| MATERIALS ENGINEERING | MATHEMATICAL

PhD Yearbook | 2024



DOCTORAL PROGRAM IN MATERIALS ENGINEERING

Chair: Prof. Chiara Bertarelli

The Ph.D. Programme in Materials Engineering provides high educational opportunities to young talents and executives who intend to become proactive professionals and researchers skilled in the design, production and application of both traditional and innovative materials, their optimization for specific applications, the prediction and assessment of their performance, and in developing new concepts and technologies in any materials-related fields.

Highlights of the Ph.D. Programme in Materials Engineering are:

- a rigorous scientific approach to address outstanding research
- an effective interdisciplinary approach
- connection with international leading scientific and technical communities
- a strong integration with the Doctorate School of Politecnico di Milano to increase knowledge with transversal courses, to gain soft skill and to join stimulating activities.

PHD CONTENTS AND PROGRAM STRUCTURE

Materials Engineering involves the investigation of correlation among materials structure, processing and functional and structural properties, and the knowledge management from materials design to final applications.

The Programme includes advanced research and training on:

- Research and development in traditional materials (*polymers, metals, ceramics, concretes, composites*) and related technologies.
- Specific application areas: materials for energy, materials for environment, materials for electronics, optoelectronics and photonics, materials for cultural heritage, materials for product design, materials for packaging, biomaterials.
- Smart, responsive and self-healing materials, nanostructured materials.
- Materials corrosion and durability, life cycle assessment, coating and surface functionalization

The achievement of the Ph.D. title in Materials Engineering requires a full-time study and research activity of at least three years which is completed by the development and defense of the Ph.D. thesis.

The PhD. students give an original contribution to increase knowledge in a material-related research field, and they acquire a problem-solving capability in complex contexts, including the ability of performing deep problem analysis, identifying original solutions, and evaluating their applicability in practical contexts. Students can use modern facilities for materials synthesis, processing and characterization available at the Politecnico di Milano or in other research laboratories.

The Ph.D. Programmes and the Ph.D. School offer courses, seminars, project workshops and laboratories. Teaching activities cover both basic research topics (problems, theories, methods) and specialistic topics related to the subjects developed in the theses. Ph.D. students are also encouraged to attend national and international Conferences Workshops and Schools and to plan a research period abroad.

PROFESSIONAL OPPORTUNITIES AND THE JOB MARKET

The Ph.D. Programme in Materials Engineering aims at training Ph.D. laureates having a common background and specialized qualifications in advanced research areas. The knowledge and skills of a Ph.D. in Materials Engineering enable graduates to pursue their career in the Manufacturing industry, given its quest for innovation in the production, processing, application and conservation of traditional materials, and for the development of innovative materials allowing radically new, currently unforeseeable applications. Moreover, the background deriving from full-time activity both in research and in education also qualifies the Ph.D. graduates for an academic career. Several graduates from the Materials Engineering Programme have been able to secure post-doctoral

research positions at high-ranking universities and

research Institutes.

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MODELING OF THE ELECTROSTATIC INTERACTION AND CATALYTIC ACTIVITY OF [NIFE] HYDROGENASES ON A PLANAR ELECTRODE

Manuel Antonio Ruiz Rodriguez - Supervisor: Guido Raos

The interest in the study of renewable energies has increased in the last decade because humanity needs to drastically reduce the use of fossil fuels as the main energy carrier. With this priority in mind, the idea has emerged to replace fossil fuels with hydrogen. This element has several technical and environmental advantages over fossil fuels, although, until the date of 2023, it is still difficult to produce.

To address the problem of hydrogen production, the use of hydrogenases, a group of enzymes with the ability to catalyze the redox reaction of hydrogen, has been proposed. In the oxidation pathway, two electrons are removed from the hydrogen molecule, releasing two protons. In the reduction pathway, two electrons are added to two protons, generating a molecule of hydrogen.

This ability could be used in different approaches in the field of renewable energies, for example producing a continuous flow of electrons (electricity), or using the reverse reaction to obtain electrons from electricity and using them for the production of molecular hydrogen. Allowing in this way to store the energy from electricity, in the form of the chemical bonds of the hydrogen molecule. This energy can be released later by other means, for example, in fuel cells. For this reason, the incorporation of hydrogenases in electrochemical devices has been explored using different approaches. One of these has been the adsorption of hydrogenases on the surface of electrodes used inside electrochemical devices. The idea of adsorbed hydrogenases on the surface of electrodes has been evaluated on a diversity of materials, such as titanium, gold, silver, or graphite, with different degrees of success. All these studies have reported diverse grades of hydrogen production, indicating that several factors have an important role in

the reaction rate.

The adsorption of hydrogenases on electrodes can be achieved by physical adsorption or covalent attachment. This study uses a computational model based on the linearized version of the Poisson-Boltzmann equation to describe the electrostatic interactions (physical adsorption) of the hydrogenase[NiFe](pdb code: 1e3d) on a planar electrode. To achieve such a goal, the interaction energy between a hydrogenase [NiFe] and an electrode with different orientations was calculated (Fig. 1). Considering such a purpose,

the effect of some experimental factors previously reported has determiners for the adsorption and orientation of the protein, such as pH, salinity, and electric potential. A secondary goal was to determine if it is possible to control the orientation of the hydrogenase on the surface of the electrode by tuning these variables, without modifying the chemistry of the electrode.

The third goal was to determine the activity of the adsorbed hydrogenase as a function of the enzyme concentration, based on the assumption that there is a relationship between the adsorption equilibria and the electron transfer between the hydrogenase and the electrode. According to the results, the adsorption of the enzyme on the electrode depends mainly on the



Fig.1 - Model used to test the protein-electrode electrostatic interaction, defining the tilt θ and azimuthal angles $\phi.$

salinity of the solution, followed by pH and the electrostatic potential of the electrode. The results show that the latter does not affect the adsorption energy of the protein too much, but it has a clear effect on the orientation of the protein (Fig. 2).

The results show that the orientations with the lowest total energies were obtained when there was a presence of charged patches on the surface of the protein; the presence of these patches depends on the solution pH. It was observed that the interaction was bigger in salt-free solutions, where electrostatic interactions are not screened by the presence of counter-ions. The total current, which measures the overall rate of the redox reaction of all the adsorbed proteins, has its maximum value when there is a positive synergy between the Boltzmann probabilities of the orientations, their electron transfer rates, and high adsorption constants (k). It was not possible to find combinations of experimental factors dominated by a single protein orientation, and it is for



Fig.2 - Orientation obtained with the highest current (120 $\theta,$ 240 ϕ angles), and the heatmap of the interaction energy under its experimental conditions (I =0.0 M, electrode potential 0.0 V).

that reason that the overall current depends on a whole population of absorbed proteins in a random distribution of orientations. While the electric potential and pH do not affect the interaction energy of the hydrogenase too much, they have a clear effect on the orientation of the protein. Due to the presence of charged patches on the surface of the enzyme, whose presence mainly depends on the solution pH. One recurrent particularity is the presence of lysine residues in the charged patches close to the surface of the electrode in the minimum-energy orientations. It could be interesting to pursue further this observation and determine the role of lysine residues in the adsorption of the hydrogenase and if it is possible to increase it by introducing more lysine residues on the exterior of the protein, at favorable positions with respect to the [3Fe4S] external cluster. The results of the adsorption curves show little difference at different pH levels, with pH=5 (Fig. 3a) yielding slightly better results due to a combination of a

higher current (J₀), determining saturation of current at high protein concentrations, and a slightly higher adsorption constant (K) determining the position of the inflection point in the Langmuir isotherms.

The plots show that there is a dependence on the pH for the results obtained in the salt-free solutions (Fig. 3b), where the cases at pH=8 and 9 are characterized by strong absorption (large K), but the values of J_0 are low, indicating that the hydrogenase is adsorbed in an unfavorable orientation for electron transfer.

Figure 3c shows the effect of modulating the electrode potential (-0.05 to 0.05V), the most visible changes occur at the two ends of the pH range, and a negatively charged protein (pH=9) has a much greater affinity for the electrode at positive potential. This study shows that the adsorption of hydrogenase can be achieved with electrostatic interactions and these are affected by ionic strength, pH, and the orientation of the protein.



Fig.3 - Dependence of current at different pH and protein osmotic pressure, at zero electrode potential. (a) salty solutions, I=0.15 M; (b) salt-free solutions, I=0.00 M; (c) for saline solutions with I=0.15 M, (-0.05 V $\leq \Phi_e \leq 0.05$ V).



Simona Sorbara - Supervisor: Piero Macchi

EVALUATION, AND APPLICATIONS

The goal of this research project was to find new and disruptive materials that could be good candidate for the miniaturization of electronic devices. Scientists and engineers try to design and fabricate new types of insulators in spite of the traditional fiberglass, which does not meet the requisite of very low dielectric constant ($\kappa =$ 3.9), to be adequate for further miniaturization of the devices. This deficiency causes, for example, a large cross-talk effect in microcircuits. To overcome these limitations, nano-porous materials and, in particular, Metal Organic Frameworks (MOFs) have recently received much attention. MOFs are typically very stable, tuneable, highly porous, and often crystalline. Indeed, these are key features for disruptive ultralow-κ materials. However, some pitfalls hamper their application, for example the ease of water adsorption, which is extremely problematic due to its high polarity, dielectric constant, and mobility. Thus, the target is fabricating a hydrophobic material which preserves the low dielectric constant of a highly porous MOF, with just a minimal loss of performance, and at the same time is sufficiently hydrophobic. Several strategies are possible, for example:

a) applying post-synthetic modifications to functionalize the MOF with linkers bearing strongly hydrophobic substituents; b) protecting the MOF pores with other materials, like layered graphenes, producing hierarchical nano-composites; c) using ligands featuring optimal hydrophobicity that (often sterically) prevent water molecules from cleaving the metal-carboxylate/metalnitrogen bonds. During the whole research project, all these three strategies have been investigated.

SUPERHYDROPHOBIC MOFS: DESIGN, PREPARATION,

a) <u>Hydrophobic MOFs using post-</u> <u>synthetic reactions (Fig.1)</u> The dielectric constant of a very well- known Metal-Organic Framework, namely Cu₃(BTC)₂ (known as HKUST-1; BTC = 1,3,5benzenetricarboxylate), was investigated before and after protection with some amines. These studies allowed us to evaluate the hydrophobic power given by different



Fig. 1 - A schematic picture of the fabrication of a superhydrophobic MOF composite by means of long-chain alkyl amines (such as OA). amines (alkyl and aromatic) to the pristine material. Moreover, we investigated the structure of HKUST-1 under a strong electric field, studying its robustness and the electron density perturbation of its guest molecules.

b) Hydrophobic MOFs through post-synthetic fabrication (Fig.2) A well-known family of four isoreticular MOFs, UiO-66, $[Zr_6(\mu_3-O)_4(\mu_3-OH)_4(BDC)_6]_n(BDC$ = 1,4-benzenedicarboxylate) and UiO-66-X, with X = NH₂, NO₂, and F₍₄₎ were subjected to a post synthetic modification with polydimethylsiloxane (PDMS). In this contest, to study their interactions

with water molecules, we

developed a new protocol

Fig. 2 - Schematic illustration of the adopted

PDMS protection strategy, primed to induce

surface hydrophobicity in MOFs that exhibit

surface hydrophilicity, pre-protection.

any type of material.

applicable more generally to

 c) <u>Hydrophobic MOFs with pre-</u> synthetic design (Fig.3) As reported in the literature,

fluorinated linkers seem to be ideal for the fabrication of hydrophobic Metal Organic Frameworks. In this context, we were able to isolate three new promising fluorinated low-κ hydrophobic Ni(II) and Mn(II) based porous systems, structurally characterized though X-ray powder diffraction. All the three seem to be promising as low dielectric constant materials, nevertheless the material characterizations are quite complex, not allowing us to find the right impedance analysis conditions, so far.

With these results, one could undertake further steps for the optimization of the material design and fabrication, having paved the way toward a better understanding and determination of the key-features necessary to prepare a superhydrophobic MOF.

Fig. 3 - Representation of the crystal structures of the new synthetized fluorinated MOFs. On the top, the two Ni(II)-based MOFs; on the bottom, the Mn(II)-based MOF. 440

MATERIALS ENGINEERING

VIBRATIONAL AND COMPUTATIONAL INVESTIGATION OF ADSORPTION AND TRIBOLOGY OF ORGANIC FRICTION MODIFIERS INTERACTING WITH STEEL SURFACES

Nicolò Simone Villa - Supervisor: Andrea Lucotti

Friction plays a major role in contributing to global energy consumption and reducing it would bring about major economic and environmental advantages. It is estimated that roughly 23% of the sample (micro-IRRAS). This is the first successful attempt at this implementation of the spectroscopic technique for this particular scope, to the best of the author's knowledge. The recorded spectra are interpreted by density functional theory (DFT) calculations and provide important information about the effect of the tribological phenomena on the adsorption state and molecular orientation of the friction modifier. Moreover, this implementation allows for a differential analysis of the state of the tribofilm of regions affected/ not affected by the tribological phenomenon. The combination of theoretical calculations and experimental measurements led to confirmation that the OFM molecules chemisorb on the surface forming monodentate, bridging bidentate, and bridging chelate configurations on the iron atoms, arranged in SAMs. By combining micro-IRRAS and DFT/ DFT-MD calculated spectra we verified that OFM molecules do indeed tilt as an effect of friction.

Through polarized IR spectra DFT calculations, the tilt angle could be estimated (Fig. 1). Classical dynamics simulations (Fig. 2) show that at low temperatures the OFM molecules undergo collective torsional and tilting motion during a friction event.

This becomes progressively easier as temperature increases, resulting in lower friction coefficients, until a temperature

a) [- micro-IRRAS before friction micro-IRRAS after friction v(C=O) monodentat ance (a.u.) v(COO⁻)a bridging (a.u.) δ(CH₂) + v(COO')s bridging v(C-O) monodentat 1000 1100 1200 1300 1400 1500 1600 1700 1800 1000 1100 1200 1300 1400 1500 1600 1700 1800 Wavenumber (cm⁻¹) Wavenumber (cm⁻¹) c) — Calculated - α = 0° Calculated - a = 20° ice (a.u.) (a.u.) o nce 1000 1100 1200 1300 1400 1500 1600 1700 1800 1000 1100 1200 1300 1400 1500 1600 1700 1800 Wavenumber (cm⁻¹) Wavenumber (cm⁻¹)

where these collective motions

cannot be maintained anymore,

leading to an increase of the

friction coefficient, which is

of disordered domains in the

the steel surface. Static DFT

calculations, combined with

experimental measurements

of friction coefficients indicate

that the strength of the packing

between OFM molecules

molecular arrangement on

accompanied by the formation

Fig. 1 - a) Experimental micro-IRRAS spectra of oleic acid adsorbed on steel before (black) and after (blue) the MTM test and b) the difference spectrum. c) Calculated polarized spectra of all-trans hexanoic acid adsorbed on hematite, with tilt angle of 0° (black) and 20° (blue) compared to the z-direction of our simulation cell and d) the difference spectrum. The calculated frequencies presented in c) and d) have been uniformly scaled by a factor of 0.98 to ease the comparison with the experiments.

determines the friction performance, rather than the adhesion interaction with the steel surface. The temperature at which the collective behavior fails coincides with the temperature at which the Gibbs' free energy of packing is found to diminish (Fig. 3).

This study enlightens the principles of the action of OFMs in reducing friction and provides quidelines for the development

of new OFMs exhibiting better performances. The results obtained pave the way for a software-assisted design of new OFMs, as well as the models for the prediction of friction performances, with the knowledge of the OFM structure as the only requirement.

TYYVE MENTINE STILL Fig.2 - Starting geometry of the MD simulation. development of machine learning

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The hydrogen atoms and the oxygen atoms of hematite have been hidden for viewing



Fig. 3 - a) Plotted DFT calculated electronic adsorption, packing, and adhesion energies for each of the OFMs investigated. b) Gibbs' free energies of packing calculated from the DFT models of the OFMs investigated.

INKJET PRINTING AS AN ALTERNATIVE FABRICATION TECHNIQUE FOR ENERGY STORAGE AND MEMS DEVICES

context, the idea to implement

IJP as a non-traditional battery

motivated this study, where the

final goal was the obtainment of a thin-film battery device, that

could retain its electrochemical

different degree of deformation.

On the other hand, the idea of

implementing inkjet printing

in the electronic fabrication

related to the production of a

polymeric vibration damping

layer on a spring present on

non-restraining resolution

traditional fabrication

MEMS. In particular, wherever

requirements are acceptable,

techniques can be substituted

by inkjet printing, in an optic of facilitating the process and

reducing material waste.

has motivated the study

production technique has

performances even under

Prisca Viviani - Supervisor: Luca Magagnin

In the framework of additive manufacturing, inkjet printing has attracted great interest both from the academic and industrial point of view. This work was focused on investigating inkjet printing as a possible alternative fabrication technique, that could guarantee simplicity, easy integrability, versatility and flexibility combined with limited material waste, typical of additive manufacturing techniques. In particular, two different fields were explored through an extensive study of how inkjet printing could be adopted in the production of energy storage devices and MEMS components. On one hand, the adoption of inkjet printing as a non-traditional fabrication technique is justified by the increasing demand in thin, flexible energy storage devices that are able to power complex-shaped objects. This is particularly relevant in the ambit of the Internet of Things, where systems and everyday objects should be able to collect and interpret data without the need of human participation. Of course, the integration of traditional rigid batteries is challenging, as their form factor as well as their adaptability to complex-shaped surfaces is in fact limited. From this

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METAL NANOSTRUCTURES DOPED ELECTROSPUN MEMBRANES FOR SERS SENSING

Ziwei Wang - Supervisor: Matteo Tommasini

Water pollution has become a serious problem on our planet, and the new emerging contaminants in wastewater include pharmaceuticals, or personal care products. Better detection strategies and wastewater treatments are required, hence sensors with excellent sensibility and simple operation are called for. Nanomaterials have various special properties, for example size effects, quantum effects and large surface area. Metal nanoparticles have an appealing property in the world of nanomaterials, which is the presence of localized surface plasmon resonances. Due to their unique optical properties, gold nanomaterials have been explored in recent years to enable the detection of many analytes. Among various sensing techniques, surface-enhanced Raman spectroscopy (SERS) is a method to effectively increase the Raman signals when the analyte is in low concentration. SERS has been widely investigated in different research fields including surface science, biology, material science and electrochemistry. In this research project, gold nanorods (AuNRs) were synthesized through a seedless growth method, and their aspect

ratios were varied between 2.4 and 4.2 by adjusting the silver nitrate concentration. The AuNRs were centrifuged and doped into poly(vinyl alcohol)(PVA) fibers through the electrospinning technique, so to produce thick membranes. After electrospinning, the composite membranes were made stable in water environment by crosslinking with glutaraldehyde (GA). Under the scanning electron microscope (SEM) the fibers were homogeneous and defectfree, with diameters of about 300 nm. The red shift of the surface plasmon resonance (SPR) peak of the AuNRs, measured by UV-Vis spectroscopy, indicated the aggregation of the AuNRs after doping into PVA fibers. The successful crosslinking was proved by Fourier Transform Infrared Spectroscopy (FTIR), while the optimal crosslinking time of 40 minutes was determined by checking with SEM the results of the crosslinking procedure for different reaction times. The composite AuNRs/PVA membranes so produced were tested as SERS active substrates for the detection of Rhodamine 6G (Rh6G) and aniline in aqueous solutions. The Rh6G solution was selected to optimize the SERS performance as a function of the concentration of the AuNRs in the

PVA matrix. With a AuNRs doping concentration of 3.36 wt%, the composite membrane could detect Rh6G at the concentration of 10⁻⁶ M, which is too low to be detected by normal Raman spectroscopy. An improved SERS measurement technique was introduced by using a customized hard disk drive as a spinning device to achieve a dynamic SERS detection mode. This allows overcoming sample degradation effects that may be often induced by a static irradiation of the SERS substrate with a focused laser power. Furthermore, the reusability of the composite AuNRs/PVA SERS membrane was proved by simply rinsing off both analytes with water. Moreover, I also discovered that the crosslinking step improves the



Fig. 1 - The schematic illustration of a SERS substrate prepared by the electrospun AuNRs/ PVA membrane after a post-processing crosslinking step. SERS performance of the AuNRs/ PVA membrane, as shown by Raman mapping measurements. The investigation of SERS detection approaches in water environment was also achieved through another strategy, which implied the preparation of the gold nanomaterials followed by phase transfer. Both gold nanoparticles (AuNPs) and AuNRs were made suitable for phase transfer in organic solvents by functionalizing the surface of the nanomaterials with 1-dodecanethiol (DDT) or 1H.1H.2H.2Hperfluorodecanethiol (PFDT). The absorption peak analyzed by UV-Vis spectroscopy showed a red shift after phase transfer. Then, an appropriate polymer, including PMMA and PEO,



Fig. 2 - The SEM photo of focusing on only one fiber doped with AuNRs. The inset photo is SEM photo of AuNRs dispersion droplet on silicon slice. was selected to support the gold nanomaterials and thus form a membrane through the electrospinning technique. Both the phase transferred AuNPs and AuNRs composite membranes were able to be applied as SERS substrates for detection of Rh6G in aqueous solutions. Due to the property of protein that interacts with various molecules, BSA decorated into the composite AuNRs/PVA membrane system to provide capture ability to the membrane, especially for the standard analyte in low concentration and the analyte which is difficult to be detected through regular SERS. Filter-based SERS is a technique combines SERS

and filtration to achieve better detection performance. Through a filtration set-up, the hybrid BSA/AuNRs/PVA membrane was able to detect Rh6G aqueous solution in the concentration of 10⁻⁷ M, which was not able to be detected through regular SERS detection introduced above. Furthermore, the hybrid BSA/PVA membrane is a good candidate as a filter for wastewater treatment to capture ketoprofen. The average diameter of BSA/PVA fiber was measured by SEM characterization. By analyzing the spectra produced from the Bradford protein assay, the

presence and amount of BSA at the fiber surface were measured. After immersing the hybrid BSA/PVA membrane into 520-Biotin solution, the decorated membrane was developed to an optical biosensing platform with the ability to capture 132 ± 28.5 µg of biotin per gram of mat mass. Hence, the BSA/ AuNRs/PVA membrane is able to detect ketoprofen solution in the concentration of 10⁻⁶ M using filter-based SERS measurement.