nanoparticles on the surface of the TiO_2 nanostructures can act as an additional separator of electron and hole pairs, which are formed under the influence of solar irradiation.

2. Experimental

2.1. Synthesis of titanate nanotubes

The titanate nanotubes were synthesized using the hydrothermal method (Table 1). Approximately 1 g of TiO_2 was transferred into a Teflon reactor and suspended in 75 mL of 10-M NaOH. The reactor was sealed and placed into an autoclave for 48 h at a temperature of 130 °C. After the synthesis the sample was washed with deionized water and filtered in vacuum until the filtrate pH was less than 8. With the aim being to prepare the titanate nanotubes in the protonated form (TiNTs), the nanotubes were suspended in 100 mL of HCl with a concentration c(HCl) = 0.1 mol/L. After three hours of soaking in the solution of HCl (with occasional mixing) the nanotubes were vacuum filtered and washed with deionised water until the pH of the filtrate was ∼5. All the samples were dried at 80 °C after washing overnight.

For the syntheses of the decorated titanate nanotubes, 250 mg of TiNTs was suspended in 100 mL of 0.05-M solution of $AgNO_3$ (Table 1). The reaction mixture was mixed and exposed to UV light for 3 h at 80 °C. After that the decorated nanotubes were separated from the solvent by vacuum filtration and washed with deionized water until the filtrate was ∼6. The silver-decorated nanotubes (TiNTs@Ag) were dried for 12 h at 80 °C.

The annealing process for both the decorated and pure nanotubes was carried out in a Carbolite CTF Tube furnace in a reducing atmosphere (H_2) at a temperature of 550 °C for 3 h (Table 1). The temperature ramping in both cases was 10 °C/min.

2.2. Methods of characterization

The structural and morphological changes of the TiNTs and TiNTs@Ag before and after the annealing in the reducing atmosphere were studied by transmission electron microscopy (TEM), Raman spectroscopy (RS), X-ray powder diffraction, X-ray Photoelectron Spectroscopy (XPS or ESCA) and UV/VIS spectroscopy.

The TEM imaging was performed in a Jeol JEM-2100-LaB_6 operated at 200 kV. For the TEM measurements, the samples were suspended in ethanol and sonicated for approximately 1 min in a low-power ultrasonic bath, dropped onto carbon-coated copper grids and dried in air.

The Raman spectroscopy (RS) measurements were performed in a Horiba, Jobin–Yvon T64000 spectrometer with an argon-ion laser Coherent, Innova 400 operating at 514.5 nm for the excitation. The Raman spectra were collected in micro-Raman mode with a multi-channel CCD detector. A laser power of 20 mW at the sample and an objective with a 100× magnification were used.

The X-ray diffraction (XRD) patterns were obtained using a Philips PW 3040/60 X'Pert PRO powder diffractometer, employing Cu Kα radiation at 45 kV and 40 mA. The incident beam passed through an X-ray mirror having a divergence slit of 0.5°. The diffracted beam was directed to the detector through the parallel-plate collimator with an equatorial acceptance angle of 0.18°. The step size was 0.02°, with a measuring time of 10 s/step.

The X-ray photoelectron spectroscopy (XPS) analyses were carried out in a PHI-TFA XPS spectrometer, exciting the sample surface with X-ray radiation from an Al monochromatic source. The samples in the form of powder were pressed on double-sided adhesive tape. The analyzed area was 0.4 mm in diameter and the analyzed depth was 3–5 nm. The energy resolution was 0.6 eV, measured for the Ag $3d_{5/2}$ core-level spectrum. The sample charging during the analysis was partially compensated by using a neutralization gun for low-energy electrons. In addition, we aligned the binding-energy scale at 284.8 eV, characteristic for C–C bonds in a C 1s spectrum, originating from surface contamination. The relative error in the composition was estimated to be about ±20% of the reported concentrations and the error in the binding-energy measurement was about 0.3 eV. The base pressure in the XPS analysis chamber was 8×10^{-10} mbar.

UV–ViS-NIR diffuse-reflectance spectroscopy was utilized for the optical absorption characterization of the pure and Ag-decorated synthesized titanate nanotubes before and after annealing in the hydrogen atmosphere. The optical absorption spectra were measured with a UV–ViS-NIR Perkin–Elmer Lambda 950 high-performance spectrophotometer with an integrating sphere of 150 mm and a wavelength range from 175 nm to 3300 nm. The analysis of the band-gap energy was made on 10 mg of catalyst powder suspended in 50 ml of distilled water. The diluted samples were sonicated for 30 s in order to homogeneously suspend the particles prior to recording the absorption spectra. The band-gap energies were estimated using a straight-line intercept to the energy axis fitted to a graph of $[\alpha h\nu]^{1/2}$ [eV cm^{-1}] versus hν [eV], where α[cm^{-1}] is the absorption coefficient. From the UV–ViS-NIR measurements, the indirect band-gap transition of the photocatalyst is estimated in accordance with the theoretical equation for the indirect band-gap of semiconductors [34,35].

Caffeine was used as a model to evaluate the photocatalytic activity of the synthesized samples. A total of 8 mg of catalyst was dispersed in 8 mL of 50 ppm water-caffeine solution. A 10-mL beaker containing the catalyst and the solution was stirred to ensure the full suspension of the particles throughout the experiment. The photocatalysis experiments were carried out at room temperature in the photocatalytic reactor under an Ultra Vitalux Lamp (300 W) – the simulator of the solar spectra. The distance between the lamp and the base of the beaker was 20 cm. Prior to irradiation, the suspensions with nanoparticles were stirred