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Evaluation of the photodiscoloration efficiency of β-Bi_2O_3 films deposited on different substrates by pneumatic spray pyrolysis

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ABSTRACT

Immobilization of β-Bi_2O_3 over corning glass and sintered silica discs was performed to evaluate a competing fixed support as an alternative to slurry based photocatalytic systems. Pneumatic spray pyrolysis technique was used to produce coatings of β-Bi_2O_3 at 450 °C. Coated substrates were characterized using X-ray diffraction (XRD) and UV–Vis diffused reflectance spectroscopy (DRS), field emission scanning electron microscope (FESEM) and energy dispersive X-ray spectrometry (EDS). The XRD analysis showed that the obtained crystalline structure of the films is tetragonal β-Bi_2O_3 for both glass and silica. DRS showed the broad absorbance spectra of the films, correlated to β-Bi_2O_3 with an energy band gap of 2.4 eV. FESEM showed that the morphology of the films was different according to the substrate. In the case of corning glass, random non-compact distribution of particles was observed while over silica discs overlapped sheets of β-Bi_2O_3 were seen. This is probably due to differences in the wetting and evaporation rate of the sprayed droplets. During photodiscoloration of anionic indigo carmine (*IC*) dye solution, the β-Bi_2O_3 coated silica was found more effective than the coated glass, response associated to the larger interaction between the dye molecules and catalysts assisted by the roughness and porosity induced by the silica. Furthermore, photocatalytic evaluation of coated silica in discoloration of other two organic dyes: cationic rhodamine B (*RhB*) and anionic acid blue 113 (*AB*) revealed that adsorption and interaction of the dye molecules with coated films could vary due to the presence of different functional and branched groups that overall affect the photocatalytic process, the kinetic rate of discoloration and the TOC analysis. Finally, after the assessment of stability of films and suitability of silica, it was confirmed that silica discs are favorable as a photocatalyst support and last long usage for photodiscoloration of organic dyes.

1. Introduction

In recent years, there has been high interest in finding efficient photocatalytic materials for degradation of organic and inorganic pollutants in aqueous phase. So far, amongst the various practical challenges the main are the efficient recovery of small particles, their filtration and reuse [1–6]. For improved photoactivity, micro and nanometric particles are preferred due to their larger surface area, better dispersion in the solution and adequate passage for activation of particles through irradiation source [7]. However, in aqueous phase, these small particles are difficult to recover and the filtration process required for recyclable use of the catalysts increased the operational costs of water purification systems. Furthermore, during the photocatalytic degradation process, the particles may undergo coagulation and agglomeration and consequently their catalytic activity is reduced [8,9]. These problems have motivated the development of non-slurry based alternative systems where the photocatalyst is supported or immobilized. The supports for photocatalysis should also fulfill certain requirements such as chemical inertness, transparency to UV or visible light irradiation and adequate specific surface area for capturing the pollutants in bulk solution [2,9]. A lot of work has been devoted for the photocatalyst immobilization on diverse materials focusing on the use of silicon, carbon and mineral based porous supports with the advantage of higher surface area that allows good interaction between the photocatalyst and pollutants. Examples of these supports are silica based [3,4,10–22], activated carbon [23–27], synthetic clay laponite [28] glass, steel mesh [29–34] and even polymers such as polyimide [35]. Most of the mentioned works, presented methods for TiO_2 immobilization on various substrates, but in general, the photoactive response was lower than the bare TiO_2 powder, due to low dispersion, reduced transparency, low mass transfer and

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less interaction of the photocatalyst with pollutants. Therefore, supported photocatalysts are still a challenge for the development of alternative non-slurry based systems.

The current study was aimed to explore potential supports for photocatalyst immobilization, which may prove to be efficient, attempting challenges of the mass transfer limitation, maximum irradiation passage and targeting the pollutants. Selected supports were porous sintered silica discs and corning glass. The sintered silica discs allow improved grid interface in targeting the pollutants for efficient photoactivity due to its uneven roughness, porosity and the intrinsic hydrophilicity of silica. The corning glass was used for the comparison of overall photoactivity using coated sintered silica, because photodegradation of dyes using ZnO, TiO_2 and Bi_2O_3 thin films grown on glass has been extensively reported [5,30–33,36–38]. The pneumatic spray pyrolysis (PSP) technique was used for thin films coating because it is a simple and cost effective technique, which leads to uniform film growth [36,39–41], in comparison to other techniques such as dip coating, CVD or MOCVD [27,37,42–47]. Along with investigating different substrates, focus was also given in utilization of visible light for photocatalytic evaluation of the films. Tetragonal Beta-Bismuth oxide (β-Bi_2O_3) was chosen as the immobilized photocatalyst since it is a promising visible-light material [36,48–55]. The photocatalytic evaluation of the coated films was based on the efficiency to discolorate organic dyes of different ionic behavior and functional groups, considering their adsorption and interaction with coated substrates.

2. Materials and method

2.1. Characteristic of substrates

Sintered silica discs of porosity grade-3 made of borosilicate glass (with an average pore size of 10–15 μm) were purchased from Pyrex®. Plain corning glass were rectangularly cut at 12 × 25 mm (length × width).

2.2. Films coating

The precursor solution was prepared using bismuth(III) acetate $Bi(CH_3CO_2)_3$ from Sigma-Aldrich dissolved in acetic acid 25 V% and deionized water 75 V% at a concentration of 0.05 M, at 45 °C under constant stirring to obtain a transparent homogeneous solution. Before growth, substrates were separately sonicated in isopropanol and acetone for 10 min. For growth of β-Bi_2O_3 precursor solution was sprayed on each dedicated substrate from a constant distance of 27 cm and at a fixed rate of 2.15 mL/min. The deposition temperature was maintained constant at 450 °C; similar conditions were previously reported in our work to successfully obtain β-Bi_2O_3 [36].

2.3. Characterization

During thin films growth on each substrate, a 1 cm × 1 cm corning glass was also placed and it was used for X-ray diffraction (XRD) and UV–vis diffused reflectance spectra (DRS) characterization of coated substrates, to avoid the background of fused silica. The phase composition of coated samples was characterized through XRD by using SIEMENS D500 X-ray diffractometer (Cu-Kα X-ray source). The diffraction patterns were analyzed using the PDXL2 software to identify phases and particle size [32,36,38,40]. The DRS were recorded on a UV–vis spectrophotometer equipped with an integration sphere (Shimadzu 2600) and using $BaSO_4$ as a reference. The spectra were converted from reflectance to absorbance by the Kubelka–Munk method to calculate the direct band-gap energy (Eg) of the films, by extrapolating the linear portion of the $(FR \times h\nu)^2$ vs $h\nu$ curves to FR = 0 [56]. Morphology of the coated and blank substrates was investigated by field-emission scanning electron microscopy (FESEM, ZEISS MERLIN 4248). An OXFORD INCA ENERGY 450 energy-dispersive X-ray spectroscopy (EDS) was used to observe film distribution and elemental mapping over coated substrates.

2.4. Photocatalysis tests

For photocatalytic investigation a reactor previously reported by some of us [57], was used. The photocatalytic activity of β-Bi_2O_3 coated and bare glass and silica was initially evaluated by measuring the photodiscoloration of anionic indigo carmine (*IC*) under white light (standard fluorescent lamp) with an irradiance of 33 Wm^{-2}, using 15 mL of the dye solution at pH = 7 and a dye concentration of 5 mg/L. For each experiment, the dye solution was initially stirred for 45 min in the dark to reach the adsorption-desorption equilibrium. The stirring rate of the dye solution was done at 600 rpm in both dark and irradiated steps. The absorbance spectra of the dye solution as a function of time were measured using a UV–vis spectrophotometer (Shimadzu 1800) taking aliquots of 3 mL and returning them to the vial after each measurement. After selecting the substrate with the best photocatalytic characteristics, evaluation was continued for the photodiscoloration of two more dyes: anionic Acid blue 113 (*AB*) at a concentration of 5 mg/L and cationic Rhodamine B (*RhB*) at concentration of 3 mg/L, to observe the photocatalytic behavior and photodiscoloration kinetic rate when dealing with dyes of different functional groups and ionic behaviors. The total organic carbon in the irradiated dye solutions was determined by using a TOC-L Shimadzu Total Organic Carbon analyzer by using NPOC method in high sensibility mode. Furthermore, the best substrate was repeatedly evaluated up to 3 cycles to analyze the stability of films and suitability of the substrate.

3. Results and discussion

3.1. Characterization of the films

3.1.1. Crystalline structure

As mentioned above, during the deposition for each substrate, a witness glass was placed. The XRD patterns of such coated glasses were alike and an example is shown in Fig. 1A. The pattern shows that the diffracted peaks correspond to the tetragonal-β-Bi_2O_3, with principal peaks at 2θ = 27.783, 32.628, 45.52 and 55.397° (JCPDS card no. 01-076-0147) ascribed to (201), (220), (222), (213) and (421) planes respectively. Similar XRD results were reported in our previous work [36], in which β-Bi_2O_3 thin films were obtained on corning glass and silica wafers by using PSP technique at 450 °C. Under strict conditions, the obtained crystalline structure of the Bi_2O_3 thin films is always tetragonal-β for all type of substrates.

3.1.2. Optical band gap

Fig. 1B shows the UV–Vis DRS analysis of β-Bi_2O_3 coated witness glass. Films exhibited a wide absorption plateau from 300 to 550 nm wavelength, the absorption edge appeared above 550 nm indicating that electron transitions from the valence band to the conduction band initiates in the visible-wavelength range. The Kubelka-Munk plot allows an estimation of the energy band-gap to around 2.4 eV (shown in inset Fig. 1B), like previously reported β-Bi_2O_3 films and powders [36,37,48,49,52,53,56,58].

3.1.3. Morphology

The FESEM and optical images of the bare and coated substrates are shown in Fig. 2. Fig. 2A shows the flat surface of the blank glass, after deposition of the β-Bi_2O_3 coating (Fig. 2B and Fig. 2C), a random non-compact distribution of crystalline sub-micrometric particles can be clearly seen. This random distribution of particles on the glass substrate could be due to the rapid evaporation of the sprayed droplets after reaching the glass surface [36,39–41]. The bare sintered silica presented a very smooth surface with regularly spaced holes (Fig. 2D), the film morphology was different to the coated glass (shown in Fig. 2E and Fig. 2F). It