

**Virginia Tech – Waseda Joint Workshop on
"Energy and Nanomaterials"
Speaker's Biography and Abstract**

Date: September 11, 2017(Mon), 10:00am-4:25pm

Venue: Takeuchi Lounge, 1st floor, 55-N Building

HOST: Energy and Nanomaterials Unit,
Top Global University (TGU) Project, Waseda University

Hiroyuki Nishide

Professor of the Department of Applied Chemistry, Leader of the Unit for Energy and Nanomaterials, TGU Project, Waseda University



Short Biography

Hiroyuki Nishide is a Professor at Department of Applied Chemistry, School of Advanced Science and Engineering, Waseda University, Tokyo, Japan. He received his PhD in 1975, and has been visiting researcher at Free University Berlin and Polytechnic University New York. He has conducted research in the field of syntheses and applications of functional polymers, recently focusing on the organic polymers for rechargeable batteries and photovoltaic cells. He has published more than 500 journal articles, and is Past-President of the Society of Polymer Science, Japan, of the Federation of Asian Polymer Societies, and of Japan Union of Chemical Science and Technology.

Tim Long

Professor of Chemistry, Director of the Macromolecules Innovation Institute, Virginia Tech



Short Biography

Tim Long is a tenured Professor of Chemistry and the Director of the Macromolecules Innovation Institute at Virginia Tech. He maintains a vigorous partnership with diverse industries, including BASF, Honeywell, Michelin, SABIC, ExxonMobil, Procter & Gamble, IBM, 3M, Kimberly Clark, Henkel, Bayer, Kraton Polymers, Toray, and Solvay. He has maintained a 20-member interdisciplinary research group and has been awarded ~\$45M in research funding over the past 18 years at Virginia Tech.

His group's research is on novel macromolecular structure and polymerization processes with the development of high performance macromolecules for advanced technologies, including: drug and gene delivery, sustainable feed stocks, adhesives and elastomers, block copolymers and living polymerization, and biomaterials.

Title

Additive Manufacturing Demands Advanced Material Design: from High Temperature Polyimides from Stereolithography to Water-Soluble Polyester Ionomers from Extrusion

Abstract

3D printing, or additive manufacturing (AM), provides diverse opportunities to create previously unattainable geometric objects through a layer-by-layer fabrication process. Novel macromolecular structures and synthetic methods in synergy with unique methods of printing demonstrated micron-scale resolution 3D part generation tunable to emerging technologies. Microstereolithography of poly(amic diethyl acrylate ester)s yielded soft 3D organogels. Upon thermal imidization, this organogel transformed into a 3D structured thermoplastic polyimide, which is unachievable in conventional manufacturing. Furthermore, the backbone of the polyimide exhibited versatility through processing of both rigid-rod, insoluble thermoplastics and amorphous, melt-processable thermoplastics. These unprecedented polyimide objects offer immediate impact in aerospace, medical, architectural, and automotive applications. The versatility of 3D printing also provides micron-scale resolution of poly(ether ester) ionomers through low temperature material extrusion for the inclusion of biologics and therapeutics. Typical melt polymerization of poly(ether ester) ionomers from poly(ethylene glycol) and sulfonated isophthalate provided water-soluble polymers capable of complete ion exchange. The incorporation of divalent counterions such as calcium, magnesium, and zinc provided an increase in melt viscosity necessary for low temperature material extrusion 3D printing. Filament of poly(ether ester) ionomers with a calcium counterion revealed successful, flexible filament for subsequent processing. 3D printed structures maintain shape upon printing without flow from the nozzle, successfully demonstrating material extrusion from filament for the first time below 80 °C. By tuning polymer structure, printing type, and printing parameters, diverse structures for vastly different applications ranging from drug delivery and controlled release fertilizers to satellites and aerospace. This lecture will highlight structure-property-processing relationships for the design of advanced materials for several additive manufacturing platforms. The synergy of chemistry and mechanical engineering will be demonstrated in each case study.

Toshinori Fujie

Assistant Professor of Waseda Institute for Advanced Study, Waseda University



Short Biography

Toshinori Fujie is an Assistant Professor of Waseda Institute for Advanced Study, Waseda University. He received his PhD (Engineering) from Department of Life Science and Medical Bioscience, Graduate School of Advanced Science and Engineering, Waseda University in 2009. He spent postdoctoral periods at the Italian Institute of Technology and Tohoku University, and served as an Assistant Professor of the Faculty of Science and Engineering, Waseda University. He is concurrently serving as a PRESTO researcher of

the Japan Science and Technology Agency since 2015.

His current interests are

Polymeric Materials, Biomaterials, Tissue engineering, Microfabrication, Bioelectronics, Implantable Device, Bio Robotics

Title

Ultra-Flexible Polymeric Devices Integrated into the Living System

Abstract

Integration of flexible devices into the living system is expected for the advancement of medical and healthcare devices, which allows for the investigation of biological information at nano-biointerface. Such devices should be compatible to physical and mechanical properties of biological tissues. In this talk, we introduce free-standing polymeric ultra-thin films (referred to as “polymer nanosheets”) as a unique platform of ultra-flexible devices, which comprise tens- to hundreds-of-nanometer thickness close to the scale of biomembranes¹⁾. Various polymers (e.g., biodegradable polymers, conductive polymers, elastomers) can be applicable as building blocks of polymer nanosheets; those are processed by spincoating, layer-by-layer and gravure coating techniques. Interestingly, the polymer nanosheet showed flexible and physically adhesive property owing to the ultra-thin structure. The polymer nanosheet is also functionalized by incorporating conductive polymers or thermo-sensitive dyes. These nanosheet-based devices can reveal several physiological properties of living organisms at different length scale from tissue to body *via* functionalized interface, exemplified by temperature map of living muscle tissues and electromyogram of human bodies^{2),3)}. We are currently working for *in vivo* recording of neuronal signals by injecting a nanosheet-based electrode into the brain, which is designed by combination of polymer nanosheets with inkjet-printing techniques. The nanosheet technology will open a new avenue in the field of biotechnology and biomedicine.

References

- 1) T. Fujie, *Polym. J.*, 2016, 48, 773.
- 2) T. Miyagawa, T. Fujie, Ferdinandus, T. T. Vo Doan, H. Sato, S. Takeoka, *ACS Appl. Mater. Interfaces*, 2016, 8, 33377.
- 3) A. Zucca, K. Yamagishi, T. Fujie, S. Takeoka, V. Mattoli, F. Greco, *J. Mater. Chem. C*, 2015, 3, 6539.

Michael J. Bortner

Assistant professor of Chemical Engineering, Virginia Tech



Short Biography

Michael Bortner is an assistant professor in Chemical Engineering at Virginia Tech and part of the Virginia Tech Advanced Manufacturing Team and the Macromolecules and Interfaces Institute. Mike has significant experience in structure-process-property relationships of polymers and polymer nanocomposites, including 10 years of industry experience with a primary focus on development and manufacturing transition of novel nanomaterials and polymer nanocomposites. The Bortner research group, known as the

Polymer and Composite Materials Laboratory, has a primary research focus on polymer nanocomposites and ways to uniquely leverage material properties and processing approaches for multifunctional, next generation “smart” materials.

Research thrusts focus on interfacial and surface science, molecular transport, phenomenological modeling, development of unique characterization tools, and structure-process-property relationships. Core research areas include cellulose nanocrystals and related synthesis, processing, characterization and application; extrusion based polymer additive manufacturing and related materials development and process modeling; thermoplastic fiber reinforced composites; and interfacial interactions in thermosetting nanocomposites.

Title

Cellulose Nanocrystal Templates for Transparent Conductive Films

Abstract

There is great interest in using biorenewable materials for sustainable, next generation technologies. Here we present the use of cellulose nanocrystals (CNCs), derived from wood pulp, as a unique template for growing conductive silver nanoparticles (Ag NPs) as a potential replacement for indium tin oxide and related transparent conductive materials. We demonstrate the potential to successfully nucleate and grow AgNPs on CNC templates in the form of a stable, optically clear and transparent aqueous colloid. Our approach to generating the Ag/CNC templated nanoparticles is unique compared to traditional metallic NP colloid growth schemes, in that we take advantage of starving the particle nucleation and growth processes to control NP size and resultant nanocomposite morphology. The co-integrated CNC templates serve as nucleation sites for NP growth. The CNC templating agent facilitates systematic alignment of conductive nanoparticles along its rigid backbone. Our results show the impact of CNC surface chemistry and functional group density on the CNC/Ag nanocomposite morphology, including Ag particle size/shape and population density on the CNC template.

We further present preliminary results to generate robust 3D percolating networks of CNC/Ag particles in the form of homogenous, optically transparent nanocomposite films and conformal coatings. Traditionally, electrical percolation requires exceeding a critical loading level with which particles are sufficiently close in a 3-D network to enable interparticle charge mobility for a conductive pathway. Our results demonstrate that the CNC/Ag colloids can be processed under ambient conditions into optically transparent films, and further shed light on the relationship of nanocomposite film structure/morphology, film formation approach, and measured electrical conductivity/optical transparency.

Ryo Kato

Assistant Professor of the Department of Applied Chemistry, Waseda University



Short Biography

Ryo Kato is currently an Assistant Professor of the Department of Applied Chemistry at Waseda University, Japan. He received his Ph.D. in 2017 from Waseda University.

His current interests are

Functional Polymers, Hydrogen- / Charge-storage Materials, Electrolytic Hydrogenation

Title

Fluorenone/Fluorenone Polymers for Cycle of Electrolytic Hydrogen-fixing and Releasing

Abstract

Fluorenone exhibits two-electron redox capability in negative potential and turns to a fluorenone, the corresponding hydrogen adduct of fluorenone, by the electrolytic reduction in aqueous electrolyte solution due to the protonation. Fluorenone polymers were synthesized and quantitatively protonated in protic solvent through the electrolytic reduction to form their hydrogenated (fluorenone) derivatives which easily evolved hydrogen gas in the presence of the iridium complex catalyst¹⁾ by just warming around 80 °C. The polymers repeatedly fixed and released hydrogen without any significant deterioration in the hydrogen evolution capacity.²⁾

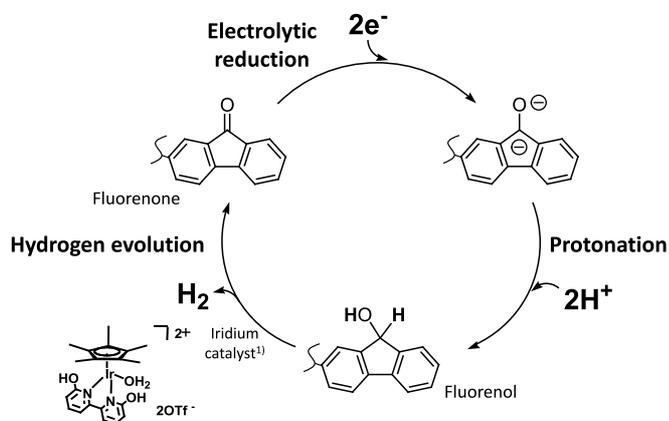


Figure Hydrogen fixing and releasing cycle

References

- 1) K. Fujita, R. Yamaguchi, et al., *J. Am. Chem. Soc.*, 2012, 134, 3643.
- 2) R. Kato, et al., *Nat. Commun.*, 2016, 7, 13032.

Yoshiyuki Sugahara

Professor of the Department of Applied Chemistry, Waseda University



Short Biography

Yoshiyuki Sugahara is currently a professor of the Department of Applied Chemistry at Waseda University, Japan. He received his Ph.D. in 1988 from Waseda University. He became a research associate in 1987 and an assistant professor in 1990 at Waseda University. Then he was promoted to an associate professor in 1992, and became a professor in 2000 at Waseda University. During his carrier, he was a post-doc at Massachusetts Institute of Technology in 1989-1990 (supervisor: Prof. Seyferth), a visiting scientist in 1998 and an invited professor in 2007 both in University of Montpellier II, France (Prof. Corriu's lab).

His current interests are

Inorganic Nanomaterials (Nanoparticles and Nanosheets), Organic-Inorganic Hybrid Materials, Surface Modification, Polymer-derived Ceramics, High-pressure Synthesis of Ceramics, Non-hydrolytic Sol-gel Process

Title

Preparation of Organic-Inorganic Hybrid Materials via Surface Modification of Oxide Nanomaterials

Abstract

Inorganic nanomaterials, in particular oxide-based nanomaterials, have been attracting an enormous amount of attention. One of their promising applications is polymer-based organic-inorganic hybrids, and they can be employed as nanofillers. Generally, affinity between a surface of an inorganic nanomaterial and a polymer matrix is insufficient. Thus, surface modification is required to achieve sufficient dispersibility in a polymer matrix to prepare a homogeneous organic-inorganic hybrid material. Silane coupling agents have been commonly employed for surface modification of oxide nanomaterials, but phosphorus coupling agents are also very suitable in particular for transition metal oxide nanomaterials. Their advantages over silane coupling agents include suppression of homocondensation under mild conditions and stability of metal-oxygen-phosphorous bonds formed.

We have been interested in surface modification of oxide nanomaterials using phosphorus coupling agents. Surface-modified niobate nanosheets can be obtained via intercalative surface modification of protonated forms of ion-exchangeable layered perovskites, typically $\text{HLaNb}_2\text{O}_7 \cdot x\text{H}_2\text{O}$, and potassium hexaniobate, $\text{K}_4\text{Nb}_6\text{O}_{17} \cdot 3\text{H}_2\text{O}$, with organophosphonic acids, and subsequent exfoliation via ultrasonication. The resulting nanosheets can be dispersed in organic solvents, typically acetonitrile, and further dispersed in polymer matrices to yield nanosheet/polymer hybrids. It is also possible to bind polymer chains on the surface of nanosheets via surface-initiated atom-transfer radical polymerization (SI-ATRP) using a phosphorus coupling agent bearing an ATRP initiator group. When we employed oxide nanoparticles, on the other hand, we can also modify their surfaces with phosphorus coupling agents. We have mainly employed TiO_2 nanoparticles, which exhibit relatively high refractive index. When we employed a methanol dispersion of TiO_2 nanoparticles, we can modify their surface in methanol with oleyl phosphate. The same surface modification can be achieved in a water-toluene system with phase transfer by employing an aqueous dispersion of TiO_2 nanoparticles. Bulk TiO_2 /PMMA hybrids can be prepared by an in-situ polymerization using PMMA-grafted TiO_2 nanoparticles prepared by SI-ATRP.

Kenichi Oyaizu

Professor of the Department of Applied Chemistry, Waseda University



Short Biography

Kenichi Oyaizu received his Ph.D. in 1995, and began as Assistant Professor at Waseda University, promoted to Lecturer in 1997, and relocated to Institute of Colloid and Interface Science at Tokyo University of Science in 2003 as Associate Professor. He returned to Waseda in 2007 and was promoted to Professor in 2012.

Title

Synthesis of Halogen-free Poly(arylene sulfide)s and Their Optical Application

Abstract

Poly(1,4-phenylene sulfide) (PPS) is widely used as an engineering plastic, because of its excellent mechanical, thermal and electric properties. Commercially, PPS is produced by the polycondensation of p-dichlorobenzene and Na₂S eliminating NaCl, using N-methylpyrrolidone as a solvent. This particular solvent is essential because of the need to dissolve PPS during chain propagation which is inherently insoluble in other common organic solvents. An alternative route has been found to yield PPS via oxidative polymerization of diphenyl disulfide (PhSSPh). This method attracted much attention because of the capability of using oxygen or air as the convenient ultimate oxidant, using a vanadyl complex-strong acid catalyst as the electron mediator. However, the oxidative polymerization for PPS has not so far been adopted as the industrial process, because of the limited molecular weights and the low cost performance due to the need to use pricy dehydrating agent such as trifluoroacetic anhydride to maintain the activity of the sulfonium electrophile.

Recently, a breakthrough has been obtained, based on the finding that molten diphenyl disulfide with a melting point of 61 °C undergo polymerization above 100 °C with the evaporation of H₂O as the reduced species of O₂, giving rise to the first anhydride-free process of the oxidative polymerization. This high-yielding reaction not only suggests the robustness of the catalyst and the propagating sulfonium electrophile at the moderately elevated temperatures, but also the possibility of developing the PPS production through a highly atom-economical process. Origin of the selectivity of the sulfonium electrophile for the formation of the 1,4-thiophenylene chain, characterized by the presence of a disulfide bond at the chain end, has been determined by the polymerization behavior and the analysis of the product together with a computational calculation, which revealed a unique chain growth-type polycondensation process. Recent development of high refractive poly(arylene sulfide)s by the oxidative polymerization will be discussed.

Amanda J. Morris

Associate Professor of Inorganic and Energy Chemistry, Virginia Tech



Short Biography

Amanda Morris is an Associate Professor of Inorganic and Energy Chemistry at Virginia Tech. She matriculated from Penn State University (B.S.) and Johns Hopkins University (M.S. & PhD). She conducted her postdoctoral work at Princeton University. She has been the recipient of many awards including the Sloan Research Fellowship, the Dreyfus Teacher-Scholar Award, the Inter-American Photochemical Society Young Investigator Award, the Kavli Frontiers of Science Fellowship, and the Ralph Powe Junior Faculty

Award. She currently serves as an American Chemical Society Expert in Sustainable Energy.

Her research interests are

Artificial Photosynthesis, Next Generation Solar Cells, Metal Organic Frameworks, and Photon Upconversion

Title

Exploring Metal Organic Frameworks for Use as Integrated Artificial Photosynthetic Assemblies

Abstract

The finite supply of fossil fuels and the possible environmental impact of such energy sources has garnered the scientific community's attention for the development of alternative, overall carbon-neutral fuel sources. The sun provides enough energy every hour and a half to power human civilization for an entire year. However, two of the remaining challenges that limit the utilization of solar energy are the development of cheap and efficient solar harvesting materials and advances in energy storage technology to overcome the intermittent nature of the sun. In the seminar, the research projects to be discussed focus on the development of an integrated artificial photosynthetic array for solar energy storage. Photosynthetic systems consist of light harvesting arrays and redox mediators that can funnel the electrochemical potential stored in a molecular excited states to catalytic centers to drive the oxidation of water and the reduction of CO₂ to sugars. Many artificial approaches to this chemistry have been reported. In the Morris group, we investigate porous coordination networks (PCNs) as both light harvesters and high surface area catalysts as photosynthetic mimics. PCNs combine the synthetic diversity possible with molecular catalysts and the ease of recovery of heterogeneous catalysis. Theoretically, the high surface area of PCNs can be exploited to produce a higher catalytic rate per geometric area than those realized by other approaches. Additionally, the incorporation of molecular chromophores into networks has been show to lead to enhanced luminescence quenching. Our studies span the scope of artificial photosynthetic chemistry and include mechanistic investigations of homo-resonance energy transfer, electron transport, and catalysis within PCNs.

Atsushi Shimojima

Professor of the Department of Applied Chemistry, Waseda University



Short Biography

Atsushi Shimojima is currently a Professor of the Department of Applied Chemistry at Waseda University, Japan. He received his Ph.D. in 2002 from Waseda University. After four years of working as post-doc at Waseda Univ. and Univ. of California Santa Barbara, he became an assistant professor at the University of Tokyo and was promoted to an associate professor in 2008. In 2013, he moved to Waseda University as an associate professor and was promoted to a full professor in 2017. His present research interests include self-assembly of nanobuilding blocks into porous materials and design of silica-based photo-responsive materials and self-healing materials.

Title

Construction of Nanoporous Materials from Cage-type Oligosiloxanes

Abstract

Nanoporous siloxane-based materials have received great interest owing to their high surface area and large pore volume that enable many potential applications including adsorption, catalysis, optics, and drug delivery systems. Bottom-up assembly of well-defined building blocks is a promising approach to construct molecularly designed architectures. Cage siloxanes, such as double-four-ring (D4R) unit (Si_8O_{12}), are particularly important as building blocks of nanoporous materials because of their rigid frameworks that can be functionalized variously. In this paper, recent progress in the syntheses of nanoporous materials consisting of cage siloxanes will be presented. A variety of microporous materials have been prepared from octa-functionalized cage siloxanes ($\text{R}_8\text{Si}_8\text{O}_{12}$) by interconnection with Si–O–Si, Si–C, C–C, and Si–O–C bonds. It has been demonstrated that rigid aromatic linkers are effective to obtain highly porous materials. Another important approach is self-assembly of mono-substituted cage siloxanes ($\text{R}'\text{Si}_8\text{O}_{12}(\text{OR})_7$, $\text{R}' =$ long alkyl or bulky alkoxy groups) into ordered structures, followed by removal of the R' groups to generate mesopores. One of the challenging issues in this field is the construction of crystalline porous materials like zeolites. Recently, we have focused our efforts on the construction of crystalline materials via hydrogen bonding of silanol (Si–OH)-functionalized cage siloxanes. Synthesis, characterization, and properties of these materials will be presented.

E. Johan Foster

Associate Professor of Materials Science and Engineering, Virginia Tech



Short Biography

E. Johan Foster is an Associate Professor and the Digges Faculty Fellow in Materials Science and Engineering at Virginia Tech. Johan's expertise are in the design, synthesis, processing and investigation of functional nanocomposites, biomaterials, supramolecular materials and polymers. His research group focuses on the chemistry and engineering of functional bio(nano)materials, imbuing materials with 'smart' functionality, often utilizing cellulose nanocrystals (CNCs) as a filler. Johan has many national and international collaborators, from countries as far reaching as Australia, Ghana, France and Switzerland. His research program is supported through federal, industrial and state research grants.

Prof Foster's research group, now the 'Advanced Materials Group' in the Materials Science and Engineering Department at Virginia Tech (<http://www.famg.mse.vt.edu/>) will continue to focus on the chemistry and engineering of functional bio(nano)materials, imbuing materials with 'smart' functionality, often utilizing cellulose nanocrystals (CNCs) as a filler. Prof Foster's group has shown a wide variety of uses of CNCs, lightening, strengthening and reinforcing materials from metals to polymers. The use of CNCs represents a potential revolution in the use of green materials, propelling the field into the 'nano-age'.

His current interests are:

nanomaterials, polymers, stimuli responsive, cellulose nanocrystals, implantable materials, processing polymers/nanocomposites, supramolecular

Title

Mechanically Adaptive Bio-nanocomposites for Implantable Materials

Abstract

Stimuli-responsive nanocomposite materials which change their mechanical properties in response to external stimuli have attracted significant interest for using in broad spectrum applications. The incorporation of high stiffness, high-surface-area nanofibers with switchable interactions into a polymer matrix has rapidly emerged as a versatile design strategy to create nanocomposites properties that react to a variety of stimuli. We will present our experimental research focused on the design, synthesis and possible applications of materials that change their mechanical properties when implanted in the body. Moreover, we will show biocompatible sensing mechanisms that can be coupled to a range of implantable materials. Ranging from optical fibers to cortical electrodes, we will show several mechanisms that allow long term implantation and sensing within the body.

Atsushi Hosoi

Associate Professor of the Department of Applied Mechanics & Aerospace Engineering, Waseda University



Short Biography

Atsushi Hosoi is currently an Associate Professor of the Department of Applied Mechanics & Aerospace Engineering at Waseda University, Japan. He received his Ph.D. in 2008 from Waseda University, and worked as an assistant professor at Nagoya University and a visiting researcher at the University of Sydney (2008-2014). Then he came back to Waseda University as a tenure-track assistant professor, and continued his research. He got tenure and joined the department in 2017.

His current interests are

Material strength, Fracture mechanics, Crack propagation, Polymer matrix composites, Nano materials, Long-term reliability

Title

Effect of 3D Nanostructure Surfaces on Adhesion Strength between Carbon Fiber Reinforced Thermoplastic Composites and Aluminum Plates

Abstract

The development of the multi material light weight vehicles is demanded for the energy saving. The application of carbon fiber reinforced thermoplastic (CFRTP) composites to the vehicles is expected because they have high specific strength and stiffness and excel in productivity and recyclability. On the other hand, there are still issues that the adhesion strength is quite low between CFRTP composites and metallic materials, especially aluminum alloys. Thus, we have developed the fabrication technique of 3D nanostructures on aluminum surface to improve the adhesive strength. In this study, the effects of 3D nanostructures on the adhesion strength between CFRTP composites and aluminum alloy were evaluated. The woven CFRTP composites with matrix resin of polyamide 6 and A1050 aluminum plates were used as the specimens. The aluminum surfaces having regular nanoporous array and regular nanospike array structures are fabricated. After that, the silane coupling treatment was processed on each aluminum surface. Finally, it was confirmed that the adhesion strength was improved by the anchor effect of nanoporous and nanospike array structures. The adhesion strength between the aluminum plates with nanospike array structure processed silane coupling treatment and CFRTP laminates was approximately 26.7 MPa. In the adhesion surface having 3D nanostructure processed silane coupling treatment, the characteristic failure morphology was observed on the fracture surfaces of CFRTP laminates.

Takeo Suga

Assistant Professor of the Department of Applied Chemistry, Waseda University



Short Biography

Takeo Suga is currently a tenured Assistant Professor of the Department of Applied Chemistry at Waseda University, Japan. He received his Ph.D. in 2007 from Waseda University, and worked as a post-doc research associate at Virginia Tech. Then he came back to Waseda as a research associate/research assistant professor, and continued his research at Research Institute for Science and Engineering (RISE) and Waseda Institute for Advanced Study (WIAS) as an assistant professor (2012-16). He got tenure and joined the department in 2016.

His current interests are

Functional Polymers, Precise Polymer Synthesis, Organic Electronic Devices, Energy-conversion/ -storage, Phase-separation and Self-assembly

Title

Precise Photo-curing: Temporal/Spatial Control of Nanostructure Formation

Abstract

UV-curing process based on photo-induced radical polymerization has been widely utilized for inks, paints, adhesives, and photo-resist materials. Especially, facile tuning of UV intensity, wavelength, irradiation area etc, has enabled their industrial applications, however the precise control of photo-polymerization is not trivial due to their too rapid reaction time (within seconds). Delicate balance of reaction kinetics, deformation (shrinkage), and phase-separation associated to polymer network formation needs to be considered.

Controlled (or living) radical polymerization techniques such as atom-transfer controlled radical polymerization (ATRP) have greatly impacted the advancement of polymer synthesis in the last 20 years, allowing well-defined polymers with precise molecular weight distribution and segment blocks. Recently, further temporal (on/off) control of polymerization via external stimuli such as photo-excitation has proposed and gained increased attention. Here we focus on organo-catalyzed iodine-transfer controlled radical polymerization, which allows reversible photo-activation of polymeric dormant without metal catalysts. In this study, we synthesized polymeric dormant with C-I endgroup and utilized to the UV-curing process to challenge the precise control of photo-polymerization and phase-segregation simultaneously. The obtained coatings were optically clear, but internal nanostructure of the coating exhibited unprecedented, bicontinuous nanodomains with gradient size distribution. The domain size was tunable with UV intensity, crosslinker content, and other processing aids. Post-functionalization of the evolved nanostructures will be also discussed.