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# High flowrate microreactors integrating in situ grown ZnO nanowires for photocatalytic degradation

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## Abstract

A high-volume, low-pressure microfluidic photocatalytic microreactor was created and demonstrated here. This high-flowrate microreactor, based on an innovative design developed by the start-up Eden Tech, was produced by a simple thermal pressing process, using Eden Tech's easy-to-use and environment-friendly thermoplastic polymer, Flexdym™. ZnO nanowires (ZnO NWs) were then synthesized *in situ*, using an environment-friendly, low-cost, two-step hydrothermal method. Varying the synthesis parameters (growth solution flowrate, time and temperature) allowed us to get an insight of the optimal synthesis conditions for photocatalytic purposes. The *in situ* grown nanowire morphology was characterized under Scanning Electron Microscopy (SEM). The photocatalytic efficiency of the as-synthesized microreactors was tested by degrading continuous streams of water polluted with Acid Red 14 (AR14), a commonly used organic dye, under UV irradiation, followed by UV-visible spectrometry. We found that the best results are obtained with the following synthesis parameters: a 1h growth time, a growth flowrate of 200 μL/min and a temperature of 80°C, as after 4 passes in the reactor, which is roughly equivalent to 40 seconds of UV light irradiation, the dye was degraded at 98%. Increasing the photocatalysis flowrate from 200 μL/min to 500 μL/min showed a small decrease in efficiency, but is still encouraging in the aim of high-flowrate degradation.

## Introduction

Due to the combined effects of growing human population, climate change and increasing industrial consumption, the pressure on water resources is steadily rising and is a hugely pressing issue. To ensure the sustainability of Humanity's water supplies, it is necessary to find efficient, low-cost and environmentally friendly ways to purify urban and industrial wastewater effluents.

One of the most studied solution for water purification is the photocatalytic process [1,2], a sustainable degradation process using a photocatalyst such as ZnO or TiO<sub>2</sub>. This process presents the advantage of using a renewable and abundant energy source: the sunlight. It also leads to the mineralization of the pollutants, preventing the risk of leaking harmful

chemicals into the environment [3]. Finally, as it is a catalytic process, the product needed to perform the depollution can easily be retrieved and reused. ZnO and TiO<sub>2</sub> are large-band-gap metallic oxides with similar photocatalytic properties [4,5], and TiO<sub>2</sub> has already been widely studied [6,7]. However, ZnO presents the advantages of being a low-cost photocatalyst, whose raw materials are abundant in nature [1]. It is even supposed to be a better photocatalyst than TiO<sub>2</sub> under visible light [4,8], and is also non-toxic and biocompatible [1,2,9,10]. Thus, in the aim of creating an environmentally friendly and efficient photocatalytic reactor, ZnO seems to be a better choice, which is why it is our photocatalyst of choice.

To increase the contact between the photocatalyst and the molecules to be degraded, nanostructures are often used, such as nanoparticles, nanorods or nanowires. Those nanostructures present high surface-to-volume ratios, which increases the contact opportunities between the material and the molecules to be degraded, and so, the photocatalytic efficiency of the samples [11].

Nanostructured photocatalysts can be used by direct dispersion into water, like a powder [12-14]. However, once the purification is done, the separation of the photocatalytic particles from the water is far from easy and often requires further filtration of the effluents, adding significant time and energy costs, both financial and environmental, reducing the effective yield of depolluted water, and making the scale-up from laboratory scale difficult [15]. Furthermore, considering the reduced size of the nanoparticles, leakage into the environment is difficult to avoid, with uncertain consequences [16].

To prevent these risks and the filtering step, the nanostructures can be immobilized on a substrate [15, 17, 18]. This, however, tends to reduce the general photocatalytic efficiency [15] due to the unfavourable surface-to-volume ratio: a large volume of water is in contact with a relatively small photocatalytic surface. On the other hand, in addition to the reduced leakage risks and the possibility to easily reuse the photocatalyst, this allows to create reactors using the ZnO nanostructures in order to try to purify bigger quantities of water. For example, several designs of photocatalytic macroreactors have already been studied [19-20].

Performing photocatalysis with immobilized nanostructures at high-efficiency is achievable by incorporating them into microreactors, as previously done by several synthesis methods, such as chemical bath deposition [21], sol-gel [22], electrospinning [23], and hydrothermal growth [24-27].

Microreactors have several very interesting properties for photocatalytic water depollution [21,22,28,29]: the reduced size of the microchannels increases the contact between the pollutant and the photocatalyst, while reducing the absorption of light irradiation by the liquid. This is especially important in the degradation of coloured pollutants. The continuous stream and small size of the microchannels also create a situation where mass transfer is no longer limiting the kinetic of the reaction, improving the reaction rate. All of these advantages imply that the reaction kinetic of the degradation is quicker in microreactors than in bigger reactors.

A major reported limitation of microreactors is the very small liquid quantities that can be treated within microchannels (often in the range of less than 1 mL/min [30]), and the high pressure required to achieve high-flowrate, making the solution costly for large treatment volumes. However, it is possible to circumvent the flowrate problem by plugging microreactors to one another in chain. Sadly, this means the pressure needed to ensure the flow of liquid will be even higher [28, 31].

The start-up Eden Tech has developed a new design of microreactor [32], in which the pressure needed to make the liquid flow inside of the reactor is minimal, allowing high flowrate without large pressure needs. This microreactor is more suitable for water purification applications which need to treat large water quantities.

We used a low-cost and environmentally friendly hydrothermal method to synthesize ZnO NWs into a microreactor composed of a Si-wafer substrate and a Flexdym™ chip, on which microchannels had been patterned by a simple thermal process. Flexdym™ is a thermoplastic polymer, developed and produced by Eden Tech, which presents very interesting properties for its use in microfluidics for the environment, such as biocompatibility, optical transparency, stable surface chemistry, low water evaporation and ease of use [33]. It has also been proven that Flexdym™ is ideally suited for the use in tough conditions [34] and does not require a clean room for its use.

The parameters of the synthesis have been investigated in order to find the optimal synthesis conditions for the photocatalytic efficiency. The microstructure of the synthesized NWs were characterized by SEM observation and their photocatalytic efficiency was studied by degrading a continuous stream of AR14-polluted water, an organic dye often found in urban, pharmaceutical and agro-food industry effluents, under UV-irradiation, followed by UV-visible spectrometry.

## **Experimental**

### ***Materials and Methods***

The reactor is composed of two different kinds of microchannels. Long microchannels, which weave from the inlet to the outlet, with a length of 575.92 mm and a height of 100  $\mu\text{m}$ , ensure the sustainability of the high flowrate. Short microchannels, with a length of 0.85 mm and a height of 10  $\mu\text{m}$ , connect the long microchannels to each other, decreasing the pressure needed to pump liquids into the reactor, as well as allowing a better contact between the pollutants and the NWs, improving the photocatalytic efficiency. The total volume of the microreactor is of 0.2 mL. The design has a circular shape, to fit 4 inches wafers, ease the stacking and allow all the outlets to be at the same distance of the inlets. During preliminary experiments, our reactor proved to be able to sustain pressures up to 1500 mbar. As we used a syringe pump in our experimental set-ups, the pressure at the inlets of the reactor could not be measured. However, as the 1500 mbar pressure lead to a

flowrate of 6.1 mL/min, we are confident in the ability of our reactors to sustain flowrates even higher than the ones presented here.

This design was printed on 2 mm thick Flexdym™ chips by vacuum thermal pressing (Sublym100™, Eden Microfluidics, France) using an epoxy mold imprinted with the negative design. First, the polymer sheet and the mold were pre-heated at the pressing temperature, 165°C, in the Sublym100™ press for 10 minutes. Then, vacuum was applied for 760 seconds, still at 165°C, before release. The molded Flexdym™ sheet was unfolded from the mold and stored between two Teflon sheets for later use.

The hydrothermal synthesis was performed following a method adapted from our previous works [Erreur ! Source du renvoi introuvable.]: first, 4-inch circular Si wafers were spin-coated ( $200 \mu\text{L}/\text{cm}^2$ ) with a precursor solution composed of 10g of poly-vinyl-alcohol (PVA) and 1g of Zinc Acetate dissolved into 100 mL of deionized (DI) water ( $R = 18.2 \text{ M}\Omega$ ). The substrates were then calcined at 500°C during 3 hours, to remove the PVA. After the calcination, the Flexdym™ chip was bound into the substrate for 4 hours at 120°C in an oven, without external pressure. The obtained non-functionalized reactor is illustrated in **Figure 1(a)**.

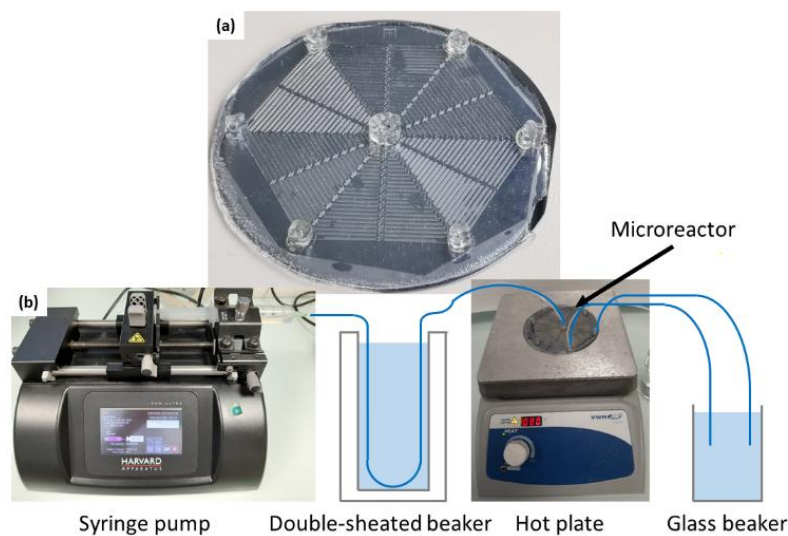


Fig. 1. Non-functionalized reactor (a) and *in situ* ZnO NWs growth set-up (b).

The *in situ* ZnO nanowire growth inside the microreactor uses the same ZnO nanowire growth solution as the one for classical samples mentioned in our previous work, made by mixing equal quantities of a 0,075 mol/L  $\text{Zn}(\text{NO}_3)_2$  solution and a 0,0375 mol/L Hexamethylenetetramine (HMTA) solution [Erreur ! Source du renvoi introuvable.].

The resulting growth solution was heated at the desired temperature (80°C, 85°C or 90°C) using a thermostated bath and injected into the microreactor with a syringe pump, at a constant flow rate (from 100 to 400 µL/min) for the desired growth time (30 min to 1h30). During the circulation of the growth solution, the microreactor was placed on a heating plate to ensure a constant temperature throughout the process. The experimental set-up is displayed in **Figure 1(b)**. As Flexdym™ cannot sustain the high temperatures of the post-annealing (350°C) we usually perform, this step was not performed in these experiments. This could lead to a small decrease in efficiency, but the biggest effect of the impossibility to anneal the samples after each experiment will more likely be a decrease in efficiency for subsequent experiments.

The obtained NWs were characterized by SEM observation, by taking apart the microreactor and imaging the NWs directly. The photocatalytic experiments were conducted by degrading a solution containing 10 µmol/L of AR14, pumped into the microreactor at a constant flow rate of 200 µL/min with a syringe pump, under UV irradiation. The surface of the tested microreactors was maintained at 10 cm of the UV lamp (Hamamatsu LC8, Japan) corresponding to an UV intensity of 35 mW/cm<sup>2</sup>. The photodegradation of the studied dye was monitored using UV-visible spectrometry (Perkin-Elmer, Lambda 35). Every time, the syringe was rinsed with DI water, and the solution was pumped back into it to resume the experiment.

## **Results and discussion**

The photocatalytic properties of our samples are given below. Each graphic shows the degradation rate versus the number of passes made for each reactor. Each pass represents 25 minutes of injection at 200 µL/min. Considering the volume of our microchannels and the flowrate, the residence time of the liquid is of 10 seconds under the UV light, meaning that 4 passes are roughly equivalent to 40 seconds of photocatalytic process in the reactor.

### **Study of flowrate on ZnO NWs growth**

Flowrate is critical to the proper growth of the NWs. A flowrate too slow can prevent the full filling of the microchannels, whereas a too fast flowrate reduces the contact with the seed layer and prevents the growth of the NWs, as the precursor molecules cannot diffuse to the wall (seed layer). The ratio between convection and diffusion is represented by the Péclet number, calculated according to the following equation [Erreur ! Source du renvoi introuvable.]:

$$Pe = H^2 \cdot v \cdot D^{-1} \cdot L^{-1}$$

Where H stands for the height of the microchannels, v stands for the velocity of the liquid in the microchannels, L stands for the length of the microchannels, and D

stands for the diffusion coefficient of the molecules. A Péclet number higher than 1 means that the diffusion time of the molecules in the liquid is slower than their advection time, thus that all the molecules don't have the time to reach the bottom of the microchannels before exiting the reactor. In our case, this could lead to a waste of precursors, as they might just pass through the reactor and not be consumed by the growth reaction. Furthermore, a too high pressure, induced by a too high flowrate, could lead to a leakage of the chip, damaging the reactor.

To ensure the integrity of the reactor and improve the chances of contact between the suspended precursor molecules and the seed-layer, the chosen flowrates were fixed at values between 100  $\mu\text{L}/\text{min}$  and 400  $\mu\text{L}/\text{min}$ , leading to Péclet numbers between 0.55 and 2.21.

The ZnO NWs were grown for 1 hour at the temperature of 80°C. Those parameters were chosen to ensure that the NWs were long enough to perform the photocatalytic degradation of the AR14, and reduce the risk of precipitation or evaporation. The effect of the flow velocity of the precursor solution on photocatalytic efficiency are shown in **Figure 2**.

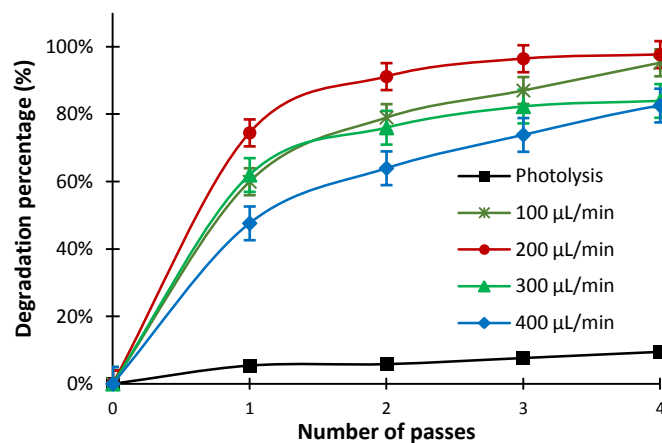


Fig. 2. Impact of the ZnO NW growth solution flowrate on the photocatalytic efficiency.

As can be seen, the best results were obtained for NWs grown at a flowrate of 200  $\mu\text{L}/\text{min}$ . This means the Péclet number is of 1.1, and so, that the diffusion transfer is almost equal to the advection transfer.

The obtained nanostructures were then characterized by SEM observation, as seen in **Figure 3**.

As shown in the SEM images, we obtained a homogenous NWs layer on our samples surface at 100 and 200  $\mu\text{L}/\text{min}$ , but at higher flowrates, the NWs seem to agglomerate and cover less surface.

The difference in efficiency between the 100  $\mu\text{L}/\text{min}$  and the 200  $\mu\text{L}/\text{min}$  samples is due to the characteristics of the NWs layer: as it is visible on the SEM image, the surface of the 100  $\mu\text{L}/\text{min}$  sample is not totally covered by NWs, whereas the surface of the 200  $\mu\text{L}/\text{min}$  sample is fully covered. Furthermore, the mean diameter of the NWs varies from  $41 \pm 5$  nm for the 100  $\mu\text{L}/\text{min}$  one to  $58 \pm 5$  nm for the 200  $\mu\text{L}/\text{min}$ , meaning their surface area is lower than the surface area of the 200  $\mu\text{L}/\text{min}$  sample. The smaller density and mean diameter of the NWs in the 100  $\mu\text{L}/\text{min}$  samples advocate for a smaller reaction rate of the NWs growth. This is because, at 100  $\mu\text{L}/\text{min}$ , the smaller velocity of the flow equals a lower regeneration rate of the precursors, leading to a reduced reaction rate. The surface coverage and the density increase of the NWs explain the difference in efficiency between the two samples.

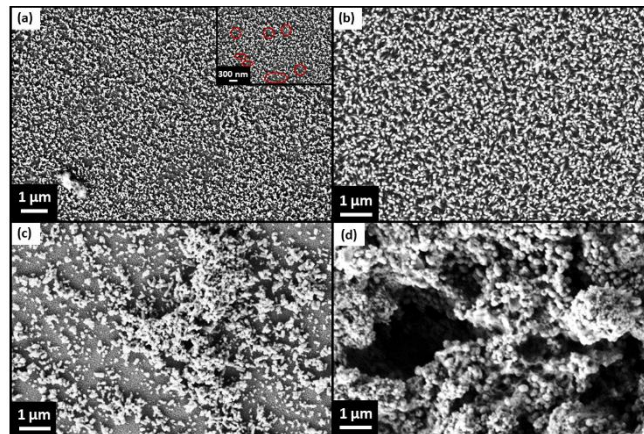


Fig. 3. SEM images of the synthesized nanostructures at the different flowrates: (a) 100  $\mu\text{L}/\text{min}$  (b) 200  $\mu\text{L}/\text{min}$ , (c) 300  $\mu\text{L}/\text{min}$ , (d) 400  $\mu\text{L}/\text{min}$ . For the 100  $\mu\text{L}/\text{min}$ , some zones devoid of NWs are highlighted in red.

When the flowrate increases, the increase of the Péclet number indicates that the relation between the advection time and the diffusion time reverses. As the velocity of the flow increases, the size of the depletion layer, defined as the layer in the flow of growth solution right above the bottom of the microchannels, where there is no precursor, as it is consumed by the growth reaction, decreases. This leads to an increase in available precursors near the bottom of the microchannels, promoting the growth and agglomeration of the ZnO nanowires in clusters. This explains the loss in photocatalytic efficiency: as the nanostructures tend to agglomerate on big clusters, the catalyst surface available for the photocatalysis decreases due to the screen effect, and such, the photocatalysis efficiency.

### **Study of growth time on ZnO NWs growth**

The second synthesis parameter we studied is the growth time. A too short growth time would lead to an incomplete NWs growth, resulting in a lack of surface area, and such, a reduced efficiency. However, a too long growth time could lead to NWs with an excessive length that may block the microchannels.

Reactions are supposed to occur faster in microfluidic reactors compared to their batch counterparts [Erreur ! Source du renvoi introuvable.]. It has already been demonstrated that reduced reaction times lead to ZnO NWs with lengths equals or even greater than ZnO NWs grown in batch conditions [Erreur ! Source du renvoi introuvable., Erreur ! Source du renvoi introuvable.]. Furthermore, the synthesis of 2- $\mu\text{m}$ -long ZnO NWs in few minutes by using a continuous flowrate in capillary tubes has been reported [Erreur ! Source du renvoi introuvable.]. Thus, we decided to investigate the reduction of the growth time, by using timeframes ranging from 30 minutes to 1h30.

We selected a temperature of 80°C and a flowrate at 200  $\mu\text{L}/\text{min}$ , conditions which previously demonstrated the highest photocatalytic efficiency. The effects of growth time on photocatalytic efficiency are shown in **Figure 4**.

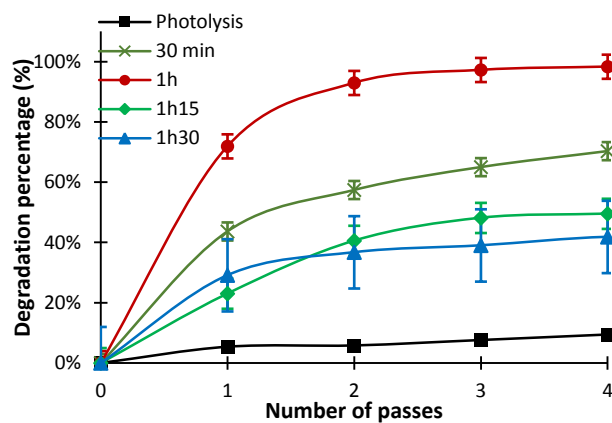


Fig. 4 Impact of the ZnO NW growth time on the photocatalytic efficiency.

The **Figure 4** indicates that the best photocatalytic performance of as fabricated microreactor was obtained for a growth time of 1h. The SEM images of the different NWs layers are presented in **Figure 5**.

The SEM images give us access to the factors affecting the efficiency of our samples, which are summarized in **Table 1**.

Those two parameters help to understand the differences in efficiency measured between the samples. Starting with the mean density, more NWs means more contact area, and should lead to an improved photocatalytic efficiency. However, when the density reaches a certain threshold, the NWs start to cover each other, preventing the liquid and the light from reaching the nanostructures. This diminishes the NWs area available for the photocatalytic reaction, and so reduces the photocatalytic efficiency.

As for the diameter, a larger diameter results in an increase of the surface area available for the photocatalysis, thus a higher efficiency. However, the mean

diameters have to be linked with the density to have an overall picture of the efficiency of the samples. The decrease in the mean diameter we can see for growth times higher than 1h is due to the apparition of very thin NWs (with diameters around 20 nm) between bigger NWs, which diameters are closer to the one measured for the 1h sample. Those small NWs crowd the sample even more, leading to the coverage we discussed earlier.

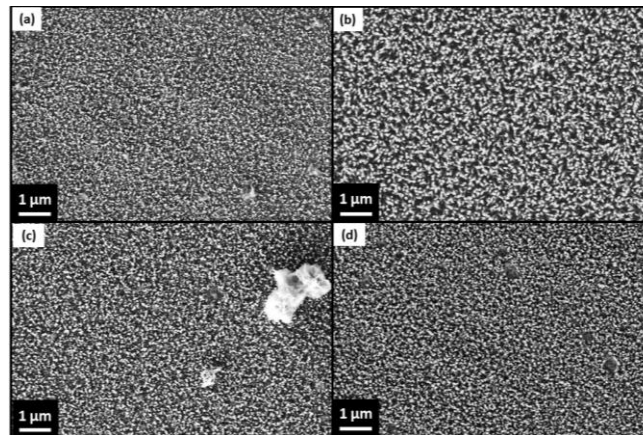


Fig. 5. SEM images of the synthesized NWs with different growth time: 30 min (a), 1h (b), 1h15 (c), and 1h30 (d).

We can also see that the mean diameter of the NWs increases to a maximum with a growth time of 1h, then decreases after 1h, due to the apparition of smaller NWs. This means that the NWs of the 30 min sample have a smaller diameter than the other, and thus, their surface area is smaller than the one of the NWs of the other sample; further explaining their lack of efficiency.

Finally, even if performing cross-sections on our samples is difficult, we managed to evaluate the length of the nanowires synthesized in the optimal conditions by observing a damaged reactor with SEM, and comparing the obtained results with theoretical results obtained from an UV-vis analysis [Erreur ! Source du renvoi introuvable.]. The theoretical length of the ZnO NWs is  $650 \pm 65$  nm, while the estimated length is  $710 \pm 50$  nm. This size is inferior to the one we obtain with our usual method, but this could be explained by the fact that the *in situ* growth was performed only for 1h, whereas the classic growth has a duration of 4h.

#### **Study of temperature on ZnO NWs growth**

Finally, the last parameter we studied was the growth temperature. This temperature should not be too low, to ensure the NWs growth is taking place [Erreur ! Source du renvoi introuvable.]. However, if it is too high, the growth solution might precipitate into the Teflon tube, or start to evaporate, creating gas bubbles into the

microchannels and blocking them in both cases. Thus, the selected growth temperatures were 80°C, 85°C and 90°C.

Growth time	Mean NWs density (NWs/ $\mu\text{m}^2$ )	Mean diameter ( $\mu\text{m}$ )
30 minutes	$74 \pm 5$	$39 \pm 5$
1h	$64 \pm 5$	$58 \pm 5$
1h15	$80 \pm 5$	$45 \pm 5$
1h30	$83 \pm 5$	$41 \pm 5$

Table 1. Morphological characteristics of the NWs according to their growth time.

The flowrate is still fixed at 200  $\mu\text{L}/\text{min}$ , and the growth time at 1h, according to the previous studies. The results of the influence of the growth temperature on the photocatalytic efficiency are presented in **Figure 6**.

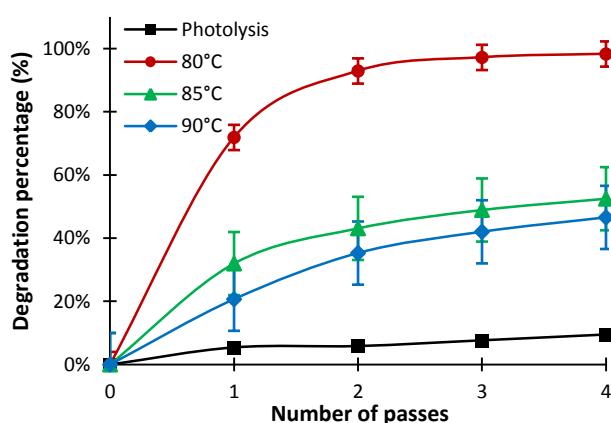


Fig. 6. Impact of the growth temperature on the photocatalytic efficiency.

The influence of the temperature is important and interesting. As the growth solution can precipitate in the Teflon tube, it can also precipitate in the microchannels, thus creating blockage in some microchannels, and even engulfing NWs, preventing the dye molecules to reach them, leading to a reduced photocatalytic efficiency. Considering the small quantities of liquid involved, it is also possible that a part of the liquid started to evaporate at higher growth temperature, creating air bubbles into the reactor, and such, areas where the NWs growth does not take place, further reducing the photocatalytic efficiency.

The nanostructures obtained via the synthesis at different temperatures have also been observed under SEM. The images are given in **Figure 7**.

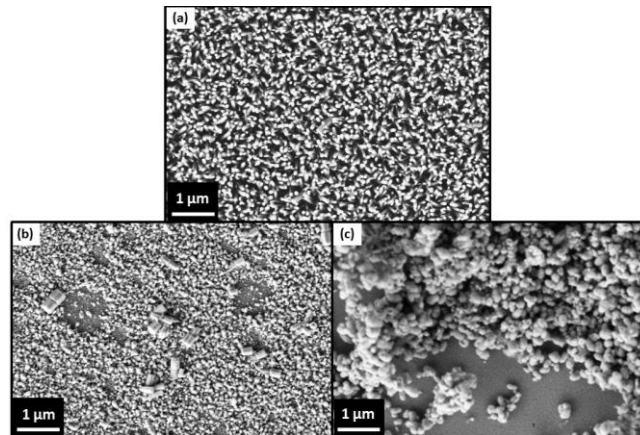


Fig. 7. SEM images of the synthesized nanostructures at different temperatures: a) 80°C, b) 85°C and c) 90°C.

The SEM images show drastic changes in the morphologies of the nanostructures with the augmentation of the temperature: increasing the temperature from 80°C to 85°C leads to the apparition of empty spaces in the NWs layer and the formation of larger structures, similar to nanorods. The NWs are also smaller than the ones synthesized at 80°C.

When increasing the temperature further, from 85°C to 90°C, we obtained nanostructures that are similar to agglomerates of nanorods, while the NWs layer seems to have disappeared. There are still some empty spaces in the nanostructure layer, and those are bigger than the ones obtained at 85°C.

Those observations are in accordance with the hypothesis that the increase of the temperature of the solution leads to the apparition of air bubbles inside of the liquid flow. Those air bubbles then stop the growth of the NWs, by preventing the growth solution to bring reagents in contact with the seeds. As the temperature of the growth solution increases, the solubility of the dissolved gases decreases, leading to the apparition of gas bubbles. Considering the growth solution is heated before entering the reactor, and as the reactor design is conceived to allow an efficient evacuation of the air bubbles that could be formed insides the microchannels, the air bubbles should be evacuated before they have an effect on the growth. However, during the reaction pathway for the ZnO NWs growth, there is formation of  $\text{NH}_3$ . Thus, the observed gas bubbles could be  $\text{NH}_3$  bubbles. As the solubility of  $\text{NH}_3$  decreases when the temperature increases, the as-formed bubbles size increases, thus leading to the holes in the NWs layer.

The bigger nanostructures and their agglomeration are most likely due to the increase in the liquid agitation with the increase in temperature, as well as the surface effects of the bubbles inside of the liquid. Those two effects lead to a strong difference between areas were the liquid is concentrated, thus more available for nanostructure growth, and zones where there is no liquid, and so, no growth. The creation of those

aggregates leads to a diminution of the available surface area for the photocatalysis, thus reducing the photocatalytic efficiency.

### **Photocatalysis at high flowrates**

The previous results have allowed us to determine the best synthesis conditions to have the best performing reactors. However, the photocatalysis flowrate have been maintained at 200  $\mu\text{L}/\text{min}$ , which is still a low flowrate, as our final goal is to overcome the usual flowrate one can expect from microreactors. Thus, we conducted further photocatalytic experiments where the polluted solution flowrate was increased from 200  $\mu\text{L}/\text{min}$  to 500  $\mu\text{L}/\text{min}$ . The growth conditions in the reactor were the optimized conditions we established in the previous paragraphs.

The results of those photocatalytic experiments are presented in **Figure 8**. As we can see, the degradation rate we obtained is lower than the one obtained at the smaller flowrate, but stays very good, at around 87% of the pollutant degraded in 5 passes, which is roughly equivalent to 20 seconds under the UV light. This is the same time as 2 passes for the previous flowrate, which gave a degradation rate of 93%, meaning the photocatalysis is less efficient at higher flowrates, but the loss in efficiency is still minimal. This can be explained by the fact that, as the pollutant spends less time in the reactor, it stays under the UV irradiation for a shorter time, and so the photocatalysis degrades a smaller quantity of pollutant, leading to a smaller efficiency.

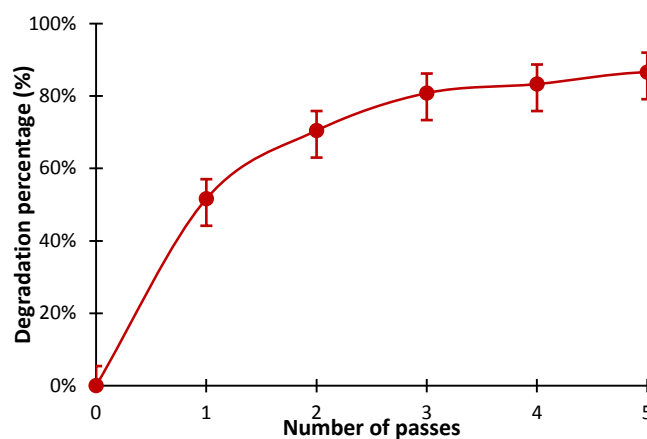


Fig. 8. Photodegradation of AR14 at a flowrate of 500  $\mu\text{L}/\text{min}$  by the optimized reactor, synthesized at 200  $\mu\text{L}/\text{min}$  and 80°C for 1h.

Those results, however, stay very encouraging, as they prove that increasing the flowrate does not lead to a drastic decrease of efficiency, meaning that our reactor should be able to ensure the photocatalytic degradation of pollutants at even higher flowrates.

### Influence of the microchannels dimensions on the nanowires characteristics

The reactor design we used is divided in two kinds of microchannels: long microchannels, which ensure the reactor is able to handle high flowrates, and short microchannels, which ensure the good distribution of the liquid inside the microreactor. Besides the length difference, the different microchannels also present a height difference: the long microchannels are 100  $\mu\text{m}$  high, whereas the short ones are 10  $\mu\text{m}$  high. Thus, we observed the NWs separately, depending on their localization into the microreactor. The SEM image of a connection between a long and a short microchannel is presented in **Figure 9(a)**.

As the image shows, there is a very clearly defined separation between the different microchannels. The entrance of the short microchannel shows an accumulation of nanostructures, which progressively disappears, as shown in **Figure 9(b)**, giving the way to an homogenous layer of NWs.

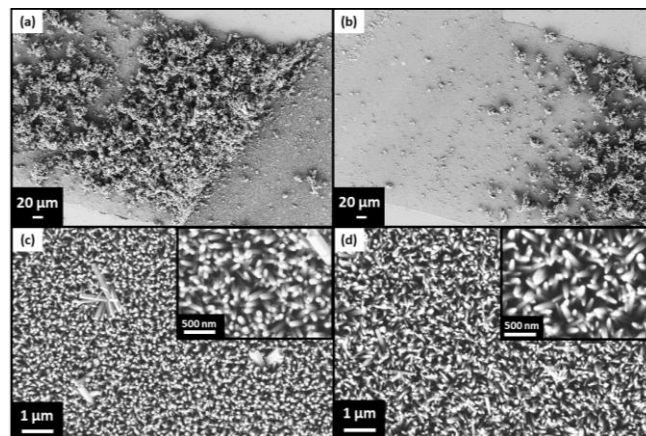


Fig. 9 SEM Images of the nanostructures grown (a) at the junction between the short and long microchannels (b) at the other end of the short microchannel and zoom on the NWs grown into the short (c) and long (d) microchannels.

This accumulation is attributed to the recirculation of the precursor solution at the entrance of the microchannel, caused by the height difference between the short and the long microchannels.

To check if the different flowing conditions had an effect on the NWs morphology, we studied their morphological characteristics and their visible aspect according to their location. The measured characteristics are summarized in **Table 2**, and the SEM images from which those characteristics were obtained are shown on **Figure 9(c) and 9(d)**.

Table 2. Morphological characteristics of the NWs grown into the short and long microchannels.

Microchannel type	Mean NWs density (NWs/ $\mu\text{m}^2$ )	Mean diameter ( $\mu\text{m}$ )
Long microchannels	$64 \pm 5$	$58 \pm 5$
Short microchannels	$61 \pm 5$	$63 \pm 5$

**Table 2** shows that the morphologies of the NWs are very similar, even when their growth occurred in the different kinds of microchannels. **Figure 9(c) and 9(d)** reveal that even if the NWs have nearly identical morphologies, the ones synthesized in the short microchannels present a flat top, whereas the ones synthesized in the long microchannels possess a sharp top. The growth kinetics of the ZnO NWs have already been studied and tends to show that the NWs will first follow a very fast growth along the vertical axis, which will start to decrease after some reaction time, due to the decrease of the precursors concentration in the growth solution [**Erreur ! Source du renvoi introuvable.-Erreur ! Source du renvoi introuvable.**]. The growth along the horizontal axis is slower than the one along the vertical axis, but follows the same pattern [**Erreur ! Source du renvoi introuvable., Erreur ! Source du renvoi introuvable.**].

The sharp tops of the NWs might be attributed to less available precursors in the long microchannels, which means that the NWs will have a very slow diameter increase with time, while the height increase stays higher, leading to sharp tops. In the short microchannels, however, the flat tops seem to indicate that the precursors are more easily available for the growth reaction, as the diameter increase seems not to be affected the same way as in the long microchannels.

This might be due to the difference in height of the microchannels: as the volume of precursors solution is bigger in the long microchannels, the precursors molecules which are consumed by the NWs growth are replaced less quickly than in the short microchannels, where the volume of precursors solution is smaller, meaning that the molecules are more easily available for the NWs growth occurring at the bottom of the reactor.

## Conclusions

We successfully created a high-volume photocatalytic microreactor by synthesizing ZnO NWs inside a microfluidic reactor, using a simple and environment-friendly hydrothermal method adapted from our previous works. The synthesis conditions were studied, and we concluded that the optimal conditions were a flowrate of 200  $\mu\text{L}/\text{min}$ , a growth temperature of  $80^\circ\text{C}$  and a growth time of 1h. Under these conditions, the reactor achieved a 98% degradation rate over 4 passes, the rough equivalent of 40 seconds under UV irradiation. We also demonstrated that even at

500  $\mu\text{L}/\text{min}$ , our reactor keeps most of its efficiency, degrading 87% of the dye in 20 seconds, against 93% at 200  $\mu\text{L}/\text{min}$ .

The next steps will be to increase the degradation flowrates, test the efficiency of the microreactors on different kinds of dye, and try to improve the efficiency even further by considering to perform an *in situ* metal doping of the NWs, as it has been proved metal doping leads to a better degradation [Erreur ! Source du renvoi introuvable.].

Those results are really promising, as they suggest that it is possible to produce environment-friendly and very efficient microreactors for the photocatalytic depollution of water, with high flowrate throughput, by using a simple production methods, easy-to-use and biocompatible polymers, and a low cost synthesis method at low temperature and atmospheric pressure.

### **Conflicts of interest**

There are no conflicts to declare.

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