1η ΗΜΕΡΙΔΑ ΠΡΟΠΤΥΧΙΑΚΩΝ ΦΟΙΤΗΤΩΝ

Εκπόνηση Διπλωματικής Εργασία στο Τμήμα Επιστήμης και Τεχνολογίας Υλικών

Πανεπιστήμιο Κρήτης, Ηράκλειο

15 Μαΐου 2023

ΒΙΒΛΙΟ ΠΕΡΙΛΗΨΕΩΝ

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Πανεπιστημιούπολη Βουτών

Αίθουσα Ε130 Τμήματος Μαθηματικών και Εφαρμοσμένων Μαθηματικών

Πανεπιστημίου Κρήτης

Οργάνωση

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ΣΥΜΒΟΥΛΟΣ ΔΙΟΡΓΑΝΩΣΗΣ

Αρματάς Γεράσιμος

ΠΕΡΙΕΧΟΜΕΝΑ

ΠΕΡΙΛΗΨΕΙΣ ΟΜΙΛΙΩΝ

Exploratory Synthesis of Complex Halide Perovskites via Solid-State Chemistry Approaches

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Perovskite is the calcium titanium oxide mineral with the formula of $CaTiO_3$. Based on this prototype, all compounds with a general formula ABX_3 and similar atom topology in the unit cell are called perovskites The simplest way to describe the perovskite is by placing a relatively large, non-bonding (ionic bonding), positively charged, atom or small molecular cation of type A in the center of a cube (in a primitive cubic unit cell). The corners of the cube are then occupied by the B atoms, which are typically small, positively charged metal ions located at the center of a perfect octahedron, covalently connected with six X anions. This configuration enables for the formation of infinite three-dimensional network of corner-connected octahedra linked via 2-coordinate X-anions. The complex perovskite structure has been extensively studied over the years, leading to a series of discoveries, notably including ferroelectricity and superconductivity for the $BaTiO_3$ and $YBa_2Cu_3O_7$ derivatives (1). More recently perovskites based on halide rather than oxide X anions have been expensively studied, due to their relevance to optoelectronic applications (2). Even though the two families present main similarities the structural and crystal chemistry of this systems presents striking differences which significantly impact the physical properties of the compounds.

With these concepts in mind, my thesis project will be focused on the exploratory synthesis targeting selected perovskite types that are well-known for the oxide families but so far have not been synthesized for any halide analogue. The target compositions are designed based on the *charge mismatch* concept, where the perfect perovskite stoichiometry is tweaked to generate imbalances in the chemical composition. Oxide analogues such as the vacancy-ordered tungsten bronzes (A_xWO_3) and/or the ordered Aurivillius-type heterostructures ($Bi_4Ti_3O_{12}$) will be actively investigated. The perovskite materials will be synthesized either via standard wet chemistry methods or via the more direct solid-state reactions. The approach that we will focus our research on is based on the stoichiometry mismatch of the reactants, taking into account the different coordination trends of heavy metals across the Periodic Table. We seek to obtain perovskite compositions with a suitable bandgap range for use in photovoltaics. The reaction products will be characterized via multiple characterization techniques (crystallography, spectroscopy, etc) and single-crystal structures will be determined in cases where sufficiently large-single crystals can be grown.

Keywords: perovskites, solid-state synthesis, crystal chemistry

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Machine Learning Models for Heterogeneous Catalysis Data

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Machine learning (ML) has become a promising approach to predict and optimize catalytic systems in recent years. By using ML models, researchers can rapidly screen and identify the most effective catalysts and reaction conditions, reducing the time and cost required for experimental trials. One of the main challenges in catalysis research is the complexity of the reaction mechanisms involved.1 ML algorithms can be used to extract useful insights from large and complex datasets, which can be used to identify key factors affecting catalytic performance. In our work, we study the potential of ML in predicting the reaction energies from density functional theory (DFT) calculations on surface systems, by obtaining those data and using various ML models, especially regression models, such as Linear Regression, Support Vector Regression, and Random Forest Regression. Overall, ML has great potential in catalysis research, and it is expected to play a significant role in the development of new catalytic materials and processes in the future. The application of ML models in catalysis data analysis can lead to a more efficient and sustainable chemical industry, with reduced environmental impact and improved economic benefits.

Keywords: Algorithms, Machine Learning, Catalysts, Catalysis

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Synthesis and Characterization of CoP/g-C₃N₄ Heter-nanostructures for Environmental Applications

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Water pollution is a serious hazard to aquatic ecosystems and human health. Toxic metals, such as Pb, Hg, As, and Cr, are some of the most severe chemical wastes. The cost-effectiveness and scalability of the photochemical conversion of the hexavalent chromium (Cr(VI)) to less toxic trivalent (Cr(III)) form make this process one of the most promising solutions for environmental remediation. The sunlight irradiation is an affordable and environmentally friendly energy source for chemical reactions. In this work, we present the synthesis of 2D/3D hybrid heterostructures composed of graphite carbon nitride (g-C₃N₄) layers and small-sized cobalt phosphide (CoP) nanoparticles and demonstrate their excellent performance in the photocatalytic reduction to Cr(VI). Using a combination of photochemical deposition method and solid-state reaction, we succeeded in preparing a series of CoP/g-C₃N₄ composite materials with different CoP content, that is, from 5 to 30 wt.%. The resulting materials were studied in terms of lattice crystallinity, chemical composition, optical properties and porosity of the structure with the techniques of electron scanning microscopy (SEM), elemental analysis EDS, X-ray diffraction (XRD), UV-VIS optical absorption and N₂ porosimetry. The catalytic activity of the CoP/g-C₃N₄ composites compared to the primary materials CoP and g-C₃N₄ is evaluated in the photocatalytic detoxification of Cr(VI)-contaminated effluents under visible light illumination ($\lambda > 420$ nm), remarkably without the use of sacrificial additives (electron donors).

Keywords: Graphitic carbon nitride, cobalt phosphide, hetero-nanostructures, photocatalysis, Cr(VI) reduction, environmental remediation.

References

Development of Ni$_2$P/NiCo$_2$S$_4$ Composite Nanostructures for Efficient Electrocatalytic Water Splitting

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In the attempt to replace the polluting fossil fuels with sustainable and clean energy sources, hydrogen is a promising solution. In this context, electrochemical water splitting is one of the most effective, environmentally sustainable and inexpensive methods for green hydrogen production. As a consequence, an important research goal in this topic is the development of highly active, stable, yet cost-effective electrocatalysts. The main purpose of this thesis is the synthesis and structural characterization of new nanostructured Ni$_2$P-modified NiCo$_2$S$_4$ heterostructures with different Ni$_2$P content (i.e., from 10 to 40 wt.%), as well as the evaluation of electrocatalytic activity of these materials towards electrochemical water splitting and hydrogen evolution reaction. The morphology, chemical composition, crystal structure and electronic structure of the Ni$_2$P/NiCo$_2$S$_4$ composite catalysts were characterized by a combination of analytical and spectroscopic techniques, such as X-Ray diffraction (XRD), electron scanning microscopy (SEM), EDS microanalysis, UV-VIS spectroscopy and electrochemical impedance spectroscopy (EIS). In the present study, we further demonstrate that by tuning the composition, Ni$_2$P/NiCo$_2$S$_4$ composite catalyst containing 30 wt.% Ni$_2$P attains excellent stability and electrocatalytic performance for hydrogen evolution.

Keywords: Thiospinels, Nickel phosphide, Electrochemical water splitting, Hydrogen evolution reaction.

References

Synthesis of Colloidal Dispersion of Wide Gap Halide Perovskite Nanocrystals for Optoelectronics

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Halide perovskites is a class of high-performance semiconductors operating in the visible spectral range. They have attracted an enormous research interest in the past decade in fields related to optoelectronics- particularly photovoltaics. However, the recent synthesis of stable colloidal solutions opened new avenues in the potential applications of the materials, emphasizing the very efficient light-emission of the materials originating from the close to 100% photoluminescence quantum yield (PLQY) (1).

In this Thesis project, we investigate the synthesis of such colloidal solutions, targeting nanocrystals that emit in the blue spectral region (400-500 nm), targeting compositions close to the phase-pure system $CsPbCl_3$. We select to focus on the all-inorganic $CsPbX_3$ system since it has been shown (1) to provide homodisperse nanocrystals the exhibit narrow emission linewidths of (10-40) nm, a wide color gamut, high quantum yields and radiative lifetimes in the range of few nanoseconds. We are particularly interested in the light halide compositions (including solid solutions) since these materials have a wide enough bandgap to emit in blue region of the visible spectrum. We discuss the potential of NCs for optoelectronic applications such as light-emitting devices for television displays and spontaneous emissions for potential lasing operation. Once synthesized the materials will be characterized via photoluminescence measurements in order to assess the particle size distribution and the homodispersity of our system, the stability of the nanocrystals upon illumination and their light emitting efficiency. In addition, auxiliary measurements (crystallography, microscopy, etc.) will be performed to analyze the phase purity and the homogeneity of the as prepared colloidal suspensions.

Keywords: perovskite, nanocrystals, semiconductors, photoluminescence

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Μελέτη της δομής, των μηχανικών και θερμικών ιδιοτήτων εποξειδικού δικτύου με βάση την κατεχόλη

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Στο πλαίσιο της έρευνας μελετήσαμε την δομή, τις μηχανικές, και θερμικές ιδιότητες ενός διασταυρωμένου εποξειδικού πολυμερικού δικτύου με επιπλέον δεσμούς σιδήρου-κατεχόλης. Το δίκτυο εκμεταλλεύεται την ιδιότητα της κατεχόλης να δημιουργεί δεσμούς συντονισμού με τον σίδηρο, έχοντας ως αποτέλεσμα ένα υβριδικό δίκτυο με ομοιοπολικούς και δεσμούς συντονισμού. Με τον τρόπο αυτό, το ελαστομερές αποκτά βελτιωμένες μηχανικές ιδιότητες. Συγκεκριμένα, μελετήσαμε τους τρόπους απομάκρυνσης της προστατευτικής ομάδας της κατεχόλης, τη δημιουργία δικτύου με διαφορετικά μοριακά βάρη του πολυμερούς, τη θερμική και μηχανική συμπεριφορά του, καθώς και τις τυχόν διαφορές στις θερμικές ιδιότητες μετά την διαδικασία του εφελκυσμού.

Λέξεις κλειδιά: Κατεχόλη, Μηχανικές ιδιότητες, Σίδηρος, Δεσμοί Συντονισμού, Υβριδικό δίκτυο

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Mesoporous Frameworks of Linked β-Ni(OH)$_2$-decorated CdIn$_2$S$_4$ Nanoparticles as Efficient Photocatalysts for Hydrogen Fuel Production

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As the growing global warming and energy demands are becoming a pressing issue, hydrogen as an alternative fuel has attracted great interest. Photocatalytic water splitting, utilizing abundant solar energy, represents a promising strategy for clean, low cost and environmentally sustainable H$_2$ production. Thiospinels constitute an interesting class of materials for photocatalytic applications due to their relatively narrow band gap, nontoxicity, and photochemical stability. In this work, synthesis of mesoporous networks of thiospinels nanoparticles as building block units is accomplished by utilizing a simple polymer-templated oxidative polymerization method. The resulting mesoporous structures is composed of linked CdIn$_2$S$_4$ nanocrystals and present a 3D open-pore framework structure with high internal surface area. Due to the large and accessible surface area and suitable band gap, which results in visible-light response, the mesoporous CdIn$_2$S$_4$ constitute an efficient catalyst in the field of photochemical water splitting. Deposition of β-Ni(OH)$_2$ nanoparticles on the surface of CdIn$_2$S$_4$ mesostructure is experimentally demonstrated as an effective way to improve the photoactivity of composite frameworks through the formation of p-n junctions. Such heterojunctions promote efficient separation and transfer of the photogenerated charge carriers and suppress their recombination. As thus, the β-Ni(OH)$_2$/CdIn$_2$S$_4$ photocatalytic system can benefit from the high reactivity of the semiconductor nanoparticles and the large density of surface active sites, presenting enhanced visible-light photocatalytic performance for water splitting and hydrogen production.

Keywords: Chalcogenide, Thiospinel, Hetero-nanostructures, Photocatalysis, Water splitting, Hydrogen evolution.

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Synthesis and crystal growth of organic-inorganic halide perovskite single-crystals

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Hybrid organic-inorganic perovskites are a class of materials that have gained a lot of attention in recent years due to their potential applications in various fields, such as solar cells, light-emitting diodes, and lasers. These materials have the general formula ABX_3, where A is an organic cation (methylammonium or formamidinium), B is a metal cation (in this case Pb), and X is a halide anion (Br, Cl, I). The synthesis of organic-inorganic halide perovskites typically involves solution-based methods, which allows for control of the chemical composition and the crystal morphology of the single crystal.

The main focus of the research project concerns the study of the different methods available for the growth of the perovskite crystals spanning different crystallization techniques. One method that can be used for the synthesis of perovskite crystals is supersaturation crystallization. During this method, the metal oxide and the organic salt precursor are dissolved in a specific hydrohalic acid in concentrations close to saturation that enables control over crystal growth via temperature control. Another method that is commonly used, called inverse temperature crystallization (ITC), involves mixing the metal halide precursors with an organic cation precursor in a polar aprotic organic solvent. The resulting homogeneous solution, is then heated to a certain temperature, which enables the initiation of crystallization due to the reduced solubility of the perovskite at elevated temperatures. A different method that can be used for the growth of perovskite single crystals is the combination of solvent/non-solvent mixtures. In this instance, the crystallization is controlled by the solvent/non-solvent ratio and the rate of mixing between the two miscible solvents. These three methods produce large-sized (several mm), euhedral crystals, which are then characterized via a series of crystallographic and spectroscopic methods, in order to assess the advantages and disadvantages of each crystal growth method.

Keywords: perovskite, halide, synthesis, crystal growth

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Two-dimensional halide perovskites for photovoltaic applications

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Halide perovskites are an emerging class of high-performance semiconductors that have drawn remarkable attention in the past decade due to their superb properties and the low fabrication cost. With $CH_3NH_3PbI_3$ as the parent prototype, halide perovskites have evolved to immense complexity in order to assist the optimal performance of photovoltaic devices -the leading technological applications. Compositions as complex as $(Cs_{(0.05)}CH_3NH_{3(0.15)}$ $HC(NH_2)_{2(0.80)})Pb(I_{2.4}Br_{0.6})$ (simply known as the "triple cation" perovskite) have been invoked for this purpose, with the main focus of these changes being to increase the chemical stability of the system for long-term photovoltaic operation (1). Although this has been a relatively successful approach, the complexity of the system often leads to phase segregation, which is likely the reason for the instability of the material. In order to address these, a derivative class of materials has been employed in the form of dimensionally reduced perovskites. This class of materials offers the added benefit of incorporating bulky organic cations which are suitable as water repellants in addition to the structural benefit they provide in texturing the materials within the photovoltaic assembly (2).

The main focus of this Thesis project will be the employment of selected two dimensional (2D) hybrid halide perovskites for the fabrication of photovoltaic devices. Specifically, we study the n=3 and n=4 values of the $(A')_2(A)_{n-1}Pb_nI_{3n+1}$ homologous series (starting for the A' = butylammonium/ a = methylammonium combo), where we investigate the synthesis of the raw materials, and the factors affecting their successful deposition onto thin-film substrates. There will be a brief comparison of the properties of n=3 and n=4 2D perovskites with those of traditional 3D perovskites to demonstrate the potential advantages of the former. Once the crystal synthesis is done, the next step is to move to the photovoltaic device fabrication, which uses the synthesized 2d perovskites and consists of a glass substrate coated with a fluorine doped tin oxide (FTO) layer, a perovskite layer, an electron transport layer (ETL), a hole transport layer (HTL) and finally a layer of Au to complete the n-i-p junction. Our results demonstrate the potential of 2d perovskites as promising candidates for use in high-performance and stable photovoltaic devices. The synthesis and application of 2d perovskites, can be used to develop efficient and cost-effective solar energy harvesting technologies.

Keywords: perovskite, thin-films, semiconductors, photovoltaics

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ΠΕΡΙΛΗΨΕΙΣ POSTER

Synthesis of AaeUPO-polymer bioconjugates

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Catalysis is among the numerous applications protein-polymer conjugates are expected to find in the field of materials science due to their ability to enhance and/or differentiate the activity of the parent enzymes. In this report, the synthesis of protein-polymer conjugates of AaeUPO, a peroxygenase isolated from the basidiomycete Agrocybe aegerita, is presented. Peroxygenases have drawn significant interest as 450 monooxygenases substitutes. As heme-thiolate enzymes, their range of reactions resembles that of P450 monooxygenases however, peroxygenases utilize hydrogen peroxide or organic peroxides as oxidants, which enables their application in non-aqueous media.[1] Therefore, UPOs are attractive biocatalysts for selective oxyfunctionalization of otherwise non-reactive carbons. A variety of monomers were utilized to synthesize hydrophobic, hydrophilic, responsive protein-polymer bioconjugates via oxygen tolerant, controlled radical polymerization approaches.[2] The synthesis and characterization of a variety of such bioconjugates will be presented together with initial studies on their response and catalytic properties.

Keywords: bioconjugates, UPO, catalysis, peroxygenase

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Ab-initio insights on adsorption on ZnO surfaces doped with Mn

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Zinc Oxide (ZnO) is a wide-bandgap semiconductor material that has been extensively studied due to its unique electronic and optical properties, which play a crucial role in a variety of applications such as batteries and photocatalytic applications to mention just a few.[2] Moreover, adsorption is a well known aspect in catalysis and in some cases the degree of adsorption can also be used as an indicator of the catalytic activity of a material. The main focus on this thesis will be the simulation of molecular adsorption on ZnO surface slabs doped with Mn. Doping is the intentional introduction of impurities into a materials to modify its properties, while Mn is considered a great candidate for ZnO surfaces due to the fact that it has similar ionic radius to Zn, allowing the improvement of the catalytic activity and properties without causing significant defect or changes in the crystal structure.Therefore, studying the simulation of molecular adsorption on Mn-doped ZnO surfaces, can provide important insight into the catalytic properties of the material and aid in the development of more efficient and selective catalysts. Surface-doping of ZnO by Mn can be used to tune the workfunction up to several eV in some cases, while preserving the atomic and electronic structure of bulk ZnO. The effect of Mn doping on the electronic and structural properties will be examined. To further test the catalytic properties of Mn-doped ZnO, we consider adsorption of model molecule such as CO and H on its surface. We focus on the adsorption energy and in particular, how it depends on adsorption site and Mn content. The simulations will be performed using the Vienna Ab-initio Simulation Package (VASP), one of the most widely used in the field of computational materials science, which performs first-principles electronic structure calculations using DFT(Density Functional Theory).[1]

Keywords: Zinc Oxide (ZnO), catalysis, adsorption energy, doping, DFT, Ab-inition calculations

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Development of Mechano Active Scaffolds for Enhanced Osteogenic Differentiation

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Bone is a dynamic tissue that undergoes continuous mechanical forces. Mechanical stimuli applied on scaffolds resembling a part of the human bone tissue could have major effect on osteogenesis [1]. Poly(3,4-ethylenedioxythiophene) (PEDOT) is a piezoelectric material that responds to mechanical stimulation producing an electrical signal that promotes the osteogenic differentiation of pre-osteoblastic cells by opening voltage-gated calcium channels [2]. In this study we examined the biological behavior of pre-osteoblastic cells when seeded onto lyophilized piezoelectric PEDOT-containing scaffolds applying uniaxial compression.

Two different concentrations of PEDOT (0.15% w/v and 0.10% w/v) were combined with a 5% w/v poly(vinyl alcohol) (PVA) and 5% w/v gelatin, casted into wells, freeze dried and crosslinked with 2% v/v (3-glycidyloxypropyl)trimethoxysilane and 0.025% w/v glutaraldehyde.

The scaffolds were physicochemically characterized by FTIR, measurement of elastic modulus, swelling ratio and degradation rate. They were subjected to uniaxial compression with a frequency of 1 Hz and a strain of 10% for 1 h every second day for 21 days. The loading parameters were selected to resemble the in vivo loading situation [3]. Cell viability and morphology on the PEDOT/PVA/gelatin scaffolds was determined. The alkaline phosphatase (ALP) activity, the collagen and calcium production were assessed.

The elastic modulus of PEDOT/PVA/gelatin scaffolds ranged between 1 and 5 MPa. The degradation rates indicate a mass loss of 15% after 21 days. The cell viability assessment displays excellent biocompatibility, while SEM images display well-spread cells. The ALP activity at days 3, 7 and 18 as well as the Calcium production is higher in the dynamic culture compared to the static one. Moreover, energy dispersive spectroscopy analysis revealed the presence of calcium phosphate in the extracellular matrix after 14 days.

In conclusion PEDOT/PVA/gelatin scaffolds support the adhesion, proliferation, and osteogenic differentiation of the pre-osteoblastic cells under mechanical stimulation, thus favoring bone tissue engineering.

Keywords: mechanical stimulation, PEDOT:PSS scaffolds, piezoelectric material, dynamic vs. static culture

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