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Analysis of the Relationship Between the Proportion of Surface Atoms and Light Emission Competition in Semiconductor Nanomaterials

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Abstract. Because of their quantum size effects and surface effects, semiconductor nanomaterials show a wide range of optical properties, making them a core part of strategic industries like high-definition displays, solid-state lighting, and biomedical detection. Its light-emitting mechanism mainly includes exciton emission and defect emission. The coexistence and competition between the two is one of the key factors affecting performance. But traditional studies mostly attribute it separately to quantum size effects and surface effects, lacking a unified structural parameter. This article introduces 'surface atom ratio' as a parameter to uniformly describe this competitive relationship, and also analyzes its role as a bridge connecting quantum size effects and surface effects. Using a theoretical analysis approach, starting from the three major effects of nanomaterials, the aim is to derive the relationship between the proportion of surface atoms and size, and explain their connection to enhanced quantum confinement and defect state density; through systematically analyzing the effects of size and surface passivation on competition, the rules of luminescence competition centered on the proportion of surface atoms are summarized. This article found that this parameter can indeed effectively regulate the coexistence and competition between the two, and provides a reference for designing nanomaterials with high luminescence efficiency in a measurable way.

Keywords: semiconductor nanomaterials, surface atom ratio, exciton luminescence, defect luminescence

1. Introduction

Semiconductor nanomaterials, especially colloidal quantum dots and nanowires, are seen as the core building blocks of next-generation optoelectronic devices because their light emission depends on their size. The quantum size effect causes exciton energy levels to shift to higher energies (blue shift) and increases oscillator strength as the material size decreases, leading to narrow-band, color-tunable exciton emission. At the same time, the extremely high specific surface area of nanomaterials introduces a lot of surface dangling bonds, creating localized defect states in the bandgap that result in broad-band, red-shifted defect emission. Two types of luminescence coexist and compete with each other, directly affecting the device's light-emitting efficiency.

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However, traditional theories explain the two types of luminescence in a relatively fragmented way, only using the quantum size effect to explain the blue shift of exciton emission, and describing the formation mechanism of defect emission from a coordination chemistry perspective through surface effects, which has obvious limitations. For example, nanocrystals of the same size may exhibit a transition from purely excitonic emission to defect-dominated emission after different surface treatments; whereas under extremely strong confinement, perfectly passivated materials can achieve nearly 100% excitonic emission efficiency. This indicates that a single dimension or specific surface area parameter cannot fully explain the essence of luminescence competition, and a unified parameter is needed to simultaneously reflect this competitive relationship.

The surface atomic fraction proposed in this paper, that is, the ratio of the number of surface atoms to the total number of atoms, can, by virtue of its dual geometric and electronic attributes, reconcile the contradictory explanations of quantum size effects and surface effects, and establish a theoretical framework capable of predicting the dominant factor in luminescence. This study is expected to provide direct parameter guidance for the rational synthesis and surface engineering of nanoluminescent materials, with significant theoretical implications.

2. Three major effects and the theory of surface atom proportion

2.1. Quantum size effects and the luminescence mechanism of excitons

The quantum size effect describes what happens when a material becomes smaller than or equal to the exciton Bohr radius. At that scale, the motion of charge carriers is confined, so the originally continuous energy bands split into discrete energy levels. This increases the bandgap of the material. As the size decreases further, the bandgap becomes larger, the emitted photons have higher energy, and the wavelength becomes shorter [1].

Exciton luminescence occurs after a semiconductor material is excited and electrons in the conduction band combine with holes in the valence band to form excitons. These excitons then undergo radiative recombination and emit photons. The photon energy released during an exciton transition matches the energy difference when the exciton relaxes from a higher energy state to a lower one. Its wavelength depends directly on both the material's bandgap and its exciton binding energy [2].

Quantum size effects directly determine the energy states of excitons and the spectral positions of recombination luminescence by altering the spacing between energy levels and the bandgap width. As the material size decreases, the enhanced quantum confinement effect leads to a widening of the bandgap, resulting in a blue shift of the emission spectrum; conversely, an increase in size causes a red shift in the spectrum. Moreover, the quantum size effect also influences the competition between exciton emission and defect emission by altering the spatial distribution and binding energy of the exciton wave function, thereby determining the luminescence efficiency. In certain materials such as carbon dots, it is the combined effect of quantum size effects and effective conjugation length; however, when the size is smaller than the exciton Bohr radius, the quantum size effect usually dominates. Therefore, the quantum size effect is the core physical mechanism for regulating exciton emission properties [3].

2.2. Surface effects and defect luminescence mechanisms

The surface effect arises when the particle size of nanomaterials is reduced to near the exciton Bohr radius, causing the ratio of surface atoms to total atoms to increase sharply, resulting in incomplete

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coordination of surface atoms, a large number of dangling bonds, and high surface energy. This high activity state makes the surface atoms extremely susceptible to reacting with atoms or molecules in the environment, forming a wide variety of surface chemical structures. As the size decreases, the specific surface area of the material increases, and the surface atoms are in a high-energy state due to the lack of covalent bonds, making them highly prone to capturing electrons or holes, forming non-radiative recombination centers or specific surface states, resulting in defect luminescence [4].

2.3. Small size effects and surface atom fraction theory

The small-size effect refers to the phenomenon in which, when the size of a material is reduced to be comparable to or smaller than the physical characteristic scales such as the wavelength of light, the de Broglie wavelength of conduction electrons, and the Bohr radius of semiconductor excitons, the periodic boundary conditions of the crystal are disrupted, leading to significant changes in macroscopic physical properties, including acoustic, optical, electrical, and thermal behaviors.

The surface atom fraction refers to the ratio of the total number of atoms on the surface of a material to the total number of atoms. It has a significant negative correlation with the geometric dimensions of the material. As the material particle size decreases from the micrometer scale to the nanometer scale, the proportion of surface atoms rises sharply; when the particle sizes are 20 nm, 10 nm, 4 nm, 2 nm, and 1 nm, the proportion of surface atoms can reach 10%, 20%, 40%, 80%, and 99%, respectively [5]. This high proportion is due to nanomaterials having an enormous specific surface area, which leads to insufficient coordination numbers of surface atoms, the presence of a large number of dangling bonds and surface defects, and can trigger significant surface effects [6]. Therefore, the proportion of surface atoms can be regarded as a bridge between the small-size effect and the surface effect.

3. Mechanism and case analysis of surface atom proportion dominating luminescence competition

3.1. Exciton emission enhancement and quantum confinement effect under size regulation

Size regulation mainly influences exciton luminescence characteristics through the quantum confinement effect. When the material size is reduced to the exciton Bohr radius, the movement of electrons and holes is restricted, causing energy levels to shift from quasi-continuous states to discrete states, thereby altering the band gap size and resulting in a blue shift of absorption and emission peaks. In addition, the quantum confinement effect increases the probability of radiative recombination by enhancing the spatial overlap of electron-hole wave functions, but an increased proportion of surface defects may introduce non-radiative recombination pathways, weakening the luminescence efficiency.

A relevant example is the quasi-2D perovskite system: the bandgap can be tuned by adjusting the number of inorganic octahedral layers, denoted as n. Low-n phases exhibit blue-shifted emission due to confinement effects, but the low-dimensional phase with n=1 has a high density of defect states, which easily leads to defect-related luminescence [7]. In addition, when metal halide single crystals are size-controlled to form nanocrystals, their luminescence efficiency can also be enhanced through the quantum confinement effect. For example, the fluorescence quantum yield of Cu(II)-based halide nanocrystals increased from 15.8% to 48.43% after size reduction and passivation with water molecules [8].

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3.2. The relationship between defect state density and defect luminescence

Defect state density refers to the number of defects present per unit area, and its correlation with defect luminescence is primarily realized through the regulation of carrier behavior by the defect states. Research shows that surface defects act as energy traps under non-equilibrium states, capturing excited state carriers and thereby altering luminous efficiency. For example, thermal treatment of ZGGO:Cr long-persistent luminescent nanoparticles synthesized by the hydrothermal method to obtain T-ZGGO:Cr long-persistent luminescent nanoparticles can eliminate surface hydroxyl adsorption and partially repair defects, prolong the afterglow duration, and improve the signal-to-background ratio [9]. Moreover, when the density of defect states is excessively high, the interactions between defect states lead to an increase in non-radiative recombination of carriers, enhancing defect-related luminescence, which in turn suppresses the overall emission intensity. For example, in ZnGa2O4:Ce3 materials, the luminescence intensity of ground and dried samples shows significant differences compared to heat-treated samples due to the retention of high-density surface defects [10].

3.3. Regulation of luminescence competition by surface passivation

The higher the proportion of surface atoms, the defect state density increases exponentially; therefore, it is necessary to perform surface passivation to regulate this relationship. Surface passivation refers to forming a protective layer on the material surface by introducing an insulating layer or functional molecules, in order to reduce the density of surface defect states. For example, the surface passivation of carbon quantum dots is achieved by coating with an insulating layer or grafting organic molecules, in order to prevent energy loss and enhance optical activity [11]. Nanomaterials with a high proportion of surface atoms are prone to forming dangling bonds and defect states due to the under-coordination of surface atoms. By introducing passivating agents that bind with surface atoms, the number of dangling bonds is reduced, thereby decreasing the density of defect states. At the same time, different degrees of passivation have different competitive effects. When the surface is almost completely passivated, the proportion of surface atoms approaches zero, defect states disappear, and exciton emission becomes the only mechanism; when the surface is partially passivated, the proportion of surface atoms is still relatively high, passivating agents preferentially occupy highly active defect sites, but residual defect states may still induce impurity-level emission [12].

3.4. Summary of the relationship between surface atom proportion and luminescence competition

The higher the proportion of surface atoms, the greater the density of defect states formed by surface dangling bonds, resulting in an enhanced ability of surface defect states to capture charge carriers, with defect luminescence becoming dominant. When the proportion of surface atoms is ≥20%, the density of defect states caused by dangling bonds increases, and the strong trapping ability of surface defect states can suppress exciton luminescence. Defect luminescence then becomes dominant. At the macroscopic scale, the proportion of surface atoms is less than 2%, and at this point, the material properties are mainly determined by the bulk electronic structure, so surface effects can be neglected [13]. Through passivation treatment, the competitive landscape can be reconstructed, and exciton emission can once again become dominant through the quantum confinement effect [14].

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4. Conclusion

The proportion of surface atoms can be used as a single parameter to describe the competition between exciton luminescence and defect luminescence in semiconductor nanomaterials. As the material size decreases, this proportion increases markedly. That matters. A higher surface-atom proportion strengthens quantum confinement effects and raises the density of surface defect states, which gives a physical explanation for the competition between these two luminescence pathways.

The examples discussed above suggest that when this proportion is below the threshold, luminescence is mainly controlled by quantum confinement, so exciton luminescence remains dominant. Once the proportion rises, especially when passivation is weak, defect luminescence tends to become dominant instead. Surface passivation changes this balance because it lowers the effective defect density and makes exciton luminescence more likely to prevail. This parameter has been shown to apply to materials such as quantum dots, perovskites, nanowires, and carbon dots. In that sense, it provides a quantitative basis for designing nanomaterials with high luminescence efficiency. It can guide the optimization of color purity and efficiency balance in display devices, and also indicates strategies for regulating the signal-to-noise ratio of biomedical detection probes, possessing strong potential for technological translation. Of course, this paper has not yet conducted an in-depth exploration of the critical behavior of competitive rules. Future research could focus on precise atomic-level observations using aberration-corrected STEM, single-particle spectroscopy, and femtosecond time-resolved techniques to quantitatively characterize the atomic arrangement, band structure, and carrier dynamics of materials.

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