



Purification of titania nanoparticle thin films: Triviality or a challenge?

Urmas Joost^{a,*}, Anu Saarva^a, Meeri Visnapuu^a, Ergo Nõmmiste^a, Kathriin Utt^a, Rando Saar^{a,b},
Vambola Kisand^{a,b}

^a*Institute of Physics, University of Tartu, Riia 142, 51014 Tartu, Estonia*

^b*Estonian Nanotechnology Competence Center, Riia 142, 51014 Tartu, Estonia*

Received 11 November 2013; accepted 10 December 2013

Available online 18 December 2013

Abstract

Although purification of titania nanoparticles is a very common process in laboratory practice the specific purification protocol is often chosen without scientific justification. In the present work the efficiency of three different and in laboratory practice widely used treatments is compared for removing organic contaminants from the surface of titania nanoparticles. The most effective purification treatment was annealing of nanoparticles below 400 °C: annealing at higher temperatures causes besides purification the growth of nanoparticles.

© 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: A. Films; A. Sol–gel process; Nanoparticles; D. TiO₂

1. Introduction

Titania (TiO₂) has attracted attention as a perspective material for many advanced applications. It has been studied extensively as a promising photocatalyst [1], solar cell material [2], biocompatible material [3], material for anti-fogging and self-cleaning coating [4,5], etc. Nanostructure, crystal structure, purity etc. all play important roles in many of titania applications.

The efficiency of TiO₂ photocatalytic properties depends besides its crystal structure also on the grain size [6]. Even the adhesion of living cells on titania films (extremely important for medical implants) depends on the nanostructure of the material [3]. The efficiency of a dye sensitized solar cell is as well influenced by the nanostructure of the material, since the grain size of the material directly influences how much dye can be adsorbed on titania surface [7].

One of the ways to control the grain size of titania is by changing the annealing temperature of the material. With increasing annealing temperature, the grain size starts to increase, but also crystal phase change occurs during annealing from the photocatalytically active anatase to inactive rutile

crystal phase [8–11]. With annealing it is possible to get larger crystallites, but it has been shown that enhanced properties of titania usually emerge with smaller particles/grains [3,6,7]. Titania can as well exist in amorphous phase but amorphous titania is not photocatalytically as active as anatase crystal phase [12]. Electron transfer is also faster between surface adsorbed dye and crystalline titania compared to amorphous material [13] and conductivity of titania is enhanced with the evolution of its crystalline structure [14].

For many applications it is feasible to synthesise titania nanoparticles with controlled size and crystal phase and subsequently manufacture the necessary object (electrode, functional coating etc.). There are numerous methods to synthesise titania nanoparticles with different sizes and crystalline phases. It is possible to obtain titania particles as small as 4 nm with well-defined crystal structure using various methods [15–17]. With different methods titania consisting of anatase [15–19], rutile [18,19] or brookite [18] crystalline phase can easily be obtained.

Synthesis methods using organic media and/or organic ligands might prove to be problematic in specific applications of titania due to excess amount of organic material adsorbed on the surface of the synthesised nanoparticles. Depending on the method used the organic material could be toxic, acidic or blocking the surface and making the material unusable for

*Corresponding author. Tel.: +372 580 17909.

E-mail address: urmas.joost@ut.ee (U. Joost).

the intended application. For this reason it is very important to investigate different methods of cleaning the synthesised material from organic residue.

Although purification of titania nanoparticles is a very common process in laboratory practice the specific purification protocol is often chosen without scientific justification. The aim of the present work is to compare efficiency of three different and in laboratory practice widely used treatments for removing organic contaminants from the surface of the nanoparticles.

2. Experimental

Titania nanoparticles were synthesised using a method described by E. Scolan et al. [15] with slightly modified parameters. Commercially available reagents were used, titanium(IV) butoxide ($\text{Ti}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4$) (Sigma-Aldrich, reagent grade), *p*-toluene sulfonic acid (PTSA) (Sigma-Aldrich, reagent plus), acetyl acetone (acac) (Sigma-Aldrich, reagent plus), butanol (Sigma-Aldrich) and deionised water were used as precursors. Since the compounds are sensitive to water, the solvent (butanol) was dried using CaH_2 and distilled before utilization. The molar ratio between PTSA and titanium (IV) butoxide was set to 0.2, the molar ratio between acac and titanium(IV) butoxide was set to 3 and the molar ratio between water and titanium(IV) butoxide was set to 10. The reaction was carried out overnight at reflux conditions. The mixture was first cooled to room temperature and after that the solvent was evaporated with a rotary evaporator at 70 °C, the solid residue was weighed and dispersed in acetone yielding a uniform and stable 10 wt% colloidal solution.

Thin films were prepared by spin-coating colloidal solution on Si(1 0 0) substrates in ambient atmosphere. The substrates were cleaned prior to coating with ethanol to remove small dust particles. The rotation frequency during spin-coating was 3000 rpm and coating time was 0.5 min. The obtained precursor films were aged at room temperature in ambient conditions for 4 days. The purpose of such ageing was to allow the remaining solvent to evaporate slowly in order to prevent the cracking of the films. After ageing the samples were annealed in a Nabertherm L5/11/S27 furnace (in air atmosphere) in order to evaporate the remaining solvent and evaporate/burn off organic species. Similar methods for preparing thin titania films (not based on nanoparticles) have been used by our group previously [20–23].

Three different and in laboratory practice widely used treatments were devised to remove organic contaminants from the surface of the nanoparticles: (i) annealing at different temperatures, (ii) annealing followed by washing with deionised water in an ultrasound bath for 10 min, and (iii) irradiation of nanoparticle film (aged, but not annealed) with UV light to degrade the organic molecules using photocatalytic properties of titania.

At the beginning of annealing all samples were put into the furnace and the temperature was increased to first set value of 100 °C by using the mean ramping rate of 1.25 °C/min. After a 1-h dwelling time, one set of samples was removed from

the furnace and the temperature was increased to the next desired value (200 °C) by using a mean ramping rate 1.7 °C/min. This was followed by annealing for one hour at that temperature and removal of another set of samples from the furnace. The procedure was repeated until the last sample was removed from the furnace after a 1-h annealing at 500 °C.

Part of samples was washed with deionised water after annealing. However films annealed lower than 200 °C were destroyed during the washing (nanoparticles were washed off the substrate), only samples annealed at 200 °C or higher could be analysed after washing. Washing off the films was conducted in deionised water for 10 min using 37 kHz frequency at room temperature (Elmasonic P 30 H).

UV light was used to photo-oxidize organic contaminants on the titania nanoparticles (aged, but not annealed). Self-made setup was used, a 6 W low pressure mercury lamp with luminous output of 1.7 W at 254 nm (according to datasheet [24]) was employed. Luminous flux at the sample surface was measured with Delta Ohm HD2302.0 lux meter equipped with an UV C sensor. Luminous flux between 220 and 280 nm was 60 W/m². Photo-oxidation experiments were conducted in Memmert CTC 256 climate chamber at 70% of relative humidity and 30 °C. It is stated that the most effective humidity conditions for photo-oxidation on titania surface is in the humidity range from 10 to 80% [25].

X-ray photoelectron spectroscopy (XPS) was used for investigating the chemical state and elemental composition of titania nanoparticle films after different treatments. XPS measurements were conducted using a surface station equipped with an electron energy analyser (SCIENIA SES 100) and a non-monochromatic twin anode X-ray tube (Thermo XR3E2), with characteristic energies of 1253.6 eV (Mg $K\alpha_{1,2}$ FWHM 0.68 eV) and 1486.6 (Al $K\alpha_{1,2}$ FWHM 0.83 eV). All XPS measurements were conducted in ultra-high vacuum (UHV) conditions. The binding energy scales for the XPS experiments were referenced to the binding energy of Ti 2p_{3/2} (458.6 eV) photoemission line. To estimate overall atomic concentrations of different compounds and elements average matrix relative sensitivity factors (AMRSF) procedure [26] and transmission function of the instrument were used. Raw data were processed using Casa XPS [27] software. Data processing involved removal of $K\alpha$ and $K\beta$ satellites, removal of background and fitting of components. Background removal was done using Tougaard background, for fitting Gauss–Lorentz hybrid function was used (GL 70, Gauss 30%, Lorentz 70%) for best fit. However the absolute amounts of different compounds and elements have to be considered cautiously and are given to outline trends and estimates only. Due to the possible surface region deviation from chemical homogeneity in the working range of photoelectron spectroscopy (surface region with thickness up to three electron mean free paths), some signals might be amplified or suppressed.

The crystalline phases of titania were examined by measuring room-temperature Raman spectra of the films prepared on a fused silica substrate using Renishaw micro-Raman setup equipped with 514 nm continuous mode argon ion laser, spectral resolution was about 1.5 cm⁻¹.

Download English Version:

<https://daneshyari.com/en/article/1461179>

Download Persian Version:

<https://daneshyari.com/article/1461179>

[Daneshyari.com](https://daneshyari.com)