

## Thin Films and Surface Modification

### Room Naupaka Salon 4 - Session TF1-WeE

#### Thin Films - Properties

Moderator: Tetsuhide Shimizu, Tokyo Metropolitan University

#### 5:40pm TF1-WeE-1 Superlubricity: Toward Design of Zero-Friction and Zero-Wear Materials, *Diana Berman*, University of North Texas INVITED

Friction and wear-related failures remain the greatest problems in today's moving mechanical components, from microelectromechanical devices to automotive assemblies and to biological systems. The critical need to reduce and eliminate the tribological failures constitutes the necessity for continuous search of novel materials and lubrication solutions. In this presentation, we overview recent advances in establishing the fundamental understanding of materials interactions at sliding interfaces and use this knowledge as a guide to developing nanomaterials solutions that enhance reliability and efficiency of tribological systems. We evaluate tribological performance of 2D materials, including graphene, molybdenum disulfide, and MXene, and demonstrate realization of superlubricity regime at macroscale. To extend the lifetime of the tribological materials, we demonstrate tribochemically-driven self-replenishment of materials inside the contact interfaces, thus enabling a zero-wear sliding regime.

Overall, the findings have not only allowed us to solve some long-standing puzzles, but could also open a new avenue for the development of new concepts and design strategies for next generation of tribologically efficient materials systems.

#### 6:20pm TF1-WeE-3 Langmuir Monolayer Studies of First-Generation Photoswitchable DASA Surfactants, *H. Kaur*, University of Saskatchewan, Canada; *S. Sumat, S. Murphy*, University of Regina, Canada; *Matthew Paige*, University of Saskatchewan, Canada

Donor-Acceptor Stenhouse Adducts (DASAs) are photochromic molecules that can be isomerized with visible light between a coloured, linear triene form to a colourless cyclic form. These compounds have garnered considerable interest for a variety of light-based applications in the field of photopharmacology and related fields. In this work, we have synthesized several first-generation DASAs with a barbituric acid-based acceptor and a dialkyl amine donor, and investigated how the chemical structure of the DASA affects fundamental structural properties of Langmuir films they form. The DASAs form stable monolayer films at the air-water interface and exhibit a classical LE-LC phase transition at room temperature. Photoillumination leads to a significant alteration in film packing, along with spectroscopic changes consistent with successful isomerization between triene and cyclic form. Film morphology at the air-water interface is also significantly impacted by the photoisomerization process, as assessed by *in situ* Brewster Angle Microscopy. We have also explored the ability to deposit films as both monolayers and multilayers onto solid substrates and characterized the deposition process efficiency and resulting film structures using a variety of techniques. Time allowing, the structure and orientation of the DASA headgroup at the air-water interface will be discussed in context of appropriate molecular modeling calculations.

#### 6:40pm TF1-WeE-4 Highly Transparent, Colorless Optical Film with Outstanding Mechanical Strength and Folding Reliability Using Mismatched Charge-Transfer Complex Intensification, *Sung Woo Hong*, Korea Institute of Industrial Technology (KITECH), Republic of Korea

The development of flexible, transparent, and colorless optical films with exceptional mechanical properties is of great interest to the advancement of flexible displays and electronics. In this study, we develop a new highly transparent, colorless optical film with outstanding mechanical strength and folding reliability for flexible displays and electronics.

Employing the concept of mismatched charge-transfer complex intensification, the newly developed optical film shows a tensile modulus of over 10 GPa, total transmittance close to 90%, and a yellow index below 3.0. To our knowledge, this is the best-recorded balance between mechanical strength and optical properties for a highly flexible optical film.

In addition, it has a superior pencil hardness grade (3H) compared to that of commercially available optical-grade engineering plastic films (under 4B). More importantly, it exhibits exceptional mechanical durability and folding reliability for over 300,000 folding/unfolding cycles at a radius of 1.5 mm, outperforming commercially available optical-grade engineering plastic films and conventional glass substrates.

These remarkable properties are attributed to a unique supramolecular structure with multiple hydrogen bonding and salt complexation

interactions, which exhibits CTC intensification. We also propose a mechanism to explain the concept of mismatched CTC intensification.

In summary, our study provides valuable insights into developing highly flexible films with significantly improved optical properties, mechanical bulk and surface strength, mechanical durability, and folding reliability for next-generation flexible displays and electronics. Our findings also offer new possibilities for the design of advanced flexible displays and electronics, with potential applications in various fields, such as wearable devices, biomedical sensors, and flexible solar cells.

#### 7:00pm TF1-WeE-5 Precise Synthesis of Covalent Organic Framework Thin Films, *Dong Wang*, Institute of Chemistry, Chinese Academy of Sciences, China

The exotic properties associated with graphene and other 2D layered inorganic materials have attracted great interests from a variety of research fields. Two-dimensional covalent organic frameworks (2D COFs), which are covalently constructed from planar aromatic building blocks based on the principles of reticular chemistry, are a class of porous crystalline material with the highly ordered porous architectures and pre-designable electronic skeletons. 2D COFs feature the extended conjugation within a 2D layer and periodically columnar arrays aligned with an atomic precision in vertical direction, which is hardly achievable in other molecular architectures. In this context, high crystallinity and closely eclipsed stacking alignment of aromatic moieties render 2D COF as an ideal plat-form for charge carrier transport. With the improved crystallinity and controllable orientation, substrate supported 2D COF film would enable fabrication of advanced architectures for electronic devices, which however remains unexplored so far.

Herein, we report the on surface synthesis of high quality 2D COF thin film. We have developed a general method for constructing COF monolayers and thin films on substrate surfaces based on gas-solid and liquid-solid interfacial reactions. We proposed a method to improve 2D polymer orderliness by remotely modulating the molecular conformation through the effect of steric hindrance. We developed a chemical vapor deposition method, and prepared highly ordered 2D polymer films with controllable number of layers by modulating the kinetic process of the reaction. We further demonstrate that it is possible to fabricate COF thin film for optoelectronic device. Two types of field-effect transistors with horizontal and vertical structures were constructed by directly growing COF films on the surfaces of hexagonal phase boron nitride and monolayer graphene, respectively, and their in-plane transverse charge transport properties and electronic properties in the  $\pi$ - $\pi$  stacking direction were investigated. We have constructed COF-based electrochromic devices, and the highly ordered structure of COF significantly enhances their performance such as response speed.

[1] Q. Hao, Z.-J. Li, C. Lu, S. Bing, Y.-W. Zhong, L.-J. Wan, D. Wang. *J. Am. Chem. Soc.* 2019, 141, 19831-19838.

[2] Q. Hao, Z.-J. Li, B. Bai, X. Zhang, Y.-W. Zhong, L.-J. Wan, D. Wang. *Angew. Chem. Int. Ed.* 2021, 60, 12498-12503.

[3] X.-R. Ren, B. Bai, Q. Zhang, Q. Hao, Y. Guo, L.-J. Wan, D. Wang. *J. Am. Chem. Soc.* 2022, 144, 2488-2494.

[4] Q. Hao, X.-R. Ren, Y. Chen, C. Zhao, J. Xu, D. Wang, H. Liu. *Nat. Commun.* 2023, 14, 578.

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