MATERIALS SCIENCE

Three-dimensional nanoscale metal, metal oxide, and semiconductor frameworks through DNA-programmable assembly and templating

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Controlling the three-dimensional (3D) nanoarchitecture of inorganic materials is imperative for enabling their novel mechanical, optical, and electronic properties. Here, by exploiting DNA-programmable assembly, we establish a general approach for realizing designed 3D ordered inorganic frameworks. Through inorganic templating of DNA frameworks by liquid- and vapor-phase infiltrations, we demonstrate successful nanofabrication of diverse classes of inorganic frameworks from metal, metal oxide and semiconductor materials, as well as their combinations, including zinc, aluminum, copper, molybdenum, tungsten, indium, tin, and platinum, and composites such as aluminum-doped zinc oxide, indium tin oxide, and platinum/aluminum-doped zinc oxide. The open 3D frameworks have features on the order of nanometers with architecture prescribed by the DNA frames and self-assembled lattice. Structural and spectroscopic studies reveal the composition and organization of diverse inorganic frameworks, as well as the optoelectronic properties of selected materials. The work paves the road toward establishing a 3D nanoscale lithography.

INTRODUCTION

Modern technological advances in electronics, photonics, and sensing rely heavily on planar fabrication approaches offered by top-down lithographic methods (1). However, in a broad range of emerging applications in optical and mechanical metamaterials, neuromorphic computing and energy materials require three-dimensional (3D) framework organization with complex material compositions and controllable nanoscale architecture (2-4). Additive manufacturing provides a route for fabricating 3D structured metals at the microscales (5). At the nanoscales, multistep planar lithography and deposition methods have demonstrated a structural control with a resolution extending to ~30 to 100 nm. The technique, however, faces challenges of incorporating a broad class of materials as well as the effort-intensive and low-throughput fabrication of 3D architecture in the sub-30-nm range (6-8). On the other side, self-assembly approaches using surfactants, polymers, and biomolecules, and shaped nanoparticles offer a rich structural diversity in 3D (9-14) that can be combined with inorganic templating, which allows for fabrication parallelization. However, these approaches typically do not offer ways to prescribe specific nanoscale architecture, and the breadth of material systems is limited.

In the past decade, DNA-based assembly methods have been increasingly proven to be capable of organizing matter on the nanoscales (15-19), noted for the ability to precisely place inorganic and biological nano-objects according to the designed parameters of the desired structures. For example, DNA origami, due to its shape and interaction programmability as well as size matching with nano-objects, Check for updates

represents a versatile approach for rational generation of diverse structural motifs that can be self-assembled in larger-scale spatially organized 3D frameworks consisting of optical, magnetic, bioactive nano-objects. However, to exploit these 3D DNA-based nanomaterials, robustness and specific functionality are typically required. Converting these 3D frameworks into inorganic architectures might introduce the framework complexity to inorganic materials.

A DNA metallization through the adsorption of ions on a charged DNA backbone was extensively investigated for potential use in molecular electronics (20–22). However, this approach typically results in nucleation and unconstrained growth (23). Recent advances in the silication of complex DNA architectures expanded the potential use of DNA-assembled materials to applications requiring robustness against temperature, environmental factors, and radiation (24–28). Concerning material diversity, DNA was shown to template biologically inspired calcium phosphate growth (29), and processing of silica into silicon carbide was demonstrated for DNA frameworks, providing feasibility of creating a wide bandgap semiconductor (30). To enable a broad range of applications, these silica-based frameworks can be used as architected 3D supports to host other functionally active material coatings.

While thermal evaporation of niobium onto silica lattice framework was demonstrated for creating niobium 3D nanostructures with superconducting properties (*31*), this fabrication approach suffers from low penetration into the 3D structure. To overcome this limitation and to establish a broadly applicable platform for creating 3D frameworks of different classes of materials, a universal strategy for 3D inorganic templating is needed. It has been shown that silica gel can be used for the sorption of metal ions from solution for a large range of metal salts (*32*). Overall, this suggested that at low pH, sorption to the silica follows the law of mass action.

Ex situ organic-inorganic hybridization techniques, including liquid-phase infiltration (LPI) and vapor-phase infiltration (VPI), are emerging as new methods for converting polymer templates into

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