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Synthesis, characterization and photocatalytic properties of sol–gel TiO_2 films

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Abstract

The application of heterogeneous photocatalysis is described as an advanced oxidation process (AOP) for the degradation of the diazo reactive dye using immobilized TiO_2 as a photocatalyst. Starting TiO_2 solutions were prepared with and without the addition of polyethylene glycol (PEG) and TiO_2 films were directly deposited on a borosilicate glass substrate using the sol–gel dip-coating method. The surface morphology and the nanoscale roughness of TiO_2 films were studied by means of atomic force microscopy (AFM). Structural properties of TiO_2 were identified by X-ray diffraction (XRD). The decomposition behaviour of organic compounds from the gels was investigated using thermal gravimetry (TG) and differential scanning calorimetry (DSC). Photocatalytic activities of TiO_2 films in the process of degradation of the commercial diazo textile dye Congo red (CR), used as a model pollutant, were monitored by means of UV/vis spectrophotometry. The kinetics of the degradation of the CR dye was described with the Langmuir–Hinshelwood (L–H) kinetic model.

The addition of PEG to the TiO_2 solution resulted in the changes in the film surface morphology, and affected the ratio of anatase–rutile crystal phases and the photocatalytic activity of TiO_2. The TiO_2 film prepared with PEG is characterized by higher roughness parameters (R_a, R_{max}, R_q, R_z and Z_{max}), a lower amount of the rutile phase of TiO_2, a higher amount of the anatase phase of TiO_2 and a better photocatalytic activity compared to the TiO_2 film without the addition of PEG.

Keywords: A. Sol–gel process; Atomic force microscopy; Photocatalysis; UV/TiO_2; Congo red dye

1. Introduction

Synthetic organic dyes are used in various industries, such as textile industry, leather tanning industry, paper production, hair dye production, etc. Wastewaters containing these dyes may be harmful to the environment and living organisms. Therefore, it is very important to remove or degrade these dyes before discharging them into the environment. In addition to standard technologies for the degradation and/or removal of dyes, several new specific technologies, the so-called advanced oxidation processes (AOPs), have been developed to eliminate dangerous compounds from polluted waters. Heterogeneous photocatalysis, as one of the AOPs, could be effective in the oxidation/degradation of organic dyes. A major advantage of using heterogeneous photocatalysis for this purpose is the total mineralization of organic dyes, which results in CO_2, H_2O and corresponding mineral acids [1–12]. The initial interest in the heterogeneous photocatalysis was aroused in 1972 when Fujishima and Honda discovered the photochemical splitting of water into hydrogen and oxygen by the UV irradiated TiO_2 [13]. After that, research on the heterogeneous photocatalysis started growing rapidly [14] in many areas of water and air treatment technologies.

Titanium dioxide generally exhibits the highest photocatalytic activity of all photocatalysts. The use of TiO_2 as a photocatalyst has been of great interest due to its high activity,

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photochemical inertness, non-toxicity, efficiency, and low cost. Other semiconductors that can be used as photocatalysts are WO_3, SrO_2, ZrO_2, ZnO, Fe_2O_3, CeO_2, CdS, ZnS, etc.

Titanium dioxide occurs in three different crystalline polymorphic forms: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). Among these, the anatase phase usually exhibits the best photocatalytic behaviour, while the rutile phase is the most stable phase. A photocatalyst may be used as a suspension in an aqueous solution or it may be immobilized onto a supporting substrate. The immobilization method is more convenient for practical use since the main problem in the usage of TiO_2 suspended in an aqueous solution is the separation of TiO_2 nanopartices after the photcatalytic reaction and their reuse. Among several deposition techniques, the sol–gel dip-coating method produces films with good photocatalytic properties, large area coatings, with low equipment and production costs [15–18]. The crystal structure and the surface morphology of films influence the photocatalytic efficiency of TiO_2. Atomic force microscopy (AFM) is a very important tool for examining the thin film surface morphology at the nanoscale. During the last decade, a considerable interest has been expressed regarding the application of AFM for structural studies of different materials [19–21].

The aim of this research was to prepare titania films, with and without the addition of PEG, on a borosilicate glass substrate by using the sol–gel dip-coating method and their use as the photocatalysts. Characteristics of these films were analyzed and indentified by means of AFM, X-ray diffraction (XRD), thermal gravimetry (TG) and differential scanning calorimetry (DSC).

Commercial diazo textile dye Congo Red (CR) was used as a model pollutant.

2. Experimental

2.1. Preparation of sol–gel TiO_2 films

TiO_2 films were deposited on two types of borosilicate glass substrates: borosilicate glass tubes (200 mm in height and 30 mm in diameter) and borosilicate glass plates with dimensions of 25 mm × 30 mm × 2 mm. Two borosilicate glass tubes were used as photoreactors and four borosilicate glass plates were used for the characterization of films by means of AFM. The substrates were carefully cleaned prior to the process of deposition. First, the substrates were ultrasonically cleaned in detergent and rinsed with water. Then, they were ultrasonically cleaned in acetone and subsequently in ethanol for 10 min, respectively. Finally, they were thoroughly rinsed with deionised water and dried.

For the preparation of solutions (TiO_2 sols), the following components were used:

- titanium (IV) isopropoxide, TIP ($Ti(C_3H_7O)_4$, $M_r = 284.25$, purity > 98%) as a titanium precursor;
- ethanol, (C_2H_5OH, $M_r = 46.07$) as a solvent;
- acetic acid (CH_3COOH, $M_r = 60.05$) as a catalyst;
- acetylacetone ($CH_3(CO)CH_2(CO)CH_3$, $M_r = 100.12$) for peptization;
- distilled water (H_2O, $M_r = 18.02$) for gelation;
- polyethylene glycol, PEG ($HO(C_2H_4O)_nH$, $M_r = 5000–7000$) as an organic/polymer additive.

In the present study, two sols (solutions) were prepared: sol 1 and sol 2. Sol 1 was prepared by dissolving titanium isopropoxide in ethanol. A magnetic stirrer was used to continuously stir the liquid. Then, acetylacetone, acetic acid, and distilled water were added successively. Sol 1 was stirred vigorously for 2 h and after that it was sonicated for 30 min. Sol 2 was prepared using the same procedure as the one described for sol 1 with only one exception, i.e. the addition of 2 g of polymer–polyethylene glycol (PEG). The molar ratios of components used to prepare both titania coating solutions are shown in Table 1.

Borosilicate glass plates were dipped into sol 1 and sol 2 by a home-made, electrically driven pulley system. Substrates were dipped into the sols at a rate of 10 mm/min, were kept there for 10 min, and then removed at the same rate. Also, sol 1 and sol 2 were each poured into a borosilicate glass tube, kept there for 10 min, and slowly poured out of them. Then, all substrates were dried, first at 100 °C for 60 min, then at 500 °C for 4 h. The dipping process was repeated three times for both solutions.

2.2. Characterization of sol–gel TiO_2 films

The surface topography and the roughness of the TiO_2 films were determined by using a Multimode AFM with a Nanoscope IIIa controller (Veeco Instruments Santa Barbara, CA) with a vertical engagement 125 μm scanner (JV). Contact mode imaging was performed under ambient conditions in air, by using silicon tips (NP, Nom. Freq. 18 kHz, Nom. Spring constant of 0.06 N/m), and at a scan resolution of 512 samples per line. The linear scanning rate was optimized between 1.0 and 2.0 Hz at a scan angle of 0°. Images were processed and analyzed by means of the offline AFM NanoScope software, version 5.12r5. Particle dimensions of the granular microstructure of the TiO_2 thin film were determined by means of the Particle Analysis option within the AFM software.

Roughness analysis software option was used to performed roughness analyses on 2 μm × 2 μm imaged surface area for each sol–gel TiO_2 film. Results are presented as the R_a, R_q, R_z, R_{max} and the Z range values.

Table 1
The composition of coating solutions (sol 1 and sol 2) and molar ratios.

Sol	Components, molar ratio					*m*, g
	$Ti(OC_3H_7)_4$	C_2H_5OH	CH_3COOH	$CH_3(CO)CH_2(CO)CH_3$	H_2O	PEG
Sol 1	1	40	0.9	1.3	12.5	0
Sol 2	1	40	0.9	1.3	12.5	2