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Nanotechnology applications in conventional lithium-ion batteries

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Abstract. Since the successful development of the first battery, it has prompted the development of the electronics industry. From only able to power small electronics, to powering fully electrical vehicles, battery technologies have developed to a promising extent, and has become ever more integral across many fields. However, conventional methods currently face challenges in improving battery performance to meet higher demands. The urgency of the issue calls for researcher to create innovate, new approaches to tackle the problem. The recent rise in nanotechnology research has prompted unique and practical solutions to some of battery technology's most major problems: low power and energy density. This article offers a comprehensive compilation and overview of recent advancements in nanotechnology applied to lithium-ion batteries and how these breakthroughs have effectively addressed critical challenges in enhancing battery performance. Emphasises in areas of nanotech research covered in this article includes silicon nanotechnology, carbon nanotechnology, and other innovative approaches to battery development.

Keywords: Lithium, Nanotechnology, Batteries.

1. Introduction

In the early 19th century, Alessandro Volta's invention of the voltaic pile, copper and zinc discs separated by cloth or cardboard soaked in brine, marked the beginning of battery technology. This pioneering creation ignited the curiosity of numerous researchers, captivating their interest in harnessing the electrochemical reaction's potential to generate a continuous voltage for power generation. However, initial explorations into practical applications revealed several formidable challenges. The first modelled battery's low power density, limited energy density, and poor cycle life rendered it ineffective for industrial adoption. In the most optimal conditions, batteries could only sustain rudimentary operations. It was until the discovery of lithium-ion batteries that a transformative shift transpired within the battery industry. This technology sought to take advantage of the high electrochemical activeness of lithium ions, which was thanks to the element being the third smallest element in the periodic table, to generate remarkable improvements in voltage and charge performance. The first ever experimented lithium-ion batteries showed to have high energy and power density, long cycle life, and relatively robust safety during testing [1].

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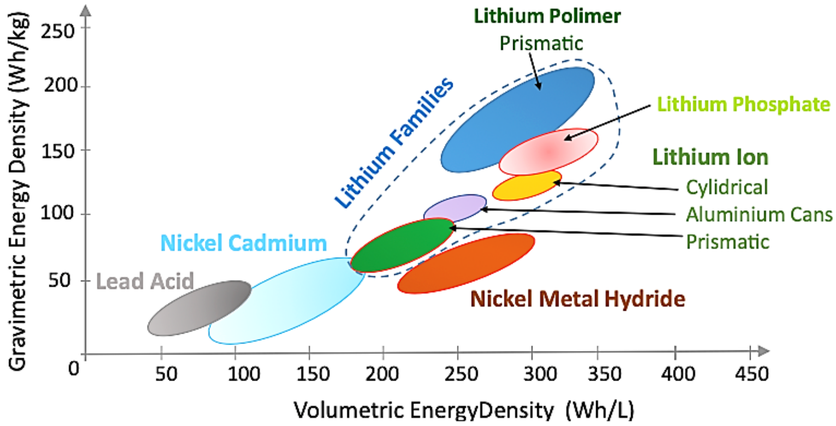

Figure 1. Energy density verses power density graph of various commercial batteries [2].

As shown in Figure 1, lithium-ion batteries achieved a ninefold increase in energy density and nearly tripled the power density in comparison to their conventional lead-acid predecessors [2]. This development allowed conventional batteries to undertake more intricate and energy-intensive tasks. However, to fully capitalize on the potential of lithium ions, commensurate advancements in anode, cathode, and electrolyte materials were required. Currently, in the market, graphite and silicon dioxide is the common material for anodes and lithium metal oxides for cathodes (Figure 2). Nevertheless, new inherent issues, such as uncontrollable lithium dendrite formation and subpar low-temperature performance, continue to restrain lithium-ion batteries performance. Furthermore, given the current speed of development in the battery and electrical vehicle industry, it is increasingly apparent that the current performance of the batteries are struggling to meet burgeoning demand [3].

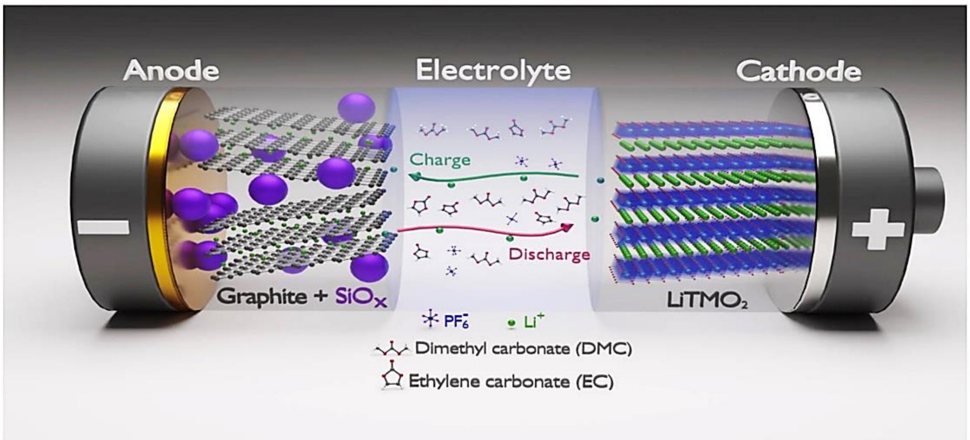

Figure 2. Schematic illustration of the internal structures of a typical battery and how the electrochemistry works [3].

Consequently, researchers are compelled to explore alternative solutions. In the recent decade, the development of nanotechnology has led to many innovative solutions across various fields, and the battery industry is among its primary beneficiaries. One major advantage nanotechnology provides is the increased contact surface area between materials thanks to the small particle size. For batteries, the increased surface area provides increased efficiency and flow, achieving a higher voltage performance. Additionally, nanotechnology allows researchers to better engineer interphases that separates the electrodes from the electrolytes, preventing the battery from short circuits and improving cell cycling life. In the recent half a century alone, there have been numerous different nanotechnology applications in batteries, each with its own unique approach to solving different problems. This comprehensive review delves into an array of nanotechnological approaches currently integrated into battery technology. Disciplines include various types of silicon technology such as silicon nanowires, and silicon nanoparticle coating; Various applications of carbon such as carbon nanotubes, and carbon nanofibers; and other nano-engineered battery technology.

2. Silicon Nanotechnology

Silicon, distinguished by its exceptional chemical properties in bonding, has garnered substantial attention within the battery industry. Being in the same group as carbon on the periodic table, silicon shares the ability of carbon: it can form giant covalent structures such as silicon dioxide (silica) and pure silicon. This structure gives silicon giant covalent structures a high boiling point and high tensile strength, which are 2 important properties of an anode. However, for a material to be an effective anode, it must also be an effective reducing agent and have good conductivity. As a semiconductor, Silicon itself has weak electrical conductivity, but it was found that it can be alloyed with lithium to form a lithium silicon complex, which allowed silicon to gain the conductivity of lithium. This discovery marked silicon complexes to be a promising anode candidate. Experimental assessments found that silicon complex batteries have a specific capacity of 3600 mAh/g, almost 10 times that of graphite batteries. Furthermore, silicon as an element is much safer and abundantly found than graphite, a costly and unstable material. However, despite decades of research integrating silicon into battery technologies since the 1970s, commercialization remains elusive. This is because of another unique property of silicon, volume expansion after charge. Experimental data reveal that silicon anodes may swell by up to more than 300% of their original volume upon discharge, severely constraining their cycling potential [4]. This long-term performance was worse than graphite batteries, placing silicon at a disadvantage.

Researchers looked at alternative approaches that investigated potentials in using silicon's volume expansion, such as decreasing ionic transport distances or unique insulating properties but found no promising results. Recent advancements in nanotechnology have reintroduced optimism among researchers regarding the incorporation of silicon into commercial lithium batteries. At the nanoscale, molecules take on a different chemical property compared to the macro scale. Notably, materials exhibit enhancements in mechanical strength due to increased surface area. Nanoscale silicon is a promising solution to volume expansion issues faced by previous researchers.

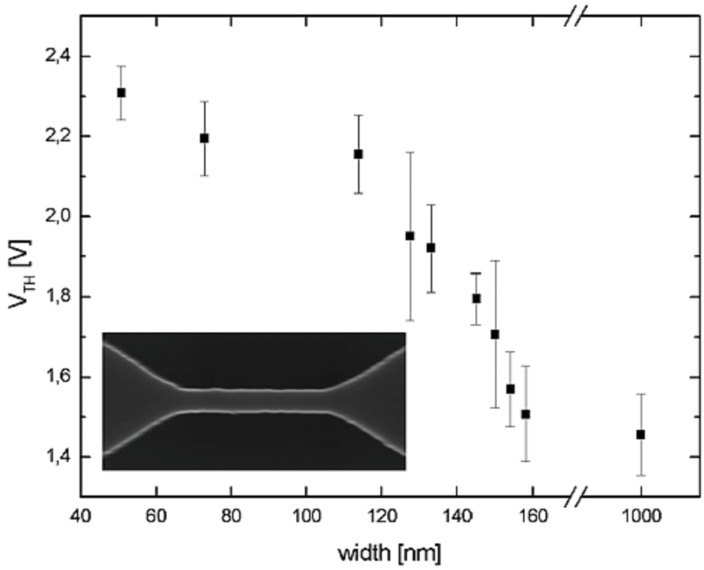

Figure 3. Threshold voltage verses widths of nanowire. Image of nanowire displayed on the bottom left of the graph [5].

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2.1. *Silicon nanowire*

Researchers chose to investigate silicon nanowires due to the research involved in silicon nanotubes, an analogous nanostructure but taking up a tube-like structure. The primary objective of research in silicon nanowires was to delve deeper into the nanoscale intricacies of silicon, specifically within the sub-50 nm range. At this length, quantum effects render silicon's conductive properties to be influenced by the local charge environment and the surface-induced field effect. This heightened sensitivity and conductivity offer considerable promise. One study conducted by Elfström and their team sought to investigate how the change in size of silicon nanowire is related to its sensitivity. The results revealed that as the size decreased, the threshold voltage correspondingly increased, indicative of an amplified surface charge effect and enhanced voltage response (Figure 3) [5]. It was also observed that silicon nanowires with dimensions below 150 nm lost this detection property entirely. Furthermore, another study looked at the Young's modulus and fracture strength of silicon nanowires and found that the former decreased while the latter increased when nanoparticle size decreased. When compared to silicon thin films, silicon nanowires exhibited a significantly higher rate of increase in fracture strength. This property is very important to silicon nanowires for being a potential anode material because when silicon swells during discharge, it cracks, compromising cycling performance [5].

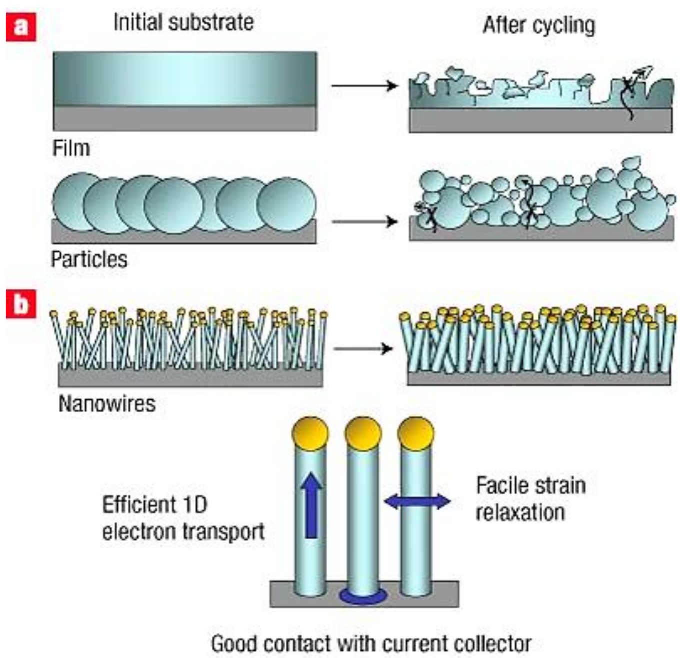

Figure 4. Illustration of structure of different nanostructure and how they are affected after cycling [6]. (a): Illustration of Common silicon substrate (film and particles) after charge. (b): Illustration of silicon nanowires after charge, further characterization of their individual structure and how they resist cracking.

A novel study conducted by Professor Cui at Stanford explored silicon nanowires and its application in batteries. Their investigation demonstrated the swelling behaviour of silicon nanowires during discharge and how this specific structure mitigated the propensity for cracking (Figure 4). Capitalizing on this structure's ability to accommodate silicon's expansion, the research group achieved remarkable results, obtaining data demonstrating the attainment of the theoretical maximum silicon capacity in the initial cycle, ranging from 3600 to 4000 mAh/g. Subsequent experimentation revealed a marked decrease in capacity of about 17%, which gave a coulombic efficiency of 90%. Fortunately, no further significant capacity degradation was observed over the subsequent ten cycles. To ensure sustained anode performance, Cui and the team evaluated the electron transport properties of silicon after cycling, revealing a resistance of only 8 MΩ, qualifying silicon nanowires' proficiency as conductors even after extended use [6]. The nanoscale dimensions of silicon nanowires have enabled comprehensive

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exploration of silicon's properties without succumbing to the challenges of swelling and cracking, establishing silicon nanowires as one promising materials for anode applications.

2.2. Silicon nanoparticle coating

Observing that nanoscale molecular structures greatly benefit silicon in its performance in batteries, there have been several other approaches in developing silicon nanostructures. One notable approach is silicon nanoparticle coatings. The theoretical idea of this approach revolves around decreasing the size of silicon to a thin-film coating that can be seamlessly applied to target surfaces. The result coating forms a net-like structure, giving it the name "silicon nanonet". In one study, researchers focused on the nanonet material $TiSi_2$ as a potential candidate as anode. In 100 cycles tested, the material demonstrated a stable specific capacity of 1000 mAh/g with a minimal 0.1% capacity fade per cycle and a fast charge/discharge rate of 8400 mA/g [7]. This meant that $TiSi_2$ did not perform as promisingly as silicon nanowires in terms of specific capacity, but its competitive advantage is that it has a higher charge/discharge rate and promising stability. While $TiSi_2$ may not represent the best silicon materials for battery anodes, its advantages should not be missed. Researchers were able to test out an effective $TiSi_2$ nanonet, and they found that the high charge and discharge rate allow $TiSi_2$ nanonets to be an efficient conductor. In photo-splitting H_2O and photo absorption techniques, the high charge and discharge rate of $TiSi_2$ nanonets allows the electrochemistry to be efficient while the setup to be lightweight and malleable. A study combined highly conductive $TiSi_2$ nanonets with a photoactive TiO_2 coating. They saw a peak conversion efficiency of 16.7%, accepting wavelengths from 300 nm~380 nm [8]. In conclusion, silicon nanoparticle coating is another interesting field of exploration for silicon nanostructures and potentially will extend its applications beyond the confines of the battery industry.

3. Carbon nanotechnology

Carbon, the 4th most abundant element on earth, plays a pivotal role in scientific exploration and technological advancement. Its extensive versatility arises from its diverse range of chemical properties, making it indispensable in various scientific disciplines. Its first known allotrope, the diamond structure, allowed carbon to be one of the best materials in terms of hardness and resistance to abrasion. In 1991, a seminal paper titled "Helical microtubules of graphitic carbon," authored by Iijima and colleagues, marked a pivotal moment in carbon research [9]. Iijima and colleagues discovered the carbon nanotubes (CNTs). CNTs is characterized by layers of carbon rings interlinked with one another, exhibiting notable electrical conductivity due to the presence of delocalized electrons within their carbon rings, a characteristic uncommon among covalently bonded carbon compounds. Subsequently, the identification of graphene, the fundamental constituent of CNTs, expanded research interest in nanoscale carbon allotropes. The common advantages shared by most carbon nanostructures are high mechanical tensile strength, lightweight, surface-to-volume ratio, and thermal conductivity. These properties underscore the significant role of carbon in advancing scientific understanding and making carbon a competitive material in battery technologies.

3.1. Carbon nanotubes (CNT)

There are many applications of CNTs in the battery, and one interesting application is to use CNTs to quench lithium dendritic formation. During discharge and charging cycles, the sudden formation of sharp, tendril-like lithium dendritic structures at the surface of the material causes punctures in the structures of the battery cell. These dendrite formations often lead to short-circuiting and poor cycling ability, and the formation mechanisms are still not well understood by researchers. This challenge poses a significant problem in the safety of lithium batteries, as these short circuits may lead to the battery's instant combustion. Only recently have researchers identified that this type of dendritic formation has a dependence on the battery's current level and flow. As battery technologies evolve towards materials with higher voltage capacities and accelerated charging rates, the issue of lithium dendrite formation has assumed greater prominence [10]. Due to the complexity of this phenomenon, researchers have instead tailored their focus to exploring alternative approaches to control lithium dendrites formation. One such

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approach is to quench lithium ions in CNT's lattice structure. In this approach, CNT acts as a harbour for the lithium dendrites, restricting the lithium dendrites to form predictably, thereby preventing short circuits. Researchers at Rice University investigated this approach and commented about how they have uniquely engineered the structure to prevent dendritic formation by making the nanotube film at as a harbour that could allow the lithium ions to diffuse in an orderly fashion. Their data demonstrated that the CNT structure implemented in their lithium-sulphur battery effectively quenched dendrite formation over 580 cycles, retaining 99.8 percent of the cell's coulomb potential [11].

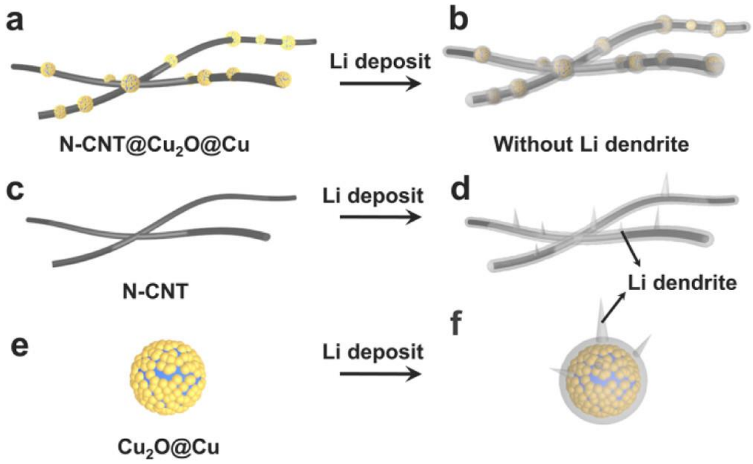

Figure 5. Schematic illustration of Li plating on various frameworks [12]. (a)&(b), Illustration of N-CNT@Cu_2O@Cu framework before and after charge, indicating no Li dendrite formation. (c)&(d): Illustration of pure N-CNT framework, indicating Li dendrite formation. (e)&(f): Illustration of Cu_2O@Cu particles, indicating dendrite formation.

Similarly, Zhang and their research team explored a 3D lithiophilic and conductive framework known as N-CNT@Cu_2O@Cu. This framework aimed to lower Li nucleation overpotential with its unique integrative material (Figure 5). From Figure 6., it can be observed that the capacity of the tested lithium battery overtime saw a lesser reduction in the N-CNT@Cu_2O@Cu framework compared to other methods tested, indicating minimal lithium loss during cycling and a reduction in dendrite formation [12]. Despite these compelling benefits and advancements, the incorporation of CNTs into the battery market remains elusive due to underlying health risks. As a nanoparticle, CNTs are easily absorbable by the human body and therefore pose inhalation and ingestion risks during manufacturing. This can potentially lead to a range of serious pulmonary diseases [13]. Consequently, while CNTs exhibit substantial potential, they grapple with real-world limitations that currently hinder their widespread adoption in the industry.

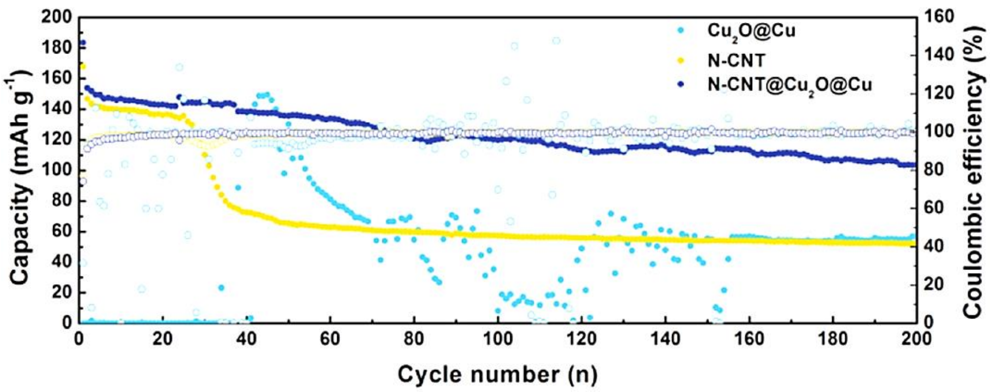

Figure 6. Capacity and Coulombic efficiency of tested Li battery over 200 cycles [12].

3.2. Carbon nanofibers (CNF)

Carbon nanofibers (CNF) are a class of CNT but with several unique properties. Unlike conventional CNTs with regular and even patterns, CNFs are structurally irregular CNTs where the graphene layers stack in uneven patterns, forming what is known as “graphene platelets” [14]. One of the standout properties of CNFs lies in their highly porous structure. Researchers at MIT investigated the incorporation of CNF into lithium-air batteries, a class of batteries designed to maximize the energy-storing capabilities of lithium oxide. The oxide is much lighter than conventional cathodes, therefore theoretically allowing more storage per unit weight. The researchers employed a chemical vapor deposition technique to engineer CNFs into a highly conductive, low-density scaffold. Through this methodology, they achieved a structure with over 90 percent void space, which is filled by reactive materials during battery operation. Experimental results demonstrated that the electrode could store the energy of four times its weight compared. Furthermore, researchers realized that although the structure is highly irregular, the irregularity appears in a relatively predictable pattern. This allowed them to conduct comprehensive observations, paving the way for in-depth investigations into the battery’s operational mechanisms and potential areas for improvement [15]. The porous structure of CNFs has also found application in one study on the sulfur cathode, where CNFs were used to capture polysulfides during cycling to enhance specific capacity and electrochemical cycling of the cell. The choice of CNFs in this context CNF stemmed from the small size of the structure, facilitating rapid diffusion within the cell. Results showed that with CNF incorporated into the battery structure, specific capacity doubled during cycling and maintained for 2 times longer than the battery structure without CNF [16]. Looking ahead, as nanotechnology continues to advance, there is a strong likelihood of further research into the integration of CNFs within battery technology, promising innovative solutions, and improvements in energy storage systems.

4. Other disciplines in battery nanotechnology

Lastly, this section aims to encompass some of the more unique breakthroughs of battery nanotechnology that introduce changes to conventional battery structures. These advancements represent significant strides in pushing the boundaries of nanotechnology, delivering innovative solutions and novel technologies to the forefront of energy storage.

4.1. Paintable batteries

In 2012, a ground-breaking development emerged from the laboratories of Rice University as researchers embarked on the journey to create paintable batteries. This innovative concept aimed to replicate the fundamental components of a battery, including the cathode, anode, separator, and current collectors, all within a paintable medium. Key constituents of this paint included lithium cobalt oxide as the main cathode material, lithium titanium oxide as the main anode material, and Kynar Flex resin as the separator material. The theoretical idea of this battery design was to layer each component paint so that it simulates the correct electrochemistry of a battery. When connected to a power generator, the battery should be able to store energy. The obvious advantage of such a design is the versatile application of the battery in any shape and environment. Therefore, the researcher’s first experiment with the paints was conducted on bathroom tiles to simulate the design operating in practical, real-world scenarios. In this initial experiment, the paintable battery was applied onto 9-bathroom tiles and, when fully charged, demonstrated the capacity to power a light for a continuous duration of six hours. The researchers at Rice noted that the primary challenge they encountered during this experimentation phase was achieving the right mechanical stability for the layers. Maintaining stability was crucial to preventing the cathode and anode layers from inadvertently fusing, which could lead to a short circuit. In their later trials, they found that adding PMMA (poly (methyl methacrylate)) gave them optimal stability [17]. Furthermore, the paintable batteries are also uniquely designed so that solar cells can easily charge the batteries. The clear advantage of paintable batteries is their freedom from energy density issues faced by conventional batteries. Their theoretical capacity is virtually unlimited, contingent upon the availability of a sufficiently large surface area to apply the battery components. On the other hand, the connection with

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solar technology could allow paintable batteries to make self-sustaining vehicles more efficient in their design. However, it's worth noting that challenges related to paint durability and corrosion resistance need to be addressed. Despite these challenges, paintable batteries represent a highly promising and versatile technology that has the potential to revolutionize the battery industry. Their adaptability to various shapes and sizes opens numerous possibilities for innovative applications.

4.2. Interdisciplinary applications across biomedical fields

One of nanotechnology's largest advantages is the nanoscale operations, which pose unique and new features in materials. Moving into the future of technology, electronics are assuming a central role in numerous fields of study. The integration of battery powered electronics into medical treatments holds the promise of enhancing the efficiency and effectiveness of many different types of treatment plans. The continued evolution of nanotechnology has been integral in driving rapid developments in this interdisciplinary field. One significant challenge in incorporating battery powered electronics into medical treatments has been the risk of infection and the body's natural tendency to reject foreign substances. This phenomenon is particularly apparent in past macro-scale operations. Nanoscale implantation offers a potential solution to mitigate these risks. While reducing the size alone doesn't eliminate the possibility of the body rejecting electronic components, it significantly decreases the contact area between the body and the device. This reduction in contact area allows for more effective control measures to minimize the body's rejection response. One example of a successful nanoscale biomedical implant is the cardiac pacemaker. These devices send electronic signals to regulate the heart's rhythm, ensuring it beats in a controlled and consistent manner. In recent years, researchers have developed high-performance inertia-driven triboelectric nanogenerators using nanotechnology. These nanogenerators, about the size of a commercial coin, are designed to harness body motion and gravity to generate power. This design allows it to be practically independent of charging, which will significantly reduce the complications of the procedure. A significant challenge in this project was creating a self-charging implant that is non-toxic to the human body. Researchers first explored several commercially available metals as conductors, such as lead, but, found that the toxic levels were still unfavourable. Eventually, they developed a nanogenerator using polyvinylidene fluoride composite nanofibers, zinc oxide, and reduced graphene oxide hybrid nanofillers. This nanogenerator could regenerate 487μJ of energy, a sufficient amount of energy to make it a promising candidate as a pacemaker [18].

Another notable nanotechnology development in the biomedical field is the bionic eye, an implantation designed for individuals with vision-limiting biological eye diseases. The bionic eye works in 2 parts: there is an outer eyepiece that will capture the image and send the signal to an intelligent controller unit, which will encode and process the image. Then it will send the signal to an implanted device wirelessly, which decodes data and sends electronic signals to the retina of the eye to simulate an artificial reconstruction of the image. Apart from the prevalent safety issues this product faces, the demand for computing power from the implanted chip is extremely high, therefore the area-to-efficiency ratio of the chip must be high. Nanotech techniques are used to overcome that challenge by designing a unique array structure for the electrode to provide efficient stimulations [19]. The biomedical field still holds many unexplored possibilities, and nanotechnology is opening avenues for further exploration. However, safety remains a paramount concern, and continued research in this field will be subject to rigorous regulations [20].

5. Conclusion

The evolution of battery technologies has been nothing short of remarkable, tracing its roots back to the 1800s. From being able to only power small electronics with relatively minimal operating abilities, batteries have made significant strides in overcoming their initial challenges, such as low power and energy density. With the integration of nanotechnology, there has been a marked enhancement in battery performance and a broader range of battery applications. Silicon nanowires and carbon nanotubes, for instance, have proven to be promising materials for pushing the boundaries of energy storage. Moreover,

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innovative designs like paintable batteries have opened many more possibilities for future battery technologies. It is evident that nanotechnology and battery research will continue to be tightly intertwined. The pursuit of higher battery performance remains to be a strong driving force, and nanotechnology will undoubtedly play a crucial role in realizing these ambitions.

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