A new type of composite material involving the in situ immobilization of tin oxide nanoparticles (SnO$_2$-NPs) within a monolithic metal–organic framework (MOF), the zeolitic imidazolate framework (ZIF)-8 is presented. SnO$_2$-NPs within a monolithic MOF, while leveraging the photocatalytic action of the nanoparticles. The composite displays outstanding photocatalytic properties and represents a critical advance in the field of treating toxic effluents and is a vital validation for commercial application. Crucially, full retention of catalytic activity is observed after ten catalytic cycles.

**1. Introduction**

The catalytic degradation of organic molecules such as toxic dye effluents and nerve agents has received considerable attention in recent years. Metal–organic frameworks (MOFs) have been proposed as promising catalysts for the degradation of these compounds. However, the possibility of incorporating catalytic nanoparticles (NPs) to create new functional composites brings vast benefits in terms of their performance. At the same time, the use of MOFs as supports for catalytic NPs has been hindered due to the powder morphology of the former, which results in poor catalyst retention and recyclability. Furthermore, the development of new applications for NPs faces difficulties owing to particle toxicity and agglomeration. Overall, shaping of powdered supports into monolithic conformations has been a long-standing challenge to the applicability of these materials. A satisfactory solution promises to address problems associated with pressure drops in adsorption columns due to MOF powder compaction and to promote the recovery of catalytic NPs from liquid phases.

In the last 20 years, the Cambridge Crystallographic Database Centre has catalogued more than 80,000 MOFs, comprising a vast variety of organic linkers, nodes, and topologies. Despite the burgeoning interest in MOFs and in the improvement of catalytic MOF composites, the development of monolithic structures for these multifunctional materials has not been explored thoroughly. Hence, for example, previous work has focused on size control, spatial distribution, and controlled encapsulation of NPs in nanocrystalline MOFs, achieving great success in terms of catalytic performance. However, in a recent major advance in MOF shaping, we presented a novel sol–gel synthetic method for producing transparent, robust, monolithic zeolitic imidazolate framework (ZIF)-8 without the need for high pressures or binders.

These monoliths are conformed (i.e., shaped) porous structures that retain the same porous texture and chemical/thermal stability of the nanocrystalline MOF but now in the form of a mechanically robust macrostructure with bulk densities and volumetric Brunauer–Emmett–Teller (BET) areas 3–4 times higher than those of the powder. This new approach to MOF synthesis presents multiple advantages over the prior art. First, it has yielded the first conformed porous material that, after successful packing and densification, reached the volumetric DOE target for methane storage. Second, compared with other pelletization methods that can lead to up to 90% of pore collapse and pore blocking due to the use of high pressures, this sol–gel synthetic protocol introduces the possibility of creating mechanically stable monoliths based on porous MOFs that can robustly incorporate highly active and potentially toxic species such as NPs.

The incorporation of catalytically active NPs into a MOF represents an important method of exploiting the combined physico-chemical properties of both constituents. However, to the best of our knowledge, there are no reports of...
NP encapsulation via a “bottom-up” synthesis involving MOF precursors resulting in mechanically stable monolithic composite (NP@monoMOF) macrostructures recoverable by simple filtration. Previous attempts to exploit the properties of MOFs for environmental remediation have focused on powdered morphologies, with their ability to degrade toxic organic compounds being poor.[11] Furthermore, compared with other monolithic samples such as 3D graphene aerogel, the preparation of our material is highly time and energy efficient: 10 min reaction at room temperature for the monolithic MOF compared to a 12 h reaction at 90 °C for the graphene aerogel.[13] In this work, we used recent advances in sol–gel synthesis to create a mechanically and chemically robust monolithic MOF able to encapsulate NPs. On the one hand, we chose the prototypical ZIF-8 (Zn(2-mIm)2·2·mIm = C6H4N2) MOF from the ZIF family.[15] ZIF-8 shows a sodalite topology with large cages and narrow windows (1.16 nm cavity diameter and flexible 0.34 nm windows),[16] boasting both high porosity (total pore volume 0.485 cm³ g⁻¹) and high chemical and thermal stability.[27] On the other hand, we chose SnO₂-NPs for encapsulation due to their nontoxic nature and track record in detoxification.[28] In addition, despite the proven benefits of SnO₂-NPs in the photocatalytic degradation of toxic molecules, they still present major challenges of recovery and reuse owing to their small size.[19] The SnO₂@monoZIF-8 composite developed here combines excellent activity in the degradation of toxic industry effluent with straightforward catalyst recyclability.

2. Results and Discussion

The synthesis of SnO₂-NPs resulted in uniform, monocristalline NPs with a mean size distribution of 5.0 ± 1.1 nm and a band gap of 3.74 eV (Figures S1–S4, Supporting Information). We then incorporated them into high-density ZIF-8 monoliths during a sol–gel process similar to the synthesis of monolithic aerogels.[20] This sol–gel process involves the formation of small primary ZIF-8 particles that aggregate, forming the gel macrostructure before being dried into a monolithic structure. Whereas pure ZIF-8 monoliths (monoZIF-8) were transparent (Figure 1a), SnO₂@monoZIF-8 appeared white (Figure 1b). Scanning electron microscopy (SEM) analysis of SnO₂@monoZIF-8 revealed a similar flat surface morphology to that previously reported for monoZIF-8 (Figure 1c).[21] Transmission electron microscopy (TEM) analysis of the mother liquor revealed a primary particle size for SnO₂@monoZIF-8 (100–150 nm) larger than that for monoZIF-8 (60–80 nm) (Figure S5, Supporting Information), suggesting that ZIF-8 exhibits slower nucleation in the presence of SnO₂-NPs.[22]

We confirmed the composition of SnO₂@monoZIF-8 using energy-dispersive X-ray spectroscopy (EDX). Figure 2 shows representative scanning transmission electron microscopy (STEM) images, indicating the presence of bright spots within the monolithic matrix. These present some agglomeration at the local level but are well distributed through the monolith. By using EDX, we confirmed the chemical nature of these bright spots (Figure 2c), so demonstrating the successful encapsulation of SnO₂-NPs.

We further investigated the subsurface features of the monolith and the presence of the SnO₂-NPs, using focused ion beam (FIB)-SEM. Figure 1c–f shows images obtained during etching, revealing SnO₂ agglomerates dispersed throughout the monolithic matrix. By providing a solid surface to which NPs with high interfacial energies can adhere, monoZIF-8 has prevented the worst excesses of NP agglomeration (Figure S1, Supporting Information). Triplicated inductively coupled plasma-optical emission spectroscopy (ICP-OES) experiments found the level of SnO₂-NP loading to be 2.0 ± 0.1 wt% (Table S1, Supporting Information). Attempts to increase the loading of NPs in the composite failed to afford a monolith, suggesting that the 2.0 wt% loading of SnO₂-NPs represents the maximum attainable while preserving the structural integrity of the composite. X-ray photoelectron spectroscopy (XPS) confirmed the results of FIB-SEM. Figure 3a shows the FIB-XPS analysis of the 3d region of Sn(IV). This revealed peaks attributable to Sn(3d₅/₂) and Sn(3d₃/₂) binding energies, centred at 486.7 and 495.5 eV, respectively, confirming the presence of SnO₂.[22] The high-energy shoulder on the Sn(3d₅/₂) peak is attributed to the presence of ZIF-8.[23] Encouragingly, we detected Sn consistently throughout etched areas, while the external surface spectrum revealed a lower Sn presence. This supports the FIB-SEM microscopic image and confirms that the majority of SnO₂ is located within the monolith. Discussion of the remaining XPS data may be found in the supporting information (Figures S6 and S7, Supporting Information).
Figure 3b compares the powder X-ray diffraction (PXRD) patterns of simulated ZIF-8 with experimental mono-ZIF-8, SnO$_2$-NPs, and SnO$_2$@mono-ZIF-8. Fresh SnO$_2$@mono-ZIF-8 revealed minimal peak variation compared with mono-ZIF-8, confirming that the SnO$_2$-NPs do not perturb the crystallinity of the MOF.

Figure 3c shows the N$_2$ adsorption isotherms for the composite; Table 1 compares the BET areas, and the micropore and total pore volumes. Both mono-ZIF-8 and SnO$_2$@mono-ZIF-8 display typical stepped ZIF-8 adsorption isotherms and an absence of mesoporosity, as confirmed by the similarity of micropore and total pore volumes. However, the adsorption capacity and BET area of the composite are ~25% lower than those of mono-ZIF-8. This is attributed to pore blocking by nonporous phases. Mercury porosimetry revealed the bulk density (envelop

---

**Figure 2.** a,b) Representative STEM-HAADF images of SnO$_2$@mono-ZIF-8. (Scale bars 100 nm, panel (a) and 20 nm, panel (b).) c) Drift-corrected EDX analysis of SnO$_2$@mono-ZIF-8, scanned over Area 1 (blue) and Area 2 (red) as illustrated by the regions defined, panel (b).

---

**Figure 3.** a) FIB-XPS binding energy spectra for the 3d region of Sn(IV) in SnO$_2$@mono-ZIF-8; quoted peak energies calculated as an average over the ten spectra. b) PXRD patterns of simulated ZIF-8 and experimental mono-ZIF-8, SnO$_2$-NPs, and SnO$_2$@mono-ZIF-8 fresh and after 1, 5, and 10 catalytic cycles. N$_2$ adsorption isotherms at 77 K for mono-ZIF-8; SnO$_2$@mono-ZIF-8 after 1 catalytic cycle; SnO$_2$@mono-ZIF-8 after 5 catalytic cycles; SnO$_2$@mono-ZIF-8 after 10 catalytic cycles; SnO$_2$@mono-ZIF-8 after 1 catalytic cycle; SnO$_2$@mono-ZIF-8 after 5 water cycles; SnO$_2$@mono-ZIF-8 after 10 water cycles on c) nonlogarithmic and d) semilogarithmic axes.
or particle density) of SnO$_2_{\text{mono}}$-ZIF-8 to be slightly higher than that of mono-ZIF-8, i.e., 1.13 g cm$^{-3}$ versus 1.05 g cm$^{-3}$, while confirming the absence of meso- and macroporosity (Figure S8, Supporting Information).

### 2.1. Photocatalytic Studies

As proof of concept to evaluate the photocatalytic activity and, most importantly, the straightforward recovery and reusability of SnO$_2_{\text{mono}}$-ZIF-8 for toxic organic molecule destruction, we monitored the catalytic degradation of aqueous methylene blue (MB) solutions over multiple catalytic cycles. Each cycle lasted 3 h, with the composite recovered each time by simple gravity filtration (Figure S9, Supporting Information) before being reused without washing. The degree of degradation was calculated according to the reduction in absorption for the major MB absorption band at $\lambda_{\text{max}} = 664$ nm

\[
\text{Degradation} \, \% = 100 \times \left(1 - \frac{C_t}{C_0}\right)
\]

where $C_0$ is the initial concentration of MB and $C_t$ is the concentration of MB after time $t$.

Table 1. BET areas ($S_{\text{BET}}$), micropore volumes ($V_{\text{m}}$), and total pore volumes ($V_{\text{TO}}$) for mono-ZIF-8 and SnO$_2_{\text{mono}}$-ZIF-8 before and after exposure to methylene blue (MB) and H$_2$O.

<table>
<thead>
<tr>
<th>Material</th>
<th>$S_{\text{BET}}$ [m$^2$ g$^{-1}$]</th>
<th>$V_{\text{m}}$ [cm$^3$ g$^{-1}$]</th>
<th>$V_{\text{TO}}$ [cm$^3$ g$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>mono-ZIF-8</td>
<td>1423</td>
<td>0.543</td>
<td>0.546</td>
</tr>
<tr>
<td>SnO$<em>2</em>{\text{mono}}$-ZIF-8</td>
<td>1055</td>
<td>0.413</td>
<td>0.417</td>
</tr>
<tr>
<td>SnO$<em>2</em>{\text{mono}}$-ZIF-8—1 cycle (MB)</td>
<td>1068</td>
<td>0.421</td>
<td>0.427</td>
</tr>
<tr>
<td>SnO$<em>2</em>{\text{mono}}$-ZIF-8—5 cycles (MB)</td>
<td>985</td>
<td>0.389</td>
<td>0.393</td>
</tr>
<tr>
<td>SnO$<em>2</em>{\text{mono}}$-ZIF-8—10 cycles (MB)</td>
<td>1027</td>
<td>0.405</td>
<td>0.411</td>
</tr>
<tr>
<td>SnO$<em>2</em>{\text{mono}}$-ZIF-8—1 cycle (H$_2$O)</td>
<td>973</td>
<td>0.384</td>
<td>0.389</td>
</tr>
<tr>
<td>SnO$<em>2</em>{\text{mono}}$-ZIF-8—5 cycles (H$_2$O)</td>
<td>991</td>
<td>0.389</td>
<td>0.393</td>
</tr>
<tr>
<td>SnO$<em>2</em>{\text{mono}}$-ZIF-8—10 cycles (H$_2$O)</td>
<td>996</td>
<td>0.385</td>
<td>0.399</td>
</tr>
</tbody>
</table>

Data obtained at $P/P_0 = 0.1$; $^{10}$P/$P_0 = 0.99.

Figure 4. a) Photocatalytically induced spectral changes to aqueous MB dye (1.55 $\times$ 10$^{-4}$ M) highlighting degradation of the absorption maximum at 664 nm in the absence of composite (red) and presence of 1.7 g SnO$_2_{\text{mono}}$-ZIF-8 (green) after 3 h of simulated solar irradiation. b) Degradation of MB in the presence of 0.4 g (cycles 1–5 and 10) and 1.7 g of SnO$_2_{\text{mono}}$-ZIF-8. Error bars are the standard deviation in triplicated readings.

MB (dimensions: 7.9 $\times$ 16.3 $\times$ 4.0 Å)$^{[24]}$ is widely used in the textile industry and represents a common toxic effluent in water supplies.$^{[25]}$ By using a dye larger than the apertures of ZIF-8 (i.e., 3.4 Å)$^{[16]}$ we have explored the accessibility of the SnO$_2$-NPs. Figure 4 shows the degradation of MB in the presence of different amounts of SnO$_2_{\text{mono}}$-ZIF-8.

A number of MOFs are known to exhibit photocatalytic properties,$^{[26]}$ with the partial degradation of MB under nanoparticle ZIF-8 previously attributed to the wide band gap of this semiconducting material.$^{[27]}$ For these reasons, it was essential to establish whether mono-ZIF-8 represented a potential source of dye degradation in this work. Triplicated control experiments revealed that mono-ZIF-8 presents no photocatalytic behavior under simulated solar irradiation, with measured dye degradation attributable to surface physisorption (Figures S10 and S11, Supporting Information). Meanwhile, low loading experiments utilizing 0.4 g of composite (i.e., 53 µmol of SnO$_2$-NPs) proved SnO$_2_{\text{mono}}$-ZIF-8 to be moderately photocative, with an average of 41.5 ± 3.0% MB degradation achieved in 3 h. Importantly, the catalytic performance was sustained, with 39.4 ± 0.6% MB degradation achieved in the 10th cycle, providing compelling evidence for NP retention by the composite (Figure S12, Supporting Information). When increasing the loading to 1.7 g of composite (i.e., 225 µmol catalyst), MB degradation increased to

\[\text{Degradation} \, \% = 100 \times \left(1 - \frac{C_t}{C_0}\right)\]
93.6 ± 2.7% in 3 h. This is a substantial improvement on previously reported semiconducting NP-(ZIF-8) hybrid materials.\cite{[31,38]}

Previous studies suggest that to achieve appreciable degradation of a dye under comparable conditions, 150–300 μmol of powdered photocatalytic NPs are typically required.\cite{[32,33]}

Interestingly, although the narrow apertures of ZIF-8 preclude the passage of MB, this is not a barrier to photocatalysis. Houas et al. have proposed the following mechanism,\cite{[34]}

where intimate contact between SnO$_2$-NPs and dye is not necessary:

\[
\begin{align*}
\text{SnO}_2 + h\nu &\rightarrow e^{-}_\text{CB} + h^+_\text{VB} & \text{1) Exciton production} \\
O_2 + e^{-}_\text{CB} &\rightarrow O_2^- & \text{2) Ionosorption and reduction of O}_2 (0 \text{ to } -0.5 \text{ eV}) \\
H_2O + h^+_\text{VB} &\rightarrow H^+ + OH^- & \text{3) Production of hydroxyl radicals} \\
O_2^- + H^+ &\rightarrow HO_2^- & \text{4) Neutralization of O}_2^- \\
2HO_2^- &\rightarrow H_2O_2 + O_2 & \text{5) H}_2O_2 formation} \\
H_2O_2 + e^{-}_\text{CB} &\rightarrow OH^- + H^+ & \text{6) H}_2O_2 degradation} \\
R + OH^- &\rightarrow R^- + H_2O & \text{7) Oxidation of dye (R)} \\
\end{align*}
\]

In this mechanism, the species active in dye degradation derive from adsorbed oxygen and water.\cite{[19]}

Even allowing for their flexibility, the narrowness of the 3.4 Å windows of ZIF-8 suggests that the dye cannot pass through its framework apertures. This considered, we propose that water, with a 2.68 Å kinetic diameter,\cite{[31]}

diffuses through the ZIF-8 windows\cite{[12]}

and interacts with SnO$_2$. Reaction with the photoinduced excitons (electrons, e$^-$, and holes, h$^+$) in the conduction (CB) and valence (VB) bands of the NPs then creates the hydroxyl and superoxide radicals required for dye degradation. A terephthalic acid (TA) probe was used to determine OH$^-$ radical production. Reaction of TA with OH$^-$ radicals generates the fluorescent species 2-hydroxyterephthalic acid (2-HTA), and the formation of this molecule was monitored using the intensity maximum at 450 nm after excitation at 315 nm. The production of 2-HTA was seen to increase with solar irradiation time (Figure S13, Supporting Information), indicating the photogeneration of OH$^-$ and strongly endorsing the photocatalytic mechanism proposed. Furthermore, the high levels of photocatalytic activity achieved using SnO$_2@$_ZIF-8 suggest that SnO$_2$ far below the monolith surface, and not only that present at the external surface, must be intrinsically involved in the catalytic cycle.

We evaluated the chemical robustness of SnO$_2@$_ZIF-8 by PXRD and N$_2$ adsorption. PXRD patterns of the composite after 1, 5, and 10 photocatalytic cycles showed no significant variations from that of fresh composite (Figure 3). However, the adsorption isotherms of N$_2$ showed a small decrease in the BET area (Table 1; Figure 3c,d). We obtained similar values of BET area (Table 1; Figure 3c,d). We obtained similar values of BET area (Table 1; Figure 3c,d). We obtained similar values of BET area (Table 1; Figure 3c,d). We obtained similar values of BET area (Table 1; Figure 3c,d). We obtained similar values of BET area (Table 1; Figure 3c,d). We obtained similar values of BET area (Table 1; Figure 3c,d). We obtained similar values of BET area (Table 1; Figure 3c,d). We obtained similar values of BET area (Table 1; Figure 3c,d). We obtained similar values of BET area (Table 1; Figure 3c,d).

Industrial applications require that materials possess the mechanical strength and toughness to withstand the stresses of friction, cyclic compression, or vibration within a container. A useful nanoindentation technique to establish that the magnitudes of both the Young’s modulus, $E$, and hardness, $H$, of SnO$_2@$_ZIF-8 (3.0 ± 0.01 and 0.4 ± 0.01 GPa, respectively) were 10% greater than those of ZIF-8 (3.00 ± 0.01 and 0.41 ± 0.01 GPa, respectively), thereby rendering the composite structurally stiffer and more resistant to permanent deformation than pure ZIF-8 (Figures S14–S17, Supporting Information). This is likely attributable to the incorporation of the SnO$_2$-NPs leading to a greater packing efficiency of the primary particles.\cite{[33]}

The thermal stability of fresh and recycled SnO$_2@$_ZIF-8 was measured by thermogravimetric analysis (TGA) (Figure 5). We found that the decomposition temperature for SnO$_2@$_ZIF-8 (450–500 °C) is lower than that of ZIF-8 (600 °C). This is expected due to the NPs disrupting the coordination bonds within the MOF.\cite{[14]}

Initial weight losses of 2.5%, 4.0%, 4.5%, 4.5%, and 5.5% at 250 °C for mono-ZIF-8, fresh SnO$_2@$_ZIF-8, and SnO$_2@$_ZIF-8 after 1, 5, and 10 catalytic cycles, respectively, were seen (Figure S18, Supporting Information). As SnO$_2$ is very thermally stable, these initial weight losses were attributed to ethanol and water adhered to the pure NPs and trapped in the composite materials. Importantly, however, the thermal stability of the composite far exceeded the application temperature and was not reduced after recycling.

To assess the generalization of the encapsulation method, other catalytically active NPs were trialed in the formation of monolithic composites. CdSe and (Au@PdO)/TiO$_2$ were prepared using modified literature procedures\cite{[15–17]}

and successfully incorporated in mono-ZIF-8, forming structurally resilient composites (Figures S19 and S20, Supporting Information). Hence, for example, optical imaging shows a change in the color from transparent mono-ZIF-8 (Figure 1a) to deep red in CdSe@mono-ZIF-8, showing that the monolith has adopted the color of the NPs. The TEM microscopic image shows the homogeneous distribution of NPs in the MOF matrix, while the PXRD pattern confirms the crystallinity of the sample (Figure S19b–c, Supporting Information).

3. Conclusion

In summary, we report a chemically and mechanically robust composite in which SnO$_2$-NPs have been controllably integrated into a monolithic MOF without the need for binders, additives, or high pressures, so avoiding structural amorphization and pore collapse. SnO$_2@$_ZIF-8 has shown high levels of photocatalytic activity and extraordinary recyclability when compared to powdered NPs or previously reported NF@MOF composites. Furthermore, the straightforward synthetic method used led to the entrapment of NPs in a way that prevented catalyst leaching. The outstanding level of recyclability coupled with the unprecedented degree of dye degradation seen under high loading of the composite has proven SnO$_2@$_ZIF-8 to be a highly effective photocatalyst. The catalytic mechanism proposed involves the diffusion of water through the apertures of ZIF-8 before interaction with the photoactive NPs, exploiting the size selective properties of the MOF. This insight has inspired new avenues of
The mixture was transferred quantitatively (dropwise) to the stannic chloride solution until a pH of 12 was achieved. Zn(NO$_3$)$_2$·H$_2$O (0.293 g, 0.985 mmol) was dissolved in ethanol (20 mL). This was added separately in ethanol (20 mL), and NPs were added (30 mg). Both resulted mixture was stirred for 15 min at room temperature and then centrifuged (4250 rpm, 10 min). The collected solid was washed in ethanol (20 mL, three times) and the pellet dried at room temperature overnight, yielding a solid monolith. This was ground into 1–5 mm pieces before activation at 110 °C in a vacuum oven overnight.

4. Experimental Section

Synthesis of SnO$_2$ Nanoparticles: SnO$_2$-NPs were prepared following a modified literature synthesis.[16] SnCl$_4$·5H$_2$O (0.787 g, 2.24 mmol) was dissolved in water (15 mL). Sodium hydroxide (0.7 g, 17.5 mmol) was dissolved in water (20 mL) and ethanol (20 mL). This was added dropwise to the stannic chloride solution until a pH of 12 was achieved. The mixture was transferred quantitatively (~40 mL) to an autoclave and hydrothermally treated (200 °C, 24 h). After cooling, the resultant precipitate was separated and washed with water and 1:1 ethanol/water mix under centrifugation (7000 rpm). The washed sample was dried in a desiccator overnight, yielding SnO$_2$-NPs as a white powder.

Synthesis of NP@monoZIF-8 Monoliths: In a representative synthesis, Zn(NO$_3$)$_2$·6H$_2$O (0.293 g, 0.985 mmol) was dissolved in ethanol (20 mL). 2-Methylimidazole (C$_4$H$_5$N) (0.809 g, 9.85 mmol) was dissolved separately in ethanol (20 mL), and NPs were added (30 mg). Both solutions were ultrasonicated for 20 min before being combined. The resulting mixture was stirred for 15 min at room temperature and then centrifuged (4250 rpm, 10 min). The collected solid was washed in ethanol (20 mL, three times) and the pellet dried at room temperature overnight, yielding a solid monolith. This was ground into 1–5 mm pieces before activation at 110 °C in a vacuum oven overnight.

Supporting Information

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

Acknowledgements

J.P.M. and T.T. contributed equally to this work. This work was funded by an EPSRC IAA Partnership Development Award (RG/75759).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

catalyst recovery, composites, metal–organic frameworks, nanoparticles, photocatalysis