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Introduction to the editor's choice collection on inorganic-biomolecule nanomaterials

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Nanoscale Horizons Scientific Editor Prof. Mark MacLachlan (University of British Columbia, Canada) introduces this hand-selected Editor's Choice collection on inorganic-biomolecule nanomaterials. This collection features some of the exciting research developments published in *Nanoscale Horizons* in the past couple of years.

Inorganic molecules and nanomaterials can furnish materials with attractive electronic, optical, magnetic and catalytic properties, among others. At the same time, biomolecules bring many complementary attractive features, including cellular targeting, chirality, and biocompatibility that can be used to modify the properties of the inorganic component. The marriage of inorganic nanomaterials chemistry with biomolecules has led to

new families of sensors, therapeutics, diagnostics, and catalysts, for example. Gold nanoparticles (AuNPs) functionalized with bioactive receptors, for instance, have been commercialized for use in COVID and pregnancy tests. Scientists are now expanding the library of organic-inorganic hybrid materials available, which is leading to innovations in nanoscience.

In this Editor's Choice collection, we highlight recent publications that have demonstrated the integration of inorganic chemistry and biomolecules to develop nanomaterials for applications

in sensing, separations, batteries, antimicrobials, cancer therapy, flexible electronics, and others.

In fact, the integration of inorganic components with biomolecules is a hallmark of many natural materials, such as bone, nacre, and crab shells. Nacre has a 2D structure in which platelets of aragonite (a polymorph of calcium carbonate) are embedded in a matrix of protein and other biomolecules. This 2D fusion of inorganic and biomolecular components gives nacre its iridescence and its impressive mechanical properties (*e.g.* toughness). In a recent review, Vural and Demirel (<https://doi.org/10.1039/d4nh00530a>) discuss many examples of natural nanocomposites and illustrate how they are being mimicked by materials scientists to develop materials with impressive properties.

Many of the innovations in the field of inorganic/biomolecule hybrid materials relate to cancer cell targeting. Fang *et al.* (<https://doi.org/10.1039/d4nh00464g>) synthesized phosphomolybdenum blue nanoparticles using single-stranded DNA as a template. The particles show good photo-thermal conversion when irradiated with near-IR light, which enabled them to be used to treat tumors.

Biagiotti *et al.* (<https://doi.org/10.1039/d3nh00063j>) reported the synthesis and characterization of cellulose

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nanocrystals (CNCs) functionalized with both AuNPs and monosaccharide head-groups that are exposed on the surface. This modular approach, which was enabled by click chemistry, allowed the authors to easily vary the sugar present on the surface of the CNCs. The same group (<https://doi.org/10.1039/d4nh00042k>) used the CNCs functionalized with sugars to guide a payload of AuNPs to cancer cells. The AuNPs, which were attached to the surface of the CNCs, could be used as radiosensitizers. This approach enabled both the targeting of cancer cells and the delivery of a large payload of AuNPs.

In many diseases, proteins are glycosylated in different locations; these modifications are called glycoforms. Discriminating different glycoforms of a protein is crucial to identifying the markers for disease, especially cancer. Neves *et al.* (<https://doi.org/10.1039/d2nh00470d>) used AuNPs as signal enhancers in biolayer interferometry. With lectin-modified AuNPs, it was possible to discriminate protein glycoforms quickly and with high sensitivity.

Metal-organic frameworks (MOFs) are porous materials that can be used to deliver payloads to cells. Molecules can be stored inside the MOF, or even chemically incorporated into the MOF itself. By functionalizing MOFs with biomolecules, many properties of the MOFs beyond bioactivity – *e.g.*, solubility, degradability – can be tuned. In a review on carbohydrate-containing MOFs, Zuliani *et al.* (<https://doi.org/10.1039/d4nh00525b>) explore the various ways that carbohydrates have been incorporated into MOFs. They discuss the limitations and potential for the different approaches that have been explored, and offer their outlook for the future.

Regulation of reactive oxygen species (ROS) for therapeutics is challenged by the insolubility of sp^2 -iminoglycolipids (IGLs), which limits their bioavailability. In work by Guerrero *et al.* (<https://doi.org/10.1039/d3nh00363a>), an IGL bearing a selenoureido fragment (DSeU) was incorporated into a matrix of ZIF-8, a type of MOF constructed from imidazole and Zn^{2+} ions. The DSeU@ZIF8 nanoparticles were able to modulate the ROS levels in endothelial cells, suggesting a

new pathway for treating diseases caused by oxidative stress.

As antibiotic-resistant pathogens, such as methicillin-resistant *Staphylococcus aureus* (MRSA), pose significant health problems, it is essential to develop innovative approaches to target them. In work reported recently, Liu *et al.* (<https://doi.org/10.1039/d5nh00137d>) created porous nanoparticles from the carbonization of ZIF-8, then loaded them with glycyrrhizic acid (GA), a potent plant-derived substance. Upon irradiation with near-IR light, the nanohybrid material released the GA, and this was demonstrated to be effective for treating intracellular antibiotic-resistant bacteria.

Nain *et al.* (<https://doi.org/10.1039/d3nh00275f>) took a related approach to target MRSA. Nanogels prepared from quercetin were lightly carbonized, then used as a template for the synthesis of CuS nanoclusters. When they were irradiated with near-IR light, the composite films were effective at destroying biofilms of MRSA. Furthermore, they showed other excellent properties, such as being anti-inflammatory. The authors suggest that these composite films are promising for wound healing.

Wiita *et al.* (<https://doi.org/10.1039/d3nh00385j>) explored a novel biomaterial-based approach to antimicrobials. In their work, they synthesized micron-sized hydrogel particles made from silk, and formed selenium nanoparticles inside. These organic-inorganic composite materials show potent activity against bacteria and fungi, and remain biocompatible with mammalian cell lines.

Many researchers have studied the coating of AuNPs with bioactive molecules, particularly for the targeting of receptors on cancer cells. In a recent study, Ghouri *et al.* (<https://doi.org/10.1039/d4nh00178h>) investigated the role of nanoparticles on the activity of protein coronas on the surface. They found that the function of the protein corona, especially its interaction with endothelial cell junctions, is strongly influenced by the properties of the underlying nanoparticles.

In their review of the cooperation between biomolecules and nanomaterials, Hong *et al.* emphasize the role of

chirality in biomolecules (*e.g.* DNA, polysaccharides, proteins) to enhance the sensitivity for chemical sensors (<https://doi.org/10.1039/d3nh00133d>). They further emphasize the role of these novel biocomposite nanomaterials for use in enantioselective separations.

Related to this, Baimanov *et al.* (<https://doi.org/10.1039/d3nh00124e>) explored the influence of chirality of AuNPs on a protein corona and its interactions with other biomolecules. They synthesized chiral AuNPs using tripeptide coatings, then investigated the bio-distribution of these particles and their stereoselective interactions with proteins. The authors found that the chirality of the surface coating on the AuNPs strongly affects the activity of interacting proteins. In addition, the chirality affects the accumulation in tissues and clearance rates of the AuNPs.

Although combinations of different enzymes have been widely explored for cascade catalysis, mixtures of enzymes with synthetic inorganic catalysts are much less explored. Chen *et al.* (<https://doi.org/10.1039/d2nh00572g>) coated CeO_2 nanoparticles with chitosan, then adsorbed these onto *Spirulina platensis*, a microalga rich in superoxide dismutase (SOD). The SOD could convert the reactive oxygen species superoxide anion radicals ($\text{O}_2^{\bullet-}$) into H_2O_2 , then the CeO_2 NPs converted H_2O_2 into water and O_2 . The tandem reaction facilitated by this biotic/abiotic hybrid system was shown to be effective for reducing inflammation in mouse models of ulcerative colitis and Crohn's disease.

As indicated above, many of the recent papers on inorganic/biomolecule nanomaterials in *Nanoscale Horizons* focus on biological applications, but there are also many exploring these materials for other applications and properties. Akter *et al.* (<https://doi.org/10.1039/d4nh00134f>) described an innovative way to create mesoscopic assemblies of nanoparticles using biomolecules. In their method, termed “bio-catalytic nanoparticle shaping,” quantum dots (QDs) functionalized with oligo-L-lysine linkers formed discrete assemblies. Afterward, the biomolecule could be degraded using trypsin, leaving the QD

assembly available for use in drug delivery or sensing. This approach could be extended to a variety of inorganic nanoparticles.

Clean energy production and storage are among the biggest challenges facing humanity. Integrating biodegradable, renewable components into these devices is a promising way to address these problems. In recent work from Ge *et al.* (<https://doi.org/10.1039/d4nh00243a>), a composite hydrogel composed of graphene oxide and biomolecules sodium alginate and iota-carrageenan was cross-linked with Zn^{2+} ions. The nanostructured

gel showed high ionic conductivity and proved to be an effective electrolyte for a zinc ion battery.

Silver nanowires are attractive components for flexible, transparent electrodes given their high conductivity, flexibility, transparency and processability. Unfortunately, silver nanowires suffer from poor adhesion to substrates, as well as low optical, thermal, chemical, oxidative, and mechanical stability. Kwon *et al.* (<https://doi.org/10.1039/d4nh00285g>) protected thin films of silver nanowires with a multilayer film of chitin and cellulose. The resulting materials showed

significantly improved stability compared to the uncovered silver nanowire films.

We hope this Editor's Choice collection highlights just some of the impactful publications related to inorganic bionanomaterials and related applications published in *Nanoscale Horizons* over the past couple of years. The exciting innovations emerging from this field are well-positioned for breakthroughs in areas ranging from energy storage to cancer therapy, and we look forward to publishing more impactful developments in the field.