

Photocatalytic ZnO based PES Membranes for AOP Water Treatments under UV and Sunlight

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Abstract

ZnO nanorods (ZnO) are grown by Chemical Bath Deposition on microfiltration polyethersulphone (PES) water membranes in order to combine photocatalytic properties of zinc oxide to adsorption properties of membranes. Degradation of a model dye (methylene blue, MB) dispersed in water is promoted by exposition of multifunctional ZnO/PES membranes to UV and solar light: in fact, ZnO decorated membrane ensures generation of reactive oxygen species (ROS) that degrade the organic pollutants dispersed in water. ZnO degradation promoted by UV irradiation is detectable by anionic meso-tetrakis(4-sulfonatophenyl) porphyrin (H_2TPPS^{4-}) that is used as effective molecular probe to sense the presence of Zn^{2+} ions due to photocatalytic leaching. Copyright © VBRI Press.

Keywords: ZnO, polyethersulphone, membranes, photocatalysis, water treatments.

Introduction

Increasing pollution, generated by global industrial and consuming society, represents a serious threat to the environment: clean air and clean water must be assured to next generations and, in this perspective, new remediation strategies are under evaluation and development [1-5]. The preferred approaches are those able to degrade most of the dispersed contaminants without using or generating toxic substances or requiring high energy consumes.

Advanced Oxidation Processes (AOP) based on semiconductive photocatalysts are suitable for water and air treatments since they are based on light activated mineralization of all class of organic contaminants [6-8]: however implementation of AOP processes requires the possibility to use solar light, which is an inexpensive, clean and endlessly form of energy, to effectively promote such photocatalytic activity of a wide selection of photoactive materials.

The main requirement for a semiconductive photocatalyst concerns its energy band-gap which must be compatible with redox potential of involved degradation reaction and light wavelength: moreover, material non-toxicity, stability and high surface area are requested for environmental application.

TiO_2 and ZnO are the most used and studied photocatalysts for water and air treatments, with an energy gap of about 3-3.2 eV, thus, activated by UV light [6, 7]. These semiconductive oxides are low cost materials largely used in AOP treatments as

nanopowders or nanostructured dispersions. Employed in this form, however, high costs of recovery are mandatory in order to avoid their dispersion in water and, consequently, immobilization of photocatalyst on solid surfaces or membranes is more proper for water purification applications [9-11].

The possibility to obtain a plethora of ZnO nanostructured architectures by low-cost bottom-up approaches at low temperature [12] allows for development of fabrication hybrid approaches to combine this nanostructured material with conventional microfiltration membranes [13, 14].

In particular, herein, we present a study on photocatalytic properties of PES water membranes decorated with ZnO nanorods grown by Chemical Bath Deposition. Spectroscopic study of Methylene Blue (MB) degradation in presence of photoactive membrane irradiated with UV and solar light irradiation has been performed to validate the activity of the ZnO/PES hybrid membranes.

Anionic porphyrins (H_2TPPS) are used as molecular probe to spectroscopically reveal and quantify Zn^{2+} leaching caused by UV irradiation of the ZnO based membranes

Experimental

Materials

The selected water filtration membranes were commercial supported Polyethersulfone membranes

(P010F) by Microdyne with a molecular mass of 10kDa. Zinc Acetate dehydrate ($\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$) and Ethylenediamine (EDA) were purchased from Sigma - Aldrich.

Materials synthesis

PES membrane was washed with distilled water in order to remove its glycol content and then dried in an oven overnight. ZnO nanorods were grown onto the surface of the PES membranes by a Chemical Bath Deposition Process (CBD) [15, 16]. The first step of this process was a seeding procedure that consists of a pre-treatment of the membrane in $\text{Zn}(\text{Ac})_2/\text{H}_2\text{O}$ solution (0.5 M). A proper support has been used to allow for a repeatable sample positioning inside the seeding solution where it remains dipped for 1 hour under stirring at ambient temperature. After dipping, the PES membrane was dried at 110°C overnight.

In a second step, the seeded membrane was immersed, using the same support employed for seeding, in a 1:1 $\text{Zn}(\text{Ac})_2/\text{H}_2\text{O}$ and EDA solution (0.1 M), and kept magnetically stirred at 80°C for 3 h. At the end, the PES membrane covered with ZnO nanorods was washed with distilled water and dried at 110°C for 1 h.

Characterization

Size and morphology of the ZnO nanorods were observed by ZEISS SUPRA-55 VP Field Emission Scanning Electron Microscopy equipped with an Oxford EDS solid state detector for Energy Dispersed X-rays Spectroscopy (EDS).

ZnO doped PES membrane and the bare membrane were dipped in a glass crystallizer containing MB aqueous solution and left in the dark. The solution was measured with an UV-VIS spectrophotometer (JASCO V-630) in a wavelength range of 200-800 nm.

Bare and ZnO treated PES membranes were dipped in a glass crystallizer containing methylene blue aqueous solution (16 ml, pH = 7) and irradiated by UV lamp (420 and 365 nm). The crystallizer was put in a box wrapped around by an aluminium foil for reflection of UV light back into the crystallizer. The irradiated solution was measured at regular time intervals with an UV-VIS spectrophotometer (JASCO V-630) in a wavelength range of 200-800 nm.

Photodegradation tests were performed under natural sunlight by dipping the PES membrane in a glass cuvette containing methylene blue aqueous solution ($50 \mu\text{M}$). The cuvette was put out of the window, covered with a quartz slide and exposed to sun light. Also, in this case, the solution was measured at regular time intervals with an UV-VIS spectrophotometer (JASCO V-630) in a wavelength range of 200-800 nm.

The degradation of MB was evaluated by the absorbance peak at 664 nm in the Lambert-Beer regime. The photodegradation rate was calculated from the linear plot of $\ln(C_0/C)$ versus the irradiation time. The decomposition of the MB dye in the absence of any photocatalyst materials was checked as a reference.

Results and discussion

ZnO nanorods are grown on conventional water filtration PES membranes to couple their mechanical separation ability with photocatalytic action. Two steps are required to achieve an extensive ZnO nanorods coverage onto the membrane surface: i) a seeding layer is firstly achieved by dipping the membrane in an aqueous solution of Zinc Acetate dehydrate (ZnAc) and by annealing it overnight at 100°C and then ii) CBD allows for the extensive growth of ZnO nanorods.

Fig. 1 shows SEM images of the membrane after CBD growth: ZnO nanorods are visible on both sides of the PES membrane, the flat front side (Fig. 1a) and the fibrous backside (Fig. 1b).

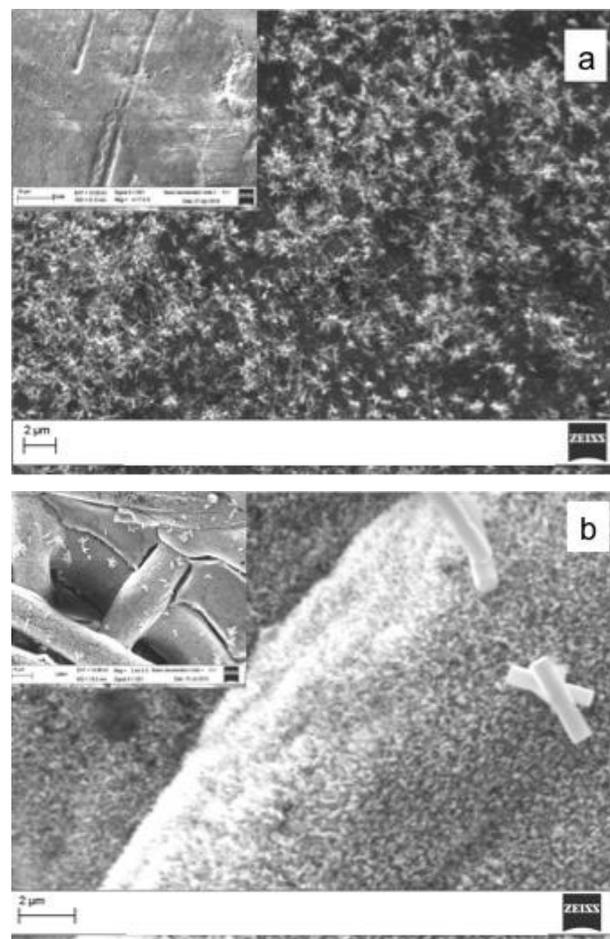


Fig. 1. SEM images of ZnO nanorods grown on water membrane (a) flat frontside (in the inset the flat side of membrane before ZnO growth is shown for comparison) and (b) fibrous backside.

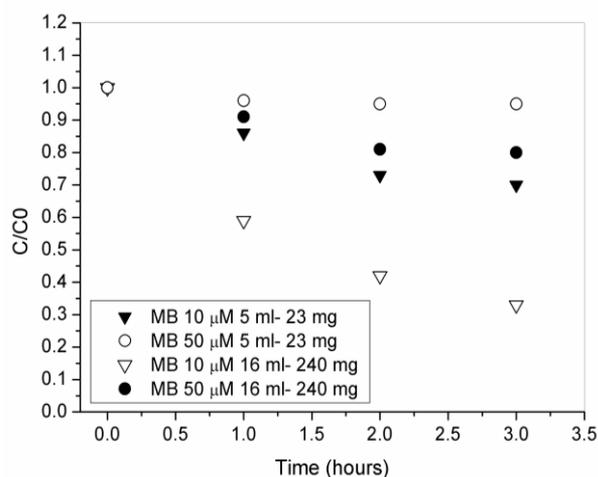


Fig. 2. MB concentration decrease (defined as C/C_0) related to adsorption on PES membrane surface.

In order to verify the absorption behaviour of bare PES membranes, dipping tests are performed upon varying membrane dimensions and MB concentration (Fig. 2).

Membrane dimension varies from $1 \times 1 \text{ cm}^2$ (about 23 mg) to $4 \times 4 \text{ cm}^2$ (about 240 mg): as expected, adsorption increase upon increasing membrane surface. Upon increasing the MB concentration from $10 \mu\text{M}$ to $50 \mu\text{M}$ any variation associated to adsorption becomes less visible since the estimated absorption capability of the PES membrane is 3 nmol/mg .

Fig. 3 shows the expected reduction of MB concentration ($C_0 = 50 \mu\text{M}$) related to absorption capability of ZnO treated membranes (23 mg), at 25°C (Fig. 3a) and 45°C (Fig. 3b).

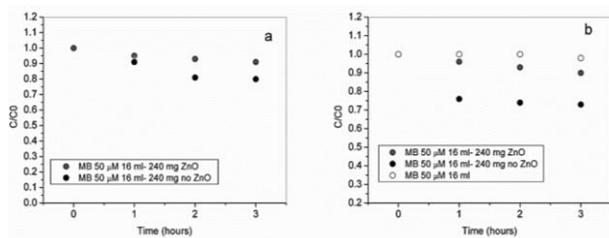


Fig. 3. MB concentration decrease (defined as C/C_0) related to adsorption on bare PES membrane (black circles) and ZnO treated PES membranes (grey circles) at (a) 25°C and (b) 45°C : MB $50 \mu\text{M}$ solution thermal resistance has been tested at 45°C (open circles).

At the end of dipping time, despite the observed colour variation from white to blue, bare membrane absorption (black circles) results in about 20% decrease of MB concentration, while the presence of ZnO nanorods (grey circles) suppresses the adsorption within the same time range. At 45°C (Fig. 3b), in order to exclude any thermal degradation of dye, MB solution behaviour is reported for comparison (Fig. 3b, open circles): bare membrane absorption rate slight increases with respect to that observed at 25°C , while the behaviour of ZnO treated membrane remains unchanged.

We can, thus, conclude that ZnO presence reduces MB absorption onto the surface of the membrane.

To test photocatalytic performances of these membranes, bare and treated samples (240 mg) are dipped in 16 ml of MB solution ($10 \mu\text{M}$) and exposed to UV light. Fig. 4 shows decrease of normalised concentration of MB (C/C_0) induced by UV light irradiation at $\lambda = 420 \text{ nm}$.

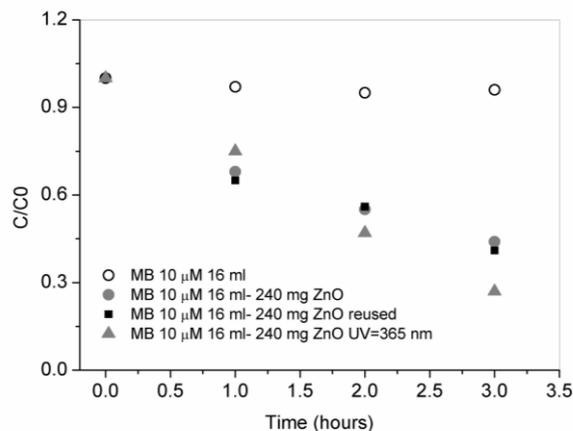


Fig. 4. MB ($C_0 = 10 \mu\text{M}$) degradation (open circles) under irradiation with UV light ($\lambda = 420 \text{ nm}$). MB degradation in presence of (a) ZnO treated PES membranes (grey circles) and (b) reused ZnO treated PES membranes (black squares). MB solution ($C_0 = 10 \mu\text{M}$) degradation in presence of ZnO treated PES membrane under irradiation with UV light at $\lambda = 365 \text{ nm}$ (grey triangles).

Upon irradiation with UV lamp at $\lambda = 420 \text{ nm}$, MB solution is not degraded (open circles) while the presence of ZnO promotes a MB degradation up to 70% (grey circles): cycling experiments confirm the possibility to reuse these multifunctional membranes (after drying it in oven at 100°C overnight) without reducing their efficiency (black squares). Finally, the photocatalytic performances of ZnO treated membrane under irradiation with UV light at $\lambda = 365 \text{ nm}$ (magenta triangles) are further increased (up to 85%) with respect to that recorded working with light at $\lambda = 420 \text{ nm}$.

ZnO treated membranes have been further tested, using UV light at $\lambda = 420 \text{ nm}$, by increasing MB concentration ($50 \mu\text{M}$), as shown in Fig. 5.

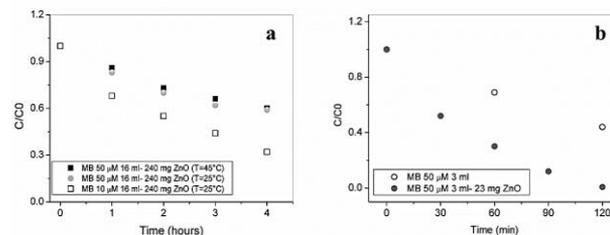


Fig. 5. (a) MB solution ($50 \mu\text{M}$) degradation under irradiation with UV light ($\lambda = 420 \text{ nm}$) in presence of ZnO treated PES membranes at 45°C (grey circles) and ZnO treated PES membranes at 25°C (black squares). MB diluted solution ($10 \mu\text{M}$) degradation under irradiation with UV light ($\lambda = 420 \text{ nm}$) in presence of ZnO treated PES membranes at 25°C (open squares) is shown for comparison; (b) MB solution ($50 \mu\text{M}$) degradation under sunlight (open circles) and in presence of ZnO treated PES membranes (solid grey circle).

As shown in **Fig. 5a**, in presence of ZnO treated membranes dye degradation is of about 40% both at 25°C (grey circles) and 45°C (black squares): therefore, photodegradation performances are not affected by temperature increasing. **Fig. 5b** shows photo degradation promoted by exposure under natural sunlight of MB 50 µM solution containing ZnO treated PES membranes. Bare MB solution is photodegraded (open black circles) under sunlight, but role of the presence of ZnO treated membrane is well evident and deals to complete degradation of MB in 2 hours (grey solid circles).

Another important data that needs to be controlled during photocatalytic testing of ZnO based materials is Zn²⁺ leaching due to irradiation. An effective test to reveal the presence of zinc ions at sub-micromolar concentration is a spectroscopic titration using water soluble anionic porphyrin. In particular, herein we use H₂TPPS as molecular probe to reveal the presence of Zn²⁺ in solution. H₂TPPS is an anionic porphyrin, well soluble in water due to the presence of the charged substituents at the meso position of porphyrinic ring, able to form ZnTPPS in presence of zinc ions in solution [17, 18].

Fig. 6 shows UV-Vis spectra of H₂TPPS in water, in absence (dotted line) and in presence of Zn²⁺ ions (solid lines).

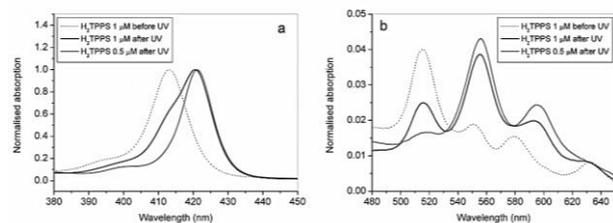


Fig. 6. Normalised H₂TPPS absorption spectra in presence of MB solution (10 µM) before (dotted line) and after UV irradiation in presence of ZnO treated PES membranes using a concentration of 0.5 µM (gray line) and 1 µM (black line): Soret region (a) and Q-bands region (b).

H₂TPPS (1 µM) aqueous solution containing ZnO treated membrane shows, before UV irradiation (dotted black line), in the 380-600 nm region the typical features associated to porphyrin free base: Soret band is centred at 413 nm (**Fig. 6 a**) and four Q-bands are visible in the 500-650 nm region (**Fig. 6 b**) [18]. After irradiation with UV light (4 hours), if solution is treated with H₂TPPS having a concentration below 1 µM (0.5 µM, grey line) Soret band is shifted at 421 nm due to the instantaneous metalation of the inner macrocycle core and formation of ZnTPP: porphyrin core metalation is further confirmed by spectral changes in the Q-bands region (**Fig. 6 b**) detectable by reduction of band number from four (for free base - dashed line) to two (for metalated derivative- solid grey line). On the contrary, band broadening of the Soret band is observed and two components are clearly visible at 413 nm and 421 nm if 1 µM H₂TPPS solution is used (black line): this evidence refers to coexistence of free base and

metalated form. Therefore, at this concentration ZnTPPS coexists with H₂TPPS, thus pointing to estimation of an overall membrane leaching, dealing with release of Zn²⁺ ions in solution, below 1 µM.

Conclusion

It has been demonstrated the possibility to grow ZnO nanorods onto the surface of conventional PES water microfiltration membrane by Chemical Bath Deposition. The presence of ZnO nanostructures inhibits the methylene blue (MB) absorption capability of PES membrane thus allowing for a spectroscopic evaluation of photodegradation performances. It has been observed that irradiation with UV light at $\lambda = 365$ nm promotes a more effective MB photodegradation than that observed at $\lambda = 420$ nm. The ZnO based PES membrane are reusable and their activity has been tested also under solar light exposure: in particular, dye photodegradation is faster upon sunlight irradiation due to two coexisting processes such as intrinsic dye photolysis and oxidation processes at the surface of ZnO nanostructures.

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