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Thin films of TiO_2 nanocrystals with controlled shape and surface coating for surface plasmon resonance alcohol vapour sensing

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Abstract

This work explores the potential of thin films composed of shape-controlled colloidal TiO_2 nanocrystals in optical gas sensing applications. To this purpose, an optical characterization of nanocrystal thin films has been performed by means of UV–vis spectroscopy and surface plasmon resonance (SPR) technique. In particular, this technique has been used as optical transduction method to test the sensing properties of the oxide films towards alcohol vapours. Numerical fitting routines have been employed to evaluate quantitatively the changes in the characteristic optical parameters for the investigated films during the sensing process. It has been found that rod-shaped TiO_2 nanocrystals provided with close-packed monolayers of long-chain surfactants on their surfaces, maximize the sensor response, as they may help to achieve a higher degree of alcohol accumulation on the active material.

Keywords: TiO_2 nanocrystals; Thin films; Optical sensors; Surface plasmon resonance; Alcohol detection; Capping layer

1. Introduction

In the past decade, thin films consisting of nanosized inorganic particles have attracted considerable technological interest due to their potential applications in several fields, such as in microelectronics, integrated optics, electro- and photo-chemistry, and in catalysis [1]. In particular, grain size reduction down to the nanometer level has been generally recognized as the most efficient strategy to enhance the sensing properties of transition metal oxides. This improvement has been attributed to the higher density of surface sites available for gas adsorption, as compared to that provided by the corresponding bulk material [2].

Among oxides, TiO_2 has received much attention for its successful employment in dye-sensitized solar cells [3] and in the photocatalytic degradation of pollutants [4,5]. Owing to its chemical stability, high refractive index, and elevated dielectric constant, TiO_2 has been widely explored as a fundamental component in a number of optoelectronic, electrochromic, and electroluminescent devices, as well as in sensors [6–8]. Based on such technological relevance, detailed studies on the optical and electrical properties of this semiconductor, particularly in the form of thin films, have become increasingly intensive [9,10].

Many deposition techniques have been developed for sensor fabrication, among which the sol–gel route has largely been the most preferred chemical method to prepare the active material [11,12]. Recent advances in wet-chemistry syntheses [13] have made gram-scale amounts of size- and shape-controlled colloidal nanocrystals available for the reproducible, low-cost realization of innovative device generations with well-tailored performances [14–17]. After their preparation, the nanocrystals

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can be indeed readily manipulated and used as the building blocks by which thin films with controlled mean grain size and/or porosity and with tailored surface chemistry can be constructed.

Recently, among the conventional methods, surface plasmon resonance (SPR) has emerged as a novel and sensitive transduction technique [18]. In a recent paper [19] we reported on the optical detection of small changes in the dielectric constant of a thin oxide layer deposited on a metal surface, that occur when any analyte adsorbs onto the active medium surface or chemically reacts with it. Although numerous studies have reported on the suitability of the SPR approach to organic-based films (e.g. polymers, porphyrins, and phtalocyanines) [20–23], so far its applicability to inorganic or hybrid organic–inorganic thin films for gas sensor applications remains less explored [24,25]. For instance, the deposition of a SiO_x film onto the gold layer has been found advantageous for biosensing [26–28]. More recently we reported about the association of SPR with films made of colloidal TiO_2 nanocrystals ([29a,b]).

In this work we report on the structural, morphological, and optical characterization of thin films made of TiO_2 nanocrystals with controlled shape and surface coating, analyzing their sensing properties for the detection of alcohol vapours by means of the SPR technique. The response of the films to the presence of either methanol or ethanol vapours has been investigated at room temperature as a function of the nanocrystals shape and of the nature of the organic molecules passivating the nanocystals surface. For comparison, the nanocrystals films have been examined after being subjected to oxidative annealing in order to remove the surfactant coating. In all cases, the changes in the values of the optical parameters for the sensing material have been extracted from SPR measurements to authenticate the process of alcohol adsorption.

2. Experimental

2.1. Materials

All chemicals were of the highest purity available and were used as received without further purification. Titanium tetraisopropoxide ($Ti(OPr^i)_4$ or TTIP, 97%), trimethylamino-*N*-oxide dihydrate ($(CH_3)_3NO{\cdot}2H_2O$ or TMAO, 98%), oleic acid ($C_{18}H_{33}CO_2H$ or OLEA, 90%), and ethylene glycol ($C_2H_4(OH)_2$ or EG, 98%) were purchased from Aldrich; *n*-tetradecylphosphonic acid ($C_{14}H_{19}PO(OH)_2$ or TDPA) was purchased from Alfa Aesar. All solvents used were of analytical grade and purchased from Aldrich.

2.2. Synthesis of TiO_2 nanocrystals

Organic-capped anatase TiO_2 rods (referrred to as NRs) were synthesized by hydrolysis of TTIP in OLEA at low temperature, as reported elsewhere [30]. Briefly, TTIP was reacted with an excess of aqueous TMAO solution. TiO_2 rods resulted from the direct injection of large aqueous base volumes into OLEA:TTIP mixtures, while spherical TiO_2 nanocrystals (referred to as NSs) were obtained upon slow in situ water release from TMAO-catalyzed esterification of OLEA and added EG. The nanocrystals were precipitated from the reaction mixture upon ethanol addition and subsequent centrifugation, washed repeatedly with ethanol, and easily redispersed in chloroform or hexane to yield optically clear solutions. Conventional surface ligand exchange procedures were applied to replace the pristine OLEA capping with tetradecylphosphonic acid (TDPA), as described previously [30].

2.3. Characterization

The structural characterization of the nanocystals was performed by powder X-ray diffraction (XRD). XRD patterns were obtained with a powder diffractometer PHILIPS, Mod. P1729, in a conventional θ–2θ reflection geometry by using filtered Cu Kα radiation ($\lambda = 1.54056$ Å). The spectra were recorded in the 2θ interval of 10–80° with an increment step of 0.02°. The powders were prepared by precipitating the purified nanocystals from the respective nonpolar stock solution upon ethanol addition, and then evaporating the residual solvent under vacuum.

For preparation of sensing layers, ~7 nm TiO_2 NSs and ~3 nm × 25–30 nm NRs in size were typically used [30]. Thin oxide films were deposited by spin coating (at 2000 rpm) suitably diluted nanocystals solutions (~0.5–0.1 M, expressed with reference to the TTIP precursor), either onto quartz substrates for spectrophotometric measurements or onto 1 mm-thick glass slides (Corning glass 7059) coated with thermally evaporated 2-nm chromium and 50-nm gold layers for SPR measurements. In order to remove the organic surface coating from the nanocystals, the films were treated at 550 °C for 2 h under O_2 flow, according to the conditions suggested by DTA and TGA analysis.

The surface topography of the nanocystals films was investigated by contact mode atomic force microscopy (AFM) by using an EXPLORER–VEECO system equipped with a Si_3N_4 pyramidal tip. To check the lateral uniformity of the TiO_2 nanocystals films, images were acquired on different areas of the sample surface and at different scan sizes.

The thickness of the films was measured with a surface profiler (Alpha Step 500, Tencor).

Room temperature UV–vis transmittance and reflectance spectra of the oxide films deposited on quartz substrates were recorded with a Varian Cary500 UV–vis-NIR spectrophotometer at normal light incidence. A clean quartz substrate was used as the reference to measure the absolute transmittance of the deposited films.

2.4. Sensing tests

SPR measurements were carried out by using an SPR equipment consisting of a home-made experimental set-up in the Kretschmann's prism configuration [31]. The prism/sample combination was placed on a θ–2θ rotation table driven by a microprocessor-controlled stepping motor (with a resolution of 0.01°). The reflectivity of 1 mW *p*-polarised (i.e. polarised parallel to the plane of incidence) He–Ne laser ($\lambda = 632.8$ nm), inducing surface plasmon excitation of the gold layer at the prism/sample interface, was measured as a function of the