EXPLORING THE MATTERVERSE USING NANOMATERIAL MEGALIBRARIES

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The discovery of new materials must address an enormous design challenge

Identifying new materials that exhibit desired properties is central to almost everything we do as a civilization. Imagine a world without catalysts, silicon, polymers, batteries, and construction materials. Although remarkable advances have been made in materials discovery, in many respects we are moving through the possibilities at a glacial pace. Indeed, when just approaching the synthesis of new inorganic materials, one must consider an enormous parameter set, including, but not limited to, the elemental composition, oxidation states, size, shape, morphology, crystal structure, and support. This design space is massive and cannot be adequately surveyed using traditional synthesis or screening methods. For example, if we focus solely on metallic nanoparticle materials containing variations of the 61 metals with stable isotopes, and we target the synthesis of four-component nanoparticles, there are 520,000 possible combinations. If we then also consider size control from 1-50 nm in 1 nm increments, there are a total of 26,000,000 potential materials. Finally, if the four-component elemental composition is controlled in 5 atom% increments, we are confronted with 25,000,000,000 possible material targets. There are many more parameters besides composition and size that influence performance; therefore, the total possible number of chemically or physically distinct nanomaterials is near infinite, which defines what we term the "matterverse".

In the context of inorganic materials, combinatorial chemistry has advanced to the point of using hundreds to thousands of thin film features for screening properties.[1-3] While important advances, these approaches do not create features that are discrete in nature and of the appropriate length scales to uncover the effects of reduced dimensionality or structure/function relationships. Indeed, while multimetallic gradient thin film libraries are attractive because they are easily prepared, they lack control over most design parameters except elemental composition. In order to fully navigate the matterverse, one must: (1) realize ultrahigh-throughput synthesis techniques that produce millions to billions of new materials per experiment with the chemical precision of traditional serial synthesis methods; and (2) develop comparably fast characterization

techniques to generate performance metrics, teaching us new lessons about materials design that can only be learned by exploring as much of the design space as possible.

Scanning probe nanolithographic techniques enable the synthesis of increasingly larger libraries of materials

Over the past two decades, we have developed several scanning probe lithography techniques that enable the high-throughput, on-chip synthesis of complex nanomaterials. This began by transitioning scanning probe microscopy (SPM) techniques from reading to writing tools, as in the case of dip-pen nanolithography (DPN).[4] SPM-based lithography allows for positionally encoded deposition of attoliter-volume nanoreactors supporting specific chemical transformations for materials synthesis (Fig. 1A).[5] The spatial confinement within a nanoreactor causes all material precursors to coalesce into a single nanostructure, affording unprecedented control over product composition and size on the single-particle scale.[6-9] Remarkably, to date a library of single heterostructured nanoparticles containing up to seven different elements has been synthesized by reductive, thermal annealing of patterned nanoreactors loaded with the requisite metal salts (Fig. 1B).[10]
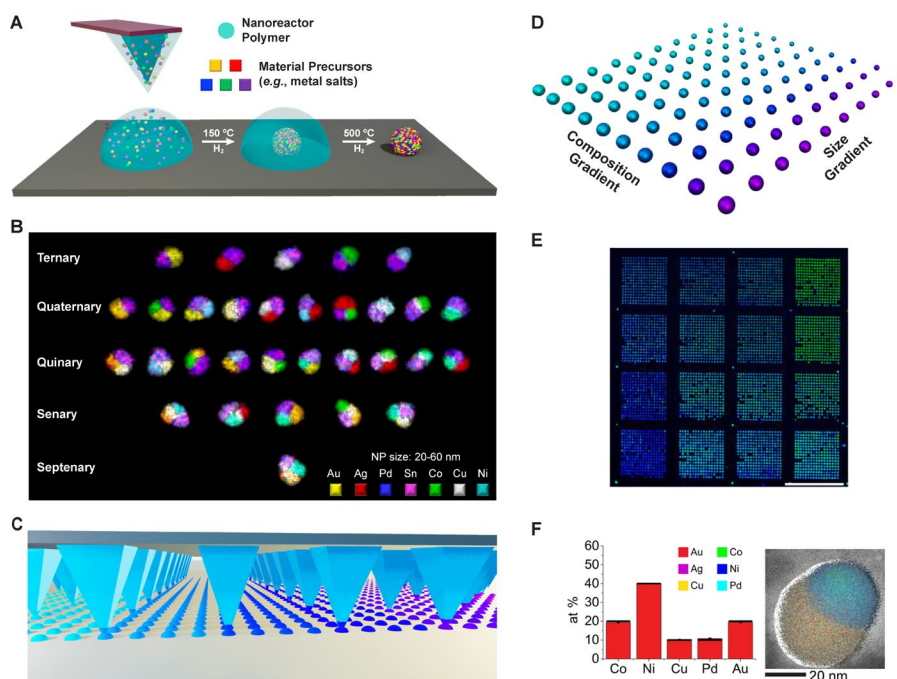

Fig. 1. (A) Scanning probe lithography of attoliter-sized nanoreactors containing materials precursors. For nanoparticle synthesis, thermal treatment induces particle formation and nanoreactor decomposition. (B) A library of polyelemental nanoparticles synthesized from nanoreactors showing elemental mapping from energy-dispersive x-ray spectroscopy (EDS).[10] (C) Parallelized nanoreactor deposition where the composition and volume of precursor at each pen is controlled. (D) A nanoparticle megalibrary schematic with both composition

and size gradients. (E) A library of more than 4,000 $CsPb(Br_{1-x}Cl_x)_3$ perovskites with varied photoluminescence behavior to optimize blue emission properties (Scale bar = 100 μm).[11] (F) AI predicted synthesis of a five-component, single-interface nanoparticle, where the bar graph shows the measured composition by EDS and the black bars represent the AI-suggested ratios.[12]

By further transforming serial nanolithography methods into cantilever-free parallel writing tools with as many as 11 million tips, we now have ways to dramatically accelerate the pace of materials synthesis (Fig. 1C).[13] For example, when precursors are distributed in pre-defined gradients across an array of pens, the composition and concentration at each pen is different, resulting in at least as many unique materials as there are pens on a single chip (*i.e.*, a nanoparticle megalibrary – a positionally encoded chip with at least a million distinct features) (Fig. 1D). Importantly, this approach can be extended to any chemistry that can be performed within a nanoreactor, of which there are many, including reactions that lead to multicomponent metallic and ionic nanoparticles as well as halide perovskites.[6-9]

To be useful, parallel synthesis must be paired with sufficiently high-throughput screening techniques. Spectroscopic methods that allow one to either rapidly interrogate the chip in a site-specific manner or, more preferably, collectively during a single analysis step are desirable. Accordingly, in one demonstration, we (collaborating with researchers from Wright-Patterson Air Force Base) used Raman spectroscopy to discover a new catalyst for the synthesis of carbon nanotubes by screening a Au-Cu nanoparticle library containing a total of 14 million nanoparticles.[14] Importantly, hundreds of new catalysts were identified, but only one was a global maximum performance-wise (Au_3Cu), which highlights the need to search a large parameter space to identify the best material for an intended use. We have also synthesized a library of 4,624 mixed halide perovskites, each subtly different in chemical composition, which was screened for blue photoluminescence (Fig. 1E).[11] From this work, $CsPb(Br_{0.6}Cl_{0.4})_3$ was identified as the highest intensity blue emitter. We now can control the precursor composition and volume at each pen tip, allowing us to pattern and synthesize at least 100,000 unique materials per square centimeter in a single experiment using commercial tools. Moreover, we are making rapid progress towards the synthesis of megalibrary chips with greater than 200,000,000 distinct particles.

Given the extraordinary complexity of the matterverse, it is imperative to take a systematic approach to megalibrary design by predicting composition spaces that are likely to exhibit properties of interest. To that end, we are interfacing the megalibrary platform with artificial intelligence (AI), combining our ability to generate large volumes of first-party data with the predictive capabilities of AI. Megalibraries provide a path to synthesizing large portions of the matterverse and acquiring massive, high quality structural and performance datasets, which then can be mined for optimized materials using AI. Thus far, in collaboration with Toyota Research Institute, we have integrated AI with libraries of heterostructured polyelemental nanostructures to successfully predict new element mixtures for biphasic nanoparticles, resulting in the most chemically

complex biphasic nanoparticles ever made: $Au_{20}Pd_{10}Cu_{10}Ni_{40}Co_{20}$ (AuPdCu-NiCo) and $Au_{10}Ag_{10}Pd_{10}Cu_{10}Ni_{40}Co_{20}$ (AuAgPdCu-PdCuNiCo) (Fig. 1F) [link].[12] Building on this foundation, we are working to integrate the multimodal structural and functional data streams produced by our high-throughput characterization tools with suitable models to harness both the predictive and analytical power of AI and allow us to comprehensively survey the matterverse.

Megalibraries and AI will accelerate materials discovery across chemistry fields

The megalibrary platform, enabled by the remarkable rise of scanning-probe nanolithography, is primed to revolutionize many aspects of materials discovery. By providing access to unexplored synthetic avenues, megalibraries offer opportunities beyond high-throughput synthesis to include screening and massive data analytics with implications far beyond the development of new screening tools and automated instrumentation. Any sufficiently automated experimentation can quickly scale beyond conventional data processing, which requires us to rethink how to acquire, store, and analyze data. This paradigm shift began a long time ago – one is already hard-pressed to find an analytical instrument that does not generate data in a digital format, and it does so at an ever-increasing rate. The integration of AI provides a way to manage these massive datasets by mining large databases, analyzing multimodal experimental results, and making predictions about new materials and their properties to inform future experiments.[15] Excitingly, this will enable a transition from automated to fully autonomous workflows, essentially digitizing a component of the workforce. In so doing, AI-integration with megalibraries will change the way we design and conduct experiments, allowing us to focus on discoveries that will tackle some of the greatest challenges we face, be it materials for fuel cell catalysts, CO_2 reduction to fuels, energy storage and conversion, chemical synthesis, or whatever the future holds – we will find important answers by mining the matterverse.

Acknowledgments

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