Hierarchical Structure of Transition Metal-based Semiconductors for Energy related Applications

Abstract

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Nanoscience and nanotechnology have emerged as the most promising field of research for the development of our society. Nanotechnology has become an extensively researched topic in various scientific domains, including physics, chemistry, biology, and engineering. The rapid pace of technological progress has inspired people to innovate and create technical solutions that are not only environmentally friendly but also cost-effective to fulfill their daily requirements. Nanomaterials have emerged as a solution to meet these demands due to their small size and improved physical properties as a result of their reduced dimensions. The physical properties of nanomaterials have been found to be significantly different and exciting from their bulk counterparts, primarily owing to the effect of quantum confinement. The electronic energy levels in nanomaterials are not continuous like they are in bulk materials. Instead, they are finite and discrete due to the electronic wave function being confined to the physical dimensions of the particles. Hence, the application potential of nanoscience and nanotechnology has significantly impacted optoelectronic devices, energy harvesting and storage devices, energy conversion devices, and more. Further, nanotechnology offers several advantages due to its ability to customize material structures at extremely small scales to meet specific requirements. This significantly expands the toolkit of materials science by enabling the creation of stronger, lighter, and more durable materials with improved reactivity, sieve-like properties, and better electrical conductivity, among other features.

The synthesis protocol of nanomaterials is the key aspect for extracting the highest performance from the pristine materials. Until now, many synthesis processes have been employed to modulate the size and morphology. Much effort has been put worldwide to innovate and improve the synthesis techniques, but still, the pristine materials suffer from shortcomings like poor electrical conductivity, agglomeration, etc. Here comes into play the hybrid or hierarchical nanostructures whose realization can mitigate all the individual shortcomings of the constituents and result in novel interface phenomena.

In the recent developments of nanoscience and nanotechnology, hierarchical nanostructure, an integrated architecture with a higher assembly-level of constituents using low dimensional nano-building blocks (viz. nanoparticles, nanorods, nanowires, nanotubes and nanosheets, etc.), has drawn a lot of interest. The organized hierarchy of nanostructures may provide several advantages like increased active sites, synergistic effects due to the variety in their building blocks and geometric complexity, and multifunctional features. Hierarchical nanostructures possess remarkable characteristics that enable the development of advanced catalysts, highly responsive sensors, and exceptional adsorption materials, which can be utilized in various technological applications.

Humankind is now facing serious energy and environmental difficulties due to the depletion of fossil fuel reserves and the conspicuous environmental degradation they cause. Hence, clean, sustainable energy generation, storage, and its use have become a significant issue for the twenty-first century, and both academic and industrial domains are paying more and more attention to this subject. This issue further promises a spectacular opportunity to achieve the idea of rebuilding energy-supplying systems that can work indefinitely and without causing pollution. The realization of cutting-edge functional materials is essential for the production, storage, and consumption of energy. The field of energy has completely changed as a result of the development of nanotechnology and the fabrication of nanodevices. Hierarchical nanostructures are regarded as exceptional candidates as they can exhibit superior qualities to ordinary nanomaterials. Multicomponent hierarchical nanostructures are ideal for energy applications in fuel cells, supercapacitors (SCs), solar cells, and other devices due to their improved electrocatalytic performance, high

energy density, high flexibility, quick charge-discharge capability, specific capacitance, and prolonged cycle life, etc. These exceptional features can further be enhanced by modulating the smart design and structure.

For the past few decades, various transition metal-based semiconductors, such as RuO_2, MnO_2, Co_3O_4, NiO, and CuO, etc., have been extensively investigated as electrode materials for SCs and electrochemical water splitting as discussed in the introduction section. Transition metal-based materials can demonstrate superior electrochemical activity compared to carbonaceous (carbon-based) materials and conducting polymers. In order to enhance the electrochemical performance of the electrode materials further, the energy research community is currently focusing on hierarchically nanostructured transition metal-based compounds. Such materials have gained popularity due to their ability to offer numerous electroactive sites that can be accessed for redox reactions. Additionally, the hierarchical nanostructure helps to shorten the ion diffusion pathway.

The primary objective of this thesis is to concentrate on the engineering of hierarchical nanostructures of transition metal-based compounds that aim to provide a range of sustainable energy and device applications. Besides chemical synthesis and integration techniques, the potential use of hierarchical nanostructures in energy generation and storage devices has been studied. In this regard, flake-like nanostructures of $CuCo_2O_4$ were synthesized on flexible carbon fabric through a hydrothermal approach. The secondary growth of MnO_2 surrounding $CuCo_2O_4$ nanoflakes was realized further to get $CuCo_2O_4$@MnO_2 hierarchy on carbon fabric. A well-optimized $CuCo_2O_4$@MnO_2 hierarchy was used as electrode materials for SC. The electrode demonstrated a high specific capacitance of 1458 F g^{-1} at a current density of 0.5 A g^{-1} in 1 M KOH electrolyte, along with excellent cyclic stability. This result is almost two-fold higher than that offered by the pristine $CuCo_2O_4$ electrode. The $CuCo_2O_4$@MnO_2 electrode was further devised to realize a flexible solid-state symmetric supercapacitor device, which offered a specific capacitance of 181.3 F g^{-1} at 2.8 A g^{-1} and a high energy density of 64.1 Wh kg^{-1} at a power density of 1.5 kW kg^{-1}. Besides, this symmetric supercapacitor device sustained a wide potential window of 1.6 V. The Symmetric supercapacitor device successfully managed to drive a number of electronic gadgets like different colored LEDs, a motor fan, a digital clock, etc.

Further, a hierarchy of nitrogen-doped carbon hollow spheres and MoS_2 (NC@MoS_2) was realized, and electrocatalytic hydrogen evolution activity (HER) was investigated. The optimized NC@$MoS_2$1100 electrode showed excellent HER activity with a low onset overpotential of 9 mV and an overpotential of 145 mV at a current density of -10 mA cm^{-2}. It also demonstrated a low Tafel slope of 39 mV dec^{-1} and excellent chronoamperometric stability.

A TiO_2@MoS_2 core@shell hierarchy was also realized and used as an electrode material for SC. This TiO_2@MoS_2 hybrid showed a specific capacitance of 152.2 F g^{-1} at 0.1 A g^{-1}, which was found to be 30-fold higher than pristine TiO_2 spheres.

Thus, this thesis highlights the importance of morphology engineering in hierarchical nanostructures of transition metal-based semiconductors to enhance electrochemical performance. The insights gained from this research may inspire future researchers to develop innovative ideas for the evolution of sustainable energy technology.

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