

Synthesis, tuning of electrical conductivity and self-assembly of niobium doped titania nanoparticles

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ABSTRACT

Crystalline niobium-doped titania nanoparticles were prepared by a solvothermal procedure using tert-butanol as a novel reaction medium. This procedure provides crystalline doped and undoped nonagglomerated titania nanoparticles, whose size can be controlled from 4 to 15 nm by changing the reaction temperature and time. The anatase lattice of these particles can incorporate more than 20 mol % of Nb ions. The nanoparticles can be easily dispersed at high concentrations in tetrahydrofuran to form stable colloidal suspensions and can be assembled into porous mesostructures directed by the commercial Pluronic block copolymer F127. The resulting mesoporous films show a regular mesostructure with a d spacing of about 17 nm, a uniform pore size of about 10 nm, crystalline pore walls, a high porosity of 43%, and a large surface area of 190 m² cm⁻³. Substitutional doping with niobium ions drastically increases the electrical conductivity of the titania particles.

Keywords: conducting transparent oxides, niobium-doped titania, nanoparticles, self-assembly, mesoporous films.

1 INTRODUCTION

Transparent conducting oxides (TCOs) with a regular mesoporosity have recently attracted attention owing to their ability to accommodate guest species in photovoltaic, electrochromic, and chemical sensing applications, where the access of both photons and charge carriers to a large interface is of key importance [1,2]. However, the range of compounds that simultaneously exhibit electrical conductivity and optical transparency in visible light is limited to doped indium, tin, zinc, or cadmium oxides; of these, only tin-doped indium oxide and antimony-doped tin oxide have been prepared with a periodic porous morphology [1,2]. The synthesis of mesoporous electrodes from other TCOs can substantially extend the library of available transparent conducting nanoarchitectures meeting the requirements of different optoelectronic applications.

In 2005, a metallic type conductivity of Nb-doped anatase titania (NTO) films was reported [3]. Thin films, epitaxially grown by pulsed laser deposition, exhibited a conductivity of 10³-10⁴ S cm⁻¹ and high optical transmittance in visible light, which makes them

comparable with the much more expensive ITO. The conductivity mechanism was explained by the formation of an impurity band overlapping with the conduction band of anatase.

As titania films with controlled mesoporous structure can be easily prepared, an increase in their electrical conductivity due to doping with Nb atoms could open a way to inexpensive TCO materials with controlled porosity. Moreover, the already known applications of titania, such as in photovoltaics, photocatalysis, and charge storage, could greatly benefit from an increased electrical conductivity of the titania framework.

Fabrication of periodic mesoporous Nb-doped titania films and disordered porous powders has been reported by several authors, but their electrical conductivity was not investigated [4]. The majority of studies involve physical processes or high temperature solid-state reactions, which are not conducive for the fabrication of periodic porous nanostructures.

Periodic mesoporous titania films with controlled porous structure can be prepared by the self-assembly of amorphous titania sols, crystalline nanoparticles, or a combination of both in the presence of surfactants acting as structure-directing agents. We have recently shown for mesoporous thin films of antimony-doped tin oxide that its nanocrystals can serve as building blocks for the assembly of nanostructured transparent electrodes [5]. Due to the intrinsic crystallinity of the building blocks, crystalline mesostructures can be obtained already at moderate temperatures. However, the use of nanoparticles as the primary units for the assembly of mesoporous conducting films implies certain requirements regarding their properties. The particles should be just a few nanometer in size with a narrow particle size distribution, feature crystallinity and electrical conductivity, and should be dispersible in various solvents to form stable colloidal solutions. The synthesis of Nb-doped titania nanoparticles meeting those criteria has not been reported so far.

Here we describe the solvothermal synthesis of crystalline monodispersed niobium-doped titania nanoparticles using tert-butyl alcohol as a novel reaction medium and an oxide source [6]. Furthermore, the ability of the obtained nanocrystals to self-assemble into complex 3D mesoporous nanostructures and the electrical conductivity of the nanoparticles and mesoporous films are investigated.

2 EXPERIMENTAL

The details of synthesis procedure are given in [6]. For the synthesis of niobium-doped titania nanoparticles, TiCl_4 and $\text{Nb}(\text{OEt})_5$ were added to tert-butanol under continuous stirring. The clear solution was kept at 100 °C in a Teflon-sealed autoclave. The reaction time was 1.5-4 h. The resulting nanoparticles were separated by centrifugation. The particles separated this way contain 25–50 % of organic residues. For the fabrication of mesostructured films, a solution of Pluronic F127 in THF was added to non-washed particles and stirred until the particles were homogeneously redispersed. Concentrated HCl was added to obtain a clear transparent solution. The mesoporous films were deposited by dip coating of prepared solutions on various substrates (Si wafer, glass) at a relative humidity of 50 - 60% and 25 °C. The films were heated in air at 300 °C for 2 hours and/or in N_2 at 500 °C for 2 hours. The average thickness of the films after heating is around 200 nm.

3 RESULTS

For the preparation of Nb-doped titania nanoparticles, titanium tetrachloride and niobium(V) ethoxide were dissolved in tert-butanol. The particles with different Nb content are designated as NPX, where X is the Nb/(Nb+Ti) molar ratio in percent. The clear solution was kept at different temperatures and different times in a laboratory oven in a Teflon-sealed autoclave. The particle size and crystallinity strongly depend on the reaction temperature. At 60 °C, the particles are completely amorphous, and an increase in the reaction temperature to 100 °C is necessary to obtain a crystalline phase. A further increase in the reaction temperature leads to larger crystalline particles.

An increase in the concentration of Nb leads to a delayed formation of particles, at 100 °C the onset of crystallization occurring after 1.5, 3, and 4 h for NP0, NP10, and NP20, respectively. This effect is attributed to the suppression of particle crystallization due to Nb doping. Furthermore, the particle size at the same reaction temperature can be varied by changing the reaction time. While NP20 particles synthesized at 100 °C for 4 h are only 4 nm in size, prolonging the reaction time to 20 h increases the particle size to 13 nm.

As we have aimed at the preparation of crystalline nanoparticles as small as possible, the reaction at 100 °C was stopped just after the onset of crystallization. The NTO nanoparticles with different Nb content prepared this way are crystalline and 4-5 nm in size (Fig. 1). The XRD patterns of both pure and doped nanoparticles with up to 20 mol % of niobium show only one crystalline phase, either anatase or a phase structurally closely related to anatase. An increase in the Nb content leads to a unit cell expansion of about 5% due to the replacement of Ti^{4+} ions with slightly larger Nb^{5+} ions according to Vegard's law.

The nanoparticles can be dispersed easily in tetrahydrofuran (THF) at concentrations of more than 5 wt % of NTO in the presence of a small amount of hydrochloric acid, forming stable transparent colloidal dispersions.

To sum up, the undoped as well as Nb-doped titania nanoparticles prepared by the solvothermal synthesis in tert-butanol are crystalline, nanosized, and dispersible, which makes them suitable building blocks for nanostructured materials assembly. We have examined the applicability of the as-synthesized nanoparticles for the assembly of mesoporous films using the commercial Pluronic F127 polymer as a structure-directing agent. Thin films designated as MS0, MS10, and MS20 were prepared from NP0, NP10, and NP20 nanoparticles, respectively. The synthesis times for the different samples were chosen such that the particle size of all samples was about 4 nm, in order to make the particles compatible with the surfactant-assisted self-assembly. In order to remove the template and to sinter the nanoparticles, the films were heated in air at 300 °C for 2 h.

The character of the mesoporous structures assembled from nanoparticles with varying Nb content differs significantly. The assembly of the undoped NP0 nanoparticles gives a worm-like open mesostructure with a homogeneous pore distribution. The films assembled from NP10 nanoparticles feature a channel-type mesostructure. Finally, the NP20 particles lead to films with a higher degree of pore ordering, resembling a cubic mesostructure with a d spacing of about 17 nm. The thickness of the films assembled from particles with different doping levels is around 200 nm.

The highly porous morphology of the films assembled from nanoparticles is apparent in TEM images (Fig. 2). The Fourier transforms of the TEM images show a ring corresponding to a mesostructure dimension of 16 nm, which is in agreement with the data provided by the small-angle XRD. The pore walls are composed of crystalline nanoparticles (Fig. 2b). The high crystallinity of the films calcined at 300 °C was also proven by wide-angle X-ray diffraction. The crystalline domain size calculated from the (101) reflection of the corresponding XRD patterns is about 7.5 and 6.5 nm for MS0 and MS20 films, respectively.

The textural properties and the accessibility of the internal surface of the thin films were studied by krypton adsorption at -196 °C. The samples assembled from nanoparticles are characterized by an open porous structure without pore blocking. The use of particles with a higher Nb content leads to films exhibiting a larger pore volume and surface area, in combination with a higher degree of uniformity of the mesostructure as could be seen in electron microscopy. The MS20 films feature the largest pore volume and a porosity of 43%, with a surface area of 190 $\text{m}^2 \text{cm}^{-3}$.

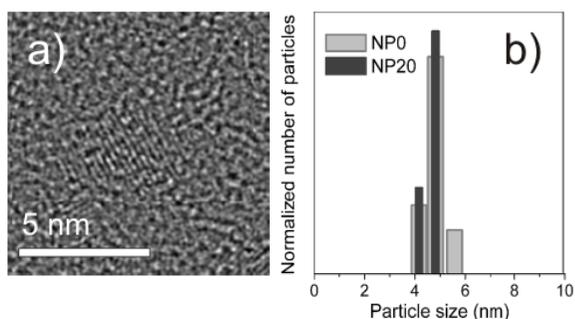


Figure 1: HR-TEM image (a) of as-made NP20 nanoparticles synthesized at 100 °C, and the particle size distribution determined by DLS in tetrahydrofuran (b).

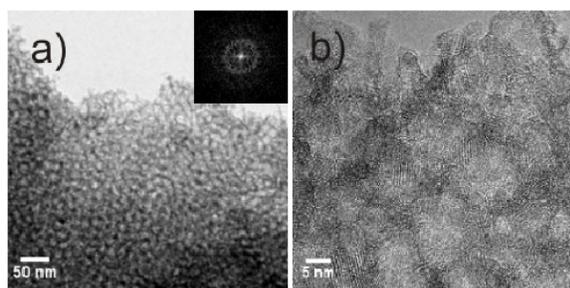


Figure 2: TEM (a) and HR-TEM (b) images of MS20 film calcined at 300 °C. The inset shows the Fourier transform of the image.

The valence state of the metal atoms in the Nb-doped titania lattice is an important indication of successful doping with regard to the electric conductivity, which is directly related to the specific defects formed in the doping process. The valence states of Ti and Nb in the nanoparticles containing 20% of Nb prepared at 100 °C were investigated using X-ray photoelectron spectroscopy (XPS). About one fifth of both titanium and niobium is found in their reduced states, Ti^{3+} and Nb^{4+} or lower. In case of effective doping by Nb, donor level electrons can reside in the form of reduced valence states of Ti or Nb. The extra electrons can be assumed not compensated by other defects. Therefore, the introduction of Nb^{5+} ions into the titania lattice leads to the donation of electrons into the conduction band and thus an increase in the charge carrier concentration.

In spite of the presence of Ti in the reduced state, the room temperature electrical dc conductivity of the crystalline nanoparticles prepared at 100 °C is still quite low, ca. $2 \times 10^{-5} \text{ S cm}^{-1}$ for NP20. This is due to a strong localization of the free electrons and their low mobility [8]. To further improve the electrical conductivity, the as-produced NTO nanoparticles have to be heated in non-oxidizing atmosphere such as nitrogen at 400-600 °C (Fig. 3). The change in the conductivity with the Nb content was

found to be nonlinear, the highest conductivity being found for NP20, for which the conductivity and the carrier concentration obtained from Hall effect measurements were 0.25 S cm^{-1} and 10^{20} cm^{-3} , respectively. The maximum conductivity was obtained for a much higher Nb concentration than for materials prepared by physical methods, for which the highest conductivity is observed already at 3% of Nb.

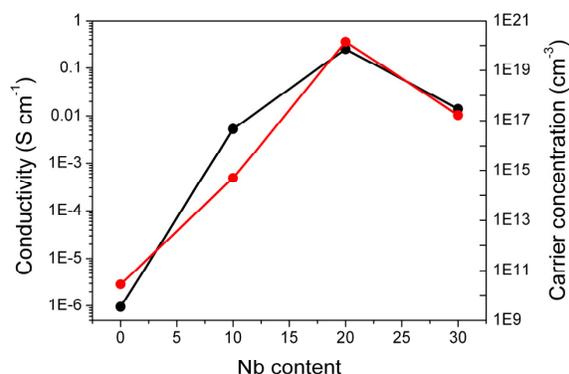


Figure 3: Specific conductivity (black) and charge carrier concentration (red) of the pellets pressed from Nb-doped nanoparticles and heated at 600 °C in N_2 , as a function of Nb content. The axes are shown in logarithmic scale.

An XPS depth profile analysis of the particles treated in N_2 at 600 °C shows that the Nb content reaches 30% at the surface and 20% in the bulk, i.e. the particle surface is enriched with niobium. In the particle core, 16% of the titanium atoms is present as Ti^{3+} , their fraction being similar to the amount of Nb^{5+} introduced in the synthesis. This indicates that most of the extra electrons generated by Nb doping are released into the conduction band of TiO_2 , leading to the formation of Ti^{3+} .

4 DISCUSSION

The developed procedure provides particles with controlled size in the range from 4 to 15 nm. Besides the pristine oxides, it is suitable for the preparation of doped nanoparticles with homogeneously distributed dopant within the host lattice. The incorporation of the guest impurities slows down the crystallization rate and leads to some expansion of the anatase lattice.

The particles can be easily dispersed in THF to form stable colloidal dispersions. This can be attributed to their surface chemistry, which also enables the assembly of nanoparticles to regular mesostructures directed by the Pluronic templates. The films assembled from doped titania nanoparticles exhibit a higher degree of mesostructure ordering than those prepared from undoped ones, which may be due to the different surface properties.

The incorporation of Nb drastically increases the electrical conductivity of the nanoparticles. The maximum conductivity at room temperature of NP20 reaching 0.25 S cm^{-1} is remarkably high for the wide band gap semiconductor titania and is achieved due to the extrinsic doping with niobium ions. The only other study published to date on the chemical preparation of conducting Nb-doped titania nanoparticles gives similar values of conductivity of as-produced nanoparticles and supports the suitability of chemical routes for the preparation of conducting titania particles. [7] Their conductivity is still much lower than that of epitaxially grown NTO films. It appears to be a general feature of the polycrystalline TCO systems prepared by chemical methods that their dc conductivity is lower than the conductivity of analogous materials prepared by physical deposition techniques. This difference is attributed primarily to grain boundary scattering in the polycrystalline material and the larger amount of defects and imperfections in the nanosized crystals. In contrast to the commonly used indium or tin oxides, which can form solid solutions with various dopants causing only limited distortion of the host crystalline lattice, the incorporation of Nb into the anatase lattice causes a noticeable lattice expansion. Moreover, donated electrons are susceptible to compensation by easily formed defects.

It appears that at least two factors are important for obtaining a highly conductive niobium-doped titania semiconductor. First, doped Nb atoms must be homogeneously distributed within the anatase lattice. Second, the formation of other defects except for the replacement of tetravalent Ti with pentavalent Nb should be avoided, as the extra electrons caused by Nb doping and existing in the form of Ti^{3+} and/or Nb^{4+} are easily compensated by titanium vacancies or oxygen interstitials. The conductivity of the as-prepared nanoparticles is rather low and can be substantially increased by a treatment at elevated temperatures in non-oxidizing atmosphere. The reasons are particle growth, particle sintering, and pyrolysis of the organic residues acting as an insulator. However, such a treatment can lead to the undesired partial surface segregation of Nb due to a "self-purification" process.

The mesoporous layers assembled from the Nb-doped titania nanoparticles show very good structural properties such as ordering of the porous system, a uniform pore size, a high pore volume, a large surface area, and crystallinity of the walls. However, the increase in conductivity due to Nb doping is much less pronounced for the mesoporous films than for the similarly treated particles. We tentatively attribute this (i) to the much smaller size of the crystals in the walls of the mesoporous films compared to that of the pressed pellets after heating (7 and 22 nm, respectively) due to the confining effect of the template, and (ii) the oxidation of a surface layer by adsorbed oxygen molecules upon exposure to air due to the high surface area of the films.

One of the ways to increase the conductivity can be the use of the bigger crystals for the mesostructure assembly, which would require larger amphiphilic polymers. Further

optimization of non-oxidizing processing methods for particle sintering is also necessary.

5 CONCLUSIONS

The solvothermal procedure developed in this study enables the preparation of crystalline-doped and undoped nonagglomerated dispersible titania nanoparticles with a narrow particle size distribution and homogeneous incorporation of doping atoms within the host lattice. The particle size and crystallinity can be controlled by the reaction temperature and time. Substitutional doping with niobium ions drastically increases the electrical conductivity of the titania particles. The particles can be easily dispersed at high concentrations in THF to form stable colloidal dispersions. The dispersibility improves with the increasing Nb content, which can be attributed to a changing surface chemistry of differently doped nanoparticles. The Nb-doped titania nanoparticles can be assembled into regular three-dimensional mesoporous structures with a narrow pore size distribution and high surface area.

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