CHAPTER 8

CHEMISTRY

Doctoral Theses

01. AGGARWAL (Tashika)

Bis(monothiolato) Mimics of the [FeFe] Hydrogenase Enzyme Active Site: Structures and Electrochemistry.

Supervisor: Dr. Sandeep Kaur

Th 25917

Abstract

Hydrogen gas derived from non-carbon sources is considered as a potential fuel for sustainable energy cycles and therefore, the quest for catalysts that can facilitate reduction of protons to molecular H2 has been a subject of great interest. [FeFe] hydrogenase (H2ase) belongs to a class of enzymes that reversibly catalyse the interconversion of protons to hydrogen and vice versa with very high TON. Considering the high efficiency of [FeFe] H2ase, a large number of model systems have been developed over the years as mimics of the enzyme by changing the bridge head atom of the dithiolate bridge, introducing other metals like Ni, Mo or Co instead of Fe, replacing CO/CN with electron-donating phosphine ligands, altering the bridging thiolate ligand by replacement of sulphur with Se or Te atoms, and using thiolate ligands without a linker between the S-atoms. Despite several advances in this field, designing stable and efficient catalysts in aqueous media functional at very low O.Ps has been challenging. Therefore, the main aim of this work was to design, develop and synthesize new and robust bioinspired mimics of the [FeFe] H2ase enzyme active site. The objective of using monothiolate and phosphine ligands was based on the fact that bis(monothiolato) iron complexes take up design principles from the catalytically active centers of both the [FeFe] and [NiFe] H2ases thus, making their structure and chemistry more fascinating.

Contents

1. Introduction and objective 2. Mono and Dinuclear mimics of the [FeFe] hydogenase enzyme featuring Bis(monothiolato) and 1,3,5- Triaza-7-phosphaadamantane ligands 3. Hydrogen evolution reaction catalysed by [FeFe] hydrogenase active site models incorporating aminophosphine ligands 4. 9-Fluorenethiolato-Bridged [FeFe] complex mimicking the Fe_2S_2 core of the [FeFe] hydrogenase: experiemental and theoretical investigations 5. [FeFe] hydogenase: 2-propanethiolato-bridged [FeFe] systems as elecrocatalysts for hydrogen production in acetonitrile -water 6. Summary and conclusion. List of publications.

02. ANKIT

Development of Flavone and Isoflavone Based Heterocycles as Antibacterial Agents.

Supervisor: Prof. Mahendra Nath

Th 25912

Abstract

The main objective of this dissertation is the design and synthesis of various flavone and isoflavone based heterocycles as antibacterial agents. Flavone and isoflavones are two important classes of oxygen containing heterocycles which have occupied a unique place in medicinal chemistry due to their numerous pharmacological profiles such as antimicrobial, antitumor, antiviral, anti-inflammatory, carbonic anhydrase inhibitors (CA), cyclooxygenase (COX)-2 inhibitors, protine kinase inhibitors and HIV protease inhibitors. Besides, these compounds are found to be useful for treating various allergic reactions. Hence, a variety of flavone and isoflavone based hybrid molecules were designed and synthesized for biological evaluations. The work presented in this thesis has been divided into four chapters. The first chapter gives an account on the synthesis and biological significance of flavone and isoflavones. The second chapter includes the synthesis, biological discussion and conclusions about all the synthesized compounds. The third chapter describes the synthetic protocols and characterization data of all the newly prepared compounds. Lastly, the fourth chapter includes all the relevant references. All the synthesized compounds were tested for their antibacterial activity against two Gram positive and two Gram negative bacterial strains. The preliminary screening results revealed that some of the synthesized compounds possessed bactericidal nature and hence may prove useful for the development of novel antibacterial agents in the future

Contents

1. Introduction 2. Results, discussion and conclusions 3. Experimental 4. References 5. Summary and publication.

03. ARUN LAL
Study of some dithiocarbamate compounds as corrosion inhibitor for mild steel in 0.5 M H_2SO_4 .
Supervisors: Prof. Gurmeet Singh and Dr. Rajkishore Sharma
Th 25899

Abstract

The thesis focusses on the study of some dithriocarbamate compounds as corrosion inhibitor for mild steel in 0.5 M H_2SO_{4-} corrosion is a worldwide destructive phenomenon in the field of science and technology. The scientific organization have paid a lot of attention over the years to understand and minimize corrosion that has caused huge economic, social and environment losses resulting from damage of highway, bridges and buildings to oil and and gas, chemical processing water and waste water systems. There is an immense opportunity to save costs due to corrosion inhibition and enhance the life of products and civil structures.

Contents

1. Introduction 2. Literature review 3. Experiemental procedure 4. Galvanostatic polarization technique 5. Electrochemical impedance spectroscopy 6. Temperature kinetics studies 7. Quantum chemical calculations 8. Surface morphological studies 9. Conclusions. List of publications and conference attended.

04. ARORA (Bhavya)

Design & Synthesis of Recyclable Magnetic Halloysite Nanotubes and Ferrite Supported Catalysts: Applications in the Degradation of Emerging Contaminants and Organic Transformations.

Supervisor: Prof. R.K. Sharma

Th 25901

Abstract

Catalysts mediated transformations represent one of the best approaches that has blossomed in the last decades and find extensive applications in the realm of rapidly growing field of techno-science. Recent advances in nanotechnology have introduced a new generation of solid-supported heterogeneous catalyst as they are highly efficient in controlling chemical reactivity and offers easy recovery. In this regard, surface engineered nanocomposites have gained wide recognition as they can be efficiently utilized as support material to generate novel "quasi-homogeneous catalysts". These nanocomposites with appealing features covers the gap between homogenous and heterogenous catalytic systems and emerges as an attractive alternative to conventional catalysts. Until now, a wide range of support materials have been explored including metal oxides, mesoporous silica, polymers, microcapsules, conducting hydrogels, carbon nanotubes etc. Amongst all, magnetichalloysite nanotubes and ferrite NPs have brought a revolutionary paradigm in the realm of heterogeneous solid supported catalysis by offering the opportunity to fabricate desired "one-size-fits-all" potent nanoscale catalysts. In addition, thanks to the inevitable properties of magnetic halloysite nanotubes and ferrite supported catalysts such as large surface area, high thermal stability, excellent mechanical stability, adequate hydroxyl groups, high porosity and tunable surface chemistry that has further helped in the wastewater treatment and organic transformations.

Contents

1. Introduction 2. Theory and principles of various physico- chemical techniques 3. *In-situ* hydroxyl radical generation using the synergism of the Co-Ni bimetallic centres of a developed nanocatalyst with potent efficiency for degrading toxic water pollutants 4. Magnetically retrievable Fe_3O_4@HNT_s supported nickel (II) complex: a sustainable and promising nanocatalyst for the efficient degradation of toxic methylviolet 6B and acid orange 7 5. Fabrication of a recyclable magnaetic halloysite based cobalt nanocatalyst for the efficient degradation of bisphenol A and malachite green 6. A susutainable gateway to access 1,8-dioxo-octahydroxanthene scaffolds *via* surface engineered halloysite based mangnetically responsive catalyst 7. Summary, List of publications and List of conference/Semeinars/Symposia participated.

05. AWASTHI (Amardeep)

Development of Naturally Occurring Chemotherapeutic Agents: Noscapinoids & MPC1001.

Supervisor: Prof. Ramesh Chandra

Th 25885

Abstract

The abstract of the thesis entitled "Development of Naturally Occurring Chemotherapeutic Agents: Noscapinoids & MPC1001" to be submitted by Amardeep Awasthi to the University

of Delhi for the award of Ph.D. Degree in Chemistry. Natural products, with remarkable chemical diversity, have been extensively investigated for their anticancer potential for more than a half-century. The collective efforts of the community have achieved the tremendous advancements, bringing natural products to clinical use and discovering new therapeutic opportunities, yet the challenges remain ahead. With remarkable changes in the landscape of cancer therapy and growing role of cutting-edge technologies, we may have come to a crossroads to revisit the strategies to understand nature products and to explore their therapeutic utility. A number of widely-used anticancer therapeutics originate from natural sources, such as irinotecan, vincristine, etoposide and paclitaxel from plants, actinomycin D and mitomycin C from bacteria as well as marine-derived bleomycin. Some of these compounds are still the mainstay of cancer therapy and will continue to play a pivotal role in the foreseeable future. Among them, camptothecin and taxol are undoubtedly the two most successful examples Despite immense achievements in developing bioactive natural products into drugs, the process to develop a potent natural product is still challenging in terms of their large-scale isolation, pharmaceutical application, and mechanistic understanding. Therefore, it is imperative to establish a short and effective synthetic route for naturally occurring chemotherapeutic agents, as well as to understand their mechanistic interactions with blood-associated proteins in an attempt to comprehend their pharmacokinetics. Disrupting the dynamics of microtubules during mitosis is an attractive target for the development of chemotherapeutic drugs against the rapid progression of cancer cells. The use of taxanes and vinca alkaloids for the treatment of numerous cancer types has verified the usefulness of microtubule-interfering medicines in cancer therapy. However, the substantial effects of taxanes and vinca alkaloids on microtubule arrays at therapeutic dosages result in a variety of adverse effects, most significantly neurologic and hematologic abnormalities. Furthermore, drug resistance develops during extended therapy owing to the upregulation of drug efflux pumps on the plasma membrane, drug target mutations, microtubules/tubulin, and a variety of additional mechanisms. It is so critical to find and develop innovative antimicrotubule drugs capable of overcoming drug resistance and having enhanced pharmacologic characteristics.

Contents

1. Introduction 2. Review of literature 3. Aim and objectives 4a. Noscapine-amino acid conjugates and to explore their potential against cancer: *in-silico* and *vitr o* studies 4b. Development of diphenylglycoluril as an organocatalyst for the chemoselective N-tert-butoxycarbonylation of aliphatic/aromatic/heterocyclic amines 5. Understanding the interaction of tryptophan conjugated noscapine with blood -associated proteins 6. Development of tubulin-HDAc-II dual inhibitor noscapine cinnamic acid conjugates 7. Antitussive noscapine and antiviral drug conjugates as arsenal against COVID-19: a comprehensive chemoinformatics analysis 8. Development of synthetic methodologies to construct the key AB ring of the MPC10001 molecule. Summary, Research publications and Certificate pf conferences.

06. AYUSHEE

KOH/DMSO Assisted Chemo-, Regio-and Stereoselective Anti-Markovnikov Hydroamidation/Hydroamination of Arylamide using Vinyl Arenes and Alkynes.

Supervisor: Prof. Akhilesh K. Verma

Th 25914

Abstract

In Chapter 1 we have briefly introduced the concept of hydroamidation and hydroamination chemistry which prove to be an example of modern sustainable organic chemistry as they are 100% atom economical and a waste-free process in which nucleophilic addition of amine or amide takes place on the unsaturated substrate. Further in Chapter 2 we have demonstrated the first example of anti-Markovnikov addition of aryl amides on styrenes to synthesize a variety of arylethylbenzamides using super basic KOH/DMSO system. This method tolerates an extensive variety of functional groups using aminobenzamides, electron-rich/ electron-deficient heterocyclic amides, and vinyl arenes to afford hydroamidated products with excellent chemo- and regioselectivity. The developed protocol also allows the late-stage modification of pharmaceutically important drug probenecid, demonstrating the efficacy of the protocol. The proposed mechanism and vital role of the solvent was well supported by deuterium labeling studies and control experiments In Chapter 3 we have described an operationally simple, efficient, and direct approach for the transformation of acetanilides into N-phenethylanilines using KOH/DMSO system in presence of vinyl arenes via a radical pathway to synthesize hydroaminated products with excellent regioselectivity. The versatility of the reaction has been demonstrated by performing controlled mono- and bis-hydroamination reaction of 1,3-divinyl benzene with acetanilide. Synthetic elaboration of bromo-substituted products by the palladiumcatalyzed cross-coupling reactions also increases the utility of synthesized products. The findings of control experiments and deuterium labeling studies provided a valuable support for the proposed mechanistic pathway. Last in Chapter 4, we have reported an elegant method for the preferential regio-, chemo- and stereoselective addition of benzamides onto electron-neutral, electron-rich, and electron-deficient alkynes to synthesize a variety of (Z)- and (E)-styrylbenzamide derivatives. The operationally simplicity of the developed protocol will make it attractive for the synthesis of biologically important stereoselective secondary enamides. The versatility of the reaction is depicted by conducting reaction with 1,3- and 1,4-dialkynes and deuterium labelling studies.

Contents

1. A brief introduction to hydroamidation and hydroamination chemistry 2. Base-mediated anti=markovnikov hydroamidation of vinyl arenes with arylamides 3. Transition-meta-free intermolecular hydroamination of styrenes with arylamides to generate N- phenethylaniline 4. Base catalysed regio-, chemo-and stereoselective intermolecular addition of benzamides onto terminal alkynes: an easy access to secondary enamides. Summary of the work and copies of the publications.

07. BINDU
Morphology Oriented Semiconductor Nanostructures for Efficient Photocatalytic Hydrogen Evolution Reaction.
Supervisor: Dr. Sasanka Deka
<u>Th 25896</u>

Abstract

The thesis entitled “Morphology Oriented Semiconductor Nanostructures for Efficient Photocatalytic Hydrogen Evolution Reaction” deals with the synthesis and characterization of

morphology-oriented semiconductor nanostructures for efficient photocatalytic hydrogen evolution reaction applications. The thesis has been divided into six chapters which are as follows. Chapter 1 This chapter mainly focused the introduction of semiconductor nanoparticles and their application in photocatalytic water splitting reaction under visible light irradiation. We have also discussed the principle of photocatalysis, photocatalytic water splitting reaction, use of co-catalysts and sacrificial reagents. Here, we also covered various semiconductor nanomaterials such as metal-free carbon nitride semiconductor nanostructures and metal-organic framework for efficient photocatalytic hydrogen evolution. Chapter 2 The second chapter describes various synthetic routes and characterization techniques for the synthesis of metal-free carbon nitride nanostructures and mixed transition metal-organic framework (MOF). The photocatalytic studies and the formulas employed to determine the band gap, decay lifetime, apparent quantum efficiency etc. are also discussed in this chapter. Chapter 3 This chapter describes the development of nitrogen-rich holey graphitic carbon nitride (g-C3N4.8) nanosheets using direct thermal polymerization approach which was characterized using XRD, HRTEM, FESEM, XPS, BET, Raman, FT-IR etc. and showed excellent photocatalytic H2 evolution activity in presence of visible light. Chapter 4 This chapter gives details about the development of highly ordered mesoporous graphitic carbon nitride (g-C3N4.5) nanosheets using a hard template approach for sustainable visible-light photocatalytic H2 evolution. Chapter 5 The fabrication of one-dimensional multichannel mesoprous graphitic carbon nitride (g-C3N4.7) nanostructure using the hard-template approach, various characterization techniques and the photocatalytic H2 evolution application are explained in detail in fifth chapter. Chapter 6 The sixth chapter describes the decoration of transition metal phosphides (TMPs; NiCoP, FeCoP) co-catalysts over ZnCo-MOF hollow rings for efficient precious metal-free visible-light photocatalytic hydrogen evolution reaction.

Contents

1. Introduction to semiconductor nanostructures for photocatalytic hydrogen evolution reaction 2. Experiemental details for the synthesis characterization and photocatalytic study of semiconductor nanostructures 3. N-rich holey carbon nitiride for promising photocatalytic H_2 evolution reaction 4. Holey and ordered graphitic carbon nitride nanosheets for feasible photocatalytic H_2 evolution reaction 5. 1D multichannel g-$C_3N_{4.7}$ nanostructure realizing an efficient photocatalytic hydrogen evolution reaction 6. NiCoP co-catalyst decorated over novel ZnCo-MOF hollow rings for precious metal free visible light hydrogen evolution reaction. Summary, Future scope and List of publications and conference attended.

08. BHAWANI SHANKAR

Synthesis of 1-(E-1-Arylpropenon-3-yl)-tri-O-benzyl-D-glycals, Pentasubstituted Chiral Chromances, Sugar-based 1-Azaindolizines and Methylidene Succinimides of Biological Importance.

Supervisor: Prof. Ashok K. Parsad

Th 25906

Abstract

Abstract of the thesis entitled: "Synthesis of 1-(E-1-Arylpropenon-3-yl)-tri-O-benzylD-glycals, Pentasubstituted Chiral Chromanes, Sugar-based 1-Azaindolizines and Methylidene

Succinimides of Biological Importance" The thesis is divided into four chapters, i.e. Chapter 1, Chapter 2, Chapter 3 and Chapter 4. A brief account of each chapter is given below: The work presented in Chapter 1 entitled "Efficient Synthesis of 1-(E-1- Arylpropenon-3-yl)-tri-O-benzyl-D-glycals and Tri-O-benzyl-1-formyl-D-glycals" describes an efficient, convenient and one-pot methodology for the synthesis of C-1 conjugated branched-chain unsaturated sugar derivatives i.e., 1-(E-1-arylpropenon-3- yl)-tri-O-benzyl-D-glycals from the reaction of C-glycosyl aldehydes and aryl methyl ketones in aqueous media using a base catalyzed Claisen-Schmidt type reaction. The unsaturated sugars are the most versatile compounds available in carbohydrate chemistry for synthetic elaborations. Unsaturated sugars have found application in medicinal chemistry as drugs, as precursors for the synthesis of other biologically important molecules and some of the natural products contain unsaturated sugars as a part of their core structures. Further, unsaturated sugar derivatives possess anti-HIV, anti-influenza properties and also serve as a precursor for the synthesis of vineomycin antibiotics. In the present work, the synthesized unsaturated sugars can emerge as potential chiral synthons for numerous organic transformations due to the presence of diene, diene-one and α,β-unsaturated carbonyl functionalities. Additionally, the synthesized C1-glucalpropenones have structural similarity with naturally occurring chalcone derivatives which are potent drug candidates making the present work more useful. The work presented in Chapter 2 entitled "Synthesis of Pentasubstituted Chiral Chromanes via Pd-Catalyzed CDC Reaction between 1-(E-1-Arylpropenon-3-yl)- tri-O-benzyl-D-glucals and Alkenes followed by Electrocyclization and in-situ 2 Aromatization" describes the efficient synthesis of pentasubstituted chiral chromenes from 1-(E-1-arylpropenon-3-yl)-tri-O-benzyl-D-glucals via palladium catalyzed cross dehydrogenative coupling reaction followed by 6π-electrocyclization and aromatization. Chromane scaffolds are important structural units often found in many natural products and bioactive compounds that exhibit anticancer, anti-HIV, antiplasmodial, antitubercular, antibacterial and antifungal activities. Chromane core makes the structural framework of complex compounds, including constituents of vitamin E, catechin, brazilin, and other pharmaceutical drugs, such as symakalin, ormeloxifene, cromakalim, etc. Among many reported strategies, reaction of salicylaldehyde and enolates or their equivalents from acetophenones has gained a prominent attention for accessing these scaffolds. In the present work, a divergent route for the transformation of 1-(E-1-arylpropenon-3- yl)-tri-O-benzyl-D-glucals into pentasubstituted chiral chromanes via Pd(II)-catalyzed CDC reaction with various alkenes followed by 6π-electrocyclization and in situ dehydrogenative aromatization has been described. The developed method is highly successful in generating a diversified library of chromanes with three inbuilt chiral centres derived from the precursor sugar for drug discovery application. The work presented in Chapter 3 entitled "Efficient Synthesis of 1-(1-Azaindolizine2-yl)-D-glycals via Solvent-catalyzed Groebke-Blackburn-Bienayme Reaction" describes the synthesis of a series of 1-(3-N-alkylamino-1-azaindolizine-2-yl)-tri-Obenzyl-D-glycals and 2-aryl/alkyl/heteroaryl-3-N-alkylamino-1-azaindolizines using a solvent catalysed and metal-free GBB reaction. Imidazo[1,2-a]pyridines or 1-azaindolizines are very well-known to demonstrate various biological activities such as antimicrobial, anti-inflammatory, antitumor, antiviral, antidiabetic, anticonvulsant, antipyretic and analgesic. These scaffolds are present in commercially available drugs such as zolpidem, alpidem, saripidem, necopidem, zolimidine, miroprofen and olprinone etc. Out of many reported strategies for the synthesis of 1-azaindolizines, the multicomponent GBB reaction between an aldehyde, 2-aminopyridine and alkyl/aryl isocyanide performed in the presence of an acid catalyst is the most preferentially used synthetic method to access these molecules. 3 In the present work, a solvent catalysed and metal catalyst-free GBB three component reaction has been developed for the synthesis of 1-(3-N-alkylamino-1-azaindolizine-2- yl)-tri-O-benzyl-D-glycals and 2-aryl/alkyl/heteroaryl-3-N-alkylamino-1-azaindolizines in excellent yields. This is the first report of GBB three component reaction attempted in hexafluoroisopropanol (HFIP) solvent in absence of an added catalyst and the protocol is highly versatile with high tolerance for a large no of substrates in term of aldehydes, 2-aminopyridines and isocyanides making the modified protocol highly useful. The work presented in Chapter 4 entitled "Solvent-free Synthesis and Molecular Docking Study of (E)-3-(β-C-Glycosylmethylidene)-N-aryl/alkyl succinimides" describes the synthesis and in silico molecular docking study of β-C-glycosylated methylidene succinimides. The sugar-based methylidene succinimides were synthesized using solvent-free Wittig olefination reaction between β-C-glycosyl aldehydes and various N-aryl/alkyl maleimides. Succinimide derivatives show pronounced biological activities, such as antibacterial, antitumor, anti-tuberculosis, anticonvulsant, antivirulence, anti-obesity, anti-arthritis and as inhibitors of various enzymes. A wide variety of succinimide derivatives are natural products, pharmaceutical drugs and agrochemicals, such as andrimid, moiramide, cladosporitin A, cladosporitin B, phensuximide, methsuximide, ethosuximide, palasimide, captan etc. The glycosylation of different bioactive compounds not only enhances their water solubility and intestinal absorption, but also decrease their toxicity. Consequently, we were interested to develop a direct method for the synthesis of C-glycosylated succinimide conjugates. The most described methods to prepare alkylidene succinimides rely on Wittig reaction performed in organic solvents. In the present work, a convenient and environment friendly methodology has been developed for the synthesis of a small library of novel β-C-glucosylated methylidene succinimide using solvent free Wittig olefination reaction. Solubility of synthesized compounds in aqueous medium makes them potential candidate for evaluation of their different bioactivity. The computational results of the in silico molecular docking studies showed good potential of the synthesized compounds as inhibitors of human papilloma virus infection which is a driver of oral cancer, HNSCC and cervical cancer.

Contents

1. Efficient synthesis of 1-(E-1-Arylpropenon-3-yl) tri-O-benzyl-D-glycals and Tri-*O*-benzyl-I-formyl-D-glycals 2. Synthesis of pentasubstituted chiral chromanes via Pd catalyzed CDC reaction between 1-(E-1-arylpropenon-3-yl)-tri-*O*-benzyl-D-glucals and alkenes followed by electrocyclization and *in-situ* aromatization 3. Efficient synthesis of 1-(1- azaindolizine-2-yl)-D-glycals via solvent catalyzed groebke-blackburn bienayme reaction 4. Solvent-free synthesis and molecular docking study of (E) -3 (β-C-glycosylmethylidene)-N-aryl/alkyl succinimides. Summary, list of publication and workshops and conferences attended.

09. CHAUHAN (Maruf)
Biogenic Synthesis of Metal Oxide Nanoparticles, Nanocomposites of Metal Oxide and their Catalytic Application.
Supervisor: Prof. Priti Malhotra
Th 25876

Abstract

The major goal of the current thesis is to explore and construct novel ways for developing economically viable, environmentally friendly, and highly active heterogeneous catalysts.

Thus to meet this target nanostructured heterogeneous catalysts were developed which were used in a number of biologically important organic reactions and degradations. The pivotal target has been to first engage biological waste and then employ the nano products towards a green approach and water remediation exercise. Chapter 1: Introduction and Review of the Literature Chapter 1 provides an overview of the greener synthesis of metal and metal oxide nanoparticles and its current status in the relevant field. This chapter focuses on the unique features of metal oxide nanoparticles/nanocomposites and their extraordinary applications in organic transformations and drug removal. The topics of interest of both homogeneous and heterogeneous catalytic frameworks have been combined in nanocatalysts. The nano catalytic framework allows for faster, more precise chemical conversions with higher yields, as well as easier catalyst separation and recovery. The ability to recover a catalyst from its framework is one of the most important properties of any catalyst before it can be used in industrial green synthesis processes. The interaction between reactants and catalysts increases dramatically at the nanoscale (this is close to homogeneous catalysis). Because of its insolubility in non-reactive solvents, the catalyst is heterogeneous and hence may be successfully separated from the reaction mixture (this is close to heterogeneous catalysis). As reported in this dissertation, we have designed various metal oxide and hybrid nanocomposites for organic transformations and the removal of drug waste. ZnO nanoparticles, Cu2O/RGO, and Cu2O/ZnO hybrid nanocomposites were synthesized using greener protocols and employed as catalysts in organic transformation reactions and their enhanced surface activity was applied for drug removal. The green methods for the synthesis of NPs and NCs together with their applications can be certainly mimicked at the bulk level to ensure major gains and productivity of the current research

Contents

1. Introduction and review of literature 2. Instrumentation analysis 3. Water chestnut peel facilitated biogenic synthesis of zinc oxide nanoparticles and their catalytic efficacy in the ring opening reaction of styrene oxide 4. In- situ biogenically synthesized Cu_2O/RGO composite using beetroot peel extract for efficient hydrogenation of cinnamaldehyde in water 5. Biogenic synthesis of Cu_2O/ZnO nanocomposites using beetroot extract and its photocatalytic application in the degradation of doxycycline 6. Conclusion. List of publication and List of Intenational/National Conferences/ Workshop and award.

10. DEEPA

Development of Organocatalysts for the Asymmetric Biginelli, Direct-Aldol and Friedel-Crafts Reactions.

Supervisor: Dr. Surendra Singh

Th 25918

Abstract

The thesis entitled “Development of Organocatalysts for the Asymmetric Biginelli, Direct-Aldol and Friedel-Crafts Reactions” reveals the synthesis of DABCO salts and chiral organocatalyst such as chiral modified MacMillan organocatalyst, chiral prolinamides, and chiral imidazolium-based α,α’-diarylprolinol. The chiral organocatalysts were applied in different organic transformations such as enantioselective Biginelli reaction, enantioselective Direct-Aldol reaction, and enantioselective FriedelCrafts reaction. Chapter 1 contains the general introduction of chirality and different methods to synthesize the chiral compounds.

Chapter 2 comprises the synthesis of racemic and enantioselective dihydropyrimidinones using organocatalysts and is divided into two sections. Section A describes the synthesis of DABCO salts as organocatalysts and the DABCO salts were applied in the Biginelli reaction. The catalytic efficiency of the DABCO triflate salt was evaluated in the Biginelli reaction of aromatic aldehydes, urea, and ethyl acetoacetate under mild reaction conditions. The resulting dihydropyrimidinones (DHPMs) were obtained in good to excellent yield in a few minutes. Section B describes the synthesis and characterization of modified MacMillan catalysts derived from amino acid esters. The synthesized modified MacMillan catalysts were explored in the enantioselective Biginelli reaction of aromatic aldehydes, urea, and βketo esters, and the resulting DHPMs were obtained in moderate to good yields (33- 77%) with enantiomeric excess (up to 30%) using ethanolamine derived modified MacMillan catalyst. Chapter 3 reveals the synthesis and characterization of (L)-prolinamides anchored to imidazolium ionic liquids and their application in the enantioselective Biginelli reaction of aldehydes, urea, and β-keto esters. A wide range of optically active 3,4- dihydropyrimidin-2-(1H)-ones (DHPMs) were obtained in 16-74% yields and 7-85% enantiomeric excesses using a chiral ionic liquid containing adamantyl moiety (5 mol%) and p-toluenesulfonic acid (5 mol%) at room temperature. Chapter 4 deals with the synthesis and characterization of chiral ionic liquid containing (L)-prolinamide and intercalated in bentonite clay and their application in the enantioselective direct aldol reaction. The prolinamides as chiral organocatalysts were successfully entrapped in the layers of the bentonite clay using the cation-exchange method. The enantioselective aldol reaction of isatin and acetone using chiral prolinamide containing hexafluorophosphate anion (10 mol%) gave the corresponding 3-substituted-3-hydroxy indolin-2-ones in 72-98% yields and 37-80% ee's and 32-69% yields with 39-88% ee's obtained with prolinamide intercalated in bentonite clay (10 mol%) at -20 °C in iso-propanol. The prolinamide intercalated bentonite clay was reused for up to four recycles with a slight loss of activity and selectivity of the catalyst. Chapter 5 contains the development of α,α-diarylprolinol derived chiral ionic liquids for the enantioselective Friedel-Crafts reaction. The Friedel-Crafts reaction of indoles and α, β-unsaturated aldehydes using 20 mol% of O-TMS protected α,αdiphenylprolinol ionic liquid, and 40 mol% of triethylamine as base additive gave the corresponding products in 62-89% yields and 47-88% ee's. The chiral ionic liquid containing α,α-diphenylprolinol ionic liquid was reused up to four recycle with a slight loss of activity and selectivity after the third recycle.

Contents

1. Introduction 2. Synthesis of racemic and enantioselective dihydropyrimidinones using organocatalyst 3. Enantioselective biginelli reaction catalysed by (L)-prolinamide containing imidazolium ionic liquid 4. Prolinamide and prolinamide tagged with ionic liquid intercalated in bentonite clay, a recyclable catalyst for enantioselective direct aldol reaction between isatins and acetone 5. O-TMS-α,α-diaryl-(S)-prolinol tagged with imidazolium ionic liquids as recyclable and recoverable organocatalysts for the enantioselective Friedel crafts reaction between indoles and *α, β*-unsaturated aldehydes. Summary, List of publication and List of Conference/Symposium/Workshops participation.

11. GARG (Charu)
Design and Development of Modified Amino Acids Containing Peptide Based Nanostructures for Biomedical Applications.
Supervisors: Prof. Alka Gupta and Dr. Ashwani Kumar Sharma
Th 25911

Abstract

Supramolecular self-assembly of peptides formed from amino acids or peptide monomers to generate organized nanostructures is an interesting area of research. In recent decades their application in the fields of biotechnology and nanomedicine has gained increasing attention. In this area a new addition is the inclusion and use of modified amino acids. These amino acids are slightly different in structure from their usual counterparts but remarkably different in the structural features and properties they possess. Prudent substitution of usual amino acids with the modified ones in the peptides of interest leads to the nanostructures being biocompatible and enzymatically resistance to proteolysis. Addition of modified amino acids can prove to be a valuable inclusion in the peptide sequence. The focus of the present research work is the synthesis of β-amino acid and α,β-dehydroamino acids containing peptide nanostructures. These structures are formed by the process of self-assembly and exhibit properties like stability against proteolytic enzymes which natural amino acids are susceptible to. So, they present themselves as ideal candidates as vehicles for the delivery of drugs and genes. The present thesis entitled "Design and Development of Modified Amino Acids containing Peptide Based Nanostructures for Biomedical Applications" includes: (i) Design and synthesis of short peptide oligomers containing modified amino acids by solution phase peptide synthesis strategy and their characterization, (ii) self-assembly of the synthesized peptides in to nanostructures and their characterization using DLS and TEM, (iii) studies of the interaction and co-assembling of peptide nanostructures with anti-protozoal drug ornidazole and anti-cancerous drug curcumin as the model drugs, and eosin and fluorescein sodium salt as model dyes, (iv) investigation of encapsulation and in vitro release kinetically of these drugs and dyes from peptide nanoassemblies, (v) conjugation of the peptide with moieties like polysaccharide and polymer, (vi) cytotoxicity profiling and investigation of gene delivery potential.

Contents

1. Introduction 2. Material and methods 3. Synthesis characterization and fabrication of self assembled nanostructures of tripeptide H-Phe Pro-β Ala-OEt and its dimer for potential use in delivery of hydrophobic drugs ornidazole and curcumin 4. Synthesis, characterization and fabrication of self assembled nanostructures of tripeptide H-Phe-Δ Phe- β-Ala -OEt and its dimer for potential biomedical applications 5. Synthesis characterization and fabrication of self assembled nanostructures of inulin conjugated tripeptide Boc-Phe-Δ Phe-εAhx-OH for colon targeted delivery of ornidazole 6. Synthesis, Characterization and fabrication of self assembled nanostructures of polyethylenimine conjugated tripeptide Boc-Phe Phe-Δ Phe-εAhx-OH for drug delivery and gene delivery applications 7. Summary and future prospects, References and List of publications/Conferences attended.

12. GOYAL (Preeti)
Design and Development of Polymeric Nanostructures as Efficient Drug Delivery Systems.
Supervisors: Prof. Alka Gupta and Dr. R. P Singh
Th 25904

Abstract

Polymeric nanostructures are the most fascinating and innovative research materials, offering several biomedical applications. These nanostructures have shown interesting findings in drug delivery applications. They exhibit many significant advantages which overcome the hurdles existing in the conventional methods of drug delivery. Majorly, polymeric nanostructures solubilize the hydrophobic drugs, prolong the blood circulation time of these therapeutic drugs and also make them target-specific. Furthermore, their projected chemical groups can be easily modified according to the desired applications. Also their stimuli responsive behaviour to temperature, light, pH, redox, biological component, and magnetic field alters their physico-chemical properties for significant biological applications. In general, biodegradable and biocompatible polymers are adopted to develop such nanoformulations, minimizing the side effects on the body. There are various kinds of natural and non-natural biodegradable polymers which have been used to fabricate the nanostructures. PEG is the most explored FDA approved hydrophilic polymer. It is popular for stealth behaviour which protects the drug delivery systems to the non-specific protein interactions and facilitates the delivery of drugs at specific site. There are many clinical and preclinical studies that have been carried out on PEG and a few PEGylated products have come in the market so far. In addition, natural polymers such as polysaccharides have been extensively investigated in drug delivery applications owing to their significant inherent properties.

Contents

1. Introduction 2. Material and methods 3. Self assembled retinoic acid methoxypolethylene glycol based nanomicelles-synthesis, characterizatio and applications in colon targeting drug delivery 4. Amphipathic methoxypolyethylene glycol-curcumin synthesis characterization and evaluation for drug delivery applications 5. Self-assembled cholesteryl-dextran nanomicelles-synthesis, characterization and applications as colon targeting delivery vehicle 6. Core-shell nanosturcures of naproxen-PEG conjugates-synthesis, characterization and evaluation as drug delivery system. Summary of the projected work and its future aspects, References and list of Publications.

13. GUPTA (Padmini)
Development of Heterogeneous Nanostructured Materials for Organic Transformations.
Supervisor: Prof. Subho Mozumdar
Th 25915

Abstract

Characterization is one of the most significant aspects in the development of catalysts. The shape, size, structure, chemical composition, magnetic property, functionalization, surface area, oxidation state, phase identification and other properties of nanomaterials could all be determined using these techniques. Some of the most prevalent spectroscopic and other methods for the characterization of heterogeneous catalysts have been introduced in this chapter. These include X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray (EDAX), Fourier Transform Infrared Spectroscopy (FT-IR), Vibrating Sample Magnetometer (VSM), CHN Analyzer, Thermo-gravimetric Analysis (TGA), Nuclear Magnetic Resonance (NMR) and HighResolution Mass Spectroscopy (HR-MS).

Contents

Introduction and review of the literature 2. Characterizaion techniques 3. Amine grafted Fe_3O_4 immobilized graphene oxide as a recyclable and effectual nanocomposite for the regioselective ring opening reaction 4. Basic ionic liquid grafted on magnetic nanoparticles: an efficient and high active green catalyst for the synthesis of β-nitroalcohols and 4H-benzo[b]py rans 5. Ionic liquid network on graphene oxide decorated with AuPd Alloy nanoparticle composites: an efficient and recyclable catalyst for the oxidative coupling of anilines 6. A biscationic imidazolium ionic immobilized on graphene oxide as an efficient heterogeneous catalyst for the synthesis of tetraketone derivtives 7. Conclusion, List of publication and List of International/ National Conferences/ Workshop and awad.

14. HANDA (Manisha)
Effect of Excluded Volume Interactions on Conformations, Rheology and Orientation of Ring Polymers in Dilute Solutions.
Supervisor: Prof. Prabati Biswas
Th 25880

Abstract

Polymers are among one of the simplest examples of physical cooperativity as they consist of many repeating units known as monomers. Based on their length, architecture and chemical nature, they constitute a commendable candidate for various sustainable materials, owing to their diverse physical, mechanical and dynamic properties. There are well developed theories for understanding the behavior of linear polymers in solutions and melts. However, the behavior of ring polymers, which are also known as cyclic polymers, remains an important area of interest which needs attention. The architecture of a ring polymer emerges when the free ends of a linear polymer joins together. In this thesis, the conformations and dynamics of the ring polymers in dilute solutions are investigated within the framework of the Rouse-Zimm theory. The dynamic aspect investigated in this thesis basically includes the viscoelastic and orientational relaxation of the rings of different degrees of polymerization. The influence of EVI on the conformational properties is explored, while the effect of both HI and EVI on the viscoelastic and orientational relaxation dynamics is examined. The basic idea is to analyze how these interactions alter the relaxation rates of the local and collective relaxation modes. This thesis offers a novel theoretical approach to model the distance dependent excluded volume interactions in polymers. The conformational features are probed through the static properties such as the mean square radius of gyration, static structure factor, scattering intensity, fractal dimensions and mean square intermonomer distances. The viscoelastic/mechanical relaxation is characterized through the mechanical properties, i.e., the storage and loss moduli, while the orientational relaxation is studied through the relaxation parameters such as the orientational autocorrelation functions, spectral density, spin-lattice and spin-spin relaxation rates. The diffusion coefficients and the characteristic relaxation times of the ring polymers with HI only and with both HI and EVI are also evaluated as a function of the ring size. Most of the quantities named above can be obtained generally through specific experimental techniques. This thesis enables the theoretical evaluation of such experimentally relevant quantities. The results are validated by comparisons with other relevant theoretical, experimental, simulation or numerical studies. The conclusions drawn from the works presented in this thesis may help in a better understanding of ring polymers in dilute solutions.

Contents

1. Introduction 2. Orientational relaxation of ring polymers in dilute solutions 3. Conformation of ring polymers with excluded volume interactions 4. Intramolecular

relaxation of ring polymers in dilute solutions 5. Segemental mobility of ring polymers in goog and poor solvents.

15. HEMLATA
Synthesis, Characterization and Electrochemical Investigations of Dinuclear {FeFe} Thiolate Complexes
Supervisor: Dr. Sandeep Kaur
Th 25893

Abstract

The thesis present work deals with the development of {FeFe} mono- and di-thiolate bridged bioinspired mimics of the [FeFe] hydrogenases. The thesis is divided into five chapters. Chapter 1 delineates the structural revelations and uniqueness of catalyzing the reversible reduction of protons to H2 by hydrogenases. Furthermore, monothiolate-, propanedithiolate- and benzenedithiolate-bridged functional mimics reported since 2009 have been discussed. Chapter 2 describes the synthesis and characterization of compounds [Fe2(CO)4(μnaphthalene-2-thiolate)2(μ-dppe)] 1 and [Fe2(CO)4(μ-naphthalene-2-thiolate)2(μ-DPEPhos)] 2 with chelating phosphines. The bridging coordination mode of the diphosphine (dppe, 1) was confirmed by SC-XRD. An ECEC mechanism (1) has been proposed for proton-reduction in the presence of acetic acid. Complex 1 showed better stability than 2 in the presence of acids. Chapter 3 explores the synthesis of mimics [Fe2(μ-pdt)(CO)5(PPh2PhNH2-o)] 3, [Fe2(μpdt)(CO)4(PPh2PhNH2-o)2] 4, [Fe2(μ-pdt)(CO)5(PPh2PhNH2-m)] 5 and [Fe2(μpdt)(CO)4(PPh2PhNH2-m)2] 6 incorporating propane-dithiolate and aminophenyldiphenylphosphines. The apical coordination mode of the phosphines in 3-6 was confirmed by SC-XRD. Monosubstituted derivatives (3, 5) studied electrochemically in organic/aqueous media were found to be efficient catalysts. Complex 3 was a better electrocatalyst than 5. Chapter 4 discusses the synthesis of complexes [Fe2(μ-bdt)(CO)5(PPh2PhNH2-o)] 7 [Fe2(μ-bdt)(CO)5(PPh2PhNH2-m)] 8 and [Fe2(μ-bdt)(CO)5(PPh2PhNH2-p)2] 9 incorporating benzenedithiolate and aminophenyldiphenylphosphines. The -NH2 containing phosphines were selected for coordination via P-atom while providing internal base adjacent to the metal centre. Furthermore, complexes 7-9 were studied as electrocatalysts in CH3CN and CH3CN-H2O. Chapter 5 describes the trimethylamine N-oxide assisted oxidative decarbonylation reaction of benzenedithiolate-bridged complex [Fe2(μ-bdt)(CO)6] I-7 with tertiary phosphines to synthesize complexes [Fe2(μ-bdt)(CO)5(PPh2PhCOOH-p)] 10 and [Fe2(μ-bdt)(CO)5(P(3,5-CH3,4-OCH3Ph)3)] 11. Molecular structure of 10 was established by SC-XRD. The reduction potentials of 10 and 11 appeared at more negative potentials than I-7. Complexes 10 and 11 were active electrocatalysts for proton reduction in dichloromethane.

Contents

1. Background and scope of the present work 2. Structural and HER studies of Diphosphine monothiolate complexes [Fe$_2$(CO)$_4$(μ-naphthalene-2-thiolate)$_2$((μ-dppe)] and [Fe$_2$(CO)$_4$(μ-naphthalene-2-thiolate)$_2$(μ-DPEPhos)] 3. Propanedithiolate-bridged {FeFe}complexes: relevance to the [FeFe] hydrogenase active site 4. Aminophenyldiphenylpohosphine (*o*, *m* and *p*-NH$_2$) ligands substituted diiron benzenedithiolate bridged complexes: synthesis, characterization and electrocatalytic activity 5. Role pf phosphine ligands on the catalytic activity of diiron dithiolate

bridged [FeFe]-H_2ase inspired complexes. Summary and conclusion. List of Publication.

16. KAUSHIK (Bhawna)

Design and Fabrication of Visible Light Responsive Zinc Based Magnetic Photocatalysts for Effective Heteroarylation Nitrobenzene Reduction and Degradation of Organic Pollutants.

Supervisor: Dr. Deepti Rawat

Th 25877

Abstract

In the era of population spurt, rapid industrialization and diminishing conventional sources of energy, there is an urgent need of a clean energy source that can make our future greener and more sustainable. Natural sunlight being an abundant and renewable form of energy possesses an untapped potential to accomplish environmental remediation and drive a wide variety of industrially important organic transformations. Introducing light as the energy source not only makes the whole catalytic process benign and environment friendly but also brings the thermodynamic equilibrium of various redox reactions towards feasibility at room temperature and reduces the possibility of thermally driven side reactions. In contrast to the conventional catalytic processes, photocatalysts can trigger both spontaneous as well as non-spontaneous reactions where Δ Go < 0. In case of spontaneous processes, the catalyst employs green and sustainable light energy to overcome the activation energy barrier at ambient reaction conditions whereas in non-spontaneous reactions, a portion of solar/light energy is stored into the reaction products in the form of chemical energy. The phenomenal establishment of the work was carried out by Honda and Fujishima for water splitting using TiO2 electrode. The work instigated a spark among the scientific community as the process offered a ray of hope to the world with limited fossil fuels and the constant pollution caused by their incessant use. Nevertheless, the utilization of ultraviolet light (UV) is the common requisite to perform such reactions in specially designed reaction containers. This UV light is not only harmful for the skin but also leads to lower selectivity of the favorable products hampering their practical applications. To overcome these shortcomings, scientists have made a shift from UV induced to visible light triggered photocatalytic reactions due to their feasibility in milder conditions and high product selectivity. Besides, visible light-mediated photocatalytic transformations have shown a promising pathway to replace conventional processes having bottlenecks such as high temperature, use of hazardous reagents, tedious separation and employment of heavy metals etc.

Contents

1. Introduction 2. Theoretical aspects of advanced instrumental techniques to characterize photocatalysts 3. Precisely engineered type II ZnO-CuS based heterostructure: a visible light driven photoctalyst for efficient mineralization of organic dyes 4. Synergetic effect of magnetic ZnO/$BiVO_4$ for enhanced visible light mediated degradation of bisphenol A and methyl violet 5. Magnetically separable type II semiconductor based ZnO/MoO3 photocatalyst: A proficient system for heteroarenes arylation and rhodamine B degradation under visible light 6. *In-situ* synthesis of 3-D hierarchical $ZnFe_2O_4$ modified Cu_2S snowflakes: exploring their bifunctionality in selective photocatalytic reduction of nitroarenes and methyl orange degradation. Summary, Copies of the publications and List of conference, workshop and seminar attended.

17. KRISHNA

Synthesis of Non-ionic Amphiphilic Architectures for Biomedical Applications & Gaur Gum Based Heterogeneous Catalyst.

Supervisor: Prof. Sunil K. Sharma

Th 25900

Abstract

Self-assembly and self-organization are the key tools in supramolecular chemistry and are being intensively used by researchers to build amazingly complex architectures. The advent of supramolecular chemistry in the last decades of the 20th century has provided chemists with a wealth of new routes toward constructing molecular structures and materials that exhibit self-assembly phenomenon due to relatively weak, non-covalent interactions, such as hydrogen bonding, π-π stacking, electrostatic and van der Waals interactions. The self-assembly of amphiphiles has been shown to be of significant importance in many research fields, such as candidates for drug delivery, artificial enzyme-mimicking, stabilizers for emulsions used for cleaning and green organic reactions. Moreover, amphiphiles show unique and newer opportunities for designing novel material for advanced applications in biomedicine and bionanotechnology. Considering various possible structures among Gemini amphiphiles, the non-ionic one is advantageous for the drug delivery applications due to reduced 2 cytotoxicity. Furthermore, the presence of two hydrophobic alkyl tails in Gemini amphiphiles allow sharp and uniform decrease in CAC value than their monomeric counterparts and thus making a valuable contribution for therapeutic applications. As a part of our ongoing efforts to explore the use of other type of competing novel moieties, we aim to explore the use of gold standard polyethylene glycol (PEG) towards the synthesis of a wide variety of amphiphiles for drug delivery applications, PEG is known for its unique properties, such as low toxicity, excellent solubility in aqueous solution, good chemical stability, ion-transporting ability, decreased interaction with blood components, etc. Herein, we report the design, synthesis, and characterization of a newer family of glycerol based non-ionic Gemini amphiphiles and study of their supramolecular aggregation into different nanostructures in an aqueous medium. Firstly, suitably protected glycerol was conjugated via its secondary hydroxyl group with the 5-hydroxy isophthalic acid via Mitsunobu reaction and the resulting diacid then undergoes esterification with propargyl alcohol to yield an A_2B_2 central core in a multiple step chemo-enzymatic approach by making use of immobilized Candida antarctica lipase (Novozym 435). The primary alcohols of the glyceryl moiety in the A_2B_2 core were first reacted with the long chain aliphatic acid, it was followed by the reaction of mPEG-azide to couple with the two acetylenic groups of the core via Click coupling. The amphiphiles thus generated by conferring hydrophobic and hydrophilic groups were studied for their transport potential.

Contents

18. KUSHWAHA (Chandra Shekhar)

Synthesis, Characterization and Electrochemical Sensing Study of Conducting Biopolymer Composites.

Supervisor: Dr. Saroj Kumar Shukla

Th 25919

Abstract

The thesis entitled "Synthesis, Characterization and Electrochemical Sensing Study of Conducting Biopolymer Composites" delivers the dissertations focusing on the study of the preparation of transition metal oxides by nitrate eutectic melt method, binary and ternary type conducting biopolymer composites (CBCs) from biopolymers (ca. chitosan, cellulose, and sodium alginate), transition metal oxides (ca. α-Fe2O3, NiO, CuO, and ZnO) and aniline after using acidified ammonium persulfate (APS) as an oxidizing agent. The characterizations of prepared CBCs for structural and morphological studies and the effect of metal oxide nanoparticles are revealing the advances in the properties of CBCs after inserting nano-size metal oxide with improved stability, electrical conductivity, adsorption capacity, and electrochemical responsiveness by significant order. Further prepared CBCs explored for potentiometric sensing of pesticides (ca. malathion, methyl parathion, and chlorpyrifos), pharmaceuticals (ca. paracetamol and amoxicillin), and heavy metal ions (ca. Cu2+, Pb2+, and Hg2+), along with the determination of different sensing parameters i.e., sensing range, sensitivity, response time, recovery time, interference and stability. The complete research work and results are presented in seven chapters from 1 to 7 with the help of schemes and illustrations.

Contents

1.Introduction 2. Material and methods 3. Characterizations of TMOs and CBCs 4. Potentiometric sensing of pesticides 5. Poteriometric sensing of heavy metal ions 6. Potentiometric sensing of pharmaceuticals7. Conclusion and future outlook. List of published research papers. List of conferences/Sympposium attended and list of books/book chapters.

19. LAKSHYA KUMAR

Development of Nanostructured Mixed Transition Metal Oxides and Layered Double Hydroxides for Energy Storage Application.

Supervisor: Dr. Sasanka Deka

Th 25891

Abstract

The thesis entitled "Development of Nanostructured Mixed Transition Metal Oxides and Layered Double hydroxides for Energy Storage Application" deals with the synthesis, characterization of mixed transition metal oxides and layered double hydroxide materials for energy storage applications. The thesis has been divided into six chapters which are as follows. Chapter 1 This chapter mainly focused on the introduction about nanoparticles, literature survey on mixed transition metal oxides and layered double hydroxides and their application in energy storage devices. We have discussed a few basic topics of nanoscience and nanotechnology and their role in various fields. We also discuss the introduction about spinels and layered double hydroxide and their application in energy storage devices. This chapter also covered various types of capacitors and their energy storage mechanisms. After

that, we discussed various electrolytes and their mechanisms to store energy in supercapacitors. Lastly, we have discussed various electrode materials used for supercapacitor applications. Chapter 2 The second chapter describes various synthetic routes and characterization techniques for the synthesis of mixed transition metal oxide nanoparticles and templatebased mixed metal layered double hydroxides (LDH). We have discussed the formation of NiCo2O4 nanoplatelets with the help of a non-aqueous colloidal route and coral shaped and octahedron shaped NiCo2O4 nanoparticles synthesized by slow ageing hydrothermal method. We have also discussed template assisted hydrothermal method to obtain CuCo-LDH polyhedrons. Various characterization techniques employed are also covered in this chapter. Lastly, we have discussed the electrochemical studies to make cells for three-electrode, coin cell and flexible supercapacitor study and the formula used to calculate capacitance, specific capacity, energy density, power density and ESR of the cell. Chapter 3 This chapter describes the development of NiCo2O4 nanoplatelets via a nonaqueous colloidal route, characterization of these nanoplatelets and their use as efficient electrode material for supercapacitor applications. The purity and crystalline phase study was confirmed by XRD, FT-IR and Raman measurements and TEM, HR-TEM and FESEM showed nanoplatelets morphology. Then, we conducted three-electrode measurements and coin-cell measurements by taking NiCo2O4 nanoplatelets as the electrode material which showed high charge-storage capability for energy applications and can be used in real-life application as the coin cell device. Chapter 4 This chapter provides insight into the synthesis of porous octahedron shaped NiCo2O4 nanoparticles, characterization of these octahedron nanoparticles and fabrication into an all-solid-state symmetric flexible supercapacitor application. The characterization techniques such as XRD, Raman, TEM and FESEM measurements revealed a pure phase and octahedron morphology. Then, we fabricated a symmetric flexible supercapacitor device by sandwiching the octahedron nanoparticles and ionic liquid electrolyte between two newly developed super flexible current collector substrate sheets. Thereafter, the electrochemical studies were done by using as the developed flexible device which showed exemplary charge storage behavior. Chapter 5 The synthesis of coral shaped NiCo2O4 nanoparticles, characterization techniques and its supercapacitor application are discussed in fifth chapter. Various characterizations revealed a pure phase with highly porous coral like morphology of NiCo2O4 nanoparticles. Thereafter, we performed three-electrode measurements and coin-cell measurements using NiCo2O4 nanoparticles as the electrode material, which demonstrated high charge-storage capability for energy applications and can be used as the device in real-world applications. The high charge-storage capability can be attributed to faster ion intercalation between electrode and electrolyte and redox faradic capacitance, high conductivity, highly porous coral morphology that decreases diffusion distances and exposure of mixed metal valence at the surface. Chapter 6 This chapter describes the synthesis of CuCo-LDH hollow nanopolyhedrons nanostructures, their characterization, and their incorporation into an all-solid-state symmetric flexible supercapacitor application. Several characterization techniques like XRD, Raman, TEM, and FESEM revealed a pure phase and porous hollow polyhedron morphology. Using CuCo-LDH hollow nanopolyhedrons, ionic electrolyte and GPPCS a symmetric flexible supercapacitor device was created. Following that, electrochemical studies were conducted using the developed flexible device, which demonstrated exceptional charge storage characteristics as accredited to high surface area furnishing abundant active sites, shortened ion diffusion length and consequent faster ion switching, synergism between balanced Cu and Co ions.

Contents

1. Introduction 2. Synthetic procedures and experimental details 3. Faster Ion switching $NiCo_2O_4$ nanoparticles electrode based supercapacitor device with high performances and long cycling stability 4. A super bending ($0-180^0$) and high voltage operating metal oxide based flexible supercapacitor 5. Coral shaped mixed metal oxide nanoparticles by oriented attachment of nanocrystal building blocks: a material for efficient charge storage 6. CuCo-layered hydroxide nanosheet based polyhedrons for flexible supercapacitor cells. Summary, Future scope and list of publication and conference attended.

20. MISHRA (Gaurav kumar)

Theoretical Models for Electron Transfer Kinetics and EDL Dynamics at Curved Nanostructured Electrode.

Supervisor: Prof. Rama Kant

Th 25907

Abstract

The electrode surface ubiquitously possesses atomic, mesoscopic, and the macroscopic scale irregularities, which anomalously govern the electronic, electrochemical interfacial ion reorganization and the transport properties. The atomic-scale surface irregularities influence the local and global electronic properties of an electrode, viz. Fermi energy, work function (WF), the potential of zero charge (PZC), adsorption of ions or molecules, heterogeneous electron transfer (HET) kinetics, and so forth. Similarly, the mesostructure (2-50 nm) of an electrode surface is known to influence the reorganization and the packing density of the ions or molecules, therefore, altering the ionic and dipolar charge distribution, the interfacial capacity, and indirectly the HET kinetics. This chapter provides a comprehensive review of the current status of various classical and microscopic aspects of HET kinetics along with the EDL structure and dynamics. This chapter reviews the following topics: (i) the ET theory including the classical Butler-Volmer equation, contemporary Marcus theory, Marcus-Hush-Chidsey theory and other approaches, (ii) the ET kinetics at lower dimensional materials, (iii) the theoretical status of charge transfer coefficient, (iv) experimental anomalies in ET kinetics and (v) factors influencing the electrochemical phenomena at the interface, such as metal jellium WF with and without solvent or the self-assembled monolayer, supporting electrolytes, electroactive species, and the atomic scale electrode surface irregularities

Contents

1. Introduction to interfacial processes: theoretical aspects 2. Semi microscopic theory of transfer coefficient in outer sphere electron transfer kinetics 4. Theory of heterogeneous electron transfer on curved nanostructures: inactivation kinetics of SARS-CoV-2 5. Theory of the influence of metal steps on potential of zero charge and electronic dipolar capacitance 6. Theory of influence of nanocorrugated atomic steps on elelctorn transfer kinetics 7. Theory of current rectification phenomenon in nanogap molecular devices 8. Modular theory of elelctrochemical impedance response of supercapacitor 9. Electrochemical impedance response for elecroscatalytic reactions: theory and expariement on exfoliated graphene 10. Summary and future perspectives.

21. MITTAL (Rupali)

De Novo Design and Synthesis of Diversified Carbon-based and Metal Oxide Materials for Functional Group Transformations in Organic Reactions.

Supervisor: Prof. Satish Kumar Awasthi

Th 25905

Abstract

The present thesis deals with the design, synthesis and applications of carbon-based and metal oxide-based materials for functional group transformations. In brief, a methodical examination has been carried out on these materials to realize their easy synthetic approaches and potential applications in the field of heterogeneous catalysis. Despite considerable progress in design and development of carbon-based and metal oxide-based materials for catalytic organic reactions, there is always a need to foster low-cost methodologies using environment-friendly and sustainable reaction conditions. This thesis is divided into five chapters. A brief account of each chapter is discussed below. Chapter 1 reports the potential of sulfonated reduced graphene oxide (SrGO) as a metal-free solid acid catalyst for the chemoselective N-t-Boc protection of various aromatic, heterocyclic and aliphatic amines under ambient and solvent-free conditions. In this study, SrGO was synthesized by the introduction of sulfonic acid-containing aryl radicals onto chemically reduced graphene oxide obtained by using sodium borohydride as the reducing agent. The authenticity of this green approach was confirmed via single crystal X-ray analysis of compound 3q. Further, SrGO could be easily recovered from the reaction mixture and reused upto seven consecutive catalytic runs without substantial loss in its activity. Chapter 2 reports an unprecedented work wherein a common catalyst, that is, metalfree sulfonic acid functionalized reduced graphene oxide (SA-rGO) has been used for the first time for the synthesis of both carboxylic acids and their bioisosteres, 5- substituted-1H-tetrazoles. Unlike the previous chapter, in this work, SA-rGO was attained by using non-toxic L-ascorbic acid as a mild reducing agent to chemically reduce the graphene oxide which was subsequently grafted with sulfonic acid containing aryl radicals prepared from the diazonium salt of sulfanilic acid. SA-rGO as a catalytic material incorporates the intriguing properties of graphene oxide material 2 with additional benefits of highly acidic sites due to sulfonic acid groups. The oxidation of aldehydes to carboxylic acids could be efficiently accomplished using H2O2 as a green oxidant with high TOF values and green chemistry metrics values close to ideal values. The 5-substituted-1H-tetrazoles could also be effectively accessed with high TOF values. The synthetic approach for 5-substituted-1H-tetrazoles was validated by single crystal X-ray analysis of compound 5k and computational calculations of the proposed reaction mechanism which correlated well with the experimental findings. Further, both the reactions could be performed proficiently at gram scale (10 g) using the SA-rGO catalyst. SA-rGO exhibited eminent reusability upto eight consecutive catalytic cycles without significant decrease in its productivity. Chapter 3 reports a synergistic silica coated magnetic Fe3O4 catalyst functionalized with nitrogen rich organic moieties and further immobilized with cobalt metal ion (FNP-5) for scalable selective oxidation of alcohols to aldehydes and ketones using tertbutyl hydroperoxide (TBHP) as oxidant. The control reactions revealed radical mechanistic pathway assisted by the synergism induced by the inorganic-organic hybrid nature of FNP-5. The catalytic role of FNP-5 material for the selective oxidation of alcohols to aldehydes and ketones has been explained unconventionally as a synergistic architecture, wherein each of its component contribute towards the catalytic activity, thus displaying practicality closer to synthesis. The prominent characteristics of this work include neat

reaction conditions, high TOF values, scalability of product and low E-factor value (1.92). Furthermore, FNP-5 could be readily separated via an external magnet, displayed recyclability over eight consecutive catalytic runs and exhibited structural integrity even after vigorous use. Overall, this work manifests the understanding of synergistic architectures as sustainable surrogates for valuable selective oxidation reactions. Chapter 4 reports a bimetallic zinc cobalt oxide (ZCO-1) material capable of accomplishing dehydrogenative oxidation of alcohols and diols to carboxylic acids and dicarboxylic acids. Primitively, novel zinc cobalt acetate hydroxide precursor was prepared which was subsequently converted to zinc cobalt oxide via thermal annealing. To attain superlative performance, the Co/Zn molar ratios were fine-tuned by preparing the material in three different ratios, viz. ZCO-1 (2:1), ZCO-2 (1:1) and ZCO-3 (1:2). 3 On comparison, ZCO-1 emerged as the finest catalyst for the dehydrogenative oxidation of alcohols to carboxylic acids exhibiting wide substrate applicability and high yield output with concomitant evolution of hydrogen gas (latent fuel) under oxidant-free conditions. The superior catalytic output of ZCO-1 sample can be imputed to the synergistic interactions originating from fine-tuned molar ratio of Co/Zn (2:1) which led to the formation of pure single-phase spinel-structured zinc cobalt oxide with sufficiently high surface area capable of furnishing large active sites resulting in faster reaction kinetics and higher productivity. Further, ZCO-1 could be easily recovered and reused upto ten consecutive catalytic cycles without significant activity loss. Moreover, the practical utility of the current protocol was displayed via ZCO-1 catalyzed gramscale synthesis of high-value chemicals like nicotinic acid, terephthalic acid and succinic acid. Chapter 5 reports the synthesis of Mn3O4-Co3O4/NC@SiO2 (MCCO) nanoreactors derived by mounting Mn3O4 nanoparticles prepared via a novel methodology at room temperature onto Co-zeolitic imidazole framework (ZIF-67) crystals coated with SiO2 followed by pyrolysis. The MCCO was used for the catalytic oxidation of C-H bonds, cycloalkanes and alcohols under air atmosphere and neat reaction conditions. The other notable aspects of MCCO catalyzed oxidation reaction include low catalyst loading (2 mg), high yield of oxygenated products and wide substrate applicability. The exceptional catalytic behaviour of MCCO can be attributed to the complementarity among Mn3O4-Co3O4 and synergistic contributions from different components of MCCO such as (a) the confinement effect of SiO2 coating which stabilizes the active sites via encapsulation and (b) the presence of graphitized carbon component which enhances the electron transport leading to faster reaction kinetics. Further, MCCO catalyst can be effortlessly recovered via an external magnetic force and exhibited exceptional reusability upto ten consecutive catalytic runs while preserving high catalytic performance and structural aspects. Moreover, the practical utility of the current protocol was depicted by MCCO catalyzed gram-scale synthesis of high-value chemicals like acetophenone and vanillin

Contents

22. NAVEEN KUMAR

Di- and Tri-Iron Models of the Hydrogenase Active Site as Electrocatalysts for the Hydrogen Evolution Reaction.

Supervisor: Dr. Sandeep Kaur

Th 25916

Abstract

Abstract of thesis entitled: “Di- and Tri-Iron Models of the Hydrogenase Active Site as Electrocatalysts for the Hydrogen Evolution Reaction,” to be submitted to University of Delhi. In nature, [FeFe], [NiFe] hydrogenase (H2ase) enzymes found in green algae and anaerobic bacteria, are known to be highly efficient biological catalysts for hydrogen evolution. These metalloenzymes, especially the [FeFe] (H2ases) (6000- 9000 TOF / s–1) have inspired the design of synthetic catalytic systems for hydrogen production in order to achieve a sustainable hydrogen economy and minimize the use of fossil fuels for a cleaner environment. Therefore, with the aim of developing new, efficient and stable monothiolate ligand-based catalysts, {FeFe}/{FeFeFe} model complexes have been synthesized by using different combinations of bridging monothiolates (electron-donating/-withdrawing) and mono/di-phosphine ligands as bioinspired mimics of the enzyme active site of the hydrogenases.

Contents

1.Introduction and aim of the work 2. 4-Nitrobenzylthiolato-bridged diiron models of the [FeFe] hydrogenase: synthesis, characterization and electrochemistry 3. Syntheischaracterization and electrochemical studies of 3-methoxybenzenethiolato-bridged diiron models of the hydrogenase active site 4. Electrocatalytic proton reduction byphosphine substituted bis (naphthalene-2-thiolato) {FeFe} complexes 5. 2-Meracaptobenzimidazole ligand-based models of the [FeFe] hydrogenase: synthesis, characterization and electrochemical studies.

23. PACHISIA (Sanya)

Molecular Assemblies and Coordination Polymers Decorated with Hydrogen Bonding Functional Groups.

Supervisor: Prof. Rajeev Gupta

Th 25909

Abstract

The thesis is divided into the following six chapters: Chapter 1. Introduction: Selected Examples of Molecular Assemblies and Coordination Polymers Offering H-bonding Functional Groups Chapter 2. Half-Sandwich Ruthenium Complexes of Amide-Phosphine Based Ligands: H–Bonding Cavity Assisted Binding and Reduction of Nitrosubstrates Chapter 3. Hg-Based Molecular Assemblies Offering H-Bonding Cavities: Influence of Cavity Structure and H-bonding on Heterogeneous Catalysis Chapter 4. Hg-Based Molecular Assemblies Offering H-Bonding Cavities: Influence of Cavity Structure and H-Bonding on Dye Adsorption Chapter 5. Zn- and Cd-based Coordination Polymers Offering H-Bonding Cavities: Highly Selective Sensing of S2O7 2- and Fe3+ Ions Chapter 6. Co-based Coordination Polymers Offering H-Bonding Cavities as the Efficient Heterogeneous Catalysts.

Contents

1. Introduction selected examples of molecular assemblies and coordination polymers offering H-bonding functional groups 2. Half-sandwich ruthenium complexes of amide-phosphine based ligands: H-bonding cavity assisted binding and reduction of nitrosubstrates 3. Hg- based molecular assemblies offering H-bonding cavities: influence of cavity structure and H-bonding on heterogeneous catalysis 4. Hg-based molecular assemblies offering H-bonding cavities: influence of cavity structure and H-bonding on dye adsorption 5. Zn-and Cd-based coordination polymers offering H-bonding cavities: highly selective sensing of $S_2O_7^{2-}$ and Fe^{3+} Ions 6. Co-based coordination polymers offering H-bonding cavities as the efficient heterogeneous catalysts. Summary and List of publication.

24. PANDEY (Jyoti)

Exploring solution-based synthesis and catalytic applications of bismuth-containing oxides with fluorite, pyrochlore structure, and layered oxychlorides with Sillen structure.

Supervisor: Prof. Rajamani Nagarajan

<u>Th 25922</u>

Abstract

Abstract of the thesis entitled "Exploring solution-based synthesis and catalytic applications of bismuth-containing oxides with fluorite, pyrochlore structure, and layered oxychlorides with Sillen structure'' to be submitted by Ms. Jyoti Pandey, Department of Chemistry, University of Delhi for the award of the degree of Doctor of Philosophy. The thesis is divided into four chapters; chapter 2 contains four subsections, and chapter 4 includes two subsections. Chapter 1: Introduction Chapter 2: Bismuth containing fluorite structured oxides and β-Bi2O3. Section 2.1: Catalytic application of oxygen vacancies induced by Bi3+ incorporation in ThO2 samples obtained by solution combustion synthesis. Section 2.2: Outcome of stabilizing β-polymorph of Bi2O3 upon doping of Th4+. Section 2.3: The emergence of bifunctional catalytic properties by the introduction of Bi3+ in defect fluorite-structured PrO1.833. Section 2.4: Bismuth and alkali, alkaline earth, and rare earth metal ions co-doped in PrO1.833. Chapter 3: Metastable Bi2Zr2O7 with pyrochlore-like structure: Stabilization, oxygen ion conductivity, and catalytic properties. Chapter 4: Hole doped Bi2YO4Cl. Section 4.1: Analysis of structure, ferroelectric, and toxin removal application of Ca - substituted Bi2YO4Cl. Section 4.2: Crystal structure and ferroelectric properties of Cd - substituted Bi2YO4Cl. Conclusions and future directions.

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1. Introduction 2. Bismuth containing fluorite structured oxides and β-Bi_2O_3 2.1 Catalytic application of oxygen vacancies induced by Bi^{3+} incorporation in ThO_2 samples obtained by solution combustion synthesis 2.2 Outcome of stabilizing of β-polymorph of Bi_2O_3 upon doping of Th^{4+} 2.3 The emergence of bifunctional catalytic properties of Bi^{3+} in defect fluorite structured $PrO_{1.833}$ 2.4 Explorations of structural changes incurred in the fluorite structured $PrO_{1.833}$ due to the co-substitution of bismuth-erbium,bismuth-sodium and bismuth-calcium 3. Metastable $Bi_2Zr_2O_7$ with pyrochlore-like structure: stabilization, oxygen ion conductivity, and catalytic properties 4. Hole substituted Bi_2YO_4CI 4.1 Analaysis of structure ferroelectric and toxin removal application of Ca-substituted Bi_2YO_4CI 4.2 Crystal structure and

ferroelectric properties of Cd- substituted Bi_2YO_4CI.Coclusion and future directions. List of publications, conferences, workshop and seminars attended.

25. PATHAK (Tribhuvan Kumar)
Synthesis and Characterization of Aerosol Forming Composite (AFC) for Fire Fighting Applications.
Supervisor: Prof. P.S. Jassal
Th 25902

Abstract

For many decades halons have been widely employed as effective fire fighting extinguishers. However, their applications have now been phased out in view of the Vienna convention (1985) and Montreal protocol (1987) on the protection of the ozone layer. Halogen based fire extinguishing agents produces significant quantities of halogen acid gas and aerosol during fire suppression and causes potential risk of depleting ozone layer and also can be life threatening. The thermal degradation of halogenated organic fire suppression compounds can produce toxic HF (hydrogen fluoride), COF_2 (carbonyl fluoride), HCI (hydrogen chloride), HBr (hydrogen bromide), or HI (hydrogen iodide) gases having high ozone depletion potential (ODP) and global warming potential (GWP). Thus, against the urgent background of their elimination has triggered the research and development efforts for halon alternatives all around the world. As a result, number of halon alternative technologies emerged out such as foam, inert gases (CO_2, N_2, Ar etc.), fluorinated chemicals (Novec 1230-$(CF_3)_2CFCOC_2F_5$, FM 200- CF_3CFHCF_3, etc.), dry powder, hydro fluorocarbons (HFCs), aerosols, water mist etc. emerged out and have gained much attention in recent years. The condensed aerosol fire extinguishing technology has been widely used in preference to other halon alternative technologies because its superior fire suppression efficacy with zero toxicity, negligible environmental impact on global warming and ozone depletion. It has small atmospheric lifetime, low residue, can be effortlessly installed without piping, occupies minimum space, and there is no requirement of storage in a pressurized vessel. It is highly efficient against various classes of fires.

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1.Introduction 2. Review of literature 3. Scope and objectivities of the present work 4. Material and method 5. Fire performance evaluation of natural antioxidants based pyrotechnic composites 6. Fire performance evaluation of aromatic nitro compounds based pyrotechnic composites 7. The significance and effect of natural binders in pyrotechnic composites 8. Summary and list of publication.

26. PROMILA KUMARI
Wet chemical synthesis and catalytic applications of Bi and Sb containing thoria, Sb, Sn, and transition metal ion (Mn, Co, Ni, and Cu) substituted yttria systems.
Supervisor: Prof. Rajamani Nagarajan
Th 25888

Abstract

Mixed metal oxides have invited extensive investigations because of their technological capabilities. Synthesis and tuning of the properties of mixed metal oxides give rise to a new set of compounds that can be further exploited in various fields. The present thesis aims to synthesize mixed metal oxides mainly belonging to bixbyite and fluorite structure and characterization and explore their use in catalysis and magnetism. A brief overview of the thesis is outlined below. Chapter 1 The chapter discusses the literature related to various aspects of mixed metal oxides, taking suitable examples of bixbyite, fluorite and pyrochlore structure type oxides and different polymorphs of Bi2O3 and correlate with the properties exhibited by them. Chapter 2 The chapter describes the work carried out on bismuth, thorium-related oxides, divided into three sections. Section 2.1 deals with the solid solution formation between thoria and bismuth oxide has been determined following a molecular precursor route exploiting the high chelating ability of NTA (nitrilo triacetic acid) and EDTA (ethylenediaminetetraacetic acid). The samples have been thoroughly characterized using powder X-ray diffraction, scanning electron microscopy, Raman, and UV-visible diffuse reflectance spectroscopy measurements. The creation of oxygen vacancies and narrowing of direct bandgap occurred on bismuth substitution. Bismuth substituted samples catalyzed the reduction of nitroaromatics following pseudo-first-order kinetics efficiently. Section 2.2 deals with the stabilization of β-Bi2O3 by codoping thorium (1-10 mol %) and carbon (cation-anion codoping) to enhance its photocatalytic activity. It was achieved by adopting the solution co-precipitation synthetic method. Carbon doping in this sample has been responsible for narrowing the bandgap. The sample exhibited a high surface area. Cation-anion codoped samples behaved good catalysts for the photodegradation of carcinogenic dye solution. Such coupled anion- n-cation doping schemes are quite rare and hence demonstrates a pathway to tailor the bandgap of a metastable polymorph together with its stabilization. Section 2.3 deals with the synthesis of antimony substituted thoria following a cocomplexation method. Antimony oxide (III) has a stereochemically active lone pair of electrons which causes an asymmetric coordination environment in the structure. The introduction of antimony causes significant changes such as the decrease in crystalline nature and compressive strain in the thoria lattice. Chapter 3 The chapter describes the work carried out on yttria, modified with a variety of metal ions and it is divided into three sections. Section 3.1 deals with the effect of chemical pressure on yttria's structure and electronic properties (Y2O3) by introducing trivalent antimony by preparing the samples by the EDTA co-complexation method. A complete transformation from ordered bixbyite to disordered fluorite structure was achieved by incorporating 20 mol % Sb3+ in yttria. Williamson-Hall analysis revealed a compressive strain in antimony substituted samples. Raman spectra of antimony substituting samples indicated extensive disorder. With the increase in the antimony content, the absorption edge moved towards the visible region. 50 mol % antimony substituted yttria sample has been utilized as a catalyst for the photodegradation of Rh-6G dye. Section 3.2 Variation in structural, optical, and luminescent properties arising from the doping of Eu3+ and Tb3+ ions in fluorite structured YSbO3 was investigated. PXRD patterns and structural refinements results confirm the fluorite phase of these samples. Eu3+ and Tb3+ doped samples emitted in reddish yellow and green regions with CIE coordinates of (0.42, 0.44) and (0.14, 0.55). Lifetime measurements of these transitions have been carried out. Section 3.3 The effect of substituting magnetic transition metal of the first row of periodic table at the place of yttrium on the structure and properties of Y2O3 are presented. 10 mol % of Mn, Co, Ni, and Cu doped Y2O3 samples have been synthesized by the sol-gel method, and field and

temperature-dependent magnetic measurements have been carried out. 10 mol % Co-doped yttria sample showed spin-glass behavior at low temperature due to competing ferromagnetic and antiferromagnetic interactions. Other transition metal ion-doped Y2O3 systems remained paramagnetic. These transition metal ion (10 mol % Mn, Co, and Cu) doped yttria was demonstrated as a heterogeneous catalyst to reduce p-nitrophenol to p-aminophenol. Section 3.4 Progressively increasing concentrations of tin in Y2O3 have been carried in this section, where the phase transformed from bixbyite to fluorite and finally resulted in a defect fluorite structural arrangement. The overall conclusions from the entire set of investigations are collected at the end. Further, a summary of how these studies can be additionally used for other practical applications is elaborated.

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1. Introduction 2. Work related fo bismuth-thorium oxides 2.1 Co-complexation method for the synthesis of $Th_{1-x}Bi_xO_{2-8}$ using NTA/EDTA as ligand 2.2 Co-compexation method for the synthesis of β-Bi_2O_3 by substituting thoria (using EDTA as a ligand) 2.3 Synthesis and characterization of antimony substituted thoria lattice by co-compexation method 3. Work related to yttrium oxides 3.1 Bixbyite to fluorite phase transformation by the antimony substitution 3.2 Synthesis and iuminescent properites of Eu^{3+} and Tb^{3+} doped $Y_{0.50}Sb_{0.50}O_y$ 3.3 Optical magnetic and catalytic properties of transition metal ion (Mn, Co, Ni, and Cu) doped yttria by the sol-gel method 3.4 Sol-gel synthesis and phase transformtionof yttris from bixbyite→fluorite→defect fluorite by tin substitution. References, Conclusion and future direction and list of publications and conferences attended.

27. RANA (Pooja)

Visible Light Mediated Cross Dehydrogenative Coupling, C-H Arylation, Cyanation and CO_2 capture via the Design and Development of Surface Engineered Nanosized Photocatalysts.

Supervisor: Prof. R.K. Sharma

Th 25890

Abstract

Sunlight is a cleaner, greener, sustainable and renewable energy source which has been utilized abundantly for different purposes throughout the history of life evolution on Earth and continues to play a significant role even today. Drawing inspiration from mother nature, artificial photosynthesis is being emulated to tackle the current energy and environmental crisis via the efficient utilization of clean and renewable energy of sunlight. To mimic nature's ability by using various visible light absorbing chromophores/photocatalysts, material scientists and engineers have evinced keen interest towards designing energy efficient artificial photocatalysts. The untapped potential of the abundant and easily available solar energy was unlocked by various scientists by harnessing it in photocatalytic process in which the solar energy is used to drive thermodynamic uphill reactions to generate targeted products. Visiblelight-driven photoredox catalysis has already proven its dominance and is experiencing a renaissance in the field of organic transformations to generate various chemical motifs due to its mild conditions for substrate activation, the potential to facilitate thermodynamically uphill reactions by harvesting non-toxic and inexpensive light energy to attain high proficiency to generate the desired products without leading to the formation of unwanted and toxic byproducts. Over the course of the preceding 35 years, there has been a substantial utilization of expensive complexes of noble metals such as Ru, Ir, Os, and Pt due to their peculiar characteristics such as: i) absorption in visible light region, ii) long life-time of the excited species and well-defined molecular structure, iii) excellent photoredox properties and iv) ability of the noble metals to circumvent the possibility of thermally induced side reactions. Despite their remarkable ability and achievements to catalyse a wide range of distinct transformations, reliance on rare and expensive noble metal complexes (eg. Ru, Ir, Os, and Pt) for efficient photosensitization presents a significant roadblock for practical photocatalytic processes due to possibility of metal contamination, difficult extraction and recyclability which impedes their practical adoption in large scale industries for future applications. Henceforth, it is highly desirable to develop well defined heterogeneous photocatalytic system which would embrace these significant features (i) based on inexpensive earth abundant metal and (ii) show bright prospects of excellent recoverability and reusability up to multiple runs. Till date, there are various reports on the design and development of semiconductor based heterogeneous photocatalysts by opting surface science and the solid-state chemistry, whose surface atoms serve as the sites for reactions. Unfortunately, the semiconductor-type photocatalysts such as TiO2 and ZnO typically require UV irradiation owing to their large band gaps. Until now, not much attention was paid to develop heterogeneous photocatalytic system from a sustainable and environmentally friendly standpoint by immobilizing the photoactive metal complex on heterogeneous support to achieve the goal of facile separation and recycling of the catalyst that can not only reduce the cost, but also fulfil the goal of circular economy.

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1.Introduction 2. Theoretical aspects of advanced instrumental techniques employed to characterize photoredox nanocatalyst 3. Cross dehydrogenative C(sp^3)-C(SP^3) coupling via C-H activation using magnetically retrievable ruthenium based photoredox nanocatalyst under aerobic conditions 4. Surface engineered iridium-based magnetic photocatalyst paving a path towards visible light driven C-H arylation and cyanation reaction 5. Earth abundant cobalt based photocatalyst: visible light induced direct (Het)Arene C-H arylation and CO_2 6. Noble metal free heterolyptic copper based photoredox nanocatalyst mediated aza-henry reaction under ambient conditions. Summary, Copies of the publications and list of conferences workshops and seminar attended.

28. SACHI
Synthesis of Nano-Heterostructures and Metal Oxides for Applications in Photocatalysis/Catalysis and Dielectric Resonators.
Supervisor: Prof. M. Thirumal
Th 25879

Abstract

Increase in the world's population results in high energy requirement. The Fossil fuels are limited source of energy and getting exhausted. The combustion of fossil fuels generates carbon dioxide that results in severe air pollution and contributes to global warming as a major greenhouse gas. Therefore, these fossil-fuel based energy systems and its limitations drive to explore attractive sustainable energy sources and technologies. In this regard solar energy is an infinite and has abundant amount of supply in all landmasses of the world. Thus the scientific community has been working to explore a solution by which the solar energy can be utilized. Recently, in the quest to explore the sustainable energy sources and

technologies, photocatalytic technology is studied as one of the most captivating and promising technologies for the direct harvest, conversion and storage of renewable solar energy. In this concern, the semiconductor photocatalysis has gained immense attention, by the researchers. Recently, ZnO, TiO2, NaNbO3, etc. wide band gap semiconductors has reported to be the potential candidates in the photocatalytic degradation of organic pollutants. However, the prospect of efficient photocatalysis could not be attained primarily due to the wide band gap associated with these semiconductors. In addition, fast recombination rate of photo-generated excitons are also responsible for low quantum efficiency of photocatalytic reactions. The solar energy is in the visible light region accounts to (44-47%) whereas the UV light accounts for 3-5% of the solar energy spectrum. In order to accomplish the maximum use of solar energy, it is essential prerequisite to utilize visible light efficiently. Several strategies have been developed by the researchers to overcome these issues. Among them, construction of semiconductor based heterostructure nanocomposite by coupling with mid/narrow band gap material is one of the promising strategies to enhance the photocatalytic efficiency under visible light irradiation. The formation of heterojunction results in migration of electrons from sensitizer to large band gap semiconductor and the hole transfers from large band gap semiconductor to sensitizer. Heterojunction band alignment results in efficient separation of photogenerated charge carriers enhancing the photocatalytic efficiency of wide band gap semiconductors in the visible light region.

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1.Introduction 2. Fabrication of AgNi nano alloy decorated ZnO naocomposite as an efficient and novel hybrid catalyst to degrade noxious organic pollutants 3. Enhanced Vis-resposive ZnSe/g-C_3N_4 heterostructure for the photodegradation of tetracycline 4. Fabrication of novel visible light active $NaNbO_3$/MGO heterojunction as an efficient photocatalyst for the reduction of Cr (VI) 5. Enhanced visible light catalytic performance of ZnO/$Ag_2V_4O_{11}$ heterostructure for the degradation of methylene blue 6. Solid solutions, composites of (1-x) $Ba_8ZnTa_6O_{24}$-(x) $Ba_8MgTa_6O_{24}$ perovskites and their characterizations 7. Conclusion and publications and conferences.

29. SAH (Digvijay)

Synthesis and Characterization of Solid Supported Nanostructured Materials for Catalysis.

Supervisor: Prof. Subho Mozumdar

Th 25878

Abstract

Abstract of the thesis entitled “Synthesis and Characterization of Solid Supported Nanostructured Materials for Catalysis” to be submitted by Mr. Digvijay Sah, Department of Chemistry, University of Delhi for the award of Doctor of Philosophy. The thesis is divided into seven chapters: Chapter 1: Introduction and review of the literature Chapter 2: Characterization techniques Chapter 3: Palladium oxide-decorated mesoporous silica on graphene oxide nanosheets as a heterogeneous catalyst for the synthesis of βsubstituted indole derivatives. Chapter 4: Ultra-small palladium nanoparticles decorated diamine functionalized graphene oxide porous sheets as an efficacious, potent and retrievable catalyst for the synthesis of amide derivatives. Chapter 5: Magnetic core-shell spherical silica fractals bearing acidic ionic liquid as retrievable nano-catalyst for the synthesis of xanthene derivatives. Chapter 6: Ruthenium oxide nanoparticles decorated L-Histidine coated fractal of silica nanospheres as a heterogeneous nano-catalyst for the synthesis of 2,3-dihydroquinazolin-4(1H)-one derivatives. Chapter 7: Conclusion.

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1.Introduction 2. Characterization techniques 3. Palladium oxide-decorated mesoporous silica on graphene oxide nanosheets as a heterogeneous catalyst for the synthesis of β-substituted indole derivtives 4. Ultra-small palladium nanoparticles decorated diamine functionalized graphene oxide porous sheets as an efficacious, potent and retrievable catalyst for the synthesis of amide derivatives 5. Magnetic core-shell spherical silica fractals bearing acidic ionic liquid as retrievable nano-catalyst for the synthesis of xanthene derivatives 6. Ruthenium oxide nanoparticles decorated L-hisitidine coated spherical silica fractals as a heterogenous nano catalyst for the synthesis of 2,3-dihydroquinazolin-4(1H)- one derivatives 7. Conclusion. List of publications and list of international conferences/workshop.

30. SAXENA (Megha)
Role of Functionalized Nanomaterials in Removal of Organic Contaminants from Water.
Supervisor: Prof. Reena Saxena
Th 25889

Abstract

This thesis entitled "Role of Functionalized Nanomaterials in Removal of Organic Contaminants from Water" discusses the synthesis, characterization and applications of functionalized nanomaterials for removal of organic contaminants from water using two methods, adsorption and catalytic reduction. Water being the most vital component of life is getting contaminated due to inhuman disposal of toxicants in water bodies. Organic compounds such as dyes, pharmaceuticals/drugs, pesticides, etc., are used for various purposes and become life threatening when dumped in water bodies without pre-treatment. The dyes such as methylene blue (MB) and malachite green (MG) are used in dyeing and printing of fabrics, cosmetics, etc., but they are highly toxic for living beings as their prolonged exposure can cause severe side effects such as nausea, abdominal pain, bladder infection, etc., and can even cause cancer. The diclofenac is an anti-inflammatory drug and it has deleterious effects on all living beings when present in excess amount in water due to its poor degradation rate. The other organic pollutant, 4-nitrophenol is used in chemical industries in the synthesis of dyes, pesticides, pigments, etc., and is considerably toxic due to its mutagenic and carcinogenic properties. The removal of these toxicants from the environment is complicated but highly essential for sustainable development. Various methods have been used for this purpose among which adsorption and catalytic reduction are most widely used because they are simple, fast, effective and inexpensive methods for the removal of such contaminants as compared to other methods. Various types of materials such as activated carbon, silica, alumina, etc., have been used for the removal of these hazardous organic pollutants but they suffer from certain limitations such as high cost, required in large quantity, more time-consuming procedures and less adsorption or catalytic tendency. Nowadays, Nanomaterials proved to be the best adsorbents and catalysts due to

their unique structural properties such as small size, large surface area and high adsorption as well as catalytic tendency. Their ease of modification, selectivity and high reusability enhances their applications for the removal of variety of organic contaminants

Contents

1.Introduction 2. Experimental 3. Synthesis and characterization of functionalized nanomaterials 4. Applications of functionalized multiwalled carbon nanotubes for adsorptive removal of dyes (MB and MG) and determination by UV-visible spectrophotometry 5. Applications of functionalized multiwalled carbon nanotubes for adsorptive removal of drug(diclofenac) and determination by UV-visible spectrophotometry 6. Applications of asparagine chitosan magnetic nanoparticles for catalytic reduction of organic pollutant (4-nitrophenol) and determination by UV-visible spectrophotometry. Summary and publication.

31. SINDHU (Anamika)
Ionic Liquids as Biocompatible Solvent Media for the Structural Stability and Activity of Proteins.
Supervisor: Prof. p. Venkatesu
Th 25894

Abstract

Proteins are biomacromolecules that perform multitudes of vital processes in the living organism. They are the biopolymers of amino acids and every protein is composed of unique sequence and number of amino acids. The biological function, evolution and cellular location of a protein are determined by its three-dimensional (3D) structure encoded by the amino acid sequence. Protein’s 3D network is sustained by various interactions comprising electrostatic, ionic, hydrogen bonding and hydrophobic interactions. As a protein can adopt numerous possible pathways, the concept of protein folding becomes complex and spontaneous. By their unique structural features, proteins perform nearly all types of biological processes in living beings. Additionally, proteins own numerous potentials for a wide range of applications varying from the synthesis of pharmaceutical intermediates to large-scale production of biofuels from renewable resources. For a protein to be biologically active, the maintenance of its native structure becomes a prerequisite. However, proteins are barely stable, even slight external stresses like temperature, shear, pH and solvent conditions could compromise the structure of protein. Any deviation in native structure of protein results in a misfolded or completely unfolded state of protein which in turn results in serious life-threatening ailments like type II diabetes, Alzheimer’s disease and Huntington’s disease. Extensive research suggests that there are numerous ways like protein immobilization, engineering and appropriate solvent conditions that could resolve the situation. Towards it, ionic liquids (ILs), the designer solvents are recognized as perfect candidates to provide a protein-friendly environment. There are multiple reports available on IL-protein interactions that suggest that modification of anions and cations of ILs affects the stability as well as the activity of proteins. Despite the voluminous research work on protein folding in presence of varied families of ILs, there is still inadequacy of outcomes that could suggest the occurrence of protein stability and refolding of denatured protein in presence of ILs. Also, there is a dearth of knowledge on the impact of ILs on protein amyloid fibril formation. Furthermore, the interactions of proteins with some families of ILs such as cholinium-based ILs ([Chn] ILs) are not well appraised.

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1.Introduction and review of the literature 2. Materials and experiemental techniques 3(a). Insight into impact of cholinium based ionic liquids on bovine β-lactoglobulin structural analysis unexpected high thermal stability of protein 3(b). Protein packaging in ionic liquid mixtures: an eco-friendly approach towards the imporoved stability of β-lactoglobulin in cholinium-based mixed ionic liquids 4. Assessing the compatibility of Mono-, Di- and Tri- cholinium citrate ionic liquids for the stability and activity of α- chymotrypsin 5. Cholinium based ionic liquids attenuate the amyloid fibril formation of lysozyme 6. Implication of imidazolium based ionic liquids as refolding additives for urea-induced denatured serum albumins 7. Coclusion.

32. SINGH (Pratibha)
Synthesis, Characterization and Sensing Studies of Transition Metal Oxides/Conducting Polymers Composites.
Supervisor: Dr. Saroj Kr. Shukla
Th 25894

Abstract

The thesis delivers the dissertations focusing on study of: synthesis of transition metals (Fe, Co, Ni, Cu and Zn) oxides (TMO) by eutectic melt method, synthesis of conducting polymers composites (TMO-PANI, TMO-PPy and TMO-PTh) by in-situ polymerization and composite formation technique. The method results the nano size transition metal oxides and binary composite with good yield and facile parameters. The chemical characterizations of prepared conducting polymers composites for structural and morphological studies and effect of metal oxides nanoparticles are revealing the advances in the properties of conducting polymers i.e. PANI, PPy and PTh after inserting nano size metal oxide with improved stability and electrical conductivity by significant order. The presence metal oxide also improves the adsorption capacity as well as electro- chemical responsiveness. These integrated properties of composites were explored in electrochemical sensing of relative humidity and ammonia concentration with improved sensing parameters and stability. Humidity sensing behavior of conducting polymers composite by resistive type sensing and ammonia sensing behavior of conducting polymers composite by resistive type sensing at 5-100 ppm range has been described. Finally, the finding explain the science behind improvement in properties and improving the limitations of conducting polymer after making the composite with transition metal oxides.

Contents

1.Introduction 2. Material and methods 3. Synthesized and characterization of TMOs, CPs and CPCs 4. Humidity sensing 5. Ammonia sensing behaviors of CPs and CPs-TMO composites 6. Conclusion and summary. Publications.

33. SINHA (Nitish Kumar)
Syntheses, Structural, Reactivity and Catalytic Aspects of Pd(II) Pincer Complexes Derived from N-Substituted Guanidines.
Supervisor: Prof. N. Thirupathi
Th 25883

Abstract

The reaction of Sym N,N',N''-Tris(2-thioanisyl)guanidine 2.1.1 with Pd(OC(O)R)2 (R = Me and tBu) in toluene at 65 °C for 6 h afforded [6,5] CNS Pd(II) pincer complexes, 2.1.3 and 2.1.4, respectively. Complex 2.1.4 was subjected to metathesis reaction with LiBr to afford 2.1.5. Complex 2.1.5 was treated with AgBF4 in MeCN to afford a cationic complex, 2.1.6. Complex 2.1.3 was utilised as catalysts for Suzuki-Miyaura reactions involving aryl bromides and phenylboronic acid. The reactions of [(ArNH)(ArN=)CN(H)(C(O)Py-2)] (Ar = 2-MeC6H4 (2.2.1) and 2-(CF3)C6H4 (2.2.2)) with Pd(OC(O)R′)2 (R′ = Me, CF3 and tBu) afforded [Pd{κ 3 (C,N,N)}(OC(O)R′)] (2.2.3, 2.2.4 and 2.2.8) and [Pd{κ 3 (C,N,N)}(μ- OC(O)R′)Pd{κ 3 (C,N,N)}] (2.2.5–2.2.7). Complexes 2.2.5–2.2.7 were treated with PPh3, 4-NH2Py and MeCN (L) to afford [Pd{κ 3 (C,N,N)}(L)] (2.2.9–2.2.12). Reaction 2.2.3 with 2.2.12 in the presence of NaOC(O)tBu in CHCl3 to afford a mixed Pd(II) pincer, [Pd{κ 3 (C,N,N)}(μ- OC(O)tBu)Pd{κ 3 (C,N,N)}] (2.2.15). Complex 2.2.3·C7H8 was used as an efficient catalyst in Suzuki-Miyaura reactions involving sterically hindered aryl bromides and arylboronic acids. The reactions of guanidines [(ArNH)(ArN=)CN(H)(CH2Py-2)] (Ar = 2-MeC6H4 (2.3.1) and 2- (CF3)C6H4 (2.3.2)) with Pd(OC(O)R')2 (R' = CF3, Me and tBu) gave Pd(II) pincer complexes [Pd{κ 3 (C,N,N)(OC(O)R')}] (2.3.3–2.3.8). The reactions of 2.3.3 and 2.3.6 with PPh3 and ArN≡C (L) (Ar = 2,6-Me2C6H3) afforded cationic Pd(II) pincer complexes [Pd{κ 3 (C,N,N)(L)}][OC(O)CF3] (2.3.10, 2.3.11, 2.3.13 and 2.3.14) while the reactions of 2.3.4 or 2.3.5 and 2.3.7 with ArN≡C afforded neutral picolinamide based Pd(II) pincer complexes [Pd{κ 3 (C,N,N)(CNAr)}] (2.3.15 and 2.3.16), respectively. The reaction of 2.3.8 with ArN≡C afforded the neutral picolyl based Pd(II) pincer complex [Pd{κ 3 (C,N,N)(CNAr)}] (2.3.17). Complex 2.3.8 was used as efficient catalysts in base free cycloisomerization of 4-pentynoic acid. All the new compounds were fully characterized and the molecular structures of 2.1.1, 2.1.4·½C_7H_8, 2.2.1, 2.2.3·C_7H_8, 2.2.4–2.2.6, 2.2.8·C7H8, 2.2.9, 2.2.10·H2O, 2.3.3·½toluene, 2.3.5·½toluene·½pivalic acid, 2.3.6, 2.3.7 and 2.3.14–2.3.16 were determined by single crystal X ray diffraction.

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1.Introduction 2. Result and discussion 3. Supporting information 4. Outlook, Synopsis, Abstract and published work.

34. SURABHI

Synthesis and Characterization of Nanostructured Materials for Organic Transformations.

Supervisor: Prof. Subho Mozumdar
Th 25921

Abstract

The thesis is divided into eight chapters: • Chapter 1: Introduction and literature review. • Chapter 2: Characterization techniques. • Chapter 3: Magnetic core-shell dendritic mesoporous silica nanospheres anchored with diamine as an efficient and recyclable base catalyst. • Chapter 4: Palladium nanoparticles decorated porous 1-(3-aminopropyl) Imidazole functionalized graphene oxide nanosheets as an efficacious and heterogeneous catalyst for oxidative amidation of aldehydes with amines. • Chapter 5: Development of double charged DABCO-based ionic liquid grafted over dendritic fibrous cubic silica nanoparticles as a highly efficient and recyclable base catalyst. • Chapter 6: Magnetic core-shell zeolitic imidazolate framework encapsulated AgCu bimetallic nanoparticles as recyclable nanocatalyst for multiple reduction and degradations reactions. • Chapter 7: Fabrication of imidazolium-based ionic liquid supported over magnetic graphene oxide as a retrievable nanocatalyst for the Knoevenagel condensation. • Chapter 8: Conclusion.

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1. Introduction and review of the literature 2. Characterization techniques 3. Magnetic core shell dendritic mesoporous silica nanospheres anchored with diamine as an efficient and recyclable base catalyst 4. Palladium nanoparticles decorated porous 1-(3- aminopropyl) imidazole functionalized graphene oxide nanosheets as a highly efficacious and heterogenous catalyst for oxidative amidation of aldehydes with amines 5. Development of double charged DABCO- based ionic liquid grafted over dendritic fibrous cubic silica as a highly efficacious and recyclable base catalyst 6. Magnetic core-shell zeolitic imidazolate framework encapsulated Ag-Cu bimetallic nanoparticles recyclable nanocatalyst for multi reduction and degradation reactions 7. Fabrication of imidazolium based ionic liquid supported over magnetic graphene oxide as a highly efficient and recyclable nanocatalyst for Knoevenagel condensation 8. Conclusion. List of publication and list of intrantional/national conference/workshop.

35. TARUN MOHAN
Application of Some Inorganic and Hybrid Nanoparticles in Light Activated Therapy and Catalysis.
Supervisor: Prof. Indrajit Roy
Th 25910

Abstract

Cancer is responsible for over 9 million deaths annually. In recent years chemotherapy, radiotherapy, surgery, and few other methods are being used for cancer treatment. Although these techniques prove to be effective, one of the main issues encountered in treatment is the destruction of healthy cells along with cancerous cells. To overcome these complications, photodynamic therapy (PDT) is actively used in treating several cancers in the clinic, along with dermatological disorders and microbial infections. PDT is a non-invasive technique in which a photosensitizer drug is activated with light for the transformation of molecular oxygen into cytotoxic singlet oxygen through a series of photophysical processes. Photosensitizer alone is usually harmless and has no impact on either abnormal or healthy tissues in the absence of light. PDT has many advantages over other therapies as it is highly localized, cost-effective, and leads to specific tumor treatment with higher cure rate for some tumors. However, owing to their poor aqueous solubility, they have been formulated in several micro and nano-sized delivery systems for stable aqueous dispersion. These delivery systems also ensure sustained release, avoid plasmatic fluctuation, reduce side effects, decrease the frequency of administration, and enhance the drug uptake by targeted tissues, thereby improving the treatment potency. For example, the hydrophobic zinc phthalocyanine was incorporated in a liposomal formulation for successful delivery. Zinc phthalocyanine has powerful absorbance in the red region of the spectrum of visible light, x and a powerful emission in the range of 600-800 nm. Light-activated NORM/ZnPc experience singlet to a triplet intersystem crossing because of charge transfer and simultaneously nonradiative decay under fixed near-infrared light irradiation wavelength. This phenomenon produces singlet oxygen in high quantum yield and with elevated photothermal efficacy.

Contents

1. Introduction 2. Literature review 3. Experiemental and characterization techniques 4. Synthesis characterization and application of NORM encapsulated zinc phthalocyanine nanoparticles as photodynamic therapeutic agents 5. Synthesis of multifunctional iron selenide (FeSe) nanorods for dual modality therapy and study their light activated therapies 6. Synthesis charcaterization and application of photosensitizer loaded UiO-66 in phto dynamic therapy 7. Nanoscale graphene oxide as a photodynamic agent in drug delivery vehicle 8. Conclusion, Publications and conferences/Workshop attended.

36. VARUN

Computational Studies on Tumor-linked Human Carbonic Anhydrase IX and its Inhibitors.

Supervisor: Prof. Rak Kishore Sharma and Prof. Rita Kakkar

Th 25881

Abstract

The research work presented in this thesis comprises in silico studies on the tumorlinked human carbonic anhydrase IX (hCA IX), a special member of the carbonic anhydrase family, and its inhibitors. The compound SLC-0111, an hCA IX selective inhibitor, is explored in terms of its various structural, electronic and non-linear optical properties, using density functional theory. The aim of this thesis is to gain an insight into the receptor-ligand interactions responsible for the selective inhibition of hCA IX and to discover novel selective hCA IX inhibitors utilizing the concept of ligand-based and structure-based drug design, two important tools of the computeraided drug design process. Carbonic anhydrases (CAs), a family of zinc metalloenzymes, are widespread in all living organisms. They catalyze a simple process, i.e. the reversible hydration of carbon dioxide to the bicarbonate ion and a proton, and are thus involved in various important physiological processes like pH regulation, chemosensing, bone resorption/ calcification, electrolytic secretion, gluconeogenesis, ureagenesis, lipogenesis, etc. Seven distinct genetic families, viz. α, β, γ, δ, δ, ε and ζ CAs have been described so far, of which the α-CAs are the most studied, owing to their presence in vertebrates, algae, protozoa, gram negative bacteria and the cytoplasm of green plants. In humans, fifteen different CAs encoded by the α-CA gene family have been identified, but only twelve are catalytically active. These isoforms are further divided into four subcategories, cytosolic (hCA I-III, VII and XIII), mitochondrial (hCA VA and VB), membrane-bound (hCA IV, IX, XII, and XIV) and secreted (VI)

Contents

1. Human carbonic anhydrases (hCAs): a review 2. Computational techniques 3. Theoretical investigation of SLC-011, a novel inhibitor of human carbonic anhydrase IX, and its anion 4. A comparative study of the binding modes of SLC-0111 and its analogues in the hCA II and hCA IX active sites using QM/MM, molecules docking, MM-GBSA and MD approaches 5. Identification of potent human carbonic anhydrase IX inhibitors: a combination of pharmacophore modelling, 3 D -QSAR, virtual screening and molecular dynamics simulations 6. A combination strategy of structure based virtual screening MM-GBSA, cross docking, molecular dynamics and metadynamics simulations used to investigate natural compounds as potent and specific inhibitors of tumor linked human carbonic anhydrase IX 7. Concluding remarks and bibliography.

37. VERMA (Vineet)

Synthesis of sugar-modified nucleoside analogues, 1,2-aminols, pyridocoumarins and their biological / photophysical studies.

Supervisor: Prof. Ashok K. Prasad

Th 25920

Abstract

Abstract of the thesis entitled: “Synthesis of sugar-modified nucleoside analogues, 1,2-aminols, pyridocoumarins and their biological / photophysical studies” The thesis is divided into four chapters, i.e. Chapter I (Parts A and B), Chapter II, Chapter III and Chapter IV. A brief account of each chapter is given below: The work presented in Chapter I (Part A) entitled “A review on synthesis and applications of double-headed nucleosides” describes the synthetic methodologies for the synthesis of double-headed nucleoside monomers and their applications. Nucleosides are the constructional subunits of deoxyribonucleic acids (DNA) or ribonucleic acids (RNA), which contain either a purine or pyrimidine nucleobase and a furanosyl moiety of pentose sugar 2′-deoxyribose or ribose. Nucleotides are constituted by addition of triphosphate group at the 5′-position of the nucleosides and these monomeric units polymerize to construct nucleic acids (DNA or RNA). These macromolecules reserve and express genetic information in all living cells and viruses. Modified nucleosides are a class of organic compounds which are unnatural and have an altered/substituted nucleobase and/or a modified pentose sugar. Synthetic accessibility of these organic molecules encouraged researchers to produce sugarmodified nucleosides and nucleobase-modified nucleosides. Modified nucleoside monomers with more than one nucleobase attached to them are called double-headed nucleosides. A thorough literature search regarding the double-headed nucleosides disclosed that these modified nucleosides were constituted with any two naturally occurring nucleobases, i.e. adenine, guanine, thymine, uracil and cytosine or one naturally occurring nucleobase and one heterocyclic/carbocyclic moiety attached directly to the sugar or via any linker. Some of these naturally occurring nucleobases have been found to be substituted by halogens or alkyl groups. On the other hand, a variety of heterocyclic/carbocyclic moieties were found to be considered as the head of these modified nucleosides. Literature revealed that most of the double-headed nucleosides have the first nucleobase attached to the anomeric carbon of pentofuranosyl/hexopyranosyl sugar moiety and an additional nucleobase/ viii heterocyclic/carbocyclic moiety attached directly or through a linker to any of the carbon of the sugar moiety either by C-N or C-C bond. However, in case of base to base double-headed nucleosides, the additional nucleobase/substituted or unsubstituted phenyl moiety/polyaromatic moiety/carbocyclic moiety/heterocyclic moiety is attached to the first nucleobase with/without a linker. Whereas, all the acyclic double-headed nucleosides had natural nucleobases or heterocyclic moieties attached at the terminal carbons only.

Contents

1 Part A. A review on synthesis and applications of double headed nucleosides Part B. Synthesis of hexopyranosyl pynimidine homonucleosides 2. Synhthesis of novel1,2,3, triazole linked hexopyranosyl pyrimidine nucleoside analogues and their anti HBV activity 3. Syntheis of 1,2 -aminole 2,6- anhydro-glucoheptitol and their molecular docking studies with $\beta_1$and β_2-adrenoceptors 4. Phosphoric-acid catalysed synthesis of fused pyridocoumarins and their acidochromic applications. Summary, List of publications and workshops and conferences attended.

38. YADAV (Anita)

Designing of Metal-Based Nanomaterials as Potential Catalysts for Adsorption and Degradation of Toxic Organic Contaminants.

Supervisor: Prof. Rakesh Kumar Sharma

Th 25903

Abstract

Responsive polymer-based materials are extensively studied over the years for diverse range of applications such as biosensing, tissue engineering and various drug delivery vehicles. Upon exposure of the responsive polymer to external stimuli, they undergo alterations in chemical and physical properties. Amid vast external stimuli (pH, temperature, ionic strength, electric field, magnetic field) temperature is considered to be the most studied stimulus. Therefore, temperature dependent polymers or more specifically thermoresponsive polymers (TRPs) have flourished the field of polymer science in recent years. In fact, TRPs are capable of undergoing instant reversible phase transition from hydrophilic to hydrophobic conformations. The phase transition can be triggered by change in conformation, change in solubility and alteration of hydrophilic/hydrophobic balance. More specifically, recent advancements are made by making conjugates of TRPs with several moieties such as proteins and nanoparticles (NPs). The hybrid materials formed by TRPs and NPs exhibit improved thermoresponsive character and can be utilized as nanocarriers in various drug delivery applications. A subsequent knowledge of undergoing interactions between TRPs and NPs is very important to meet the requirements of advanced scientific community. In this context, efforts have been devoted to fabricate the potential new hybrid materials of TRPs and NPs. Examining and understanding the monitoring of phase transition behavior and interactions of TRPs with NPs are the primary step to develop TRPs-NPs hybdrid scaffolds. Moreover, TRPs offer an effective platform to better disperse the NPs which further provide the application in originating the nanoconjugates with improved characteristics. Among various NPs studied so far, carbon nanotubes (CNTs) and gold nanoparticles (AuNPs) find their utility in developing the potential hybrid structures with TRPs. Herein, we have demonstrated the effect of these nanostructures on the conformational behavior of TRPs, which is the primary step to understand the ongoing molecular interactions between TRPs and NPs. Apparantely, the impact of distinct shapes of AuNPs such as gold nanospheres (AuNSs), nanorods (AuNRs), nanocubes (AuNCs) and trisoctahedrals (AuTRs) is described in the present work of thesis.

Contents

1.Introduction and literature survey 2. Experiemental techniques and characterizations 3. Synthesis of nesoporous iron gallate nanocomplex for the adsorption and degradation of toluidine blue and rose Bengal 4. Laser induced morphology change in copper sulphide nanoparticles and its catalytic activity 5. Magnesium-PAP metal-organic framework based photoswitcher for the degradation of chlorpyrifos 6. Copper based nanoparticles as catalysts for degradation of organic dye 7. Conclusion, List of publication and list of conference and presentations.

39. YADAV (Dileep Kumar)

Exploration of Layered Honeycomb Oxides and Layered Double Hydroxides Possessing Interesting Structures and Physical Properties.

Supervisor: Prof. Sitharaman

Th 26459

Abstract

The development of multifunctional material has become an important area of research in the modern solid-state scientific community in order to attend to the growing demands specifically in the energy and environment sectors. In the quest for such materials the aim of the present thesis has been to study the layered honeycomb oxides and layere double hydroxides because of their rich crystal chemistry, tunable electrochemistry, exotic magnetic and highly flexible topological phenomena. To study such material several synthetic methods such as high temperature solid state, sol-gel, combustion, coprecipitation ion-exchange, microwave-assisted method, etc have been employed.

Contents

1.Introduction 2. Sodium containing layered honeycomb oxides 3. Lithium containing honeycomb oxides 4. Lithium containing layered double hydroxides. Overall summary and future directions. List of publications, conferences, workshops and seminars attended.

40. YADAV (Priya)

Design, Fabrication and Application of Silica-Coated Magnetic Nanocatalysts and Metal-Functionalized Covalent Organic Frameworks: Highly Stable and Efficient Catalysts for C-H Activation and Multicomponent Reactions.

Supervisor: Prof. Anju Srivastava

Th 25898

Abstract

Development in the field of synthetic organic chemistry using magnetic nanocatalysts as catalytic entities has gained incredible attention. They possess unique characteristics such as high surface area, easy dispersion in reaction media, easy recyclability with the aid of external magnet and excellent stability. Silica coated magnetite nanocatalysts provides magnificent platform for versatile modifications due to their numerous advantages such as chemical stability, inertness and prevention from agglomeration. Till now, magnetic nanocatalysts have opened the door for a wide range of research including, C-C, C-N, C-S, and C-O cross-coupling, oxidation, reduction, multicomponent and many other reactions. Therefore, it is considered as one of the major growing areas in catalysis domain. Alternatively, covalent organic frameworks (COFs) have also emerged as porous and partly crystalline organic materials that allow sufficiently precise atomic integration of organic molecules into ordered structures. They possess unique characteristics such as tuneable molecular design, high porosity with controllable pore size, adjustable electronic/physical properties and excellent stability. These properties have provided COF materials with superior potential in the field of gas and energy storage, adsorption, and catalysis applications. In this context, a variety of synthetic methods have been developed so far including solvothermal, ionothermal, mechanochemical, sonochemical, microwave and light promoted synthesis. In terms of catalysis, many researchers have exploited the porous nature of COFs in order to support metal species and other catalytic entities, which enhances the efficiency of their use as heterogeneous catalysts. COFs allow large availability of functional groups onto their surface, which can strongly coordinate with metals. This diminishes the possibility of metal leaching and subsequent contamination of product stream. Moreover, this type of catalysts can be easily recovered from the reaction media via simple

centrifugation or filtration, thereby allowing recycling without a significant loss of catalytic activities. Offering these advantages, COFs have been widely used in a variety of organic transformations including C-C coupling, oxidation, reduction, asymmetric synthesis and many others. Even, tandem reactions are performed by developing bimetallic docked COFs.

Contents

1.Introduction 2. Theory of instrumentation techniques used 3. Fabrication of copper-based magnetic nanocatalyst for efficient one-pot synthesis of chalcones *via* A^3 coupling of aldehydes alkynesamines 4. One pot synthesis of propargylamines using aldehydes-amines-accetylene *via* an official nickel-based silica-coated magnetic 5. Synthesis of phenol esters by direct C-H activation of aldehydes using highly efficient and reusable copper immobilized polymide covalent organic framework (Cu@PI-COF) 6. Unlocking the catalytic potence of highly efficient and reusable cobalt immobilized polyimide covalent organic framework (Co@PI-COF) for one pot synthesis of amidoalkyl naphthols. Summary, Spectral data and list of publication and conference attended.

41. YADAV (Priyanka)
Diversified Catalytic Applications of Surface Modified Cobalt Ferrite Nanoparticles and Biophysical Study of Antimalarial Compounds.
Supervisor: Prof. Satish K. Awasthi
Th 25892

Abstract

The present study includes a sequential analysis of interaction mechanism of these two potent antimalarial tetraoxane analogs (TO1 and TO2) to HSA, using different spectroscopic and computational techniques. The hyperchromicity obtained in UV-vis spectra displayed the interaction of tetraoxanes with HSA. Fluorescence quenching results confirmed the static nature of quenching mechanism as the values obtained for quenching constant (~1012) were greater than scatter collision (~1010). The values of binding constant (~104) demonstrated a moderate and reasonable binding of TO1-2 to HSA, divulging that their clearance from kidneys and diffusion into the tissues decreases. The results obtained from circular dichroism confirmed that these tetraoxanes induced conformational changes in the secondary structure of HSA upon interaction. Further, molecular docking studies concluded that these analogs binds with strong affinity to HSA, at Sudlow site IIA in the close proximity to Trp-214, through hydrophobic interaction and H-bonding

Contents

1.Design and synthesis of nitrogen enriched biguanidine functionalized cobalt ferrite nanoparticles as heterogeneous base catalyst for Knoevenagel condensation under solvent free conditions 2. Probing catalytic activity of highly efficient sulfonic acid fabricated cobalt ferrite magnetic nanoparticles for clean and sclalable synthesis of dihydro, spiro and bis quinazolinones 3. Application of sulfonic acid fabricated cobalt ferrie nanoparticles as effective magnetic nanocatalyst for green and facile synthesis of benzimidazoles 4. Pd immobilized on magnetic cobalt ferrite nanoparticles as recyclable nanocatalyst for hydrogenation of nitroarenes 5. Interaction between the antimalarial drug dispiro tetraoxanes and human serum albumin: a combined study with spectroscopic methods and computational studies. Summary and list of publications.

42. YADAV (Ritu)

Influence of Nanopartciles on the Phase Transition Behaviour of Smart Polymers in Aqueous Media.

Supervisor: Prof. P. Venkatesu

Th 25882

Abstract

Responsive polymer-based materials are extensively studied over the years for diverse range of applications such as biosensing, tissue engineering and various drug delivery vehicles. Upon exposure of the responsive polymer to external stimuli, they undergo alterations in chemical and physical properties. Amid vast external stimuli (pH, temperature, ionic strength, electric field, magnetic field) temperature is considered to be the most studied stimulus. Therefore, temperature dependent polymers or more specifically thermoresponsive polymers (TRPs) have flourished the field of polymer science in recent years. In fact, TRPs are capable of undergoing instant reversible phase transition from hydrophilic to hydrophobic conformations. The phase transition can be triggered by change in conformation, change in solubility and alteration of hydrophilic/hydrophobic balance. More specifically, recent advancements are made by making conjugates of TRPs with several moieties such as proteins and nanoparticles (NPs). The hybrid materials formed by TRPs and NPs exhibit improved thermoresponsive character and can be utilized as nanocarriers in various drug delivery applications. A subsequent knowledge of undergoing interactions between TRPs and NPs is very important to meet the requirements of advanced scientific community. In this context, efforts have been devoted to fabricate the potential new hybrid materials of TRPs and NPs. Examining and understanding the monitoring of phase transition behavior and interactions of TRPs with NPs are the primary step to develop TRPs-NPs hybdrid scaffolds. Moreover, TRPs offer an effective platform to better disperse the NPs which further provide the application in originating the nanoconjugates with improved characteristics. Among various NPs studied so far, carbon nanotubes (CNTs) and gold nanoparticles (AuNPs) find their utility in developing the potential hybrid structures with TRPs. Herein, we have demonstrated the effect of these nanostructures on the conformational behavior of TRPs, which is the primary step to understand the ongoing molecular interactions between TRPs and NPs. Apparantely, the impact of distinct shapes of AuNPs such as gold nanospheres (AuNSs), nanorods (AuNRs), nanocubes (AuNCs) and trisoctahedrals (AuTRs) is described in the present work of thesis

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