

Virginia Tech – Waseda Joint Workshop on "Energy and Nanomaterials"

Date: June 7, 2019 (Fri), 9:20am-3:10pm

Venue: 55S-407

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

Moderator: Takeo Suga, Assistant Professor, Waseda University

Time	Lecture Time	Title	Speaker
9:20am	5 min	Opening & Introduction of TGU Project and Research	Prof. K. Oyaizu (Unit Leader of TGU/ Dept. App. Chem., WU)
9:25am	5 min	Introduction of Virginia Tech Research Activities	Prof. J. Foster (Dept Mater. Sci./MII, VT)
9:30am	20min	Design of Photoresponsive Siloxane-based Nanomaterials by Self-assembly	Prof. A. Shimojima (Dept Appl. Chem., WU)
9:50am	30min	Block Copolymer-based Porous Carbon Fibers and Plasmonic Polymer Nanocomposites	Assist. Prof. Greg Liu (Dept Chem. Eng., VT)
10:20am	20min	Surface Modification of Oxide-based Nanomaterials using Biphasic Systems	Prof. Yoshiyuki Sugahara (Dept Appl. Chem., WU)
10:40am	10min	Coffee Break	
10:50pm	30min	Polymer Sequestrants for Environmental and Biological Applications	Assist. Prof. Michael Schultz (Dept Chem., VT)
11:20am	15min	Mechanistic Understanding of Liquid-liquid Interfacial Reactions using the Micro Channel Device and the Quantum Chemical Calculation: Boric Acid Ester Formation, as a Case Example	Assist. Prof. M. Kunimoto (Dept App. Chem., WU)
11:35am	15min	Predicting conductivity of polymer electrolytes by machine learning approaches	Assist. Prof. K. Hatakeyama-Sato (Dept App. Chem., WU)
11:50pm	70min	Lunch (& Poster Session)	
1:00pm	20min	Efficient production of carbon- and silicon-based materials for solar-cells	Prof. S. Noda (Dept. App. Chem., WU)
1:20pm	30min	3D printing of Mechanically Responsive Cellulose Nanocrystal Thermoplastic Urethane Composites	Assoc. Prof. Michael Bortner (Dept. Chem. Eng., VT)
1:50pm	20min	Polymeric Hydrogen Carriers: Reversible Hydrogen Storage with Redox Polymers	Prof. K. Oyaizu (Dept. App. Chem., WU)
2:10pm	30min	Bioproducts as Bioinspired Materials for Healing	Assoc. Prof. E. J. Foster (Dept. Mater. Sci. & Eng., VT)
2:40pm	20min	Photo-active Polymeric Dormant: Precise Synthesis and Controlled Photo-curing	Assist. Prof. T. Suga (Dept. App. Chem., WU)
3:00pm	5 min	Closing	Assist. Prof. T. Suga

Speakers Short Biographies

Atsushi Shimojima



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 4 years of working as a post-doc at Waseda Univ. and Univ. of California, Santa Barbara, he became an assistant professor of 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

Design of Photoresponsive Siloxane-based Nanomaterials by Self-assembly

Abstract

Siloxane-based materials are useful in many applications because of the high stability and transparency of the Si–O–Si networks along with diverse organic functionalities that can be introduced by Si–C bonds. Self-assembly of molecular building blocks is a promising approach to well-designed architectures. Recently, we have focused our efforts on the creation of photoresponsive siloxane-based nanomaterials by the self-assembly processes. Ordered photoresponsive hybrids with lamellar structures have been obtained by self-assembly of azobenzene-functionalized alkoxy silanes ($\text{RSi}(\text{OEt})_3$ and/or $(\text{EtO})_3\text{Si-R-Si}(\text{OEt})_3$, R = azobenzene groups) during hydrolysis and polycondensation.^{1,2} The lamellar films showed reversible changes of the interlamellar spacings and macroscopic bending–unbending motions upon UV/Vis irradiations by partial *trans-cis* photoisomerization of the azobenzene groups. High thermal stability and mechanical property as compared with conventional photoresponsive organic polymers have been demonstrated. Cage-type siloxanes are also useful as a siloxane moiety. A mesostructured film consisting of cylindrical assemblies were formed by the self-assembly of an azobenzene derivative bearing a cage siloxane unit ($-\text{Si}_8\text{O}_{12}(\text{OEt})_7$).³ The azobenzene groups in the film exhibited reversible and efficient *trans-cis* isomerization upon UV/Vis irradiation. The bulky cage played an important role in both the formation of cylindrical assemblies and the improvement of the photoisomerization behavior. A variety of photoresponsive materials can be created by the further molecular design, and some other examples will be presented.

1. S. Guo, A. Sugawara-Narutaki, T. Okubo, and A. Shimojima, *J. Mater. Chem. C*, **1**, 6989 (2013).
2. S. Guo, K. Matsukawa, T. Miyata, T. Okubo, K. Kuroda, A. Shimojima. *J. Am. Chem. Soc.*, **137**, 15434 (2015).
3. S. Guo, J. Sasaki, S. Tsujiuchi, S. Hara, H. Wada, K. Kuroda, A. Shimojima, *Chem. Lett.*, **46**, 1237 (2017).

Guoliang (Greg) Liu



Greg is an Assistant Professor of Chemistry and an affiliated professor of Chemical Engineering at Virginia Tech. He is also an assistant professor of Virginia Tech's newly launched Nanoscience program in the Academy of Integrated Science. He is affiliated to the Macromolecules Innovation Institute and Virginia Tech Center for Sustainable Nanotechnology. He received his Ph.D. in 2011 from the University of Wisconsin-Madison, and worked as a postdoctoral fellow in International Institute for Nanotechnology at Northwestern University. He also worked at the Hitachi Global Storage and Technology in San Jose, CA.

Liu holds more than 15 issued patents. Among them, four are assigned to SABIC; four assigned to Hitachi Global Storage and Technology; one licensed to Intel®; and one licensed to Waves Audio (Israel). Liu has been named an Inventor of the Month at Virginia Tech (2017/07). Liu is a recent recipient of NSF CAREER award, Air Force Young Investigator Program (YIP) Award, ACS PRF Doctoral New Investigator (DNI) award, ACS PMSE Young Investigator award, Macromolecular Rapid Communications Young Talent, and Emerging Young Investigator of Journal of Materials Chemistry, Polymer Chemistry, and Molecular Systems Design and Engineering.

His current interests are Block copolymers, Polymer nanocomposites, Carbon fibers, Energy conversion and storage, and Desalination

Title

Block Copolymer-based Porous Carbon Fibers and Plasmonic Polymer Nanocomposites

Abstract

First, I will describe the synthesis of a new type of porous carbon fibers from block copolymers. Carbon fibers possess high surface areas and rich functionalities for interacting with ions, molecules, and particles. However, the control over their porosity has remained challenging. Conventional syntheses rely on blending polyacrylonitrile with sacrificial additives, which macrophase-separate and result in poorly-controlled pores. Here we use the microphase-separation of block copolymers to synthesize porous carbon fibers (PCFs) with well-controlled mesopores and micropores. Without infiltrating any precursors or dopants, block copolymers are directly converted to nitrogen and oxygen dual-doped PCFs. Owing to the optimized bimodal pores and interconnected porous network, the block copolymer-based porous carbon fibers exhibit outstanding ion transport properties and ultrahigh capacitances in supercapacitors. The use of block copolymer precursors revolutionizes the synthesis of PCFs. The advanced electrochemical properties signify that PCFs represent a new platform material for electrochemical energy storage.

Second, I will present the design of plasmonic polymer nanocomposites for tinted glass. The state-of-the-art commercial tinted glass is coated with a full layer of metalized film to decrease the transmittance of electromagnetic waves. Besides the high cost of the metal layer, the key limitation of such light-reflecting glass is the lack of spectral selectivity. To date, there has been no demonstration of stable and spectral-selective glass that covers the entire visible and near-infrared (NIR). To address the challenge, by judiciously controlling the planar orientation of 2D plasmonic silver nanoplates (AgNPs) in polymer nanocomposites, we effectively harness the transmittance, reflectance, and filtration of any wavelength across the visible and NIR. In contrast to the conventional bulk polymer nanocomposites where plasmonic nanoparticles are randomly mixed within the polymers, our thin-film polymer nanocomposites employ a minimal amount of planarly oriented metal nanoparticles and yet efficiently manage light across the visible and NIR.

Yoshiyuki Sugahara



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 (Prof. Seyferth group), a visiting scientist in 1998 and an invited professor in 2007 both in University of Montpellier II, France (Prof. Corriu group).

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

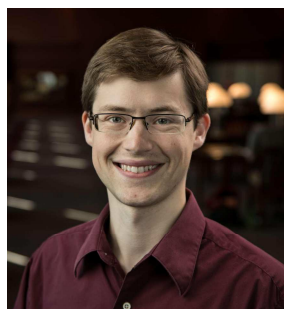
Title

Surface Modification of Oxide-based Nanomaterials using Biphasic Systems

Abstract

Oxide-based nanomaterials have been attracting an enormous amount of attention. One of their promising applications is polymer-based organic-inorganic hybrids, where 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. We have been interested in modifying surface of oxide nanomaterials using phosphorus coupling agents. Their advantages over silane coupling agents which have been commonly employed for surface modification of oxide nanomaterials include suppression of homocondensation under mild conditions and stability of metal-oxygen-phosphorous bonds formed. Among surface modification methods, liquid-liquid biphasic systems consisting of two immiscible liquids have been employed, partly because phase transfer phenomena can be involved during surface modification. A several attempts have been reported for metals, and a limited number of studies have also been reported for metal oxide nanoparticles. We utilized an aqueous dispersion of TiO_2 nanoparticles or nanosheets from ion-exchangeable layered perovskite, $\text{HLaNb}_2\text{O}_7 \cdot x\text{H}_2\text{O}$ and organic solvents, toluene or cyclohexane, where oleyl phosphate, a mixture of monoester and diester, was dissolved, for the formation of biphasic system. As surface modification proceeded, the aqueous phase became clear and the organic phase became turbid, indicating the occurrence of phase transfer. Detailed characterization of the products in organic phases clearly showed that the oleyl phosphate moieties were bound to the surfaces of TiO_2 and the nanosheets derived from $\text{HLaNb}_2\text{O}_7 \cdot x\text{H}_2\text{O}$.

Michael Schulz



Michael D. Schulz is currently an Assistant Professor in the Department of Chemistry at Virginia Tech. Before beginning his independent career, he concurrently received a PhD in Organic and Polymer Chemistry and an MS in Pharmaceutical Science at the University of Florida, where he worked in the group Ken Wagener. During graduate school he spent three months conducting research at Kyoto University in the lab of Yoshiki Chujo. From 2014 to 2015 he was a Fulbright Scholar at the Max Planck Institute for Polymer Research in Mainz, Germany. He was subsequently a postdoctoral scholar in the group of Robert Grubbs at Caltech. His current research interests are diverse and include biomedical materials and devices, antiviral polymers, metal-chelating polymers, radiotherapy-enhancing materials, and polymerization catalyst development.

Title

Polymer Sequestrants for Environmental and Biological Applications

Abstract

Polymeric materials can be specifically designed to bind to targeted compounds in complex environments. Often, this capability is based on the ability of multiple pendant groups on the polymers to simultaneously bind to a targeted moiety, a concept known as polyvalency. Three vignettes will be presented on developing polymer sequestrants for biological toxins, heavy metals, and chemotherapy agents. The first will cover our efforts to develop materials that can bind to toxins produced by *Clostridioides difficile* (previous known as *Clostridium difficile*) in the gastrointestinal track. The second will describe metal-chelating polymers and the connection between polymer architecture and metal-binding capabilities. The final vignette will describe our work developing a method to filter off-target chemotherapy agents from the bloodstream before they cause side-effects. These three stories will illustrate the potential of using polymers to sequester specific targets in a wide range of contexts.

Masahiro Kunimoto



Masahiro Kunimoto is an Assistant Professor of Department of Applied Chemistry, Waseda University. He received his Ph.D from Waseda University in 2012. His research focus is reaction analyses of electrochemical systems, based on interfacial spectroscopy and theoretical calculation. He has been applying those skills for mechanistic understanding of electrochemical deposition, development of a new synthesis process of solar grade silicon, and electrode analyses of secondary batteries. He worked as a CREST researcher from 2013 to 2016, and worked for national research project funded by NEDO in 2017. His current interests are, theoretical and spectroscopic analyses of interfacial reactions (including electrode reactions), surface enhanced Raman spectroscopy, density functional theory, and battery electrode analyses.

Title

Mechanistic Understanding of Liquid-liquid Interfacial Reactions using the Micro Channel Device and the Quantum Chemical Calculation: Boric Acid Ester Formation, as a Case Example

Abstract

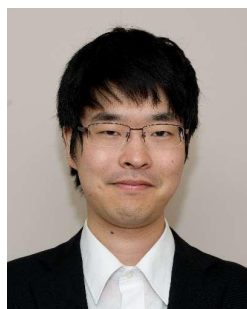
Micro channel devices are of great advantage for the control of chemical reactions: (i) high controllability of temperature, which gives homogeneous distribution of products in the reactor, (ii) high interfacial area, which is favorable for the efficient interfacial reactions, (iii) high safety, etc. Besides, it works well as a powerful tool for reaction analysis, because its micro space leads to the flow with lower Reynolds' number, producing ideal laminar flow that is easy to be mathematically modeled. We have created the micro channels as both reactors and analysis tools, by using micro-nano fabrication for Si substrate.

Great progress has been made in the quantum chemical calculation methods in these several decades. It shows the possibility of analyzing molecular level mechanism of various kinds of reactions. But the question often raised here is, how we should relate the result from the calculation to that from experiments. One of the typical ways is to perform spectroscopy, but in most cases spectroscopy study alone is not able to make connection between them sufficiently.

We present the method to compare the quantum chemical calculation result with the experimental results, by using micro channel device as an analysis tool. Here mathematical modeling for the solution flow in the device plays a key role [1]. As a case example, the method was employed in mechanistic understanding of boric acid ester formation reaction at the liquid-liquid interface. The results led to the conclusion that water molecules significantly affects the reaction rate of the ester formation. The detail of this mechanism will be shown in the presentation.

[1] M. Kunimoto, D. Bothe, R. Tamura, T. Oyanagi, Y. Fukunaka, H. Nakai, T. Homma, *J. Phys. Chem. C*, **122**, 10423-10429 (2018).

Kan Hatakeyama-Sato



Kan Hatakeyama-Sato is currently an Assistant Professor of the Department of Applied Chemistry at Waseda University, Japan. He received his Ph.D. in 2018 under the supervision of Prof. K. Oyaizu and Prof. H. Nishide from Waseda University.

His current interests are Functional polymers, organic batteries, materials informatics, solid polymer electrolytes

Title

Predicting conductivity of polymer electrolytes by machine learning approaches

Abstract

The accurate prediction of the properties of polymers and their composites is important because of their industrial importance; however, it is exceptionally difficult to treat these complex systems. Traditional approaches, such as analytic models and simulations, cannot fully predict polymer properties due to a number of nonlinear molecular interactions at each nano/meso/micro/macrosopic level. A recently developed statistical approach, artificial intelligence (AI), has partially succeeded in predicting the features of simpler materials, such as ceramics and small organic compounds. However, most polymer properties, except for some basic or easy to simulate features (e.g., transition temperature, ionization potential, and permittivity), could not be predicted accurately even by AI due to the lack of the appropriate methodology and databases for polymer informatics.

In the present work,^{1,2} we constructed a database for Li⁺-conducting polymers and predicted their ionic conductivity accurately with a probabilistic machine learning model. The database covered almost all chemical structures for Li⁺-conducting polymers reported up to 2018, and involved 10⁴ conductivity data plots for all temperature ranges. A stacked deep neural network model, which was pretrained to recognize polymer structures, and Gaussian processes were developed to achieve the reliable prediction of even unprecedented chemical structures. Our model forecasted the properties of future samples (i.e., reported in early 2019) with high accuracy of over 90% by automatically extracting the unrevealed statistical trends in the database.

References

1. Hatakeyama-Sato, K.; Tezuka, T.; Nishikitani, Y.; Nishide, H.; Oyaizu, K., Synthesis of Lithium-ion Conducting Polymers Designed by Machine Learning-based Prediction and Screening. *Chem. Lett.* **2019**, *48* (2), 130-132. (editor's choice)
2. Hatakeyama-Sato, K; Nishide, H; Oyaizu, K., Machine learning for predicting properties of solid polymer electrolytes to discover unexpected chemical species. *Under review*.

Suguru Noda



Suguru Noda received his PhD in 1999 from The University of Tokyo, Japan, became an assistant professor and associate professor there, and then joined Waseda University in 2012 as a full professor. He is a chemical engineer conducting research in the field of materials processes. He is recently focusing on practical production of carbon and silicon nanomaterials such as carbon nanotubes and silicon films/nanoparticles, and applying those materials to energy and electronic devices including rechargeable batteries.

Title

Efficient production of carbon- and silicon-based materials for solar-cells

Abstract

To efficiently use renewable energy at larger scale and support society, energy devices should be produced at lower cost using abundant chemical elements. Carbon nanotubes (CNTs), which are composed of only carbon, are attractive due to their properties including high specific surface area, fairly high electric conductivity, lightness, flexibility, thermal/chemical stability, and good compatibility with solution processing. We focus on their use as passive electrode materials in combination with various active materials in energy devices.

Photovoltaics (PV) is now indispensable for green electricity. Various types have been extensively researched, however the conventional bulk crystalline silicon cells still account for >90% [1]. Although the cell price has been reduced significantly, it is important to decrease the cost further to enhance the installation. The energy pay back time is about 3.3 and 2.1 years for mono-crystalline Si and multi-crystalline Si PV systems in Germany, and the Si wafer accounts for about 2/3 and 1/2 of them, respectively, due to the energy intensive production process [1]. We have developed “rapid vapor deposition and in situ melt crystallization” process that yields large-grain crystalline Si films in 1 min with reduced Si consumption [2]. Simple and quick junction formation is also important to make the cells at lower cost. CNT-Si heterojunction is an emerging technology, which enables quick junction formation at ambient temperature. We have proposed the repetitive dispersion-centrifugation process and realized efficient conversion of CNTs (>90%) into high-quality transparent conductive films (TCFs) (80% transmittance and 50 Ω /sq resistance with HNO₃ doping) using a small amount of CNTs (5–10 mg/m²) [3]. We used such solution-processed CNT-TCFs to fabricate CNT-Si heterojunction solar cells and realized ~10% photoconversion efficiency with flat n-Si wafer with HNO₃ doping and with textured n-Si wafer without doping [4]. Low-cost production of high-quality CNTs is also important. Our flame-assisted chemical vapor deposition method that yields 1 nm-diameter single-wall CNTs [5] will also be introduced.

[1] ©Fraunhofer ISE: Photovoltaics Report, updated: 14 March 2019.

[2] Y. Yamasaki, et al., *CrystEngComm* **18**, 3404 (2016).

[3] H. Shirae, et al., *Carbon* **91**, 20 (2015).

[4] E. Muramoto, et al., *RSC Adv.* **6**, 93575 (2016).

[5] S. Okada, et al., *Carbon* **138**, 1 (2018).

Michael J. Bortner



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. His current research efforts at Virginia Tech are focused on development of materials and process technologies to advance the state of the art in 1) polymer based additive manufacturing, 2) cellulose nanocrystals: production, characterization and CNC/polymer nanocomposite materials development, and 3) fiber

reinforced polymer matrix composites.

Title

3D printing of mechanically responsive cellulose nanocrystal thermoplastic urethane composites

Abstract

Improving material selection for the fused filament fabrication (FFF) process has gained significant attention in recent years. Several researchers and companies have been pushed by consumers and industry to stretch the capabilities of the FFF process. FFF was originally developed as a prototyping tool and is now progressively challenged each day to produce end use parts for a wide variety of applications. We have built on the development of a smart mechanically dynamic material, one which can respond to changes in environment with minimal energy input, to potentially increase design freedom and realize new opportunities for expansion of FFF into new functional products.

This study focuses on the production of thermoplastic urethane (TPU)/ cellulose nanocrystal (CNC) filaments for use in FFF. We investigate the influence of various melt processing parameters on the stimuli-responsiveness of the adaptive thermoplastic nanocomposite filament. The composite system analyzed is composed of Texin® RxT70A with 10 wt% dispersed CNC, generated through a master batching process. Randomly oriented film samples are created via solvent casting and uniaxially oriented samples are created via single screw melt extrusion. The orientation of each sample is characterized by both polarized Raman spectroscopy and small angle X-ray scattering (SAXS). Dynamic mechanical analysis results indicate that uniaxial orientation does not significantly impact dry or wet state modulus, likely resulting from a change in the percolating nature of the CNCs. Thermal history imparted by the single screw extrusion process has a negligible impact on the functionality of the CNCs and the corresponding responsiveness of the composite. These results directly translate to the observed shape memory and shape fixity response of 3D printed parts, providing significant insight into process design for successful printing of functional parts.

Kenichi Oyaizu



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

Polymeric Hydrogen Carriers: Reversible Hydrogen Storage with Redox Polymers

Abstract

Electron transfer process of quinoid molecules with electrochemical reversibility and rapid reaction rates were employed to develop organic electrode-active materials, based on self-exchange reactions in polymer layers. Polymers bearing anthraquinones as pendant group per repeating unit gave rise to efficient charge transport properties to allow fabrication of organic rechargeable air battery

Negative charging of the electroneutral redox polymers result in a significant increase in basicity to allow hydrogenation of each redox-active site in the polymer. Hydrogenated organic compounds have been studied as hydrogen storage materials. However, they suffer from safety issues of toxicity, flammability, and volatility, and are usually hydrogenated with hydrogen via highly energy consuming processes. We present here hydrogenated (i.e. hydroquinone and alcohol) polymers which evolve hydrogen by warming under mild conditions with an Ir catalyst. The dehydrogenated quinone and ketone derivatives reversibly store hydrogen via a simple electrolytic hydrogenation in water at room temperature. The hydrogenation also proceeds by simply reacting the polymer with hydrogen gas at 1 atm. The reversible hydrogenation/dehydrogenation cycle allowed the use of the polymers as a new class of polymeric hydrogen carrier.

- [1] T. Kawai, S. Nakao, H. Nishide, K. Oyaizu, **Bull. Chem. Soc. Jpn.** 2018, *91*, 721.
- [2] R. Kato, T. Oya, Y. Shimazaki, K. Oyaizu, H. Nishide, **Polym. Int.** 2017, *66*, 647.
- [3] R. Kato, K. Yoshimasa, T. Egashira, T. Oya, K. Oyaizu, H. Nishide, **Nature Commun.** 2016, *7*, 13032.

E. Johan Foster



E. Johan Foster is an Associate Professor in Materials Science and Engineering at Virginia Tech. Johan's expertise are in the design, synthesis, processing and investigation of functional nanocomposites, bioproducts, biomaterials, and polymers. His research group focuses on imbining 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, Kenya, France and Switzerland. Johan is an elected member of the American Chemical Society Division of Polymer Chemistry, an active member in the Technical Association of the Pulp and Paper Industry Nanotechnology Division and an expert for the organizer of several international symposia and workshops. His research program is supported through federal, industrial and state research grants.

Title

Bioproducts as Bioinspired Materials for Healing

Abstract

We present bio-based, bio-compatible nanocomposites designed to act as responsive materials to engineer healing. With the goal of creating smart, stimuli-responsive materials, bioproducts such as cellulose nanocrystals (CNCs) can provide not only the structural component needed to replace damaged tissue, but also provide chemical cues that aid in healing. CNCs are mechanically stiff, high-aspect-ratio, biorenewable fibers which can serve as both a reinforcing filler in nanocomposites, as well as a convenient handle for imbining material with stimuli responsiveness. We combine structural aspects, along with chemical cues, to create 3D scaffold components, all of which lead to a very specific materials tailored to perform in a specific location in the body. In addition to healing within the body, we look at tailoring interactions at the nano-filler / matrix interface, to create materials that are 'self-healing'. By controlling alignment, directionality of cells and 3D structure is essential to create functional material that mimics nature, for use in regenerative medicine.

Takeo Suga



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

Photo-active Polymeric Dormant: Precise Synthesis and Controlled Photo-curing

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. Telechelic polymeric dormant was also successfully prepared by single unit monomer insertion reaction.

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.