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Design and photocatalytic ability of ordered mesoporous TiO_2 thin films

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Highlights

- Applicability of new highly ordered mesoporous TiO_2 thin film for photocatalytic degradation of selected organic pollutants was tested.
- Complete degradation of methylene blue **(**MB**)** and crystal violet **(**CV**)** was achieved.
- Kinetic parameters of photodegradation reactions were correlated to the properties of mesoporous TiO_2 films.
- Dip coating was proved to be effective technique to obtain desired morphology of ordered mesoporous TiO_2 thin films by using polymer templates.

Abstract

Homogeneous and crack-free TiO_2 films with templated mesoporosity were prepared by **the** dip coating technique using **an** evaporation-induced**,** self-assembly method. The synthesized mesoporous TiO_2 films were characterized using SEM/TEM, BET and XRD techniques. Degradation reactions of methylene blue and crystal violet dyes were used to test **the** photocatalytic capability of mesoporous TiO_2 films. **The d**egradation kinetic**s** of methylene blue

and crystal violet **were** investigate**d over a b**road range of initial concentrations of **the** organic dyes. The kinetic data were correlated with **the** specific surface area and thickness of mesoporous TiO_2 films, as well as number of reaction cycles.

KEYWORDS: A. nanostructures, A. thin films, B. sol-gel chemistry, C. transmission electron microscopy, D. catalytic properties

1. Introduction

Water pollution is currently a major problem of global significance. Recalcitrant organic dyes are widely used in **the** textile and photographic industries and present worldwide environmental problem**s**. It is projected that from 1 to 20% of dyestuffs, used in dyeing process**es**, are released in wastewaters [1,2]. **Even** small concentrations of textile dyes considerably influence the water environment [3]. They can have carcinogenic and mutagenic effects, thus **they are** harmful pollutants for **both** humans and **aquatic** organisms**.**

Traditional wastewater treatments are not particularly effective for colored effluents. During the past two decades, researchers have been **assessing** unconventional, cost-effective and promising solution**s** for the complete decolorisation of dye-based contaminants in **the** natural environment. In this context, heterogeneous photocatalysis is considered to be one of the most promising technologies for treatment of water contaminated with toxic organic substances.

Due to their favorable properties TiO_2 based thin films have found extensive commercial applications in water and air refining processes [4-6], as self-cleaning coatings [7], gas sensors [8], electrochromic devices [9], and as TiO_2-dye composite materials in manufacturing of photovoltaic cells [10,11]. Most of th**e foregoing** applications **have been a**chieved **because of the** porous**,** nanocrystalline structure and large specific surface area of TiO_2 thin films. Several preparative techniques such as sol-gel [12], chemical vapor deposition [13], electrodeposition [14], electrophoresis [15], and ultrasonic spray pyrolysis [16,17] have been developed in order to obtain TiO_2 films with **the** desired properties. The film morphology can be controlled by preparation process parameters such as composition of precursor solution, deposition time, withdrawal rate, etc. Mesoporous TiO_2 films can be deposited either by doctor-blad**e** [18]**,** dip

coating [19,20] **or** spin coating technique**s** [21,22]. Recently, **the** evaporation-induced self-assembly method [20,23,**24**] **using** various precursors and templating **polymers have been used** in order to prepare mesoporous TiO_2 films**; it is accepted that the polymer templates have a significant influence on the porosity of the final material.**

In the present study **the** photocatalytic activity of homogeneous and crack-free TiO_2 films with templated mesoporosity, prepared by using **two different** polymer**s** as mesopore directing/generating agent**s**, was tested. **The d**egradation kinetic**s** of methylene blue (MB) and crystal violet (CV) dyes **were** investigated as a function of pore size, film thickness and number of reaction cycles.

2. Experimental

2.1. Preparation of templated TiO_2 thin films

Silicon wafers of W5 quality (dimensions: 25 x 10 x 1.5 mm) were used as substrate**s** **c**leaned in acetone and ethanol, and then dried at 35 ºC for 30 min, before use.

All chemicals were of the highest purity, an**d u**sed as received. Dip coating solutions were typically prepared by dissolving about 6.0 ml of $TiCl_4$ in 50 ml of dry ethanol (98%) under an inert atmosphere in **a** glove box. During this exothermic process followe**d t**he increase **in** solution temperature, formation of TiO_2 colloid takes place. After 1 hour, when **the** precursor solution cooled-down to ambient temperature, **an** alcohol-water mixture (50 ml of ethanol and about 10 ml of water) containing either Pluronic F127 tri block copolymer ($EO_{106}PO_{70}EO_{106}$; m.w. = 12600) or PSM02 polymer (PEO-PBD-PEO; molar weight of PBD part is 10000) was added. **The m**olar ratio between $TiCl_4$ and F127 was adjusted **to 1** : 0.001, while the molar ratio between $TiCl_4$ and PSM02 was 1 : 0.01. These solutions were stirred at room temperature for 24 hour**s** an**d t**he addition of deionized water molar ratio between selected solution constituents was adjusted t**o T**iCl_4 : EtOH : H_2O = 1 : 30 : 10.

The TiO_2 films were deposited onto silicon substrates by dip coatin**g c**ombined with **the** evaporation-induced self-assembly method. **The d**ip coating procedure was performed in a climate chamber at 25 °C with a withdrawal rate of either 60 or 200 mm/min. **The r**elative humidity in **the** climate chamber was adjusted t**o 4**0%. All deposited films were initially conditioned at 70 °C for 3 hours **using** synthetic air flow (10 cm^3/min). Then, calcinatio**n** of the

TiO_2 films **was** carried out at 400 or 450 °C for 30 min**, again using** synthetic air flow. In both thermal procedures a heating rate **of** 1 °C/min **was employed.**

2.2. Characterization of templated TiO_2 thin films

The surface morphology and microstructure of the calcined TiO_2 films was studied by scanning electron microscopy (SEM, JEOL 7401F operated at acceleration voltage of 5.0 kV). The **use** of ImageJ software enabled **the** determination of pore size distributions by using **a** statistical approach based on **the** diameter measurement of at least 100 pores **diameters**.

The specific surface area of TiO_2 films was evaluated by using **a** low temperature adsorption/desorption BET method **(**Micromeritics ASAP 2010 instrument**)** in N_2 physisorption experiments. **The s**pecific surface area is expressed as BET m^2 of TiO_2 film per m^2 of substrate planar dimensions.

X-ray diffraction (XRD) measurements were performed using **a** Philips PW-1710 diffractometer with Cu-anticathode and a monochromator **set** at 40 kV and 55 mA. Scherrer's equation was used in order to calculate **the** average crystallite size.

2.3. Photocatalytic degradation of organic dyes

Photocatalytic ability of mesoporous TiO_2 thin films was studied using organic dyes, methylene blue (MB) and crystal violet (CV), as model systems. The photochemical reactor consisted of **a** UV lamp (Roth Co., 16W, 2.5 mW/cm^2, λ_{max} = 366 nm) positioned annular to the 50 ml quartz flask. The rates of photocatalytic degradation of both organic dyes, MB and CV, were followed for different initial concentrations in th**e 0**.005 to 0.03 mM **range.** The blank experiments, direct photolysis of MB and CV, were also performed and used as a correction factor. In order to test **the** performance of **the** mesoporous TiO_2 films under long run working conditions, **the** photocatalytic degradation of organic dyes was studied in repeated cycles. The acidity of solutions was not adjusted and pH values were in the range **of** 6.7 to 7.0.

Initial concentrations of organic dyes, as well as their decreas**e** during photodegradation reaction**s** were determined using **a** UV/Vis spectrophotometer (Perkin Elmer Lambda 25).

3. Results and Discussion

Typical SEM images of the calcined TiO_2 films deposited onto silicon substrates, obtained by using two different template polymers and two different substrate withdrawal rates, are shown in Figure 1. **The t**op view of the TiO_2 film prepared by using Pluronic F127 polymer as template (Figure 1a) indicated **a** complete crack-free surface coverage of substrate. **The e**xtensive porosity of **the** TiO_2 film **is noticeable**, characterized **by a** narrow pore size distribution**,** with **an** average pore size of about 8 nm. Image of the cross-section of mesoporous TiO_2 film (Figure 1c) reveale**d a** short range, cubic-like ordering of **the** interconnected pore structure.

On the other hand, **the** dip coating proces**s using P**SM02 polymer**,** as a template**,** leads to the formation of crack-free mesoporous TiO_2 films with larger pores (20 - 22 nm) compared to Pluronic F127 polymer **(F**igure 1b). It is obvious that **the use** of **the** polymer with **the** larger molecular mass and consequently larger volume result**s** in **the** formation of film**s** with larger pore size**s**. Image of the cross-section **(F**igure 1d) of **the** mesoporous TiO_2 film indicated **the** elliptical shape of pores and **a** lower level of their interconnectivity, which can reduce diffusion of reactants through the film during catalytic reactions.

Cross-section imaging of mesoporous TiO_2 films provided **opportunities** to determine the film thickness as a function of **the** dip coating withdrawal rate **(F**igures 1c and 1d). Based on a limited number of experiments, linear proportionality between film thickness and withdrawal rate was found. For example, **a** three times thicker TiO_2 film was obtained when **the** dip coating withdrawal rate was somewhat over three times larger (compare TiO_2 films shown in Figures 1c and 1d). This effect is **a** consequence of **the** larger viscous force when **the** substrate is pulling up **the** precursor sol at **a** larger dip coating withdrawal rate. Because of **the foregoing, a** thicker layer of liquid precursor is deposited over **the** substrate surface. These results are in agreement with literature data concerning **the** importance of the substrate withdrawal rate and sol viscosity for **the** preparation of uniform TiO_2 films using **the** dip coating technique and titanium alkoxide as a precursor [**25**].

Corresponding BET surface areas of mesoporous TiO_2 films obtained by **the** dip coating technique in the presence of F127 and PSM02 templates after calcinatio**n** at 400 °C were found to be 95.7 and 23.4 m^2/m^2, respectively. These results are in agreement with **the** estimated pore size **obtained by using a statistical software ImageJ. The average pore size is determined by using the Barrett-Joyner-Halenda (BJH) method [26].** On the other hand, calcinatio**n** at 450

°C led to **a** decrease **in** surface area (47.3 and 19.2 m^2/m^2 for samples prepared in the presence of F127 and PSM02, respectively). **The d**ecrease **in** specific surface area is a consequence of extensive particl**e** sintering during **the** calcination process performed at higher temperature. Similar BET surface areas of **T**iO_2 films, obtained by dip coatin**g, have been** reported in **the** literature [**27-30**], while differences in reported values can be explained in terms of **the** different prepa**ration** history (substrate type and its roughness, TiO_2 precurso**r, c**omposition of coating solution **and** template used in (conventional) **the** evaporation-induced self-assembly method).

The crystalline phase composition of the calcined TiO_2 films was analyzed by XRD. The XRD pattern of TiO_2 film**s,** with **sufficient t**hickness to obtain reliable data (270 nm)**,** is shown in Figure 2. The XRD analysis revealed the presence of anatase phase (peaks at 25.3, 37.8, 48.05 and 53.9 °) and **a** small amount of nonstoichiometric Ti_2O_3 (peaks/shoulders at 33.1 and 34.8 °). The calculated grain size, based on the broadening of the XRD diffraction peak**s**, using Scherrer's equation**,** was found to be 12 nm. This result is in agreement with data obtained by other authors [**30,31**]. Also, it is important to point out that TiO_2 particles whose size is smaller than 20 nm instead of octahedral have square pyramidal surface structure with one double Ti=O bond [**32,33**]. Under-coordinated surface titanium atoms are basically active sites with **the** capability to efficiently adsorb solutes from **the** surrounding media**, thus** improvin**g the p**hotocatalytic ability of TiO_2.

It is well-known that **the** specific surface area has **a** significant influence on the photocatalytic efficiency of TiO_2 [**34,35**]. In order to quantify this effect **the** photocatalytic degradation of two different organic dyes (MB and CV) was investigated under the same experimental conditions using mesoporous TiO_2 films of the same thickness, prepared in the presence of two different polymer templates (F127 and PSM02), having distinct specific surface areas (95.7 and 23.4 m^2/m^2, respectively). **The p**hotocatalytic degradation kinetics of MB and CV are shown in Figure 3a and 3b, respectively. In the case of both organic dyes, faster degradation kinetic**s** was observed when mesoporous TiO_2 film**s** with larger specific surface area **were** used as a photocatalyst. In addition, **the** photocatalytic activity of mesoporous TiO_2 films was tested as a function of their thickness. As expected, thicker films, due to the larger amount of photocatalyst, induced faster photodecomposition of organic dyes (results are not shown).

Photocatalytic degradation of MB and CV over mesoporous TiO_2 films was investigated as a function of initial concentration of organic dyes **in the** 0.005 to 0.03 mM **range**. The

degradation kinetic curves for different initial concentrations of MB and CV with usage of mesoporous TiO_2 prepared in the presence of F127 polymer (specific surface area = 95.7 m^2/m^2) are shown in Figure 4a and 4b, respectively. Complete decolorization of both organic dyes, under illumination no longer then 1 day, was observed only when **the** initial concentration was sufficiently low. The mesoporous TiO_2 films were pealed-off from the substrate after photocatalytic experiments in order to check their **mass**. For all TiO_2 films used in photocatalytic experiments **a mass** of 30±2 mg was found.

The photocatalytic degradation of organic dyes **follows** Langmuir-Hinshelwood **k**inetics [**36**], which can be described by **the** following equation:

$$- dC/dt = k_r \cdot K \cdot C_{eq} / (1+K \cdot C_{eq}) \quad (1)$$

where k_r is the apparent rate constant, K is the adsorption coefficient of the substance to be degraded and C_{eq} is the equilibrium concentration. For very low concentrations **of solutions/pollutants** the Langmuir-Hinshelwood equation simplifies to a pseudo-first-order **kinetic behavior**:

$$- dC/dt = k \cdot C \quad (2)$$

where k is the pseudo-first-order rate constant.

The pseudo-first-order rate constants determined for different initial concentrations of MB and CV in the photocatalytic degradation reaction using mesoporous TiO_2 films with different specific surface areas (95.7 and 23.4 m^2/m^2) but of the same **mass** (30 mg) are collected in Table 1. Based on th**e kinetic** data **for degradation** some general features can be recognized. First**ly, under the same experimental conditions, the** photocatalytic degradation of CV is slower compared to **the** degradation of MB**.** Second**ly**, as expected, the degradation of both organic dyes is faster when **the** photocatalyst **exhibits a** larger specific surface area. Third**ly**, the relative decrease of **the** rate constant wit**h i**ncrease **in** initial concentration of both organic dyes is larger for the photocatalyst with **the** smaller specific surface area. This effect can be easily explained **in terms of the greater** occupancy of TiO_2 surface sites with smaller specific surface area by organic dyes. Also, it should be mentioned that in all experiments **the** pH of the solutions wa**s**

between 6.7 and 7.0. It is well known that TiO_2 is ampho**te**ric and that the zero point charge is at $pH_{zpc} \approx 5.9$ [**37**]. Under **such** experimental conditions, **the** electrostatic attraction between positively charged organic dyes and negatively charged, i.e. deprotonated surface –OH groups is **the** driving force for adsorption of organic dyes.

In order to test **the** photocatalytic ability of mesoporous TiO_2 films under long run working conditions, **the** degradation of both organic **dyes** was **ascertained** in repeated cycles without **the photocatalyst being subject to any cleaning treatments**. The subsequent degradation kinetic curves **for** MB after its complete decolorization are shown in Figure 5. Identical behavior was also observed in the experiments with CV (results are not shown). It **is noticeable** by comparing, for example, the first and the third kinetic cycl**e the** photocatalytic ability of TiO_2 film is not significantly diminished under long run working conditions.

4. Conclusion

The dip coating technique with **the use** of templating polymers proved to be **a** simple way to obtain mesoporous TiO_2 films with **the** desired properties. Variation of synthetic parameters (composition of precursor solution, withdrawal rate, temperature, etc.) makes **it** possible to control **the** basic characteristics of TiO_2 films (homogeneity, pore size and their interconnectivity, thickness). The organic dyes (MB and CV), **over a** broad range of initial concentrations, were used as a model system in order to probe **the** photocatalytic capability of synthesized TiO_2 films. Special attention was paid **to** the influence of pore size and thickness of mesoporous TiO_2 films, as well as the number of reaction cycles **in terms of** the photocatalytic degradation kinetics of **the** organic dyes. Additional experiments are underway in our laboratories in order to optimize experimental conditions that will improve **the** efficiency of **the** desired photocatalytic reactions.

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Figure Captions

Figure 1. SEM images of mesoporous TiO_2 films obtained in the presence of (a) F127, and (b) PSM02 polymer template (top view). Cross-section of mesoporous TiO_2 films obtained at (c) 60 mm/min, and (d) 200 mm/min withdrawal rate of substrate.

Figure 2. The XRD pattern of TiO_2 film with thickness of 270 nm on silicon wafer substrate.

Figure 3. Degradation kinetic of MB (a) and CV (b) using mesoporous TiO_2 films as a photocatalyst with different specific surface area (95.7 and 23.4 m^2/m^2).

Figure 4. Degradation kinetic of MB (a) and CV (b) using mesoporous TiO_2 films as a photocatalyst with 95.7 m^2/m^2 specific surface area as a function of initial concentration of organic dyes.

Figure 5. Degradation kinetic of MB using mesoporous TiO_2 film with 95.7 m^2/m^2 specific surface are as a function of repeated cycles (initial concentration of MB was 0.01 mM).

Table 1. The pseudo-first-order rate constant for different initial concentrations of MB and CV in the photocatalytic degradation reactions over mesoporous TiO_2 films obtained using two different templating polymers

	k_{MB} (h^{-1})		k_{CV} (h^{-1})	
C_0 (mM)	**F127**	**PSM02**	**F127**	**PSM02**
0.005	0.154	0.145	0.139	0.122
0.0075	0.112	0.108	0.100	0.086
0.01	0.079	0.072	0.065	0.058
0.03	0.027	0.022	0.017	0.016

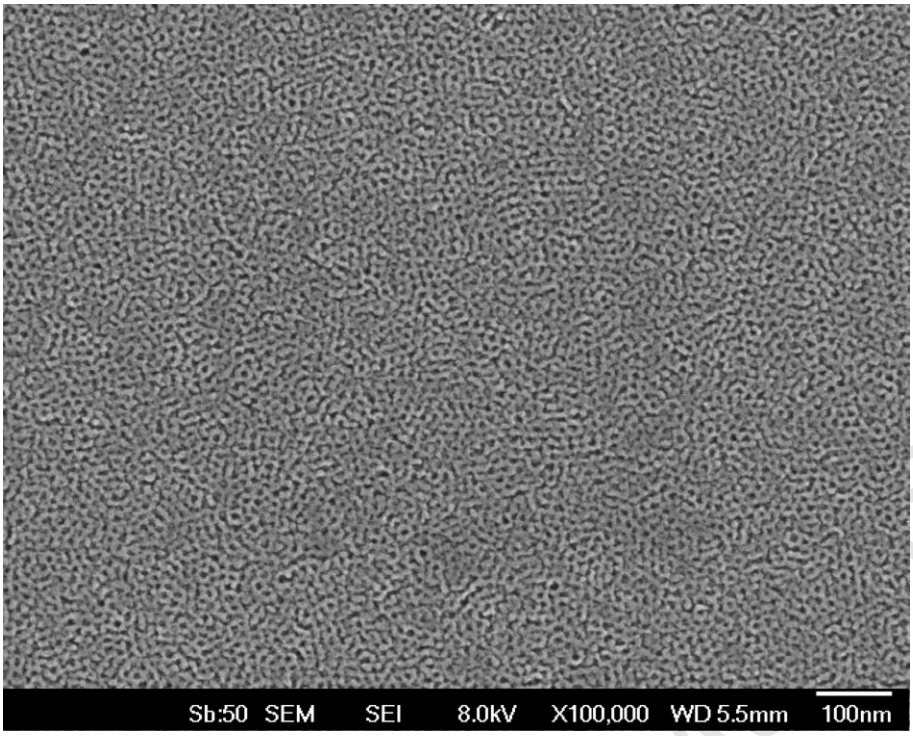

Fig 1a .

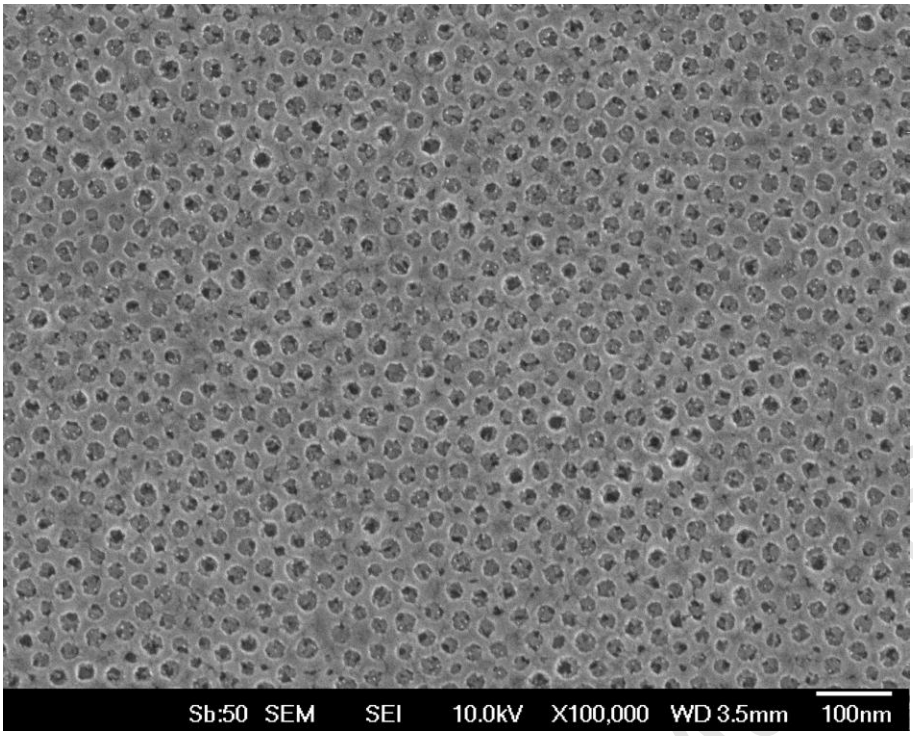

Fig 1b .

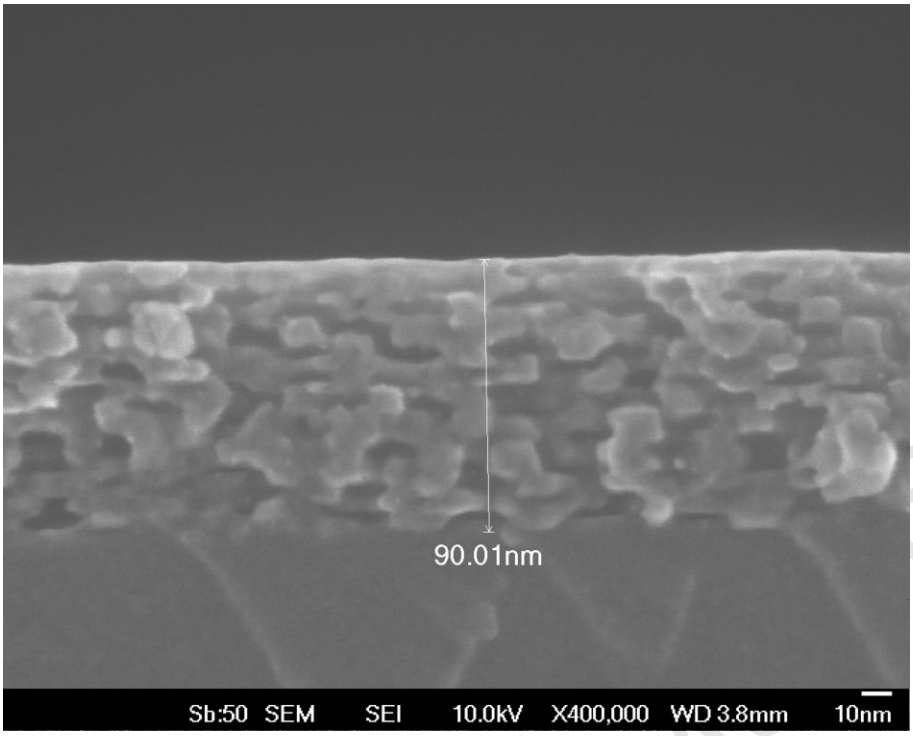

Fig 1c .

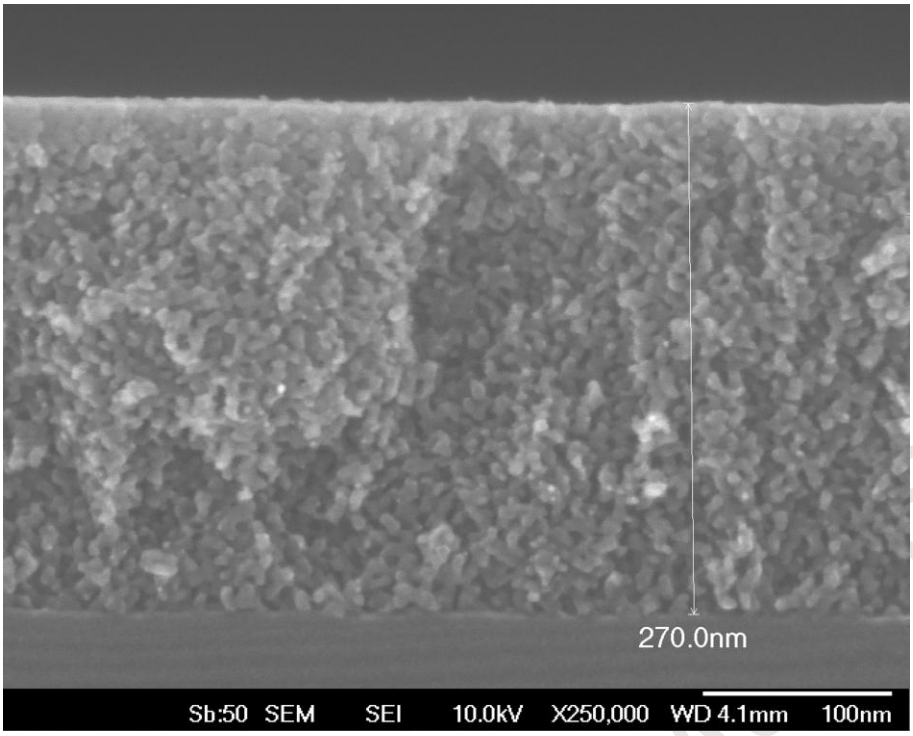

Fig 1d .

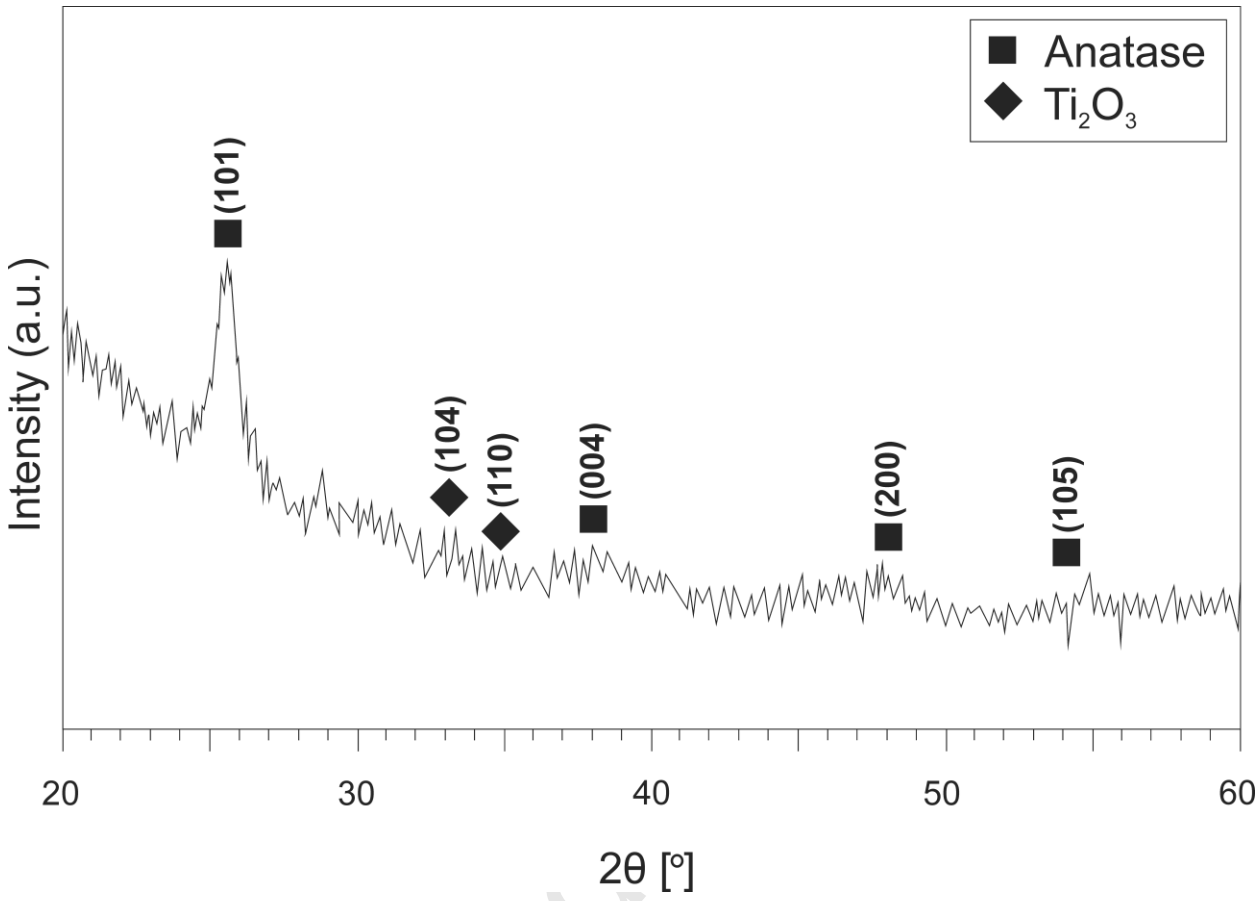

Fig 2 .

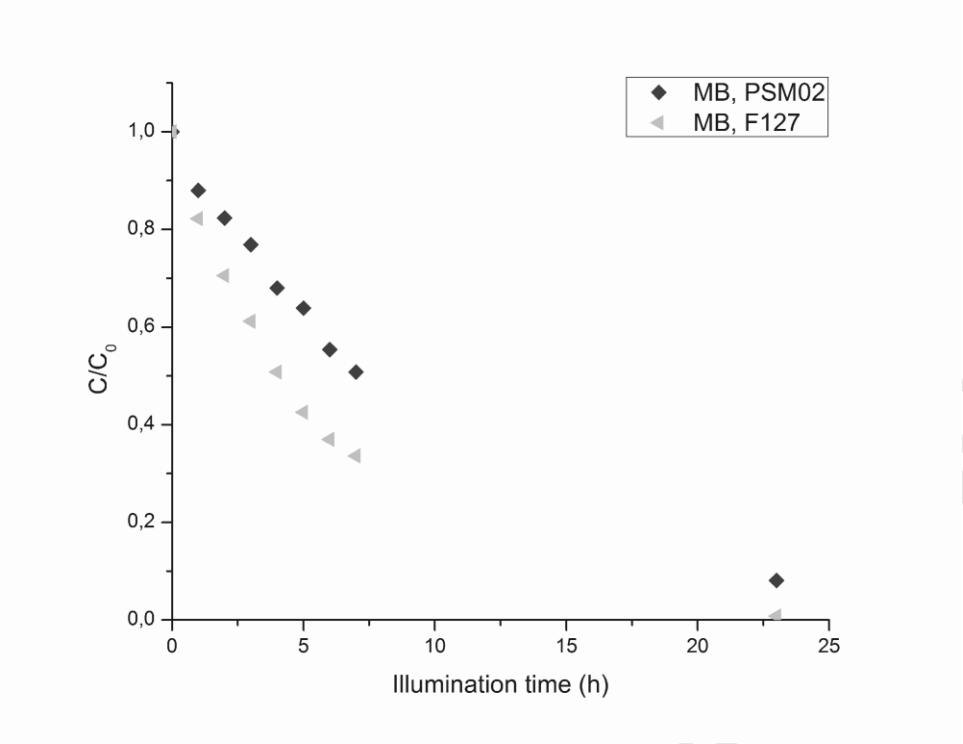

Fig 3a .

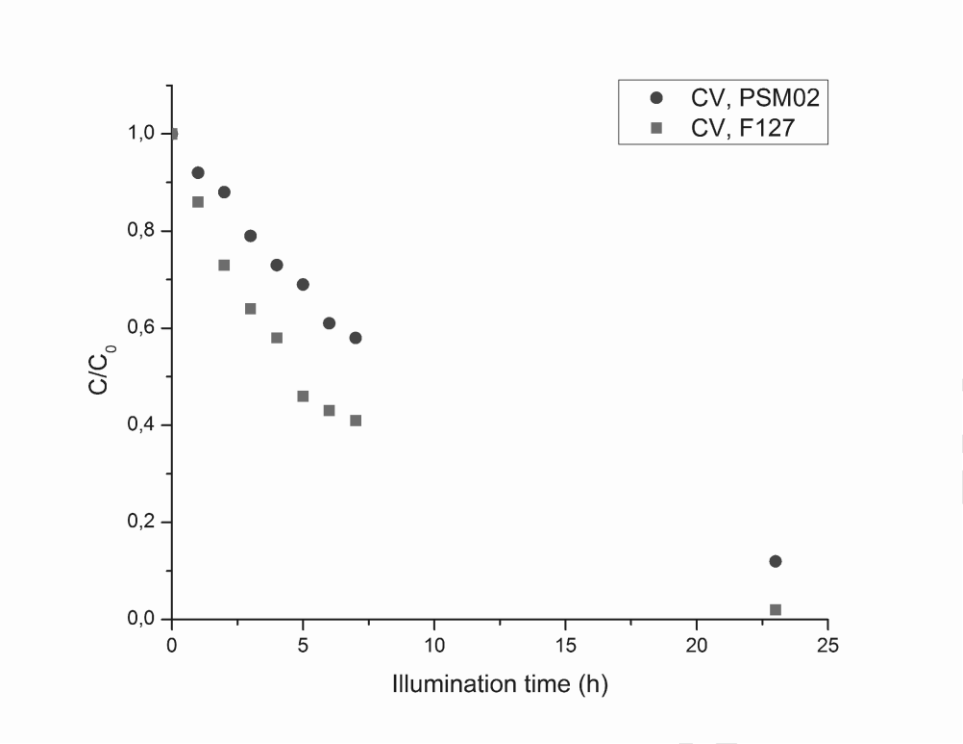

Fig 3b .

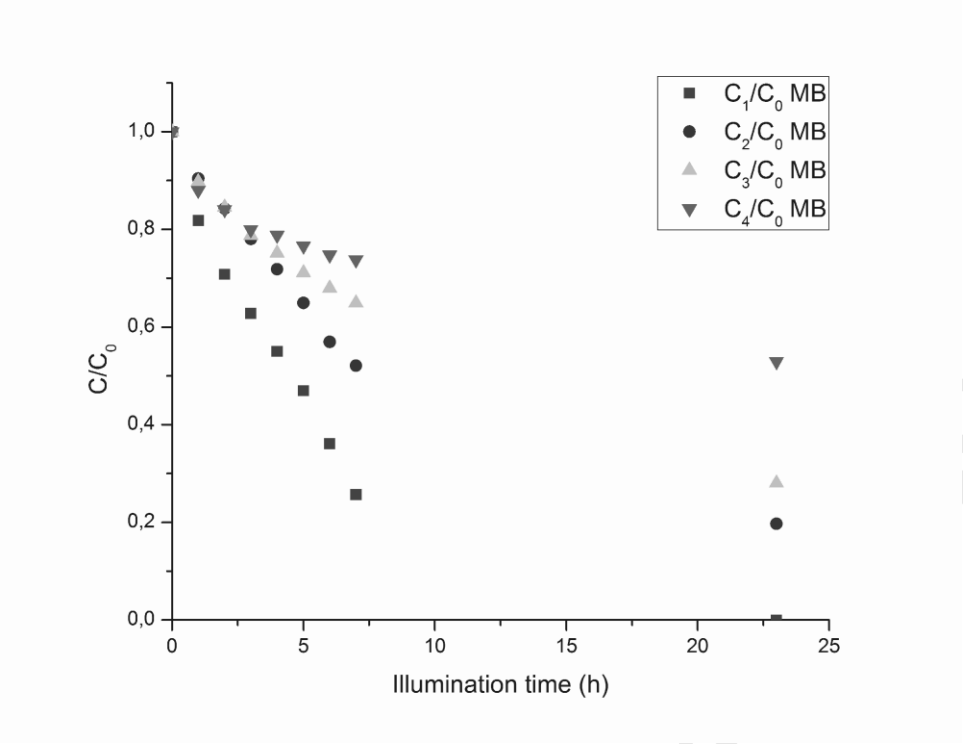

Fig 4a .

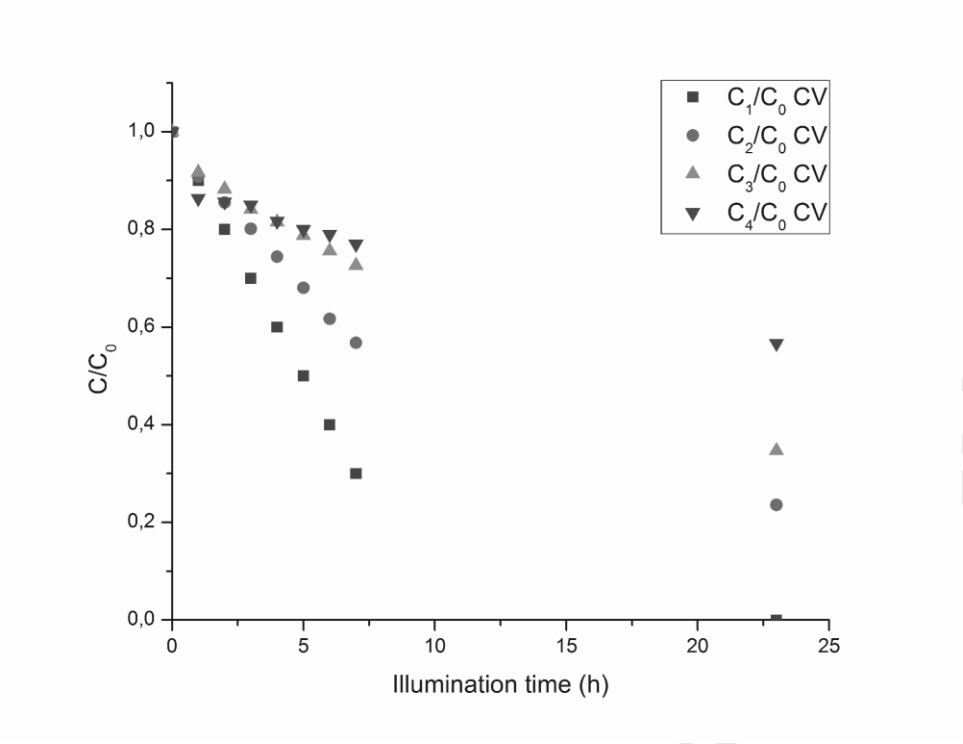

Fig 4b .

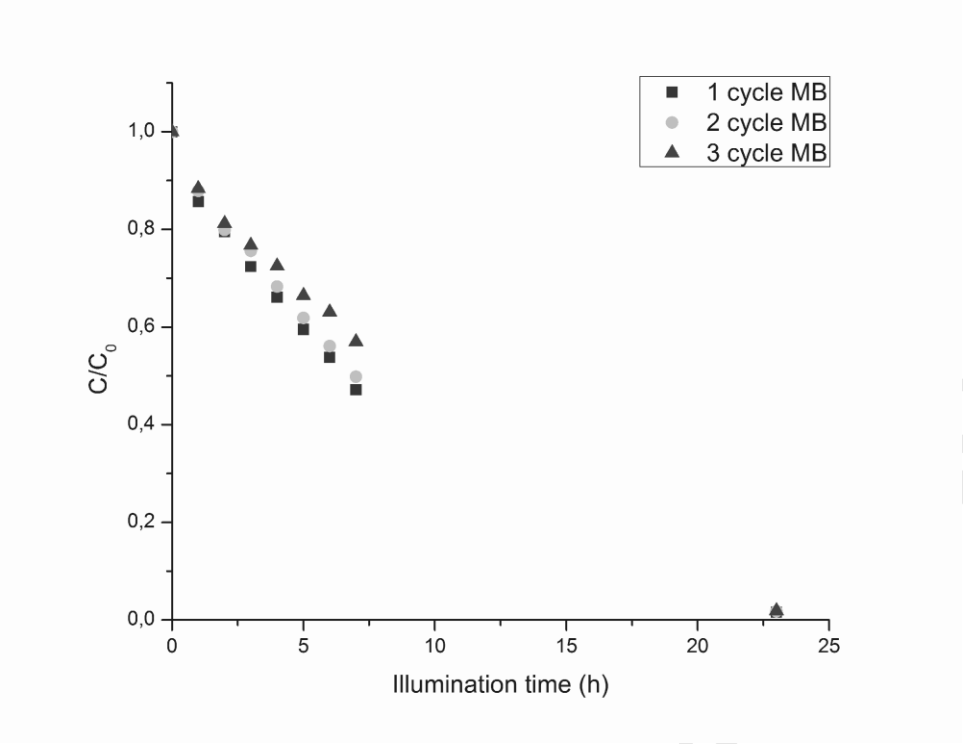

Fig 5 .