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Surface engineering of nanomaterials for improved energy storage – A review

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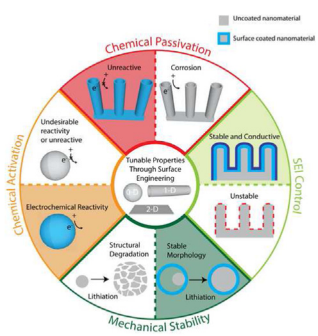
HIGHLIGHTS

- Surface engineering decouples bulk and surface properties relevant to energy storage.
- Surface engineering is critical for nanostructured materials in energy storage.
- Recent advances in energy storage build from four mechanistic roles of surface engineering.
- Future innovation in energy storage centers on advances in surface engineering methods.

GRAPHICAL ABSTRACT



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ABSTRACT

Nanomaterials bring extreme promise for a future wave of energy storage materials with high storage capacity, fast recharging capability, and better durability than bulk material counterparts. However, this promise is often overshadowed by greater surface area and higher reactivity of nanostructured active materials - obstacles that must be overcome to be practical. Specifically for energy storage systems, many materials that exhibit promise in bulk form for high capacity or energy density exhibit surfaces that are unstable or reactive in electrochemical environments when downsized to nanometer length scales. As a result, surface engineering can be a powerful tool to decouple bulk material properties from surface characteristics that often bottleneck energy storage applications of nanomaterials. This review discusses advances made toward the surface engineering of nanostructures in the context of four mechanistic roles that surface engineering can play. This includes (i) chemical activation, where the surface layer plays the active role in facilitating a Faradaic chemical process, (ii) solid electrolyte interphase (SEI) control, where a surface layer can lead to a stable artificial interface for Faradaic processes to occur, (iii) chemical passivation, where near atomically thin surface protective layers can protect from corrosion or unwanted electrochemical reactions at interfaces, and (iv) mechanical stability, where a thin layer can provide mechanical support to inhibit fracturing or mechanical failure. This review elucidates surface engineering as a multi-faceted tool for engineering materials for energy storage that intersects the quest for new materials and the rediscovery of old materials to break new ground in energy storage applications. The discussion concludes by highlighting key current challenges in surface engineering for pure metal anodes in metal-ion batteries and polysulfide immobilization in lithium-sulfur batteries.

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1. Introduction

In 1959, renowned physicist Richard Feynman gave a historical talk entitled "There's Plenty of Room at the Bottom," where he proceeded to predict how systems engineered at the nanoscale can radically change the landscape of scientific research efforts (Feynman, 1960). Just short of seven decades later, the average researcher whose efforts overlap with nanoscience has the capability at their fingertips to engineer materials and their surfaces with atomic scale precision. Whether it is recognized as such or not, the abundance of research tools that can engineer surfaces of materials and still maintain the integrity of the bulk interior material has unlocked a whole new frontier of research in the area of *surface engineering*. From this concept emerges an engineering approach for heterogeneous material systems where the surface properties can be engineered separately from the bulk material properties to harness the true application potential of material systems. This approach can be synergistically applied alongside the search and discovery of new nanoscale materials or can be a technique to rediscover materials with extraordinary bulk properties that were overlooked many decades ago due to the inability to overcome limitations of reactive or poorly suited surface/interface characteristics.

For the specific case of energy storage applications with nanomaterials, surface engineering becomes a critical component of functional electrode design. Despite years of research on nanoscale materials for energy storage, commercial batteries still make use of micro-scale materials for electrodes. This is due to a combination of both (1) manufacturing challenges for nanoscale materials, but also (2) the reactive nature of nanoscale materials that leads to high irreversible capacities associated with solid electrolyte interphase (SEI) formation (Armand and Tarascon, 2008). New nanoscale materials exhibiting improved performance compared to bulk materials often lead to lower performance at the cell-level due to the increased electrolyte consumed while forming a stable electrode-electrolyte interface. This is one of many challenges that can be addressed and overcome through surface engineering. However, beyond the limits of this one challenge, surface engineering is a tool highly applicable to a broad scope of energy storage materials due to the native function of energy storage devices that require an electrode-electrolyte interface that is stable. In the case of electrochemical supercapacitors, this interface must be stable to prevent Faradaic charge transfer reactions and sustain an electric double layer. In the case of batteries and pseudocapacitors, this interface must facilitate Faradaic charge transfer reactions that store and release energy without degradation. The premise of engineering electrode materials for these applications without tools to perform surface engineering experiments requires a researcher to isolate materials among a limited set where the bulk properties are favorable for high performance (storage capacity, internal resistance, etc.), but in addition to this, the electrochemical interface between these materials and the electrolyte is *also* favorable. Surface engineering therefore dramatically decreases the complexity of the engineering challenge by allowing a researcher to identify a material with ideal bulk properties, and then independently engineer the surface properties to be stable. This opens a trajectory for faster, more efficient, and more intelligently designed progress toward improved energy storage systems that can overcome many of the key bottlenecks limiting their advancement today.

This review will first lead into advancements in surface engineering by providing a brief introduction into the most common

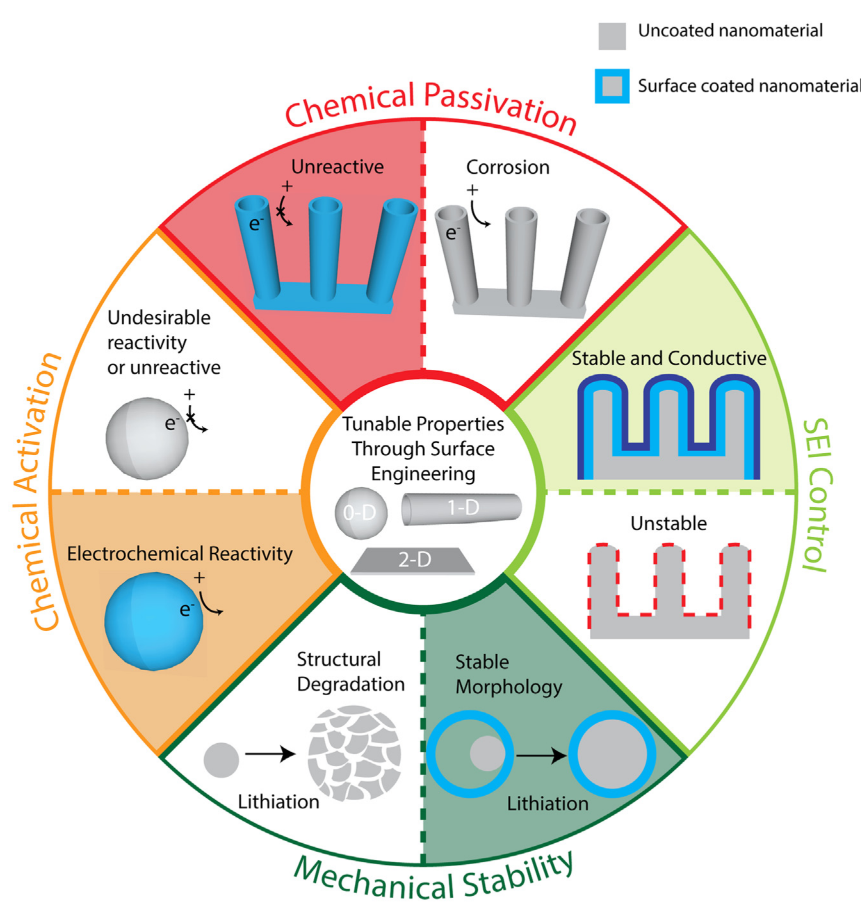

Fig. 1. Schematic representing the different properties of nanostructures that can be controlled through surface engineering.