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Fabrication, characterization and photocatalytic activity of TiO_2 layers prepared by inkjet printing of stabilized nanocrystalline suspensions

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ABSTRACT

Titanium dioxide (TiO_2) colloidal dispersions were synthesized by hydrothermal synthesis in acidic pH under various process conditions. Phase structure of prepared TiO_2 was identified as pure rutile by X-ray diffraction analysis and crystallite sizes determined by the Scherrer equation were in the range of 10–25 nm. These values correlated with particle sizes observed by transmission electron microscopy (TEM). Afterwards, the prepared TiO_2 dispersions were used for the formulation of stable inkjet printable "inks". Thin layers of nanocrystalline TiO_2 were deposited by inkjet printing onto soda-lime glass substrates. After sintering at 500 °C, thin patterned films were obtained. Their basic physicochemical properties were characterized by standard methods. Optical microscopy and SEM imaging revealed highly structured topography of samples surface. Layer hardness was equivalent to the B pencil as determined by the "Pencil Hardness Test". The topology and roughness were examined by atomic force microscopy and RMS roughness was in the range of 40–100 nm. Band gap energy of TiO_2 determined by UV–vis reflection spectroscopy was consistent with known rutile values. The photocatalytic activity of printed layers was evaluated on the basis of 2,6-dichloroindophenoldiscoloration rate monitored by UV–vis spectroscopy and did not exceed the performanceof Aeroxide P-25. Despite average photocatalytic performace of this particular TiO_2 type, inkjet printing proved to be an efficient method for the fabrication of patterned titania films originating from nanocrystalline precursor.

1. Introduction

Heterogeneous photocatalysis being a promising water and air purification technique, has attracted a great deal of attention in the last years [1–6]. The main advantage of this method compared to the traditional wastewater treatment, such as chlorination or ozonolysis is that a lot of persistent contaminants, (e.g. phenol, 4-chlorophenol, trichloroethylene and chlorobenzene) can be completely mineralized including their potentionally problematic degradation byproducts [7–9]. Among various oxide semiconductorsefficient for photocatalysis, titanium dioxide is the bestphotocatalyst because of its strong oxidizing power, nontoxicity and relatively long-term photostability [10].

Absorption of UV light causes the generation pair of an electron and a hole. The excited electrons are trapped by O_2 to form superoxide radical ion (O_2). The holes can react with adsorbed water to form reactive hydroxyl radicals (•OH). These radicals are considered to be the major active species responsible for the photocatalytic oxidation reaction. These hydroxyl radicals can by quantitatively detected by photoluminescence [11].

Three main different crystalline phases of titanium dioxide exists: anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic). However, only anatase and rutile have been used in most photocatalytic studies and the photocatalytic activity of amorphous titania is negligible [12]. Anatase phase shows a higher photocatalytic activity than rutile due to its lower recombination rate of photo-generated electrons and holes [13,14].

It is well known that the photocatalytic activity of TiO_2 strongly depends on the preparation methods and post-treatment conditions, since they both have a decisive influence on the chemical and physical properties of TiO_2 [15–16]. Many approaches to improve the photocatalytic activity of TiO_2have been proposed. Generally, modification of its morphology, crystal composition, crystallinity, and surface area are the most common [17–24]. Of these approaches, hydrothermal treatment is one of the most widely used methods for increasing the crystallinity of TiO_2 [25,26].

The hydrothermal method of TiO_2 particles preparation has many advantages. A major advantage of using the hydrothermal

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process is the ability to produce different crystalline phases without the need of subsequent thermal treatment as it provides the capacity to grow good-quality crystals and to control the crystalline composition simultaneously [27]. By changing the hydrothermal reaction conditions, such as the reaction temperature, pH values, reactant concentrations and molar ratio, crystalline products with different compositions, structures and morphologies have been obtained.

Nanocrystalline dispersions of titanium dioxide, either of the hydrothermal or any other origin, are very efficient for the photocatalytic degradation of various pollutants. However, photocatalytic reactions utilizing the slurried form of catalyst are burdened by the need for catalyst recovery. Therefore, photocatalyst immobilised onto suitable support is usually the preferred form for practical application. Although titania coatings have been fabricated by countless different processes, wet coating techniques constitute a very popular approach. At the same time, hydrothermally synthesized nanocrystalline titania dispersions are excellent raw materials for wet coating formulations, providing a good level of control over the crystallinity of the resulting layer.

Many different wet-coating techniques have been proposed, such as dip-, spin- or spray-coating, doctor blade spreading, roller etc [28]. However, recently a new promising wet coating technique has become available. This novel approach is usually termed inkjet material deposition or shortly material printing. The technique shares the basic principles with conventional inkjet printing, i.e. tiny droplets of a low-viscosity liquid are precisely deposited onto a substrate by means of thermal or piezoelectric printhead. In the case of material printing, the ink is a specially formulated liquid used for transporting a functional component onto the substrate surface [29–33].

Material printing has been successfully employed for the deposition of a great variety of functional materials, titanium dioxide including. Generally, two different approaches can be identified when discussing titania printed layers: The printing "ink" can be based on the sol–gel chemistry utilizing an organometallic precursor in the form of stable sol. Printed ink dries to form a xerogel layer which is further processed into oxide layer usually by calcination at 300–500 °C [34–40]. The second route relies on the formulation of stable colloidal suspension of nanocrystalline TiO_2 followed by a delivery of this suspension onto substrate by means of the inkjet printing [41–47]. Naturally, the free-standing nanoparticles have only very limited adhesion to substrate and need to be fixed e.g. by heat sintering or the addition of suitable binder [48].

In this paper, we report the influence of different hydrothermal conditions on the physical properties and photocatalytic activity of prepared TiO_2. Hydrothermally prepared titania slurries were deposited onto soda-lime glass substrates by material printing and effect of layers thickness was investigated.

2. Experimental

2.1. Hydrothermal synthesis of TiO_2

Colloidal dispersion of titanium dioxide was prepared by hydrothermal synthesis using titanium oxochloride($TiOCl_2$) as a precursor. $TiOCl_2$ was added dropwise to 480 mL of potassium hydroxideaqueous solution with concentration 5 mol L^{-1} to neutral reaction. KOH was used as the precipitation agent. Mixture was washed several times to remove excess of chloride ions which can have a negative influence on final TiO_2 photocatalytic activity [49]. According to our previous finding, acidic environment is much better for photocatalytic activity of colloidal TiO_2 than basic medium [50]. So HCl (p.s.)(0.9 mL) was added to TiO_2 mixture for decreasing final pH value to 1. The mixtures were hydrothermally treated under different conditions. The influence of temperatures and duration of hydrothermal synthesis on the final properties of prepared samples was investigated. We used temperature 110 °C and 160 °C. These particular temperatures were selected arbitrarily to include samples processed at a temperature close to the boiling point of water (which is favourable from the practical engineering and energy consumption point of view) and a sample set processed at a significantly higher temperature. According to our previous experience the difference of 50 °C was expected to be sufficient to induce significant differences in the properties of prepared samples. Treatment duration was 6 h, 24 h and 48 h yielding 6 samples of nanocrystalline titania dispersions.

2.2. Thin layer printing

Soda-lime glass platesof size 50 mm × 50 mm × 1.1 mm were used for TiO_2 immobilization. Firstly, it was necessary to pre-treat the soda-lime glass plates in sulphuric acid in order to prevent sodium ions diffusion which would have caused a reduction of photocatalytic activity [51,52]. Just after and before the layer coating, the plates were washed in an aqueous surfactant solution to remove of dust, grease and other residues which might have contaminated the surface during plate storage.

Titania application was performed in an innovative way utilizing an experimental printer FUJIFILM Dimatix (Dimatix Materials Printer DMP-2831). In order to fully exploit the full potential of this device, printing inks needed to be formulated and optimized proving stable and reliable jetting:1 mL of hydrothermally synthesized TiO_2dispersion was mixed with 1 mL HCl (p. s.) and 1 mL surfactant (see Section 3.4. for surfactant choice discussion) and 1 ml H_2O, respectively.

The prepared formulation was stable and was used directly as the printing ink. Before filling the cartridge ink tank, it was necessary to sonicate the ink for 5 min and filter it through a 0.45 μm size syringe filter in order to eliminate any aggregates and solid contaminants which may 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 to 40 °C which was beneficial for further viscosity reduction without increasing the evaporation rate from printing nozzles too much. Nozzle span was set to 20 μm, i.e. 2500 drops per mm^2. Dimatix model liquid 2 waveform was used and the piezo driving voltage was set to 22 V.

One-layer and two-layer samples were coated by this method for all six samples. The printing of two layers was performed in the so called "wet-to-dry" manner, meaning that the first layer was completely dry before printing the second one. Simultaneously with the synthesized TiO_2, we printed also one- and two-layer samples with an ink prepared from commercial TiO_2 (Evonik Aeroxide P-25) which was used as a comparative standard. A simple 4 cm square pattern was printed in the middle of the 5 cm square glass plate. Finally, the printed substrates were placed into a calcination furnace and printed titania layers were fixed by heating with a ramp of 3 °C/min and keeping at 500 °C for 30 min.

2.3. Characterization

Crystallinity of TiO_2 was examined from X-ray powder diffraction pattern measurement by using Cu Kα as the radiation source. We used X-ray diffractometer Empyrean, Panalytical for this analysis. The titania powder was prepared by drying the hydrothermally synthesized colloidal dispersion at the temperature of 50 °C to constant weight.

Subsequently, the crystallite size was calculated using Scherrer Eq. (1), where B is constant equal 0.94, λ is the wave length which is equal to 1.54 Å and β is the width of peak at a half of maximal height.