NUCLEATION AND GROWTH OF ZIF8 AND MIL FRAMEWORKS ON SILICON-BASED SUBSTRATES AND COPPER FOILS.

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Metal Organic Frameworks (MOFs) have become increasingly promising materials for a wide range of technologies because of their high surface area, versatility, and chemical stability. MOFs are hybrid porous complexes in which periodic arrangements of metal clusters are connected by organic ligands. Among all possible MOFs topologies, ZIF8 that consists of $Zn(MeIm)_2$ (HMeIm: 2-methylimidazolate), can be considered the zeolyte network more easily to obtain due its intrinsic structure and has great potentialities for gas and energy storage, chemical sensing and nanodevices. Several synthesis methods based on direct approaches, like solvothermal or microwave-based and electrochemical protocols, and on layer by layer deposition (LBL) carried out by employing OH or NH_2-terminated surfaces, have been proposed to obtain ZIF8 film. Here, through direct synthesis and by changing the solvent, it has been studied the role of surface chemistry on ZIF8 film growth. Si (100), Quartz, amorphous Si (a:Si) and silicon with native oxide have been employed as surfaces. The film preparation was carried out through sequential one-pot method, without additive, at room temperature and using a mixed Zn nitrate and imidazole solution either in MeOH or EtOH. Films were characterized by ellipsometry, XRD, SEM and XPS. Using MeOH a solvent, fast ZIF8 nucleation was observed both in solution and on the surface leading to powders and thick films. Well-grown films were, hence, obtained on quartz, a:Si and Si(100), while a poor coating was formed on SiO_2. From ethanol solution, slower grow rates occurred, so that the crystal formation in solution was negligible and thinner films compared with the ones in MeOH were deposited. The lower polarity of ethanol slows down the homogenous nucleation and allows to detect the

substrate effect. The different surface reactivity towards ZIF8 functionalization is attributable to the diverse silanol densities on the various surface and, in turn, to the different Lewis basic strength which can accelerate imidazole deprotonation. Si(100), being the surface with lower silanols density and exhibiting more basic behaviour, promotes the imidazole deprotonation, key step of ZIF8 formation. Indeed, Si results the most reactive surface towards ZIF8 functionalization and the growth rates on the diverse substrates increases according to the following order SiO_2 < quartz < amorphous Si < H-terminated Si.

Another promising subclass of MOFs is Fe-based MIL (Material of Institute Lavoisier) built from trivalent Fe^{3+} centers and carboxylate ligands. Particularly, MIL-101 and MIL-88 are framework isomers shaped from the same precursors but with different connectivity. Synthesis conditions, like temperature, reaction time, pH and the presence of additive, drive the deprotonation of carboxylic linkers and condition the MOF morphology leading to specific networks. Several examples of MIL-101 and MIL-88 (Fe-based) crystals have been obtained mainly by microwave-assisted and solvothermal route in presence of polymer and/or stabilizing agents, and characterized by long reaction times (12-24 hours) for hydro-thermal synthesis. Whereas, there are few examples of MIL films, carried out through coating techniques like Langmuir Blodgett and spin-coating which are usually polymer-assisted to optimize the surface adhesion and, through direct growth on pre-functionalized surfaces after long immersion time. In this study, in addition to the ZIF-8 film growth, it has been investigated the role of the acid additive and SAMs functionalization on the MIL phase, the surface coating and growth rate. Particularly, Fe-based MIL-101 and MIL-88 film were directly grown from solution on Si (100) surface through three different protocols in order to implement a new fast and facile synthesis route. MIL film with different morphology, crystallinity and coverage have been obtained and characterized by chemical, structural and optical data.

Then, either ZIF-8 and MIL films have been grown on copper foils through different synthesis protocols in order to study the electrochemical properties. In addition, ZIF8 coating copper foils have been also doped with lithium salts, in order to investigated how the doping can influence the charge/discharge profile of lithium ion cell.