

# Nanomaterials as well their applications and effects in batteries

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**Abstract.** In recent years, with the increasing awareness of environmental protection, electric vehicles have appeared in front of the public, and there is a trend to replace fuel vehicles. However, the reason why fuel vehicles have not been completely replaced until now is that there are many problems in the batteries of electric vehicles, such as low speed of charging, low capacity, and so on. Therefore, it is necessary to optimize the electric vehicle battery. In this paper, by summarizing nanomaterials and their applications in batteries, the optimization direction of batteries and the problems to be avoided are clarified. By reviewing the types, properties, advantages, disadvantages, and applications of common nanomaterials, as well as summarizing the application of nanomaterials in batteries, it is concluded that nanomaterials have many obvious advantages in the field of batteries, which can improve the reaction rate, energy, capacity, etc. However, at the same time, it inevitably brings disadvantages. The future work will be to take advantage of nanomaterials while avoiding or reducing the impact of disadvantages. This paper can provide researchers with a macro perspective on the application of nanomaterials in batteries, so that stakeholders can more accurately design ideal battery electrode materials, thereby promoting the development of electric vehicles and further improving the trend of global warming.

**Keywords:** Environmental protection, fuel vehicle, electric automobile, nanostructured material

## 1. Introduction

With the emergence of different electronic devices, people's requirements for energy storage technology are also greatly improved. Therefore, fuel cells, supercapacitors, lithium-ion batteries, redox flow batteries, and hybrid supercapacitors are widely studied as future energy storage devices. Among these devices, supercapacitors, despite their relatively high power density, are still limited by low energy density. In contrast, Li-ion batteries with excellent rate capability, high energy density, and high cycle stability have been recognized as a promising option, which can also be applied to various aspects such as mobile phones, notebook computers, and digital cameras. To explore the large-scale applications of Li-ion batteries, most researchers continuously strive to improve energy density and cycle life.

However, the problems of lithium-ion batteries cannot be ignored. The problems of the commonly used lithium-ion batteries include poor safety, poor battery life, long charging time, high price, and so on. The safety problem is mainly for the case where the internal temperature of high-power charging and discharging is too high. Secondly, since the electrolyte is a flammable organic solvent, if a strong collision occurs, the leakage of the electrolyte can easily cause the battery to burn. Poor battery life and long charging time are mainly due to the low capacity of lithium-ion batteries and their low charging/discharging efficiency. All of the above prove that the performance of lithium-ion batteries needs to be further optimized.

In order to effectively solve the existing problems of lithium-ion batteries, nanotechnology is combined with lithium-ion batteries, making full use of the advantages of nanotechnology, by obtaining high specific surface area, to promote the speed of chemical reactions, thereby improving electron conversion efficiency and energy density, and battery performance such as cycle life. The research topic of the combination of nanotechnology and lithium-ion batteries is very important for the research field of advanced lithium-ion batteries, which can greatly solve the problems of low electric capacity and low charging/discharging efficiency of lithium-ion batteries. At the same time,

it can further expand the application field of nanotechnology, and provide a broader platform and environment for further exploration and research of nanomaterials.

Currently, no review articles on nanomaterials and their applications in Li-ion batteries were found. At present, relevant literatures focus on the application of specific nanomaterials in a specific field, for example, the application of biological nanomaterials in the medical field, the application of electronic nanomaterials in the field of electronic devices, and so on. Nowadays, the review articles on nanomaterials and their applications in Li-ion batteries urgently need to be summarized, because this can provide researchers in related fields with a broader, comprehensive, and summarized overview, which will help them innovate and construct new research directions based on this article.

The main purpose of this article is to summarize and enumerate common nanomaterials and examples of their applications in Li-ion batteries to improve and optimize battery performance. Firstly, an overview and classification of commonly used nanomaterials are introduced, including nanotubes, nanowires, nanosheets, and nanoparticles. Secondly, the application direction of nanomaterials in batteries is given. Finally, the disadvantages of nanomaterials are summarized and the future work direction is proposed.

## 2. Nanomaterials

Due to its size in the range of 1-100 nanometers, which is closed to the coherence length of electrons, nanomaterials have many special properties, including electrical conductivity, thermal conductivity, magnetic, optical properties, and so on. Since its inception, nanomaterials have gradually been sought after by the scientific community and play an important role in the contemporary scientific community. It is one of the most active research fields in materials science today. Correspondingly, nanomaterials are widely used in various fields. According to their different sizes and properties, they have great potential for development in the fields of electronics, construction, biomedicine, environmental protection materials, optical materials, aerospace materials, and ultrasonic materials [1-2]. This section will firstly introduce the concept of nanomaterials, followed by a detailed description of the properties, advantages, and application examples of nanotubes, nanowires, nanosheets, and nanoparticle materials. Finally, the common disadvantages of nanomaterials are introduced.

### 2.1. The concept of nanomaterials

When the material reaches the nanometer scale, in the space of about 0.1-100 nanometers, the properties of the material will undergo mutation and special properties will appear. This kind of material with special properties that are different from the original composition of atoms, molecules and macroscopic substances is called nanomaterials. In the past, people only paid attention to atoms, molecules or cosmic space, and often ignored this intermediate field, which actually exists in large quantities in nature, but the performance of this scale range was not recognized before. The first to really recognize its properties and cite the concept of nanometers were Japanese scientists, who prepared ultrafine ions by evaporation in the 1970s, and discovered by studying its properties: after reaching the nanometer scale, an electrically and thermally conductive conductor made of copper or silver loses its original properties and exhibits neither electrical conductivity nor thermal conductivity. The same is true for magnetic materials, such as iron-cobalt alloys, when it is made into a size of about 20-30 nanometers, the magnetic domain becomes a single magnetic domain, and its magnetic properties are 1000 times higher than the original. In the mid-1980s, people officially named such materials as nanomaterials [3-6].

### 2.2. Classification of nanomaterials

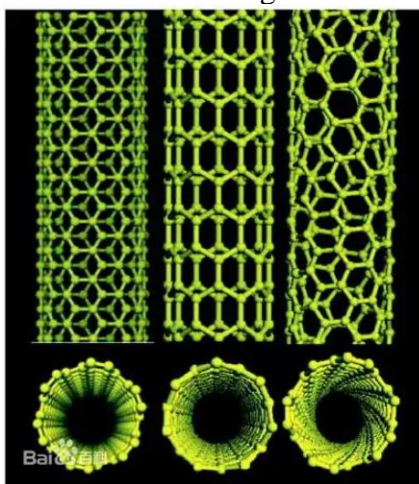
There are many types of nanomaterials, which can be roughly divided into nanotubes, nanowires, nanosheets, nanoparticles and so on according to the shape of the material. In this section, these five

different forms of nanomaterials will be introduced, from the concepts, properties, advantages, application examples, etc.

### 2.2.1. Nanotubes

Nanotubes are nanomaterials with a tube wall thickness in the range of 1-100 nanometers that are shaped like pipes, and the length of nanotubes can reach thousands of times their thickness. Nanotubes are 10,000 times thinner than a human hair.

There are many kinds of nanotubes, such as, silicon nanotubes, carbon nanotubes, nickel-plated carbon nanotubes and meteorite carbonaceous crystalline nanotubes. Different arrangements will also form nanotubes of different shapes, and there will be some differences in performance accordingly. Figure 1 shows carbon nanotubes with different arrangements.



**Figure 1.** Top and front views of carbon nanotubes with different arrangements [7].

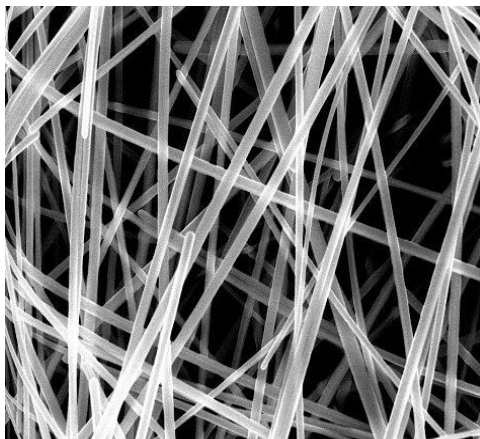
Nanotubes have lots of excellent performance. They have high hardness which is 100 times harder than steel. In addition, they can withstand temperatures as high as 6500°F (3593°C). Nanotubes can be used both as metal electrical conductors, which are much more conductive than gold, and as semiconductors which are necessary to make computer chips, because they have high thermal conductivity and high electrical conductivity. Nanotubes are also extremely flexible, strong, resilient and superconductive at extremely low temperatures.

Nanotubes can be used in many fields. In the application of silicon chips, the capacity of silicon chips is limited by physical barriers, and researchers hope to use nanotubes in them to reduce the size of circuits. At the same time, nanotubes can be used to make smaller, lighter and more efficient fuel cells. The hollow tubes of single-walled carbon nanotubes can store and stabilize hydrogen molecules, and can be used to prepare light and portable hydrogen storage containers. Due to their light weight and hollow structure, carbon nanotubes can be used as outstanding containers for storing hydrogen, which is even denser than liquid or solid hydrogen. With proper heating, hydrogen can be slowly released. By taking advantage of their ultra-high conductivity, nanotubes can be made into switches or transistors used in computers. Due to their extreme flexibility, strength and resilience, nanotubes enable the synthesis of high-performance sports and aerospace materials. Due to their strong tension, they have the special property of bending without returning to their original shape. In addition, nanotubes can be used in materials that need to withstand extremely high temperatures, such as panels on the exterior of aircraft and rockets [7].

### 2.2.2. Nanowires

A nanowire can be defined as a one-dimensional structure with a diameter limited to less than 100 nanometers (no limit on length). Suspended nanowires refer to nanowires whose ends are immobilized under vacuum conditions. Typical nanowires have aspect ratios above 1000, therefore, they are often referred to as one-dimensional materials.

According to the different constituent materials, nanowires can be divided into different types, including metal nanowires (such as: Ni, Pt, Au), semiconductor nanowires (such as: InP, Si, GaN) and insulator nanowires (such as: SiO<sub>2</sub>, TiO<sub>2</sub>). Molecular nanowires are composed of repeating molecular elements, which can be organic (e.g., DNA) or inorganic (e.g., Mo<sub>6</sub>S<sub>9</sub>-xIx). Figure 2 below shows silver nanowires.



**Figure 2.** Silver nanowires [8].

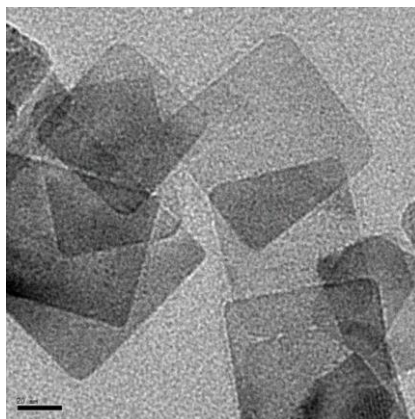
Nanowires show many good properties. With its size decreasing, nanowires can show better mechanical properties than bulk materials, such as, high strength and high toughness. Silver nanowires have recently attracted extensive attention. Silver nanowires are considered to be the most likely material to replace the traditional ITO transparent electrode. Compared with other materials, it has the characteristics of good conductivity, good light transmission, excellent flexibility, low cost and good stability. The discovery of silver nanowires has made it possible to realize bendable LED display and touch screen, and a large number of studies have applied it to thin film solar cells. Besides, because of the large aspect ratio effect of silver nanowires, it also has excellent advantages in the application of conductive adhesives and thermal conductive adhesives.

Nanowires play an important role in electronics, optoelectronics and nanoelectronic mechanical devices. For example, nanowires can be used as additives in composites, wiring in quantum devices, field emitters, biomolecular nanosensors, electrode materials in microbatteries, and the preparation of high-strength and tough materials such as silica nanowires are 15 times harder than high-strength steel and 10 times stronger than traditional Fiber Glass Reinforced Plastic (FRP). The photons emitted by resonance are more concentrated (the conversion of solar energy is achieved in the process of emitting photons), which is beneficial to improving the conversion efficiency of solar energy, thus making nanowire-based solar cell technology a real improvement.

### 2.2.3 Nanosheets

Nanosheets refer to sheet-like nanomaterials with a thickness ranging from 1-100 nanometers. A typical example of nanosheets is graphene, the thinnest (0.34 nm) two-dimensional material. The hexagonal grid of carbon atoms is obtained by arranging in the form of monolayer flakes [9].

There are many kinds of nanosheets, such as, graphene nanosheets, metal nanosheets, oxide nanosheets, titanium dioxide nanosheets (figure 3), boron nitride nanosheets and so on. The structure of hexagonal boron nitride nanosheets is very similar to that of graphite. In brief, its structure can be regarded as that C atoms in graphite are replaced by B atoms and N atoms in turn [10].



**Figure 3.** Titanium dioxide nanosheets [11].

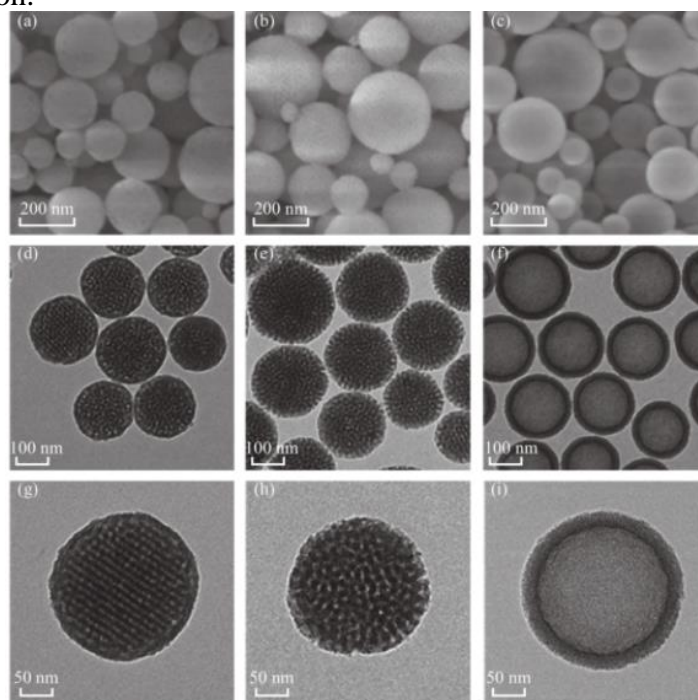
Good performance is reflected in nanosheets, for instance, high thermal conductivity, high electrical conductivity, low expansion coefficient, good thermal insulation at high temperature, good chemical stability, and excellent lubricity.

Due to its high conductivity, it can be used in sensors and energy production technology. It can also be used as a filler for insulating and thermally conductive materials, raw materials for lubricants, catalysts, in the cosmetics industry, electrical insulation industry, PCB copper clad laminate, LED and other industries [10].

#### 2.2.4 Nanoparticles

Nanoparticles refer to particles of nanometer scale. It is defined as particles smaller than 100 nanometers in at least one dimension.

Nanoparticles can be metal or alloy particles, carbide particles, nitride particles, composite metal oxide particles, inorganic salt nanoparticles (figure 4 shows silica nanoparticles), organic nanoparticles, and so on.



**Figure 4.** TEM images of three hierarchical porous silica nanoparticles [12].

Due to its high specific surface area, suspension stability, high solvent affinity, high catalytic activity and high strength [13-14], they can be used in catalyst, drug carrier, gene delivery carrier, etc.

## 2.3. Disadvantages of Nanomaterials

Technology is a double-edged sword. While nanomaterials have many advantages, they also have their disadvantages.

### 2.3.1. Harmful to human health.

Nanomaterials are widely used in cosmetics, clothing, paint, and other industries, which not only bring convenience to these industries, but also damage the health of related processing personnel. Because the particle size of nanomaterials is too small, it is easy to remain in the lungs of the human body, such as medical staff (nano-silver is used in disinfectants), construction personnel (nanomaterials are present in building materials), laboratory researchers (experimental materials are present in nanomaterials) and so on.

### 2.3.2. Harmful to environment

Because the particle size of nanomaterials is too small, floating in the air pollutes the environment. Filters are unable to filter it out, allowing nanomaterials to flow into nature, pollute the environment, and exist in drinking water [15].

## 3. Application of nanomaterials in batteries

Nanomaterials are widely used in various fields due to their excellent properties. In the automotive field, nanotechnology can be applied to almost every important part of the car, thereby greatly optimizing the performance of the car and improving the experience and feeling of the driver and passengers. As shown in figure 5, nanotechnology has been widely used in everything from appearance parts to function parts, from interior trim to exterior trim. This section only selects the application of nanomaterials in electric vehicle batteries to summarize the application direction of nanomaterials in electrodes.

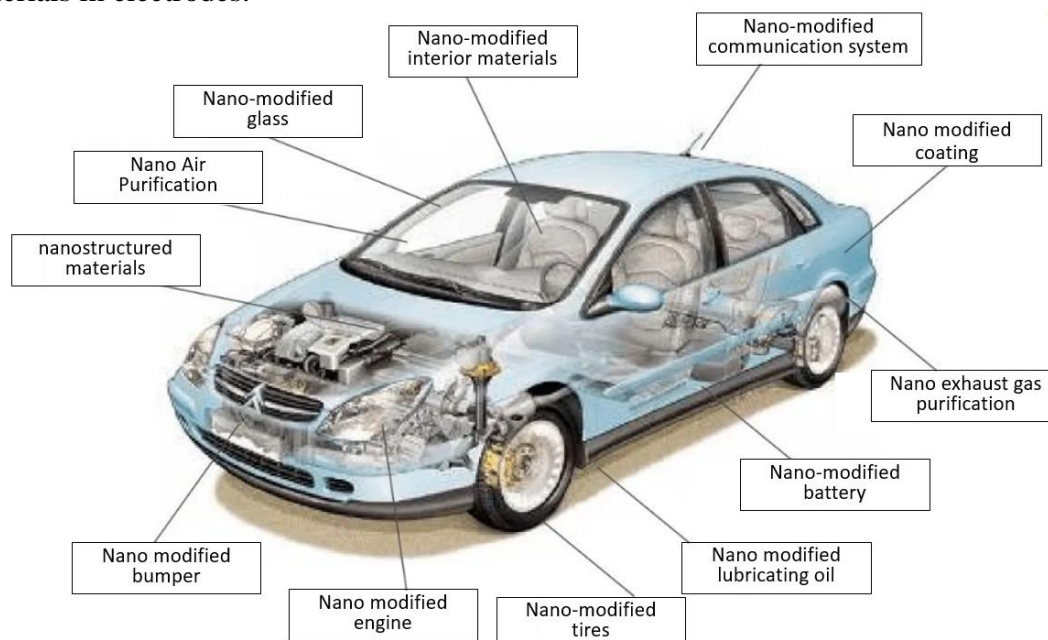


Figure 5. Application of nanomaterials in automobile.

### 3.1. Nanostructured materials as main active materials in electrodes

#### 3.1.1. Improve particle transmission speed and efficiency

Improvement and optimization of the electrochemical properties of LIB active materials can utilize nanostructured materials. Nanomaterials can significantly enhance the chemical reaction rates of anode and cathode materials, as well as the overall power transfer due to their size reduction (e.g., <100 nm). By scaling down the size of the active material (e.g., particle/crystallite size), the transport

time of charge carriers (Li ion,  $e^+$ ) in the battery is reduced. According to the formula (1), since the distance  $L$  transported by the charge carriers in the active material decreases, the time  $\tau$  decreases accordingly [16].

$$\tau \propto \frac{L^2}{D} \quad (1)$$

### 3.1.2. Increase the specific surface area

Nanoscale active materials can increase the surface-to-volume ratio, which improves the rate of chemical reactions. Relative to the innermost material of the nanomaterial, an increase in the number of atoms belonging to the position of the surface will change the surface free energy, thereby making the surface more reactive. The morphological features of nanomaterials are sometimes used to build 3D structures, which also greatly increase the reaction area and thus the reaction rate. But this behavior that affects the electrode material has both advantages and disadvantages. The advantage is that it can promote electrochemical reactions, and the disadvantage is that it also promotes side reactions, negative reactions, including electrolyte degradation and/or electrode surface passivation.

### 3.1.3. The increase of surface defects improves the electrochemical activity

Firstly, there are many surface defects in nanomaterials, such as the extent of vacancies, steps, edges, corners, and grain boundaries. These can significantly increase the diffusion rate of charge carriers in the active material in the electrode, which can also improve the electrochemical activity. Secondly, due to the increase of dangling bonds (because of the sudden termination of the crystal at the surface due to the lattice, each atom in the outermost shell of the surface will have an unpaired electron, i.e. there will be an unsaturated bond and this bond is called a dangling bond), the local chemical potential of the material will also be increased, thereby improving the chemical reactivity. This effect of surface defects is significant, which can be reflected in, for example, altering the electrochemical deposition process, the nucleation process, and enhancing the formation and growth of the SEI layer.

### 3.1.4. The increase in toughness and strength enhances the adaptability to volume changes

The mechanical properties of nanomaterials change as the size of the material decreases. Its strength and toughness will be improved. Correspondingly, the tailored nanostructures can better withstand the volume changes that occur in the electrode during chemical reactions, and the associated strain/stress build-up. When Si is used as an electrode material, the volume will change significantly, but if spherical Si nanoparticles are used, the volume change will be smaller. At the same time, Si spheres with an amorphous structure are more effective in resisting volume changes. There is data shows that amorphous Si spheres up to 870 nm in diameter do not fracture, while crystalline Si spheres have a critical fracture size of 150 nm [16]. This is mainly because the amorphous structure undergoes an isotropic volume change, which affects the stress evolution process and delays the onset of fracture, and the Li ion diffusion kinetics also change during electrochemical reactions.

## 3.2. Nanomaterials as auxiliary materials in electrodes - decorative active materials

A common strategy to decorate active materials with nanomaterials is surface coating. Mainly from the following three aspects to improve the electrode performance.

### 3.2.1. Improve electron transfer efficiency

Surface coatings can actually greatly improve electron transfer efficiency in two ways. Firstly, the improved particle-to-particle electron transfer efficiency stimulates the availability of electrons in all active particles in the electrode. Secondly, to expand the available area of electrons on the active particles. If the electrons are only available in a limited area of the active particle, the electron transfer efficiency is greatly reduced, but if the electrode material surface is covered with a uniform surface coating that can conduct electricity, the reaction will take place over the entire surface of the material

particle. Therefore, the use of a suitable conductive coating can greatly optimize the conductivity of the electrode.

### **3.2.2. Inhibit the dissolution of active particles**

The coating can inhibit the dissolution of the active material particles or reduce the dissolution rate. Because the surface of the material interacts with the electrolyte, the active material degrades. But preparing an effective coating is not an easy task, and there are two things to note. Firstly, the coating needs to be as thin as possible to avoid the coating blocking the passage of lithium ions and electrons. Secondly, the coating needs to be free of structural defects, which is to prevent leakage of transition metals from the inside of the active material [17].

### **3.2.3. Prevent the agglomeration phenomenon in the process of electrochemical reaction**

Coatings can also prevent agglomeration of nanoparticle materials, prevent nanoparticle growth, can also act as spacers to provide additional porosity, and so on [18-19].

## **3.3. Advantages and disadvantages of nanomaterials in batteries**

### **3.3.1. Advantages**

The advantages of nanomaterials in batteries are numerous. Firstly, due to the reduction in the size of the material, the transmission distance of the loaded particles is reduced, thereby reducing the transmission time, improving the transmission efficiency and increasing the reaction rate. Secondly, due to the increase of the specific surface area, the surface activity increases, thereby improving the chemical reaction activity, and also increasing the reaction rate and degree of reaction. Thirdly, due to the increase of vacancies, grain boundaries, etc., in nanomaterials, the activity of the materials is greatly enhanced, which will increase the chemical reaction rate. Fourthly, due to the reduction of the material size, the mechanical properties of the material are improved, for example, the strength and toughness are improved, which increases the volume tolerance of the electrode material, prevents the electrode material from breaking, and so on. Fifthly, since the material does not require additional energy to undergo the crystalline-to-amorphous transition, amorphous nanoparticles can also act as a buffer in volume changes. Sixthly, with the help of the surface coating, the electron transport efficiency can be improved, the active material can avoid dissolving in the electrolyte to a certain extent, and the agglomeration and growth of nanomaterials can also be avoided to a certain extent, and so on [16].

### **3.3.2. Disadvantages**

While nanomaterials bring advantages, they also bring some disadvantages. Firstly, compared with bulk materials, nanomaterials with controlled size, composition, and shape are difficult to produce, the production process is not environmentally friendly, and the cost is high. The mass production process is difficult. Secondly, the stability of the reactive material will decrease due to the high specific surface area, high particle conduction efficiency, etc. This can have the side effects of electrolytes, such as, being consumed faster and gas escaping. Thirdly, nanostructured materials are difficult to compact and contain in dense electrode coatings, and the resulting excessive porosity is detrimental because the voids are filled with electrolyte, which reduces the energy content of the electrode. Fourthly, the control of crystallinity and defects in nanomaterials is challenging. Fifthly, nanomaterials grown on current collectors are fragile and the active mass that can be loaded is limited, which leads to electrodes fabricated from such materials that are easily damaged during battery assembly. In addition, SEI will grow around broken nanostructures, thereby forming a thick insulating film, resulting in irreversible loss of active material [16].

## **3.4. Challenges**

Although nanomaterials have been widely used in batteries, they still face many challenges. Firstly, when preparing electrode materials, the advantages and disadvantages of nanomaterials need to be considered primarily, and this needs to be weighed according to the desired performance of the

electrode and battery, and finally a battery with more advantages than disadvantages is designed. It is not sensible that only focusing on all the advantages of nanomaterials but ignoring their disadvantages. Secondly, complex nanomaterial production and control processes are costly and time-consuming. In order to solve this problem, it is necessary to select elements that are abundant in nature (for example, Si, Al, Fe, Ti, Mn, Zn, C). The same manufacturing methods also need to be considered, namely "top-down" and "bottom-up", which as well can be combined to some extent. According to the needs of production requirements, it is necessary and important to formulate a suitable preparation method [20]. Thirdly, for microelectronic devices such as semiconductors, fine and rigorous preparation methods and standards for nanomaterials are not an option, but a necessary condition. This means that a high level of control is required for the fabrication of nanostructured materials, especially when it comes to 3D electrodes with complex features [21]. Fourthly, it is difficult to compact nanomaterials into high-quality electrode coating materials, because their density is usually low, and the stored energy of the battery is correspondingly reduced [16].

#### 4. Conclusion

Nowadays, nanomaterials are widely used in all aspects of human life. With the strengthening of human's awareness of environmental protection, electric vehicles have entered the stage, but the performance of the battery still has many defects, which cannot meet the needs of consumers. This article firstly summarizes the types, properties, advantages and disadvantages of common nanomaterials, as well as application examples. Secondly, the application directions of nanomaterials in batteries are summarized, which are mainly divided into two categories, one is nanomaterials as the main reactive active materials, and the other is nanomaterials as surface decoration materials of active materials. Finally, nanomaterials have many advantages, but also bring some disadvantages due to their special size, structure, etc. The direction of future work about nanomaterials is to overcome their disadvantages, or make trade-offs between advantages and disadvantages. Preparation and processing technology also needs to be improved and refined to meet the requirements of high-precision devices and large-scale production. This article provides some improvement suggestions and a summary of advantages and disadvantages for nanomaterials in the field of battery applications, so that readers can view nanomaterials from a more objective and comprehensive perspective.

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