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# Copper-induced synthesis of zinc imidazolate metal-organic framework (ZIF-8) crystals and coatings

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**Abstract.** Zeolitic imidazolate framework-8 (ZIF-8) is one of the most stable Metal Organic Frameworks currently available, with promising properties in adsorption, separation and catalysis. Herein, we report a method for the rapid production of ZIF-8 crystals at room-temperature from methanolic solutions containing sodium acetate and metal salts. Of the different metal salts tested, copper nitrate presence prompted formation of cubic shaped ZIF-8 crystals within 5 minutes. Derived from this finding, an adaption of the synthesis route was implemented over copper foils and copper based metallic/non-metallic substrates, which yielded high quality shape- and size- controlled ZIF-8 crystal coatings. The outcomes also revealed a significant impact of sodium acetate as modulator and of copper ions released in the reaction media as triggering agent/co-modulator. Together these chemical species are understood to be involved in a multitude of coordination complex formation and deprotonation equilibria, thus largely determining the ZIF-8 crystal morphology and growth, especially near the copper releasing sites. Overall, this work presents an important platform for rapid and controlled synthesis of ZIF-8 crystals and coatings over metallic/non-metallic substrates, which can be adapted for advanced applications such as device integration.

**Keywords:** ZIF-8, direct in-situ synthesis, sodium acetate, copper ions, continuous and patterned coating.

## 1. Introduction

The research interest in metal organic frameworks (MOFs), especially zeolitic imidazolate framework-8 (ZIF-8), has grown considerably in the last decade[1]. ZIF-8 is a microporous material with a tetrahedral framework formed via coordination bonds between zinc atoms and imidazolate linkers[2]. It forms a sodalite (SOD) topology with large cages of 1.16 nm in diameter interconnected via narrow 6-ring windows of 0.34 nm in diameter[3,4]. Owing to its analogous structure to aluminosilicate zeolites, ZIF-8 possesses properties of both MOFs and zeolites, thus exhibiting large pore volume and surface area, exceptional thermal and chemical stability and negligible cytotoxicity[2,5,6]. It can be obtained via simple and reproducible synthesis routes and several groups have reported diverse approaches in order to find a more facile and cost-effective method[5,7].

Of the various methodologies reported, aqueous synthesis methods are widely employed owing to their simplicity[8]. Various factors affecting the properties of ZIF-8 such as reaction time[9,10], solvent[11], zinc salts[12], and reactant molar ratio[8,13] have been examined. By modifying these parameters, the controlled synthesis of MOF crystals can be achieved[14,15]. Another strategy which has been explored intensely to achieve this goal entails the incorporation of additives, also known as modulators. From synthesis point of view, the presence of modulators can affect the nucleation and growth rates[16]. Their role consists of modulating coordination (competing with organic linker, reducing the nucleation points and thus, increasing the crystal size) and/or deprotonation equilibria (accelerating the nucleation rate and thus, decreasing the crystal size). The net result of the presence of a modulator depends on its coordination strength towards the metal, its concentration and its basicity[16,17]. So far, different types of modulators such as sodium formate, 1-methylimidazole, n-butylamine and sodium acetate have been explored[17–19]. However, a synthesis route comprising modulators and co-modulators/triggering agents such as metal salts for controlled synthesis of ZIF-8 crystal with well-defined morphology have not been reported. Therefore, in this work we report a direct *in-situ* synthesis method performed at room temperature in the presence of sodium acetate as modulator and metal salts as triggering agents/co-modulator to obtain ZIF-8 crystals.

Typically, MOFs are synthesized as powders and possess ultrahigh porosity and surface area with uniform and tuneable pores, however anchoring them to a solid support is necessary for applications such as sensors, microreactors, optoelectronics and structured adsorbents[20–22]. Thus, with the goal of synthesizing structured adsorbents, focus was afterwards oriented towards ZIF-8 based composites. So far, numerous studies have been performed where different substrates such as silica wafers[23,24], porous titania[25], alumina[26–31], polymers[32–35], metal induced templates[36] and supramolecular assemblies[37] have been investigated. However, reports on ZIF-8 coating over metal substrates are still scarce. Papporello et.al. have studied growth of ZIF-8 films and found good film growth is possible on copper and aluminium substrates when placed in a mixture of composition  $Zn:Ac \geq 1:2$  at high temperature (120 °C)[38,39]. In case of copper, the authors reported a film growth of 17  $\mu m$  after seeding the substrates with ZIF-8 nanocrystals (via secondary growth) after 12 h[38]. Meanwhile for aluminium, substrate etching with NaOH or HCl was suggested before the *in-situ* ZIF-8 growth and an average total layer thickness of around 10 – 12  $\mu m$  was informed[39]. Thus, as next step the technique was transformed into a generic route to achieve direct *in-situ* ZIF-8 coating over different metal substrates at room temperature, followed by synthesis mechanism proposal and a modified version of the synthesis route to get patterned ZIF-8 coating over any copper-based metallic/non-metallic substrate.

## **2. Materials and Methods**

### **2.1. ZIF-8 crystals synthesis via metal salts**

First, the technique referring to the synthesis of ZIF-8 crystals in the presence of metal salts as triggering agents/co-modulator is discussed. In here, different metal salts such as aluminium nitrate nonahydrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), iron nitrate nonahydrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), cobalt nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), nickel nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), copper nitrate hexahydrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ), and zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) were added to the methanolic synthesis mixture of Zn:Hmim:Ac:MeOH = 1:2:1:200, where Zn corresponds to zinc nitrate hexahydrate (as metal ion), Hmim to 2-methylimidazole (as linker), Ac to sodium acetate (as modulator), and MeOH to methanol (as solvent). To trigger the precipitation in the synthesis mixture, a pipette containing metal salt (Figure S1) was placed in the reaction mixture at room temperature. A video recording to capture the change/material formation was performed for each metal salt and the material formed inside was collected via centrifugation for further characterization. The supplementary information (S.I.) provides more details regarding the materials, the methodology and a link for the video recordings.

## 2.2. ZIF-8 coating over metallic foils

In the second part, the metal salts were replaced with metal foils with the aim of growing ZIF-8 crystals over their surface. For that, a room-temperature direct in-situ approach was implemented, where a pre-treated metal foil was placed vertically in the synthesis mixture Zn:Hmim:Ac:MeOH = 1:2:1:200, after leaving the mixture to age for 24 h. The ageing was done to ensure absence of crystal growth in the bulk solution. Further, after placing the metal substrate in the solution, the vial was left (partially) open to air. Pre-treatment of the metal substrate involves thorough soap washing, etching with sandpaper (P180), washing with deionised water and drying with compressed air to remove any dirt. The different metal substrates used were aluminium, copper, zinc and stainless-steel foils. After 24 h, the sheets were washed with methanol and acetone respectively and dried in an oven at 363 K for 16 h. See supplementary information (S.I.) for materials and detailed methodology.

## 3. Results and discussion

### 3.1. ZIF-8 crystals synthesis via metal salts

For each of the six metal salts (Al, Fe, Co, Ni, Cu, Zn), in the first instances after their addition, gas bubbles were noticed inside the liquid in the pipette followed by the dissolution of the salt (S.I.). This phenomenon could be related to the air trapped inside the pipette. Subsequently, cloudiness due to precipitate formation either inside the pipette or at the bottom of the vial was noted. Figure S3 displays the images of these vials after 60 minutes for each metal salt. An example is shown in Figure 1, where the precipitate formed inside the vial containing copper salt is exhibited, along with a SEM image of this material. Excluding the case of nickel salt, where even after 24 h no change was noticed, the swiftness of this appearance/change differed unevenly for other cases. For Fe and Cu salt, a rapid

precipitation was seen within 3 minutes, meanwhile for Zn salt, it was noted after 6 minutes. In case of Al and Co salt, the slowness of this trend extended to 20 minutes and 40 minutes respectively (S.I.). Interestingly, the coordination strength of divalent metal ions with acetic acid in aqueous solution also increases in the order of  $\text{Ni}^{2+} \cong \text{Co}^{2+} < \text{Zn}^{2+} < \text{Cu}^{2+}$ [40], thus explaining the above trend. Figure S4 exhibits SEM images of the precipitate formed in these vials. In each case, a different morphology was seen. For cobalt salt, only flake like amorphous material was observed, meanwhile for aluminium, iron and zinc salt, cubic shaped crystals were noticed along with the presence of non-crystalline material. With copper salt, cubic shaped crystals of size varying between 4 – 15  $\mu\text{m}$  were noticed (Fig. 1b and Fig. S7).

Apart from the precipitate collected, a white coating on each pipette was also observed (Fig. S5). For further characterization, the precipitate obtained was analysed via X-ray diffraction and compared with pure ZIF-8 powder. Figure S6 displays the PXRD pattern of the material formed inside the pipette along with pure ZIF-8 powder. Only in the case of copper and zinc salt, together with other phases the result indicated presence of ZIF-8 crystals. For both cases, this was confirmed by the characteristic peaks at  $2\theta = 7.4^\circ, 10.4^\circ, 12.7^\circ, 14.7^\circ, 16.4^\circ, 18.0^\circ$ [35]. The additional low intensity peak seen in the case of copper at  $43.5^\circ$  could be corresponding to the unreacted copper nitrate salt[41] (S.I.). For other metal salts, even though crystalline material was observed in SEM images, no confirmation of ZIF-8 could be made. Overall, these results demonstrate a triggered synthesis of MOF crystals due to the addition of a metal salt, where especially with copper salt high quality and zinc-based MOF crystals i.e., ZIF-8 can be obtained at room temperature in order of minutes.

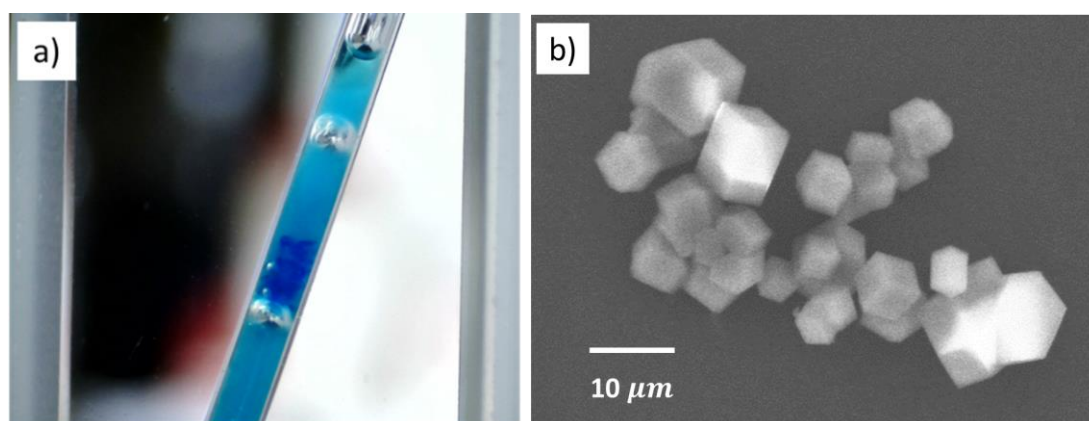


Figure 1: a) Photograph of pipette with  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  salt in the reacting mixture of molar composition  $\text{Zn}:\text{Ac}:\text{Hmim}:\text{MeOH} = 1:1:2:200$ , after 10 min., b) SEM images of as-synthesized crystals obtained from the pipette.

### 3.2. ZIF-8 coating over metallic foils

In above the findings demonstrated that the ZIF-8 crystals can be grown at lower acetate concentration i.e.,  $\text{Zn}:\text{Ac} = 1:1$  and at room temperature. Thus, following the methodology, different metal foils such

as aluminium, stainless steel, copper and zinc, were subjected to the mixture Zn:Ac:Hmim = 1:1:2 at room temperature and without any seeding/pre-treatment, in an open air environment. The open-air strategy permits oxygen diffusion which would react and consequently, lead to release of metal ions in the reaction mixture as observed above with metal salt addition. Of all the tested metal substrates, similar to metal salts, only on copper and zinc foil a new phase (crystals) was observed on both sides (Fig. S8 and S9). No coating or crystal growth was noticed over aluminium and stainless-steel surface (Fig. S8c,d and S9c,d) or in the bulk synthesis solution. This finding indicates that the crystal growth is caused by the presence of the metal substrate and not due to crystal formation in the liquid bulk phase in the absence of metals. Prior to the addition of the metal substrate, the solution was left to age for 24 h to confirm no precipitation in the liquid bulk phase. Regarding the crystal morphology, over the zinc foil, cubic shaped crystals of size around  $3\ \mu\text{m}$  were observed (Fig. S8b), whereas over the copper foil, truncated rhombic dodecahedral shaped crystals of size around  $30\ \mu\text{m}$  were noticed (Fig. 2a). Furthermore, for both foils an accumulation of crystals was seen at different locations on the front side, resulting in a continuous yet non-uniform coating (Fig. 2a and S8b). In both cases, a small amount of precipitate was also observed at the bottom of the vial. Regarding ZIF-8 film thickness, while a thin film of thickness around  $5 - 6\ \mu\text{m}$  was noted over zinc substrate (Fig. S10), a thicker film varying between  $35 - 60\ \mu\text{m}$  was noticed over the copper foil (Fig. 2b).

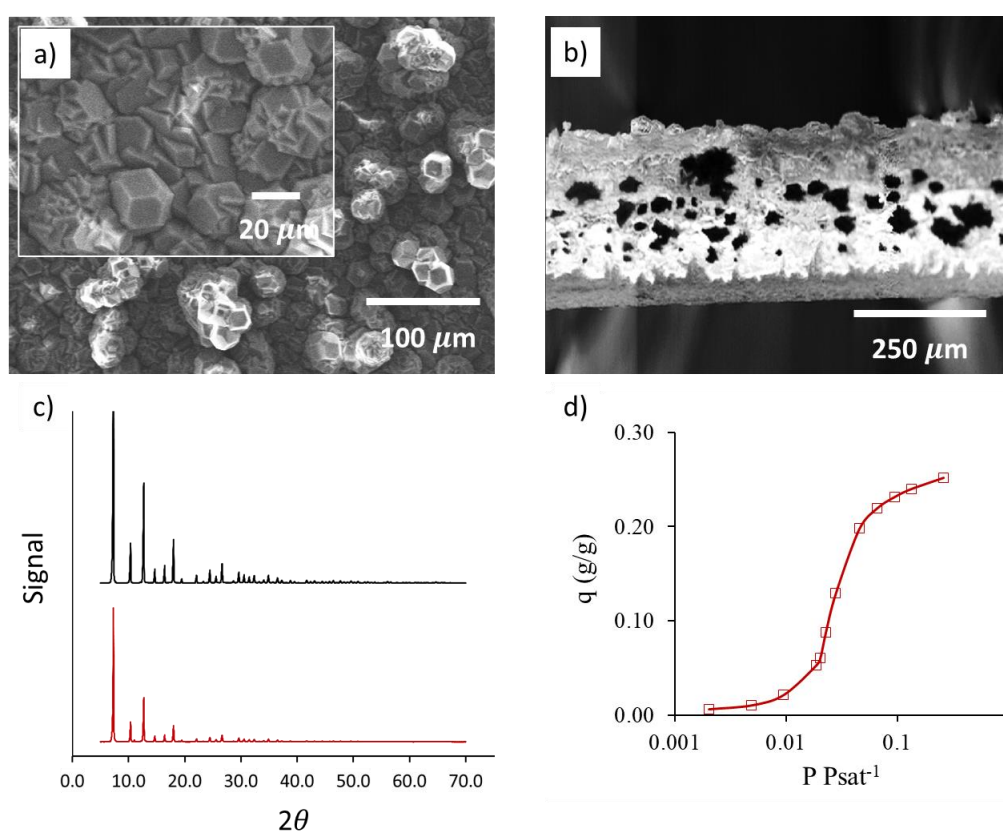


Figure 2. SEM image of copper sheet treated in the reacting mixture of molar composition Zn:Ac:Hmim = 1:1:2 for 24 h a) in top view and b) in side view, c) Powder X-Ray diffraction (PXRD) patterns of

crystals collected from coated copper foil (below) and of commercial ZIF-8 crystals purchased from BASF (above), and d) Vapor phase adsorption isotherm of n-butanol on ZIF-8 collected from coated copper foil at 323 K.

Another observation was the change in colour of the synthesis mixture in the case of copper from transparent to blue (Fig. S11). It is understood to be caused due to support leaching[38]. To examine the coating over the copper sheet, it was removed by scratching and characterized via powder X-ray diffraction (PXRD) and alcohol vapor-phase adsorption. Figure 2c shows the comparison between the XRD pattern of coating scratched from copper substrate and commercial ZIF-8 powder (Basolite Z1200, BASF). All peaks were sharp and well defined, confirming the film coating consists of ZIF-8 with fully crystalline nature. A similar conclusion can be made from Figure 2d, in which the vapor-phase adsorption isotherm of n-butanol show an S-shaped profile, in accordance with the n-butanol isotherm on the material in powder form, as a result of the hydrophobic nature of ZIF-8 [42]. Furthermore, the adsorption capacity (0.25 g/g) is in good agreement with literature[42] indicating a high-quality sample. Next, mechanical and thermal stability of the composite was analysed. For that, coating scratched from the copper foil was subjected to thermal gravimetric analysis (TGA) (Fig. S12). A little weight loss (0.2 %) before 200 °C was observed which could be attributed to the removal of solvent (methanol) from the pores and other species (e.g., Hmim). The coating was stable up to 400 °C, which correlates with the literature[43]. For evaluation of thermo-mechanical stability, the coated copper substrate was subjected to five cycles of thermal stress i.e., sharp heating up to 250 °C from 25 °C and then sonicated for 1 h. The mass loss was negligible (in the order of the error of the balance) and no damage or erosion was observed on the coating surface (Fig. S13). These findings indicate very good adhesion of the ZIF-8 coating to the substrate surface. Overall, this synthesis route allows to grow thick and thermo-mechanical stable ZIF-8 coatings over copper foils via direct in-situ synthesis at room temperature.

### 3.3. Interaction between modulator, co-modulator and environment

So far, the results of the experiments have revealed that ZIF-8 crystals are grown when copper ions, either from salt addition or from copper sheet, are released into a synthesis mixture comprised of equimolar sodium acetate and zinc nitrate concentrations in an open-air environment. This presents as a great opportunity towards synthesizing high-quality ZIF-8 crystal coatings-based composites/structured adsorbents. Furthermore, these results contradict the findings reported by Papporello et.al., where though similar coating results on copper foils were mentioned, no ZIF-8 growth was stated with reaction mixture Zn:Ac:Hmim = 1:1:2[38]. Additionally, film thickness over the copper foil was lower i.e., 17  $\mu\text{m}$  with Zn:Ac:Hmim = 1:4:2. The authors suggested that ZIF-8 nuclei obtain highly deprotonated surfaces due to presence of acetate, which interact favourably with the copper surface owing to the state of charges at the surface of copper support. However, this reasoning only

refers to the role of surface chemistry and lacks clarity regarding the role of sodium acetate as modulator on ZIF-8 morphology and film thickness. Additionally, it does not explain the absence of ZIF-8 crystals on copper foil when the mixture composition was Zn:Ac = 1:1. Consequently, in the context of understanding ZIF-8 crystal and coating synthesis, experiments were carried out to study the role of the modulator (i.e., sodium acetate), the copper ion/surface which acts as trigger/co-modulator and the aerobic environment.

Starting with sodium acetate, three synthesis mixtures were prepared: i) Zn:Ac:Hmim = 1:0:2, ii) Zn:Ac:Hmim = 1:2:2, and iii) Zn:Ac:Hmim = 1:4:2, in to which copper foil was placed vertically. **Figure S14** displays SEM images for each of these cases along with SEM images for Zn:Ac = 1:1. In absence of acetate, a non-continuous coating of cubic shaped nanocrystal was spotted (**Fig. S14a and Fig. S15a**), whereas with excess of acetate, i.e. Zn:Ac = 1:4, a continuous and uniform coating of thickness around 100  $\mu\text{m}$  was formed with cubic shaped crystals of size around 5 – 7  $\mu\text{m}$  (**Fig. S14d and Fig. S15d**). A similar coating of thickness around 40 – 55  $\mu\text{m}$  was seen with a synthesis mixture with a higher Zn:Ac ratio of 1:2, but with an increase in crystal size to 20  $\mu\text{m}$  (**Fig. S14c and Fig. S15c**). These outcomes suggest the role of the sodium acetate as mildly basic modulator. In small amount i.e., Zn:Ac = 1:1, it competes with the linker molecule for the coordination sites present at the metal centres of the forming crystals, or modulating in coordination equilibria and lead to big ZIF-8 crystals (truncated rhombic dodecahedral shaped crystals of size around 30  $\mu\text{m}$ ) caused by thermodynamically driven nucleation process. Meanwhile, in higher concentration (Zn:Ac = 1:4) it act as a base facilitating the deprotonation of the organic linker, and leading to smaller cubic shaped crystals of size 5 – 7  $\mu\text{m}$ [5,17–19,44–46]. A schematic model explaining the effect of sodium acetate as modulator on the ZIF-8 crystal morphology is depicted in **Figure S16a**.

However, in the above experiments, the reaction mixture colour turned to blue due to copper leaching. Additionally, for the reaction mixture with low sodium acetate concentration (Zn:Ac = 1:1), addition of copper salt triggered ZIF-8 precipitation. Combining the above information confirms that copper ions released in the reaction mixture, especially with low sodium acetate concentration, play an important role in the ZIF-8 crystal formation too. To confirm this, reaction mixtures were prepared with different sodium acetate concentration i.e., Zn:Hmim:Ac:MeOH = 1:2:x:200, where x = 0, 1, 2, and 4 and left to age without any substrate/salt. Except for the mixture with Zn:Ac = 1:1, where no change was noticed even after 72 h, in all the other cases a white precipitate was noticed within 2 h. Further, the appearance of precipitate was swifter at higher amount of sodium acetate. This suggests that at low concentration of sodium acetate i.e., Zn:Ac = 1:1, there is a possibility of coordination modulation and at higher concentrations i.e., Zn:Ac  $\geq$  1:2, deprotonation equilibria exists. The triggered formation of ZIF-8 crystals seen in the synthesis mixture Zn:Ac = 1:1, with copper ions release, whether from salt or substrate leaching, hints towards the disruption of this possible (coordination) equilibrium, thus leading to the formation of ZIF-8 crystals next to the copper releasing sites. To confirm this disruption



caused by the coordination between acetate and copper ions, UV/Vis spectroscopy of the reaction mixture after the synthesis was performed, which revealed the presence of copper acetate complex in it (Fig. S19). Overall, the effect of copper ions (as triggering/co-modulator agent) in the presence of modulator on the ZIF-8 coating is important and a schematic model explaining this effect is displayed in Figure S16b.

The major improvement of the synthesis technique is being environment-friendly and cost-effective as it is performed at room-temperature and in open-air environment. The initial reasoning behind the open-air strategy was to enable the oxygen diffusion for later release of  $\text{Cu}^{2+}$  ions, also seen after the addition of copper salt in the reacting mixture (Zn:Ac:Hmim = 1:1:2). However, for better understanding of this parameter, a synthesis was performed in an inert environment ( $\text{N}_2$  box). In a vial containing the above reaction mixture a copper foil was placed vertically. Afterwards, the vial was closed and left in the nitrogen box with controlled atmosphere ( $\text{H}_2\text{O} < 10$  ppm and  $\text{O}_2 < 10$  ppm). After 24 h, no coating was observed. Later, the vial was opened inside the nitrogen box and left standing for another 24 h. As previously, no coating was observed on the copper sheet again. But when the open vial was brought in contact with air, within 2 h copper leaching was observed along with formation of a white precipitate and cubic crystals of size around 1  $\mu\text{m}$  formed over the sheet (Fig. S17). This clearly explains the contradictory results with the literature, where the synthesis was carried out in a confined environment (autoclave). In an open-air environment, it is speculated that the oxygen diffuses, reacts, and consequently lead to release of copper ions in the reacting mixture (Fig. S17). Due to their higher preference towards acetate than zinc ions, these copper ions form acetate complexes[40,47,48], subsequently disrupting the equilibria between the chemical species present in the reacting mixture and set in motion the reaction between zinc ions and imidazolate to form ZIF-8 crystals, seen as precipitation in the bulk liquid and over the copper sheet surface after 2 h (Fig. S17). Another approach to confirm the role of copper oxidation was done by performing a control test with copper oxide ( $\text{CuO}$ ) (S.I.). Similar observation of change in colour was observed when  $\text{CuO}$  was added in the synthesis mixture (Zn:Ac:Hmim = 1:1:2). Figure S18 shows the image of the reacting mixture after 24 h, before and after separating the precipitate from the solution via centrifugation. The SEM image revealed cubic shaped crystals and XRD analysis confirmed the presence of ZIF-8 in the precipitation along with copper oxide (Fig. S20). Overall, the ZIF-8 growth mechanism involves a multitude of coordination complex formation and deprotonation equilibria, with a significant impact of modulator and co-modulator largely determining whether crystalline ZIF-8 forms under largely thermodynamic or kinetic control to yield equilibrium or non-equilibrium shapes, especially near the copper releasing sites. Based on the above understanding, a plausible mechanism showing the evolution of the copper sheet with time after being placed in the reacting mixture is shown in Figure 3.

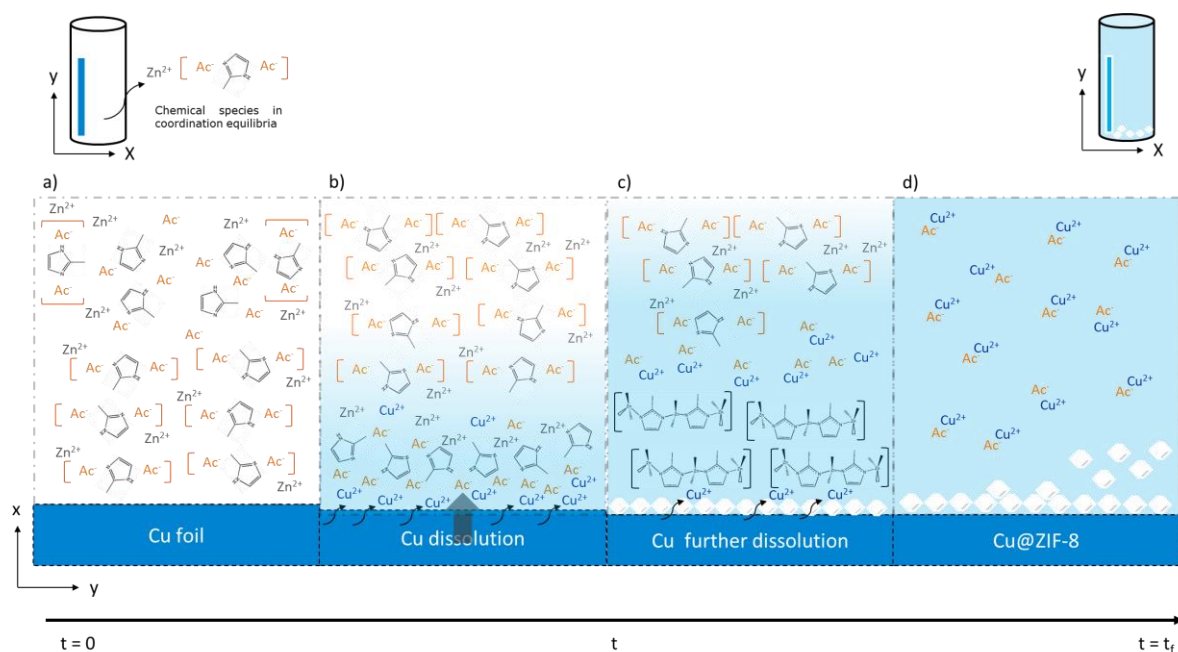


Figure 3. Scheme of the proposed mechanism showing evolution of ZIF-8 growth over time over copper foil: a) at  $t = 0$ , a copper foil is introduced into the reaction mixture composed of zinc, imidazolate and acetate ions. When present in composition  $\text{Zn}:\text{Ac}:\text{Hmim} = 1:1:2$ , coordination equilibria could exist between these chemical species, b) copper ions release from the copper foil into the reaction mixture and form a complex with acetate ions, thus disrupting the equilibria, c) copper acetate complex formation leads to reaction between zinc and imidazolate ions causing formation of ZIF-8 crystals next to copper ions release sites (the foil surface) and d) finally at  $t = t_f$ , accumulation of crystals is observed in the reacting mixture and at bottom of the vial due to continuous release of copper ions. At higher concentration of sodium acetate, imidazolate tend to self-nucleate and form individual crystals in the reacting solution.

### 3.4. Patterned ZIF-8 growth over copper-based substrates

It has been revealed that copper ions, along with sodium acetate, play an important role in defining ZIF-8 growth over copper substrates. To extend this understanding into real-world applications such as device integration, the possibility of growing ZIF-8 on other metallic/non-metallic substrates was investigated. For a description of the detailed methodology, please consult the S.I. In brief, two substrates, a) stainless-steel rod and b) cyclic olefin co-polymer (COC) chip were prepared. Regarding the stainless-steel rod, first copper was selectively electroplated over it to create a patterned surface. The partially electroplated rod was then placed in the synthesis mixture,  $\text{Zn}:\text{Ac}:\text{Hmim} = 1:4:2$ , for 24 h. **Figure 4a** displays the steel rod before and after copper electroplating, followed by ZIF-8 coating, which was predominantly formed over the electroplated copper zones. Apart from the visual observation, the selective growth of ZIF-8 over the steel rod was also noticed in SEM images, where

cubic shaped microcrystals of size  $\sim 1 \mu\text{m}$  were noticed (Fig. 4b). To be mentioned, after synthesis, no copper was left on the steel rod and the colour of the solution changed to blue as in the previous cases.

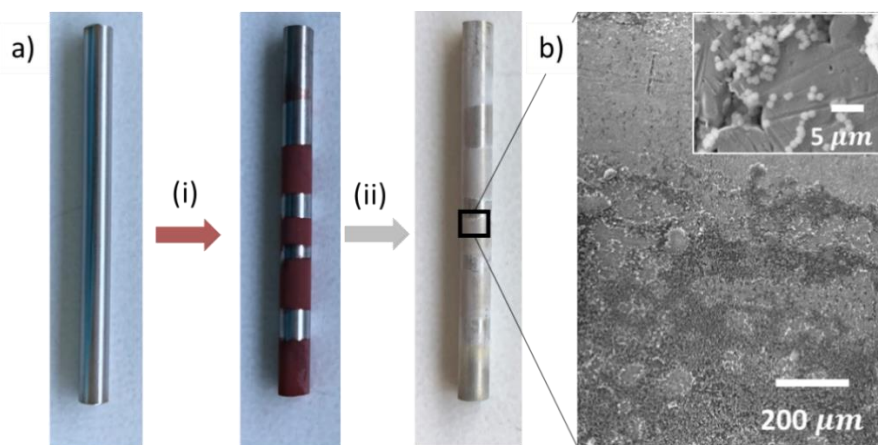


Figure 4. a) Photographs showing the two-step synthesis route to achieve ZIF-8 coating on a stainless-steel rod, where (i) corresponds to copper electroplating and (ii) corresponds to direct in-situ synthesis, and b) SEM image of the marked zones.

A similar approach was intended by embedding copper pieces in the COC chip via chemical etching and pressing (see also S.I.). Afterwards, the chip was placed vertically in the reaction mixture of composition  $\text{Zn}:\text{Ac}:\text{Hmim} = 1:2:2$  for 24 h. Figure 5a displays the COC chip with copper pieces embedded in it, followed by a close up image before (left) and after (right) coating (Fig. 5b). The presence of ZIF-8 crystals was also detected by SEM analysis, where cubic shaped crystals with truncated edges of size  $\sim 9 \mu\text{m}$  were seen (Fig. 5c). Still, smaller cubic crystals of size  $\sim 5 \mu\text{m}$  was also observed over the non-metallic part of the COC chip (Fig. S21). This is believed to be caused by the deposition of the crystals formed in the reaction medium. These findings demonstrate a promising approach to obtain a high-quality shape- and size-controlled ZIF-8 crystal coating on metallic/non-metallic surfaces.

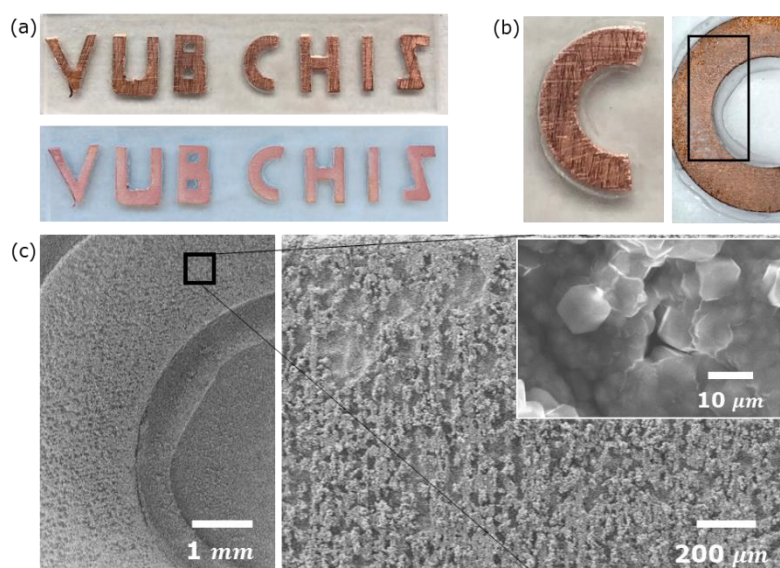


Figure 5. a) Photograph of COC chip embedded with copper pieces, before (up) and after (down) placing in the synthesis solution of composition Zn:Ac:Hmim = 1:2:2 for 24 h and b) photograph of the letter C before (left) and after (right) ZIF-8 coating along with (c) SEM images of the marked zones.

#### 4. Conclusions

In conclusion, we present a novel method for rapid synthesis of ZIF-8 crystals at room temperature by incorporating metal salts as triggering agent/co-modulator, along with sodium acetate as modulator. Especially with copper salt, a rapid production of ZIF-8 crystals in less than 5 min. was noticed at room temperature. Adaption of this synthesis route to a direct in-situ method allowed to achieve continuous and thick ZIF-8 coatings on copper supports at room temperature without any pre-treatment. Furthermore, the results also demonstrate the importance of sodium acetate molar ratio and of copper ions in the crystallization kinetics and evolution of ZIF-8 crystals. Overall, a conceptual advance in understanding the ZIF-8 formation mechanism is provided. Moreover, an extended trajectory of a synthesis route, from obtaining morphologically controlled ZIF-8 crystals in sustainable conditions to optimizing the route for synthesis of ZIF-8 continuous coatings on metallic/non-metallic substrates with thickness varying between 5 – 100  $\mu\text{m}$  have been delivered.

#### Author Contributions:

Ravi Sharma (Conceptualization, Formal analysis, Investigation, Methodology, Writing – original draft, review & editing), Tom R.C. Van Assche (Supervision, Validation, Visualization, Writing – review & editing), Gino V. Baron (Resources, Validation) and Joeri F.M. Denayer (Funding acquisition, Project administration, Resources, Supervision, Validation, Writing – review & editing).

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### Conflicts of interest

There are no conflicts of interest to declare.

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