

A Review: Application of Nanomaterials in New Energy Batteries

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Abstract: The advancement of nanomaterials is propelled by technological progress, multidisciplinary studies, and the practical requirements for application, backed robustly by governmental and industrial entities. Nanomaterials exhibit great potential in sectors like electronic devices, information technology, energy, the environment, and biomedical studies. This article examines how nanomaterials can be utilized in the development of new energy batteries. The current market has extensively utilized lithium-ion batteries, but they face issues such as cost, resource limitations, and safety concerns. These challenges have driven scientists to research alternative new energy batteries, such as lithium-sulfur batteries. Nanomaterials, with their unique properties and various classifications, have the potential to improve the efficiency of novel energy batteries and propel the progression of renewable energy. The article details the progress of nanomaterials in battery separators, electrodes, and other areas, addresses some of the challenges faced, and provides an outlook for the future.

Keywords: Nanomaterials, New Energy Batteries, Lithium-Ion Batteries, Lithium-Sulfur Batteries

1. Introduction

Secondary batteries are also called rechargeable batteries. It differs from primary batteries. The recyclability of secondary batteries makes them highly favored by the public [1]. There is a diverse array of secondary battery types. Lithium-ion batteries (LIBs) represent a fairly prevalent variety of secondary batteries in today's market [2-4]. Since its inception in 1990, due to its long life cycle, the product rapidly entered the commercial market and reached commercial levels. This is extensively employed in areas including electric vehicles and mobile electronics, with its development potential being highly extensive. Despite efforts, lithium-ion batteries continue to encounter numerous challenges, including elevated prices, a scarcity of lithium resources, and a lack of adequate safety measures. Such issues have significantly hindered its continued advancement. Conversely, sulfur's affordability and plentiful reserves have garnered interest from both domestic and international experts and academics [5-7]. Aiming for advancement in the innovative, high-energy density battery system, numerous scientists dedicate themselves entirely to advancing and researching lithium-sulfur battery technology to address the demands of extensive energy storage and power batteries, thus tackling the progressively serious issues of ecological harm and energy shortages [8-9].

Nanomaterials refer to solid materials with characteristic sizes at the nanometer scale (1 - 100nm), or materials composed of these as basic units. That is to say, materials of this size at the nanometer level are called nanomaterials [10,11]. Nanomaterials themselves have unique features that help them exhibit unique properties in terms of optical properties, magnetism and chemical reactivity. According to the geometric structure of nanomaterials, nanomaterials can be divided into zero-dimensional (0D) nanomaterials with nanoscale structures in all three dimensions, one-dimensional (1D) nanomaterials with a fiber structure, two-dimensional (2D) nanomaterials with nanoscale in the thickness direction, and three-dimensional (3D) nanomaterials with at least one dimension at 1 - 100nm. According to the difference in materials, they can also be divided into metal nanomaterials, inorganic nanomaterials and organic nanomaterials. According to the different uses of nanomaterials, nanomaterials can also be divided into functional nanomaterials and structural nanomaterials [12-17].

Utilizing nanomaterials can enhance the efficiency of new energy batteries, thus hastening the replacement of conventional fossil energies. In response to the escalating worldwide need for clean energy, the development of effective new energy batteries becomes crucial for transforming the energy structure. The use of nanomaterials can enhance the energy, power, and lifespan of batteries, enabling extensive energy storage capacity.

This paper delves into the use of nanomaterials in innovative energy batteries via a review approach. It specifically details the advancements in research on lithium-sulfur batteries, photoelectrochemical cells, and lithium-ion battery separators, among others, and examines the characteristics and roles of associated nanomaterials. The study offers a guideline on employing nanomaterials in the development of innovative energy batteries, aiding in the advancement of this domain. Investigating the effectiveness and function of varied nanomaterials in battery development offers valuable insights and direction for crafting new, more dependable and potent energy batteries. It contributes to fresh concepts and guidance in addressing issues related to energy and the environment.

2. Overview

2.1. Lithium-sulfur batteries

Kim et al. developed a highly effective BN-carbon separator multifunctional membrane that can efficiently inhibit the shuttle of polysulfides (PSs), resulting in an impressive electrochemical performance for Li-S batteries (Figure 1a-c). The separator is composed of boron nitride layers combined with carbon layers, leading to high Coulombic efficiency, long cycle life, and stable capacity.

Fan et al. developed a multifunctional separator. Let commercial Celgard separators integrate with Functionalized BN nanosheets (BNNSs) which had negatively charged groups (Figure 1d-f). The resulting separator effectively eliminates the shuttle effect, enhances electron transfer speed, and increases Li^+ diffusion rate, achieving high electrochemical performance.

The pure BNNT separator developed by Kim et al. promotes ion transfer, mitigates the cathode shuttle effect, and protects the lithium metal anode from forming dendrite, resulting in superior performance for Li-S batteries. By incorporating an appropriate amount of purified BNNT to modify traditional polypropylene (PP) separators and forming a three-dimensional (3D) spider-web-like structure with one-dimensional (1D) purified BNNT randomly stacked on the PP separator, the modified separator shows significantly better conductivity of ionic and diffusion coefficient compared to the PP separator.

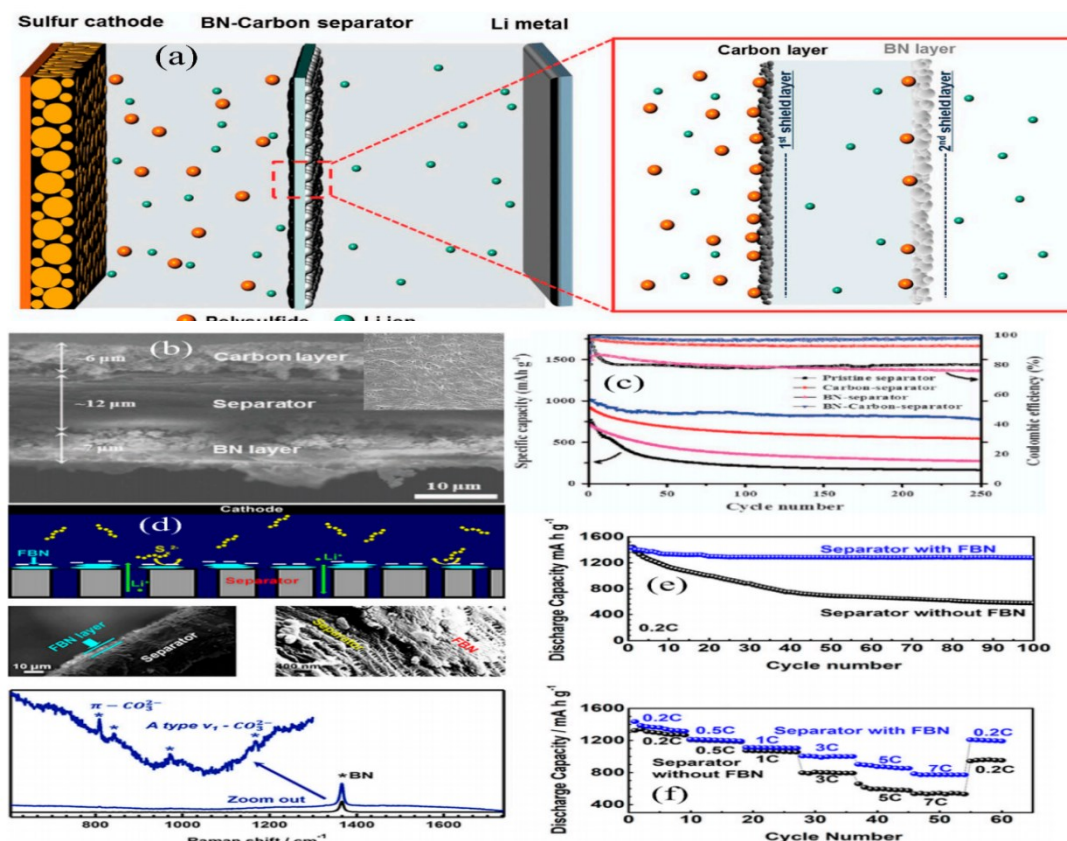


Figure 1: The performance of lithium-sulfur batteries

In Figure 1, (a) is the diagrammatic depiction of the role of the BN-carbon separator in the cycling process, (b) is the scanning Electron Microscopy (SEM) depiction (depicting carbon, separator, and BN layers, with the inset revealing an unaltered separator), (c) shows the comparison of electrochemical efficiency at 0.5C across various separators, (d) is the diagrammatic representation of the Li-S cell made using FBN separator, SEM visuals (cross-sectional view of the coating layer and FBN separator surface), along with the Raman spectrum of FBN nanosheets, (e) illustrates the conducting of a cyclic examination of two cells, both with and without the FBN separator, at a temperature of 0.2C for a maximum of 100 cycles, and (f) is for evaluating the performance rate of the cells, both in the presence and absence of FBN..

2.2. Photoelectric chemical cell

A photoelectric chemical cell converts light energy into electrical energy without resulting in any net chemical changes [18] (Figure 2). As photons possessing energy surpassing the bandgap create electron-hole pairs, Negative charge carriers move across the semiconductor material in the direction of the current collectors and the external circuit [18]. Positive holes ascend to the surface where the diminished state of redox mediator molecules (R) neutralizes them, converting them into oxygen through the reaction: $h^+ + R \rightarrow O$ [18]. Electrons from the external circuit subsequently revert the oxidized O back to R. Presented here are intriguing instances of one-dimensional nanomaterials utilized in photoelectrochemical cells.

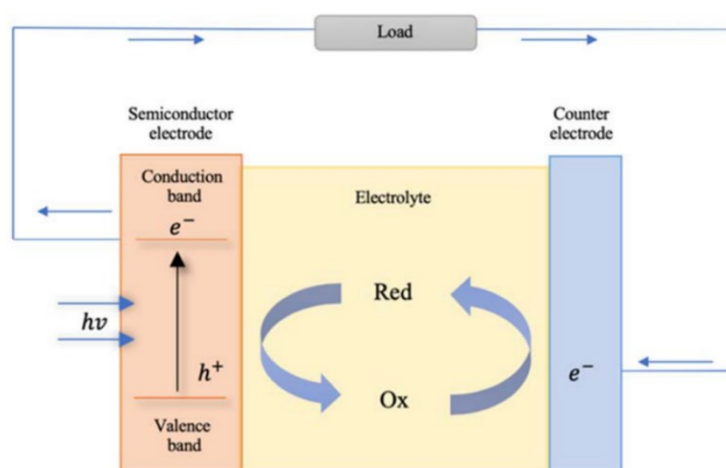


Figure 2: Schematic of a photoelectrochemical cell

Over the past five years, one-dimensional materials (Figure 3) have made significant progress in energy applications. For instance, $\text{Bi}_2\text{O}_3/\text{BiAl}$ oxide nanowire (NWs) arrays (Figure 3) have been shown to significantly enhance photoelectrochemical (PEC) performance, achieving a hydrogen production rate of up to $696 \mu\text{mol cm}^{-2}$ with 93% Faradaic efficiency[19]. CuO nanowire photoelectrodes, prepared via a hydrothermal method, exhibit a photoelectric current of approximately 1.4 mA cm^{-2} under AM 1.5G illumination, which is among the highest photoelectric currents for bare CuO photoelectrodes[20]. Hydrogenated TiO_2/ZnO heterojunction nanorod arrays show a photoelectric current density close to 2.5 mA cm^{-2} in PEC energy applications, demonstrating their potential as PEC cells[21]. ZnO/CdS nanotube arrays, altered with gold (Au) nanoparticles (ZnO/CdS/Au NTAs), demonstrate a photoelectric current density of 21.53 mA/cm^2 at 1.2 V (compared to Ag/AgCl), and a light conversion efficiency (PCE) of 3.45% when exposed to visible light ($\lambda > 420 \text{ nm}$)[22].

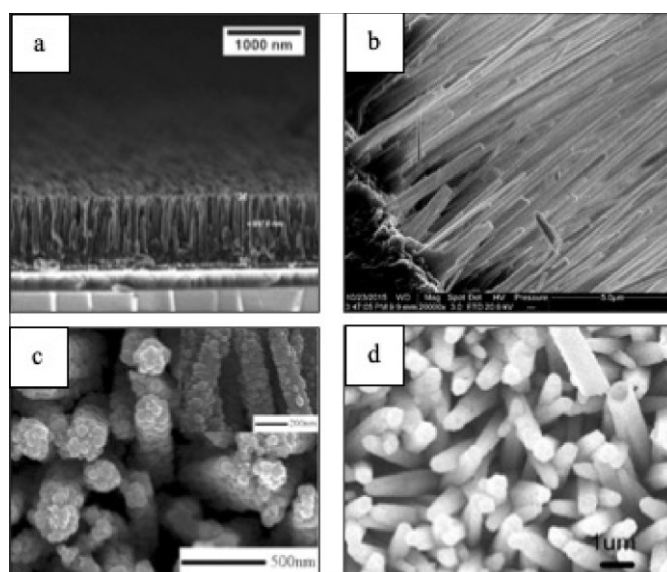


Figure 3: SEM characterizations

Figure 3 shows the SEM characterizations of (a) Bi:Al 21:1 photocathode, (b) CuO NWs, (c) Hydro-genated TiO₂/ZnO heterojunction (TZ10-H), and (d) ZnO/CdS/Au NTAs [19-22].

One-dimensional materials (Figure 4) are also integrated into PEC cells for sensing applications [23-26]. For instance, the Au-NiO_{1-x} ($0 < x < 1$) composite nanowire arrays serving as glucose detectors, which exhibit an exceptionally high sensitivity of $4.061 \text{ mA cm}^{-2} \text{ mM}^{-1}$, featuring a minimal detection threshold and an extensive glucose concentration detection spectrum from 0.005 to 15 mM [23].

Additionally, TiO₂ nanowires synthesized via a sol-gel template method exhibit practicality for hydrazine photoelectrochemical sensors, with a detection limit (LOD) of $1.91 \text{ }\mu\text{M}$ and a quantification limit (LOQ) of 8.91 mM [24]. Advanced anatase-branch@hydrogenated rutile TiO₂ nanorods act to detect chemical oxygen demand (COD) in wastewater, featuring a detection limit of 0.2 ppm and a broad linear detection range from 1.25 to 576 ppm [25]. Sensors for Gallic acid propyl ester PEC, utilizing zinc oxide nanorods and molybdenum disulfide flakes, exhibit a broad linear spectrum, spanning from $1.25 \times 10^{-7} \text{ mol L}^{-1}$ to $1.47 \times 10^{-3} \text{ mol L}^{-1}$, and can detect quantities down to $1.2 \times 10^{-8} \text{ mol L}^{-1}$ [26].

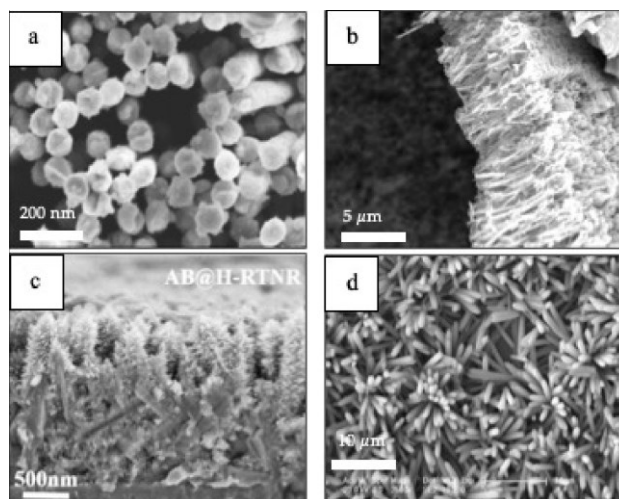


Figure 4: one-dimensional materials

Figure 4 illustrates some one-dimensional materials such as (a) Au-NiO_{1-x} ($0 < x < 1$) hybrid nanowire arrays, (b) TiO₂ nanowires, (c) anatase-branch@hydrogenated rutile nanorod TiO₂, and (d) ZnO nanorods and MoS₂ flakes [26]

2.3. Lithium-ion battery separator

In 2015, Luo et al. improved a commercial separator by applying a thermally conductive boron nitride nanosheet (BNNS) coating. The analysis revealed that the BNNS separator exhibited excellent compatibility with organic carbonate-based electrolytes, achieving an impressive coulombic efficiency of 92%, compared to just 88% for the original separator under the same conditions. Rahman and his colleagues introduced a long, thin boron nitride nanotube (BNNT)-based separator, which enhanced traditional polyolefin separators (Figure 5a-g). Employing elongated, slender BNNTs in this research guaranteed that the Li⁺ ion diffusion pathways within the separator remained unobstructed, which is crucial for high-performance separators. BNNTs also demonstrated outstanding thermal conductivity and flame retardancy. These properties indicate that BNNTs are exceptionally well-suited inorganic nanomaterials compared to others, capable of effectively

upgrading traditional separators to ensure stable operation under harsh conditions. The BNNT separator exhibited excellent thermal stability at 150°C, ensuring stable operation of LIBs in high-temperature environments. $\text{LiFePO}_4/\text{Li}$ batteries made with this BNNT separator showed satisfactory performance under different electrical current densities and higher temperatures (50°C and 70°C). Under conditions of elevated temperature and current, the BNNT separator batteries functioned as usual (Figure 5f, g), this suggests the BNNT separator remains stable in harsh environments, owing to its capacity to soak up and disperse extra heat throughout its cycle. In contrast, commercial PP separators failed to operate reliably under similar testing conditions.

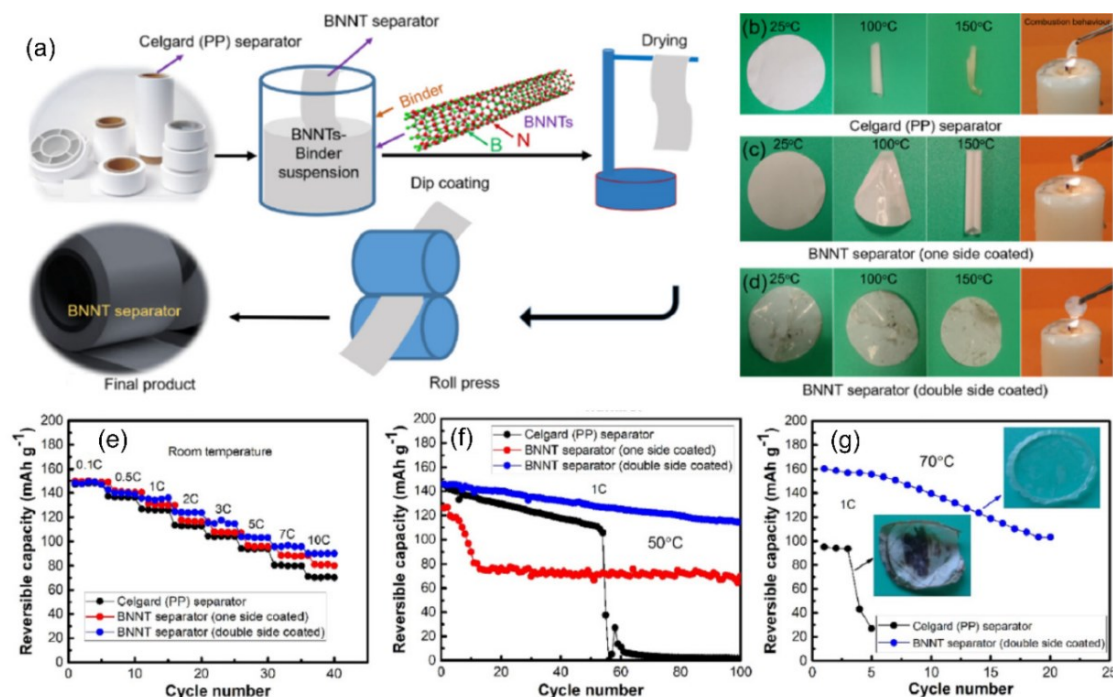


Figure 5: the BNNT separator batteries functions

Figure 5 illustrates (a) Diagrammatic representation of the production procedure for the BNNT separator, (b) Commercial separator (Celgard-PP), (c) A separator with one side coated in BNNT, (d) Dual-sided coated BNNT separator, (e) Assessing rate capabilities at diverse current densities, (f) Bicycling at a temperature of 50°C and 1C, and (g) Bicycling at a high temperature (70°C) with a temperature of 1C

Due to its natural insulating characteristics, Boron nitride (BN) cannot be used as an anode electrode in rechargeable batteries. However, various techniques and methods, such as creating vacancies, doping, introducing defects, and compositing, can make this material conductive [27-29]. In 2013, Lei et al. successfully created a few layers (ranging from 2 to 6 atomic layers) of carbon-infused boron nitride (BCNs) nanosheets and first applied them as an anode in lithium-ion batteries (LIBs) (Figure 6a-d) [29]. Surprisingly, this structure demonstrated significant potential for lithium-ion storage. Following 100 cycles, the achieved capacity reached 390 mAh g^{-1} with a current density of 30 mA g^{-1} . The material maintained a consistent capacity of approximately 100 mAh g^{-1} at 2 A g^{-1} , even following 5000 cycles. The research underscores the substantial advancements achieved in the application of boron nitride-based light element anode substances for secondary batteries. Reports also indicated the creation of a sheet-like anode, made from chemically bonded hexagonal boron

nitride (h-BN) and silicon carbonitride (SiCN), through pyrolysis, serving as a high-efficiency LIB anode (Figure 6e-g).

In contrast to market-available anodes like graphite, lithium titanate oxide (LTO) anodes exhibit multiple limitations, notably their diminished inherent electrical conductivity and a restricted range for electrochemical activity. Such constraints hinder their practical use. The integration of reduced graphene oxide (r-GO) has resolved numerous problems with LTO materials, yet this method continues to demonstrate swift capacity deterioration at elevated current densities (exceeding 5C) attributed to its substantial internal resistance. Lately, a successful technique integrating r-GO and boron nitride (h-BN) has been applied to develop a tri-dimensional structure of LTO (Figure 6h-k). The composite electrode of crafted LTO/r-GO/h-BN sustains its form steadiness even under intense current densities of 20C, showcasing standard charge-discharge graphs (Figure 6h). Relative to alternate electrode varieties, the LTO/r-GO/h-BN electrode exhibits enhanced capacity, improved stability, and superior performance in rate (see Figures 6i,j). Findings show the altered electrode (LTO/r-GO/h-BN) possesses reduced impedance relative to LTO and LTO/r-GO electrodes, hinting at enhanced ion movement efficiency via the LTO/r-GO/h-BN electrode (Figure 6k). The given framework enhances the efficiency in electron movement, the storage of Li^+ , and the diffusion of ions. For peak efficiency, the loading speed of h-BN is a vital element.

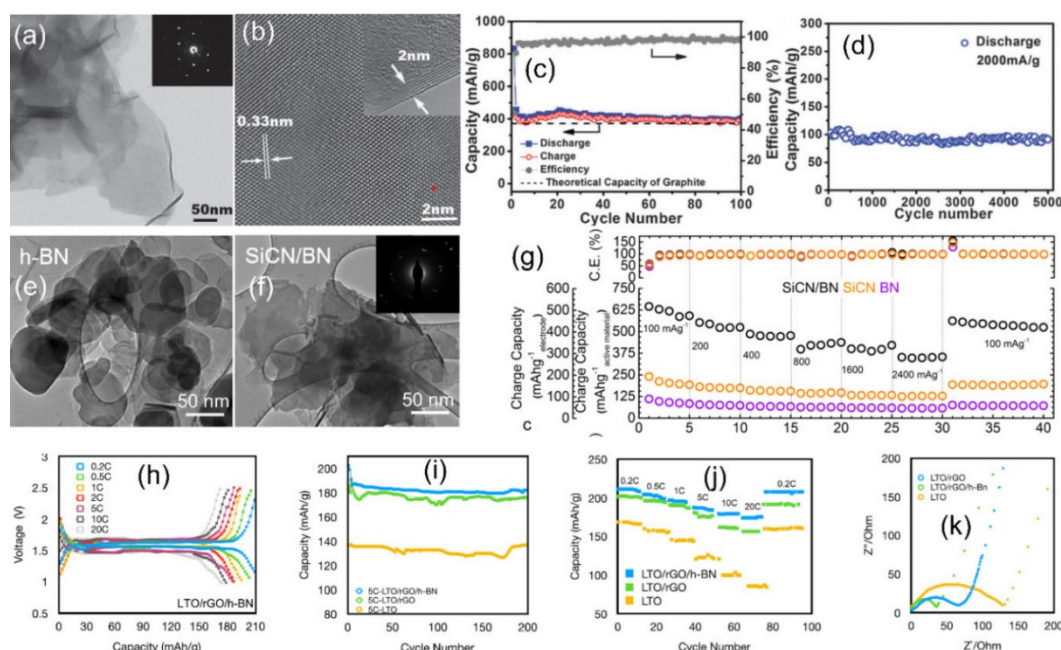


Figure 6: BCNs nanosheets as an anode in lithium-ion batteries

Figure 6 shows (a) The nanosheets' bright-field TEM imagery and SAED design (inset), (b) High-Resolution Transmission Electron Microscopy visuals of a nanosheet with a folded edge (inset), (c) Stability in cycling and Coulombic efficiency at a current of 30 mA g^{-1} over 100 cycles, (d) The cyclic efficiency of the BCN nanosheet electrode with a few layers at a current of 2 A g^{-1} , (e) Transmission Electron Microscopy depiction of the newly acquired BN sheets, (f) Synthetic SiCN/BN composite material in its original form (inset illustrates the SAED pattern), (g) Comparative analysis and performance in electrochemistry, (h) Graph depicting the charge-discharge relationship at varying speeds of LTO/r-GO/h-BN electrodes, (i) Evaluating the stability of cycling across various electrodes, (j) Evaluating rate capabilities across various electrodes, and (k) Analysis of electrochemical impedance.

3. Discussion

3.1. Utilizing Boron Nitride-Based Nanomaterials in Battery Tech

Presently, a limited number of synthesis methods exist for the mass production of diverse BN nanomaterials. Sophisticated synthesis techniques are essential for customizing BN materials for their immediate use as conductive nanomaterials in batteries. In Li-S batteries, the shuttle effect is considered a core issue, thus requiring advanced composite solid-state electrolytes development that with the desired properties to replace traditional liquid electrolytes. Meanwhile, conventional separators for LIBs/SIBs face challenges related to ion diffusion in extreme environments. The emergence of unstable SEI layers and the expansion of Li dendrites at the junction of Li anode and electrolyte pose major safety risks. To gain a deeper insight into interface chemistry, sophisticated techniques for characterization, both in-situ and ex-situ, are required. There is limited research on the BN materials using as anodes for LIBs/SIBs and as sulfur hosts in Li-S batteries. Developing sophisticated anodes and sulfur cathodes is essential by combining various BN nanomaterials with different conductive additives and high sulfur contents.

3.2. Photorechargeable Batteries

Key factors contributing to the inefficiency of photorechargeable batteries are the inadequate absorption of light by nanomaterials, considerable charge recombination, insufficient storage space, and low reversibility of cycles. Moreover, battery efficiency is affected by factors like the excessive potential of metal anodes, corrosion and passivation of polymer electrolytes (PE), and the light-triggered deterioration of organic substances. Enhancing battery efficiency can be achieved through methods like refining heterojunctions or nanostructures to minimize charge recombination, choosing n-type semiconductors, or altering the surface of active substances to boost charge storage capacity. From a morphological standpoint, one-dimensional nanostructures such as nanotubes, nanowires, or nanorods prove more advantageous in improving battery efficiency. Merging various nanostructures to create heterojunctions or nanocomposites can enhance overall performance. Moreover, the implementation of hole scavengers, applying anti-light-corrosion coatings, or investigating affordable nanomaterials can tackle the difficulties encountered by these batteries. There is currently a lack of standardized experimental conditions and characterization criteria for photorechargeable batteries, rendering the direct comparison of outcomes and the formulation of conclusions challenging. It is essential to establish relevant standards, encompassing efficiency in converting photo to electrical energy, round-trip performance, and the ability to charge and discharge.

Additionally, it's essential to confirm the properties of nanomaterials seen in half-cells when applied to entire cells. Emphasizing the importance of in-depth theoretical research on the matching of parameters like voltage, current, energy, and power are vital among various elements in storage systems. This approach aims to predict photobattery performance and facilitate rational design.

4. Conclusion

Despite the significance of boron nitride-based nanostructures in nanomaterials owing to their unique characteristics, their use in diverse energy storage systems is less common compared to other nanomaterials. The distinct features of BN-based nanomaterials, including their exceptional chemical, thermal, and mechanical robustness, along with their inherently superior insulating qualities, render them more suitable for the use in battery technology. As a result, even with the progress in employing nanostructured BN regarding battery technology, the research outcomes remain in their initial stages, yet they constitute a significant field of study. Advancing requires tackling various obstacles associated with synthesis, characteristics, and the use of batteries.

This research investigates the use of nanomaterials in innovative energy batteries, such as lithium-sulfur batteries, photoelectrochemical cells, lithium-ion battery separators, among others. However, it highlights certain shortcomings, including the inadequate methods of creating BN nanomaterials, the lack of adequate research on these in certain batteries, and the absence of uniform experimental setups and benchmarks for characterizing photorechargeable batteries. Moreover, studies on incorporating nanomaterials into new energy batteries are at a nascent phase, with multiple challenges in synthesis, properties, and battery application yet to be overcome.

Thinking about the development in the future, future generations of photobatteries will inevitably rely on nanostructured materials to achieve higher energy and photo-to-electric conversion efficiencies. Despite the ongoing difficulties in producing affordable, stable, and efficient photoelectrodes, expansion in this sector is anticipated to pave the way for feasible commercialization strategies.

With the continuous advancements in energy storage systems, especially in battery and capacitor technologies, autonomous energy storage has now been achieved, which is crucial for most of the devices we use daily. One-dimensional nanostructured materials have shown great promise in improving efficiency across all these applications and are poised to become key drivers in promoting sustainable human development.

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