Antimicrobial and photocatalytic activity of $BiVO_4$ thin films targeting water treatment

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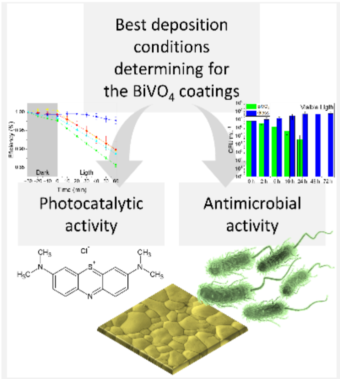

The aim of this work was to investigate operational parameters for $BiVO_4$ photocatalytic coatings production, and their influence on chemical, physical, optical, and, consequently, visible light-driven photocatalytic properties, as well as assess antimicrobial properties of the material for water treatment applications. The thin films were deposited by reactive magnetron sputtering. Bismuth (Bi) and vanadium (V) target were used. Taguchi design type L9 array was used to determine the best deposition conditions on glass for the following parameters: pressure, pulse frequency, duty, and deposition time. The samples were characterized by SEM/EDX, XRD, TEM and UV-vis spectroscopy. The photocatalytic activity and the reusability were assessed with methylene blue degradation test under visible light. The reaction mechanism was investigated using the scavengers. At last, the antimicrobial tests were performed with *E. coli*, following the British Standard (BS) ISO 27447:2009.

Introduction

The availability of adequate drinking water quality and quantity is a public health issue. The World Health Organization (WHO) estimates that at least 2 billion people worldwide consume drinking water sources contaminated with microorganisms [1]. This results in nearly one million annual deaths from waterborne infections, primarily among children under five. Heterogeneous photocatalysis could be a building block to achieving safe water treatment. However, this process still faces some problems concerning operation and efficiency [2]. In trying to solve such issues, one strategy is immobilizing catalysts in thin film form [3,4]. This way offers several advantages, such as reduced material usage and potential toxicity, lesser physical interference, and improved long-term performance [5]. Bismuth vanadate ($BiVO_4$) catalyst-based has attracted significant interest due to its characteristics, including a low band gap, non-toxicity, and corrosion resistance, resulting in consistent photocatalytic activity under visible light [6,7]. Despite its merits, limited literature explores optimization in $BiVO_4$ thin film production. Precise control of deposition parameters could enable control of film properties that impact photocatalytic activity, such as morphology, porosity, bandgap, and crystalline structure [8]. Thus, this work aims to investigate operational parameters for $BiVO_4$ thin film production and their influence on chemical, physical, optical, and, consequently, photocatalytic properties, as well as assess their antimicrobial properties targeting the water treatment application.

Material and Methods

The thin films were deposited in a single step under a high vacuum using the Teer UDP 350 sputtering reactor. A bismuth (Bi) and a vanadium (V) target were used. The distance between the target and the substrate was 50 mm. The argon flow was kept constant at 40 sccm, the oxygen flow at 20 sccm, and the time-averaged power applied to the magnetron was 50 W to Bi and 800 W to V. The Magnetron was powered by dual-channel Advanced Energy Pinnacle Plus source in pulsed DC mode. A Design of Experiments Taguchi type L9 array was used to determine the best deposition conditions for the parameters: pressure, pulse frequency, duty, and deposition time. The factors and levels analyzed are shown in Table 1. A 25 x 75 mm soda-lime glass slides were used as substrate.

Table 1. Factors and levels for L9 Taguchi design of experiments in determining the best operating condition of BiV thin film deposition.

Factors	Levels		
	1	2	3
Pressure (µTorr)	4	6	8
Frequency (kHz)	100	200	300
Duty (%)	60	75	90
Time (h)	0.5	1.0	2.0

To define the best production condition, the samples were characterized by SEM/EDX, 3D profilometry, and UV-vis spectroscopy. In addition, photocatalytic tests were performed with methylene blue (MB) (20 µmol L^{-1}) under visible light (400 – 800 nm).
Using the best determined deposition conditions, upon visible light photocatalytic activity, the reusability of the material was tested. To assess the reaction mechanism through the scavengers, 4-hydroxy-TEMPO was used to scavenge superoxide radicals ($O_2^{\cdot -}$), isopropanol for hydroxyl radicals (OH•), sodium oxalate for holes (h^+), and sodium nitrate for electrons (e^-). Moreover, antimicrobial tests were performed with *E. coli* until 72 h exposure,

following the British Standard (BS) ISO 27447:2009 protocol.

Results and Discussion

Analysing the results of the $BiVO_4$ deposition conditions, a strong influence of deposition time on the thickness of the coatings can be seen (Tab. 2). The band gap values (Tab. 2) are slightly lower than those reported in the literature ~2.4 eV [9]. Especially in samples with a shorter deposition time and, consequently, a lower thickness. This characteristic reduces the material light absorption and, consequently, its photocatalytic activity.

Table 2. Production conditions tested, bandgap, thickness, and pseudo-second-order kinect of MB removal in visible light from L9 Taguchi design for $BiVO_4$.

Sample	Pressure (µTorr)	Frequency (kHz)	Duty (%)	Deposition time (h)	Band gap (eV)	Thickness (nm)	k (10^{-5} L µmol^{-1} s^{-1})
S01	4	100	60	0.5	1.8	65	1.22
S02	4	200	75	1.0	2.0	255	1.76
S03	4	300	90	2.0	2.2	599	4.26
S04	6	100	75	2.0	2.1	336	4.85
S05	6	200	90	0.5	2.1	125	1.61
S06	6	300	60	1.0	2.2	656	2.26
S07	8	100	90	1.0	2.2	307	3.73
S08	8	200	60	2.0	2.3	742	3.39
S09	8	300	75	0.5	1.9	186	1.48

In terms of composition, determined through the EDX analysis, it was possible to verify that the stoichiometry of the produced material corresponds to $BiVO_4$. Regarding the morphology of the samples, through the SEM, the coating had a well-defined crystal structure. As the deposition time increased, crystal growth was also noted (Fig. 1).

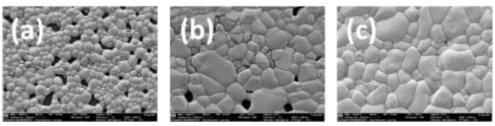

Figure 1. Surface SEM micrographs of samples of: a) 0.5 h (S05), 1 h (S06), and 2 h (S04).

The photocatalytic activity, assessed from the first-order kinetic constants of MB degradation (Tab. 2), a positive and linear influence on duty and deposition time can be observed (Fig. 2). On the other hand, a negative linear influence for pressure was observed. The frequency factor did not show linearity, but the results indicated that better photocatalytic activity was associated with lower frequency. So the best conditions for film production were defined as: 4 µbar pressure, 100 kHz frequency, 90% duty, and 2 hours of deposition.

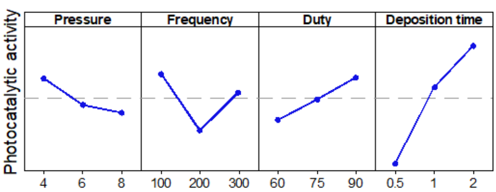

Figure 2. Main effect plot for the factors that influence in photocatalytic activity tested in L9 Taguchi design.

With the coating produced under the best determined conditions, it was found that both $OH^{\bullet}$ and $O_2^{-\bullet}$ are involved in the oxidation reactions, but the latter was more significant. The reusability material was also tested up to the fifteenth cycle, and no significant reduction in efficacy was observed ($\alpha = 0.05$).

As for the antimicrobial activity of $BiVO_4$, in the presence of visible light, there was a reduction in the concentration of *E. coli* over time, from a high initial inoculum reaching values lower than the method's detection limit (<DL) within 48 h (Fig. 3a). This data suggests more efficient antimicrobial action over other bismuth oxides, such as bismuth oxide and bismuth tungstate [4]. Furthermore, even in the dark control tests, there was an antimicrobial activity of $BiOV_4$, reaching values <DL within 72 h (Fig. 3b) suggesting some innate antimicrobial action.

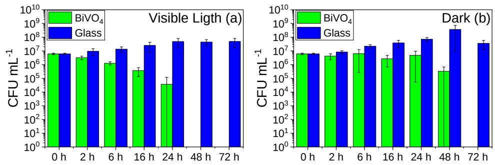

Figure 3. Number of microbial cells (CFU mL-1) recovered from the glass and BiVO4 surfaces (a) under visible light and (b) in the dark.

Conclusions

The design of experiments was of great importance to adjust the properties of $BiVO_4$ and achieve significant photocatalytic and antimicrobial activity. The latter is an innovation because no references were found in the literature that reported the antimicrobial activity intrinsic to $BiVO_4$ without light activation. This result places the material in high esteem for application in water treatment. Since it is activated by visible light, it can be applied under sunlight, and even in the absence of light, at night, it can continue working in the disinfection process.

Acknowledgments

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