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Flower-like nanoarchitecture assembled from Bi_2S_3 nanorod/MoS_2 nanosheet heterostructures for high-performance supercapacitor electrodes

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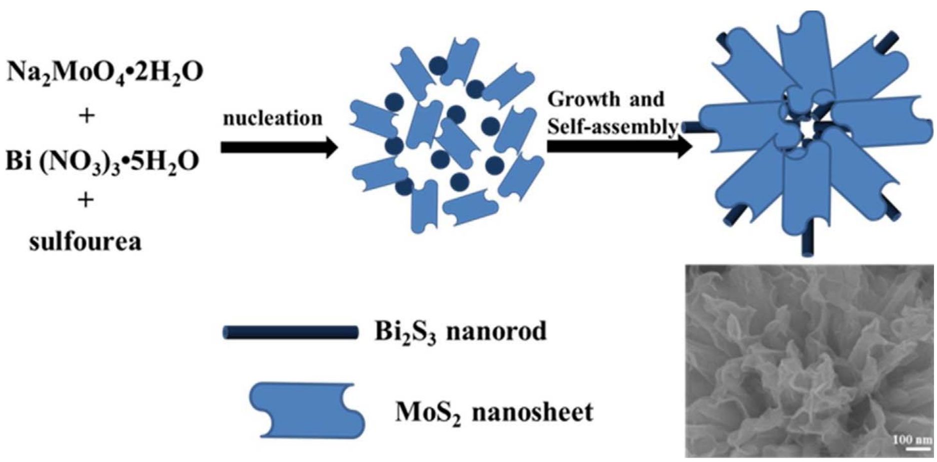
GRAPHICAL ABSTRACT

Flower-like Bi_2S_3/MoS_2 nanohybrids with high-quality heterostructures and three-dimensional asile exhibit a remarkable electrochemical performance for supercapacitors.



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ABSTRACT

Three-dimensional (3D) flower-like Bi_2S_3/MoS_2 nanohybrid is synthesized using a facile one-pot hydrothermal method. In the nanohybrid, MoS_2 nanosheet is tightly attached to the surface of the Bi_2S_3 nanorod to form a superior heterointerface, facilitating the electron transfer. Three-dimensional nanoarchitecture gives rise to large spaces and voids, fastening the ion diffuse. With the unique structural features of high-quality heterostructures and 3D aisles, the as-prepared flower-like Bi_2S_3/MoS_2 nanohybrid exhibit excellent electrochemical performance with a high specific capacitance of 3040 F g^{-1}, a remarkable rate capability (1258 F g^{-1} at a current density of 30 A g^{-1}), and an outstanding cycle stability (92.65% capacitance retention after 5000 cycles at 10 A g^{-1}). These promising results bring a new strategy to design advanced electrode materials for high-performance supercapacitors.

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1. Introduction

The continual increase in the global human population and the rapid development of industrialization are accelerating environmental pollution and the depletion of fossil fuels, which are increasingly serious issues. The vigorous development of clean and renewable energies sources (such as solar, wind, tidal power) has become extremely urgent. With this development, an important factor is energy conversion and storage technologies, which are critical for fully utilizing sustainable energy sources. Meanwhile, fast-growing applications in portable electronic devices and hybrid electric vehicles have made it essential to develop high-efficiency electrical energy storage (EES) devices. Supercapacitors have been considered as one of the most promising candidates owing to various desirable properties, including high power density, fast charge-discharge characteristics, excellent cycle stability and low maintenance cost [1,2]. According to different charge storage mechanisms, there are two main types of supercapacitors: (a) the electrochemical double layer capacitors (EDLCs), which store charges via reversible ion adsorption and desorption at the electrode/electrolyte interface, and (b) pseudocapacitors, which store their charges via reversible faradic reaction occurring at the surface of the electrode materials [3,4]. Among the potential electrode materials, transition metal sulfides (TMDs) have attracted substantial attention because of their intrinsic properties, including rich redox sites, high theoretical capacitance and earth-abundancy [5–8]. Molybdenum dichalcogenides (MoS_2) have a typical layered structure. In each layer, sublayers of Mo in a hexagonal array are sandwiched between S to form the S-Mo-S layer, where Mo atoms and S atoms within the sublayers are bonded covalently. S-Mo-S layers are vertically stacked through weak van der Waals interaction, which allows bulk MoS_2 to be easily exfoliated to 2D, atomically thin nanosheets [9]. Nanosheet structures not only greatly increase the utilization of active materials but also significantly shorten electronic and ionic transfer paths, and thus lead to an enhanced electrochemical performance [10]. Meanwhile, layered MoS_2 can deliver a relatively very high theoretical specific capacitance, so it has been widely explored in energy conversion and storage and has been suggested as a promising electrode material for supercapacitors [11–13]. However, with its poor conductivity, the MoS_2 as an electrode material suffers from low energy density and unfavorable cycling stability. In addition, 2D MoS_2 nanosheet is prone to re-stacking and aggregation, which would greatly reduce its predominant performances in practical applications. To address these issues, various strategies have been developed to improve the electrochemical performance, such as combining MoS_2 with conductive matrix materials (*e.g.,* conducting carbonaceous materials and conducting polymers) to enhance the conductivity [14–16], and tuning the morphologies to various three-dimensional (3D) nanoarchitectures to improve the reaction activity and stability [17–19]. Despite significant progress, the advantageous electrochemical performance of MoS_2 is still not fully realized, which spurs further development and investigation to advanced MoS_2-based electrode materials for supercapacitors.

In recent years, heterostructures materials with various geometrical and energy band alignments usually exhibit new fascinating properties compared with their constituent materials because the high-quality heterointerface can realize efficient electron-hole separation, and thus facilitating fast charge transfer [20,21]. They have been considered as promising candidates with practical significance in various applications such as tunneling transistors, photocatalysts, memory devices and ultrathin photodetectors [22–25]. Heterostructures materials have opened up new domains in materials science, device physics and engineering. Presently, heterostructures are based mainly on TiO_2, ZnO, SnO_2, CeO_2, and Ag_3VO_4 and there has been little research based on metal sulfides [26]. In fact, transition metal sulfides are more appropriate in terms of the band gap, cost, stability, toxicity, and catalytic efficiency compared to the abovementioned heterostructures [26]. Creating heterostructures between proper transition metal sulfide semiconductors can promote spatial charge separation, improve electrical conductivity through band engineering, and bring the synergistic effects between the two components, thus leading to significantly improved electrochemical performances [27]. There are several studies focusing on the development of transition metal sulfides based heterostructures to improve the capacitance behavior and increase the charge efficiency. These nanohybrids have exhibited excellent pseudocapacitive behavior. For example, Luo et al. [28], designed and synthesized Ni_3S_4-MoS_2 heterojunction by a convenient, self-assembly, ionic liquid-assisted method, which is demonstrated to have a relatively high specific capacitance of 985.21 $F\ g^{-1}$ at a current density of 1 $A\ g^{-1}$ and excellent cycle stability. Wang et al.'s [29], work demonstrates the general and targeted synthesis of hybrid heterostructures by the integration of porous transitionmetal oxides (TMOs, e.g. NiO, Co_3O_4 and Fe_2O_3) and 2D MoS_2 nanosheets. The as-prepared hybrids exhibit an excellent pseudocapacitive performance, such as a high specific capacitance and long cycling durability due to a favorable synergistic effect. Ansari et al. [26], reported that three-dimensional flower-like SnS_2 was grown on a g-C_3N_4 sheet by a facile solvothermal process and the SnS_2-g-C_3N_4 heterostructure exhibited superior electrochemical performance with a higher specific capacitance and cycling stability than those of the bare materials. Good quality heterostructures can be fabricated by heteroepitaxial growth between various kinds of materials ranging from one-dimensional (1D) to three-dimensional (3D) ones as constituents even under the existence of large mismatch so long as the interface between constituent materials has Van der Waals nature and does not form direct chemical bonds [30]. The heteroepitaxy means the epitaxial growth of one crystal on the surface of another crystal, which is the most frequently used, and most important and effective approach to construct heterostructures with controlled orientation and morphology [31–33]. Bismuth sulfide (Bi_2S_3), another important transition metal sulfide with a narrow direct band gap of 1.3 eV, has attracted intensive attention because of its potential application in diverse fields, such as optics, electrochemical hydrogen storage, photocatalysis, magnetics, lithium ion batteries, and biomolecular detection [34–36]. 2D MoS_2 nanosheet and 1D Bi_2S_3 nanorod have no dangling bonds on their surface. Thus, a high-quality heterointerface can be formed between MoS_2 nanosheet and Bi_2S_3 nanorod via Van der Waals epitaxy growth. In addition, the morphology and microstructure also strongly influence the electrochemical performance of the electrode materials in supercapacitors. Hybrid materials with three-dimensional (3D) porous architectures have received more attention because of their increased exposed active sites and short ion diffusion path lengths [17–19,37–39].

In this work, based on the above discussions, we design and synthesize a 3D flower-like nanoarchitecture assembled from Bi_2S_3 nanorod/MoS_2 nanosheet heterostructures (flower-like Bi_2S_3/MoS_2 nanohybrid). Owing to the following advantages: (i) the 2D super thin nanosheets structure of MoS_2 greatly increase the active sites for increased reactions, as well as shorten the electronic and ionic transfer paths; (ii) the heterointerface improves the electronic conduction; (iii) the 3D porous structure not only facilitates ion transfer but also preserves the mechanical integrity during prolonged charging/discharging, the as-prepared flower-like Bi_2S_3/MoS_2 nanohybrid exhibit a prominent electrochemical performance. As electrode materials for supercapacitors, the specific capacitance reaches 3040 $F\ g^{-1}$ at a current density of 1 $A\ g^{-1}$, and the capacitance remains at 1258 $F\ g^{-1}$ when the current density is increased up to 30 $A\ g^{-1}$. The retained capacitance of the as-prepared flower-like Bi_2S_3/MoS_2 heterostructure is maintained up to 92.8% at 10 $A\ g^{-1}$ after 5000 cycles, showing excellent cycling stability. All these results demonstrate the potential application of the as-prepared flower-like Bi_2S_3/MoS_2 nanohybrid in high energy storage systems. This work also develops a simple and fast method to fabricate transition metal sulfide heterostructures with a novel 3D architecture, not only for advanced energy storage applications but for other fields, such as photocatalysis, electrocatalysis, etc.