Magnetic Cores with Porous Coatings: Growth of Metal-Organic Frameworks on Particles Using Liquid Phase Epitaxy

*Martin E. Silvestre, Matthias Franzreb, Peter G. Weidler, Osama Shekhah, and Christof Wöll**

A novel method for the homogeneous coating of magnetic nanoparticles with metal organic frameworks (MOFs) is reported. Using a liquid phase epitaxy process, a well-defined number of $[Cu_3(btc)_2]nH_2O$, HKUST-1, layers are grown on COOH terminated silica magnetic beads. The structure and porosity of the deposited MOF coatings are studied using X-ray diffraction and BET analysis. In addition, size and shape of the fabricated composites are analyzed by transmission electron microscopy. Potential applications of particle based MOF films include catalytic coatings and chromatographic media.

1. Introduction

Metal-organic frameworks (MOFs) are highly ordered porous materials which have attracted a great interest due to their tunable pore structures and chemical functionalities.[1] This novel class of hybrid materials has been used for the storage[2] and separation[3] of gases, in catalysis,[4] sensor technology[5] and drug delivery.[6] MOFs consist of organic ligands and metal or metal-oxo nodes and are formed using solvothermal processes at elevated temperatures. For a number of applications, homogeneous dense and pinhole free coatings are required, for example, with regard to membranes, sensors or for electrochemical applications. Since the typical powder materials resulting from the conventional solvothermal synthesis process are not well suited for fabricating high-quality coatings, recently, a liquid phase epitaxy (LPE) process has been introduced to the field of MOFs by Shekhah et al.[7] Using an appropriately functionalized organic surface as a (two-dimensional) nucleation template and adding in a step-by-step fashion the organic ligand and the metal precursor yields crystalline, oriented and homogeneous films of HKUST-1 with exceptionally high quality.

The LPE process is not restricted to planar substrates but can, in principle, be applied to any solid particle. This will be demonstrated in the present paper by coating magnetic nanoparticles with surface-attached metal-organic framework multilayers (SURMOFs). MOF coated nanoparticles are particularly interesting for a large variety of applications, e.g., catalytic or chromatographic applications as well as tumor therapies.[8] When nanoparticles are used for catalytic or sorptive applications, the suspended nanoparticles normally have to be separated from the suspension by centrifugation or filtration in order to

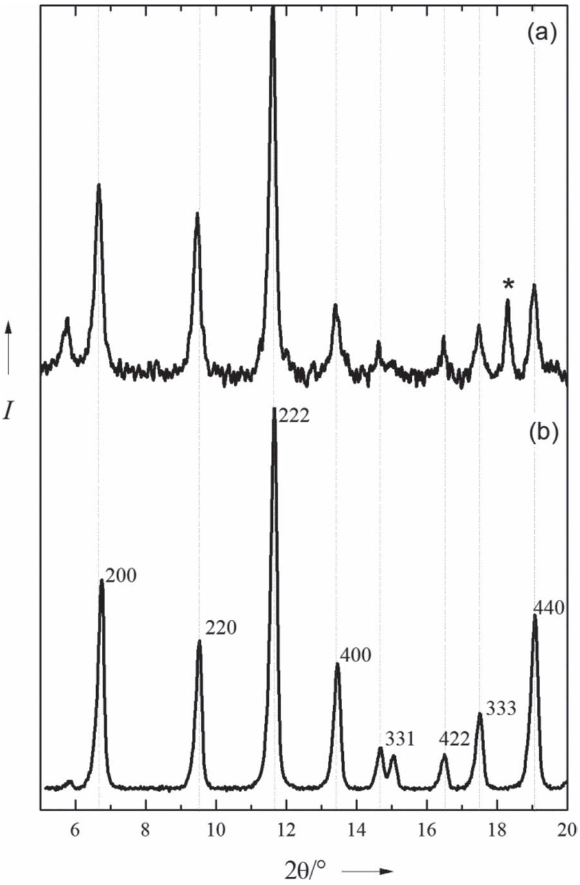

Figure 1. XRD data for: a) HKUST-1 grown on COOH terminated magnetic nanoparticles and b) HKUST-1 bulk; ∗ denotes the Fe_3O_4 (111) Bragg-peak (Cu Kα1,2).

Dr. M. E. Silvestre, Prof. M. Franzreb, Dr. P. G. Weidler, Dr. O. Shekhah, Prof. C. Wöll
Institute of Functional Interfaces
Karlsruhe Institute of Technology
Herrman-von-Helmholtz-Platz 1,
76344 Karlsruhe, Germany
E-mail: christof.woell@kit.edu

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be regenerated or recycled. An elegant way to avoid this time consuming and costly processes is to use magnetic nanoparticles together with magnetic separation techniques. Magnetic separations are fast, scalable and easily automated,[9] which is why they this technology has received considerable attention in recent years. A number of successful applications have been reported, including minerals processing, wastewater treatment, molecular biology, cell sorting and clinical diagnostics.[10]

The first incorporation of magnetic particles into porous MOFs was reported by Lohe et al.[11] Three different types of MOFs (Al-based DUT-4 and DUT-5, HKUST-1) were synthesized from solutions to which superparamagnetic nanoparticles were added. As a result of the fairly low (≈15 wt%) content, the magnetic saturation of the resulting composite particles falls below 35 A m^2 kg^{-1}, a value which is too low for straightforward applications in industrial magnetic separators.[12]

Herein, we introduce a novel class of highly defined magnetic MOF (magMOF) core/shell nanoparticles where the MOF coating is very homogeneous and of the same, well-defined thickness for all particles. The method is based on a modification of the LPE process described above and is demonstrated here for the case of HKUST-1. For coatings with other types of MOFs the reader is referred to the Supporting Information. The crystalline structure of the MOF coatings deposited on the magnetic nanoparticles is demonstrated using X-ray diffraction (XRD). In addition, particle shape and morphology were investigated with electron transmission microscopy (TEM), while the magnetic properties of the magMOF particles were analyzed by the use of an alternating-gradient magnetometer (AGM), the porosity and pore size distribution were studied using BET analysis. Finally, we provide a proof-of-concept for the use in chromatography by filling a small high-pressure liquid chromatography (HPLC) column with magMOF nanoparticles and then separating different organic molecules such as toluene, xylene,[13] and pyridine.[14]

2. Results and Discussion

In **Figure 1** we compare typical XRD data for HKUST-1 magMOF particles prepared using 60 cycles of the LPE method (Figure 1a) with data for HKUST-1 powder particles fabricated by the conventional solvothermal process.[15] The XRD patterns clearly demonstrate the success of the adapted LPE method; clearly MOF material has been deposited on the magnetic nanoparticles. The reflection at $2\theta = 18.3°$ is characteristic for the magnetite (Fe_3O_4) core of the magMOF particles. The magnetite nanoparticles exhibit the characteristic octahedral shape (shape (**Figure 2**a,b), after applying the LPE process a more transparent shell of uniform thickness corresponding to the MOF material is visible (Figure 2c). The observed thickness after 40 LPE-cycles amounts to between 20 and 25 nm, corresponding to 0.5–0.6 nm per cycle. Although this value is close to the theoretically predicted LPE growth thickness along the [100]-direction of HKUST-1, this is only half the value normally observed for the growth of HKUST-1 SURMOFs applying the LPE method[16] and clearly much less than the value of around 10 nm per cycle which was recently observed when growing SURMOFs by a sequential spray process.[17]

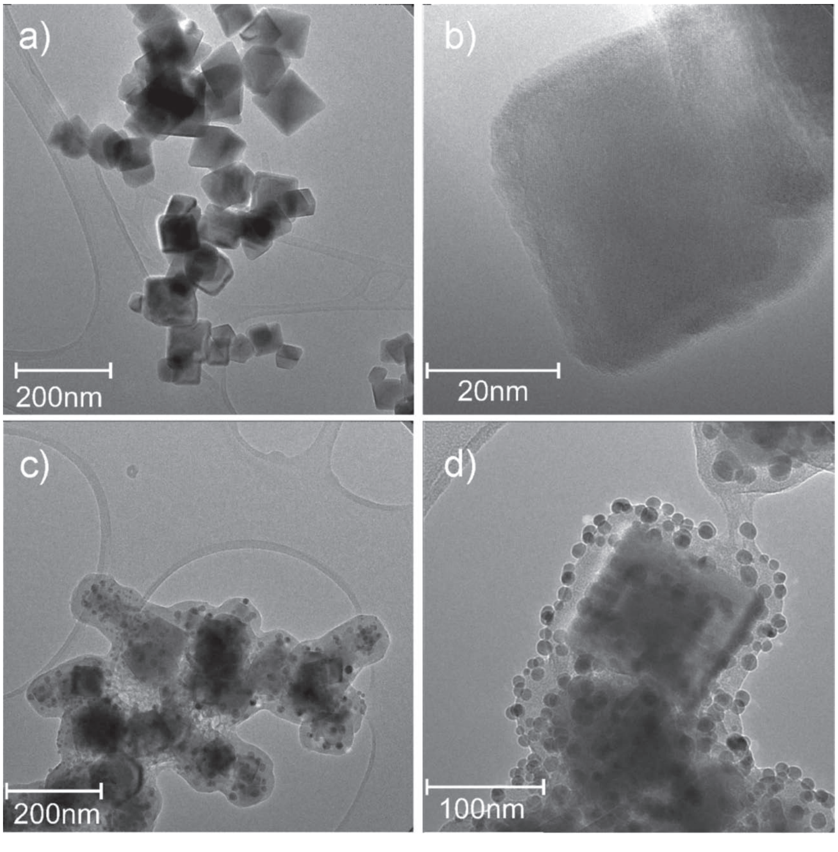

Figure 2. TEM pictures of pure MagPrep Silica nanoparticles (a,b) and HKUST-1 grown on COOH terminated MagPrep Silica after 40 cycles of the LPE method (c,d).

TEM images recorded at higher magnifications (Figure 2d) show that the transparent MOF coating contains additional small particles with sizes of about 10 nm. These particles are most likely CuO particles resulting from electron induced beam damage.

One of the most characteristic features of MOFs is their extraordinarily large specific surface area and their narrow pore size distribution, which can be determined in a straightforward fashion by BET.[18] A corresponding characterization of the magMOF particles using a non-local-density functional theory (NLDFT) equilibrium model[19] clearly shows the expected increase of surface area with the number of deposition cycles. The uncoated MagPrep silica particles possess a specific surface area of about 17 m^2 g^{-1}. With increasing numbers of LPE-cycles the specific surface area of the magMOF particles increases from 17 m^2 g^{-1} until it approaches the HKUST-I bulk value of around 1150 m^2 g^{-1} (200 cycles). The solid line in **Figure 3** was computed for a simplified core-shell model assuming a spherical shape, a core size of

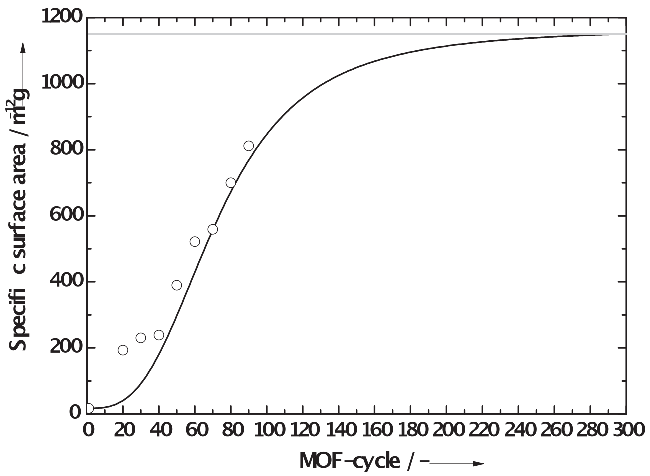

Figure 3. Brunauer–Emmitt–Teller (BET) analysis using a non-local-density functional theory (NLDFT) equilibrium model of HKUST-1 magMOFs generated by different numbers of LPE cycles. Specific area as a function of the number of cycles (O), calculated specific surface area of HKUST-1 magMOF (black line) and measured pure HKUST1 bulk (gray line).

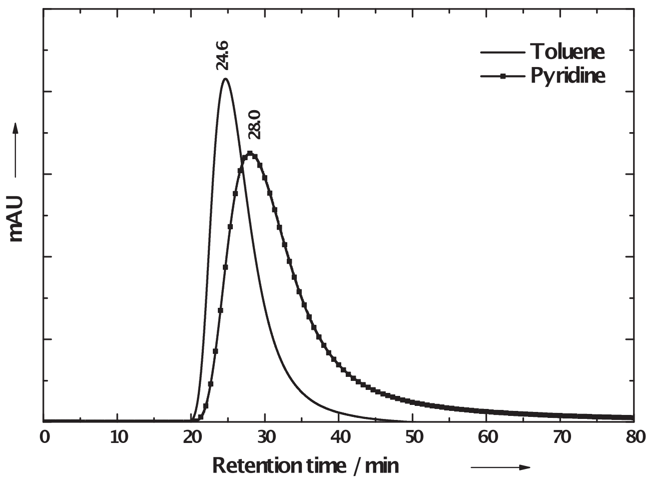

Figure 5. Isocratic elution profile after injection of a mixture of pyridine 0.01% v/v and toluene 0.002% v/v in ethanol into a HPLC column packed with magMOF HKUST-1 particles. The elution profiles of toluene and pyridine could be measured simultaneously using a DAD detector recording the signal at wavelengths corresponding to the absorption maxima of the two components (254 nm in case of pyridine and 215 nm in case of toluene, see also Figure S4 in the Supporting Information).

60 nm and densities of 4.8 g cm^{-3} for the magnetic particle and of 1.22 g cm^{-3} for HKUST-1 bulk.[20] Compared to conventional magnetic adsorbents,[21] the BET values of magMOFs are more than an order of magnitude higher, thus offering the possibility of novel applications as catalytic or sorptive materials which are easy to handle in suspension while possessing high binding capacities.

Finally, we investigated the magnetic properties of the magMOF particles since this is a key parameter for applications. **Figure 4** shows the resulting magnetization curves of MagPrep silica nanoparticles before and after applying the LPE method (60 cycles). The saturation magnetization of the pure MagPrep silica nanoparticles is found to be 72 A m^2 kg^{-1}, which decreases to 34 A m^2 kg^{-1} for HKUST-1 magMOF (60 cycles) NPs, indicating that the mass fraction of iron oxide in the composites is about 52 (wt%). Whereas saturation magnetizations > 35 Am^2kg^{-1} guarantee high efficiencies within industrial magnetic separators,[10] saturation magnetizations as low as 2–5 A m^2 kg^{-1}, as reported by Lohe,[11] may become critical.[22] Moreover, magMOF HKUST-1 particles keep the low coercivity values observed for MagPrep silica, indicating that there is no change within the magnetic properties of the iron oxide during MOF deposition.

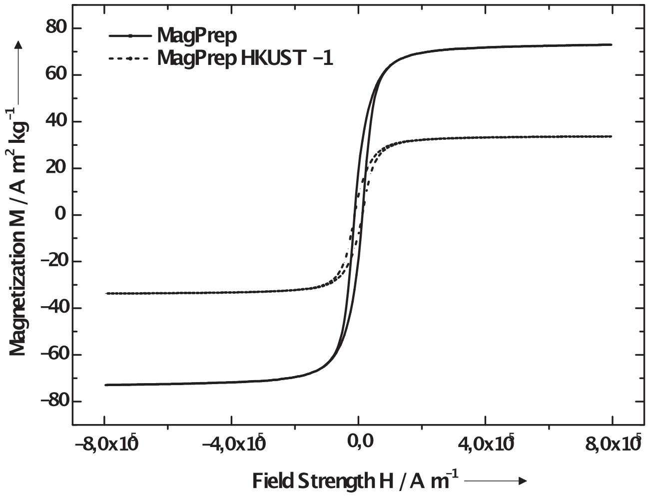

Figure 4. Magnetization curves of pure MagPrep silica and magMOF HKUST-1 (60 cycles).

In a final proof-of-concept, the synthesized magMOF particles coated with HKUST-1 were tested as chromatography media with regard to the separation of two environmentally problematic aromatic compounds (toluene and p-xylene) as well as pyridine. The chromatogram of a mixture of both compounds is shown in **Figure 5**. A comparable chromatogram resulting from a mixture of pyridine and xylene is included in the Supporting Information (Figure S5). The retention times of pure toluene and pyridine were found to be 25.2 and 28.3 min, respectively. Despite its smaller size, pyridine reached longer retention times due to its capability to coordinate to the Cu(II) atoms of the HKUST-1 framework.[14] In the case of applying a mixture of the analytes, the differences in the retention times remained largely unaffected, revealing the potential of magMOFs to form the basis of a new class of well defined chromatographic materials for small molecules. Future work will concentrate on the improvement of the chromatographic performance of magMOF material by increasing the pore size of the used MOF in order to enhance mass transfer kinetics, increasing the size of the core particles to reduce the resulting back pressure as well as advancing chromatographic resolution by the use of longer columns.

3. Conclusions

We have reported the successful growth of homogeneous metal organic frameworks (MOF) coatings with well-defined thickness on magnetic nanoparticles using the liquid phase epitaxy method. The magMOF nanoparticles resulting from the synthesis process were analyzed including a variety of different analytical methods. XRD measurements clearly revealed the crystalline structure of the generated MOF films, whereas the TEM pictures demonstrate the presence of an onion-like structure with the magnetic cores surrounded by a MOF multilayer. The produced magMOF nanoparticles show very high BET surface areas with a narrow pore size distribution. After the coating process, the saturation magnetization is still sufficiently high for straight forward separation processes using existing magnetic technology. In addition, we demonstrated the potential of magMOF particles as a HPLC medium by the separation of two organic compounds. Our results demonstrate that this new class of magnetic/MOF core/shell nanoparticles carries a huge potential for applications in catalysis, chromatographic separation, as well as for drug delivery systems.[8,23]

4. Experimental Section

The synthesis of HKUST-1 thin film layers on pretreated nanoparticles was conducted using the stepwise liquid phase epitaxy process introduced by Shekhah et al.[7] Zacher et al.[15] reported the successful fabrication of a thin HKUST-1 film on SiO_2 wafers using COOH-terminated self-assembled monolayers. In our case, the growth of HKUST-1 was carried out directly on COOH-terminated magnetic beads. Two milligrams of MagPrep silica nanoparticles with COOH functionalization were transferred into an Eppendorf tube and washed two times with ethanol to remove residual water. For MOF growth, 2 mL of 1 mM $Cu(CH_3COO)2\cdot H_2O$ ethanol solution and 2 mL of 1 mM of 1,3,5-benzenetricarboxylic acid (H_3btc) in ethanol were alternately added. In both cases, the suspension was kept for 5 min in an ultrasound bath guaranteeing complete mixing and fast mass transfer at the solid-liquid interface. After completion of the treatment in the ultrasound bath, the magnetic nanoparticles were separated from the solution by placing a permanent magnet for 2 min outside the Eppendorf tube (see Scheme S2, Supporting Information). After removing the metal precursor solution from the Eppendorf tube, rinsing, a crucial step in the LPE-method,[7] was accomplished by backfilling the Eppendorf tube with ethanol once.

Supporting Information

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

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