Contract No:

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Disclaimer:

Nano-Additive Manufacturing

We design and demonstrate the construction and operation of a simple automated flow-throughput domain process, based on a unique small-scale fluidics concept, that enables a uniform reaction environment for production of high-quality nanomaterials in large quantities. Nanomaterials were subsequently printed on various surfaces through reliable surface functionalization approaches.

Awards and Recognition

NA

Intellectual Property Review

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publically published in its current form.

SRNL Legal Signature

Signature **Date**

Title: Nano-Additive Manufacturing

Project Team: Simona Murph (Primary), and Tommy Sessions

Subcontractor: Greenway

Thrust Area: NS

Project Start Date: June 1, 2019
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We designed and demonstrate the construction and operation of a simple automated flow-throughput domain process, based on small-scale fluidics concept, that enables a uniform reaction environment for production of high-quality materials in large quantities. Nanomaterials were subsequently printed on various surfaces through reliable surface functionalization approaches.

FY2019 Objectives

- Design and purchase the parts, components, and materials needed to build the automated flow-throughput domain process (AFTDP) technology.
- Assemble and build the AFTDP technology.
- Demonstrate precise fabrication and surface functionalization of nanomaterials via AFTDP technology.

Introduction

The design and controlled fabrication of colloidal materials with functional properties has flourished over the last few decades. The beauty and distinctiveness of nanoscale materials is rooted in their unique properties that emerge at the 1–100 nm scale. In this transitional regime, a material's physical, chemical, and biological properties may differ in fundamental ways from the properties of both bulk matter and the constituent atoms or molecules [1].

Metallic nanoparticles are particularly attractive materials because they can be easily synthesized and chemically transformed. They are significantly different from the same materials in the bulk because as their size decreases, they exhibit quantum size effects. Metallic nanoparticles interact strongly with light waves, even though the wavelength of the light may be much larger than the particle. In metal nanoparticles, "plasma oscillations" driven by external electromagnetic fields are localized and lead to strong resonances at specific wavelengths that are dependent on the particle size, shape and the local dielectric environment [1]. Plasmonic properties of metallic nanoparticles find applications in plasmon-enhanced spectroscopy, near-field imaging, sensing, and nanophotonic devices. The plasmon band of gold and silver nanoparticles is tunable throughout the visible and near-infrared region of the spectrum as a function of particle shape, size and the local refractive index of the medium. Anisotropic metal nanoparticles can absorb and scatter light along multiple axes; therefore, metal nanorods and nanowires display both longitudinal and transverse plasmon bands. In the case of nanorods, two plasmon bands emerge, corresponding to light being absorbed (and scattered) along the short axis (the transverse plasmon band) and the long axis (the longitudinal plasmon band) [2].

For decades, a staggering amount of research has focused on the creation of novel nanomaterials and the elucidation of their unique property-structure correlations. Highly reliable bottom-up and top-down synthetic routes that produce increasingly complex nanomaterials with highly ordered and complex geometries have been developed. Complications in scaling up and uniformity have hampered widespread application of nanomaterials. While some of these shortcomings have been addressed to some extent, small variations of the operational parameters, such as the rates of reagents addition, times, stirring rates, uneven temperatures, etc. can still have a strong negative effect on the final product. Ultimately, the quality of the nanomaterials obtained can vary greatly from one batch to the next.

Here, we propose the construction and operation of a simple automated flow-throughput domain process (AFTDP), based on a unique small-scale fluidics concept, that enables a uniform reaction environment for production of high-quality materials in large quantities. Nanomaterials were used “ink” and “printed” on various surfaces through reliable surface functionalization techniques.

Approach

Nanomaterials of various sizes, shapes and compositions were prepared through a solution chemistry, through the reduction of molecular precursors in the presence of surfactants, and capping agents. The reduction rates of the metal precursors, reductant-to-precursor ratio, ligands and strength of reductant all were used to manipulate the final have an effect on the shape, size, and crystallinity, which affect the optical and physical properties. The ligands on the surface are used to stabilize the NPs and change the surface energy at certain facets through preferential adsorption to achieve shape control. By automatically varying the amount, volumetric flow rates, timing, location, size of the capillaries/tubings, etc. of the injected reagents, highly reliable and uniform nanomaterials can be produced. Continuous operation of the system will allow production of nanomaterials in large quantities. Once produced, nanomaterials could be printed by drop casting or by chemically binding on various supports.

Results/Discussion

The route for the bottom-up manufacturing of metallic nanoparticles (NPs) employed here is based on the reduction of molecular precursors. We found that the nanoparticle’s size and optical properties can be tuned by simply changing the reaction rate, flow rate and the $M^{n+/}$reducing agent ratio.

One interesting finding observed during the operation of the AFTDP is that the small reaction volumes enable reactions to be performed with higher yields than can typically be achieved with conventional reactors. It is possible that the applied stress (stress-induced crystallization) increases of the interaction among nano-objects, nucleation density makes the nanoparticles prone to enhanced structural arrangements and crystallization.

To create uniquely shaped morphologies, anisotropic growth of nanoparticles of interest was investigated. Crystalline symmetry was broken through the use of shape directing ions and/or facet specific binding coordinating compounds. Nanostars and nanotriangles were successfully produced.

Bimetallic nanoparticles are of long-standing interest because they can exhibit catalytic, electronic, and optical properties distinct from either of their constituent monometallic nanoparticles. The importance of the relative surface alloying or layering arrangements of metals on single-crystal substrates has been recognized, including the “near surface alloy” model of metal adlayer on metal substrate [3]. By using a co-precipitation approach, metallic nanoparticles of various compositions were produced. Once produced, nanomaterials were subsequently printed on various surfaces through reliable surface functionalization approaches.

FY2019 Accomplishments

- Demonstrated the construction and operation of a simple automated flow-throughput concentric capillaries processing technology (based on unique small-scale fluidics concept), that enables a uniform reaction environment for production of high-quality materials;
  - Large volumes of nanomaterials could be produced under continuous operations.
  - Demonstrated the production of structures of various compositions and morphologies.
- Created isotropic and anisotropic nanoscale structures in solution and on various supports.
  - The metallic nanoparticle’s size and optical properties can be tuned by simply changing the reaction rate, and the M^{n+}/reducing agent ratios;
- The small reaction volumes enable reactions to be performed with higher yields than can typically be achieved with conventional reactors.

Future Directions

- Nanomaterial’s fabrication optimization and production of uniquely shape size and composition nanostructures via AFTDP technology;
- Patterning with nanomaterials via the 3D Nano-Additive Printing technologies.

References

1. Hunyadi Murph, S.E.; et. al. “Anisotropic and Shape-Selective Nanomaterials: Structure-Property Relationships”, Nanostructure Science and Technology series, Springer Publisher, 2017, 1-470.
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3. Hunyadi Murph, S.E. (Invited) et al. “Synthesis, Functionalization, Characterization and Application of Controlled Shape Nanoparticles in Energy Production”, Fluorine-Related Nanoscience with Energy Applications, ACS Symposium Series, Volume 1064, Chapter 8, 2011, 127-163.

Acronyms

Automated flow-throughput domain process (AFTDP)

Intellectual Property

Invention disclosure – submitted.