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COMMUNICATION

Automated growth of metal-organic framework coatings on flow-through functional supports

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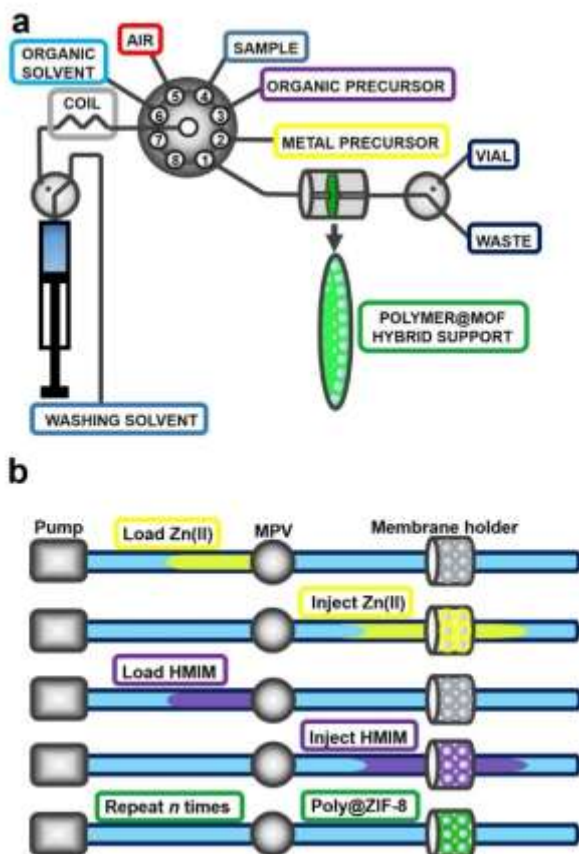
A fully automated method for the controlled growth of metal-organic framework coatings on flow-through functional supports is reported. The obtained hybrid flow-through supports show high performance for the automated extraction of water pollutants.

Metal-organic frameworks (MOFs) are an emerging class of highly porous materials based on the coordination of metal ions or clusters with organic ligands.¹ Due to their easily tunable structures, high surface area and permanent and well-defined porosity, MOFs have been widely investigated during the previous years for gas storage² and separation³, catalysis⁴, and drug delivery and sensing.⁵ Recently, MOFs have shown a great potential for analytical applications such as separation, sampling and analyte enrichment.⁶ In order to improve the performance of metal-organic frameworks in analytical applications, the preparation of MOF-based hybrid materials, such as MOFs contained in flow-through devices is desirable. Up to date, flow-through MOF-based composite materials have been applied satisfactorily for the purification of biomolecules,⁷ or as stationary phases for high-performance liquid chromatography.⁸ Many of the previous examples are based on directly embedding the MOF crystals in a polymer or silica matrix,^{8c-g} which makes difficult to obtain homogeneously distributed hybrid materials. In-situ MOF synthesis on a functional support is also difficult due to the lack of control over the growth of the coating, leading to non-homogeneous films.⁹ Improved results are obtained by immersing a self-assembled monolayer (SAM) in aged precursor solutions containing both, the metal and the organic ligand,¹⁰ or by implementing a layer-by-layer (LBL) approach based on liquid phase epitaxy.¹¹ The LBL approach is based on the sequential immersion of the SAM in the metal and the organic ligand precursor solutions, enabling a precise control over the growth of a uniform MOF thin film. Apart from flat substrates, the LBL approach has been implemented for the incorporation of MOFs into porous polymer monoliths,^{7d} mesoporous silica foams,¹² polymer or silica micro- and nanospheres,^{7a,13} silica spheres with magnetic cores,^{7c,14} and metallic micro- and nanoparticles.^{7a,15} In order to improve the control over the growth and distribution of the MOF coating, the LBL approach on SAMs has been automated by the computer-controlled spraying of the precursor solutions,¹⁶ exploiting digital microfluidics,¹⁷ and using a robot for the batch immersion of the

SAM into the precursor solutions.¹⁸ However, these methods are only applicable to planar surfaces, while in many important applications the use of a flow-through support is advantageous. Moreover, the use of flow chemistry for the preparation of advanced materials is an expanding field,¹⁹ including the continuous-flow preparation of MOFs,²⁰ or their incorporation into hollow fibers and tubular membranes,²¹ although as far as we know, it has not been exploited yet for the preparation of hybrid flow-through separation devices containing them.

Herein we report a new automated mesofluidic approach for the controlled growth of MOF coatings on flow-through supports. The developed approach is described for the preparation of the Zeolitic Imidazolate Framework-8 (ZIF-8)²² on different functional supports and is likely to be adapted to the growth of other MOFs and coordination polymers on different functional surfaces. We also demonstrate the utility of the prepared ZIF-coated hybrid supports as advanced sorbents for the extraction and preconcentration of environmental organic pollutants.

Using the fully-automated sequential injection analysis²³ system shown in Scheme 1, we control the growth of the ZIF-8 on a flow-through functional support (Polymer@ZIF-8).²⁴ The use of this system enables the sequential and bidirectional precise control of the flow, decreasing the consumption of reagents and solvents and increasing the versatility and the number of possibilities for controlled flow manipulation. A multiposition valve (MPV) interfaces the different reagents involved in the process and the flow-through holder containing the functional support (Scheme 1a), while the different fluids are precisely manipulated using a bi-directional syringe pump hyphenated to a 3-way valve. The metal and the organic precursor solutions are sequentially loaded into a coil, and subsequently injected through the functional support using a LBL approach (Scheme 1b). The excess of non-retained precursors are removed by washing the support with an excess of the solvent contained in the syringe. The detailed parameters of the automated procedure are available in Table S1 (ESI). Under the selected working conditions, a complete ZIF-8 cycle is accomplished in approximately 5 min and requires the use of 2.4 mL of solvent.



Scheme 1 a) Illustration of the developed instrumental approach for the flow-based automation of the growth of supported MOF coatings. b) Scheme of the developed sequential flow method for the LBL growth of ZIF-8 on a functional polymeric support.

After a careful optimization of the operational parameters, treatment of a flow-through support with the automated coating procedure using methanolic solutions of zinc nitrate (100 mmol/L) and 2-methylimidazole (HMIM, 50 mmol/L) resulted in the formation of a uniform ZIF-8 layer. Fig. 1a shows the XRD diffraction patterns of the polymeric support before and after a different number of growth cycles. It can be observed that the original peaks from the polymeric support gradually disappear indicating the progressive coating of the support. After only 25 cycles, the peaks corresponding to the polymeric substrate have almost fully disappeared and the X-ray diffraction lines of the ZIF-8 structure are already observable, suggesting the rapid coating of the beads forming the support with a thin film of coordination polymer. The low intensity of the ZIF-8 X-ray diffraction pattern at this point is probably due to the lack of sufficient network periodicity at this stage. After 75 cycles, all the diffraction peaks present in the diffractogram correspond to the ZIF-8 structure, confirming the presence of a crystalline and highly ordered ZIF-8 film formed by randomly oriented crystallites with the same structure as observed for the bulk ZIF-8. Up to 190 deposition cycles were performed satisfactorily without apparent back pressure or clogging of the flow-through support. The successful coating of the surface was also confirmed by FTIR microscopy. The spectrum showed the typical bands of the ZIF-8 metal-organic framework

while the infrared absorption bands from the support were practically absent (Fig. S1, ESI).

A larger number of cycles was required in order to fully cover the support with ZIF-8 when more diluted precursor solutions are used (see Fig. S2, ESI). However, the use of higher concentrations does not lead to a further improvement for the growth of the ZIF-8 coating. Crystalline ZIF-8 coatings were also obtained using a sulfonic acid-functionalized polymer support (Fig. S3, ESI), showing that the developed approach is implementable to other functional supports.

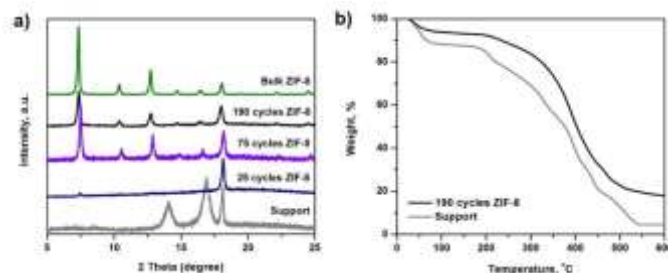


Fig. 1 a) XRD patterns of pure ZIF-8 crystals (see ESI for synthesis details) and of the support before and after 25, 75 and 190 cycles of coating with Zn(II) and Hmim solutions. b) TGA curves of the support before and after 190 coating cycles. Precursors: 100 mmol/L Zn(II) and 50 mmol/L Hmim. Solvent, methanol.

To measure the Zn(II) loading, thermogravimetric analysis (TGA) in air of the polymeric support with or without a ZIF-8 coating were performed. Fig. 1b shows the TGA curves of the polymeric support before and after 190 ZIF-8 growth cycles. The first weight loss, below 373 K, corresponds to the removal of the remaining solvent in the support, while the next gradual weight loss, between 473 and 823 K, is attributed to the combustion of the polymer support and the HMIM present in the case of the hybrid support. The weight of the residue at 873 K gradually increased with the number of growth cycles of ZIF-8 (Fig. S4, ESI), reaching a value of 13.7% after 190 cycles, an increment which is attributed to the formation of ZnO²⁵ as a result of the combustion of the metal-organic framework.

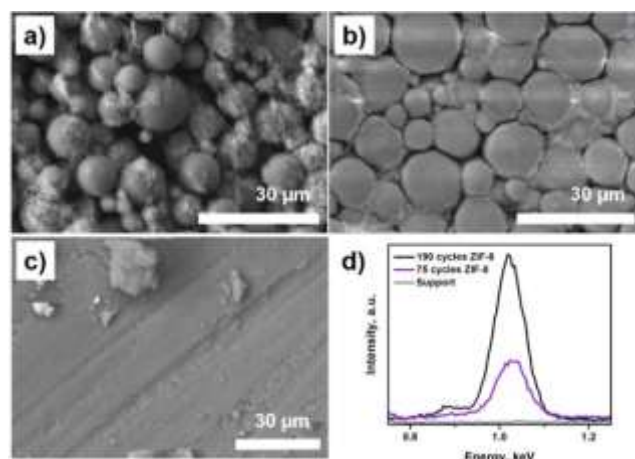


Fig. 2 SEM images of the surface of the support a) before and b) 75 and c) 190 coating cycles. d) EDS results showing the Zn peak at 1.012 KeV of the support before and after 75 and 190 coating cycles.

Fig. 2 shows the SEM images of the bead-based polymeric support before (Fig. 2a) and after 75 and 190 growth cycles of ZIF-8 (Fig. 2b and 2c). It can be observed that, after 75 cycles, the beads of the support are fully coated with a layer of ZIF-8 maintaining their original spherical morphology (Fig. 2b). An increment of the number of cycles allows the complete coating of the surface of the support with a uniform film of metal-organic framework with no evident visible defects (Fig. 2c and S5). The presence of Zn on the polymeric substrate was detected using energy dispersive X-ray spectroscopy (EDS), which showed an increase of the Zn loading with the number of growth cycles of ZIF-8 (Fig. 2d).

As a proof of concept of application of the automatically prepared hybrid supports, their performance for the extraction and preconcentration of trace amounts of 6 phthalate esters, catalogued by the US Environmental Protection Agency as priority environmental pollutants (chemical structures shown in Fig. S6, ESI), was evaluated. Low-levels of phthalate esters in water were enriched simultaneously on the solid support, attaining a higher or lower enrichment factor on depending of their affinity to the solid-phase materials. The same mesofluidic platform developed for the preparation of the hybrid supports was used for the automated solid-phase extraction of the mixture of phthalate esters (see method in Table S2, ESI). Additional ports of the MPV were used to load the aqueous sample, air,²⁶ and an organic solvent (employed for the elution of the preconcentrated targets) into the system. After elution from the support, the eluate was injected into a GC-MS for the separation and quantification of the targets.

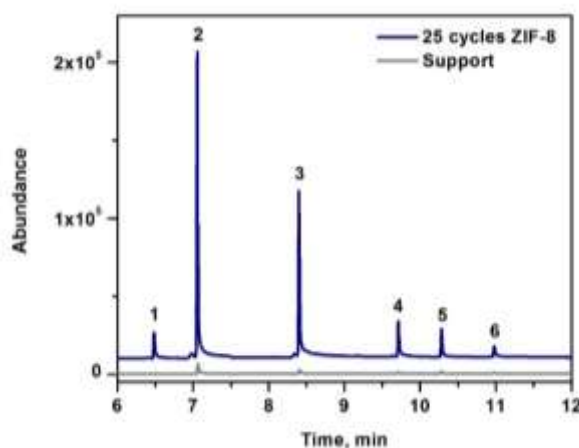


Fig. 3 GC-MS chromatograms of a mixture of 6 phthalate esters at a 20 µg/L level after extraction using a support before and after 25 coating cycles. Peaks: 1) dimethyl phthalate; 2) diethyl phthalate; 3) di-n-butyl phthalate; 4) Bis(2-ethylhexyl) phthalate; 5) butyl benzyl phthalate; 6) di-n-octyl phthalate.

Best results were obtained when coating the support with a thin layer of ZIF-8, maintaining its excellent flow through properties but ensuring a sufficient surface coverage of the support to modify its adsorption affinity towards the analytes. In Fig. 3, the GC-MS chromatograms (experimental conditions detailed in the ESI) corresponding to the preconcentration of the six phthalate esters using an unmodified support and a modified support after 25 coating cycles are shown. Using an unmodified support a certain preconcentration degree of up to 30-fold was obtained for the more hydrophobic phthalate esters. Much better results were obtained when using the coated support as shown by the increase in the peak intensity of the 6 phthalate esters in the corresponding

chromatogram. The increment was especially significant in the case of the more hydrophobic phthalate esters, for which enrichment factors up to 500 were achieved. We attribute this improvement in the extraction performance of the coated support to an increment of the adsorption affinity between phthalate esters and the surface of the support after coating it with the hydrophobic ZIF-8 metal-organic framework, although the contribution of other factors, such the presence of network defects, inherent to the step-by-step preparation approach, specially when a small number of growth cycles is performed, cannot be discarded.

In summary, ZIF-8 coatings have been engineered in flow through supports in a completely automated manner. The proposed approach is based on a computer-controlled sequential mesofluidic platform, which enables the precise control over the growth of metal-organic framework coatings. The developed hybrid supports have showed a high performance towards the automated extraction and preconcentration of trace levels of mixtures of environmental organic pollutants. The time and volume of organic solvent required per cycle can be further minimized by the careful optimization of the coating conditions, and the procedure can be easily implemented to the growth of other MOFs and coordination polymers on different functional surfaces.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Materials, instrumentation, procedures and additional figures and tables. See DOI: 10.1039/c000000x/

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