

Synergistic effect of doping with nitrogen and molybdenum on the photocatalytic properties of thin titania films



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ABSTRACT

Doping of titania with metal and non-metal elements provides a simple and efficient pathway to significant enhancement of photocatalytic properties. In this work titania thin films co-doped with molybdenum and nitrogen were prepared by reactive magnetron sputtering. Additionally, coatings doped only with nitrogen were prepared under identical deposition conditions for comparison purposes. Coatings were annealed at 873 K in air and analysed by Raman spectroscopy, XRD and XPS. Photocatalytic properties of the coatings were evaluated on the basis of the photodegradation rate of methylene blue dye under UV, fluorescent and visible light. It was found that the photocatalytic activity of co-doped samples was significantly higher than that of N-doped coatings. Unlike N-doped titania films, co-doped coatings exhibited high photocatalytic activity under the fluorescent light source and noticeable activity under visible light. The possible mechanism for the enhancement of the photocatalytic activity of Mo–N co-doped titania coatings is discussed.

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1. Introduction

Titanium dioxide (or titania) is widely used as a photocatalyst, with its photocatalytic properties being discovered more than 60 years ago [1]. It finds applications in various areas, such as building materials, antibacterial coatings, self-cleaning surfaces, etc. However, the application of titanium dioxide is restricted due to its high band-gap value (3.2 eV for anatase), which means that UV irradiation is required for its excitation. As UV constitutes just 1–2% of the solar spectrum, for many practical applications it is necessary to shift the photocatalytic activity of titanium dioxide into the visible range. Several methods of achieving this are described in the literature, with doping of titanium dioxide with either metallic or non-metallic elements as one of the most promising and well-studied.

Doping titanium dioxide with non-metal atoms, such as carbon, nitrogen, phosphorus, etc. narrows the band-gap due to a mixing of the dopant p-states with the p-states of oxygen forming the valence band of titanium dioxide [2]. Of the range of possible non-metal

dopants, nitrogen is one of the most described in literature to improve the photocatalytic activity of titanium dioxide [3–5] and extend activity into the visible range. The nitrogen atom has a size comparable with the size of an oxygen atom, thus it can be easily introduced into the titania structure in either substitutional or interstitial positions [6].

Doping with transition metal ions is reported to create impurity levels near the conduction band, that may perform as trapping centres, which extend the lifetime of photogenerated electrons and holes [7]. At present, there is no uniform theory explaining the choice of the doping element to maximise the photocatalytic properties in the visible range. However, there are some reports, which enable a reasoned choice for the doping elements. It is reported that the best results for transition metal doping can be achieved when the ionic radius of the doping metal is close to that of titanium [8], to enable incorporation into the titania lattice. Of the variety of candidate metals described in literature, transition metals such as tungsten [9], chromium [10], vanadium [11] and molybdenum [12] are mentioned as efficient dopants for shifting the activity to the visible range.

However, both metal and non-metal doping have limits to their application due to some restricting factors. Excessive metal doping may lead to the formation of recombination sites for photogenerated electrons and holes, thus reducing the photocatalytic activity. Excessive nitrogen doping leads to the formation of extra

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nucleation sites, that may lead to anatase-to-rutile transformation at lower temperatures [13], which results in a significant decrease of photocatalytic activity.

The idea of simultaneously co-doping titania with metallic and non-metallic elements has been rapidly explored by many researchers in the past few years. Nitrogen is typically used as the non-metallic element, while the metals chosen may vary. Several works have recently been published on the co-doping of titanium dioxide with both molybdenum and nitrogen, using a variety of methods to produce the coatings, such as sol–gel [7], hydrolysis-precipitation [14], etc. However, in this work, titanium dioxide coatings co-doped with molybdenum and nitrogen were deposited by reactive magnetron sputtering. Co-sputtering from a host target and a dopant target in the presence of a reactive gas is proven to be a convenient and scalable technique, which provides straightforward control over the dopant levels in the host material. The doped coatings were compared to pure titania coatings, as well as coatings singly-doped with nitrogen and molybdenum only.

2. Experimental

2.1. Coating deposition

The coatings were deposited by reactive magnetron sputtering in a Teer Coatings Ltd. UDP 450 system (Fig. 1). Three 300 mm × 100 mm type II unbalanced planar magnetrons were installed vertically opposed through the chamber walls; two magnetrons were fitted with titanium targets (99.5% purity) and one with a 99.95% pure molybdenum target. The magnetrons with the titanium targets were in the closed field configuration and driven in mid-frequency (100–350 kHz) pulsed DC mode using a dual channel Advanced Energy Pinnacle Plus supply at a frequency of 100 kHz and a duty of 50% (in synchronous mode) at a constant time-averaged power of 1 kW each. In order to achieve the desired doping level, the magnetron with the molybdenum target was driven at 100 W in continuous DC mode using an Advanced Energy MDX power supply. Previous work by the authors has shown that the best results obtained for molybdenum-doped coatings were for those containing 2.4 at % of molybdenum [13]. The reactive

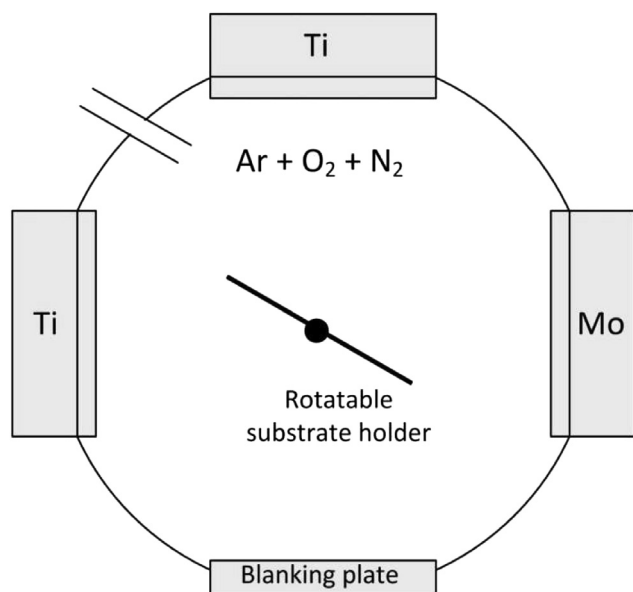


Fig. 1. Schematic representation of the Teer Coatings Ltd. UDP450 sputtering rig with three planar magnetrons.

sputtering process was carried out in an argon:oxygen atmosphere at 0.3 Pa, and was controlled by optical emissions monitoring using an operating set point (15% of the full metal signal) previously found to produce stoichiometric TiO₂ coatings [15]. The glass substrates were ultrasonically pre-cleaned in propanol and placed onto the substrate holder, which was rotated continuously during the deposition process at 4 rpm at a distance of 100 mm from the magnetrons. The nitrogen flow was controlled using a mass flow controller in the range from 0 to 10 sccm to vary dopant levels. Two arrays of coatings were deposited during this work: titania doped with nitrogen at different levels (sample IDs N1–N10), and titania with a fixed molybdenum content and varying nitrogen levels (sample IDs MoN1–MoN10). Undoped titania coatings were additionally deposited for the purpose of photocatalytic and structural property comparisons. Coatings singly doped with molybdenum (deposited under identical conditions) were described earlier elsewhere [13].

2.2. Coating characterization

The crystallinity of the annealed coatings was analysed by grazing incidence X-ray diffraction (GIXRD) (Panalytical Xpert, angle of incidence = 3°) and Raman spectroscopy (Renishaw Invia, 514 nm laser). XPS analysis was also carried out using a VG Multilab 2000 system employing an AlK α source with the pass energy of 25 eV. Transmittance of the coatings used for calculation of the band-gaps was measured with Ocean Optics USB 2000 + UV–visible spectrometer.

2.3. Evaluation of photocatalytic activity

The determination of photocatalytic activity was carried out using the methylene blue (MB) degradation test. MB is an organic dye with molecular formula C₁₆H₁₈ClN₃S, and is often used as an indicating organic compound to measure the activity of photocatalysts. An aqueous solution of MB shows strong optical absorption at approximately 665 nm wavelength. Changes in the absorption peak height are used for monitoring the concentration of MB, and hence its degradation in contact with a photocatalytic surface.

Prior to the photocatalytic measurements, coating samples of equal size (1.5 × 2.5 cm²) were immersed for 30 min in a conditioning solution of methylene blue in the dark for pre-absorption of MB on the test surfaces to exclude the effect of absorption during the photocatalytic experiment. The photocatalytic measurements were carried out for 1 h in continuous mode. Samples were immersed into 40 ml of MB aqueous solution; the concentration of methylene blue solution used in the work was 1.5 μ mol/l – this concentration was defined experimentally to be able to detect photocatalytic response of each tested coatings in 1 h experiment. The absorption peak height of methylene blue solution was measured with an Ocean Optics USB 2000 + spectrometer with continuous magnetic stirring. Each coating was tested both under UV and fluorescent light sources; 2 × 15 W 352 nm Sankyo Denki BLB lamps were used as the UV light source and 2 × 15 W Ushio fluorescent lamps as the fluorescent light source. Selected coatings were additionally tested under a visible light source. The visible light source was simulated by combining a fluorescent light source with a Knight Optical 395 nm long pass UV filter. The natural decay rate of methylene blue (without the photocatalyst present) under each type of light source was measured for reference purpose, as well as the degradation rate of methylene blue in contact with photocatalytic surface but without light irradiation (i.e. in the dark). In both cases the decay rate of methylene blue was of zero order and, thus was neglected in the following calculations, meaning any

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