Photocatalytic ZnO Foams for Micropollutant Degradation

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Photocatalytic foams can concomitantly overcome the disadvantages of slurry and immobilized photocatalysts in water treatment. However, foams have, so far, been restricted to nanoparticles grafting onto inert foam substrates, with the consequent risk of nanoparticle release into the environment. In this work, self-supporting, highly porous photocatalytic zinc oxide (ZnO) foams are produced using a combination of liquid templating and sintering for the first time. Systematic changes in sintering times and temperature affect the foams’ morphology and structure, in turn controlling their photocatalytic activity and stability. Sintering at 900 °C and decreasing sintering times from 20 to 6 h lead to a doubling in surface-area-to-volume ratio and a 30% increase in pore diameter, resulting in a near doubling of the overall quantum yield and degradation kinetics. However, photocorrosion and Zn leaching increase markedly for the shortest sintering time. Optimal sintering conditions at 900 °C for 12 h yield foams capable of effectively degrading the model micropollutant carbamazepine under UV irradiation with high stability, showing no performance decrease over five irradiation cycles corresponding to 20 h of use. This study paves the way to producing self-supporting, highly stable photocatalytic foams for the removal of organic micropollutants in water treatment.

1. Introduction

With mounting evidence of the potential risk to human health and aquatic ecosystems represented by the presence of micropollutants in the water cycle,[1] there is a pressing need to develop effective and energy efficient methods to remove these substances before they can enter the environment. Micropollutants, found at very low concentrations (µg L⁻¹ or even ng L⁻¹) in wastewater, ground, and surface water, include pesticides, flame retardants, solvents, phthalates, and pharmaceuticals, with the number and type of substances to monitor or remove periodically updated by regulators, e.g., EU watch list of contaminants of emerging concern.[2] For pharmaceuticals, their concentration and geographical location,[3] with removal rates variable due to seasonal changes, water types, and wastewater treatment plant (WWTP) configurations.[4] This is a global problem, with widespread presence of micropollutants in both influent and effluent from WWTPs in Asia, North America, and Europe.[4,5] However, conventional wastewater treatment plants both in urban and industrial areas are unable to effectively remove organic micropollutants.[5] Tertiary treatment for the removal of micropollutants, including advanced oxidation processes (AOPs), has been implemented in some countries, but remains expensive and energy intensive.[6] Among potential AOPs, photocatalysis has been shown to be effective at degrading pesticides, hormones, pharmaceuticals, and endocrine disruptors.[7] However, its implementation has, so far, been hampered by cost and safety concerns associated with the use of slurries on one hand,[7,8] and the low activity of immobilized photocatalyst configurations on the other.[9] The use of highly porous inorganic foams as supports for photocatalytic nanoparticles has been an attempt to address these twin issues.[10] Foams are 3D macroporous materials with defined porosity,[11] whose properties, e.g., pore size, shape, and permeability,[12] can be controlled during their synthesis.[13]

Alumina foams have been used as a support for grafting of titania (TiO₂) nanoparticles, showing higher photocatalytic efficiency than TiO₂ slurries in a pilot-scale photocatalytic oxidation reactor under UV irradiation.[14] The photocatalytic removal of the herbicide paraquat was performed using TiO₂/SiC foams, with TOC removal of 90% achieved in a flow reactor under UV irradiation.[14] A TiO₂ foam, prepared using a polymeric sacrificial layer, was used for the degradation of several organic pollutants including hexadecane, phenol, atrazine, RhB, and thioencarb, under visible light irradiation, showing better removal performance than a slurry using P25 TiO₂ nanoparticles, with high stability and mineralization degree.[15] Complete mineralization of phenol was achieved using TiO₂ nanoparticles grafted onto Al₂O₃ foams, with higher photocatalytic activity than the corresponding powder dispersion.[16] Further improvements in photocatalytic performance have been achieved by increasing the loading of TiO₂ nanoparticles onto the foam supports.[17]

Regardless of their presence, as slurries or supported, the practical impossibility of ensuring that there is no leaching of nanoparticles from WWTPs, has induced the EU and other regulators to restrict their use in water treatment.[18] A potential alternative, proposed here, is to create foams that are inherently photocatalytic, i.e., made of a material that is photoactive,
thereby negating the need to graft any photoactive nanoparticle that could then leach off.

Traditional methods to fabricate foams include the direct-foaming approach, the replica technique, and the use of sacrificial templates.[11] All of these techniques involve multiple process steps,[19] the use of scaffolds,[20] or the addition of polymeric phases to be removed after formation.[21] More complex methods, including freeze drying[15] and 3D printing,[22] have also been reported. In contrast, liquid foam templating is attractive due to its simplicity and scalability given by controlling the composition of particle suspensions.[23] This method has been successfully applied to produce foams using carbon and alumina particles,[13,23,24] but not zinc oxide. The method allows tailoring macroporous materials by controlling the properties of the liquid template including porosity, pore size, morphology, and distribution.[13,25] The surface tension of the liquid template is governed by the nature of the surfactants used, their concentration, and the type of particles used. The combination of those parameters affects the stability and foamability of the suspensions.[13] The total porosity is relative to the amount of gas incorporated into the suspension while the stability of the liquid template before setting determines the final pore size.[11]

Although TiO$_2$ is the most used photocatalyst, ZnO particles have demonstrated better photocatalytic performance than TiO$_2$ P25 under UV light for the removal of organic pollutants.[26] Immobilized ZnO photocatalyst revealed faster photodegradation kinetics and adsorption capacity of dyes than titania.[27] Moreover, ZnO can absorb a wider spectrum of light including in the solar range and more light quanta than other metal oxides.[28] Despite these advantages, ZnO does suffer from photocorrosion under UV irradiation, which has limited its use in water treatment, due to the toxicity of Zn$^{2+}$ ions, with a maximum concentration of 3.0 mg L$^{-1}$ recommend by the WHO.[29]

Significant efforts have been made to improve the stability of ZnO, with ZnO engineered films showing increased stability under UV irradiation,[30] and reduced toxicity on microalgae compared to nanoparticles under visible light irradiation.[31]

The aim of this work was to develop a self-supporting, highly porous ZnO photocatalytic foam obtained via a modified liquid template method to address the limitations of both slurry and immobilized photocatalysts. This aim was reached via the following objectives: i) tailoring the structure and morphology of the ZnO foams by adjusting the particle–polymer–surfactant (PSS) composition of the starting suspension; ii) controlling the crystallinity, porosity, and pore size distribution of the foams by changing in sintering conditions, such as temperature and holding time; and iii) testing the photoactivity of the foams via the photocatalytic degradation of carbamazepine (CBZ), a model pollutant chosen due to its recalcitrance to direct photodegradation by UV, and to allow comparison with other slurry and immobilized photocatalysts. Linking conventional characterization methods to structural analysis via microcomputed tomography (micro-CT), it was possible to establish correlations between sintering conditions, materials properties, and photocatalytic performance, resulting in foams with high chemical stability and reusability over 20 h of photocatalytic degradation.

2. Results and Discussion

2.1. Foams Synthesis and Characterization

ZnO 3D macroporous structures were produced using ZnO particles as the starting material (Figure 1). First, the liquid template, composed of a particle–polymer–surfactant suspension, was produced and air incorporated into the mixture.

![Figure 1. Schematic representation of the ZnO foams synthesis process: from powder to 3D macroporous structures.](image-url)
Faster conversion of the liquid template into the solid foam is essential to retain the incorporated air within the structure. After complete drying, the green body was sintered.

The synthesized ZnO foams were self-supporting, highly porous, exhibiting both micro- and macroporosity (Figure 2I–III). The macrostructure was formed after gelation under heating...
conditions and drying of the liquid templates (Figure 1). Once the air was incorporated in the liquid template, increasing the stability of the liquid template is essential to maintain the open porosity upon drying, i.e., conversion to the green body. Here, this was achieved using a combination of particles and surfactant, using hexadecyltrimethylammoniumbromide (CTAB) to produce foams with open porosity and spherical pores. Additionally, faster gelation and longer drying steps also favored green body overall porosity. Subsequently, the sintering process burned out the polymer within the structure, increasing porosity (Figures 1 and 2I). Raman analysis of the foams showed negligible presence of residual carbon from the burnt polymer (Table S1, Supporting Information). The walls of the pores were composed of flakes (Figure 2II,III), themselves composed of fused micrometer-sized particles (Figure 2IV), which enhance the mechanical stability of the pure ZnO foam.

The sintering process caused significant changes in the formed monoliths, with higher sintering temperature and longer sintering times leading to higher densification (Table S2, Supporting Information). Materials sintered at 900 °C generally present higher overall porosity and flake size distribution than those sintered at 1000 °C (Figure 3I). Foams sintered at 900 °C for 12 and 15 h present similar morphologies (Figure 3II), with the flakes presenting more defined edges (Figure S1, Supporting Information), which can significantly improve the photocatalytic performance of materials. Further increasing the sintering time to 20 h reduced flake average size distribution (from ≈13 to ≈7 µm) and formed more irregular flakes (Figure S1, Supporting Information). Temperature also affected the morphology of the flakes as the presence of edges was no longer observed at 1000 °C (Figure S1, Supporting Information).

After sintering, shrinkage of the materials was clearly observed (Figure 1) and confirmed by measurements of the foams (Table S2, Supporting Information). The behavior of the foams in the present work is well in agreement with literature on sintering of ceramics, controlled by grain boundary diffusion, lattice diffusion (from the grain boundary), and plastic flow. Grain boundary diffusion can be clearly observed in the samples sintered at 900 °C for 12 and 15 h, as confirmed by the formation of necks between particles (Figure 2IV). This was the primary densification mechanism. For extended sintering at 20 h, this led to significant shrinkage (Figure S2, Supporting Information). Samples sintered at 1000 °C showed substantial densification, with larger particles, most likely the result of Ostwald ripening, with the shape of the final flakes losing in regularity (Figure S1, Supporting Information).

X-ray diffraction (XRD) analysis showed that all produced foams contain wurtzite-type crystals (Table S3 and Figure S3, Supporting Information). The intensity of (101), (100), and (002) peaks is in agreement with reported data from JCPDS No. 36-1451. The sintering process also induced a significant increase in crystallinity compared to the precursor ZnO microparticles (Figure S3, Supporting Information). As the relation between particles shape and photocatalytic activity of ZnO is widely reported, changes in the relative intensity of the main ZnO peaks were studied to obtain information on the shape of the sintered particles. Relative intensities of the peaks increased for all conditions studied, indicating a possible degree of particle anisotropy. At 900 °C, a clear correlation could be observed, with an increase in sintering times leading to a decrease of the (100)/(002) relative intensity. As photocatalytic activity is also related to the ratio of polar to nonpolar crystal facets, rod-shaped particles demonstrated poorer photocatalytic performance compared to hexagonal plate structures, as the former have a larger amount of nonpolar facet parallel to the rod axis, whereas the latter have more polar surface exposed with higher surface energy. In turn, the presence of surface charges favored the adsorption of HO• ions, consequently increasing photocatalytic activity. In addition, the presence of [0001] facets in ZnO nanomaterials was reported to improve the photocatalytic activity due to a more negative conduction band potential and higher superoxide (O2−) generation. The presence of [0001] and [0002] facets, represented in green and blue, respectively, were clearly observed from micrographs of ZnO foams (Figure 2IV). No significant difference in surface area was observed between the foams sintered at 900 °C for 12 h and the ZnO starting material (Figure S4, Supporting Information). This latter aspect highlights that surface area is not necessarily the key optimization parameter for foams as is for...
photocatalytic nanoparticle slurries, as shown later when discussing photocatalytic performance.

### 2.2. Effect of Foams Microstructure on Photocatalytic Activity

Initially, the photocatalytic degradation of carbamazepine, as a model micropollutant, was monitored for 10 h using the foams sintered at 900 °C for 12 h as photocatalyst (Figure 4). This time was sufficient to completely degrade CBZ and of its toxic byproducts, acridine (AI) and acridone (AO). Results presented here are in agreement with the literature.[38] Given the pseudo-first order degradation kinetics of CBZ up to ≈67% removal, subsequent experiments were conducted within the linear range only, i.e., for 4 h of irradiation time.

The effect of the foams' microstructure, prepared at different sintering conditions, on their photocatalytic activity was studied by integrating photodegradation experiments (Figure 5 I,II) with in-depth structure characterization (Table 1). Micro-CT was used to reconstruct the foams' internal structure (Figure 2V–VIII), allowing direct measurement of foam volume, pore volume, size and sphericity, and surface area. From this data, the surface area to volume (SAV) ratio could also be calculated. The micro-CT also allowed differentiating between closed and interconnected pores within the structures. This is particularly useful as only interconnected pores participate in photocatalysis, i.e., are in contact with the pollutants. As such, results are discussed here only for interconnected pores (Table 1), whereas results for all pores (interconnected + closed) are shown in Table S4 in the Supporting Information.

It is important to note that since the micro-CT has a resolution in the micrometer range, the porosity value derived from it is not representative of the actual material where microporosity is clearly present (Figure 2). As such, in Table 1 only the porosity obtained using Archimedes' principle is reported.[39] Nonetheless, porosity measurements from micro-CT clearly showed the effect of different sintering times (Table S4, Supporting Information).

From Figure 5, it is clear that shorter sintering times yielded better photocatalytic performance for both sintering temperatures. For the foams sintered at 900 °C, in particular, there is a strong correlation between photocatalytic activity and porosity, mean pore diameter, and surface area to volume ratio (Table 1). Higher porosity and larger pores are associated with higher penetration of light into structured photocatalyst,[16,40] in contrast to photon penetration which, for polycrystalline materials, is in the order of a tenth of a micrometer.[41] Improved light penetration translated into a higher overall quantum yield for shorter sintering times (Table 2). Furthermore, a higher porosity will also reduce mass transfer resistances for the liquid penetrating into the foam. The mean diameter of interconnected pores is significantly higher than the mean diameter of all pores (cf. Table 1 and Table S4 in the Supporting Information), suggesting that the smaller pores formed in the monoliths are mostly closed pores while the larger pores are generally interconnected. This hypothesis is supported by looking at porosity...
values measured using the micro-CT (which cannot detect pores smaller than 20 μm) where macroporosity decreases from 73% to 58% as sintering time increases (Table S4, Supporting Information). There is a very weak correlation between photocatalytic activity and surface area, as previously observed for other immobilized photocatalyst (Table 1).[41] Given the large size of the pores, surface area values are small and, unlike the SAV, cannot capture changes in porosity and pore diameter which, as discussed, have a strong effect on photocatalytic activity. Such changes in porosity, pore diameter, and SAV strongly correlate to the overall quantum yield calculations (Table 2). Greater porosity and SAV, as a result of shorter sintering times, are both responsible for significantly higher normalized quantum yield (Table 2).

Increasing the sintering temperature marginally affected the photocatalytic performance of the foams, but with a reduction in the reproducibility of the data (Figure S1I). This effect can be attributed to differences in morphology between foams sintered at different temperatures, with those sintered at 900 °C having a more uniform structure than those prepared at 1000 °C (cf. Figure 2 and Figure S1 in the Supporting Information). It can be also seen in the larger errors associated with repeats in photocatalytic activity tests at 1000 °C than at 900 °C (Table 1). This is in agreement with previous observations for TiO2 nanoparticles immobilized on alumina foams.[14]

Furthermore, the presence of edges in the particles is known to improve photocatalytic activity due to better interaction with light.[13] A higher symmetry of the flakes, increased flakes size distribution (Figure 3I), the presence of pores within the flakes, and the degree of organization in the foams sintered at 900 °C all contribute to better light activation due to enhanced light propagation. As such, the foams sintered at 900 °C for 12 h were considered having the optimal structure-performance of all the conditions tested, with a first order kinetic constant of 2.3 × 10⁻³ min⁻¹.

| Sample ID | Foam sintering condition | k [×10⁻³ min⁻¹] | PAM [%]b | Do [μm] | Sphericity [%]c | SA [cm²] | SAV (m³ cm⁻³) |
|-----------|--------------------------|-----------------|----------|---------|----------------|----------|--------------|
| h         | 900 °C 6 h               | 1.6 ± 0.2       | 94       | 266.7 ± 2.1 | 0.93           | 6.6 ± 0.1 | 127.1 ± 4.1  |
| e         | 1000 °C 12 h             | 3.2 ± 0.2       | 93       | 376.2 ± 7.2 | 0.86           | 5.2 ± 0.2 | 96.4 ± 13.6  |
| f         | 1000 °C 15 h             | 2.8 ± 0.2       | 92       | 262.7 ± 2.3 | 0.92           | 6.1 ± 0.2 | 90.3 ± 4.3   |
| g         | 20 h                     | 2.3 ± 0.3       | 91       | 285.1 ± 13.7 | 0.89    | 6.3 ± 0.3 | 93.5 ± 8.3   |
| –         | Correlation 1000 °C –    | 0.997           | 0.714    | –0.443  | –0.914        | 0.417  |

a)The associated error is <10⁻²; b)SAV was calculated as a ratio of measured surface area relative to the volume of material in the monolith.

2.3. Foams Light Interaction and Kinetics

Although a precise comparison of different photocatalytic systems is challenging due to the many variables involved in a photocatalytic experiment (UV dose, quantum yield, etc.), a systematic analysis of the degradation of CBZ in batch reactors using either ZnO nanoparticle suspensions or immobilized ZnO (Table S5, Supporting Information) shows that the results obtained here are comparable with what was obtained for ZnO nanoparticle suspensions (e.g., k = 3.3 × 10⁻³ min⁻¹ for 0.5 g L⁻¹ of ZnO NPs and [CBZ] = 10 mg L⁻¹),[42] but lower than commercial TiO2 P25 nanoparticle slurries. While the latter result is expected, the former is quite remarkable as

Table 2. Overall quantum yield and normalized over the catalyst’s properties surface area (SA), surface area to volume (SAV), and porosity as a function of the pseudo-first order reaction rate constant (k), foams sintering time, and degradation conditions.

| Sample ID | Foams conditions | Degradation conditionsa) | k [×10⁻³ min⁻¹] | Φ overall quantum yield | Φ normalized quantum yield |
|-----------|-----------------|--------------------------|-----------------|--------------------------|--------------------------|
| –         | –               | Photolysis               | 0.6[5]          | 0.13                     | –                        |
| b         | 900 °C 12 h     | PC                       | 1.5[5]          | 0.35                     | 2.4 × 10⁻⁴               | 0.37                     | 0.24                     |
| h         | 900 °C 6 h      | PC O₂                    | 3.0 ± 0.4       | 0.85                     | 5.7 × 10⁻⁴               | 1.72                     | 0.63                     |
| b         | 900 °C 12 h     | PC O₂                    | 2.3 ± 0.7       | 0.88                     | 5.9 × 10⁻⁴               | 1.42                     | 0.60                     |
| c         | 900 °C 15 h     | PC O₂                    | 2.2 ± 0.0       | 0.72                     | 4.7 × 10⁻⁴               | 0.97                     | 0.44                     |
| d         | 900 °C 20 h     | PC O₂                    | 1.6 ± 0.2       | 0.49                     | 3.3 × 10⁻⁴               | 0.63                     | 0.29                     |
| –         | Correlation     | –                        | 0.944           | 0.882                    | 0.963                    | 0.932                    |

a)Photocatalysis under atmospheric conditions (PC); photocatalysis under oxygen saturation (PC O₂); b)The associated error is <10⁻².
2.4. Foam Stability and Reusability

The stability of the foams produced at 900 °C for 12 h under nitrogen saturation, oxygen saturation, and under atmospheric conditions was investigated (Figure 6). A significant improvement was achieved under oxygen saturation, whereas nitrogen saturation lowered the photocatalytic activity of ZnO foams. Oxygen is known as electron scavenger, minimizing electron/hole (e−/h+) recombination thus improving the catalyst performance.[46,48] The experiments performed under atmospheric condition showed not only a low PCA, but also a significant photocorrosion, as measured by the [Zn] in the solution after 4 h of photocatalysis. This is due to depletion of oxygen in the solution caused by photocorrosion.[47]

Photocatalytic efficiency is a complex compromise among several parameters including photoactivation, charge carrier transport, and mass transfer. Light activation is one of the key parameters for high photocatalytic performance as chemical reactions rely on successful energy conversion of light into charge carriers (e−/h+).[44] As photocatalytic reactions occur at the catalyst’s surface, photoactivity in slurry systems can be directly correlated to the SA of the powder catalysts.[45] In immobilized photocatalysts, however, SA is generally lower than slurries, but light interaction is dependent on light penetration through the films’ nanostructure. As such, in these systems, a higher surface area does not necessarily imply a higher photocatalytic activity.[41] The effectiveness of light penetration becomes even more important when 3D structures as foams are used as photocatalysts.[40] Furthermore, while these systems have an SA, which is intermediate between slurries and immobilized systems, their photocatalytic performance can be higher than that of slurries, as discussed in the introduction. As such, rather than using SA, in this work, the surface area per volume property of self-supporting foams has been used as a more relevant parameter to optimize photocatalytic activity. The SAV concept captures the combination of relevant properties, i.e., porosity, pore diameter, and 3D structure on the foams’ performance. This is shown by a high correlation of photocatalytic activity (0.940) with SAV compared to SA (0.246) for the foams sintered at 900 °C (Table 1). Furthermore, the higher correlation between SAV and quantum yield demonstrates how efficiently an increased pore diameter improved the photoactivation (Table 2), linking the foams’ microstructure to their photocatalytic activity. In particular, an improved quantum yield (Φ) was observed for foams sintered for shorter sintering times. This could be related to both better electronic properties associated to carrier mobility in a 3D interconnected structure and charge transport dynamics due to high crystallinity.[44]

\[
\text{ZnO} + 2\text{h}^+ \rightarrow \text{Zn}^{2+} + 1/2 \text{O}_2
\]  

In contrast, saturating the solution with nitrogen increased stability but lowered PCA. Saturation in oxygen increased PCA with stability in between the other two cases, representing the optimal solution conditions for the foams (inset, Figure 6).

Under oxygen saturation, photocorrosion significantly decreased with increasing annealing time (Table 3). This can be attributed to a higher proportion of smaller particles and less densification for shorter sintering times (Figure S1, Supporting Information). A strong correlation (0.939) is observed between zinc concentration and sintering times (12, 15, and 20 h). In addition, overall quantum yields markedly improved from 0.35 to 0.88 under saturated conditions for foams sintered at 900 °C and 12 h (Table 2).

All zinc concentrations after photocatalytic degradation studies indicated levels in the ppb range, significantly lower than the recommended 3.0 mg L−1 in drinking water according to World Health Organization (WHO).[29]

| Sample ID | Foam sintering condition | k [×10^−5 min⁻¹] | [Zn] [ppb] |
|-----------|--------------------------|------------------|------------|
| h         | 900 °C 6 h               | 3.0 ± 0.4        | 767.8 ± 0.1|
| b         | 12 h                    | 2.3 ± 0.7        | 278.1 ± 0.1|
| c         | 15 h                    | 2.2 ± 0.0        | 261.5 ± 0.1|
| d         | 20 h                    | 1.6 ± 0.2        | 144.5 ± 0.1|
|          | Correlation 900 °C      | –                | 0.939      |
| e         | 1000 °C 12 h            | 3.2 ± 0.2        | 249.5 ± 0.0|
| f         | 15 h                    | 2.8 ± 0.2        | 234.5 ± 0.1|
| g         | 20 h                    | 2.3 ± 0.1        | 174.2 ± 0.1|
|          | Correlation 1000 °C     | –                | 0.964      |

The experiments performed under atmospheric condition showed not only a low PCA, but also a significant photocorrosion, as measured by the [Zn] in the solution after 4 h of photocatalysis. This is due to depletion of oxygen in the solution caused by photocorrosion.[47]
2.4.1. Reusability

The ZnO foams demonstrated good robustness, with minimal loss in photocatalytic activity and stable photocorrosion over five cycles of photocatalytic degradation (Figure 7I), corresponding to over 20 h of use. No structural changes or loss of material were observed. No morphological changes were observed either (cf. Figures 2II and 7II). Although long-term stability is essential for any practical use of photocatalytic foams, there are relatively few results reported in the literature and mostly for titania nanoparticles grafted onto alumina foams. In one study, significant results reported in the literature and mostly for titania nanoparticles grafted onto alumina foams. In one study, significant loss of foam performance was observed after the removal of phenol and formic acid,[49] whereas others observed no material loss.[50] A minor change in photocatalytic performance was observed for titania NP foams for the reduction of nonylphenol, with the introduction of a washing step between uses re-establishing the photocatalyst’s performance.[51] Very little is reported on the photocatalytic stability of ZnO nanostructures, with, e.g., sheet-like ZnO photocatalyst demonstrating good stability after five cycles of 90 min each for dyes removal.[52]

3. Conclusions

Self-supporting, highly stable photocatalytic ZnO foams were successfully synthesized by liquid templating without the use of any support from particle–polymer–surfactant suspensions in water. Control over sintering conditions allowed tailoring foam structure and morphology. Computed microtomography analysis, unlike conventional techniques as Brunauer–Emmett–Teller (BET), proved to be a key technique in establishing correlations between a foam’s microstructure and its photocatalytic activity. The best performance was obtained for a combination of high (open) porosity, pore diameter, and SAV ratio. Such properties improved quantum yields as light penetration was facilitated through the 3D structure. The use of the SAV to optimize a foam’s microstructural properties and to maximize its photocatalytic performance has been proposed here. Photocatalytic studies revealed that oxygen saturation not only enhanced the degradation of carbamazepine as a model organic micropollutant but also reduced the photocorrosion of the ZnO foam under UV irradiation.

Photocatalytic foams can enable the use of photocatalyst in practical applications by simultaneously overcoming key limitations of current technologies, i.e., nanoparticle slurry downstream removal, poor efficiencies of immobilized catalysts, and nanoparticles leaching into the environment.

4. Experimental Section

Materials: High purity ZnO powder (99.999%; average particle size 5.0 μm) was purchased from Goodfellow. Polyvinyl alcohol (PVA) 87.0–89.0% hydrolyzed (M.W. 13 000–23 000), nitric acid, and phosphoric acid were acquired from Acros. The cationic surfactant, CTAB, and the crosslinker 2,5-dimethoxy-2,5-dihydrofuran (DHF) were supplied by Sigma-Aldrich (Germany). Acetonitrile was purchased from Fisher. Carbamazepine, used here as a model pollutant, was supplied by Sigma-Aldrich and stored in a cold room. All solutions were prepared using ultrapure water (Veolia Purelab Chorus with resistivity 18.2 MΩ).

ZnO Foams Synthesis: The ZnO foams were synthesized using a modified liquid templating process described in Figure 1. An aqueous surfactant–polymer solution was prepared by dissolving CTAB and PVA (0.9 and 5.0 wt%, respectively) in water. The solution was maintained under magnetic stirring for a few hours and further sonicated for 1 h. This suspension was stirred overnight prior to use. To prepare the liquid templates, ZnO particles (40.0 wt%) were added to the surfactant–polymer solution and stirred for 5 h. After that, the particle–polymer–surfactant suspension was heated to 45 °C for 1 h on a hot plate (IKA C-MAG HS7). The gelling process was started by adding nitric acid (16.0 vol%) and further stirring for extra 20 min followed by the addition of the crosslinker (4.3 vol%). The liquid templates were produced after air incorporation into the mixture using a homogenizer (IKA, Ultra-Turrax T 25 basic) at 11 000 rpm for 4 min. The material was immediately transferred to a preheated muffle oven (Carbolite CWF 1100) and sintered in air at 900 °C for 12 h. Each temperature was maintained under magnetic stirring for few hours and further sonicated for 1 h. The produced green body was further dried in air for 48 h inside the beaker and finally also sintered in air at 900 °C for 12, 15, and 20 h.

Figure 7. I) Reusability and chemical stability of the ZnO foams sintered at 900 °C for 12 h after five consecutive cycles of 4 h each. II) FESEM micrograph of the ZnO foam after photocatalytic degradation experiments.

ZnO Foam Characterization: The crystallographic structure of the foams was investigated using a STADI P XRD diffractometer (Cu radiation) in transmission mode for 2θ values between 20° and 80°. The composition of the foams was studied using Raman spectroscopy in a Renishaw inVia system. The analysis was performed using a green laser, 100% laser power, and 2.6 s exposure. The chemical stability of the materials was analyzed using inductively coupled plasma mass spectrometry (ICP-MS) in a Thermo Fisher Scientific X-Series II instrument. All samples, standards and blanks, were spiked with internal
standard elements Be, In, and Re. The Zn concentration was calibrated using six synthetic standards prepared from 1000 ppm Inorganic Ventures (VA, USA) standard. The associated error was typically lower than 1.0%.

The morphology of the ZnO foams was analyzed using both a JEOL JSM-6480LV coupled with EDX and a JEOL JSM-6301F FESEM. Image J software was used to calculate flakes size distribution from FESEM micrographs. Histograms were produced expressing counts (number of structures) versus flake size. The surface area of the samples was determined using the BET method in an Autosorb-IQ-C by Quantachrome Anton Paar. Samples were degassed for 480 min at 150 °C at 10−3 mbar.
The foams’ porosity was calculated according to Archimedes’ principle[50]:
\[
\rho_f = \frac{(\rho_0 - \rho_w)}{\rho_f}
\]
where \( \rho_f \) is the foam porosity; \( \rho_0 \) is the weight of the wet foam (g); \( \rho_w \) is the weight of the dry foam (g); \( D_f \) is the water density (g cm−3) at 15 °C; \( D_{ZnO} \) is the ZnO density (g cm−3).

Microcomputed tomography analysis was performed using a Nikon XT H 225ST scanner. The scanner records a series of 2D cross-sections from various angles around the object. These images are then reconstructed to produce a 3D rendered volume.[31] 3D visualization and data processing were done using Avizo software. The images were “binarized” and the surface area was calculated according to the triangulation of surface elements method.[31] The samples were probed in three different areas considering the same internal volume (0.5 × 0.5 × 0.5 cm) in order to assess their uniformity. The settings used were: 170 kV voltage, 130 μA current, 0.708 s exposure, no filter material, 3141 projections (four images per projection, which were then averaged), 18 gain, and tungsten target. The obtained resolution under these conditions was 20 μm, which meant that smaller porosity could not be captured with this technique. Correlations between the foam properties and synthesis conditions were evaluated statistically, using Pearson’s correlation coefficient (Pearson’s r).

Carbamazepine Photocatalytic Degradation Experiments: The photocatalytic activity of the ZnO foams was studied using 250 mL of carbamazepine solutions (10 mg L−1) in a stirred batch reactor. The mass of photocatalyst used was 0.5 g of material per liter of solution. The temperature was controlled at 10 ± 1 °C using a water-cooled bath (Thermo Scientific) and a jacket vessel of 250 mL. The system was continuously stirred (2000 rpm; Fisher FB15045) and irradiated from the top at a fixed distance of 3.0 cm between the foam and the UV-lamp (Aquatix pond UV lamp, 254 nm, 5 W). A UV light intensity of 6.2 mW cm−2 was measured using a UV radiometer (International Light Technologies-ILT 1400). The experiments were performed under saturated conditions in the presence of oxygen or nitrogen (flow rate 0.25 SL min−1) and without any gas purging. The dissolved oxygen content was monitored using an Orion Versastar Thermo Scientific meter.

CBZ removal was monitored from aliquots collected (not exceeding 10% of the total volume) during degradation experiments using high-performance liquid chromatography (HPLC). Chromatographic analyses were performed on a Thermo Scientific Ultimate 3000 liquid chromatograph using a UV detector. For carbamazepine analysis, a Thermo Scientific Acclaim 120 C18 column (3.0 × 75 mm, particle size 3.0 μm) and Thermo Scientific Acclaim 120 C18 guard column (R) 120 C18 (3.0 mm × 10 mm particle size 5 μm) were used. The mobile phase was composed of 5.0 mmol L−1 phosphoric acid and acetonitrile 70:30 (v/v). The flow rate was 0.8 mL min−1, injection volume was 20 μL, and the detection wavelength was set at 285 nm. Alternatively, CBZ degradation and subsequent phototransformation products acridine and acridone were monitored with HPLC (Thermo Scientific Dionex Ultra High Performance Liquid Chromatography) coupled to mass spectrometry (MS) using a Bruker MaXis HD ESI-QTOF MS. For MS analysis, the phosphoric acid was replaced with pure water in the mobile phase, while HPLC conditions remained unchanged. Acridone and acridine were verified semiquantitatively based on known m/z patterns[34] and peak areas.

CBZ absorbs light in the UV region exhibiting absorption peaks at 220 and 285 nm.[51] At 254 nm, CBZ has a molar extinction coefficient (ε) of 6072 m−1 cm−1,[39] and a quantum yield Φ254, nm of 0.060 × 10−2 mol Einstein−1 for direct photolysis.[39] Despite being considered as photoresistant, direct photolysis of CBZ was 14% after 4 h, which was in line with values from the literature using similar conditions.[31,35] Adsorption and removal of CBZ under dark conditions were found to be negligible. (C/C0) was calculated after 240 min of reaction time. Pseudo-first order reaction rate constants k (min−1 or s−1) for CBZ removal were calculated via the Arrhenius equation [In(C/C0) = −kt] by using linear regression of the logarithmic normalized concentration versus time.

UV Dose and Quantum Yield Calculations: The UV dose was calculated to enable comparison of the photocatalytic efficiency of foams sintered at different conditions rather than the light intensity emitted by the lamp.[39] The equations and calculations are described in the Supporting Information. The overall quantum yield (Φoverall) is defined as the reaction rate relative to the number of photons absorbed by the photocatalyst (κ).[56] according to the IUPAC recommendation.[56] The reaction rate (s−1) represents the pollutant conversion into degradation products. In a photocatalytic reaction, the overall quantum yield can be calculated considering the photon flux (E0) impinging at the catalyst surface and assuming negligible light scattering losses in the reaction cell according to the following equation

\[
\Phi_{\text{overall}} = \frac{k}{q'}
\]

The normalized quantum yield, i.e., the ratio between photon flux and either SA, SAV ratio, or porosity, showed a correlation coefficient (Pearson’s r) above 0.9 (Table 2).

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are openly available in University of Bath open access data archive at https://doi.org/10.15125/BATH-00799.
