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3D-printed polyamide structures coated with TiO_2 nanoparticles, towards a 360-degree rotating photocatalytic reactor

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ABSTRACT

3D-printed polyamide structures coated with TiO_2 nanoparticles were obtained by a simple impregnation method. This novel type of 3D reactor was evaluated for its photocatalytic activity towards the degradation of methylene blue under UV light using a 360-degree rotating stage. Rotation improved the photocatalytic activity under UV light for all the 3D structures. The best photocatalytic structure showed a 94.1 % methylene blue degradation, after 180 min under UV irradiation with 360-degree rotation.

1. Introduction

Titanium dioxide (TiO_2) is still one of the most promising photocatalysts for environmental applications such as removal of organic contaminants from wastewater and polluted air [1,2] as well as other energy related applications [3,4]. TiO_2 has been widely studied and used as a photocatalyst mainly due to its chemical stability, nontoxicity as well as its low price and commercial availability as powder. In practical applications, immobilized photocatalysts are more likely to be used since they eliminate the need for filtration or replenishment. On the other hand, compared with suspended particles, supported photocatalysts have less surface area and mainly suffer from mass transfer limitations during the photocatalytic reactions.

In the early 2000 Dionysiou *et al.* developed a new concept based on the rotating disk photocatalytic reactor (RDPR) [5,6]. Rotating a drum or a disk with a photocatalytic layer has been found to enhance the photocatalytic activity towards the degradation of several pollutants in water [7]. Mixing of the solution is achieved by rotation of a disk while the photocatalytic reactions occur on the irradiated TiO_2 loaded disk surface. This technique has been further developed as batch contactors for the mineralization of a chlorinated volatile organic compound [8] or as a photoelectrocatalytic (PEC) reactor for wastewater treatment [9]. The influence of other photocatalysts such as ZnO [10] or BiOBr [11] on the rotating disk reactor has also been investigated. A semi-pilot rotating reactor with supported TiO_2/Ag catalyst has also been tested as a viable option for the treatment of organic pollutants [12].

3D printing technology has become a powerful tool to produce structures in many types of applications. In particular, catalytic and photocatalytic reactors have gained much attention in this field and are developing rapidly [13–16]. The emergence of 3D printing technology has opened the way to the preparation of new and complex structures that could enhance and open new opportunities in the field of photocatalytic reactors. In this work, we deposited TiO_2 nanoparticles on 3D printed polyamide open structures using a simple impregnation method. The photocatalytic activity towards the degradation of a common standard dye (methylene blue) was performed in static mode (sample at a fixed angle compared to incident light) but also using a simple 360-degrees rotating system to maximise the irradiation distribution within the whole surface of the reactor. To the best of our knowledge, no comprehensive work was dedicated to such an approach using a tailored 3D structure together with a rotating reactor to maximize the irradiated surface area.

2. Experimental

Three different 3D structures were printed in polyamide by selective laser sintering (SLS) [17] and further used to deposit TiO_2 nanoparticles. The samples, hereby referred to as S1, S2 and S3, are described in Table 1 below. Further 3D visualizations and pictures are found in the supplementary information.

The deposition of TiO_2 nanoparticles onto the 3D structures was performed by immerging the structures into a TiO_2 suspension similarly

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to Hajiesmaili *et al.* [18]. First, a suspension of TiO_2 nanoparticles (40 g/L, TiO_2 P25 from EVONIK) in water/ethanol (1:1) was prepared under mechanical stirring and sonication for 20 min in a sonicating bath. The polyamide structures were thoroughly cleaned with distilled water and ethanol, then immersed in the TiO_2 suspension for 2 min and dried at 60 °C for 20 min. The impregnation process was repeated 3 times. The impregnated sample was then submitted to a sonication treatment for 2 min in distilled water to remove the weakly anchored TiO_2 nanoparticles, and finally dried at 100 °C for 2 h.

Surface morphology of the samples was observed with scanning electron microscopy (SEM) using a FEI Nova NanoSEM 650 FEG-SEM microscope.

Photocatalytic testing was performed in a 150 mL quartz beaker using methylene blue (MB, 10 mg/L, 120 mL) as a model compound. The 3D sample was first left in MB in complete dark for a minimum of 30 min to ensure complete adsorption equilibrium. The rotation experiments were performed using a motorized rotating camera mount (TurnsPro), where the quartz beaker containing the photocatalytic sample was simply placed on the rotating stage and rotated at a speed of 45°/min. The sample was then perpendicularly irradiated with a xenon-mercury lamp (Oriel Newport 200 W, ozone-free) equipped with a visible light cut-off bandpass filter (between ca. 400–700 nm). The quartz beaker was placed at 4 cm from the lamp's edge and covered by a watch glass. After a certain amount of time, a MB sample was taken out of the beaker and the MB absorption curve was measured between 250 and 800 nm using a UV–vis spectrophotometer (Agilent CARY 5000). The absorption value at 665 nm was used to follow the kinetic of degradation. For comparison, all samples were also tested without any rotation movement, further described as "static".

3. Results & discussion

3.1. 3D printed samples

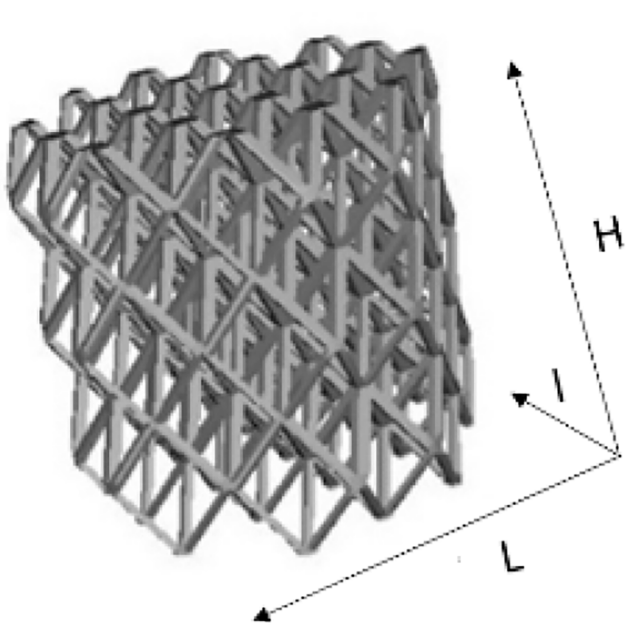
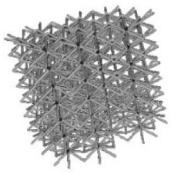
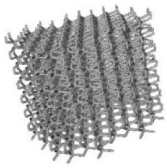
All 3D printed structures were coated with a commercial photocatalyst (TiO_2 P25 from EVONIK) by a simple impregnation-drying technique. The surface morphology of the 3D-printed and TiO_2 impregnated samples was studied by SEM. Fig. 1 shows SEM images of the 3D printed polyamide structure surface, before (1a and 1c) and after (1b and 1d) deposition of TiO_2 nanoparticles. After deposition of the nanoparticles, a rather small number of aggregates were spotted, and several cracks appeared probably due to rapid evaporation of the solvent (Fig. 1b). We could observe that the whole surface of the polyamide surface was covered with TiO_2 nanoparticles. The TiO_2 loading on the polyamide 3D structures was measured using a gravimetric method (weight before/after TiO_2 deposition) giving the following results: 2.3 wt% for S1, 5.4 wt% for S2 and 3.4 wt% for S3.

3.2. Photocatalytic activity for the degradation of MB

The photocatalytic activity of all prepared samples was evaluated by the degradation of methylene blue, a common model dye compound. The kinetic curves of degradation of methylene blue in contact with the 3D samples under UV light in static and rotating mode is presented in Fig. 2. The degradation of MB in the absence of a photocatalyst (i.e. photolysis) is insignificant and could be neglected under these experimental conditions (Fig. 2a–c, black dots). The photocatalytic activity of all prepared samples (S1, S2, S3 impregnated with TiO_2 nanoparticles) showed enhanced photocatalytic activity under rotating conditions. After 180 min under UV irradiation with 360-degree rotation, the MB degradation was 88.5 % for S1 and 94.1 % for both S2 and S3. The similar photocatalytic activity for S2 and S3 can be attributed to their structural similarity, while S1 has a much larger unit cell structure.

Reuse of the photocatalyst is an important parameter when developing future photocatalytic materials. To assess the reusability of the prepared materials, the photocatalytic structures were, after the first photocatalytic test, carefully rinsed with distilled water and dried. The photocatalytic structure was then subjected to the same photocatalytic test. Fig. 2 shows the result of 5 consecutive photocatalytic reuse tests using sample S2 as an example. Results showed a good stability of the photocatalytic structures, with a small decay of the photocatalytic activity after the 5th run, probably due to a slight loss of TiO_2

Table 1
Samples description.

Sample name	S1	S2	S3
3D structure			
description	Lattice structure	Hexagonal prism vertex centroid	Hexagonal prism diamond
L × L × H	54.3 × 54.0 × 50.4 mm^3	54.7 × 47.1 × 47.9 mm^3	50.4 × 43.9 × 44.3 mm^3

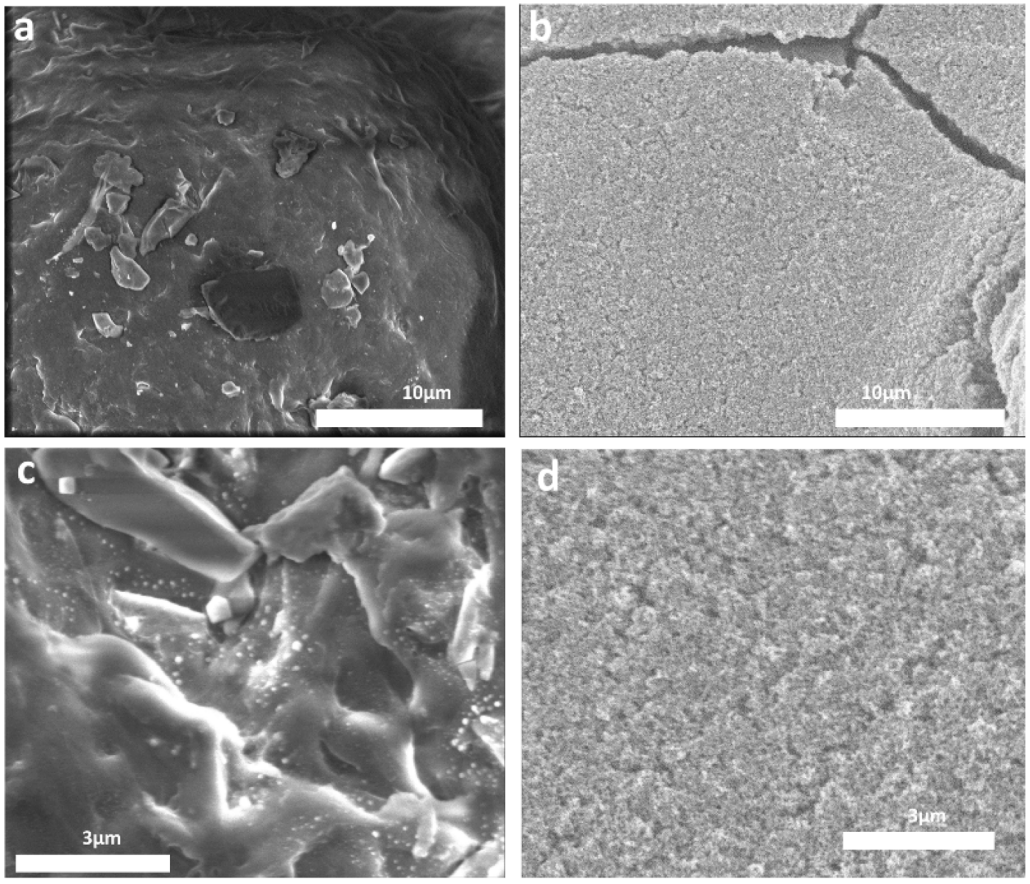


Fig. 1. SEM pictures of the surface of sample S2 at two different magnifications (a and c, scalebar 10 µm and 3 µm, respectively) and the same surface after impregnation with TiO_2 nanoparticles (b and d).

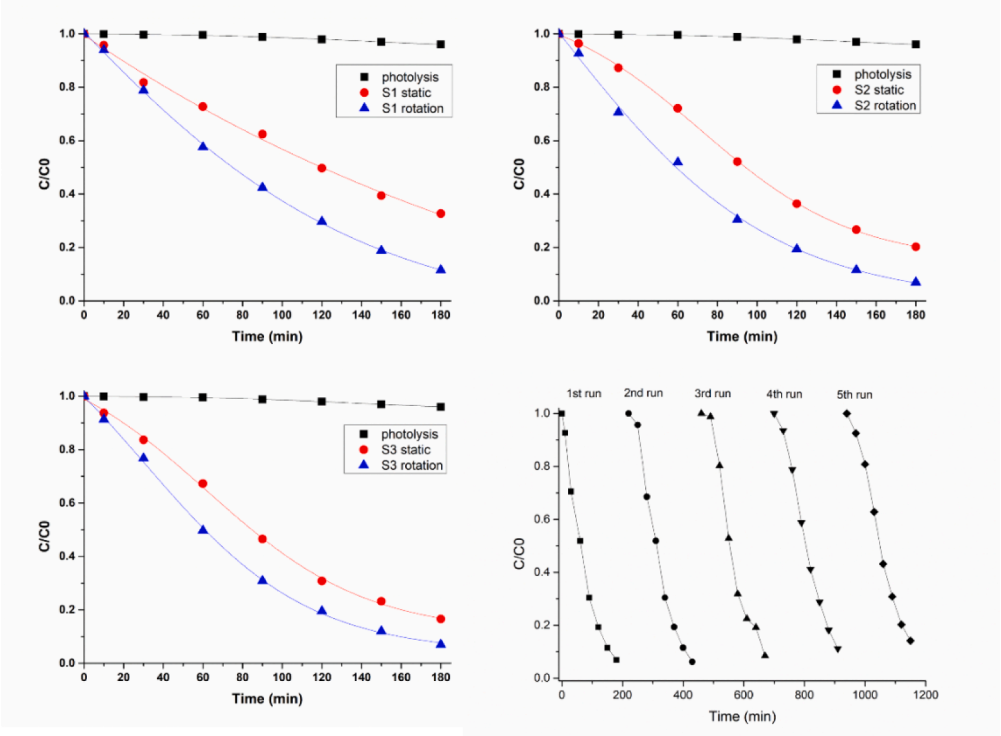


Fig. 2. Photocatalytic degradation of S1, S2 and S3 in static and rotating conditions (a, b, c). Reusability test of S2 (d).

nanoparticles during the rinsing step.

In general, the photocatalytic efficiency of a material is greatly influenced by the amount of light received on the surface of the photocatalyst. Using 3D structures, there is naturally a large proportion of the photocatalyst surface that is not irradiated at all, and therefore a loss of electron/hole pairs photogenerated under irradiation. We propose here to rotate the 3D structure to take advantage of the entire surface of the photocatalytic structures and therefore maximise the irradiation on the whole surface of the reactor. Using this simple strategy, we observed enhanced photocatalytic activity and we therefore propose a new approach for future photocatalytic reactors.

In future work it will be important to analyse further the interaction of the polyamide substrate with TiO_2 since degradation of the TiO_2/polymer interface has been reported [19], to investigate other photocatalytic materials, especially absorbing visible (solar) light as well as the rotation speed.

4. Conclusion

In summary, TiO_2 nanoparticles were deposited on 3D printed polyamide open structures by using a simple impregnation method. The TiO_2 nanoparticles were uniformly distributed on the polyamide structures, and their photocatalytic activity towards the degradation of methylene blue was tested under UV light, in static and 360-degree rotating conditions. All samples prepared in this study showed enhanced photocatalytic degradation of methylene blue in rotating mode. This new concept of 360-degrees rotating photocatalytic reactor offers a promising way for practical applications.

CRediT authorship contribution statement

Mathieu Grandcolas: Conceptualization, Methodology, Investigation, Writing – original draft, Writing – review & editing, Project administration, Funding acquisition. **Anna Lind:** Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matlet.2021.131044.

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