Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

Electron transport in surface modified TiO$_2$ nanoparticles

V. Lionas[a], T. Georgakopoulos[a], N. Todorova[b], S. Karapati[b], K. Pomoni[a,*], C. Trapalis[b]

[a] Department of Physics, University of Patras, 26504 Patras, Greece
[b] Institute of Nanoscience and Nanotechnology, National Centre for Scientific Research "Demokritos", 15343 Ag. Paraskevi, Attikis, Greece

ARTICLE INFO

ABSTRACT

Surface modified nanoparticles of P25 Evonik Degussa TiO$_2$ with silane coupling agent 3-(2-aminoethylamino) propyltrimethoxysilane (AAPTMS) were prepared at low temperature conditions. The samples were characterized using the BET technique. Their temperature dependent dc electrical conductivity was investigated in the temperature range 195–440 K. In order to investigate the influence of the environment, measurements were conducted in vacuum and in air. A change of conductivity with the molar ratio of AAPTMS/P25 is shown. Moreover, a decrease of conductivity is exhibited when compared to that of P25 nanopowder, attributed to the presence of silica in AAPTMS. The modified samples show a significant decrease of conductivity in air. In addition, the conductivity dependence on temperature differs from that in vacuum, suggesting the competition between the adsorption of oxygen and water from the surrounding atmosphere. It was demonstrated that the electrical conduction was controlled by the grain boundaries and the small polaron hopping at the high and intermediate temperatures whereas Mott's variable range hopping was the main conduction mechanism at the lower temperature regime.

1. Introduction

Titanium dioxide (TiO$_2$) is one of the more fascinating materials with a wide range of applications in several fields such as photocatalysis [1–4], gas sensors [5–7], air purification [8–10], solar cells [11–13], removal of inorganic and organic pollutants [14–16], self cleaning [17,18] etc. TiO$_2$ is an inexpensive, nontoxic wide-band gap semiconductor ($\sim$ 3.2 eV) with physical and chemical stability, and high photocatalytic efficiency. It crystallizes in three different crystalline phases, anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic) [19]. Intensive efforts have been made to overcome the low photoefficiency and the lack of visible light activity of bare TiO$_2$. To date, surface modification is one of the most effective approaches on promoting the TiO$_2$ photocatalytic performance. Surface modification can be achieved by several techniques. Among them is the loading of nanosized metals as Pt, Au, Pd and Ag at TiO$_2$ surface via photodeposition [20–22], the partial replacement of oxygen by doping with transition metals [23–25] and non-metallic elements [26–28], the polymer TiO$_2$ nanocomposites [29], and the morphological control, specifically the exposed {001} facets [30,31]. The surface charge of TiO$_2$ can also be modified using metal oxides such as silica, alumina and zirconia. The surface charge modification influences the photocatalytic reaction rate and mechanism and silica is one of the common inorganic surface charge TiO$_2$ modifiers [4]. The last years a number of

studies with silica as TiO$_2$ surface modifier have been conducted which confirm the enhancement of photocatalytic properties [4,32,33]. On the other hand, the suppression of the photocatalytic activity was reported by some others [34–36] that was attributed to the creation of coating around TiO$_2$ nanoparticles because of the formation of Ti–O–Si chemical bonding at the interface of TiO$_2$ and SiO$_2$. Karapati et al. modified commercial titania P25 nanoparticles modified with alkaline surfactant AAPTMS [3-(2-aminoethylamino) propyltrimethoxysilane] in water media [10]. The results demonstrated that during modification TiO$_2$ interacted with the amino-groups (–NH$_2$) of AAPTMS and a coating of –SiOH groups was formed around the TiO$_2$ nanoparticles. The modified titania powders exhibited improved photocatalytic activity in NO oxidation and NO$_x$ removal.

Apart the study of the optical and structural properties of transition metal oxides, the understanding of their electrical transport mechanisms is essential for the successful fabrication, performance and efficiency of semiconductor devices. The studies of the electrical conductivity of the modified TiO$_2$ are limited when compared to the considerable amount of research work carried out to improve its photocatalytic activity. The most of them refer to the influence of doping with transition metals and non-metallic elements and the results depend on the preparation technique, the TiO$_2$ phase, the kind and amount of doping element as well as on the annealing temperature. Joskowska et al. have found an increase of more than three orders of

---

magnitude in conductivity in the case of nanocrystalline Nb modified TiO$_2$ sol–gel thin films (0–40 mol% Nb), heat-treated at 800 °C [37]. In another work, Liu et al. report that PANI/TiO$_2$-SiO$_2$ exhibited an increase of at least one order of magnitude in conductivity than that of PANI/TiO$_2$ and TiO$_2$-SiO$_2$ [38]. Yu et al. report a change of about an order of magnitude in pure anatase N-doped TiO$_2$ (4 at%) prepared by plasma-assisted molecular beam epitaxy technology [39]. Our group has conducted electrical conductivity measurements on anatase (0.8 at %) N-doped TiO$_2$ sol-gel thin films and an increase of about six orders of magnitude was noticed for samples heat-treated at 600 °C [40]. In our recent study of the electrical conductivity of anatase TiO$_2$ nanoplates with silver nanoparticles photodeposited on {101} crystal facets prepared by a solvothermal method, we have found an increase of three orders of magnitude for the samples photodeposited for 5 min [41].

The types of conduction mechanisms contributing to the electrical conductivity depend on the temperature range of measurements. Therefore, the study of the temperature dependence of the conductivity is a key issue for the understanding of the involved mechanisms and it is fundamental for obtaining significant information on charge transport in TiO$_2$.

Based on the literature review up to now, no research has been reported on the electrical properties of commercial titania P25 modified with surfactant AAPTMS in water media. In these conditions, the presence of surfactant's amine group ensures the bonding between the surfactant molecule and TiO$_2$ [10]. The aim of the present work was to study the electrical conductivity mechanisms of the modified samples prepared at several molar ratios of AAPTMS/P25 and discuss the influence of the environment.

2. Experimental details

2.1. Preparation of the modified TiO$_2$ nanoparticles

The samples were prepared using commercial TiO$_2$ powder P25 (Evonic Degussa) and 3-(2-aminoethylamino) propyltrimethoxysilane (C$_8$H$_{22}$N$_2$O$_3$Si) from Sigma-Altrich as a modifying agent. 2 g of P25 were dispersed in 200 ml distilled water (pH $\sim$ 5) using tip sonicator (Hielseher, UP100hd) functioning at 50% amplitude for 5 min [10]. Samples with different AAPTMS/P25 molar ratios were prepared by addition of adequate amounts of 3-(2-aminoethylamino) propyl-trimethoxysilane to P25 titania powder and the obtained emulsions with pH $\sim$ 11 were aged at 50 °C for 18 h under vigorous stirring. The modified TiO$_2$ powders were collected by centrifugation and subsequently washed with acetone and ethanol. Finally, the powders were dried at room temperature for 24 h and designed as samples A3, A6, A9 and A18 according to the AAPTMS/P25 molar ratio (Table 1).

2.2. Characterization

The porosity of the modified samples was examined by liquid N$_2$ adsorption/desorption isotherms using the Quantachrome Autosorb-iQ instrument. The specific surface area (S$_{BET}$) and pore size distribution were determined by the Brunauer-Emmett-Teller (BET) technique and the Barrett-Joyner-Halenda (BJH) method, respectively.

Table 1
Molar ratio of AAPTMS/P25 (MR), BET specific surface area (S$_{BET}$), main pore radius (R$_m$) and average pore radius (R$_{av}$) of bare and modified TiO$_2$ samples.

Samples	A3	A6	A9	A18	P25
MR	0.3	0.6	0.9	1.8	–
S$_{BET}$ (m^2/g)	59.8	48.6	45.6	44.5	43.0
R$_m$ (nm)	12.4	34.4	17.7	32.5	23.1
R$_{av}$ (nm)	18.1	25.0	25.4	25.2	14.4

2.3. Dielectric and electrical conductivity measurements

The electrical conductivity of the modified samples was measured in different ambient environment, in vacuum and in air at the temperature ranges 195–440 K and 245–440 K respectively. The bare TiO$_2$ (sample P25) and the modified powders were pressed into disks with a diameter of 10 mm and two coplanar silver electrodes with length 7 mm and a gap between them 0.8 mm were vacuum deposited on. The thickness of the samples was 0.40, 0.40, 0.35, 0.45 and 0.48 mm for A3, A6, A9, A18 and P25 respectively. The current-voltage behavior was Ohmic in the range 1–10 V and therefore a constant bias voltage of 5 V was chosen to be applied on the samples. An Oxford ITC502S temperature controller and a Keithley 6517A electrometer were used for the temperature adjustment and the current record, respectively. For the elimination of persisting effects of previous light exposure, the samples were annealed at 440 K for 90 min and left to cool down slowly at room temperature. Subsequently, they remained in the dark for 24 h before performing any measurement.

The sample A18 was dielectrically characterized by Broadband Dielectric Spectroscopy (BDS) in the frequency range of 0.1 Hz to 1 MHz, using an Alpha-N Frequency Response Analyser, supplied by Novocontrol Technologies GmbH (Hundsangen, Germany). The amplitude of the applied ac voltage was 1.0 V.

3. Results and discussion

3.1. Textural properties and morphology

Fig. 1a illustrates the adsorption-desorption isotherms of sample A9, while its pore size distribution plot is given in Fig. 1b. For this sample, as well as for the rest of the samples (not presented due to similarity) the isotherms display the typical type IV curve, according to the IUPAC
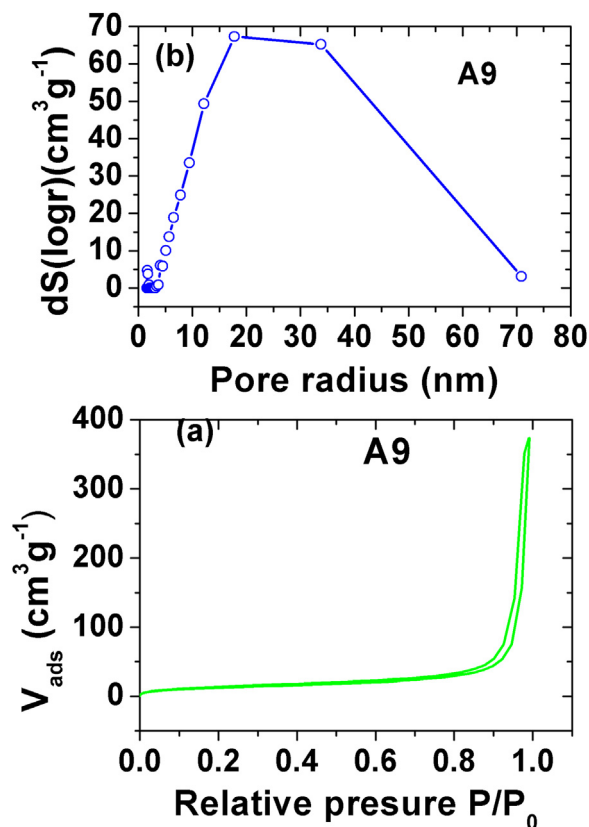

Fig. 1. (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution curve from Barrett-Joyner-Halenda (BJH) method, for the modified A9 sample.