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Synthesis and Application of Zero-Dimensional Metal Oxide Composites in Energy Chemistry

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Abstract: Against the backdrop of increasingly prominent global energy shortages and environmental issues, the development of efficient energy conversion and storage technologies has become crucial. Zero-dimensional (0D) metal oxide composites exhibit significant application value in the field of energy chemistry due to their unique properties, such as quantum size effect and high specific surface area. From a broad perspective, this paper reviews the main synthesis methods of these composites, including sol-gel method, hydrothermal/solvothermal method, precipitation method, and template method, while analyzing the characteristics of each method. It further discusses their applications in photocatalytic hydrogen production, fuel cells, lithium-ion batteries, and supercapacitors. Additionally, the current challenges, such as material dispersibility and interface bonding, are pointed out, and future development directions are prospected, aiming to provide references for related research.

Keywords: Zero-dimensional metal oxide; Composite material; Synthesis method; Energy chemistry; Energy conversion; Energy storage

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1. Introduction

The rapid development of industrialization has led to the extensive use of fossil energy, resulting in an energy supply-demand imbalance and severe environmental problems such as the greenhouse effect and pollution, which seriously restrict the process of sustainable human development. The research and development of renewable energy as well as efficient energy conversion and storage methods have become key energy research topics worldwide. Nanomaterials demonstrate excellent performance in energy chemical reactions due to their unique properties such as size effect and surface effect. Three-dimensional nanomaterials are important members of the nanomaterial family; when their size is $\leq$ 100 nm, they are referred to as zero-dimensional nanomaterials, which exhibit a prominent quantum size effect [1].

Zero-dimensional (0D) metal oxides (such as TiO_2, ZnO, etc.) have attracted widespread attention in the energy field due to their chemical stability, abundant reserves, and low cost. However, single 0D metal oxides usually suffer from drawbacks such as low electrical conductivity and high recombination probability of photogenerated electrons and holes, which limit the improvement of their performance. Composites formed by 0D metal oxides with carbon materials, polymers, and other substances can regulate the material structure and improve performance through the interaction between components. For example, composites with graphene can accelerate electron migration, and those with carbon nanotubes can address the volume expansion issue. Therefore, summarizing and introducing the preparation of 0D metal oxides and their composite structures, as well as their applications in energy, is conducive to understanding the formation of 0D nanomaterials and effectively promoting the sustainable development and application of energy materials from the perspective of preparation.

2. Synthesis methods of zero-dimensional metal oxide composites

The synthesis of zero-dimensional metal oxide composites is the basis for their performance, and different methods affect the particle size, morphology, and interface state of the materials. The following are four common and representative synthesis methods.

2.1. Sol-gel method

The sol-gel method is a classic synthesis technique. It uses metal alkoxides or inorganic salt aqueous solutions as precursors, which undergo hydrolysis and polycondensation to form a sol. The sol then aggregates into a gel, and finally, the composite material is obtained through drying and calcination [2].

In the synthesis process, precursors such as tetrabutyl titanate and zinc nitrate are selected as raw materials. Composite components, such as graphene oxide, are first dispersed and mixed. For example, in the synthesis of TiO_2/graphene composites, graphene oxide is dispersed in a tetrabutyl titanate ethanol solution, then a catalyst is added to initiate hydrolysis and polycondensation to form a sol. The sol is further converted into a gel, and the product is obtained after drying and calcination [3].

The advantages of this method include low reaction temperature, easy control of particle size and morphology, realization of molecular-level mixing of components, simple process, and suitability for the synthesis of various composite materials. However, it has shortcomings such as a long synthesis cycle, easy volume shrinkage and agglomeration during drying and calcination, and high cost of some precursors [4].

2.2. Hydrothermal/solvothermal method

The hydrothermal/solvothermal method is carried out in a closed high-pressure reaction kettle, using water or organic solvents as the medium, and promoting reactions through high temperature and high pressure to prepare composite materials. When water is used as the medium, it is called the hydrothermal method; when organic solvents are used, it is called the solvothermal method.

The synthesis process is as follows: Metal salt precursors, precursors of composite components, and surfactants are dispersed in the medium, then placed into a reaction kettle. The reaction temperature is controlled at 100–300°C, and the reaction time ranges from several hours to dozens of hours. After cooling, centrifugation, and filtration, the product is obtained.

This method can prevent the introduction of environmental impurities, resulting in pure products. The crystallinity, particle size, morphology, etc., of the desired product can be accurately controlled by adjusting reaction conditions, and it is applicable to various composite systems. However, it requires special high-pressure equipment, which leads to high costs and relatively high risk. In addition, the reaction time is long, and it is not suitable for sensitive composite components.

2.3. Precipitation method

The precipitation method involves adding a precipitant to a metal salt solution to convert metal ions into precipitates, which are then mixed with composite component precursors to obtain composite materials. Among various precipitation techniques, the coprecipitation method is the most widely used.

In the coprecipitation preparation process, solutions of two or more metal ion salts are mixed with a precipitant (such as sodium hydroxide or sodium carbonate). Under specific conditions (e.g., certain pH and temperature), a mixed precipitate is formed, which undergoes washing, drying, and calcination to produce the composite material. For example, to synthesize the Co_3O_4/NiO mixed compound, a mixed solution of cobalt nitrate and nickel nitrate is dropped into a sodium carbonate solution to obtain a mixed carbonate precipitate, which is then calcined to yield the Co_3O_4/NiO mixed compound [5].

This method features a simple process, convenient operation, no need for complex equipment, low cost, and easy industrialization, and can regulate the material composition and particle size. However, the difference in precipitation rates of different metal ions tends to cause uneven component distribution, and the precipitates are prone to agglomeration during drying and calcination, resulting in low crystallinity.

2.4. Template method

The template method regulates the structure and morphology of composite materials using templates with specific structures (hard templates or soft templates). Precursor assembly reactions are guided by the template, and the target material is obtained after template removal.

Hard templates are rigid solid materials (e.g., mesoporous silica, carbon spheres). Precursors are introduced into the template's pores or onto its surface, and the template is removed after the reaction. For instance, using mesoporous silica SBA-15 as a template, tetrabutyl titanate and graphene oxide are injected into its pores; after calcination and template removal, a mesoporous TiO_2/graphene composite is obtained. Soft templates are ordered aggregates (e.g., micelles) formed by surfactants, polymers, etc. They guide precursor reactions, and the product is obtained after template removal.

The template method can precisely regulate the structure, morphology, and pore size of materials, prepare composite materials with special structures, and improve transport performance. However, hard templates are complex to prepare, high in cost, and their removal is likely to damage the structure; soft templates have poor stability, are greatly affected by reaction conditions, and involve complex synthesis processes, which are not conducive to large-scale production [6].

3. Application of zero-dimensional metal oxide composites in energy chemistry

Zero-dimensional metal oxide composites are widely used in the field of energy conversion and storage, as they can enhance energy utilization efficiency and storage performance. Below is an introduction to their applications in four typical areas.

3.1. Photocatalytic energy conversion

Photocatalytic technology converts solar energy into chemical energy, playing a significant role in hydrogen production and CO_2 reduction. Single 0D metal oxides have limited photocatalytic performance, but their performance is significantly improved after compositing.

Composite materials can expand the light absorption range and facilitate the separation of photogenerated carriers. In photocatalytic hydrogen production, take the TiO_2/graphene composite as an example: TiO_2 absorbs photons to generate electron-hole pairs, while graphene enables rapid electron transfer, reducing the recombination of electron-hole pairs in the composite and thus improving catalytic efficiency. In photocatalytic CO_2 reduction, composite materials can convert CO_2 into organic fuels as a resource. For instance, the carbon quantum dot/ZnO composite uses carbon quantum dots to enhance the light absorption and electron transport of the composite, thereby accelerating the rate of CO_2 conversion into methane and methanol and reducing greenhouse gas content [7].

3.2. Fuel cells

Fuel cells convert chemical energy into electrical energy through electrocatalytic reactions, featuring high efficiency and cleanliness. The oxygen reduction reaction is a crucial step in the cell reaction, and the activity of the catalyst directly affects the efficiency of the fuel cell. 0D metal oxide composites can be used as fuel cell catalysts or catalyst supports to improve the catalytic activity and stability of fuel cell catalysts.

By compositing Pt-based catalysts with 0D metal oxides (such as CeO_2 and Fe_3O_4), the metal oxides can modify the electronic configuration of Pt to enhance catalytic activity, while also dispersing the catalyst, reducing the amount of Pt used, and lowering catalyst costs. As supports, composite supports composed of carbon materials and 0D metal oxides (e.g., carbon nanotube/Fe_3O_4) possess both electrical conductivity and stability, providing good support for catalysts, accelerating the diffusion of reactants and electron transport, and extending the service life of fuel cells [8].

3.3. Lithium-ion batteries

Lithium-ion batteries are commonly used energy storage devices, widely applied in electronic equipment and electric vehicles. The performance of electrode materials determines the battery's capacity and cycle stability. Zero-dimensional metal oxide composites find applications in both cathode and anode materials.

Regarding anode materials, the Si-based anode material composite with zero-dimensional TiO_2 allows TiO_2 to suppress the volume expansion of Si during charging and discharging, thereby enhancing cycling stability; meanwhile, the electrical conductivity of zero-dimensional TiO_2 improves the electron transport property of Si, boosting the rate performance of the battery. For cathode materials, the $LiFePO_4$ cathode material composite with zero-dimensional ZnO enables ZnO to increase the electronic conductivity and ion diffusion rate of the cathode material, which in turn improves battery capacity and charge-discharge efficiency, while also enhancing material stability and extending battery lifespan.

3.4. Supercapacitors

Supercapacitors possess characteristics such as high power density, fast charge-discharge rate, and long cycle life. Electrode materials are a crucial component of supercapacitors, and zero-dimensional metal oxide composites, when used as electrode materials, can enhance capacitive performance and stability.

On the one hand, composites have a high specific surface area, which can provide more active sites for charge storage. Take MnO_2/carbon material composites as an example: zero-dimensional MnO_2 has high pseudocapacitance, while carbon materials improve electrical conductivity and specific surface area; the synergistic effect of the two can increase the specific capacitance of supercapacitors. On the other hand, the excellent electrical conductivity and structural stability of composites can accelerate the charge transfer rate and reduce structural damage during the charge-discharge process. For RuO_2/graphene composites, graphene's good electrical conductivity promotes charge transfer, and RuO_2 provides high pseudocapacitance, enabling supercapacitors to achieve both high power density and high energy density [9].

4. Current research challenges and future outlook

4.1. Current research challenges

First, materials exhibit poor dispersibility and significant agglomeration. Zero-dimensional metal oxide particles have high surface energy, making them prone to agglomeration during synthesis and application. This reduces their specific surface area and inhibits the exertion of their performance. Although measures such as surface modification and the introduction of dispersants have alleviated the issue to some extent, the effect is not obvious, and controlling their dispersibility remains more difficult.

Second, the interface bonding strength is low. The interface bonding state of different components in composites determines their electron transport and synergistic effects. Weak interface bonding can easily lead to component separation of composites, reducing material stability and performance. At present, the approaches for interface regulation are relatively single, making it difficult to achieve strong and stable interfacial bonding between different components [10].

Third, large-scale preparation and industrial application are difficult. Most of the existing synthesis methods are only suitable for small-batch preparation in laboratories, such as the sol-gel method and template method. Meanwhile, factors such as long synthesis time, high preparation cost, and complex preparation methods make these methods unable to meet the needs of large-scale industrial production. Additionally, the performance stability and consistency of materials are difficult to guarantee in large-scale production, and industrial application is hindered due to limitations in material preparation.

4.2. Future outlook

In terms of material structure design and performance improvement, it is possible to precisely regulate the particle size, morphology, and component distribution of materials to form special structures (core-shell structures, porous structures), thereby further increasing the specific surface area and electron transport performance of materials. Additionally, the mechanism of synergistic effects between components can be further explored, and new composite systems can be developed—such as composites with two-dimensional materials or metal-organic framework materials—to further expand material properties and application fields.

Regarding the innovation of synthesis technologies, first, it is necessary to break through and master synthesis technologies for high-yield, low-cost, and large-scale production. Combining the concept of green chemistry, low-toxicity reaction systems should be developed to reduce energy consumption. Second, greater efforts should be made to explore the automation and intellectualization of the synthesis process to achieve the consistency and stability of products, so as to meet the needs of industrial production. Furthermore, in the promotion of industrial applications, it is essential to advance industry-university-research technology alliances and promptly translate basic laboratory research and development into industrialization. Specific composite materials should be produced according to different energy application needs, such as high-capacity lithium-ion battery electrodes and high-efficiency fuel cell catalysts. In addition, material performance evaluation standards and material quality standards should be established to ensure material performance and safety, thereby realizing more applications of zero-dimensional metal oxide composites in energy chemistry.

5. Conclusion

The unique structural and performance advantages of zero-dimensional metal oxide composites bring broad application prospects to the field of energy chemistry. Their preparation processes and related application explorations are of positive significance for alleviating the energy crisis and promoting sustainable development. This paper summarizes the sol-gel method, hydrothermal/solvothermal method, precipitation method, and template method, and presents the advantages, disadvantages, and applicable scopes of each synthesis technology. Meanwhile, it points out the applications and values of zero-dimensional metal oxide composites in photocatalytic energy conversion, fuel cells, lithium-ion batteries, and supercapacitors, and clearly identifies the current existing problems and challenges, including the inhomogeneity of such materials, interface connection, and large-scale fabrication. Furthermore, the paper looks forward to future structural design, preparation technology, and commercial applications. It is believed that with the continuous research and expansion of researchers on zero-dimensional metal oxide composites in energy chemistry, these materials will achieve greater economic and social benefits in practical applications, thereby making due efforts for the construction of a clean energy environment and an efficient energy system.

Disclosure statement

The author declares no conflict of interest.

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