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Advanced functional materials and manufacturing processes

Jessica O. Winter, *[a] Jawwad A. Darr *[b] and John Wang *[c]

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Advanced functional materials (AFMs), including nanoparticles of AFMs, play an important role in catalysis, optoelectronic and quantum materials, biomaterials, and energy harvesting, storage, and conversion materials. AFMs can be designed, synthesized, or modelled to possess different arrangements, and therefore can possess a wide range of properties. For example, using additive manufacturing or electrospinning processes, nanoparticle/cluster attributes such as bulk and/or defect structures and surface properties can be varied. AFMs can be further consolidated into larger hierarchical arrangements with specific nano-/micro-structures or surface characteristics that can impart new or unexpected functionality. However, discovering and translating AFMs from the bench to commercial products can be challenging.

Discovery synthesis approaches for new AFMs require materials to be made faster and more consistently, so that their properties can be compared within compositional space. Furthermore, during any subsequent scale-up, replicating properties can pose a number of challenges. Scale-up can result in inhomogeneous mixing and uneven mass and heat gradients that influence material function. Structure–property-composition relationships can be strongly dependent on manufacturing method (*e.g.*, thermodynamic *vs.* kinetic limitations). Consequently, there is a need to better understand the

[a] *William G. Lowrie Department of Chemical and Biomolecular Engineering, Department of Biomedical Engineering, 151 W. Woodruff Ave., Columbus, OH 43210, USA. E-mail: winter.63@osu.edu*
[b] *Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, UK. E-mail: j.a.darr@ucl.ac.uk*
[c] *Department of Materials Science and Engineering, National University of Singapore, 9 Engineering Drive 1, 117575 Singapore. E-mail: msewangj@nus.edu.sg*

Jessica O. Winter

Dr Jessica O. Winter is a Distinguished Professor of Engineering in the William G. Lowrie Department of Chemical and Biomolecular Engineering and the Department of Biomedical Engineering at Ohio State University. Her research interests include nanoparticles for cancer imaging, diagnostics, and drug delivery; and cell migration in the brain tumor microenvironment. She has held several leadership roles in the American Institute of Chemical Engineers, is co-founder and Chief Scientific Officer of Core Quantum Technologies, and is a fellow of BMES, AAAS, AIMBE, AIChE and the RSC and senior member of the IEEE.

Jawwad A. Darr

Dr Jawwad A. Darr is a Professor of Materials Chemistry at University College London. He joined UCL in 2007 and was Vice Dean Enterprise for MAPS faculty at UCL from 2016 to 2021. His research group is one of the leading exponents of lab to pilot scale continuous reactors for the production of nanoceramics and advanced functional materials. Professor Darr has strong interactions with UK industry related to the discovery and scaleup of new ceramic nanomaterials in energy (solid oxide fuel cells, Na and Li ion batteries, hybrid supercapacitors, transparent conducting oxides), materials discovery/catalysis (reduction of CO_2, water splitting/oxidation catalysis), and healthcare applications (biomedical ceramics, adjuvants).

relationship between materials synthesis and consolidation parameters at different length scales in order to control and obtain the desired functional properties.

This themed issue explores the latest developments in advanced inorganic functional materials synthesis, modelling, and simulation, including novel manufacturing processes, scale up approaches, and property evaluation and optimization. One area in which AFMs have high potential is in the area of electrochemical energy storage. Battery materials require precise placement of components in a semi-porous matrix to maximize energy storage and transfer performance. Materials manufacturing and processing are crucial to the Structure–property-composition relationships of these materials.

This collection highlights both anode and cathode materials development for Li- or other metal based batteries, including potential of Ca-based materials. In Dong *et al.*, a dual cation substitution process is used to turn disordered rock salt into $Li_{1.2}Ni_{0.4}Mo_{0.2}Mg_{0.2}O_2$ materials suitable as cathodes (**https://doi.org/10.1039/D2MA00981A**). These materials demonstrated a discharge capacity of 195 mA h g^{-1} over 10 cycles, alternating between disordered and ordered structures with cycling. Xu *et al.* address a correlated problem on the anode side in $Li_4Ti_5O_{12}$ materials (**https://doi.org/10.1039/D2MA00741J**). Such materials are promising as anode materials; however, high reactivity reduces their efficacy. They examine the use of additives, particularly fluoroethylene carbonate, as stabilizers in the electrolyte to improve usability of lithium anode materials. This additive suppressed aluminum corrosion within the half-cell, enabling capacity retention of up to 64% after 10 000 cycles at 2 °C. Despite these improvements, Li-ion batteries present risks, most notably fire hazards. Tinker *et al.* review the state-of-the-art of Ca-ion battery alternatives (**https://doi.org/10.1039/D2MA01034H**). Ca-ion batteries offer great promise to move beyond Li materials, and this review outlines the challenges that need to be surmounted in order to realize their potential.

AFMs are also making great strides in environmental applications. Yang *et al.* explore UiO-67(Zr) metal oxide frameworks (MOFs) as supports for amino-polymers useful for carbon capture (**https://doi.org/10.1039/D2MA01020H**). The unique structure of the MOF materials, combined with internalized polymers, permitted direct from air capture of CO_2, while stabilizing the polymers against degradation. The polymer loading-mass transfer studies in this work provide important guiding principles for further development of MOF-supported carbon capture materials. From CO_2 capture to degradation to CO_2, Iborra-Torres *et al.* explore the use of 3D printed perovskite-like materials for treatment of aqueous organic pollutants (**https://doi.org/10.1039/D2MA01076C**). In their report, the photocatalytic properties of $SrNbO_2N$ result in the generation of reactive oxygen species that rapidly oxidize organic materials toward CO_2 constituents. The report combines experiment and theory to show that aromatic nitrogens in the methylene blue model organic pollutant, interact most strongly with electrons generated in the perovskite-like material. The 3D printed structure provides precise manufacturing capabilities and easy recovery compared to dry powders.

Health applications also benefit from the precision control of AFMs. In particular, nanomaterials are used to encapsulate and deliver drugs, which is an area of increasing interest in the pharmaceuticals market. Paul *et al.* review nanomaterials for encapsulated drug delivery across an array of disease conditions, providing a broad overview (**https://doi.org/10.1039/D2MA01075E**). Then, Beri reviews silicon quantum dot nanomaterials for bio-imaging (**https://doi.org/10.1039/D2MA00984F**). Such materials offer many advantages for imaging, including bio-compatibility, ease of synthesis, and ability to be combined with photothermal therapy for theranostic treatments. Their review also discusses crossover of such materials into other optoelectronic applications, showing the versatility of AFMs across various fields. Demonstrating this versatility, Liu *et al.* present nanozymes for peroxidase-mediated biodetection (**https://doi.org/10.1039/D2MA00844K**) *via* similar MOF supports to those reported in this themed issue by Yang *et al.* for CO_2 capture. Here, UiO-66 MOFs are used to support gold nanoparticles with peroxidase-like activity. The gold particles were grown *in situ* in MOF templates, permitting size control and generating an even distribution. These materials could detect glucose, dopamine, and thiol ions *via* catalytic reaction *via* gold using 3,3′,5,5′-tetramethylbenzidine (TMB) as a reporter with sub-millimolar limits of detection.

These material developments rely on concomitant advances in manufacturing processes. Materials can be manufactured from top-down or bottom-up processes, with much recent interest in bottom-up manufacturing *via* self-assembly or additive manufacturing. Lin *et al.*, (**https://doi.org/10.1039/D3MA00021D**) reviews the current state of the art of nanomanufacturing for micro/nanoparticles for delivery of biologics. In

John Wang

*Dr John Wang is a Professor of Materials Science and Engineering at the National University of Singapore (NUS), and Principal Scientist II, Institute of Materials Research and Engineering, A*Star, Singapore. His research foci include: energy materials and devices, 2D materials chemistry, and nanostructured materials for energy and water technologies. Professor Wang has been a Clarivate Highly Cited Researcher for the past three consecutive years (2020, 2021, and 2022). He is an elected Fellow of the Singapore National Academy of Science, Fellow of the Academy of Engineering Singapore, Academician of the Asia Pacific Academy of Materials (APAM), Fellow of the Institute of Materials, Minerals and Mining (IOM3, UK), and Fellow of the Royal Society of Chemistry.*

Vigil *et al.*, fundamental studies of a silicatein enzyme provide guidance on its use for biomineralization materials manufacturing (**https://doi.org/10.1039/D2MA00938B**). Silicatein is a natural enzyme found in marine organisms that can be used to generate silica and ceria bio-inspired materials *via* self-assembly. However, for silicatein to be made *via* an effective manufacturing route, its solubility and yield must be increased. This work describes optimal conditions and enzyme design to achieve maximum silicatein activity, providing an important advance toward its manufacturing potential. Apart from bio-inspired self-assembly, additive manufacturing is rapidly becoming a cornerstone technique for producing AFMs. Additive manufacturing "ink" materials are printed onto a substrate where they can be cured by exposure to light or other stimuli. For AFMs, polymer ink resins are often combined with other materials, *e.g.*, nanoparticles or powders, to obtain the desired structural properties. Wang *et al.* examine composites derived from thermosetting elastomers, determining the role of wetting in composites with a high degree of particulate loading (**https://doi.org/10.1039/D2MA00892K**). This report teaches that wettability of the resin is a critical component in obtaining materials with high strength, highlighting the importance of interfacial energy in forming AFMs.

This collection provides important guidance on the design and fabrication of AFMs. Such materials can be applied across a diverse range of fields. Here, we highlight applications in energy storage, environmental engineering, and healthcare, but many other applications are possible. Further progress in manufacturing techniques would enable translation of these materials toward commercial products and create routes to materials with increasingly complex structures, representing the next horizon in this field. As AFMs mature, they will enable transformational advances spanning many fields through their power to combine multiple components into synergistic constructs.

