



Environment-Enhancing Technology and Material Science Conference

Edited by
Zheng-Qian Xuan and Yixiang Shi



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Edited by

Zheng-Qian Xuan and Yixiang Shi



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Yixiang Shi



Preface

The 1st Environment-Enhancing Technology and Material Science International Congress was held successfully on Minhang Campus of Shanghai Jiao Tong University on 6-8th December, 2013. This conference was organized by the School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Chinese Center for Resource Comprehensive Utilization Technology, China Industry-University Research Institute Collaboration Association and China Technology Innovation Strategic Alliance for Environment-Enhancing Industry, and co-sponsored by University of Hawaii, China Agricultural University, Zhejiang University and University of Arizona.

The Environment-Enhancing material science and technologies should be economically viable, environmentally sustainable and have the potential to ultimately meet the human need for liquid fuel. Energy production and environmental protection are two of the greatest challenges facing mankind in the 21st century. The shared responsibilities to meet these grand challenges are unprecedented. Economic development demands energy, yet energy consumption has historically led to increased environmental pollution. In the context of our modern society, the relationship between 'environment' and 'energy' has been more often antagonistic rather than harmonious co-existence. To sustain our economy and environment, our energy sources must be environmentally enhancing. We envision that Environment-Enhancing material science and technology should be explored aiming at meeting our entire fuel need, achieving net-zero carbon emission and water use, and recycle the nutrient in the feedstock. Except for above-mentioned fields, some works in fundamental research such as theoretical and computational studies are included as well.

In recent years, the environment-enhancing technology has been applied in several countries across the world, such as USA, China, Norway, Saudi Arabia, Philippine and Chile.

In Norway, collaborating with the Biopharmia LLC, Professor Joel Cuello's team applied the Accordion technology at the University of Agder Grimstad. In Saudi Arabia, the same team applied the xylophone photobioreactor technology at the King Abdulaziz City of Science and Technology. In Philippine, they tested macroalgae bioethanol production at the University of the Philippines Diliman. In Chile, at Universidad de Magallanes, algae is harnessed from Patagonia and Antarctica for biofuels and other high-value products.

During this congress, the attending scholars presented the applications of environment-enhancing technologies, especially those related to material science, in China and other parts of the world. Every submission has been peer reviewed and commented by two independent reviewers on the quality, originality, creativity and significance of its contributions and improvements. In the end, 18 papers are accepted in the *Advanced Material Research Supplementary*, which cover fields such as polymer, inorganic chemistry, material field even theoretical research. We would like

to thank all the authors who submitted their manuscripts and the reviewers for their selfless contributions to the peer review process.

In “A Review on the Synthesis and Controlled Release Properties of Novel Responsive Carrier”, Zhu and Huang reviewed the state-of-the art in smart responsive carriers for controlled drug delivery applications and the preparation methods of different responsive materials, sustained and controlled release performance. Huang also reviewed glass transition and technology limitation on characterization on glass transitions on thin film.

In Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Cui's group synthesized polyacrylic acid (PAA) by solution polymerization. MBA dosage, acrylic acid percentage, neutralization degree and surface crosslink on PAA have been analyzed. The experimental evidence obtained that lower acrylic acid percentage is helpful to these three properties. Indexes increase at first and then decrease with neutralization degree raise. MBA dosage is against to absorptivity and retention capability, but useful to absorptivity under pressure. Scanning electron microscopy (SEM) was used to observe the surface of the PAA powder, and prove that surface crosslink promote form a kind of honeycomb structure.

In Ren's group in Zhejiang University, Yu prepared single-crystal pre-perovskite PbTiO_3 (PP-PT) nanofibers by PVA/PVP-assisted hydrothermal method, in which polyvinyl alcohol (PVA) and polyvinyl pyrrolidone (PVP) acted as surfactants. Poly(vinylidene fluoride)/ pre-perovskite PbTiO_3 nanofibers (PVDF/PP-PT) nanocomposite thin films were successfully fabricated by a spin-coating method. PP-PT nanofibers have been shown a good distribution in PVDF matrix. Moreover, α -phase coexisted with β -phase in the PVDF and PVDF/PP-PT nanocomposite thin films. The dielectric properties of the PVDF/PP-PT nanocomposite thin films were measured.

In the paper of “Synthesis and Applications of Gold Nanoparticles”, Zhao reviewed the synthetic methods of gold nanoparticles. The applications of gold nanoparticles in nanoprobe, drug delivery systems, photonic crystals were discussed.

In “Study on Luminescent properties of YAG: Ce^{3+} , $\text{Gd}^{3+}/\text{La}^{3+}$ prepared by co-precipitation method”, Guan prepared the YAG: Ce^{3+} , $\text{Gd}^{3+}/\text{La}^{3+}$ yellow phosphors by co-precipitation, and the crystal structure, morphology, luminescent properties were studied in detail.

In Lin's group in Fujian Normal University, Shi prepared multifunctional $\text{Ag}_2\text{S-Ag}$ heterogeneous porous nanorods by the irradiation of microwave. The nanorods were characterized by scanning electron microscopic (SEM) and X-ray diffraction (XRD). The photocatalytic activity for degradation of crystal violet and the lowest detectable limit of crystal violet were investigated further. The results indicate that the $\text{Ag}_2\text{S-Ag}$ heterogeneous porous nanorods would be a promising material for environmental protection.

In “The Study on Evolutive Model of Heavy Metal Pollution in Urban Surface Soil and Design of Time-Series Database”, Shi established a spatial-temporal model of heavy metal pollution to track its evolution, and the Fourier transform has been

used to derive its analytical solution. The approach is innovative and the results they obtained are interesting.

Packaging technology is widely used in the production process of semiconductors, which makes a lot of wasted components stay intact and reused. In “Fill sealing material removal in electronic components using laser cutting”, Song reported that laser cutting technology was applied to remove material from PCB resin potting material. Using precision laser cutting technique, the resin potting material of waste PCB circuit can be removed, so as to expose entirely electronic components and all the solder joints. The technology has high economic benefit by ensuring electronic component function intact for reuse and improving the utilization rate of resource.

In “Chemo-mechanical Grinding for K9 Optical Glass”, Dai presented that chemo-mechanical grinding (CMG) was applied to process the K9 optical glass. High surface and subsurface qualities on the K9 optical glass specimen were obtained as the polished results by the CeO₂-CMG tools. Surface roughness and material removal rate were used to evaluate the grinding performance.

In “Study on Preparation of a High-strength and High-toughness Low-alloy Steel for Cross Member of Forklift Mask”, Yi designed a new type of high-strength and high-toughness low-alloy steel by multi-element alloying. The optimized heat treatment technique is obtained through orthogonal testing.

In “Casting Transformers APG Manufacturing Technology”, Chen studied APG (Automatic Pressure Gelation) process of epoxy resin casting transformer, which was developed toward epoxy resin vacuum casting process. The factors that influences the partial discharge experiment of transformer were analyzed, particularly the body making and casting processes.

In “New High Strength and Heat Resistance Aluminum Alloy Material for Engine Cylinder Head”, Li and Su studied the effect of Cu, Ni, Fe, Mn on the mechanical properties of Al-Si alloy by orthogonal experiment method. The ratio of Fe and Mn was controlled to prevent the appearance of β phase, and reduce herringbone Fe phase. The best content of Cu, Ni, Fe, Mn was obtained, which improved high temperature strengthening of the alloy.

In “Study on the Relativity between Intrinsic Coercivity and Microstructure of the Nd-Fe-B Magnet Treated by the Optimized Aging Process”, Ding reported that the aging process optimization was carried out to increase the intrinsic coercivity of the Nd-Fe-B magnets. The microstructures and the fractures of the Nd-Fe-B magnets treated by the optimized aging process were also investigated by optical microscope, thermal field emission scanning electron microscopy and energy disperse spectroscopy.

In “An Association of Reaction Time with bone Quantitative Ultrasound”, Mao examined the relationship between choice reaction time and calcaneus quantitative ultrasound. The results indicate that CRT may be associated with bone status, which suggests an effect of artificial bone on nervous system should be considered when it is produced.

Chitosan and its derivatives have attracted more and more attention due to their biological activities and potential applications in food, pharmaceutical, agricultural

and environmental industries. Xu reviewed antioxidant and free radical scavenging activities based upon chitosans and discussed the free radical scavenging mechanisms. Jiang investigated the antimicrobial effect of nano-SiO₂ particles in gelatin and chitosan based wound dressing materials. The impact of the nano-SiO₂ and antimicrobial agents on the water uptake ratio, water vapor permeability and the antimicrobial effect was evaluated. In biomaterials field, Liu compared solvent-casting and melt-compounding blended polylactide-polyethylene glycol mixture as drug carrier. The former offers fast degradation and drug releasing, the latter gives controlled drug release which requires better miscibility and longer release time. Degradation experiments and characterization such as XRD and SEM have been carried out to study degradation behavior, crystallization and miscibility.

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A Review on the Synthesis and Controlled Release Properties of Novel Responsive Carrier

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Keywords Biomaterials, Drug Carrier, Controlled Release, Single Stimuli-Responsive, Multiple Stimuli-Responsive

Abstract Interest in the stimuli-responsive polymers has been going on for decades, and a lot of work has been dedicated to the development of environmentally sensitive macromolecules that can be crafted into novel responsive carrier materials. This article reviews the state-of-the art in smart responsive carriers for controlled drug delivery applications. And the preparation methods of different responsive materials, sustained and controlled release performance are summarized. The significance and future of smart responsive materials are also commented.

1. Introduction

Intelligent controlled drug release system has attracted widespread attentions in recent years^[1]. Compared with traditional drug delivery methods, the sustained release and controlled release technology allows the drug to maintain the effective concentration range in the long term at a slow or constant release rate in accordance to certain rules. As a well solution to the problems that the burst-released drug in the early and later stage cannot be fully released in the periodic dosing way, it improves not only the efficiency of the drug, but also reduces the side effects of drugs.

Typically, the stimuli-responsive polymer drug-carrier materials can only react to a stimuli, namely the single response vector. The stimuli can be internal, such as physiological or pathological variations in the target cells/tissues, or external such as electric or magnetic fields, ultrasound, light, enzymes, changes in pH, temperature or redox state^[2-9]. Also some carrier materials can respond to multiple external stimuli, such as pH / temperature dual response^[10], pH / optical dual stimuli-responsive system^[11], etc. Various stimuli provide the inspiration for the design and development of stimuli-responsive carrier materials which release the drug in a controlled and predictable way.

2. Single Stimuli-Responsive Materials

Several kinds of recently developed stimuli-responsive materials classified by the mechanism of response to particular stimulus are reviewed in this section.

2.1 pH-Responsive Materials

The human body presents the pH changes along the gastrointestinal tract from the stomach (pH 2.0–3.0), to the small intestine (pH 6.5–7.0), to the colon (pH 7.0–8.0), and also in some specific

areas such as tumoral tissues (pH 6.5–7.2)^[12]. Therefore, the research and development of pH-responsive drug carrier materials has practical significance in the field of controlled drug release.

Vivek and co-workers^[13] reported the smart pH-responsive drug delivery system (DDS) based on chitosan nanoparticles for its potential in enabling more intelligent controlled release and enhancing chemotherapeutic efficiency of Tamoxifen. In their studies, Tamoxifen was loaded onto chitosan-nanoparticles by forming complexes and results shown that Tamoxifen was released from the DDS much more rapidly at pH 4.0 and 6.0 than at pH 7.4, thus it can be used to tumor-targeted drug delivery system. As a similar example, Shen and co-workers^[14] constructed a polyelectrolyte multilayer capsule filled with bovine serum albumin gel (BSA-gel-capsule) by a layer-by-layer assembly technique and thermally induced gelation of BSA. Due to the charge variability of BSA changes at different pH, the microcapsules not only have significantly increased drug loading, but also displayed an excellent pH-controlled drug loading and release properties.

2.2 Temperature-Responsive Materials

The preparation of drug loading/release carriers often involves high temperature processing^[15,16], thus the studies on temperature-responsive materials are also very important. The general idea of temperature-responsive carrier preparation is to introduce temperature-sensitive polymer poly-N-isopropyl acrylamide (PNIPAAm) as an assembly component. Overstreet and co-workers^[17] synthesized temperature responsive graft copolymers of N-isopropylacrylamide and Jeffamine® M-1000 acrylamidehese, and the results shown that the control swelling and drug release are nearly independently of LCST. Liu and co-workers^[18] successfully combined hollow silica particles and PNIPAAm microgels by utilizing the cross-linking reaction and copolymerization. And the results shown that the hollow silica microgels show considerable potential for the application as temperature responsive drug delivery system.

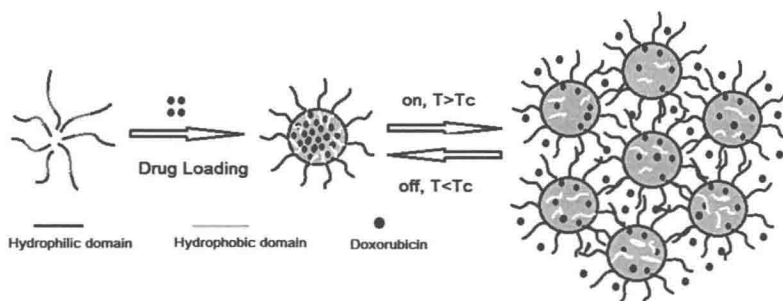


Fig.1 Flexible control of drug release from the tailor-made temperature-responsive poly(ether-urethane) particles. Reprinted from [19].

Another idea to constitute a temperature-responsive system is to introduce the general polyelectrolytes as assembly components. Recently, Wang and co-workers^[19] synthesized a series of linear amphiphilic poly(ether-urethane)s with alternative hydrophilic/hydrophobic segments based on PEG-diisocyanates and aliphatic diols (Figure 1). The copolymers show sharp temperature-responsive phase transition, and the phase transition temperature could be easily modulated by the length of hydrophilic or hydrophobic segments of the polymer.

2.3 Redox/thiol-Responsive Materials

Redox/thiol sensitive polymers are another class of responsive system that gained extensive attention recently, especially in various fields of intracellular triggered gene and drug delivery. The design of redox/thiol-responsive polymers usually involves incorporation of disulfide linkages in the main chain, at the side chain, or in the cross-linker, due to disulfide bonds can be reversibly converted to thiols by exposure to various reducing agents and/or undergo disulfide exchange in the presence of other thiols^[20,21] (Figure 2). Therefore, the polymers containing disulfide linkages can be considered to be both redox and thiol-responsive.

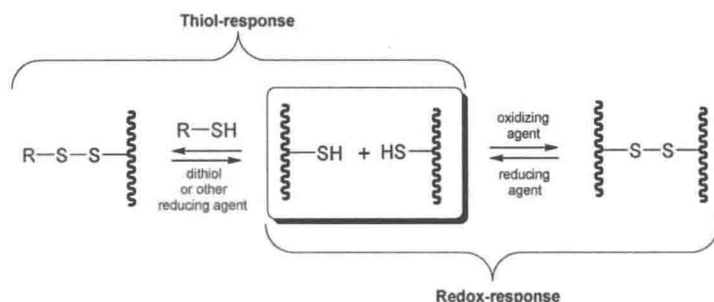


Figure 2. Redox/thiol-responsive behavior capable of being exploited in polymeric systems. Reprinted from [22].

Glutathione (GSH), the most abundant low-molecular-weight biological reducing agent in animal cells, has a typical intracellular concentration of about 0.5-10 mM, whereas its concentration is only about 2–20 μ M in the cellular exterior^[23]. The large difference in concentration has been utilized to design thiol/redox-responsive drug delivery systems that specifically release therapeutics upon entry into cells. For instance, Lee and co-workers^[24] synthesized shell cross-linked (SCL) micelles via thiol-reducible disulfide bonds to serve as biocompatible nanocarriers, results shown that these SCL micelles preferentially release anticancer drugs in the reducing conditions characteristic of cancer tissues. In a similar way, Wang and co-workers^[25] developed reversible shell cross-linked (SCL) micelles based on PEG-bPPESH -b-PCL triblock copolymer (PPESH: thiol-functionalized polyphosphoester). And these SCL micelles allow the facilitated release of entrapped anticancer drugs in the cytoplasm in response to the intracellular reductive environment, thus to be promising as a drug carrier for cancer chemotherapy.

3. Multiple Stimuli-Responsive and Multiple Drug Controlled Release

In recent years, with fast increasing of practical requirement on the functions and performance of polymer carrier materials, synthesis and developing carrier materials with double or multiple responsive and multiple drug controlled release become an important and intensive-studied field. In this section we will review several types of multiple stimuli-responsive and multiple drug controlled release materials that were recently developed.

3.1 Stimuli-Responsive Hydrogels

Smart hydrogel swelling behavior and physicochemical property can change with the environment variables (pH, temperature, ionic strength, magnetic, optical, ultrasonic, etc.), and subsequently can be used for drug controlled release system. Numerous single-responsive hydrogels had been reported, and in recent years with the improvement of functional requirements of the carrier materials, hydrogels with dual or multiple responsive have attracted widespread attention.