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Reactive magnetron sputtering deposition of bismuth tungstate onto titania nanoparticles for enhancing visible light photocatalytic activity

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A B S T R A C T

Titanium dioxide – bismuth tungstate composite materials were prepared by pulsed DC reactive magnetron sputtering of bismuth and tungsten metallic targets in argon/oxygen atmosphere onto anatase and rutile titania nanoparticles. The use of an oscillating bowl placed beneath the two magnetrons arranged in a co-planar closed field configuration enabled the deposition of bismuth tungstate onto loose powders, rather than a solid substrate. The atomic ratio of the bismuth/tungsten coatings was controlled by varying the power applied to each target. The effect of the bismuth tungstate coatings on the phase, optical and photocatalytic properties of titania was investigated by X-ray diffraction, energy-dispersive X-ray spectroscopy (EDX), Brunauer–Emmett–Teller (BET) surface area measurements, transmission electron microscopy (TEM), UV–vis diffuse reflectance spectroscopy and an acetone degradation test. The latter involved measurements of the rate of CO_2 evolution under visible light irradiation of the photocatalysts, which indicated that the deposition of bismuth tungstate resulted in a significant enhancement of visible light activity, for both anatase and rutile titania particles. The best results were achieved for coatings with a bismuth to tungsten atomic ratio of 2:1. In addition, the mechanism by which the photocatalytic activity of the TiO_2 nanoparticles was enhanced by compounding it with bismuth tungstate was studied by microwave cavity perturbation. The results of these tests confirmed that such enhancement of the photocatalytic properties is due to more efficient photogenerated charge carrier separation, as well as to the contribution of the intrinsic photocatalytic properties of Bi_2WO_6.

1. Introduction

The presence of volatile organic compounds (VOCs) in the ambient air is a major environmental concern. As the level of pollution may vary significantly depending on the location, the choice of depollution method presents an important task [1]. Photocatalytic depollution is proven to be a process that could potentially replace conventional methods of VOCs destruction; through the process of photocatalytic oxidation, it leads to the formation of simple and non-toxic end products, such as H_2O and CO_2. Consequently, the capability of photocatalytic materials in VOC destruction is often used for testing their efficiency as photocatalysts. Of the model VOCs pollutants, photocatalytic materials are most frequently tested for their ability to destruct acetone [1–5], formaldehyde [6], methanol [1,7], benzene [5,8], phenol[9,10] and toluene [5,9,11,12].

Of the known photocatalytic materials, titanium dioxide, or titania, in anatase form is typically the photocatalyst of choice for various environmental remediation processes, due to its low cost, chemical stability and low toxicity. However, TiO_2 possesses some remarkable drawbacks often mentioned in the literature. Thus, the relatively high band gap value of TiO_2 (3.2 eV for the anatase phase) means that only the UV part of the spectrum (around 4% of sunlight) can be used for its activation. Moreover, titanium dioxide is characterised with low separation efficiency of photoexcited charge carriers, which makes its use a rather challenging task for real industrial waste management. Various strategies for the modification of titanium dioxide have been proposed to date, with doping with transition metals [13–15] and non-metallic [15,16] elements being the most conventional methods. However, the photocatalytic activity of modified materials is often not comparable with that of unmodified TiO_2, due to higher rates of photogenerated charge carrier recombination.

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Coupling titanium dioxide with narrow band semiconductors is a method currently being widely explored; it typically results in enhancement of optical abilities of the material, as well as improved separation of photogenerated charge carriers. Thus, titanium dioxide is reported as having been coupled with such materials, as CdS [17], WO_3 [18], Cu_2O[19], etc. Bismuth tungstate (Bi_2WO_6) is gaining increasing popularity as a narrow band gap semiconductor that exhibits good photocatalytic properties under visible light irradiation [20,21]. Several successful attempts to couple bismuth tungstate with titanium dioxide have been reported recently. The main preparation methods described are a hydrothermal method [10,22–24], electrospinning [25,26] and dip-coating [27]. Synergistic effects between TiO_2 and Bi_2WO_6 are reported to promote more efficient separation of photogenerated electrons and holes [24], as well as introducing visible light activity to the composite material, as Bi_2WO_6 can be excited by visible light and its photogenerated holes can move to the valence band of TiO_2.

Magnetron sputtering represents a well-established technique for the deposition of metallic and ceramic coatings onto various substrates [28]. It has been shown recently that reactive co-sputtering of bismuth and tungsten targets can be used for the deposition of visible light-active photocatalytic bismuth tungstate coatings [29]. Magnetron sputtering, though, is not typically used for deposition onto powders, due to the difficulty of achieving uniform coverage from a predominately “line of sight” process. However, the use of an oscillating bowl taken from a vibrating bowl feeder mechanism [30] enables the deposition of materials onto nanoparticulates in a single stage process. The bowl oscillates vertically, but springs connected between the electromagnet and the base plate are designed to also impart a lateral moment to the oscillation. The resulting motion causes particles in the bowl to roll or hop in a circular path around the bottom of the bowl, underneath a pair of magnetrons. In the present work, magnetron sputtering from a dual source was used to deposit bismuth tungstate onto titanium dioxide anatase and rutile nanoparticulates, which were oscillated in the bowl positioned under the magnetrons. This is a new technique, and to the best of our knowledge, reactive co-sputtering of bismuth and tungsten from metallic targets onto titania nanoparticulates has not been previously reported elsewhere in the literature.

The present study, therefore, describes the deposition of bismuth tungstate onto commercially available titanium dioxide nanoparticles (Crystal Global PC500 and Sigma Aldrich rutile titania) and the testing of the materials for their ability to degrade acetone as a model VOC compound (and one of the most important air pollutants [31]). Charge carrier dynamics of the titania powders before and after coating was studied with a microwave cavity perturbation method [32,33].

2. Materials and methods

2.1. Deposition

The bismuth tungstate coatings were deposited in a single stage process in a vacuum coating system that included two 300 mm x 100 mm planar unbalanced type II magnetrons [28] installed on the top of the chamber facing the oscillator bowl in a closed field configuration. The schematic representation of the setup if given in Fig. 1. The bismuth target was fitted to one of the magnetrons, and the tungsten target to the other one (both targets were 99.5% purity and bonded to copper backing plates). The targets were sputtered in reactive mode in an argon/oxygen atmosphere, at a partial pressure of 0.4 Pa. The flow of gases was controlled with mass flow controllers (10 sccm of Ar and 20 sccm of O_2). The magnetrons were powered in pulsed DC mode using a dual channel Advanced Energy Pinnacle Plus power supply; a pulse frequency of 100 kHz and duty of 50% (synchronous mode) were used for all the deposition runs. The powers applied to the targets were varied to vary the Bi/W content in the films (100–200 W for the Bi target and 400–450 W for the W target).

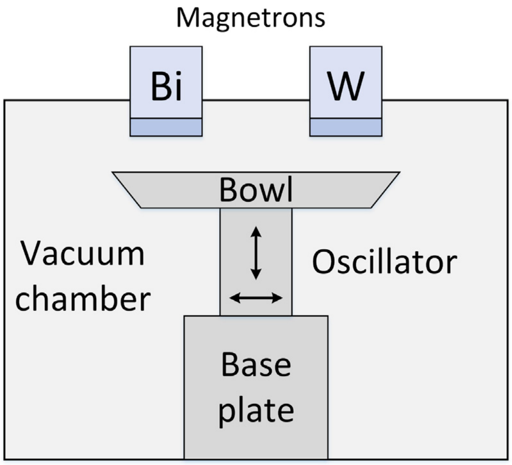

Fig. 1. Schematic representation of powder coating sputtering rig in dual co-planar configuration.

For each run, a 10 g charge of titania particles was loaded into the bowl, and then the chamber was evacuated to a base pressure of lower than 1×10^{-3} Pa. The particles used were PC500 anatase titania from Crystal Global (particle size 5–10 nm); an additional set of identical coatings was also deposited onto rutile titania (Sigma Aldrich) with a particle size of $\leq$100 nm. The deposition time was 1 h for all the coatings studied.

2.2. Characterization

The X-ray diffraction patterns of the samples were obtained using a Panalytical Xpert diffractometer with CuKα1 radiation at 0.154 nm over the range 20 to 70° 2θ; the accelerating voltage and applied current were 40 kV and 30 mA, respectively. The composition of the powders was determined using EDX (EDAX – Trident on Zeiss Supra 40 FEGSEM). The specific surface areas of the materials were determined with Brunauer–Emmett–Teller (BET) surface area measurements, which were made using a Micromeritics ASAP 2020 system. Samples were heated for 12 h at 300 °C prior to analysis and surface areas were calculated from nitrogen adsorption data in the range of relative pressures between 0.05 and 0.3 using the BET model. Optical properties of the materials were determined from UV–vis diffuse reflectance spectra recorded with an Ocean Optics USB4000 spectrometer equipped with a diffuse reflectance probe. Selected samples have been analysed with TEM (FEI Tecnai FEGTEM Field Emission gun TEM/STEM fitted with HAADF detector, FEI, Cambridge, UK).

2.3. Photocatalytic activity assessment (acetone degradation test)

The photocatalytic activities of the powders were assessed using an acetone degradation test. The degradation of acetone was performed in purpose-built reaction cell equipped with a quartz glass window. The fixed amount of photocatalyst was evenly spread over a 55 mm glass plate and placed into the reaction cell; 1 ml of liquid acetone was introduced to the cell with a syringe. The amount of photocatalyst was varied, depending on the substrate used, to get a detectable response during a 1 h experiment. For this work 1 g of the anatase powders and 10 g of the rutile powders were used for each measurement.