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Sol–gel synthesis of titanium dioxide-based films possessing highly ordered channel structures

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The structural conversion of a titanium dioxide–polyethylene glycol monooleate hybrid thin film applied from an alcohol sol to the glass substrate surface into ordered periodic lattice framework induced by the heat treatment is reported.

The synthesis of mesoporous and macroporous thin TiO_2 films of anatase phase has attracted considerable interest because of their potential applications in photocatalysis, photovoltaics, gas sensing, lithium ion batteries and photonic crystals.[1–7] Mesoporous materials have a pore size of 2–50 nm, whereas macroporous materials possess a pore size larger than 50 nm. Macroporous TiO_2 films have been reported when a sol–gel process is accompanied by phase separation; however, these results are not satisfactory because the pores are just randomly oriented and the pore size distribution is poorly controlled.[8,9] In our opinion, the main difficulty in the synthesis of macroporous films is mainly due to restrictions in the accessible molecular weight of polymers, which is often too low to form structures with a size of hundreds of nanometers thus limiting the facile use of polymer to smaller template structures. However, porous structures tend to collapse at temperatures above 450 °C because the wall thickness is commonly too thin.[10,11] Because of these restrictions, ordered macroporous TiO_2 films are mainly achieved *via* an alternative strategy based on colloidal crystal templates.[11–13] Templates of polyethylene glycol (PEG) are of considerable interest for the development of hybrid TiO_2 nanocomposites and mesoporous titania.[14–17] The aim of this work was to study the formation of ordered titanium dioxide film structures during the sol–gel synthesis using polyethylene glycol monooleate (PEG/MO) and phase changes in the synthesized material with temperature. The structural conversion of titanium dioxide–PEG/MO hybrid organic–inorganic material thin film applied from an alcohol sol to the glass substrate surface into ordered periodic lattice framework constructed by the titanium dioxide nanosized channels induced by the temperature effect is reported.

Isopropanol (Aldrich) was used as a solvent. The 0.5 g PEG/MO (Aldrich 99.98%, M_n ~460) shot was added to 80 ml of isopropanol with stirring. The solution was heated to 70 °C and stirred for 24 h. The 10 g titanium isopropoxide (Aldrich, 98%) shot was added to the above solution drop by drop. The final solution was stirred for 5 h at 70 °C. This solution was then used for applying the films to the glass surface by dipping method. The glass surface was cleaned by ethyl alcohol and dried in air at 100 °C. The hydrolysis of a precursor on the glass surface proceeded as a result of interaction with air moisture.

The film obtained was kept at 550 °C for 1 h. A portion of solution was exposed to hydrolysis in air obtaining a sol that was dried at 60 °C to the formation of a light-yellow powder. According to the thermal analysis of this powder [derived system Q1000 (MOM); temperature range, 20–800 °C; heating

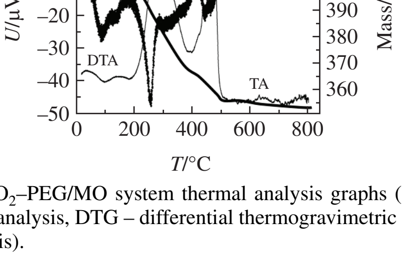
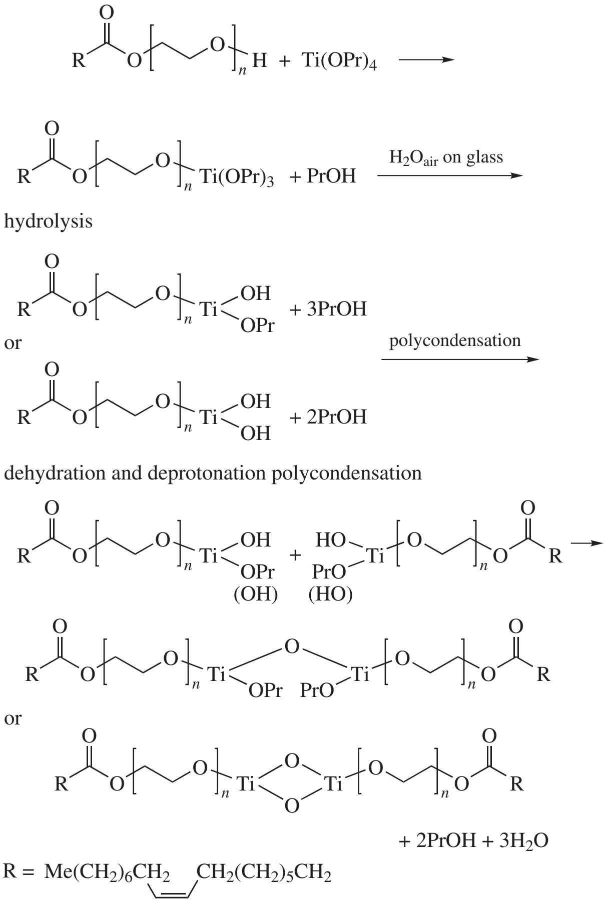


Figure 1 TiO_2–PEG/MO system thermal analysis graphs (DTA – differential thermoanalysis, DTG – differential thermogravimetric analysis, TA – thermoanalysis).



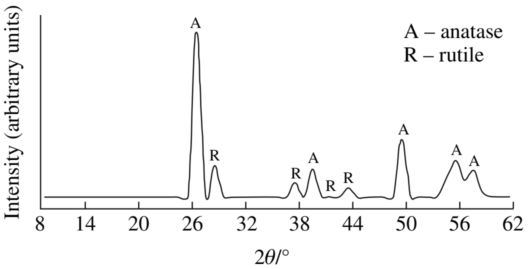


Figure 2 XRD analysis of TiO_2–PEG/MO powder calcinated at 550 °C.

rate, 7 K min^{-1}; and analyzed sample weight, 100 mg] the total mass decrease was 45%, phase change from amorphous titanium dioxide to anatase is accompanied by an exothermic peak at 310 °C, phase change from anatase to rutile is accompanied by an endothermic peak at 415 °C, the complete removal of organic phase occurred at 500 °C (Figure 1).

For carrying out the XRD analysis, the powder was calcined in air at 550 °C for 1 h. The XRD analysis of TiO_2 powder was performed using a DRON-2 diffractometer with CuKα radiation (Figure 2). For the calculation of the size of crystallites obtained during thermal processing at 550 °C and maintaining within an hour, we used the Scherrer equation $d = B\lambda/\beta\cos\theta$, where d is the mean crystallite size, B is the Scherrer constant (0.94), λ is X-ray wavelength, θ is the diffraction angle of phase under investigation, β is the peak width at half height. The Scherrer equation is only a rough approximation of the crystallite size, which is an overestimation, and it concerns only isotropic size determination of microstrain-free crystallites, which can be a biased measure in films as demonstrated by Morales.[18] Thus, the mean crystallite size of powder was 22 nm. The powders obtained are characterized by an anatase : rutile phase ratio of 4 : 1. The powders obtained after drying were X-ray amorphous.

The film surface analysis was performed using an SPM Solver P47H–PRO atomic force microscope with different resolutions. The results are shown in Figure 3.

The films containing titanium dioxide were obtained on the polished glass surface by a dipping method. During the process of hydrolysis of isopropanol solution containing PEG/MO and titanium isopropoxide, by interaction with water vapour from air, after solvent evaporation an amorphous film formed by hybrid organic–inorganic material TiO_2–PEG/MO remains on the glass surface. This is indicated by IR spectroscopy data. The analysis of the film surface structure by scanning probe microscopy has revealed the TiO_2–PEG/MO film surface to be amorphous and to possess a homogeneous relief [Figure 3(*a*)] deprived of orderliness. After thermal treatment the film gains orderliness in the form of periodically arranged channels [Figure 3(*b*)], with their width and wall thickness of about 0.9 μm and a depth of about 200 nm.

The revealed structural change in the films may be induced by various reasons. For example, the initial film formed by sol–gel method may be originally structured due to the appearance of convection currents while drying and removing the solvent. Thus obtained ordered channels formed by titanium dioxide hydroxo forms are filled with the surfactant and remaining solvent molecules and are not identified by scanning probe microscopy. Upon the film calcination the organic phase is removed and the channel structure develops. On the other hand, the structural change observed may occur in originally non-structured film and be because heating upon the calcination of glass substrate with the film takes place under non-isothermal conditions favouring the convection transfer of the film substance. This transfer may be due to the presence in the film structure, apart from titanium dioxide hydroxo forms bonded to PEG/MO molecules, of up to 20% of isopropyl alcohol as indicated by the thermal analysis data. Such a composition leads to changes in the surface tension and viscosity of the film upon the temperature change, providing the conditions for substance convection (by evaporating isopropyl alcohol from the film) and leading to the ordering of the material structure. Convection currents being directed along the vector of PEG/MO orientation in the film hybrid material structure are supposed to lead to the formation of ordered channels.

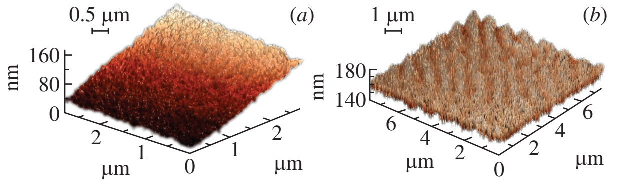


Figure 3 (*a*) The surface of amorphous TiO_2 film; (*b*) the surface of calcined TiO_2 film.

Results of this work show the peculiarities of formation of ordered titanium dioxide film structures during the process of sol–gel synthesis using polyethylene glycol monooleate (PEG/MO). Thermal processing of these coverings leads to formation of the microscopic ordered structures of titania films, constructed as channels, apparently induced by formation of convection currents as described by Rayleigh and Benard.[19] Thus, the results show the distinctive mechanism of titania films formation with the use of PEG as a structure forming material, for which the primary structure of the material keeps safe in the course of roasting.

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