Application Analysis of Zinc Oxide Nanomaterials Based on Quantum Dots in Energy Environment

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Abstract. Nano-zinc oxide is a new type of multifunctional inorganic material. Nano-ZnO has excellent photocatalytic performance, which can effectively convert harmful pollutants into inorganic substances such as H\textsubscript{2}O and CO\textsubscript{2}, and can effectively remove many refractory substances, thus having great application potential in pollution control. In this paper, ZnO quantum dots are selected as the research object, the nanostructures and various morphologies of ZnO quantum dots are introduced, and various methods for preparing ZnO nanomaterials and their applications in the field of energy and environment are summarized.

1. Introduction
The research of zinc oxide (ZnO) semiconductor materials began in 1930s. In the following years, scientists focused on the preparation and doping of ZnO materials [1]. Because quantum dots are limited in three dimensions, the movement of electrons and the interaction between atoms will be affected by the size, such as melting point, magnetic properties, electrical properties, optical properties, mechanical properties and chemical activity, which are quite different from those of traditional materials. Quantum confinement effect began to play a leading role in the properties of materials. The quantum confinement effect mainly originates from the fact that the size of nano-materials is smaller than the mean free path of electrons in the material, so it is particularly significant when the size of the material is smaller than the exciton Bohr radius of the material [2]. Because of its excellent electrical and optical properties, ZnO nano-materials have a wide range of potential applications in nano-devices such as light-emitting diodes, ultraviolet detectors, gas sensors and field effect transistors.

Nano-zinc oxide is a new type of multifunctional inorganic material. Scholars have found that it has special functions in optics, magnetism, catalysis and many other fields in recent years, which makes it have important application value in many fields such as environment. However, nano-zinc oxide has excellent adsorption and photocatalytic properties, and has the outstanding advantages of low energy consumption, simple operation, mild reaction conditions and reduction of secondary pollution, which can effectively convert harmful gases and organic pollutants into inorganic small molecules such as H\textsubscript{2}O and CO\textsubscript{2}. The application of zinc oxide nanomaterials in energy environment is studied in order to improve the preparation efficiency, reduce the cost, apply to more fields and promote the development of corresponding fields.
2. Structure and Properties of ZnO

2.1 Crystal structure of zinc oxide

Zinc oxide has three main structures (Figure 1, in which gray and red balls represent Zn and O atoms, respectively.)(3]. The most common ones are hexagonal wurtzite structure and tetragonal sphalerite structure, and there is also a rock salt structure, which can be formed under high pressure. Under certain conditions, these forms will transform each other. Due to the existence of quantum size effect, surface chain effect, valence state effect, etc., gold quantum dots show fluorescence emission phenomenon, which can be well detected by burning light spectrometer.

![Crystal structure diagram of zinc oxide](image)

The lattice constants and basic physical parameters are shown in Table 1. Each Zn atom is alternately arranged along the C axis with four O atoms to form a tetrahedron arrangement, in which the bottom surface of the tetrahedron is parallel to the C(0001) plane, and the vertex angle of the tetrahedron faces the C(000-1) plane. This tetrahedron coordination makes ZnO a polar crystal structure with non-central symmetry [4].

| Physical properties              | Numerical | Physical properties              | Numerical |
|---------------------------------|-----------|---------------------------------|-----------|
| Stable phase at 300K            | Wurtzite type | Lattice constant (nm) | a=0.3250;c=0.5205 |
| Density (g/cm³)                 | 5.675     | Heat conductivity (W/cm K)      | 0.6       |
| Melting point (°C)              | 1975      | Heat capacity (J/g K)           | 0.494     |
| Heat of fusion (KJ/mol)         | 64.9      | Bond energy (KJ/mol)            | 284.1     |
| Static dielectric constant      | 8.656     | Electron/hole mobility (cm²/Vs) | 200 (electrons)/5 ~ 50 (holes) |

In ZnO hexagonal wurtzite crystal, each O ion forms a Zn-O tetrahedral structure by covalent bonds with the surrounding four Zn ions, while Zn ions form a tetrahedral structure by covalent bonds with the surrounding four O ions. O ions are closely packed in hexagonal shape, Zn ions fill half of tetrahedral voids, and each zinc atom or oxygen atom forms a regular tetrahedral structure with adjacent atoms as its center. ZnO material is transparent in the wavelength range of 400~2000 nm, and the visible light transmittance can be as high as 90%, which is an ideal material for preparing transparent conductive films [5].

2.2 Properties of ZnO

2.2.1 Electrical properties of ZnO

The molecular formula of zinc oxide is ZnO, commonly known as zinc white powder or zinc oxygen powder. ZnO is insoluble in common solvents, such as water, absolute ethyl alcohol, acetone and ammonia water. At room temperature, the band gap is as high as 3.37 eV, and the carrier concentration is extremely low, about 106cm- 3, which is an insulating material. Transparent ZnO thin films with high
conductivity of IIIA elements such as Ga and In are expected to become potential substitutes for transparent conductive thin films of indium tin oxide (ITO) because of their price advantages. In a sufficiently low electric field, the electron energy of the applied electric field is less than the heat balance energy of electrons, so the energy diffusion of electrons is not affected by the external electric field. According to the electron diffusion equation, the scattering rate determines the electron mobility, so the electron mobility is not affected by the external electric field and follows Ohm's law. In addition, ZnO is an active transition metal oxide, which can be synthesized by various chemical or physical methods, and can also be modified by doping or coating [6].

2.2.2 Gas sensing properties of ZnO

In recent years, with the development of nanotechnology, especially the emergence of various advanced preparation methods and many sophisticated characterization instruments, the research on ZnO began to focus on crystal films, nanoparticles, nanowires, nanorods, nano-arrays, quantum wells and quantum dots. ZnO is a kind of gas sensitive material with good performance, which has special gas sensitive characteristics. The gas in the surrounding environment will affect ZnO, which will change some characteristics of ZnO, such as carrier density, and thus change the conductivity of ZnO. By measuring the change of its resistance, some sensitive gases can be detected [7]. When nanoparticles enter the sub-nanometer size, metal nanoclusters no longer support plasma because of their small size, and then turn into molecular properties. Luminescence produced by electron transition between ZnO conduction band and valence hole, energy band and defect level.

2.2.3 Photocatalytic performance

With the rise of nanotechnology, inorganic material ZnO began to receive wide attention. Some polymers will have some new properties after modifying ZnO. Whether there is chemical bond between ZnO quantum dots and polymer is taken as the standard. In the aqueous phase, the migration rate of surfactant into solution is increased due to the decrease of concentration, which makes it unable to effectively coat ZnO quantum dots, and can not exist stably in aqueous solution. Photocatalyst is a material that converts absorbed light energy into chemical energy without changing itself [8]. Photocatalytic processes can be divided into three categories: photocatalytic degradation of organic matter to convert it into harmless carbon dioxide and water, photolysis of water to generate hydrogen and new energy, and photosensitivity synthesis of compounds. The Mn-doped ZnSe / CdSe core/shell nanoparticles are used to control the spatial distribution of electron carriers and hole carriers in the nanoparticles, thus realizing the control of the exchange between Mn ions doped in the particles.

3. Preparation Technology of Nanometer Zinc Oxide

3.1 Gas phase method

Gas-phase method is a process of directly utilizing gas or taking measures to make reactants undergo physical changes or chemical reactions in the gaseous state, and condense into nano-particles in the cooling process, thus obtaining nano-ZnO. Compared with photocatalytic degradation of pollutants, the controlling factors of photolysis of aquatic hydrogen have the same parts: they are all based on absorbing photons to generate charged loads, which initiate redox reaction when they reach the surface. In the preparation process, various parameters such as the type of raw materials, evaporation temperature, collection temperature, pressure, carrier gas and the use of catalyst are controlled to realize the preparation of different ZnO nanostructures.

Fig. 2 shows the UV-vis absorption spectrum of ZnO quantum dots. It can be observed that ZnO quantum dots have an obvious exciton absorption peak at 58nm, which is due to the large exciton binding energy of ZnO bulk materials at room temperature, while the large blue shift of exciton absorption peak relative to bulk materials is due to quantum confinement effect of quantum dots [9].
In order to optimize the conversion efficiency of dye-sensitized cells, it is necessary to improve the adsorption rate of dye molecules on the surface of semiconductor nanoparticles. It is easy to modify different kinds of functional groups on the surface, so that they can be coupled with biomolecules and analyze biomolecules effectively; ZnO quantum dots coated with PVP can excite stronger ultraviolet light and weaker visible light. Among them, PVP is helpful to perfect the crystallization of ZnO quantum dots, thus reducing surface defects.

3.2 Liquid phase method
Adding precipitant to zinc salt solution for precipitation treatment, and then heating and decomposing the precipitate to obtain nano ZnO (fig. 3). Precipitation method can be divided into direct precipitation method and homogeneous precipitation method [10]. The diameter of ZnO spheres was controlled by adjusting the ratio of triethanolamine to deionized water. This not only protects ZnO, but also ensures that quantum dots can be dispersed in water. The quantum yield of the olive structure nanoparticles is higher than 50%. A part of the purified precipitate was dissolved in ethanol and water for optical test and characterization. Part of the precipitate was vacuum dried at room temperature. In addition, semiconductor quantum dots often only have narrow luminescent bands, so two luminescent materials with different luminescent bands form core/shell structure imaging quantum dots, which can realize dual-wavelength detection. Irradiate under light for a certain time, then put it into a centrifuge for centrifugal separation, take out the centrifuge and measure its absorbance at the maximum absorption wavelength of reactive brilliant red at 58 nm, and calculate the adsorption rate (%) through the concentration C1 of absorbance in reactive brilliant red.

Figure 3 Schematic diagram of process flow for synthesizing nano zinc oxide by homogeneous precipitation method
ZnO nanosheets are a kind of special materials with lamellar structure, which are grown by ZnO in two dimensions. The materials have large specific surface area, so they have potential applications in gas sensing, pollutant photocatalysis, solar cells and other fields. Under illumination, the nanowire
produces electron and hole pairs, which are separated in the consumption area on the surface of the nanowire. The holes move to the interface between the nanowire and electrolyte to oxidize OH- groups to produce O2, while the electrons move to the cathode to reduce H+ groups to produce H2. From simple nanostructures such as nanobelts, nanorods, nanowires and nanotubes to complex structures such as nanobows, nanorings, nanocages, nanospirals and nanopropellers. By changing the type and thickness of the shell, the electronic structure of quantum dots can be changed, thus changing their optical, electrical and magnetic properties. Aging in a water bath at 65 ℃, then cooling to room temperature, washing the white colloid of zinc oxide isopropoxide after centrifugal separation with deionized water, and finally drying and grinding the product to obtain nano-Zn O.

4. The Application of Nanometer Zinc Oxide in Energy and Environment Field

4.1 Application of ZnO in the field of solar cells

Because of the good optical, electrical, gas-sensitive and photocatalytic properties of Zn-O nano-materials, it has been widely concerned and studied. In the past decades, more and more researchers have continuously reported various synthesis methods and characterization methods of luminescent gold quantum dots, which have been used in chemical detection and biological applications. This is because the ZnO with special morphology has a large specific surface area, which can load more dyes and absorb and capture more photoelectrons. The recombination between charges can be reduced along the direction of multiple branches of the crystalline ZnO nanotree, thus improving its photoelectric conversion efficiency and providing more energy. For example, its adsorption performance and photocatalytic performance can adsorb mercury in flue gas, oxidize inorganic substances, kill most germs and viruses, and thus remove some pollutants harmful to human beings. Using ITO/PEN as the counter electrode, the conversion efficiency of this special dye-sensitized solar cell to solar energy is 2.19%, while the conversion rate of pure ZnO nanoparticles is only 1.80%. At the same time, it can avoid using toxic mercury vapor like fluorescent lamps, thus realizing energy-saving and environment-friendly high-efficiency solid-state lighting.

Photoluminescence spectroscopy is a method to detect the electronic structure of materials. When irradiated to the tested sample, the laser will be absorbed, and its excess energy will be transferred to the sample, and finally consumed in the form of luminescence, which is the photoluminescence process. In this synthesis method, the core nanoparticles are not separated, and then continue to grow the shell material in the same system. The location and intensity of infrared absorption peaks reflect the characteristics of molecular structure, which can be used to identify the structural composition of unknown substances or determine their chemical groups. The absorption intensity of absorption band is related to the content of chemical groups, which can be used for quantitative analysis and purity identification. The hydroxyl groups on the surface of the silicon dioxide layer can satisfy the dispersion of ZnO quantum dots in water phase, and can also be used as reaction points for functionalization, thus meeting the requirements of biological probes and other application fields. With the continuous development of quantum dots, they have many advantages such as low price, wide absorption range and stability. People use this characteristic of quantum dots to improve the conversion efficiency of solar cells, and quantum dot sensitized solar cells have gradually developed.

4.2 Environmental application

ZnO, as a wide band gap semiconductor, has high activity because of its small size, large specific surface area, incomplete atomic coordination on the surface, and different surface bonds from those inside the particles. Ultraviolet and visible light irradiates the substance, and the absorption of different wavelengths of light by molecules or ions of the substance results in the difference of ultraviolet and visible light, thus obtaining the ultraviolet and visible light absorption spectrum. Ultraviolet visible absorption is caused by the transition of valence electrons. Electrons transition from valence band to conduction band, resulting in electron-hole pairs. Electrons and holes migrate to the surface of semiconductor respectively, and undergo reduction or oxidation reaction with substances adsorbed on
the surface. Because ZnO with one-dimensional nano-array structure has a large specific surface area, it can make atoms on the surface have more opportunities to participate in surface reactions, so it has high sensitivity to adsorbed species. Adding other specific materials into zinc oxide for compounding can improve the light absorption response capability of ZnO, promote the effective separation of photogenerated electrons and holes, improve the photocatalytic activity, and enhance the photocatalytic activity, photochemical stability and corrosion resistance of ZnO. Nano-ZnO has antibacterial and deodorizing effects, and can clean the air in closed spaces. For example, the use of plastic parts and some adhesive materials in automobiles will produce bacteria and pungent odor, so nano-ZnO is expected to be widely used in the field of automobile interior cleaning.

ZnO quantum dots (QDs) are a kind of nano-particles which have been studied by polymer-nano composite materials in light shielding materials. In the process of shell growth, there are two nucleation paths of shell materials. One is to nucleate independently to form another kind of nanoparticles independent of the core nanoparticles, forming a mixture of two kinds of nanoparticles. Piezoelectric nano-generator can be constructed by using piezoelectric characteristics to supply power to other nano-devices; ZnO is also characterized by abundant reserves, low price, easy preparation and environmental friendliness. However, ZnO is similar to other transition metal oxides when applied to the negative electrode of lithium ion battery, with poor cycle performance and low rate performance. If ZnO is compounded with another semiconductor, a built-in electric field will be formed at the interface due to the difference of Fermi energy levels between the two semiconductors, thus improving the separation efficiency of photo-generated carriers and photocatalytic efficiency. The good photocatalytic function of nano-ZnO also enables it to remove small molecular organic matter which is difficult to remove by ordinary water treatment technology.

5. Summary
Nanometer ZnO has been widely used in various fields in recent years, bringing great benefits to human life. Therefore, this paper chooses ZnO quantum dots as the research object, and elaborates the modification methods of ZnO quantum dots and their applications in polymer materials from the structure to the preparation process. The special three-dimensional hierarchical structure can alleviate the expansion and contraction of the material volume in the process of lithium ion insertion and extraction, and improve the structural stability of the material. These studies will also play a positive role in promoting the research and development of related fields, especially nanotechnology.

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