Patterned growth of zeolitic imidazolate frameworks by solvent-free transformation of preprinted metal oxide patterns

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Zeolitic imidazole frameworks (ZIFs) are among the most studied metal-organic frameworks because of their mild synthesis conditions, high chemical and thermal stability and interesting characteristics for diverse applications. To realize the potential of ZIFs beyond typical gas storage and separation applications, in which they are typically employed as a bulk material, shaping and deposition methods are needed. One of the first steps in the systematic fabrication of ZIF-based devices is the deposition of patterned thin films of ZIFs on a substrate. Until now, Spatially controlled film growth to coat only the active region of for instance a sensor has only been performed via selective surface functionalization of the support (e.g. thiol-based SAMs on a gold-coated substrate). The use of simple cover masks without chemical modification of the surface is not feasible for current Zn-salt solution-based growth methods. Here it is demonstrated how spatially controlled deposition of zinc oxide (ZnO) and subsequent conversion to ZIFs is a straightforward route to patterned ZIF films applicable to diverse substrates without the need for chemical modification. Patterned ZnO deposition can be performed using various techniques such as atomic layer deposition or calcination of precursor patterns (deposited by e.g. inkjet printing, stamping or spin coating in the presence of a cover mask). In this study, ZIF-8 (Zn(2-methylimidazolate)$_2$) patterns were synthesized by localized solvent-free transformation of ZnO patterns on glass, alumina and silicon wafer supports. This transformation was performed by bringing the ZnO patterns in contact with melted 2-methylimidazole. Because of the insolubility of the ZnO precursor in the melted ligand, the ZnO patterns are successfully transformed into ZIF-8 patterns with high fidelity. It is hypothesized that the good adhesion of the ZIF crystals to the supports is the result of the existence of a thin ZnO layer which connects the two.

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