Flash synthesis for conformal monolithic coatings of the Zr-based metal-organic framework (UiO-66-NH$_2$) on non-modified surfaces: Applications in thin-film electrode systems

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ABSTRACT

Synthesis of conformal coatings of MOFs, especially water stable ones, on different surfaces is of paramount interest due to their potential applications including electrocatalysis, sensing, and separation. Despite previous efforts that resulted in successful deposition of thin-films of MOFs on flat surfaces, a rapid, low cost, and atom-efficient synthesis of such thin-films is still challenging. Herein we report a flash synthesis to produce conformal coatings of the water-stable UiO-66-NH$_2$ on different flat or patterned surfaces, including Si and Au-coated Si wafers, glass slides, TLC silica plates, carbon-coated and FTO-coated electrodes. The flash synthesis presented herein is accomplished within ten minutes reaction time, utilizing minimal amounts of solvent and reagents, and thus is a greener synthesis to attain conformal coatings of such MOF on solid surfaces. The versatility of the approach is demonstrated by successful conformal coatings of the UiO-66-NH$_2$ on Si, Au, glass, silica, as well as carbon surfaces, all achieved through drop-casting on the respective substrate at 100 °C for 10 min. The utility of such thin layer coating of microporous solids in supercapacitor applications, thin layer chromatography, as well as detection of heavy metal ions in aqueous solutions is also demonstrated.

1. Introduction

The progress in utilizing the rapidly evolving hybrid microporous solids [1], best represented by metal organic frameworks (MOFs), in real world applications is hampered by their poor processability [2]. Being extended (network) solids, once formed from their soluble molecular precursors it is not feasible to formulate MOFs into desirable shapes/forms due to insolubility in any common solvent. Moreover, being a highly cross linked polymeric crystalline material does not allow for employing the commonly utilized polymer processing techniques including heat press or melt extrusion for their shaping. Despite their *par excellence* chemistry [3], allowing for application tailored design and synthesis of a specific MOF [4 6], the commonly isolated form of crystalline powder of MOFs is not suitable for many applications, specifically if incorporation of MOFs into devices is sought. Therefore, attempts to address this limitation in shaping/deposition of MOFs into usable forms are of high interest.

The recent reports of liquid phase epitaxial growth of MOF thin films on flat supports [7,8], inkjet printing [9,10], 3D printing [11], formulation of moldable monoliths [12 14], and construction of MOF silica [12] and MOF graphene composites [15], represent major advances to address this very limitation of MOF material. However, to the best of our knowledge, such techniques require prior functionalization of the surfaces for MOF deposition, extended reaction time, usually done in multi step fashion [16,17], and/or require relatively large amounts of reactants and solvents.

Herein, we report on a method that is fairly rapid, highly efficient, and requires minimal amount of reactants and solvents for the con struction of conformal monolithic coatings of the Zr based MOF (UiO 66 NH$_2$) of excellent crystallinity. This method is also highly versatile, producing targeted MOF on different types of solid surfaces, and don't require pre treatment of the surfaces, scheme 1. Moreover, this method can produce monolithic film coating on patterned surfaces, commonly utilized in nowadays' nanotechnology devices. The choice of UiO 66 NH$_2$ as the target of this study is justified by its promising potential and performance in a myriad of bench scale tests demonstrating high chemical and thermal stability, coupled to notable performance in cata lysis, water treatment, and gas storage and separation. The aqueous stability of the Zr carboxylate UiO 66 MOF can be traced to the relative inertness of the $Zr_6(O)_4(OH)_4$ cluster at wide pH range and the ro bustness of the Zr(IV) carboxylate interactions [18]. Despite this ex cellent chemical stability, especially in aqueous medium, utilization of this MOF in industrially relevant setup is cumbersome due to the commonly isolated form of micro to nano crystallites in the range of few hundred nanometers. Therefore, targeting UiO 66 NH$_2$ with the quest for rapid and efficient synthesis of conformal, monolithic coatings

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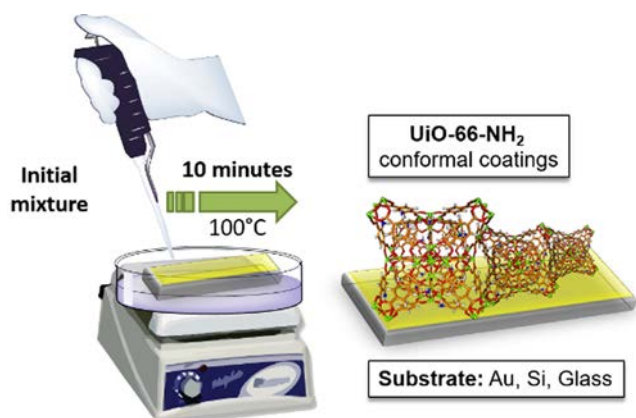
Scheme 1. Flash synthesis of UiO-66-NH$_2$ from its soluble precursors producing conformal monolithic coatings on several substrates. The synthesis utilizes minimal amounts of solvent and reagents, and does not require specific surface treatment or functionalization of the substrate.

is obviated.

2. Experimental

Screen printed electrodes (SPE) were purchased from LAN Printech (Electrode LPC12D1/001, Carbon as WE and CE, Ag as RE) and used as received. Electrochemical Measurements were conducted on FTO as working electrode, Pt wire as counter electrode and calomel electrode (3.5 M KCl) as reference electrode using a Bio Logic SP 50 potentiostat/galvanostat.

2.1. Flash synthesis of UiO 66 NH$_2$ monolithic coating

The UiO 66 NH$_2$ monolithic films synthesis was attempted on Si wafer, Au coated Si wafer, glass substrate, and silica gel thin layer chromatography (TLC) plates. The surface of the substrate (except the TLC plates) was first washed with DI water then cleaned by Ozone in UV activation chamber for 10 min prior to directly being utilized in the synthesis. The flash synthesis on FTO electrode was conducted without Ozone treatment.

2.2. Flash synthesis of conformal UiO 66 NH$_2$ monolithic films through sol gel

The substrates were placed on clean glass microscope slides within a Petri dish on the hotplate and the temperature was adjusted to 100°C. In two separate glass vials, two solutions were prepared. The first vial contained the metal ion solution, prepared by dissolving ZrCl$_4$ (175 mg) in 2.5 mL DMF, added to it 0.5 mL of glacial acetic acid. The second vial contained the ligand solution, prepared by dissolving 2 aminoterepthalic acid (182 mg) in 2.5 mL DMF and 0.15 mL H$_2$O. A mixture of 600 μL of DMF, 200 μL of glacial acetic acid, and 100 μL from each of the linker and metal ion solutions was prepared, immediately mixed and casted on the substrate while hot. The reaction was maintained covered with glass lid at 100 °C for 10 min, where to increase the thickness of the deposited film more castings can be deposited on the substrate before the previous casting reached dryness. A thin yellow film was formed. The samples were then allowed to dry at 100 °C for extra 10 min while open to air, removed from the hotplate, and allowed to cool naturally to room temperature then washed with acetone.

2.3. Flash synthesis of conformal UiO 66 NH$_2$ nano coatings

A solution of zirconium(IV) propoxide, Zr(OPr)$_4$ 70 wt% in 1 pro panol (100 μL) in DMF (7 mL) and glacial acetic acid (4 mL) was prepared in a glass vial and the vial was then capped with silicon septum. The solution was hydrolyzed by heating at 130 °C for 90 min, and then cooled to room temperature. The substrates to be coated with the MOF were placed on clean glass microscope slides within a Petri dish on the hotplate, and the temperature was adjusted to 100 °C. A portion of 1 mL from the above prepared solution was transferred to a separate vial containing 8 mg of 2 aminoterepthalic acid and sonicated briefly, and was then immediately casted on the substrates while hot, the dish was covered and held at 100 °C for 5 min, then it was opened to air to dry for extra 5 minutes yielding a faint yellow glassy thin film on the substrate. The samples were then removed from the hotplate, and allowed to cool naturally to room temperature then washed with acetone prior to further characterization.

3. Results and discussion

Key to the successful flash synthesis of conformal coatings of the UiO 66 NH$_2$ is: (i) selectively inducing nucleation on the substrate surface through heating the substrate rather than the bulk, (ii) use of relatively high concentration facilitating rapid nucleation and forma tion of sol gel at the substrate solution interface. When compared to one of the most reproducible bulk synthesis of UiO 66 and its deriva tives [19], this flash synthesis method is different regarding the con centration of the precursors in the initial mixture, the type of acid used as modulator, and the reaction time and temperature, as well as most significantly the relatively large portion of the reaction mixture in contact with the high surface area of the substrate allowing for surface heterogeneous nucleation and crystal growth. The rapid nucleation and sol gel formation is demonstrated by inspecting the scanning electron microscopy imaging of the sample, Fig. 1. The SEM images in Fig. 1 clearly demonstrate the uniform conformal coating on large area of the substrate as well as homogeneous size distribution of UiO 66 NH$_2$ na nocrystallites (average dimension of 40 50 nm). The construction of the UiO 66 NH$_2$ pure phase was ascertained from the X ray diffraction pattern recorded for the samples constructed on glass, Si, and Au sub strates, Fig. 2, for samples made from ZrCl$_4$ and Zr(PrO)$_4$ as the Zr(IV) metal ion source. All the investigated samples demonstrated excellent crystallinity as indicated by the observed diffraction peaks, showing the most intense two peaks at 2θ = 7.3 and 8.5 degrees at comparable relative intensities to the corresponding diffraction peaks calculated for
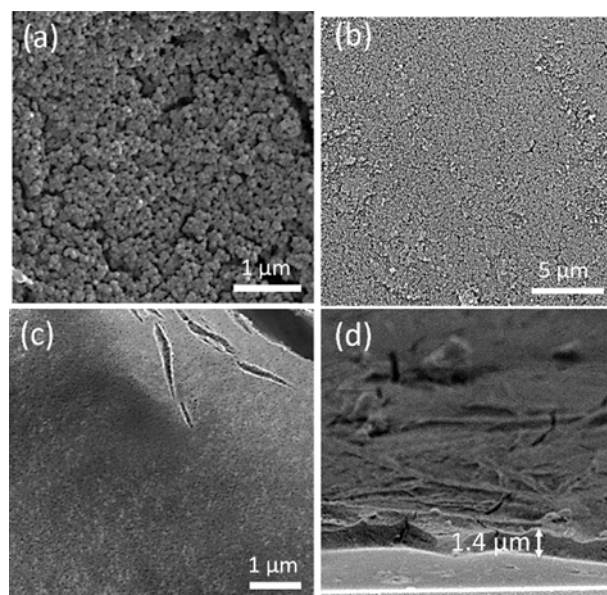
Fig. 1. SEM image for UiO-66-NH$_2$ monolithic coating on Au-coated support (a) and (b) synthesized from Zr(OPr)$_4$ and (c) and (d) from ZrCl$_4$ showing smoother surface due to much smaller crystallite size.
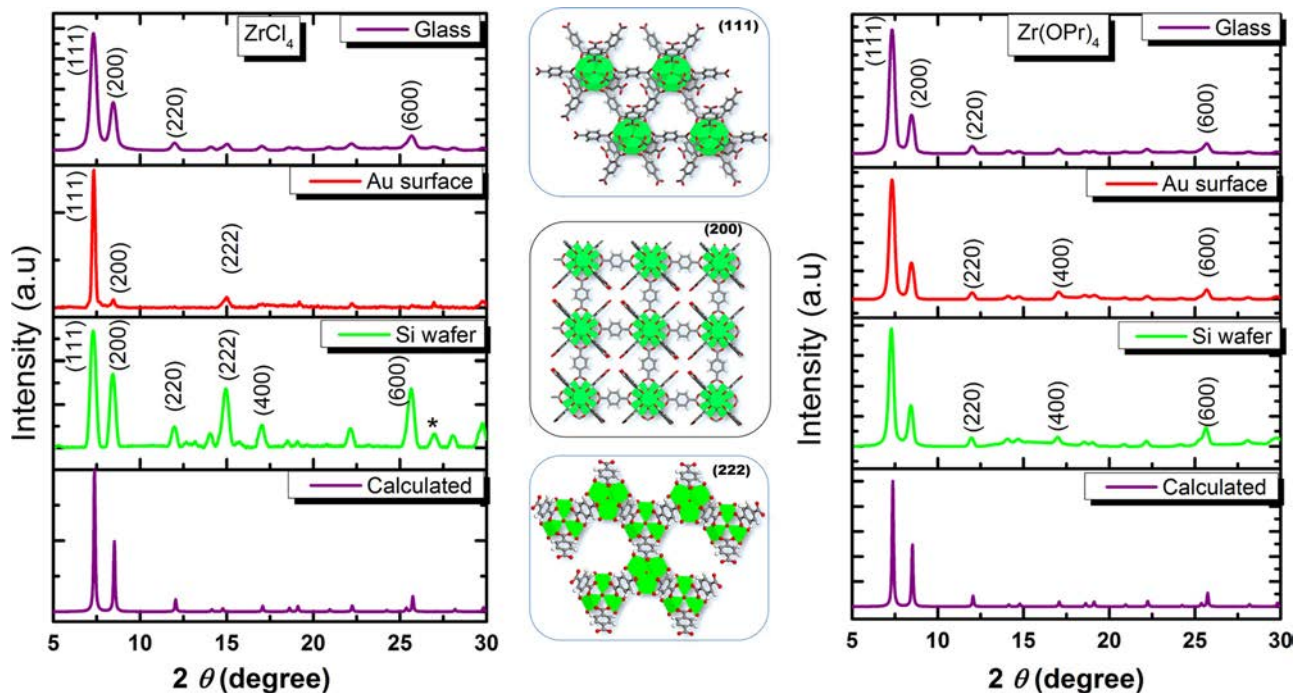
Fig. 2. XRD patterns for the UiO-66-NH$_2$ deposited on different surfaces and the calculated pattern based on crystal structure of the UiO-66. The XRDs for the UiO-66-NH$_2$@Si/Au/Glass demonstrate well resolved peaks for the reflections from several planes including the (111), (200), and (222) planes (inserts showing the corresponding planes) of the UiO-66-NH$_2$ crystallites. The two panels show XRDs for samples prepared from ZrCl$_4$ (left) and those from Zr(PrO)$_4$ (right)

the UiO 66 crystals. The observation of these two peaks indicated non preferred orientation of the monolithic coating on the solid substrate, consistent with the rapid nucleation growth process utilized herein. However, one exception was noticed, where the sample grown from ZrCl$_4$ salt on the Au coated substrate demonstrated much enhanced intensity for the (111) diffraction peak observed at 2θ =7.3°. This observation can be ascribed to preferred nucleation/growth of the polar (111) surface on the Au surface. The fact that this preferred orientation for the MOF growth on Au surface was not as much prominent in the sample prepared from Zr(PrO)$_4$ can be ascribed to the presence of preformed Zr acetate clusters, constructed while preparing the starting mixing solutions prior to mixing with the linker and deposition on the substrate, therefore leading to non preferred orientation for the buildup of the MOF crystallites on the Au surface. The enhanced orientation of the UiO 66 NH$_2$ constructed from ZrCl$_4$ solution on Au surface can be attributed to the high wettability of Au surfaces with DMF [20]. In this setup, the DMF dissolved Zr(IV) species and the linker molecules spread over the Au surface, and oriented growth can be initiated from nu cleation at the solution solid interface due to heating of the substrate. The FTIR spectra of the samples prepared demonstrated the char acteristic peaks for the MOF from 650 1600 cm^{-1} including the sym metric vibration peak for the O Zr O at 663 cm^{-1}, asymmetric stretching of carboxylate groups at 1568 cm^{-1}, the C=C stretching at 1501 cm^{-1}, and the symmetric CO$_2$ stretching at 1429 cm^{-1}, Fig. 3 [21]. As shown in Fig. 3, no significant differences can be observed for the MOF thin layer deposited on the three types of support (glass, si licon, and gold), in agreement with the XRD results shown earlier to indicate single phase and high purity of the MOF monolithic coating. To probe the porosity of the thin film constructed through the flash synthesis technique, a scaled up synthesis was conducted in petri dish (area of 78.5 cm^2) and the solid collected was found to be microporous with a surface area of 727 m^2/g using the Brunauer Emmet Teller (BET) model to fit the isotherm. This clearly demonstrated the main tained porosity of the resulted UiO 66 NH$_2$ and in good agreement with previously reported 700 m^2/g, calculated surface area for UiO 66 NH$_2$ containing 12 linkers per node [19]. Although enhanced surface area of
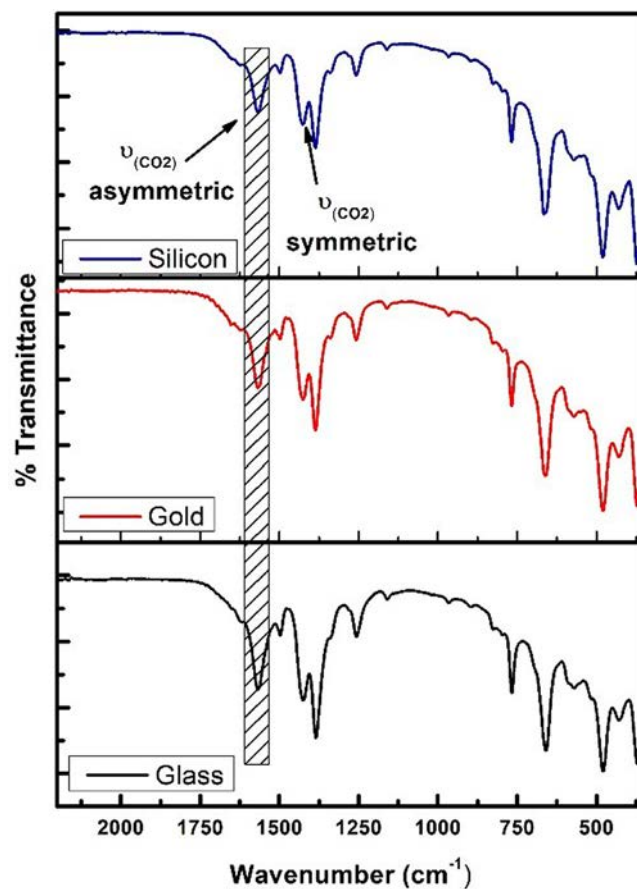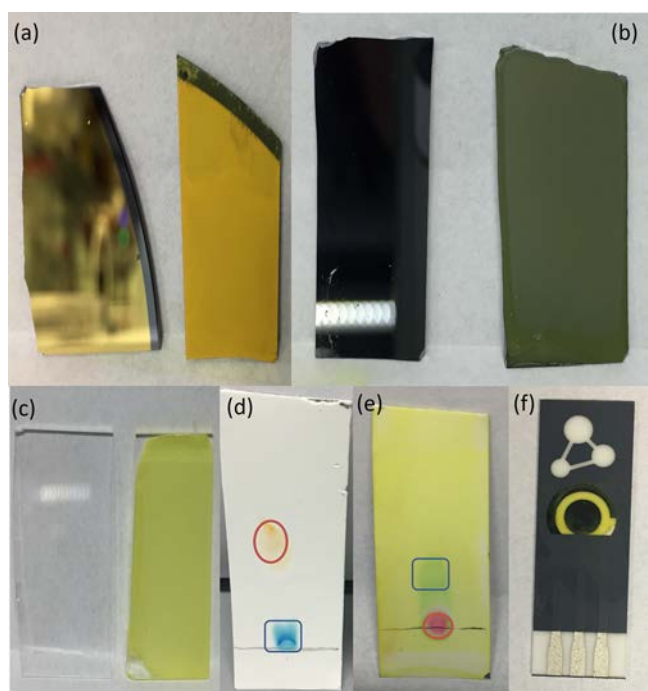

**Fig. 3.** FTIR spectra of the UiO-66-NH$_2$ at different surfaces deposited from Zr (PrO)$_4$.

Fig. 4. Optical images of UiO-66-NH$_2$ conformal coatings on (a) Au-coated substrate, (b) Si surface, (c) glass surface, in each image the surface before coating is shown on the left and after coating on the right side of the image. The image for (d) control silica gel TLC and (e) the UiO-66-NH$_2$@TLC demonstrate the difference in retention factors between MB (blue rectangle) and MO (orange circle), (f) shows coating of the MOF on screen printed electrode. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 5. Areal capacitance of two Au electrodes with (red) and without (black) coating of UiO-66-NH$_2$, showing much enhanced capacitance for the MOF-coated electrodes. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

UiO 66 NH$_2$ was reported when the synthesis contained HCl, this en hancement was ascribed to defective structure of the MOF, containing 8 linkers per the Zr node, and induced by the addition of HCl to the synthesis mixture [19]. The synthesis we report here excluded addition of HCl to avoid damage that can result from such harsh conditions to the different substrates utilized for constructing the thin films. To de monstrate the practical applicability of this method, the UiO 66 NH$_2$ was constructed on thin layer chromatography (TLC) plate. A TLC plate of silica gel on aluminum foil was conformly coated with a thin layer of the MOF utilizing the flash synthesis technique starting from ZrCl$_4$. A common spot of methylene blue (MB) and methyl orange (MO) dyes (1:1 mixture) was spotted on the MOF@TLC slide. Utilizing acetonitrile as the mobile phase, the MOF@TLC plate demonstrated efficient se paration of the MB and MO, notably in inverse order as compared to the non coated TLC plate. In the case of the MOF@TLC plate, preferential adsorption of the MO was noted, while MB moved on the plate with the mobile phase. The opposite trend was observed for the silica gel TLC plate, Fig. 4. The preferential adsorption of MO on the UiO 66 NH$_2$@TLC plate can be ascribed to the enhanced H bond interactions of the sulfonate groups of the MO with the amine/ammonium function alities lining the cages of the UiO 66 NH$_2$. The reverse order of pre ferential adsorption observed on the silica gel TLC can be justified in terms of the absence of functional groups capable of H bond interac tions with the sulfonate part of the MO, and potentially to the negative zeta potential of silica as well, contributing to the hindered migration of MB on the silica gel TLC.

Additionally, the benefit of the flash synthesis technique was de monstrated in enhancing capacitive behavior of the Au electrodes coated with the UiO 66 NH$_2$. A capacitor setup was made using two Au electrodes (or MOF@Au), and a filter paper separator wetted by 1 butyl 3 methyl imidazolium hexafluoro phosphate, BMIM(PF$_6$). As shown in Fig. 5, the areal capacitance calculated from the cyclic
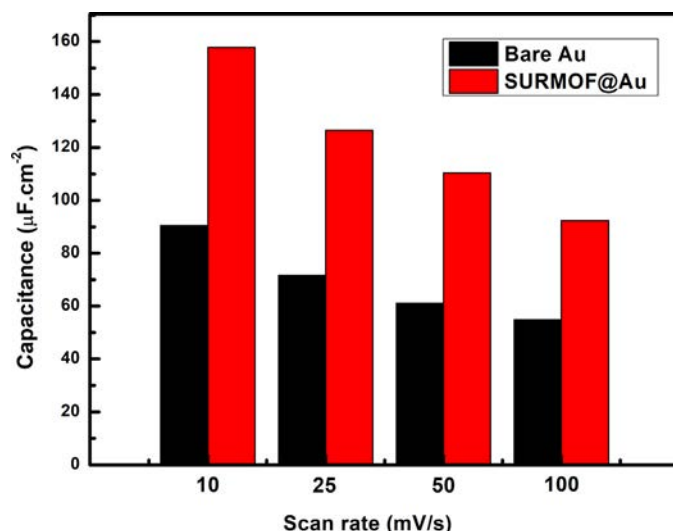
voltammograms of the MOF@Au and the Au electrodes showed great enhancement for the MOF coated electrodes, reaching to 158 μF/cm^2 for the MOF@Au electrode as compared to 90 μF/cm^2 for the bare Au electrode, at a scan rate of 10 mV/s. This can be ascribed to the higher surface area of the capacitor plate where a thin layer of microporous MOF is deposited on the Au electrode. This observation hints to the wide potential of the flash synthesis method to produce conformal coating of microporous UiO 66 NH$_2$ type material on flat surfaces with direct potential applications in electrode surface modification, highly relevant to constructing supercapacitors elements.

Furthermore, to demonstrate the usability of this approach for rapid construction of functional thin film coating of UiO 66 NH$_2$, an FTO (fluorinated tin oxide) electrode was coated with the MOF thin film to be utilized in heavy metal ion sensing. The MOF@FTO electrode de monstrated a linear response towards Pb(II) ions present in acetate buffer solution, Fig. 6, with a distinguishable redox couple centered around −0.56 V vs. Hg/Hg$_2$Cl$_2$ electrode. The MOF@FTO electrode
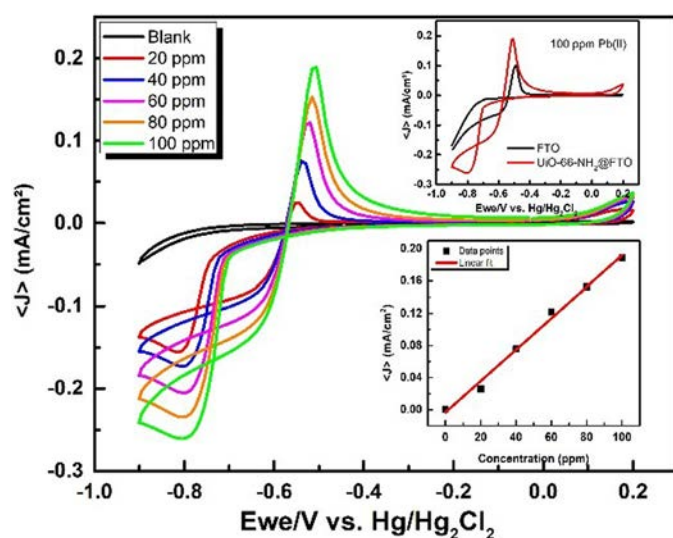
Fig. 6. Electrochemical sensing of Pb(II) ions using UiO-66-NH$_2$@FTO elec trode in acetate buffer solution, cyclic voltammetry scans (CVs) were recorded at 100 mV/S scan rate in acetate buffer solution (0.2M, pH 5) using Hg/Hg$_2$Cl$_2$ (3.5M KCl) as reference electrode.

demonstrated a linear response to the Pb(II) ion concentration with a correlation of 99.8% for a linear fit (insert in Fig. 6). The enhanced response of the MOF coated electrode as compared to bare FTO electrode is clearly demonstrated in the insert in Fig.6, boosting the detection capability of the Pb(II) ion concentrations in aqueous media. This can be ascribed to the porous functional cages of the MOF, acting to pre concentrate the Pb(II) ions in close proximity to the electrode surface from the bulk, and therefore enhancing the signal response to the same concentration of analyte under detection. This example clearly demonstrates the ability to utilize this flash synthesis approach in aqueous electrochemical sensing applications, due to combining the known stability of the Zr carboxylate UiO 66 NH$_2$ MOF and the preparation of such functional electrodes in a time and material efficient approach.

4. Conclusion

The flash synthesis method reported herein is fairly rapid and highly versatile (capable of depositing conformal monolithic coatings of UiO 66 NH$_2$ material on a variety of surfaces), in matter of minutes, using minimal amounts of reagents and solvents, as well as requires no prior specific surface treatment of the substrates. The induction of crystallization at the solid liquid interface, and the optimized conditions including solvent polarity and boiling point, modulator concentration, as well as the reaction time and temperature, resulted in high quality conformal coatings of the Zr based MOF on the solid substrates. This approach was also demonstrated to afford highly conformal MOF monolithic coatings on different surfaces for applications including thin layer chromatography, electrode coatings for supercapacitors to enhance the electrode surface area, as well as functional porous electrode coating for electrochemical detection of heavy metal ion in aqueous medium.

Author contribution

Salma Begum, Rana R. Haikal, Ahmed H. Ibrahim, Mohamed A.E. Safy, Mohamed H. Alkordi (investigation, data analysis), Manuel Tsotsalas and Mohamed H. Alkordi (Funding acquisition, supervision, writing the manuscript), Mohamed H. Alkordi (conceptualization), All authors (revising the manuscript)

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

References

[1] S. Wuttke, D.D. Medina, J.M. Rotter, S. Begum, T. Stassin, R. Ameloot, M. Oschatz, M. Tsotsalas, Bringing porous organic and carbon-based materials toward thin-film applications, Adv. Funct. Mater. 28 (44) (2018) 1801545.

[2] A. Dhakshinamoorthy, A.M. Asiri, H. Garcia, 2D metal–organic frameworks as multifunctional materials in heterogeneous catalysis and electro/photocatalysis, Adv. Mater. 31 (41) (2019) 1900617.

[3] M.Y. Masoomi, A. Morsali, A. Dhakshinamoorthy, H. Garcia, Mixed-metal MOFs: unique opportunities in metal–organic framework (MOF) functionality and design, Angew. Chem. Int. Ed. 58 (43) (2019) 15188–15205.

[4] M.H. Hassan, A.B. Soliman, W.A. Elmehelmey, A.A. Abugable, S.G. Karakalos, M. Elbahri, A. Hassanien, M.H. Alkordi, A Ni-loaded, metal–organic framework–graphene composite as a precursor for in situ electrochemical deposition of a highly active and durable water oxidation nanocatalyst, Chem. Commun. 55 (1) (2019) 31–34.

[5] M.H. Alkordi, Y. Belmabkhout, A. Cairns, M. Eddaoudi, Metal-organic frameworks for H(2) and CH(4) storage: insights on the pore geometry-sorption energetics relationship, IUCrJ 4 (Pt 2) (2017) 131–135.

[6] A. Dhakshinamoorthy, A. Santiago-Portillo, A.M. Asiri, H. Garcia, Engineering UiO-66 metal organic framework for heterogeneous catalysis, ChemCatChem 11 (3) (2019) 899–923.

[7] E. Virmani, J.M. Rotter, A. Mähringer, T. von Zons, A. Godt, T. Bein, S. Wuttke, D.D. Medina, On-surface synthesis of highly oriented thin metal–organic framework films through vapor-assisted conversion, J. Am. Chem. Soc. 140 (14) (2018) 4812–4819.

[8] A. Bétard, R.A. Fischer, Metal–organic framework thin films: from fundamentals to applications, Chem. Rev. 112 (2) (2012) 1055–1083.

[9] J.-L. Zhuang, D. Ar, X.-J. Yu, J.-X. Liu, A. Terfort, Patterned deposition of metal-organic frameworks onto plastic, paper, and textile substrates by inkjet printing of a precursor solution, Adv. Mater. 25 (33) (2013) 4631–4635.

[10] C.-H. Su, C.-W. Kung, T.-H. Chang, H.-C. Lu, K.-C. Ho, Y.-C. Liao, Inkjet-printed porphyrinic metal–organic framework thin films for electrocatalysis, J. Mater. Chem. A 4 (28) (2016) 11094–11102.

[11] J. Lefevere, B. Claessens, S. Mullens, G. Baron, J. Cousin-Saint-Remi, J.F.M. Denayer, 3D-printed zeolitic imidazolate framework structures for adsorptive separations, ACS Appl. Nano Mater. (2019).

[12] W.A. El-Mehalmey, A.H. Ibrahim, A.A. Abugable, M.H. Hassan, R.R. Haikal, S.G. Karakalos, O. Zaki, M.H. Alkordi, Metal–organic framework@silica as a stationary phase sorbent for rapid and cost-effective removal of hexavalent chromium, J. Mater. Chem. A 6 (6) (2018) 2742–2751.

[13] B. Bueken, N. Van Velthoven, T. Willhammar, T. Stassin, I. Stassen, D.A. Keen, G.V. Baron, J.F.M. Denayer, R. Ameloot, S. Bals, D. De Vos, T.D. Bennett, Gel-based morphological design of zirconium metal–organic frameworks, Chem. Sci. 8 (5) (2017) 3939–3948.

[14] T. Tian, Z. Zeng, D. Vulpe, M.E. Casco, G. Divitini, P.A. Midgley, J. Silvestre-Albero, J.-C. Tan, P.Z. Moghadam, D. Fairen-Jimenez, A sol–gel monolithic metal–organic framework with enhanced methane uptake, Nat. Mater. 17 (2017) 174.

[15] M.H. Hassan, R.R. Haikal, T. Hashem, J. Rinck, F. Koeniger, P. Thissen, H. Stefan, C. Wöll, M.H. Alkordi, Electrically conductive, monolithic metal–organic framework–graphene (MOF@G) composite coatings, ACS Appl. Mater. Interfaces 11 (6) (2019) 6442–6447.

[16] O. Shekhah, H. Wang, S. Kowarik, F. Schreiber, M. Paulus, M. Tolan, C. Sternemann, F. Evers, D. Zacher, R.A. Fischer, C. Wöll, Step-by-step route for the synthesis of metal organic frameworks, J. Am. Chem. Soc. 129 (49) (2007) 15118–15119.

[17] O. Shekhah, J. Liu, R.A. Fischer, C. Wöll, MOF thin films: existing and future applications, Chem. Soc. Rev. 40 (2) (2011) 1081–1106.

[18] M.E.A. Safy, M. Amin, R.R. Haikal, B. Elshazly, J. Wang, Y. Wang, C. Wöll, M.H. Alkordi, Probing the water stability limits and degradation pathways of metal–organic frameworks, Chem. – Eur. J. 26 (31) (2020) 7109–7117.

[19] M.J. Katz, Z.J. Brown, Y.J. Colón, P.W. Siu, K.A. Scheidt, R.Q. Snurr, J.T. Hupp, O.K. Farha, A facile synthesis of UiO-66, UiO-67 and their derivatives, Chem. Commun. 49 (82) (2013) 9449–9451.

[20] J. Cognard, Adhesion to gold: a review, Gold Bull. 17 (4) (1984) 131–139.

[21] L. Valenzano, B. Civalleri, S. Chavan, S. Bordiga, M.H. Nilsen, S. Jakobsen, K.P. Lillerud, C. Lamberti, Disclosing the complex structure of UiO-66 metal organic framework: a synergic combination of experiment and theory, Chem. Mater. 23 (7) (2011) 1700–1718.