Tuesday Morning, June 30, 2026

Emerging Materials and Processes
Room Tampa Bay Salons 1-2 - Session EM2-TuM

Vapor Phase Infiltration

Moderators: Jiyoung Kim, University of Texas at Dallas, **Il-Kwon Oh**, Ajou University

11:00am **EM2-TuM-13 Vapor Phase Infiltration as a Route to Precise Atom Number Cluster Synthesis and Cation Substitution***, Kihoon Kim, Nuwanthaka Jayaweera, Taylor Harville, Cong Liu,* ***Alex Martinson****,* Argonne National Laboratory

The energetically favorable formation of atomically precise clusters enables nanoscale synthesis with exquisite uniformity. We report the synthesis of InS- and CdS-core clusters via vapor infiltration of atomic layer deposition precursors directly into polymer thin films. Sequential infiltration of trimethylindium vapor and hydrogen sulfide gas into poly(methyl methacrylate) (PMMA) allows growth of clusters uniform properties consistent with a magic size cluster–$In_6S_6(CH_3)_6$. Most recently we demonstrate that post-synthetic vapor phase cation substitution into InS-core clusters as deposited in the polymer film is possible for a limited number of ALD precursors, consistent with DFT modeling. Gas phase dimethyl cadmium and hydrogen sulfide precursors infiltrated into poly(4-vinylpyridine) thin films also results in the 3D-nucleation of clusters consistent with a cubane-type Cd_4S_4 core with variable ligand capping. Most recently, we have utilized in situ UV/visible reflection/absorption spectroscopy to observe in real-time the nucleation and growth of CdS clusters for greater mechanistic insight, further supported by DFT. Together the novel approach and in situ characterization methods allow access to and insight into cluster syntheses previous restricted to the solution phase, with the added benefits of rapid byproduct elimination through purging under low vacuum as well as avoidance of the purification, concentration, and film casting required for solution phase cluster syntheses.

11:15am **EM2-TuM-14 Activated Direct Reaction between Carbonyl Groups in Poly(Methyl Methacrylate) (PMMA) and Diethylzinc (DEZ) During Vapor-Phase Infiltration***, Nikhil Tiwale,* Brookhaven National Laboratory*; Ashwanth Subramanian, Sayantani Sikder,* Stony Brook University*; Xiaohui Qu, Guillaume Freychet,* Brookhaven National Laboratory*; Eliot Gann, Cherno Jaye,* National Institute of Standard and Technology*; Kim Kisslinger, Jorge Anibal Boscoboinik,* ***Chang-Yong Nam****,* Brookhaven National Laboratory

Vapor-phase infiltration (VPI) enables organic–inorganic hybrid materials by allowing organometallic precursors to diffuse into polymer matrices and react with specific functional groups. In poly(methyl methacrylate) (PMMA), infiltration using highly reactive trimethylaluminum (TMA) is well established, whereas diethylzinc (DEZ) is generally considered insufficiently reactive toward PMMA carbonyl groups and therefore requires alumina priming. The prevailing model assumes that ZnO_x growth proceeds exclusively through reactions between DEZ and hydroxyl groups generated during the AlO_x priming step.Here, we show that alumina priming directly activates neighboring carbonyl groups in PMMA, enabling a previously unrecognized, direct reaction pathway between DEZ and the polymer backbone during VPI [1]. Using in situ quartz crystal microbalance measurements, cross-sectional scanning transmission electron microscopy, infrared reflection-absorption spectroscopy (IRRAS), near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, and density functional theory (DFT) simulations, we elucidate the mechanism responsible for accelerated ZnO_x infiltration in AlO_x-primed PMMA.AlO_x infiltration rapidly saturates due to near-surface free-volume clogging caused by hyperbranched AlO_x network formation, whereas ZnO_x infiltration exhibits increasing mass uptake and deeper, more uniform penetration over successive cycles. Spectroscopic analyses reveal progressive carbonyl consumption during ZnO_x cycles and the emergence of formate-like species, inconsistent with a hydroxyl-only mechanism. DFT calculations support the formation of a stabilized cyclic Zn-Al-O adduct involving an AlO_x-activated carbonyl group, which lowers the energetic barrier for DEZ binding.These results establish a revised mechanistic framework in which alumina priming electronically activates polymer functional groups, enabling direct DEZ-carbonyl reactions and sustained ZnO_x infiltration, with implications for the design of high-fidelity infiltration-based hybrid materials.

[1] N. Tiwale et al., *Chem. Mater.*, in press (2026), https://doi.org/10.1021/acs.chemmater.5c02584

11:30am **EM2-TuM-15 Atomic Layer Processes for UV-Stable Polymers: Synergistic Effects of Infiltration and Deposition of ZnO***,* ***Gil Menasherov****, Nidaa S. Herzallh, Tamar Segal-Peretz,* Technion Israel Institute of Technology, Israel

Ultraviolet (UV) radiation is the major cause for polymer degradation in outdoor environments, accelerating mechanical failure and color change, leading to plastic waste accumulation. Effective UV-protective strategies that preserve polymer functionality are therefore critical for extending material longevity in UV-intense environments. Here, we present a synergistic approach combining vapor phase infiltration (VPI) and atomic layer deposition (ALD) to engineer nanoscale zinc oxide (ZnO) coatings on poly(lactic acid) (PLA), a UV-sensitive polymer. Individually, ALD and VPI offer minimal enhancement in UV stability; however, their sequential application enables the formation of conformal, polycrystalline ZnO films that dramatically improve UV resistance in both 3D-printed structures and thin-film PLA models. In situ microgravimetry and cross-sectional electron microscopy reveal that VPI introduces ZnO nucleation sites within and atop the polymer matrix, promoting a >10-fold increase in ZnO growth per ALD cycle. The resulting ZnO–PLA hybrids absorb over 90% of incident UV-C radiation while maintaining high optical transparency in the visible range. This low-temperature, scalable process provides a promising platform for the development of transparent, durable UV-barrier coatings on polymers for use in environmentally demanding applications.

11:45am **EM2-TuM-16 Vapor Phase Infiltration of ZnO Nanocrystals into Biodegradable Fibers for Dermatologic Applications***,* ***Martina Rihova****,* CEITEC Brno University of Technology, Czechia*; Susan Azpeitia,* CIC nanoGUNE, Spain*; Denisa Fenclova, Zbynek Heger,* Mendel University in Brno, Czechia*; Mato Knez,* CIC nanoGUNE; IKERBASQUE, Basque Foundation for Science, Spain*; Jan Macak,* CEMNAT, University of Pardubice; CEITEC Brno University of Technology, Czechia

Vapor Phase Infiltration (VPI) enables the incorporation of metal oxides into polymer materials (1,2). Among other applications, allows the development of active antibacterial polymer-inorganic composites (3,4) and photocatalysts (5).

In this study, VPI was used to infiltrate polyvinyl alcohol or cellulose acetate (CA) fibers with ZnO for the treatment of *Acne vulgaris*. The fibers were prepared from biodegradable polymers using an innovative centrifugal spinning technique (6) and subsequently subjected to VPI using diethyl zinc and water, leading to the formation of ZnO both within the fibers and on the fiber surfaces. (3,4)

The fibers were infiltrated with ZnO via VPI using 1 to 128 cycles. Since ZnO-infiltrated CA fibers do not release ZnO nanocrystals, these fibers were treated with oxygen plasma to modify their solubility (4) The resulting fibers with infiltrated ZnO nanocrystals were comprehensively characterized using SEM, TEM, XRD, and XPS. Antibacterial testing revealed that both CA and PVA fibers infiltrated with ZnO nanocrystals starting from 32 VPI cycles effectively inhibited the growth of acne-causing bacteria. Moreover, the homogeneous distribution of ZnO nanocrystals within the fibers enabled the immediate release of Zn^{2+} ions while preserving the fibrous structure, in contrast to fibers containing ZnO nanoparticles, which directly blended into the spinning solution. (3,4)

The presenation will demonstrate that fibrous carriers combined with active ZnO nanocrystals prepared via VPI represent a highly promising material, showing significant potential for the treatment of *Acne vulgaris*.

References:

1. Azpitarte and Knez. "Vapor phase infiltration: from a bioinspired process to technologic application, a prospective review." *Mrs Communications* 8.3 (2018): 727-741.

2. Lee, et al., “Greatly increased toughness of infiltrated spider silk,”*Science* 324, no. 5926 (2009), 488-492.

3 Rihova et al. "Centrifugally spun and ZnO-infiltrated PVA fibers with antibacterial activity for treatment of Acne vulgaris." *Journal of Controlled Release* (2025): 113777.

4. Rihova et al."Cellulose Acetate Fibers with Infiltrated ZnO Nanocrystals: Activation of Antibacterial Properties against *Acne vulgaris* by Oxygen Plasma Treatment" *Small*, Ms submitted.

5. Chennam et al. "Carbon fibers with infiltrated TiO2 nanocrystalline layers: photocatalytic performance." *Nanoscale* (2026).

6. Hromadko et al. "Nanofibers: where they are where we need them to be." *Frontiers in Nanotechnology* 7 (2025): 1706183.

Author Index

Bold page numbers indicate presenter

— A —
Azpeitia, Susan: EM2-TuM-16, 1
— B —
Boscoboinik, Jorge Anibal: EM2-TuM-14, 1
— F —
Fenclova, Denisa: EM2-TuM-16, 1
Freychet, Guillaume: EM2-TuM-14, 1
— G —
Gann, Eliot: EM2-TuM-14, 1
— H —
Harville, Taylor: EM2-TuM-13, 1
Heger, Zbynek: EM2-TuM-16, 1
— J —
Jayaweera, Nuwanthaka: EM2-TuM-13, 1
Jaye, Cherno: EM2-TuM-14, 1
— K —
Kim, Kihoon: EM2-TuM-13, 1
Kisslinger, Kim: EM2-TuM-14, 1
Knez, Mato: EM2-TuM-16, 1
— L —
Liu, Cong: EM2-TuM-13, 1
— M —
Macak, Jan: EM2-TuM-16, 1
Martinson, Alex: EM2-TuM-13, **1**
Menasherov, Gil: EM2-TuM-15, **1**
— N —
Nam, Chang-Yong: EM2-TuM-14, **1**
— Q —
Qu, Xiaohui: EM2-TuM-14, 1
— R —
Rihova, Martina: EM2-TuM-16, **1**
— S —
S. Herzallh, Nidaa: EM2-TuM-15, 1
Segal-Peretz, Tamar: EM2-TuM-15, 1
Sikder, Sayantani: EM2-TuM-14, 1
Subramanian, Ashwanth: EM2-TuM-14, 1
— T —
Tiwale, Nikhil: EM2-TuM-14, 1