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Cerium-modified TiO_2 nanocrystalline films for visible light photocatalytic activity

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ABSTRACT

Cerium modified thin nanocrystalline TiO_2 photocatalytic films for visible light utilization, are prepared via sol–gel route at 500 °C on glass substrates. The synthesis involves a simple procedure employing nonionic surfactant molecule as pore directing agent along with the acetic acid-catalyzed sol–gel route without direct addition of water molecules while cerium was present at different concentrations. Drying and thermal treatment of the films led to the formation of TiO_2 nanoparticles with homogeneous particle size distribution. The presence of cerium induced a decrease of the TiO_2 nanoparticle size. Nanocomposite films were formed without cracks and consisted of anatase crystal phase and small crystallite size ranging from 7 to 10 nm. All materials were characterized by microscopy techniques, UV–vis and porosimetry methods in order to examine their structural properties. The Ce-modified TiO_2 films with various cerium contents were evaluated as visible light photocatalysts for the photo-oxidation of potential organic pollutants in water.

1. Introduction

Heterogeneous photocatalysis for the degradation of hazardous pollutants in air and water assisted by wide band gap semiconductors under UV or solar light has been extensively studied [1–3]. TiO_2 is a relatively inexpensive semiconductor, which demonstrates high photocatalytic activity, non-toxicity and stability in aqueous solutions [4–6]. Moreover, the synthesis of mesoporous nanocrystalline anatase TiO_2 particles, films or membranes has extended its use in environmental remediation [7]. Titania powders with high particle surface area have good photocatalytic activity since reactions take place on the surface of the nanocatalyst. However, powders can easily agglomerate in larger particles, therefore, adverse phenomena to their photocatalytic activity may be observed while highly dispersed TiO_2 powders cannot easily be recovered from aquatic systems when they are used for water treatment. The most critical parameters for high photocatalytic activity of the as-prepared titania films and powders are: specific surface area, particle morphology and possible aggregation, phase composition and number of –OH surface groups [8,9]. The higher surface area usually affects to better photocatalytic efficiency as more active centers are available but it is not the only factor that promotes a catalyst. Mesoporous TiO_2 films have been extensively studied as photoanodes for dye-sensitized solar cells but seem to be equally effective for photocatalytic degradation applications [10]. Despite of the number of applications and high photocatalytic rates measured for nanoparticulate TiO_2 powders and films, there are two critical factors that limit its photocatalytic activity. These are related to solar energy utilization which is limited to the UV region (3–5% of total solar spectrum) and fast recombination of photogenerated electron–hole pairs created after absorption of UV light. For this particular problem several methods have been proposed in the past in order to enhance the photocatalytic activity of the TiO_2. Among these methods noble metal deposition [11,12] non-metal doping with sulfur [13], nitrogen [14] and fluorine [15], surface modifications [16] and coupling with other metal oxides such as WO_3 [17], MoO_3[18], Fe_2O_3 [19], ZrO_2 [20] and SnO_2 [21] with suitable energy levels compared to TiO_2 are generally proposed. The above strategies have led to more efficient photocatalysts for solar energy utilization for specific pollutants

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extending light absorption edge. However, the investigation of new materials and methods is still an imperative. In this respect, TiO_2 modification with rare earth metals is considered as an alternative idea, since transitions of d and f orbital electrons affect absorption characteristics and assist reduction of recombination rate of electron and hole pairs in the semiconductor [22–24].

In the present work, we aim at the preparation of a visible light activated photocatalyst in the form of thin nanocrystalline films on glass composed with highly porous anatase TiO_2 nanoparticles which are modified with Cerium. We examined the structural properties and photocatalytic behavior of Ce modified TiO_2 in different rare earth ratios for the discoloration of azo dye Basic Blue 41 in water under UV and visible light. It must be mentioned at this point that azo dyes are an abundant class of organic compounds that frequently appear in waste water generated from textile, leather and dyestuff industries and they thus pose a major threat to the ecosystems owing to their toxicity and carcinogenic nature [25] and their limited biodegradability.

2. Experimental

2.1. Chemicals and Materials

Commercially available Triton X-100 (X100, polyethylene glycol tert-octylphenyl ether), titanium tetraisopropoxide (TTIP), acetic acid (AcOH), Cerium(III) nitrate hexahydrate, Basic Blue 41 (BB-41) and all solvents were purchased from Sigma–Aldrich. Double distilled water with resistivity 18.2 MΩ (Millipore) was used in all experiments.

2.2. Sol synthesis

Triton X100, a nonionic long chain surfactant, was selected as a pore directing agent in a sol. Compared to other commonly used toxic and ionic templating agents, X100 is relatively inexpensive, non-toxic, and easily removable. Such amphiphilic molecules exhibit ordered mesophase and the ability to adjust large inorganic clusters in aqueous condition [26,27]. A suitable amount of X100 was homogeneously dissolved in ethanol (EtOH). Before adding alkoxide precursor, AcOH was added into the solution. Then, titania precursor, TTIP was added during vigorous stirring. The molar ratio of the materials was optimized at X100:EtOH:AcOH:TTIP = 1:69:6:1 in accordance to previous published results [28]. Cerium(III) nitrate was finally added to the previous solution in various quantities with Ce–TiO_2 weight ratio ranging 0.5%-12%. After several minutes, the dispersion was ready to be used on glass slides. Films prepared on glass slides for various Ce–TiO_2 weight ratios will be referred as X% Ce–TiO_2 where $X = 0$–12 respectively.

2.3. Formation of TiO_2 thin films

Borosilicate glasses with size of L75 mm (effective L60) × W25 mm × T1 mm were used as substrates for fabricating X% Ce–TiO_2 thin films. Before coating, the substrate was thoroughly cleaned with detergent and washed with water and acetone and finally dried in a stream of nitrogen. A home-made dip-coating apparatus equipped with a speed controller to maintain a withdrawal rate of ~10 cm/min was used to dip in and pull out the substrate from the sol. After coating, the films were dried at room temperature for 1 h, calcined in a multi-segment programmable furnace (PLF 110/30, Protherm) at a ramp rate of 5 °C/min to 500 °C and cooled down naturally.

2.4. Materials characterization

A Bruker D8 Advance diffractometer with CuKα ($\lambda = 1.5406$ Å) radiation and Bragg–Brentano geometry was employed for X-ray diffraction (XRD) studies of the X% Ce–TiO_2 photocatalyst. Nitrogen sorption/desorption curves were measured with a Micromeritics Tristar 3000 and the surface area, porosity, and pore size distribution were derived by differentiating them according to BET method. The values were obtained from thick films after scratching the material due to the difficulty of sample collection from the thin films. Nanostructure morphology of the films was studied by microscopy (FESEM, Zeiss SUPRA 35VP) and HR-TEM JEOL (JEM-2100). Absorption spectra of the (transparent) thin films in the UV–vis region were carried out with a Hitachi U-2900.

2.5. Photoreactor and photocatalytic activity of TiO_2 and Ce/TiO_2 modified films

A cylindrical reactor presented in a previous publication [29] was used in all experiments. Air was pumped through a gas inlet using a small pump to ensure continuous oxygen supply to the reaction solution while simultaneously agitating it. Four Black light or Fluorescent tubes of 4 W nominal power were placed around the reactor for UV or visible light illumination respectively. The whole construction was covered with a cylindrical aluminum reflector. Cooling was achieved by air flow from below the reactor using a ventilator. The catalyst was in the form of four borosilicate glasses, covered on one side with nanocrystalline X% Ce–TiO_2 films. The total surface of the photocatalyst films was approximately 60 cm^2 while the catalyst mass was approximately 50 mg. The film thickness is approximately 200–300 nm according to cross sectional SEM images depending to the cerium concentration level in the sol. The reactor was filled with 80 ml of 2.5×10^{-5} M BB-41 aqueous solution. This dye is strongly adsorbed on pure or cerium modified TiO_2 films. For this reason, we stored the solution in the presence of the photocatalyst in the dark for an hour and all of our photocatalytic results were obtained after equilibrium. The photocatalytic discoloration process for the dye was examined by monitoring the absorption maximum of the BB-41 solution (610 nm) at various irradiation times. Photocatalytic discoloration rate of BB-41 was calculated by the formula: $r = (C_0 - C)/C_0$ as the concentration of the dye is proportional to the absorbance for low concentration values. Where C_0 is the initial concentration of BB-41 solution and C is the final concentration after irradiation with UV light. Discoloration efficiency is determined as $\text{eff}\% = (C_0 - C)/C_0 \times 100\%$. For repeated use of the photocatalysts, the films were washed with distilled water and dried at 80 °C while no further treatment was followed for the films. Adsorption of BB-41 on X% Ce–TiO_2 films was examined under dark and after one hour of films' presence in dye's aqueous solution.

3. Results and discussion

3.1. Structural properties of cerium modified nanocomposite films

3.1.1. X-ray diffraction analysis

X-ray diffraction patterns were used to identify the crystal phase and size of synthesized nanocatalysts while lattice parameters were also calculated. The polycrystalline X-ray diffraction patterns for pure and 0.5%–12% Ce modified TiO_2 calcined at 500 °C are presented in Fig. 1. It is obvious that in all cases anatase is the main phase of the pure and Ce modified material appeared at $2\theta = 25.3^\circ$, 37.8°, 48.03°, 62.7°.

Especially in the case that Ce ions were present (0.5–12%, w/w) a new peak at $2\theta = 30.8^\circ$ was also observed among the characteristic