Controlled Synthesis And Characterization Of Nobel Metal

Recent research has evidenced that nanotechnology may bring about a material revolution which sweeps through different scientific fields and leads to dramatic changes in the use of natural resources and our everyday life. Compared to their bulk counterparts, the nanomaterials may exhibit significantly improved physical properties by shrinking their size to nanometer scale. Metal silicide are distinguished by their features of combining advantages of both metals and semiconductors which promises superior performance various fields. Despite the progress in the synthesis methods of nanomaterials, it still remains a big challenge in controlled synthesis of 1D silicide nanostructures due to the difficulties of well-controlled synthesis conditions. In this study, synthesis process of NiSix and CoSix with different morphologies using CVD method have been analysed and determined. Synthesis of different structures of NiSix on a number of substrates has been investigated. The mechanisms behind the growth of these nanostructures have been studied for better understanding of the synthesis of these silicides. The detailed characterization techniques such as SEM, TEM and XRD were used.

Controlled Synthesis and Characterization of Some One-dimensional Semiconductor NanomaterialsControlled Synthesis and Characterization of Silicon NanocrystalsControlled Synthesis and Characterization of Hierarchically Structured Inorganic Materials for Membrane ApplicationsControlled Synthesis and Characterization of One-dimensional II-VI NanomaterialsControlled Synthesis and Characterization of Metal Oxide Nanowires by Chemical Vapor Deposition on Silicon and Carbon SubstratesControlled

Synthesis and Characterization of One Dimensional NanomaterialsCarbon Nanotubes and Titanium Oxide NanowiresControlled Synthesis of Nanoparticles in Microheterogeneous SystemsSpringer Science & Business Media

Metal Oxide Nanoparticles in Organic Solvents discusses recent advances in the chemistry involved for the controlled synthesis and assembly of metal oxide nanoparticles, the characterizations required by such nanoobjects, and their size and shape depending properties. In the last few years, a valuable alternative to the well-known aqueous sol-gel processes was developed in the form of nonaqueous solution routes. Metal Oxide Nanoparticles in Organic Solvents reviews and compares surfactant- and solvent-controlled routes, as well as providing an overview of techniques for the characterization of metal oxide nanoparticles, crystallization pathways, the physical properties of metal oxide nanoparticles, their applications in diverse fields of technology, and their assembly into larger nano- and mesostructures. Researchers and postgraduates in the fields of nanomaterials and sol-gel chemistry will appreciate this book's informative approach to chemical formation mechanisms in relation to metal oxides.

As a material is reduced down to sub-100 nm dimensions, its interaction with light, with heat, and with other matter changes due in part to increased confinement of free charges and to an increased surface area relative to volume. In practice, different materials and their characteristics can be tuned to control bulk-system properties like optical transparency, free charge generation, electric field enhancement, and localized thermal enhancement. In this dissertation, I will discuss the controlled synthesis and characterization of three different nanoparticle material systems: yttria-stabilized zirconia (YSZ), copper-zinc-tin-sulfide (CZTS), and zirconium nitride (ZrN). I

will additionally discuss the viability of using the produced materials in proposed applications, namely: YSZ as the basis material for transparent sintered ceramic disks for use as cranial implants; CZTS as the basis material for earth-abundant, inexpensive, polycrystalline thin film photovoltaics; and ZrN as a visible spectrum plasmonic absorbing material for use in light-induced localized field enhancement applications.

Extracting multifunctional benefits by combining multiple nano-scale materials has driven materials science to develop nano-heterostructures, which are known as nanohybrids (NHs). Many such composite materials have been researched for applications in the energy sector and in biomedical devices and processes. Among these NHs, carbon nanotubes combined with metal oxides (MOs) are one of the most studied materials that provide unique advantages as electrocatalyst supports, and are currently being commercialized as embedded electrodes for fuels cells. NHs are not only a new class of complex materials but also brings in novel physicochemical properties that most likely cannot be captured by the sum of the properties of their components materials. Thus, understanding the environmental health and safety (EHS) of this new class of composite NHs is imperative. The first challenge that the nano-EHS community faces is to synthesize these materials with a range of MO loadings or composition under a controlled and comparable set of experimental conditions. In this dissertation, a set of carbonaceous-metal oxide NHs have been synthesized and characterized under comparable synthesis conditions. After synthesis, the underlying mechanisms of metal oxide formation on multiwalled carbon nanotubes (MWNT) surfaces has been enumerated, and finally, aggregation behavior of a select NH and its components has been assessed as a function of the metal oxide loading. A modified sol-gel

technique has been developed to grow TiO2, ZnO, Er2O3, and Pr6O11 nanocrystals on MWNT surfaces. The novelty of this technique is that, by varying reagent composition, metal oxide content on the MWNT surfaces can be controlled, keeping all other parameters unchanged. The modified synthesis protocol has been successfully developed to produce a relatively large amount of NHs (100s of mg per batch of synthesis), adequate for systematic nano EHS studies. Following detailed characterization of the materials, underlying hybridization and MO crystal formation mechanism(s) have been enumerated. Furthermore, standard electron potential of the metal species (while considering electron transfer between their oxidized state to zero valent form) has been found to be the controlling factor for the formation of metal or metal oxide crystals from the precursors on MWNT surfaces, using the sol-gel synthesis technique. Self-aggregation, one of the dominant environmental processes that particles undergo upon release into aquatic environment, has been assessed for one of the most used and commercialized NHs MWNT-TiO2 and its components. This study investigated the role of TiO2 loading on the aggregation behavior, MWNT-TiO2 NH with three different TiO2 loadings. Results suggested that TiO2 loading on MWNT surfaces control aggregation behavior of the composite NHs. NHs with all TiO2 loading demonstrated strong dependence on electrokinetics. Deoxygenation of the NHs with decreased TiO2 loading due to the NH synthesis process appeared to be a key contributor on the electrokinetics of the NHs. The van der Waals interaction forces of the NHs decreased with decrease in TiO2 loading. This study also concluded that classical DLVO theory may be inadequate to capture the aggregation behavior of the NHs. The controlled synthesis technique developed during this research, as well as the mechanisms of metal vs. metal oxide

formation identified will be valuable to prepare a large set of NHs for nano-EHS studies. Aggregation behavior of the composites can be very complex in nature and cannot be predicted form the sum of the behavior of their component materials. The deviation of DLVO prediction from the experimental aggregation data calls for further investigation on direct measurement of other complex surface properties of the NHs upon hybridization such as surface roughness and surface charge heterogeneity

Synthesis of silver nanostructures has been an active research area for many decades because of their importance in biological sensing, imaging, electronics, optoelectronics and catalysis. In particular, much effort has been devoted to the controlled synthesis of silver nanowires because of their potential use as interconnects or active components in fabricating nanoscale devices. The solution phase method is used here to form Ag nanoparticles by reducing silver nitrate with ethylene glycol heated to 160°C. The additional presence of polyvinyl pyrrolidone plays a role of stabilizer to prevent an agglomeration and/or a capping agent to produce highly anisotropic nanowires. Silver nanoparticles are extracted from the highly viscous ethylene glycol through centrifugation, filtration, decanting and dilution in de-ionized water. The monodispersed silver nanomaterials are self-assembled into ordered arrays on a glass substrate by the drop-coating method. SEM and AFM micrographs are presented to characterize the

microstructure of these nanomaterials and their arrays. Their physical characterizations are discussed by using evanescent microwave microscopy. In particular, values of resonant frequencies and Q-factors of silver nanoparticle arrays measured by evanescent microwave microscope are used to fit to theoretical model allowing calculation their relative local conductivities. Nanomaterials have attracted significant interest in the past decade due to their unique structure and properties compared to their bulk counterparts. Nanomaterials-based solutions can address challenges in various technologies such as proton exchange membrane fuel cells (PEMFCs). PEMFC is an innovative energy conversion technology to directly convert chemical energy to electrical energy by using hydrogen as fuel. However, the current PEMFC system still faces significant technological roadblocks which have to be overcome before the system can become economically viable. A major impediment to the commercialization of PEMFC is the high cost of materials and manufacturing and stability, which is primarily associated with the cost of Pt catalysts and their support in membrane electrode assembly (MEA). One approach in addressing these issues is the controlled synthesis and application of nanostructured Pt-based catalysts and their support in PEMFCs. The objective of this thesis is to synthesize and characterize various

nanostructures (e.g. metal oxides and metal silicides or composites) and evaluate their performance as Pt supports used in the PEMFCs. Various advanced characterization techniques such as high resolution scanning and transmission electron microscopy, X-ray absorption spectroscopy and electrochemical characterization methods have been used to understand growth mechanism of obtained nanostructures and their roles in PEMFCs. We also reported the synthesis of WSi2 and Ta5Si3 heterostructures using a low pressure chemical vapor deposition (LPCVD) method. The morphologies of these nanostructures were found to be sensitive to the concentration of reactive species and silica vapor in the CVD chamber. The results indicated that the morphology of WSi2 and Ta5Si3 nanostructures varied from nanowires, networked nanoribbons to nanosheets with the control of the oxygen concentration. A vapor solid growth mechanism based on silica sheath formation was proposed for the synthesis of these nanostructures. To take advantage of unique properties of carbon nanotubes, metal oxide and metal silicides as catalyst support, a new method was developed for the synthesis of composite nanostructures. TiSi2Ox-NCNTs and TiO2-NCNTs nanocomposites were synthesized using a combination of CVD process and magnetron sputtering and their performance as catalyst supports in PEMFCs were studied. Pt

nanoparticles deposited on these nanostructures showed enhanced catalytic activity compared to commercial Pt/carbon electrodes. The electronic structure of Pt on the catalyst supports was investigated using X-ray absorption spectroscopy, to obtain insight into the interaction between the catalyst supports and Pt nanoparticles. As an example of well controlled synthesis of nanostructures, one-dimensional tungsten oxide nanostructures (W18O49) have been synthesized using a conventional chemical vapor deposition method (CVD). The morphology of the nanostructures such as diameter and length, were controlled during the synthesis process via sulfur doping. The dependence of morphology, composition and structure of tungsten oxides on the sulfur flow rate has been studied. Further, one step synthesis of tungsten sulfide/tungsten oxide nanocables (WS2/W18O49) have been achieved for the first time using tungsten and sulfur powder as the starting materials. In summary, the research work presented in this thesis aims at contributing to the development of various novel nanostructured catalyst supports and probing the correlation between synthesis approach, fine structure, and catalytic performance of the nanostructures as well as exploring their potential applications in highly active electrocatalysts for PEMFCs.

In this thesis, I will focus on the synthesis of

transition metal oxide/sulfide-based composite materials for different types of environmental and sustainable energy applications under ambient conditions. Controlled synthesis of these catalysts with unique crystalline structures, physical, and chemical properties will be carried out to achieve an improved catalytic activity. The correlations between the material structure and catalytic activity will be investigated by various characterization techniques. Finally, the catalytic activities for the resulting materials will be evaluated for environmental friendly photocatalytic dye degradation and electrochemical water splitting reaction, respectively.

Systematically summarizes the current status and recent advances in bimetallic structures, their shape-controlled synthesis, properties, and applications Intensive researches are currently being carried out on bimetallic nanostructures, focusing on a number of fundamental, physical, and chemical questions regarding their synthesis and properties. This book presents a systematic and comprehensive summary of the current status and recent advances in this field, supporting readers in the synthesis of model bimetallic nanoparticles, and the exploration and interpretation of their properties. Bimetallic Nanostructures: Shape-Controlled Synthesis for Catalysis, Plasmonics and Sensing Applications is divided into three parts. Part 1 introduces basic chemical and physical knowledge of bimetallic

structures, including fundamentals, computational models, and in situ characterization techniques. Part 2 summarizes recent developments in synthetic methods, characterization, and properties of bimetallic structures from the perspective of morphology effect, including zero-dimensional nanomaterials, one-dimensional nanomaterials, and two-dimensional nanomaterials. Part 3 discusses applications in electrocatalysis, heterogeneous catalysis, plasmonics and sensing. Comprehensive reference for an important multidisciplinary research field Thoroughly summarizes the present state and latest developments in bimetallic structures Helps researchers find optimal synthetic methods and explore new phenomena in surface science and synthetic chemistry of bimetallic nanostructures Bimetallic Nanostructures: Shape-Controlled Synthesis for Catalysis, Plasmonics and Sensing Applications is an excellent source or reference for researchers and advanced students. Academic researchers in nanoscience, nanocatalysis, and surface plasmonics, and those working in industry in areas involving nanotechnology, catalysis and optoelectronics, will find this book of interest.

The first book to paint a complete picture of the challenges of processing functional nanomaterials for printed electronics devices, and additive manufacturing fabrication processes. Following an introduction to printed electronics, the book focuses

on various functional nanomaterials available, including conducting, semi-conducting, dielectric, polymeric, ceramic and tailored nanomaterials. Subsequent sections cover the preparation and characterization of such materials along with their formulation and preparation as inkjet inks, as well as a selection of applications. These include printed interconnects, passive and active modules, as well as such high-tech devices as solar cells, transparent electrodes, displays, touch screens, sensors, RFID tags and 3D objects. The book concludes with a look at the future for printed nanomaterials. For all those working in the field of printed electronics, from entrants to specialized researchers, in a number of disciplines ranging from chemistry and materials science to engineering and manufacturing, in both academia and industry.

This book focuses on the use of semiconducting metal oxides as gas sensing materials, including the sensing mechanism and sensing materials modification approach, while also providing a comprehensive introduction to semiconductor gas sensing devices. As an essential part of IoT (Internet of things), gas sensors have shown great significance and promising prospects. Therefore, studies on semiconducting metal oxides, one of the most important gas sensing materials, have increasingly attracted attention from various disciplines. The book offers a valuable reference

guide to metal oxide gas sensing materials for undergraduate and graduate students alike. It will also benefit all researchers who investigate metal oxides nanomaterials synthesis and gas sensing with relevant frontier theories and concepts. Engineers working on research and development for semiconductor gas sensors will also find new ideas in sensor design.

Flow visualization using polystyrene microspheres (PSL)s has enabled researchers to learn a tremendous amount of information via particle based diagnostic techniques. To better accommodate wind tunnel researchers needs, PSL synthesis via dispersion polymerization has been carried out at NASA Langley Research Center since the late 1980s. When utilizing seed material for flow visualization, size and size distribution are of paramount importance. Therefore, the work described here focused on further refinement of PSL synthesis and characterization. Through controlled variation of synthetic conditions (chemical concentrations, solution stirring speed, temperature, etc.) a robust, controllable procedure was developed. The relationship between particle size and salt concentration, MgSO4, was identified enabling the determination of PSL diameters a priori. Suggestions of future topics related to PSL synthesis, stability, and size variation are also described.

Solution methods of materials synthesis have found application in a variety of fields due to the diversity of products accessible, facility of process scalability, and the ease of tuning their properties through prudent selection of reaction conditions. Control of experimental variables during the formation of colloidally stable nanoscale solids within a liquid matrix allows for tailoring of the particles' characteristics, including shape, size, composition, and surface chemistry. In this dissertation, I will discuss how the manipulation of reaction chemistries can be used to synthesize shape-controlled metal and semiconductor colloidal nanocrystals. Further, I will elaborate on the mechanisms by which these particles form from molecular precursors and describe how their properties can differ from their bulk analogues through extensive characterization, especially using transmission electron microscopy. These studies contribute to the continued development of chemical routes to nanocrystals and their application as functional materials.First, I will review recent advances in the synthesis and characterization of shape-controlled nanocrystals, as well as highlight their promising applicability in a number of emerging technologies. These principles will then be leveraged to the specific case of catalytically-active rhodium nanocrystals, which can be synthesized with morphological and dimensional control using a polyol solution-mediated strategy. I

describe an innovative shape-controlled synthesis to monodisperse colloidal rhodium icosahedra, cubes, triangular plates, and octahedra using this route. Additionally, new insights into the important role of the polyol reducing solvent on the synthesis of these nanocrystals are revealed, and how these might be exploited to engender superior reaction control and novel products.Next, I will describe how a crystallization mechanism was established for the synthesis of numerous morphologies of noble metal nanocrystals. I present a thorough analysis of the synthesis of shape-controlled rhodium nanocrystals, using extensive transmission electron microscopy characterization, and relate these findings to one of the primary synthetic levers available in the polyol synthesis: the anionic ligands present. Further, I show that the crystallization process proceeds by a nonclassical mechanism in which cluster particles serve as a stable intermediate between molecular precursors and the final product. I then apply these principles to the shape-controlled synthesis of other noble metal nanocrystals before expounding a generalized formation mechanism in the polyol synthesis of colloidal metal nanocrystals. Finally, I will highlight my efforts in the designed synthesis and characterization of colloidal tin(II) sulfide (SnS) semiconducting "quantum dot" nanocrystals. I describe a route for the solution synthesis of monodisperse colloidal SnS nanosheets,

nanocubes, and nanospherical polyhedra in high yield. Further, detailed crystallographic characterization of these nanocrystals using transmission electron microscopy indicates that their atomic structure possesses a previously-unreported nanoscale deviation from the bulk phase. Additionally, I show that their electronic and photocatalytic properties of these quantum dots are both shape-dependent and distinct from bulk SnS. Because of their structural and dynamical properties, microheterogeneous systems have been employed as solvent and reaction media both to synthesize and stabilize nanoparticles. Following this route, inside their nanometer-sized heterogeneities the nanoparticles of many different substances have been incorporated. The book shows the distinct advantages of this synthetic strategy over that of many other methods. Moreover, it furnishes to the reader a collection of theoretical and experimental facts allowing him to reduce the number of trial and errors necessary to arrive at an optimal synthetic protocol.

Fourth, a size-controlled synthesis of water soluble DPPH (1,1-diphenyl-2-picrylhydrazyl) nanoparticles has been developed. Importantly, these nanoparticles exhibit size-dependent absorption spectra and fast-exchange-narrowed single-line EPR spectra with linewidths of ~1.5- 1.8 G. Furthermore, the EPR linewidth can be controlled by partially

reducing the DPPH radical. These water-soluble DPPH nanoparticles are a perfect standard EPR labels for biological and biomedical systems.
A novel synthetic method of polymer brushes using polymer single crystals (PSCs) as solid-state templates is introduced in this study. PSC has a quasi-2D lamellae structure with polymer chains fold back-and-forth perpendicular to the lamellae surfaces. During crystallization, the chain ends are excluded from the unit cell onto the lamellae surfaces, which makes the material extremely versatile in its functionality. Such structure holds the unique capability to harvest nanoparticles, or being immobilized onto macroscopic flat surfaces. After dissolving PSCs in good solvent, polymer brushes are chemically tethered on either nanoparticles or flat macroscopic surfaces. Because the chain-folding structure can be conveniently tailored by changing the molecular weight of polymer and the crystallization temperature, the thickness, grafting density and morphology of resulted polymer brushes can be precisely controlled. As a model system, poly(Îæ-caprolactone) with thiol or alkoxysilane terminal groups was used, and polymer brushes were successfully prepared on both nanoparticles and glass/Au flat surfaces. The structure-property relationships of the as-prepared polymer brushes were studied in detail using multiple characterization techniques. First of all, when functionalizing

nanoparticles, by engineering the chain-folding structure of the PSCs, interesting complex nanostructures can be formed by nanoparticles including Janus nanoparticles and nanoparticle dimers. These unique structures render hybrid nanoparticles very interesting responsive behavior which have been studied in detail in this dissertation. When grafted onto a flat surface on the other hand, not only the molecular weight and grafting density can be precisely controlled, the tethering points of a single polymer chain can also be conveniently tailored, resulting polymer brushes with either tail or loop structures. Such difference in brush structure can significantly alter the properties of functional surface. By using atomic force microscopy based force spectroscopy (AFM-FS) and macroscale shear adhesion measurements, it is thus demonstrated that when polymer loops are grafted, the surface could exhibit much stronger adhesion compared with regular polymer tails when free-dangling polymer chains are allowed to interact with the surface, which is believed to mimic the Velcro-like behavior where polymer loops can withhold strong entanglement with free chain ends upon breaking of the physical bonding.

Carbon nanotubes (CNTs) are advanced materials that have numerous novel and useful properties. Controlling the synthesis and properties of CNTs is the major challenge toward their future applications.

This thesis addresses this challenge with several contributions. This thesis begins with the brief introduction of CNTs, including the history of their discovery, their geometric structure, unique properties and potential applications. Then focus is laid on the subsequent three sections: characterization, synthesis, and manipulation of CNTs. Chapter 2 describes three characterization tools: AFM, SEM and Raman, which are commonly used to analyze CNTs and other nanomaterials. They offer both qualitative and quantitative information on many physical properties including size, morphology, surface texture and roughness. Also, they can be used to determine the structure of CNTS. Chapter 3 addresses the synthesis of CNTS, because synthesis is an important and indispensible process to study CNTs experimentally. Specifically, two controllable synthesis techniques are realized, which are capable to produce iron catalyst nanoparticles for single-walled carbon nanotube (SWNT) growth. Iron nanoparicles of different sizes obtained from both wet chemistry and electrodeposition can be used for diameter-controlled synthesis of SWNTs. Following synthesis, two manipulation methods of CNTs are discussed in Chapter 4. Firstly, effort of electrical breakdown of CNTs is introduced. Both SWNTs and MWNTs (Multi-walled carbon nanotubes) are cut using this method. Moreover, SWNT kink is shown using AFM tip

manipulation. These two manipulation methods provide us a possibility to fabricate large cavity from a MWNT for our purposes. In the end of this thesis, conclusions on my master work in research field of CNTs are drawn and future research directions are proposed.

(Cont.) A method of electrospinning was used to encapsulate magnetic nanoparticles in a polymeric matrix to create field responsive nanofibers for various applications. The magnetization properties of the nanofibers were also characterized and their behavior under an applied magnetic field was modeled.

Providing a range of information on polymers and polymerization techniques, this text covers the gamut of polymer science from synthesis, structure and properties to function and applications. It analyzes speciality polymers, including acrylics, fluoropolymers, polysiplanes, polyphosphazenes, and inorganic and conducting polymers. The book examines the stereochemistry of polymerization and the stereoregularity of polymers.

A variety of methods were used to make polymers with different architecture and functionalities. The linking chemistry of vinyldimethylchlorosilane (VDMCS) with poly(styryl)lithium (M[subscript n] = 1,700-3,000 g/mol) was studied. The average degree of branching varied from 7.5 to 9.4 with an increase in concentration of VDMCS (1.2 to 5.2 eq).

The intrinsic viscosities and melt viscosities (at 160°C) of the star polymers were found to be less than half of that of the corresponding linear polystyrenes. [alpha]-Pyrrolidine-functionalized polystyrene (M[subscript n] = 2,700 g/mol, M[subscript w]/M[subscript n] = 1.03, 92.5%) was successfully synthesized from [alpha]-chloromethyldimethylsilane-functionalized polystyrene (M[subscript n] = 2,600 g/mol, M[subscript w]/M[subscript n] = 1.02) based on NMR spectroscopy, MALDI-TOF and ESI mass spectrometry. The stability of silyl hydride groups under atom transfer radical polymerization conditions was proven by copolymerizing methyl methacrylate and (4-vinylphenyl)dimethylsilane (VPDS). Tapered block copolymers of isoprene, VPDS, and styrene with narrow molecular weight distributions (1.04 and 1.05) were synthesized via anionic polymerization. Evidence regarding the topology of cyclic polybutadienes was obtained by Atomic Force Microscopy of grafted polymers obtained by grafting an excess of silyl hydride-functionalized polystyrene (M[subscript n] = 8,300 g/mol, M[subscript w]/M[subscript n] =1.01) onto cyclic polybutadiene (M[subscript n]=88,000 g/mol, M[subscript w]/M[subscript n] = 2.0). The reactivity of polyisobutylene carbocations was compared with respect to competitive electrophilic addition to a vinyl group versus silyl hydride transfer by investigating

the reaction with VPDS. Based on GPC results, and 1H and 13C NMR spectroscopy, no evidence for any vinyl group addition was observed. A successful attempt was made to prepare electrospun fibers from fluoro-functionalized styrene-butadiene elastomers. The water contact angle of these surfaces was found to be 162.8° [plus or minus] 3.8° for the fibrous mat of the fluorinated polymers as compared to 151.2° [plus or minus] 2.4° for the analogous fibrous mat of the non-fluorinated polymers. In-chain functionalization of tapered styrene butadiene rubber using chloromethydimethylsilane was quantitatively done via a hydrosilation reaction. Pyrrolidine-functionalized styrene butadiene rubber was obtained in 71% yield after reacting pyrrolidine with chloromethyldimethylsilane-functionalized styrene butadiene rubber. In-chain, silyl hydride-functionalized, deuterated polystyrene (M[subscript n] = 2,100 g/mol, M[subscript w]/M[subscript n] = 1.01) was functionalized with allyl cyanide in the presence of Karstedt's catalyst to obtain in-chain cyano-functionalized, deuterated polystyrene (45% based on the mass of in-chain, cyano-functionalized deuterated polystyrene obtained).

"Reversible-deactivation radical polymerization (RDRP), also referred to as controlled/"living" radical polymerization (CRP) has been developed over the past 20 years. RDRP promotes the synthesis of well-defined polymeric materials with controlled molecular weights

and molecular weight distributions, complex topologies and functionalities. In the past decade, the Matyjaszewski and Kowalewski groups pioneered the work of synthesizing nanostructured carbon by pyrolysis of polyacrylonitrile (PAN) containing polymeric precursors prepared via RDRP. My contribution to this topic was primarily focused on the following aspects: (1) optimization of the synthetic procedure, (2) deeper investigation of the structures, (3) exploration of the surface chemistry with particular emphasis of nitrogen functionality, (4) and energy related applications. This thesis first focuses on addressing current challenges in RDRP particularly in atom transfer radical polymerization (ATRP), one of the most robust RDRP techniques. Based on the development of a deep mechanistic understanding of RDRP's, ATRP was then used for the synthesis of PAN containing block copolymers followed by applying a series of analytical tools to provide detailed physical characterization. Finally, these materials were utilized as precursors for the formation of nanocarbons that were evaluated in various energy related applications. The development of nanostructured carbon materials from PAN precursors is discussed in Chapter 1. Particular emphasis is placed on the rational structural design of PAN containing polymeric precursors developed in the Matyjaszewski and Kowalewski groups, while the detailed synthetic methodology will be discussed in the subsequent chapters. Controlled synthesis is the prerequisite for many applications. The successful preparation of block copolymers via RDRP requires preparation of a macroinitiator with preserved

chain end functionality (CEF). Work described in Chapter 2 resulted in the establishment of a universal rule for quantifying the CEF in all RDRPs, which is also the most important criterion for determining the "livingness" and degree of control over the polymerization. The parameters affecting the level of CEF preservation are determined. Another challenge in ATRP is diminishing the concentration of catalyst employed during the polymerization procedure in order to reduce the cost and simplify the purification steps. Chapter 3 describes the systematic study of RDRP in the presence of zerovalent copper, which offers significant advantages in this regard. The contribution of all of the potential reactions occurring in an ATRP carried out in the presence of copper zero were evaluated, and a supplemental activator and reducing agent (SARA) ATRP mechanism is concluded to precisely describe this system. How to conduct and optimize SARA ATRP system is then demonstrated. Chapter 4 is focused on another aspect of the robust capability of ATRP : controlling the molecular weight distribution. Activator regeneration electron transfer (ARGET) ATRP was employed to prepare polystyrene-block-poly(methyl acrylate) copolymers with tunable dispersity in the range of 1.32 to 2.0 for each block. Knowledge attained from the studies discussed in Chapter 2 to 4 has been extensively utilized in the studies of nanocarbons. Chapter 5 discusses the preparation of a series of PAN containing diblock copolymers that were used as precursors for the preparation of nanocarbons. The block copolymers undergo phase separation and then the poly(n-butyl

acrylate) serves as a sacrificial segment upon pyrolysis. Both thin film and bulk nanocarbons with diverse morphologies, resembling the original phase-separated copolymer precursors, were prepared. The carbonization of bulk copolymer precursors with branched PAN domains was of particular interest; which resulted in the formation of porous nanocarbons with large surface area and highly accessible nitrogen functionality originating from PAN. Chapter 6 illustrates how porosity and accessible nitrogen functionality in the nanocarbon introduced in Chapter 5 can be utilized for CO2 capture. The main emphasis was placed on the surface area and nitrogen content's influence on adsorption capacity and selectivity was studied. Chapter 7 discusses the application of PAN-derived nanocarbons as electrode materials for supercapacitors. Materials displaying both high energy density and high power density were achieved. This excellent performance was partially due to the mesoporous structure with high specific surface area, in combination with the pseudocapacitance originating from graphitic edge nitrogens. Evidence of electrochemical activity of the nitrogen heteroatoms provided the motivation to explore the performance of copolymer templated nanocarbon as an electrocatalyst for oxygen reduction, as described in Chapter 8. A desirable 4-electron transfer process with a low overpotential system was achieved by as-prepared nanocarbon film with porous morphology; which again, demonstrates one of the unique properties of nanocarbons prepared from PAN containing block copolymer precursors. Finally, a summary is provided in

Chapter 9 and some future directions regarding synthesis and utility of heteroatom-enriched nanocarbons are discussed."--Pages ii-v.

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In this thesis, I will focus on the design and synthesis of metal oxides as adsorbents and catalysts for different types of environmental applications,such as water remediation, biogas cleanup. Controlled synthesis of these materials with unique crystalline structures, physical, and chemical properties will be carried out to achieve an improved performance. Correlations between

the material property and performance will be investigated by varieties of characterization methods. In the first part, I will employ perovskite materials for catalytic wet air oxidation (CWAO) reactions for water remediation. LaNiO3-Î ? (LNO) was applied for degradation of methyl orange (MO) azo dye in aqueous solutions under dark ambient conditions (room temperature, atmospheric pressure) without additional lights or chemical stimulants. The mechanism behind MO degradation by LNO under dark ambient conditions was unraveled by a series of characterization methods. Considering the large variety of perovskites in terms of constituents and composition, an excellent perovskite material should be tailorable for water remediation applications. Fuel cell performance for the double perovskite material PrBaCo2O5 (PBC) was briefly shown. In the second part, I will demonstrate a facile way for synthesizing mesoporous aluminas (MAs) with uniform and monomodal pores via a modified inverse micelle synthesis method. The effects of reaction times, surfactant chain lengths, and heat treatments on the textural properties of MA were adjusted to optimize the texture properties for biogas cleanup. The tuned MA of the large mesopore volume achieved high octamethylcyclotetrasiloxane (D4 siloxane) adsorption capacity, and maintained approximate 85% of its original adsorption capacity, demonstrating a sustainable adsorption performance and high potential for related industrial applications. Arsenic adsorption was performed to illustrate the application of MA for heavy metal removal. The third part, I supported transition metals on

optimized mesoporous alumina for methane oxidation. The texture properties were summarized and Temperature-programmed studies were used for understanding the mechanism for methane partial oxidation. Different ratios of copper supported on alumina were designed for methane combustion and exhibited improved performance with regard to the loading amount, which was explained by further characterization methods.