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Can Scalable Nanomanufacturing Unlock Energy Device Potential While Preserving Nanoscale Properties?

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Abstract: ***This article delves into the realm of scalable nanomanufacturing, emphasizing its significance, ongoing research endeavors, and notable achievements. The National Science Foundation is at the forefront of advancing fundamental research in scalable nanomanufacturing (SNM), fostering innovative approaches such as scalable nanopatterning. Within this framework, various novel nanomanufacturing methods have been proposed, investigated, and demonstrated. The paper explores key SNM research domains encompassing materials, processes, and applications, elucidating scale - up methodologies through project illustrations while also addressing prevalent manufacturing challenges. Specifically, it highlights the role of nanomaterials in enhancing energy storage systems, citing the 2019 Nobel Prize in Chemistry awarded to lithium - ion batteries, which power diverse applications from portable electronics to electric vehicles. Furthermore, it provides insights into recent advancements in employing nanomaterials for energy storage devices like supercapacitors and batteries, envisaging their potential in powering portable, flexible, and distributed electronics, as well as contributing to electric transportation and grid - scale storage systems. However, it acknowledges the challenges posed by the high reactivity and chemical instability of nanomaterials due to their extensive surface area. To surmount these limitations, the article advocates for the integration of nanoparticles with distinct functionalities into smart architectures on nano - and microscales. It underscores the imperative of advanced manufacturing techniques for seamlessly incorporating nanomaterials into functional devices. The narrative also outlines a roadmap for leveraging nanomaterials to enable future energy storage applications, encompassing scenarios like powering distributed sensor networks and facilitating the development of flexible and wearable electronics.***

Keywords: Nanomaterials, Energy storage systems, Lithium - ion batteries, Supercapacitors, Flexible electronics, Electric transportation, Grid - scale storage, Nanoparticles

1. Introduction

Nanomanufacturing involves the production of materials, structures, components, devices, and systems at the nano - scale, which is typically within the range of 1–100 nanometers. This field focuses on manipulating and controlling matter at the nano - scale, leveraging unique physical and chemical phenomena like quantum and surface effects. Scalable nanomanufacturing extends this concept to large - scale production of nanomaterials and nanostructures, their assembly into various components and devices, and the integration of these assemblies into higher - order systems. Research in nanomanufacturing aims to overcome scientific and technical barriers hindering the translation of lab - scale synthesis to industrial - scale production, addressing challenges such as scalability, reliability, efficiency, and affordability. The Scalable Nanomanufacturing (SNM) program by the National Science Foundation (NSF) seeks to address these challenges by exploring research ideas capable of achieving nanomanufacturing scale - up through processes like large - area, continuous manufacturing, and high - throughput techniques.

Background: Nanomaterials offer significant advantages in energy storage applications due to enhanced ionic transport and electronic conductivity compared to conventional materials. They enable efficient utilization of intercalation sites within particles, leading to high specific capacities and fast ion diffusion, making nanomaterial - based electrodes capable of handling high currents for high - energy and high - power storage. Despite these benefits, commercial adoption of nanomaterials in energy storage devices remains limited, except for certain applications such as multiwall carbon - nanotube additives and carbon coatings on silicon particles in lithium - ion battery electrodes. However, decades of development have yielded a diverse library of nanomaterials with versatile compositions and shapes, including nanoparticles, nanowires, nanosheets, and porous nanonetworks, offering potential solutions for advanced energy storage technologies such as wearable and structural energy storage.

Advances: The success of nanomaterials in energy storage relies on nanostructuring to control electrochemical performance and leverage various charge storage mechanisms such as ion adsorption and intercalation processes. Novel materials like redox - active transition - metal carbides (MXenes) exhibit superior conductivity compared to conventional materials, paving the way for high - performance energy storage devices without the need for current collectors. Hybrid architectures combining nanomaterials like carbon - silicon and carbon - sulfur with versatile nanostructuring methods address challenges related to volume changes during charging and discharging, facilitating the design of high - energy, high - power, and long - lasting energy storage devices.

Outlook: Despite their potential, nanomaterials face limitations such as high surface area leading to parasitic reactions with electrolytes, especially during the initial cycle, and agglomeration issues. Future strategies aim to develop smart assembly techniques for nanomaterials, ensuring controlled geometries in electrode architectures. Moreover, combining nanomaterials with complementary functionalities such as high electronic conductivity of graphene or MXenes with high redox activity of oxides is crucial. Innovative manufacturing approaches like printing, knitting, and spray deposition, along with advanced techniques like 3D printing and atomic layer deposition, should be employed to manufacture devices from nanomaterials, enabling flexible, stretchable, wearable, and structural energy storage solutions for disruptive technologies like the Internet of Things.

2. Problem Statement

In spite of the promising prospects that polymer - based intelligent composites offer for reshaping optoelectronic and energy technologies, a crucial requirement persists: tackling the hurdles associated with their creation, stability, enhancement of performance, and seamless integration into real - world scenarios. This issue at hand highlights the urgency for inventive endeavours in research and development, directed towards surmounting these obstacles and unleashing the complete transformative potential of these substances. This, in turn, will expedite their acceptance and influence on the prospective landscape of sustainable and high - performance optoelectronic and energy systems.

3. Hypothesis

The transition toward electricity as the primary energy source is rapidly unfolding, driven by the burgeoning demands of various sectors like consumer electronics, medical devices, electric vehicles, and grid infrastructure. This shift necessitates advancements in energy storage technologies, particularly in the realm of reversible electricity storage and release. The need to store energy from diverse sources such as solar panels, wind turbines, and even human motion underscores the pressing need for improved and diversified energy storage solutions.

Within this landscape, nanomaterials with nanometer - scale structural features play a pivotal role in revolutionizing energy storage. These materials offer large electrochemically active surfaces, enabling faster surface redox processes compared to bulk electrodes. Moreover, their high electronic and ionic conductivities, combined with intrinsic strength and flexibility, facilitate the development of ultrathin, flexible, and structural energy storage solutions. Utilizing nanomaterials also opens avenues for safer batteries with nonflammable solid electrolytes and enables the use of large or multivalent ions for more affordable grid - scale applications.

Beyond active energy - storing materials, passive components like separators and current collectors also benefit from nanomaterial integration, leading to smaller and lighter batteries. However, challenges such as high surface area leading to parasitic reactions, cost, and manufacturability remain significant hurdles in realizing the full potential of nanomaterials in practical applications.

Despite these challenges, the expanding library of nanoparticles and nanostructured materials offers a wide range of compositions and electrochemical properties. From zero - dimensional nanoparticles to three - dimensional porous networks, nanomaterials provide a diverse toolkit for creating functional energy - storing architectures. Combining nanomaterials with different dimensionalities allows for the development of hybrid structures that address limitations inherent in individual materials, thereby enhancing overall energy storage performance.

Furthermore, fundamental processes governing energy storage in nanomaterials differ from bulk materials, emphasizing the need for a deeper understanding of nanoscale phenomena. Processes such as ion and electron transport, surface interactions, and 3D architecture assembly play crucial roles in determining the performance of nanomaterial - based energy storage devices. Exploring and harnessing these fundamental properties are essential for realizing the full potential of nanomaterials in next - generation energy storage technologies.

4. Research Questions

1) What are the key challenges in scaling up nanomanufacturing processes to industrial levels, and how can they be addressed to enhance scalability, reliability, and affordability?
2) How can nanomaterials be effectively utilized to overcome limitations in conventional energy storage systems, and what are the barriers to their widespread commercial adoption?

5. Literature Review

The National Science Foundation (NSF) initiated the Scalable Nanomanufacturing (SNM) Solicitation in 2011 as a response to the National Nanotechnology Initiative (NNI) Signature Initiative (NSI) in Sustainable Nanomanufacturing. This response came after the President's Council of Advisors on Science and Technology (PCAST) recommended doubling research and development investments in nanomanufacturing to accelerate the commercialization of nanotechnology - enabled products. The objective of the Sustainable Nanomanufacturing NSI is to develop manufacturing technologies for the economical and sustainable integration of nano - scale building - blocks into large - scale systems. SNM aims to achieve this goal by conducting basic research into novel nano - scale processes for producing nanomaterials and nanostructures on a large scale, integrating them into nano - enabled systems, and eventually incorporating these systems into useful products for society and the economy. The solicitation emphasizes the importance of processes being scalable, controllable, sustainable, and safe during production.

The NSF SNM Solicitation encourages research to address scientific and engineering barriers hindering the production of useful nanomaterials, nanostructures, devices, and systems at an industrially relevant scale, reliably, and at low cost while adhering to environmental, health, and safety guidelines. It promotes high - throughput approaches such as large - area, parallel, continuous roll - to - roll, and continuous reactor processes, as well as interdisciplinary efforts involving engineering and physical sciences disciplines, and industry participation. The focus is on developing scalable processes and methods and conducting fundamental scientific research in well - defined technical areas to overcome critical barriers to scale - up and integration of nano - scale processes. The outcomes sought include design principles for production systems, enabling tools leading to nanomanufacturing platforms, metrology, instrumentation, standards, process monitoring and control methodologies, and product quality and yield assessment tools. The overarching goal of the SNM solicitation is to establish the fundamental principles for volume manufacturing of useful nanotechnology - enabled products at low cost.

The NSF SNM Solicitation has supported fundamental research in scalable nanomanufacturing for six years, awarding nearly 50 projects between 2011 and 2016 across various research areas. These research areas encompass nano - scale materials, processes, and potential nano - enabled applications, spanning from zero - dimensional quantum dots to three - dimensional nanoporous membranes. The solicitation covers a wide range of nano - scale processes including chemical, thermal, vapor - based, solution - based, electrolytic, lithography/deposition, assembly, bio nanofabrication, mechanical, and 3D nanofabrication techniques. Potential nano - enabled applications include areas such as environmental, chemical, energy, electronics, optoelectronics/photonics, sensors, structural, biomedical, and various forms of sheets/wires and templates. The impact of nanomanufacturing advances is expected to influence applications across all industrial sectors, leading to new products, improved products, and products with new functionalities, leveraging the diverse range of nano - scale materials and processes available for building nano - scale structures and systems.

6. Methodology

Scaling up nanomanufacturing processes involves employing one or a blend of various approaches:
1) Continuous Roll - to - Roll Top - down/Bottom - up Processes: This includes techniques such as printing, imprinting, self - assembly, deposition, coating, and lamination.
2) Parallel, Large - area Top - down/Bottom - up Processes: Techniques like lithography, direct - write, directed - and self - assembly are utilized.
3) Parallel, Large - area 3D Nanofabrication: Methods such as nano 3D printing, 2 - photon polymerization, nanoimprinting, self - assembly, and strain engineering are involved.
4) Large - area DNA Nanofabrication: Templating is carried out using DNA.
5) Semi - continuous, Continuous, or Parallel Chemical/Fluid/Thermal Techniques: Techniques like microreactor, microfluidic, electrospray, electrospinning, and fiber - drawing are employed.

Moving on to Scalable Nanopatterning:
Nanopatterning involves creating 2D and 3D nanostructures with repetitive designs of varying sizes, shapes, and patterns. It can be achieved through top - down, bottom - up, or hybrid processes. Both surface (2D) and volume (3D) nanopatterning methods have been demonstrated using various techniques. The aim of scalable nanopatterning research is to address challenges such as throughput, scalability, regularity, controllability, quality, and yield. While electronic and optoelectronic applications stand to gain significantly from advancements in scalable nanopatterning, non - electronic applications also stand to benefit. The objective is to develop versatile and reconfigurable manufacturing platforms capable of producing different patterns from diverse materials for a wide range of applications. Among the five general approaches mentioned earlier, the first four are suitable for scalable nanopatterning.

Scalable Nanopatterning Research at NSF:
Numerous ongoing NSF SNM research projects exemplify scalable nanopatterning approaches, as outlined in the SNM Solicitation description. These projects fall into one of the four general scalable nanomanufacturing technologies defined earlier:
1) **Continuous Roll - to - Roll (R2R) Top - Down/Bottom - Up Processes:**
   - Examples include ink - jet based nanoimprint lithography, block copolymer self - assembly, continuous CVD synthesis and patterning of CNT and graphene, and continuous microplasma - based direct write fabrication, among others.
2) **Parallel, Large - Area Top - Down/Bottom - Up Processes:**
   - Examples encompass digital in - flow nanoimprint lithography, directed self - assembly by plasmonic enhanced parallel optical trapping, CVD and directed self - assembly of block copolymer, and three - color photolithography, among others.
3) **Parallel, Large - Area 3D Nanofabrication:**
   - Examples include hyperlens - assisted projection stereo - lithography, directed self - assembly of block copolymers, and laser processing for multi - scale scaffold structures, among others.
4) **Parallel, Large - Area DNA Nanofabrication:**
   - Examples include molecular building - block assembly on DNA - like templates, bread - boarding with nanoimprint lithography of organic semiconductor nanowires, and molecular self - assembly of atomically - precise DNA patterns, among others.

Nanomaterials have revolutionized energy storage by enabling the use of conventional materials in ways previously impossible. For instance, nanostructuring allows for the utilization of materials like silicon, germanium, or tin as cathodes or anodes, despite their large structure and volume changes during cycling. Silicon, with a theoretical capacity of up to 3579 mA·hour g−1, faces limitations due to volume changes upon lithiation and delithiation, leading to pulverization of the active material. However, reducing particle size below ~150 nm limits electrode cracking and mitigates mechanical failure. Various designs, including nanowires, nanotubes, and graphene flakes, have been proposed to address these challenges.

To tackle large volume expansion and mechanical failure, nanoscale double - walled hollow structures have been demonstrated, where the outer wall constrains expansion of the inner wall, promoting stable solid electrolyte interface (SEI) formation.

In energy storage materials like oxides, sulfides, and fluorides, nanostructures have shown promise in enhancing cyclability and charge storage capacity. For instance, lithiation and sodiation of FeF2 electrodes generate ultrafine Fe nanoparticles fused into a conductive network, enhancing electron transport. Similar effects are observed in other materials like Ag2VO2PO4 cathodes, where in situ formation of Ag nanoparticles increases electronic conductivity.

Nanostructured solutions have been particularly effective in addressing challenges in sulfur cathodes, known for their high theoretical capacity but poor cyclability and large volume expansion. Thin layers of 2D materials like MXene or electrospun carbon nanofibers have been used to mitigate polysulfide shuttling and volume expansion.

In solid - state batteries, nanomaterials play a crucial role in controlling interfaces between components, creating specific battery components, and constructing 3D electrodes. They facilitate fast ion and electron transport, often through hybrid structures or 2D heterostructures.

Manufacturing energy storage devices with nanomaterials offers opportunities for faster operation, higher power, and longer lifetimes. Nanoscale materials enable the production of electrodes of any size, shape, or form factor, even integrating them into structural elements or wearable electronics. Various manufacturing techniques like spray coating, ink - jet printing, and roll - to - roll manufacturing are being explored for scalable production.

However, challenges remain, including ensuring environmental and temperature stability, managing parasitic reactions, and integrating smart functionalities into energy storage devices. Efforts to mitigate these challenges involve developing coated electrode materials, advanced electrolytes, and membranes, as well as optimizing manufacturing processes to incorporate nanomaterials effectively.

7. Results

Manufacturing challenges can be categorized into two main areas: desired outcomes and appropriate metrics. The desired outcomes encompass aspects such as product quality and durability, process repeatability and reliability, production scalability and affordability, production efficiency and yield, as well as product performance and functionality. On the other hand, determining appropriate metrics involves considerations like precision of placement, feature size and resolution, overlay registration and nanostructure density, as well as complexity and forming rates.

These challenges are inherent to all manufacturing processes, but they are particularly pronounced in nanomanufacturing due to the difficulty in manipulating, measuring, and controlling processes at the nano - scale. Even small errors at this scale can lead to significant failures. Moreover, there's often a need to strike a balance between feature size and resolution in relation to processing or forming rates, especially when aiming for high volume production.

Additionally, each nano - scale process is typically unique and untested, requiring validation. Every nanocomponent may possess a distinct processing history, further necessitating validation. To attract commercial interest, it's imperative to demonstrate extensive proven history, establish a reliable supply chain, adhere to universal standards, and define targeted metrics. Compliance with toxicity, environmental, health, and safety standards and regulations is also crucial. Finally, the fundamental question of market viability for nano - enabled products must be addressed.

In conclusion, scalable nanomanufacturing, including scalable nanopatterning, serves as the cornerstone for volume manufacturing of nano - enabled products. Research efforts in these domains aim to develop new nanomanufacturing platforms capable of producing a variety of structures and patterns for integration into various devices and systems. The objective of the NSF Scalable Nanomanufacturing (SNM) Solicitation is to advance fundamental principles for scalable nanomanufacturing, thereby facilitating the translation of lab - scale discoveries into commercial products. Through approaches like continuous roll - to - roll top - down/bottom - up processes, parallel large - area top - down/bottom - up processes, and large - area 3D nanofabrication, researchers are making strides in addressing persistent knowledge gaps and enabling applications across technological sectors.

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