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Preparation and characterization of doped titanium dioxide printed layers

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ABSTRACT

Thin layers of doped titanium dioxide on Pyrex glass were prepared by the material printing technique. Titanium dioxide was synthesized by the sol–gel method employing titanium(IV)isopropoxide as the precursor. A dedicated experimental inkjet printer Fujifilm Dimatix 2831 was used for the coating process. The influence of various solvents onto sol jettability was investigated. The mixture of absolute ethanol and 2-butanol was finally adopted because of its optimum viscosity and rate of evaporation. A series of experiments with different printing conditions was carried out, the optimum printing settings were determined. Consequently, iron and silver dopants were incorporated into the sol. The influence of doping on the photocatalytic activity of TiO_2 as well as the shift of absorption edge towards high wavelengths was investigated. The quality of all layers was studied by optical microscopy. The surface topology was evaluated by atomic force microscopy. The study of surface structure was performed using scanning electron microscopy. Crystallite phases of prepared TiO_2 were investigated by X-ray diffraction analysis. Band gap energy was determined by UV–vis reflection spectroscopy. The photocatalytic activity of printed thin films was examined as a degradation rate of stearic acid and 2,6-dichloroindophenol under UV radiation.

1. Introduction

In recent papers, photocatalytics decomposition of dye compounds [1–4] as well as simple organic compounds [5–8] has been thoroughly discussed. The most usual photocatalyst is titanium dioxide due to its specific properties, mostly the optical and electronics ones, chemical stability, non-toxicity and relatively low cost. When the TiO_2 is illuminated by an appropriate light source, the photocatalyst generates pairs of electrons and holes inside its crystalline lattice. Free electrons are produced in the conduction band and the holes in the valence one. Because TiO_2 has a large band gap (anatase form of titania about 3.2 eV) only a small fraction of solar light (about 5%) from the UV region can be utilized. Therefore, a lot of studies have tried to develop a photocatalytic system which can be activated under visible light irradiation [9–11]. Many reports have been dedicated to the modification of TiO_2 by doping of different elements, using metals as well as non-metals. The aim of this work was to shift the absorption edge into the visible light region which can consequently lead to higher activity [12–15]. The most usual non-metals dopants for modification of the physical properties of TiO_2 such as optical and photoelectrochemical properties are N [16], Cl [17], S [18], F [19]. On the other hand doping by metal ions is performed to extend the spectral response of TiO_2 to the visible light region. Transition metal ions such as Fe, V, Mo, W, Cr have been reported as possible dopants of titanium dioxide [20–23].

The photocatalytic activity of TiO_2 strongly depends on the preparation methods and on the post-treatment conditions. It has decisive influence on the chemical and physical properties [24,25]. Sol–gel is one of the most successful techniques how to prepare nanosized metallic oxides with high photocatalytic activity [26]. In the sol–gel process, titanium dioxide is usually prepared by the reaction of hydrolysis and polycondensation of titanium alkoxides ($Ti(OR)_n$) to form oxopolymers, which are consequently transformed into an oxide network [27]. Controlled hydrolysis has to be ensured during whole process to obtain homogeneous titania network. Therefore, some of the chelating agents have to be added to the precursor [28]. Condensation reaction is usually followed by a gelation process and subsequently by calcination.

Titanium dioxide photocatalyst can be used in different forms: as a powder or as an immobilized layer on various substrates. A lot of various wet coating techniques have been proposed, such as dip-coating, spin-coating, spray-coating and many others. One of the

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novel deposition methods is material printing. The term "material printing" refers to the material deposition by (e.g. inkjet) printing where traditional colour ink is replaced by a liquid media. Comparison of material printing with other deposition techniques generally favours this method due to a lot of advantages. The most important of them is the possibility of direct pattering. Printhead can be used to focus the liquid media droplets on a specified place of the substrate and thus create various patterns directly, without any mask or lithographic processing.

The final surface topology of printouts depends on both the drop formation mechanism and surface properties of the substrate used. Various dynamic phenomena have been observed on the three-phase boundary after droplet landing such as splashing, spreading, receding, bouncing and crown formation. Rioboo et al. [29] have identified the phases of drop spreading: kinematic phase, spreading phase, relaxation phase and wetting phase. Drop dynamics and film formation can be to a certain degree predicted by theoretical descriptors such as Weber number ($We = \delta v^2 d/\sigma$), Ohnesorge number ($Oh = \eta/\sqrt{(d\sigma\delta)}$), Z number ($Z = \sqrt{(d\sigma\delta)}/\eta$) and Reynolds number ($Re = \delta v^2 d/\eta$), where δ is the density, v is the drop velocity, d is the diameter of nozzle, σ is the surface tension and η is the viscosity of printable liquid. While these models were developed for Newtonian fluids, most commercially available inks are non-Newtonian fluids since they contain different additives. Nevertheless, it seems reasonable to apply these models also for non-Newtonian fluids in order to assess the printability of the inks [30–33].

2. Materials and methods

2.1. Sol synthesis

Titanium tetraisopropoxide (TTIP) (p.a.) was used as a precursor for the preparation of titanium dioxide by the sol–gel synthesis. Firstly, 20 mL of 2-butanol was mixed with 1.9 mL of acetyl-acetone (p.a.). Acetyl-acetone (AcAc) was used as a chelating agent to prevent uncontrolled hydrolysis. This mixture was added dropwise under a continuous stirring to 5.15 mL of TTIP. Consequently, absolute ethanol (22.5 mL) with small amount of water (0.343 mL) was added drop by drop to the prepared mixture to start the hydrolysis and condensation reaction. Finally, polyethylene glycol (p.s.) with the average molecular weight 1500 was added. PEG was used as an anticracking agent. The concentration of PEG was set to 4 g/L as the most suitable for printing deposition [34]. Final printing mixture consisted of 3 mL of titania solution and 2 mL of α-terpineol (96%, Sigma–Aldrich).

The goal of this work was to investigate the doping influence by iron as well as silver on the photocatalytic properties of final TiO_2. The influence on band gap energy as well as on the shifting of the absorption edge towards higher wavelength was examined. Different amount of iron (III) acetylacetonate was added to prepared titania sol (mole concentration 3%, 5%, 7%). The samples were noted Ti; 3Fe; 5Fe; 7Fe. Silver nitrate was dissolved in the sol with mole concentration 2% and the samples were noted Ag; Ag_3Fe; Ag_5Fe; Ag_7Fe.

The viscosities, densities and surface tension of the resulting formulations were measured by automatic viscosimeter AVMn (Anton Paar), density meter DMA4500 (Anton Paar), and by rheometer AR-G2 (TA Instruments), respectively. Printability of all formulations was evaluated on the basis of theoretical models and confirmed by printing tests.

2.2. Printing deposition

Pyrex glass substrates of size 30 mm × 30 mm × 3 mm were used for titania immobilization. Firstly, it was necessary to pre-treat the glass plates in aqueous solution of detergent Neodisher (BMT, Czech Republic) in an ultrasound for 10 min to remove all dust and fat and other residues which could contaminate the surface. Consequently, these substrates were immersed to solution of Abesone (commercial dodecylbenzene sulphonic acid based surfactant) to enhance their wetting by the printed sol.

Titanium sols were deposited onto the Pyrex plates using an experimental printer FUJIFILM Dimatix (Dimatix Materials Printer DMP-2831). During filling the cartridge ink tank by the printing formulation, it was necessary to filter it through a 0.45 μm mesh size syringe filter in order to eliminate any aggregates and solid contaminants which might clog the printhead nozzles. The Dimatix 10 pL printhead containing 16 nozzles was attached to the filled ink tank and mounted into the Dimatix printer. The nozzle temperature was set up to 30 °C and the piezo driving voltage was set to 22 V. The "model liquid 2" waveform proved to be well useful for our sols. We studied the influence of different coating conditions on final structure of thin layers. We compared three droplet pitches (20 μm, 30 μm, 40 μm), three substrate temperatures (30 °C, 40 °C, 50 °C) and four levels of film thickness (from 1 to 4 layers printed in the "wet-to-wet" manner, i.e., the following layer was printed immediately after the previous one without any delay for drying). Finally, the printed substrates were placed onto a hot plate (temperature 110 °C) for 30 min to quickly evaporate the solvents and fix the layer. Subsequently, they were calcinated at 450 °C for 4 h with the ramp of 3 °C/min. After that, the samples were carefully investigated and the best deposition conditions were determined.

2.3. Characterization

The structure and quality of prepared layers were examined by optical microscope Nikon Eclipse E200. All prepared titania thin films were optically transparent, smooth and shiny. In the case of iron-doped samples we observed yellowish colouring. The TiO_2 layers adhered well to the Pyrex glass substrates after the calcination process. Optical micrographs were recorded by a digital camera Nikon D5000 mounted on the optical microscope.

Afterwards, the sample structure as well as homogeneity of titania thin layers were investigated by scanning electron microscopy (SEM Carl Zeiss Ultra Plus). Simultaneously, analysis of chemical composition was carried out by EDS (Oxford X-max with silicon drift detector). The influence of iron and silver doping was evaluated. The surface topology was further studied by atomic force microscopy (AFM NT-MDT Prima).

Crystal phase composition of TiO_2 was investigated by X-ray diffraction pattern measurement by using Cu Kβ as the radiation source. The samples were analyzed as prepared by printing, i.e., thin layers on the Pyrex substrate, and the scan range was from 20° to 90°. We used X-ray diffractometer SmartLab, Rigaku. Consequently, the crystallite size was calculated according to the Scherrer equation, where B is constant equal 0.94, λ is the wavelength which is equal to 1.54 Å and β is the width of peak at a half of the maximum height.

$$d = \frac{B\lambda}{\beta \cos\theta} \quad (1)$$

The analysis of band gap energy was performed by a reflectance measurement of powdered samples. The remaining volume of sols with different amount of iron and silver which had remained after printing was transformed to powdery oxide phase by calcination at the temperature of 450 °C for 4 h. Resulting powders were finely ground and used reflectance measurement carried out using a UV–vis spectrometer equipped with a reflectance fibre probe. The optical path consists of several optical fibres where six of them are connected with the lamp providing illumination of the sample (xenon strobe lamp) and one reading fibre connected to the