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Transparent titania-ziconia-silica thin films for self-cleaning and photocatalytic applications

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ABSTRACT

Highly transparent thin films of TiO_2-ZrO_2-SiO_2 composites on glass were prepared by sol-gel process, wherein different amounts of zirconia precursor were mixed with titania precursor solution (0–20 mol% Zr with regard to Ti). For better adhesion of the films on glass supports, a silica binder was added to the mixture of alkoxides (27 mol% Si *vs.* Ti). The prepared samples were characterized by various techniques to obtain information on their structural, optical and surface properties. The presence of anatase titania polymorph as the only crystalline phase was detected. Unexpectedly, the higher loading of Zr promoted the growth of anatase particles with progressive spherical shape and concomitant decrease of specific surface area, which adversely influenced the photocatalytic activity. Decrease of the photodegradation activity with increasing amount of Zr was evidenced by contact angle measurements of a fatty deposit, spectrofluorometrically using terephthalic acid probe and by EPR spectroscopy monitoring indirectly the non-persistent radicals generation. On the other hand, the higher content of Zr improved the mechanical stability of resulting thin films. An optimal Zr content around 10 mol% appears to be a good compromise between photocatalytic activity and mechanical robustness of the films.

1. Introduction

Photocatalysis is gaining increasing attention because of its potential in improving the efficiency and selectivity of various industrially important chemical conversions. Most photocatalysts tend to employ semiconductors with band gaps in the visible or near UV portion of the solar spectrum. So far more than 190 various semiconductors were assayed as suitable photocatalysts [1]. Among the materials that are considered for applications in photocatalysis, TiO_2 has been the favorite because; i) it has strong catalytic activity, ii) it is biologically and chemically inert, iii) photostable, and iv) inexpensive [2]. The origin of photocatalytic activity of TiO_2 is attributed to the separation of electron-hole pairs that are formed on its surface upon UV irradiation [3]. Thin films with photocatalytic properties are not only exploited for air and water purification, but are also used in order to achieve anti-fogging, self-cleaning and antibacterial properties of different surfaces. The self-cleaning property arises from one of the two phenomena; hydrophobic (lotus effect) or hydrophilic. The self-cleaning feature of TiO_2, however, represents a combination of photocatalysis and photoinduced superhydrophilicity. The dirt is removed by uniform spreading of water over the surface of photocatalyst and photocatalytic decomposition of organic contaminants [4]. Photocatalytic thin films are considered to be sustainable materials, because they only need sun light and oxygen for activation and regeneration [5].

According to several reports, coupling TiO_2 with ZrO_2 increases the surface area, stabilizes anatase phase and inhibits the recombination of electron-hole pairs [6–9]. The presence of zirconia stabilizes the size of TiO_2, increases the mechanical stability and decreases ageing effect [10]. ZrO_2 has a relatively high permittivity, large band gap, high negative value of conduction band potential [11] and good thermal and chemical stability. Incorporation of zirconium dioxide may stabilize TiO_2 in the anatase crystal phase and their size even during heat treatment at elevated temperatures, suppressing titania crystallites growth [12,13]. Some

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investigations show improved photocatalytic activity when titania is coupled with zirconia or doped with Zr [6,7,14–20]. The efficiency of coupled/doped photocatalyst depends on various factors such as sources, process conditions and ratio between involved species.

Our aim in this study was to prepare photocatalytically active zirconia modified titania thin films on glass and examine properties such as mechanical and long term stability. Furthermore, we employed a low-temperature annealing procedure (150 °C), so that it can be applied e.g. on existing inbuilt surfaces or thermosensitive substrates. To achieve this aim, a silica-based binding component was added into titania-zirconia composites. Their functional and physico-chemical properties were studied by using spectroscopic methods (UV–vis, IR ATR, EPR), XRD, SEM, BET surface area and TGA measurements.

2. Experimental

The chemicals in this study were used as purchased; tetraethyl orthosilicate (TEOS, 98%) from Acros Organics; titanium isopropoxide (TTIP), zirconium(IV) butoxide (ZTB, 80 wt.%), methyl stearate (97%) from Aldrich; terephthalic acid (TPA) from Alfa Aesar; ethanol absolute, hydrochloric acid (37%), 2-propanol from Carlo Erba; hydroxyethyl-cellulose (HEC) from Fluka; ethanol 96% from Itrij; Levasil 200/30% from Obermeier; perchloric acid (70%), 2-propoxyethanol, 1-propanol, free radical 4-oxo-2,2,6,6-tetramethylpiperidine *N*-oxyl (Tempone), spin trapping agent 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO), 4-hydroxy-2,2,6,6-tetramethylpiperidine *N*-oxyl (Tempol) from Sigma-Aldrich; NaOH; *n*-hexane from VWR and toluene SeccoSolv® from Merck.

2.1. Preparation of photocatalysts

Initially a colloidal solution, primary sol, was made by dissolving titanium(IV) isopropoxide (15 mL) in absolute ethanol (2.5 mL). To obtain films with pre-determined Ti/Zr ratios, appropriate amount of zirconium(IV) butoxide was added into solution of TTIP and absolute ethanol (nTi: nZr = 100:0, 50:1, 20:1, 10:1, 5:1). The peptizing agent (prepared by adding 1 mL perchloric acid to 45 mL of deinozied water) was then slowly added to mixed metal alkoxide solution. The exothermic hydrolysis of TTIP and ZTB solutions resulted in the formation of an amorphous white precipitate. After refluxing for 48 h (intended to promote crystallization process), a stable primary sol was obtained [21].

SiO_2 binder was prepared by mixing tetraethyl orthosilicate (1.11 mL) and colloidal SiO_2 Levasil 200/30% (1.7 mL), to which 37% HCl (30 μL) was added under stirring. After about one hour of stirring, 2-propanol (5 mL) was added and was left to stir for an additional time of 12 h, so that TEOS underwent sol-gel reactions. The role of silica binder was to provide better mechanical and adhesion properties with higher optical transparency of the thin films. Solution for application on glass substrate was prepared by mixing the primary sol and SiO_2 binder (1:1 volume ratio) followed by dilution of resulting solution with 1-propanol (1:1 volume ratio) and 2-propoxyethanol (3.25:1 vol ratio = mixture of primary sol plus SiO_2 binder: 2-propoxyethanol).

Thin films were deposited on microscopic glass slides (LLG Labware, 70 mm × 25 mm × 1 mm) using dip-coating method with a pulling speed of 10 cm/min. Before the deposition, glass slides were cleaned with ethanol. After dip coating, the samples were dried in an oven (EUP-K 6/1200, Bosio, Slovenia) at 150 °C for one hour. On each glass substrate 3 layers were deposited and after the third layer deposition glass slides were heat treated for 3 h at 150 °C.

The films are labelled according to nominal Zr content with respect to Ti, namely TixZr, where x represents molar percentage of Zr vs. Ti (0, 2, 5, 10 or 20). Powder analogues for XRD, TGA and BET measurements were also prepared from the corresponding sols and heat-treated at 150 °C.

2.2. Material characterization

X-ray powder diffraction (XRD) patterns were obtained with RIGAKU MiniFlex 600 with copper source, providing X-rays of wavelength of 1.54 Å. The diffraction data was collected in the 2Θ range of 20–80°. Average crystallite size was determined by Scherrer equation [22].

Scanning electron microscope JEOLJSM 7001 operating at 20 kV was used to obtain SEM images for characterizing the morphology of the samples. Prior to the measurement, samples were properly prepared, sputtered with gold/palladium.

Multi-point BET specific surface area of powder samples was determined with Quantachrome NOVA 2200e, by measuring the nitrogen adsorption–desorption isotherms at 77 K. Samples were outgassed under vacuum for 3 h at 423 K. UV–vis transmission spectra in the range from 200 to 800 nm were collected using LAMBDA 650 UV/Vis spectrophotometer, Perkin Elmer. Thermogravimetric properties of powders from 40 to 600 °C were measured with TGA/DSC 2, Mettler Toledo, while the FT-IR spectra from 400 to 4000 cm^{-1} were obtained by Perkin Elmer 100 with GladiATR™ Single Reflection ATR Accessory. Mechanical stability was determined by Hardness Pencil test (also named Wolf-Wilborn test) with ELCOMETER 501, Elcometer. Thickness measurements of the films were performed on Ambios XP2 Profilometer, Ambios Technology, Inc.

2.3. Photocatalytic activity tests

Information on the radicals produced upon UVA exposure of films were obtained by EPR spectroscopy by monitoring the elimination of stable nitroxide radical Tempone in toluene or using the spin trapping agent DMPO in toluene or water. All EPR experiments were carried out using an EMX Plus X-band EPR spectrometer with High Sensitivity Probe-head (Bruker).

The choice of a method for photocatalytic activity determination depends mainly on desired application of the photocatalysts. For photocatalyst with a self-cleaning purpose, solid organic compound as a model contaminant or dye-solution is laid over the surface and certain characteristics that change during the photocatalytic process are followed [23]. In the present study, activity was determined with two different model substances that were subjected to photocatalytic oxidation.

2.3.1. Model contaminant: methyl stearate

Methyl stearate was dissolved in *n*-hexane (0.2 M) and deposited on the catalyst surface with dip-coating technique (withdrawal speed 20 cm/min). The sample with organic contaminant was then irradiated with UVA light (λ_{max} = 365 nm, 2.3 mW/cm^2) until a stable value of contact angle (Contact Angle Meter CAM-100, KSV Instruments) was observed. This method is time consuming due to the slow degradation process of solid fatty deposit. Each sample was irradiated with UVA light (λ_{max} = 365 nm, 2.3 mW/cm^2) before the deposition of model organic contaminant, to remove any surface impurities that occur due to ageing of the samples. The contact angle of water droplet was measured at five different points on the samples.

2.3.2. Model contaminant: terephthalic acid [24]

A mixture containing terephthalic acid, aqueous solution of NaOH and ethanol based hydroxyethyl-cellulose solution was deposited on the catalyst surface with dip-coating technique (withdrawal speed 10 cm/min). Before the deposition samples were

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