Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information for

Synthesis of Photocatalytic Pore Size-Tuned ZnO Molecular Foams

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Table S1: Table of conditions investigated in research for MolFoam production

Parameter	Initial condition	Preliminary findings	Final condition
Zinc source.	$Zn(Ac)_2$ used as Zn salt.	Issues of solubility and basicity lead to structurally weak foams.	Zn $(AcAc)_2$ selected as alternative Zn salt.
Use of surfactant	No surfactant used.	Foams shorter than reported here, very little porosity seen in MicroCT.	CTAB 5mM added to solution.
Flow rate of air	0.5 sL min^{-1}	Higher flow rates of air (0.5-, 0.25- sL min^{-1}) lead to faster evaporation of EtOH causing poor gelling and fragile foams.	0.1 sL min^{-1}
Calcination step	Foams calcined at 500 ^{o}C for 3 hours prior to sintering.	Calcining to remove organics unnecessary due to sintering and additional heating/cooling cycle leads to weaker foams	Calcination step removed, 12 hours sintering step only.
Sintering time	12, 15, 18, 20 hours sintering	Batch degradation experiments showed 20 hours sintering at 900 ^{o}C lead to greatest photocatalytic activity	900 ^{o}C ,20-hour sintering step
Sintering profile	Single step sintering process	Foams unsuitable for use within recirculating reactor.	Two step sintering condition adopted 1,000 ^{o}C ,0.5-hour + 900 ^{o}C ,20-hour
Sintering parameters	Two step sintering condition 1,000 ^{o}C ,0.5-hour + 900 ^{o}C ,20-hour	Multiple conditions (1,000 ^{o}C ,1 -hour + 900 ^{o}C ,20-hour / 950 ^{o}C ,0.5 - hour + 900 ^{o}C ,20-hour/ 950 ^{o}C ,1.0 - hour + 900 ^{o}C ,20-hour) analysed using degradation experiments, No significant change in degradation results, but original sintering conditions resulted in larger, more mechanically stable foams.	Two step sintering condition adopted 1,000 ^{o}C ,0.5-hour + 900 ^{o}C ,20-hour

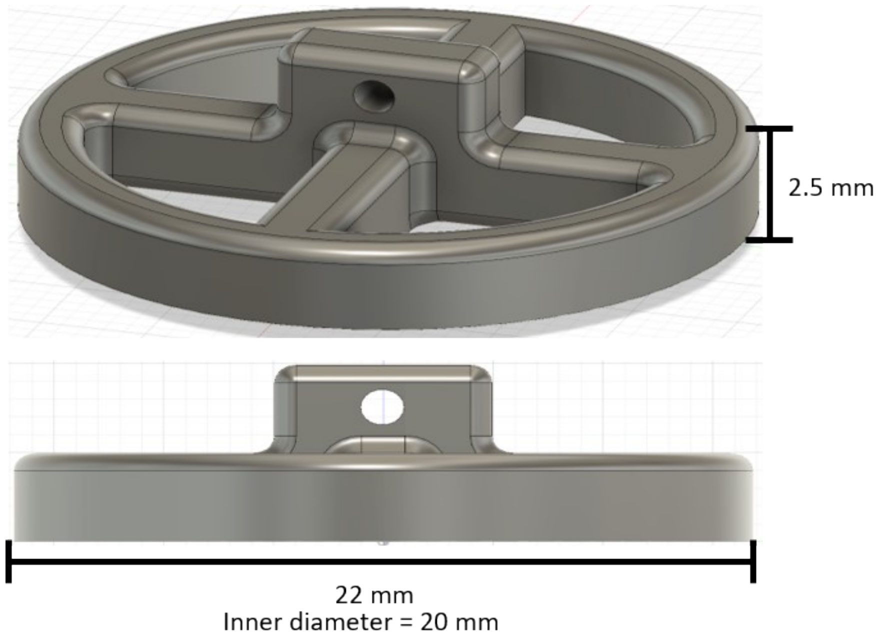

Figure S1: 3D model of printed buffer included inside reactor cartridges.

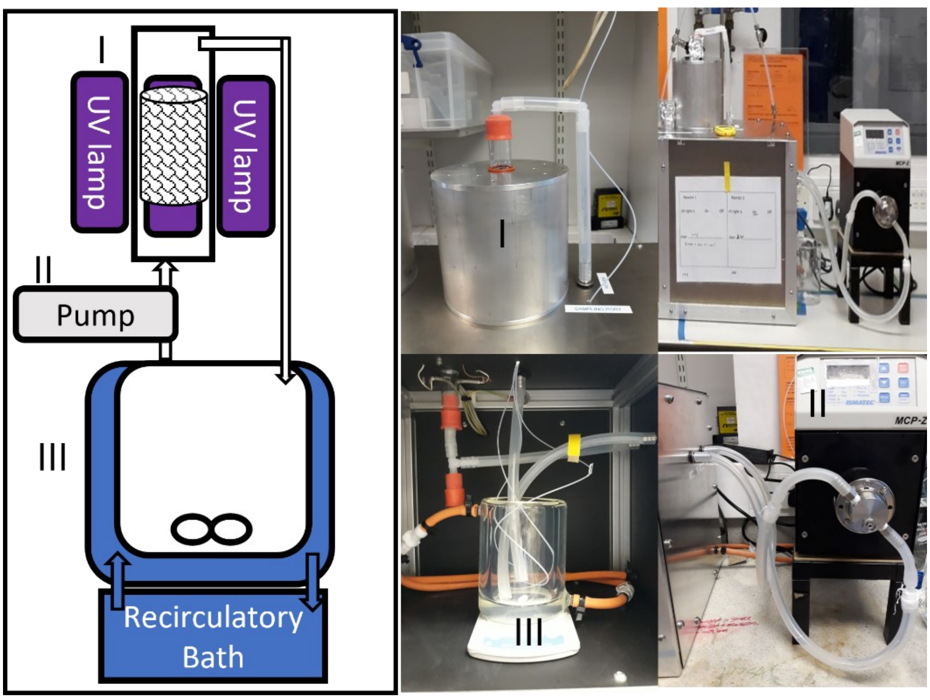

Figure S2: Schematic diagrams for recirculating photocatalytic reactors. Labelled are I) quartz tube containing foam surrounded by UV lamps, II) gear pump Ismatec, MCP-Z with a pump head Model GBS.P23.JVS.A-B1 and III) reservoir 500 mL)

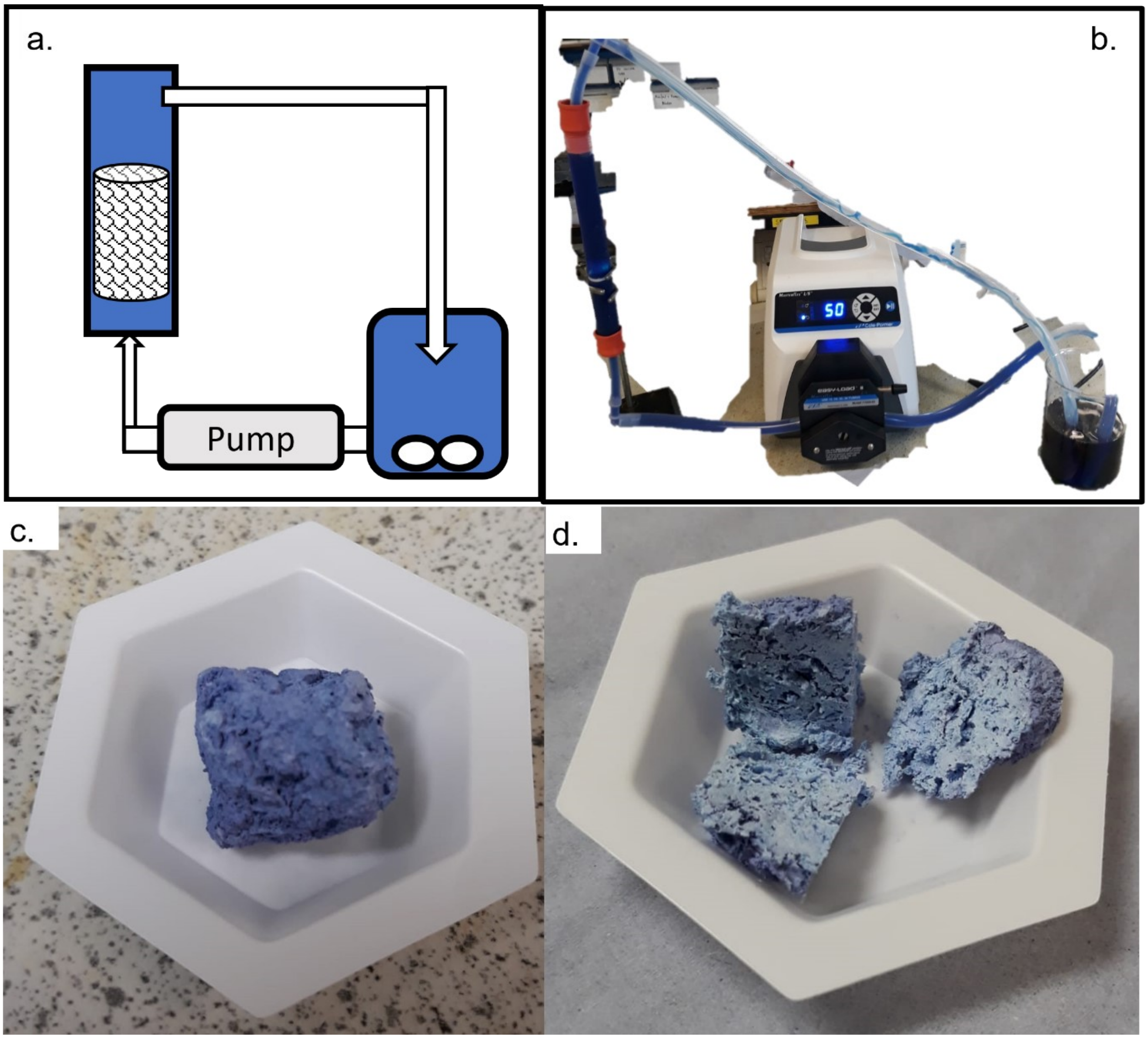

Figure S3: a) schematic diagram of bespoke dyeing rig to test dye uptake into MolFoam pores. b) photograph of dyeing rig in operation. c, d) A dyed MolFoam before and after being cut open.

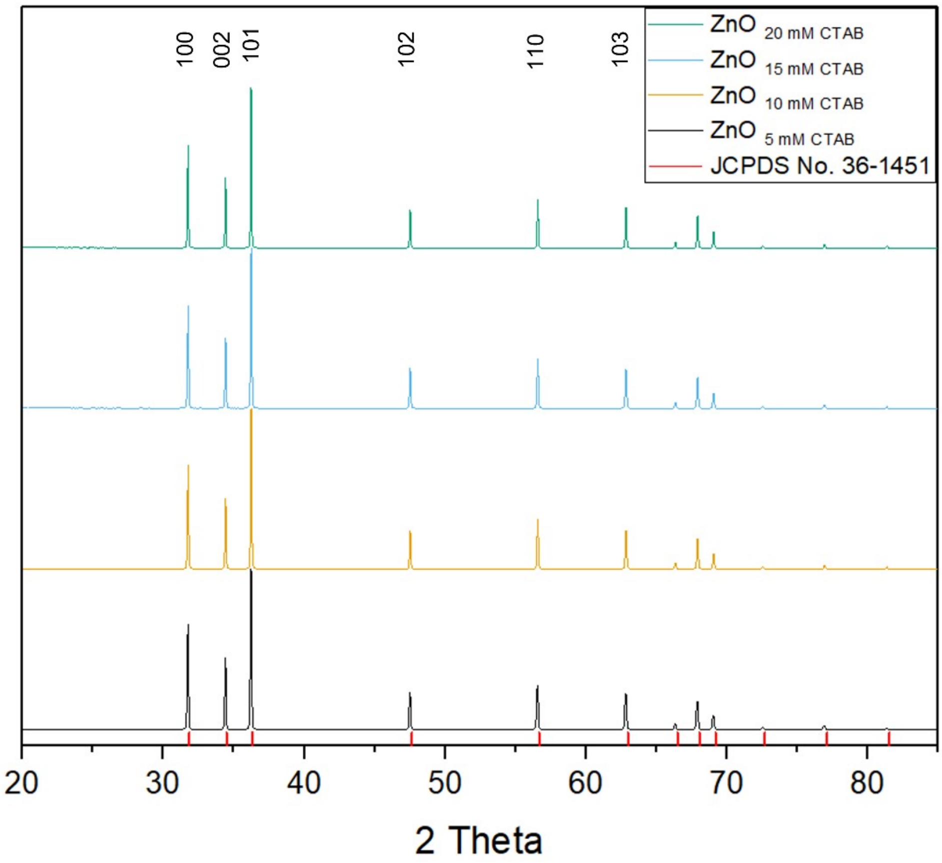

Figure S4: XRD pattern of ZnO MolFoams synthesised using different CTAB concentrations. Tick marks correspond to peaks reported from JCPDS No. 36-1451 [1]

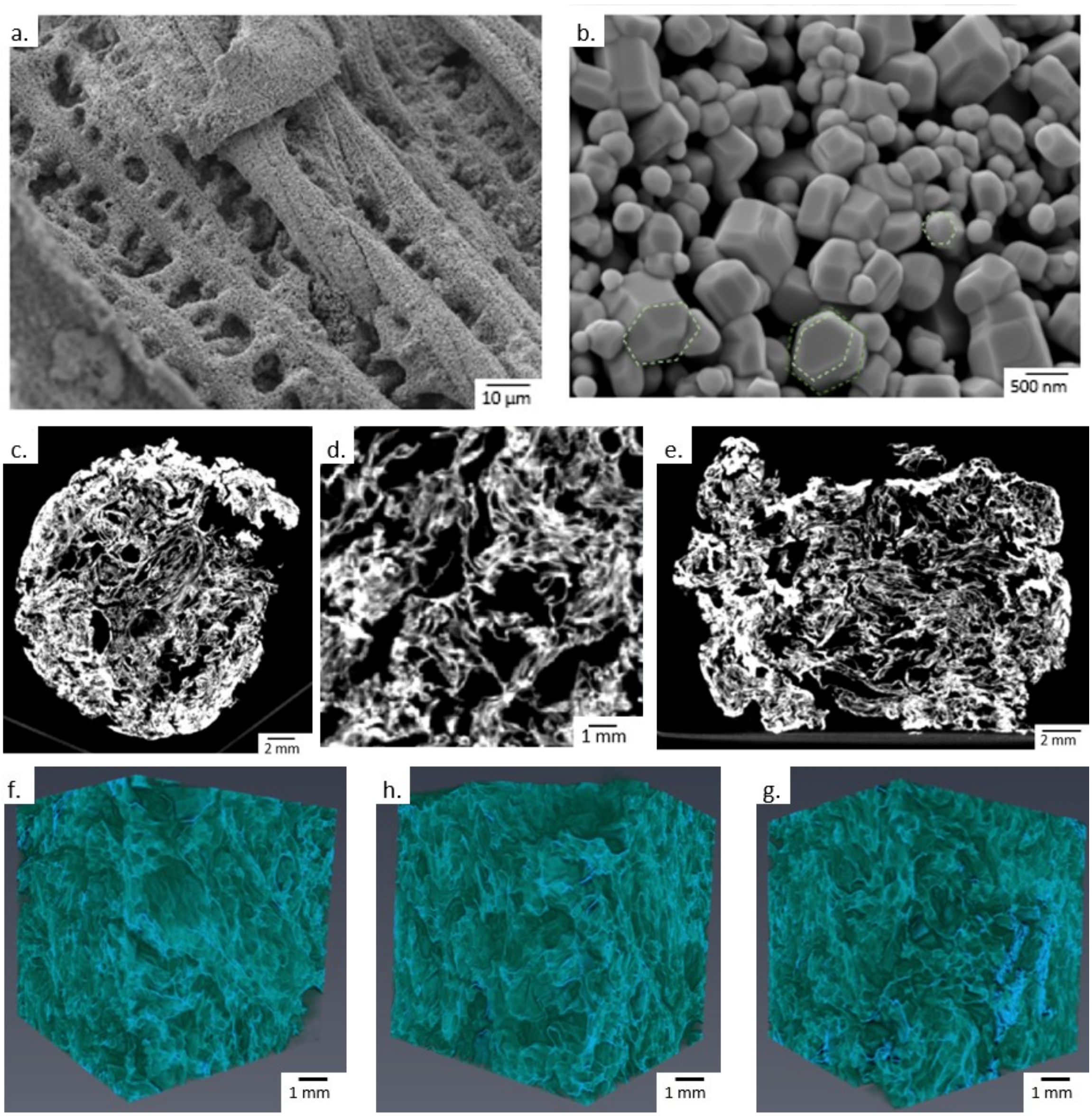

Figure S5 Various characterisations of ZnO MolFoams synthesised using 5 mM CTAB solutions a,b) FESEM c-e) MicroCT slices and f-g) 3D reconstructions based on MicroCT.

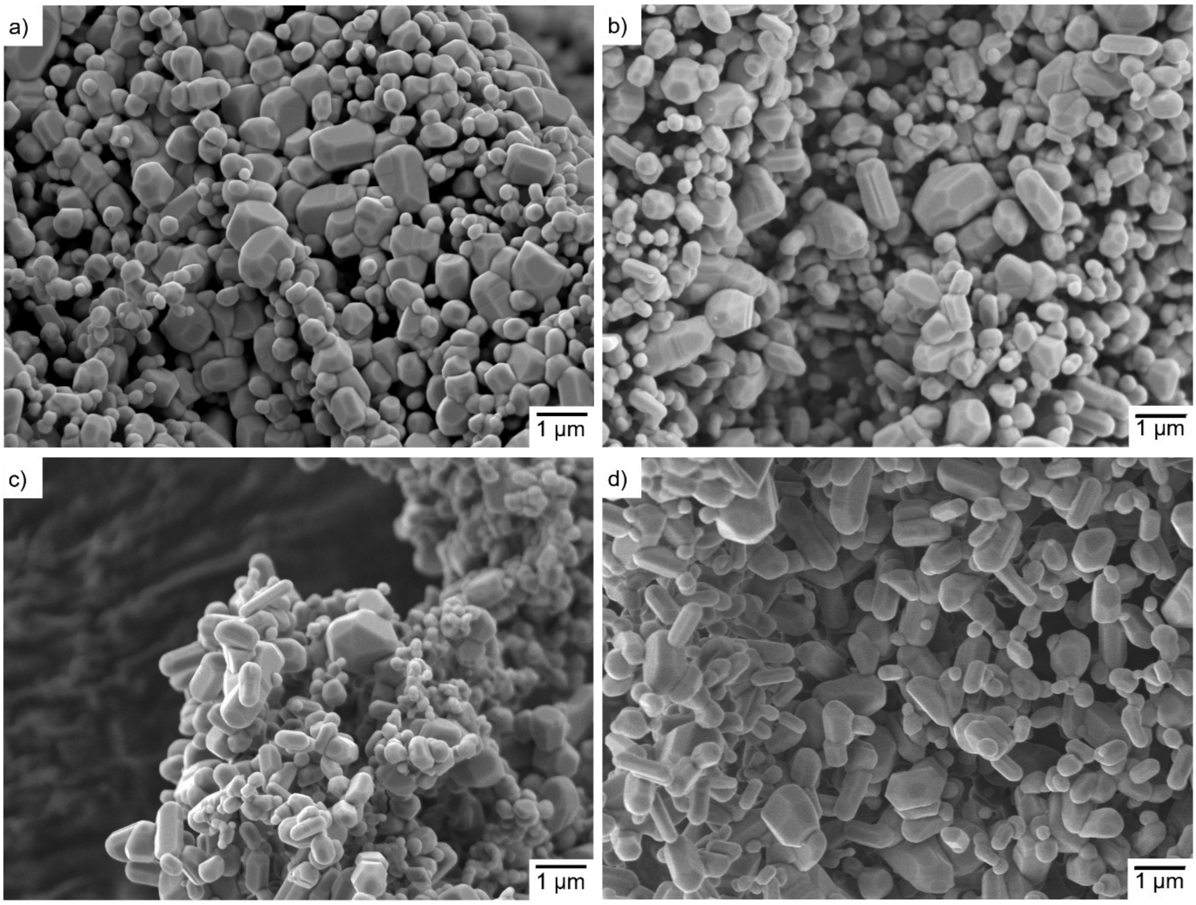

Figure S6: FE-SEM micrographs of ZnO MolFoams synthesised using a) 5mM, b) 10 mM, c) 15 mM and d) 20 mM CTAB solutions.

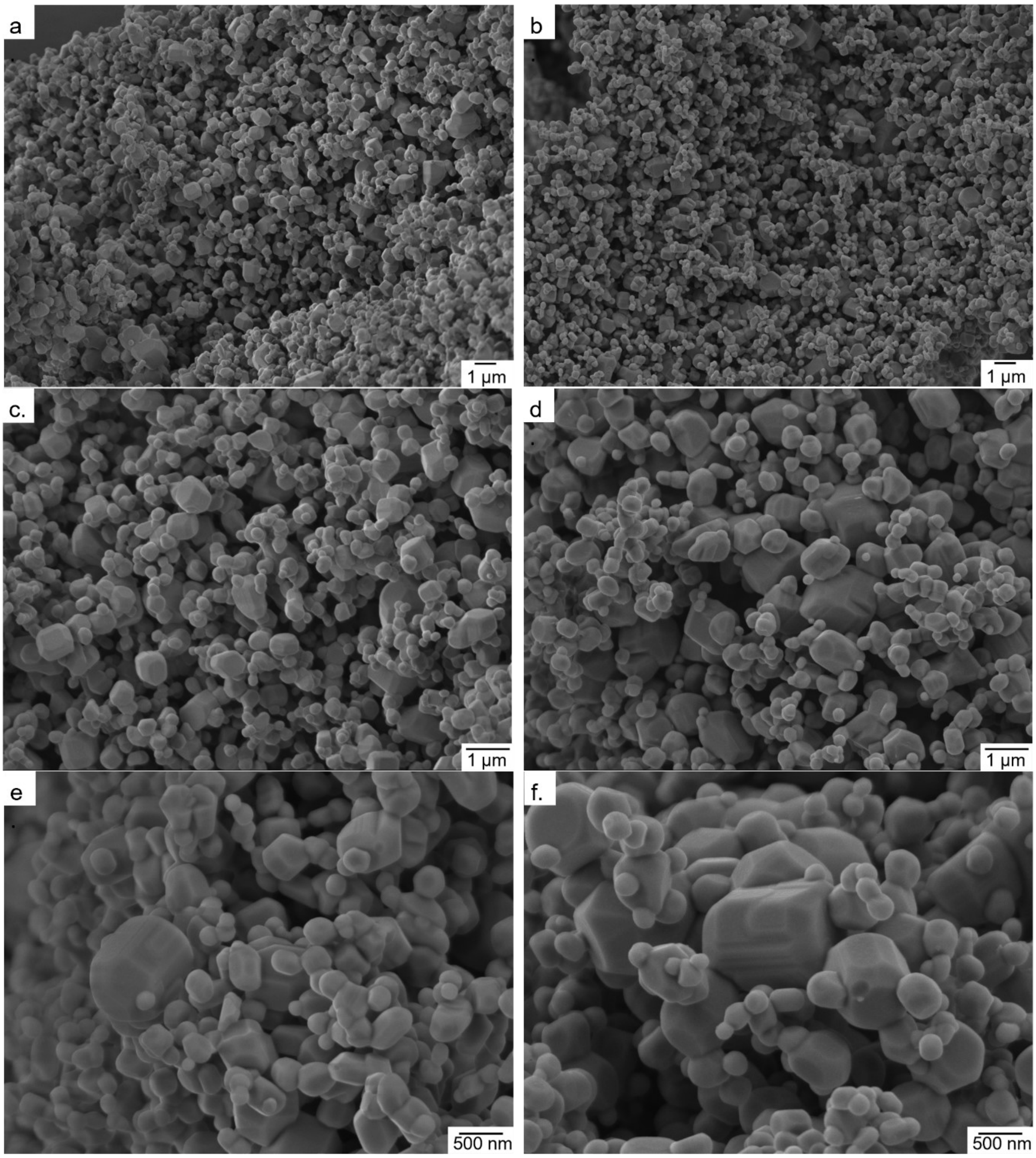

Figure S7: FE-SEM micrographs of ZnO MolFoams(a, c,e) before and (b,d,f) after application within reactor for photocatalytic CBZ degradation

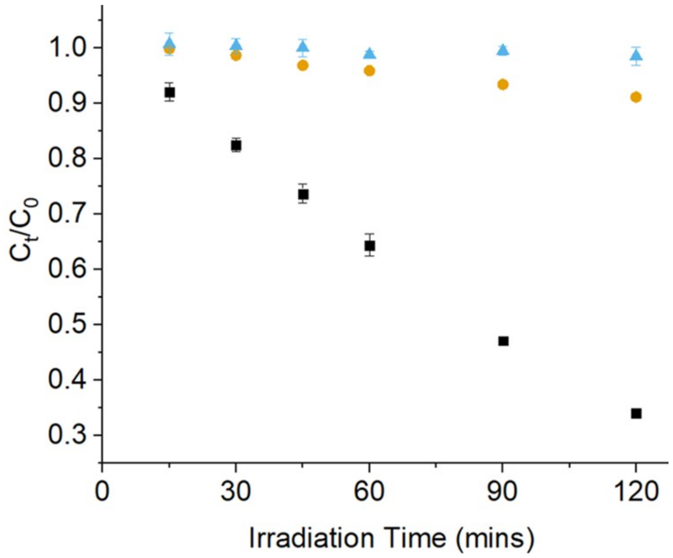

Figure S8: Removal of CBZ using MolFoams synthesised using 10 mM CTAB within a recirculating reactor operated at flow rate of 250 mL min⁻¹ [■ Photocatalysis , ● Photolysis , ◻ Adsorption].

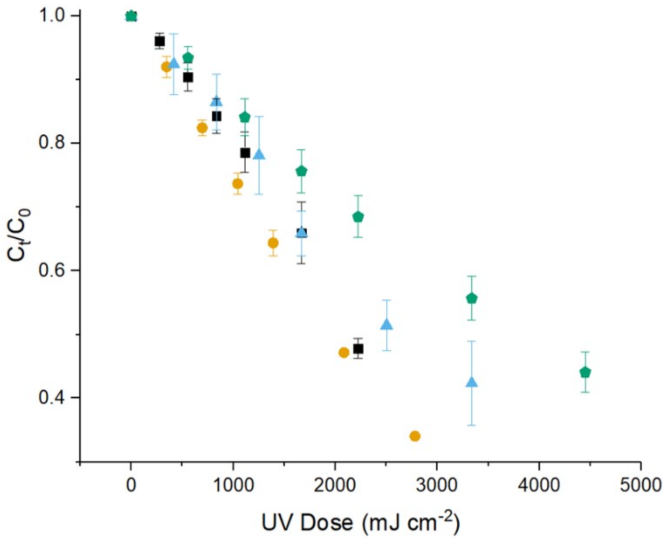

Figure S9: Photocatalytic degradation of CBZ using MolFoams synthesised using 10 mM CTAB within a recirculating reactor operated at various flow rates [■ 200 mL min⁻¹ , ● 250 mL min⁻¹ , ◻ 300 mL min⁻¹ , 400 mL min⁻¹]

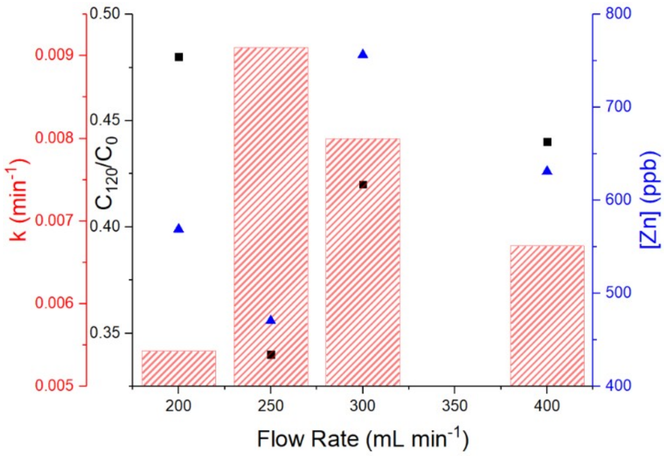

Figure S10: Comparison between ■ photocatalytic CBZ degradation after 120 mins, pseudo first order reaction kinetics (bar) and ◻ zinc concentration post PCA of MolFoam reactors operating at various flow rates.

Text S1. UV dose and quantum yield calculations

Within a recirculating reactor, the entire solution volume is not irradiated at any one time as with a batch reactor. The UV dose was calculated in equation S1 and the light attenuation calculated as shown in equation S2.[2]

$$UV\ Dose\ [\ mJ\ cm^{-2}] = \ Irradiation\ time\ [s] * I_{0\lambda} * (\tau * \frac{V_r}{V_0})\ [mW\ cm^{-2}] \quad \text{(S1)}$$

$$I_{\alpha\lambda} = \ I_{0\lambda}(1 - 10^{((\epsilon H_2O * [H_2O] + \epsilon CBZ * [CBZ])L)} \quad \text{(S2)}$$

Where $I_{0\lambda}$ is the incident light emitted by the UV lamps (mW cm^{-2}), τ is total residence time within the foam (s), V_r is the volume receiving UV dose within the foam per second (mL s^{-1}) and V_0 is the total volume of the reservoir (mL).

The measured light intensity was 10.4 mW cm^{-2}, τ was 4.5 seconds, V_r was dependent of flow rate and tabulated below, and V_0 was 500 mL. These conditions are exclusive to wavelengths of 254 nm only.

Table S2: Tabulation of V_r for corresponding flow rates.

Flowrate (mL min^{-1})	Volume of liquid exposed to UV within the foam per second (mL s^{-1})
100	1.67
200	3.33
300	5.00
400	6.67
500	8.33

Table S3: Tabulation of UV dose for recirculating reactors at various flow rates.

Time (s)	**UV Dose (100 mL min^{-1}) (mJ cm^{-2})**	**UV Dose (200 mL min^{-1}) (mJ cm^{-2})**	**UV Dose (250 mL min^{-1}) (mJ cm^{-2})**	**UV Dose (300 mL min^{-1}) (mJ cm^{-2})**	**UV Dose (400 mL min^{-1}) (mJ cm^{-2})**	**UV Dose (500 mL min^{-1}) (mJ cm^{-2})**
0	0	0	0	0	0	0
900	139	278	348	417	556	695
1800	278	556	695	834	1112	1391
2700	417	834	1043	1251	1669	2086
3600	556	1112	1391	1669	2225	2781
5400	834	1669	2086	2503	3337	4172
7200	1112	2225	2781	3337	4450	5562

The calculations for the quantum yield are based on the energy and photon flux of the system. [3]

Planck's equation was used to convert the energy value of the lamps into photon flux, Equation S3.

$$E_p = \frac{h * c}{\lambda} \quad \text{(S3)}$$

Where h is Planck's constant (6.626 X 10 $^{-34}$ J s), c is the speed of light (2.998 X 10 $^{-8}$ m s^{-1}) and λ is the wavelength of light (m) from the lamps used in these experiments. Considering the wavelength of 254 nm (2.54 X 10 $^{-7}$ m) from the light source in this study, the calculated energy was 7.82 X 10^{-19} J.

Using this, the number of photons can be calculated using Equation S4.

$$N_P = \frac{E}{E_P} \quad \text{(S4)}$$

Where E_p was calculated previously, E is the incident light intensity with attenuation (W m^{-2}). The number of photons was calculated to be 1.32 X 10 ^{20} (m^{-2} s^{-1}).

The photon flux can be determined as the ratio of number of photons (N_P, see above) and Avogadro's number (6.02 X 10 ^{23} mol^{-1}) The photon flux, calculated using Equation S5 was 2.19 X 10^{-4} mol m^{-2} s^{-1}.

$$E_{qf} = \frac{N_P}{N_A} \quad \text{(S5)}$$

Text S2. Photocatalytic reactor energy consumption calculations.

To assess the viability of scaling up of the system, the energy consumption of the reactor was accounted for by using the electrical energy per order (E_{EO}), defined as the kilowatt hours of electrical energy needed to decrease the concentration of a pollutant by an order of magnitude (90%) in one cubic metre of solution: [4]

$$E_{EO} = \frac{P * t * 1{,}000}{V(\log {}^{C_0}/_{C_t})} \quad \text{(S6)}$$

Where: P is the total power output of the 3 lamps onto the 12 cm long quartz tube (kW), t is the irradiation time (hrs) V is the volume of reservoir (L) and C_0 and C_t are the initial and final concentrations of pollutants respectively. As the foam occupied only a fraction of the quartz tube, the total power of the lamps, which act on the whole quartz tube, was multiplied by the volumetric fraction occupied by the foam (i.e. foam volume/quartz tube volume), to provide the effective power used for photocatalysis, considering that the contribution of photolysis is negligible. This is rendered necessary by the recirculating nature of the reactor, unlike a simple batch reactor, where the entire reservoir would be irradiated. In the present work, the external diameter of the foam corresponds to the internal diameter of the tube, so that the volumetric fraction is equivalent to the ratio of the foam's length to the total length of the quartz tube: 2 cm/12 cm = 0.17.

For the recirculating MolFoam reactors, three 5 W lamps were used, giving a P value of 15 X 10^{-3} kW, irradiation time was 120 minutes, volume of solution was 0.5 L, and the volumetric fraction 0.17.

Table S4: Degradation, pseudo-first order kinetics, quantum yield and E_{EO} data for MolFoams synthesised using 5 mM CTAB

Flow Rate (mL min^{-1})	C_{120}/C_0	k (X10^{-3}) (min^{-1})	$\Phi_{Overall}$	E_{EO} (KWh m^{-3})
100	0.64	4.18	0.32	49.84
200	0.54	4.45	0.34	39.71

300	0.54	5.77	0.44	37.37
400	0.43	6.24	0.48	27.28

Table S5: Degradation, pseudo-first order kinetics, quantum yield, zinc concentration and E_{EO} data for MolFoams synthesised using 10 mM CTAB

Flow Rate /mL min^{-1}	C_{120}/C_0	k (x10^{-3}) /min^{-1}	$\Phi_{Overall}$	[Zn] [ppb]	E_{EO} /KWh m^{-3} order^{-1}
200	0.48 ± 0.02	5.43 ± 0.36	0.41	569	31.37 ± 1.85
250	0.34 ± 0.01	9.08 ± 0.44	0.69	471	21.34 ± 0.59
300	0.42 ± 0.06	8.01 ± 0.41	0.61	757	26.54 ± 4.83
400	0.44 ± 0.03	6.74 ± 0.12	0.51	631	28.05 ± 2.45

Text S3. Hydrodynamics calculations.

Table S6: Hydrodynamic data and calculations for 5 mM CTAB foams

flow rate	flow rate	flow velocity	Re_{Dh}	Pe	Sc	Sh
(mL min^{-1})	(m^3 s^{-1})	(m s^{-1})				
100	1.67×10^{-6}	4.39×10^{-3}	3	4913	1.75×10^3	5
200	3.33×10^{-6}	8.77×10^{-3}	5	9826		7
250	4.17×10^{-6}	1.10×10^{-2}	7	12283		8
300	5.00×10^{-6}	1.32×10^{-2}	8	14739		9
400	6.67×10^{-6}	1.75×10^{-2}	11	19652		11
500	8.33×10^{-6}	2.19×10^{-2}	15	24565		12

Table S7: Hydrodynamic data and calculations for 10 mM CTAB foams

flow rate	flow rate	flow velocity	Re_{Dh}	Pe	Sc	Sh
(mL min^{-1})	(m^3 s^{-1})	(m s^{-1})				
100	1.67×10^{-6}	4.39×10^{-3}	2	4036	1.75×10^3	4
200	3.33×10^{-6}	8.77×10^{-3}	4	8071		6
250	4.17×10^{-6}	1.10×10^{-2}	5	10089		7
300	5.00×10^{-6}	1.32×10^{-2}	7	12107		7
400	6.67×10^{-6}	1.75×10^{-2}	9	16143		9
500	8.33×10^{-6}	2.19×10^{-2}	12	20179		10

$$Re_D = \frac{\rho Q D_p}{\mu A \varepsilon} \quad \text{(S7)}$$

$$Pe = \frac{u D_p}{D} \quad \text{(S8)}$$

$$Sc = \frac{\mu}{\rho D} \quad \text{(S9)}$$

$$Sh = 1.029 * Sc^{0.33} * Re_{D_h}^{0.55} * \left(\frac{L}{D_p}\right)^{-0.472} \quad \text{(S10)}$$

Where Q is the volumetric flow rate of the fluid, D_p is the macropore size of the foams, μ is the dynamic viscosity of the fluid, A is the cross-sectional area of the foam, ε is the porosity of the foam, u is the mean velocity of the fluid, D is the diffusion coefficient of Carbamazepine, [5, 6] ρ is the density of the fluid and L is the length of the foam. Re, Pe, Sc and Sh are the dimensionless numbers, Reynolds, Peclet, Schmidt and Sherwood.

Reynolds number for the foam system (Eq S7) was calculated as reported by Mohsen Karimian et al. [7]

Text S4. Comparison with literature.

Table S8: CBZ photocatalytic degradation kinetics for slurries and immobilised systems reported from literature.

Material	Photocatalyst	Degradation conditions	$[CBZ]_0$	Kinetics	Eeo	QY	Ref
ZnO	0.1 g L^{-1} NP suspension	Batch reactor 100 mL volume Temperature: 25 ºC Xenon Lamp, (5 KW, 5.5 W cm^{-2}, 6000 K, 483 nm)	50 mg L^{-1}	3.7 X 10^{-3}	46.48	0.0003	8
$ZnFe_2O_4$				36.7 X 10^{-3}	4.69	0.0020	
TiO_2	1.0 g L^{-1} NP suspension	Batch reactor 60 mL volume LED lamp (λ_{max} 417 nm, 450 W cm^{-2})	0.75 mg L^{-1}	4.7 X 10^{-3}		0.0050	9
$g\text{-}C_3N_4$				566.8 X 10^{-3}		0.60	
$g\text{-}C_3N_4/TiO_2$ composites	1.0 g L^{-1} NP suspension	Batch reactor 100 mL volume LED lamp (50 W, 475 nm)	10.0 mg L^{-1}	5.5 X 10^{-3}	187.09		10
N-doped TiO_2-SiO_2-Fe_3O_4	1.0 g L^{-1} NP suspension	Batch reactor 250 mL reactor Compact fluorescent lamp (9 W, 320 µW cm^{-2}, 365 nm)	2.0 mg L^{-1}	2.2 X 10^{-3}	188.24		11
TiO_2	57 mg L^{-1} NP supported on PVDF dual layer hollow fibre membrane	Recirculating reactor, flow rate 100 mL min^{-1}, 500 mL volume Hg lamp (40 W, 45.0 W cm^{-2}, 254 nm)	0.4 mg L^{-1}	22.1 X 10^{-3}	153.00	0.39	12
TiO_2	P25 commercial NPs dispersed in MeOH before electrospray onto steel mesh (2.5- X 5.0 cm)	Batch reactor 50 mL volume Six 4-W blacklight blue lamps (4 W, Sankyo Denki F10T8, Japan) 365 nm	2.4 mg L^{-1}	32.2 X 10^{-3}	395.48		13
TiO_2	TiO_2 films obtained through plasma electrolytic oxidation of Ti meshes (geometric area 327.5 cm^2)	Batch reactor 1,000 mL volume Lamp (30 W low-pressure Hg vapor UV-C, 254 nm.)	0.1 mg L^{-1}	17.9 X 10^{-3}	37.01		14
TiO_2	0.5 g L^{-1} NP suspension (P25)	Recirculating reactor, flow rate 83.3 mL min^{-1}, 1,000 mL volume A blacklight-blue lamp (HQPower Lamp15TBL, nominal power 15 W, 365 nm)	5.0 mg L^{-1}	23.4 X 10^{-3}	4.05		15
TiO_2	TiO_2 drop coated onto α-Al_2O_3 microfiltration membranes	Flow photocatalytic membrane reactor Volume 200 mL Xenon lamp(300 W, 76.7 mW cm^{-2})	1.0 mg L^{-1}	4.0 X 10^{-3}	2994.01	0.02	16
TiO_2	1.0 g L^{-1} NP suspension	Batch reactor 50 mL volume Hg Lamps (6 X 8 W, 1.6mW cm^{-2}, 365 nm)	12.0 mg L^{-1}	15.4 X 10^{-3}	191.01	0.25	17
ZnO				30.1 X 10^{-3}	624.49	0.49	
C- TiO_2	0.1 g L^{-1} NP suspension	Batch reactor 400 mL volume Tungsten lamp (150 W, 6.3mW cm^{-2}, 400 nm)	0.05 mg L^{-1}	2.3 X 10^{-3}	166.39	0.18	18
TiO_2	12.5 g L^{-1} NP supported on sand	Batch reactor 500 mL volume Xe high intensity lamp (55 W, 1.26 mW cm^{-2}, 475 nm)	5 mg L^{-1}	0.5 X 10^{-3}	12902.72	0.17	19
ZnO	1.5 g L^{-1} foam	Recirculating reactor, flow rate 250 mL min^{-1}, 500 mL volume Lamps (3 X 5 W, 10.3 mW cm^{-2}, 254 nm)	2.4 mg L^{-1}	9.1 X 10^{-3}	21.34	0.69	This work

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