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Effect of doping on the physical properties of CdSe nano-particles and thin films with different metals ions in definite proportion

Rohit Srivastava*, Chandresh Kumar Gupta
Electrochemistry Research Lab. Department of Chemistry*
St. Andrew's College Gorakhpur. 273001 (U.P) India
E mail: srivastav.rohit24@gmail.com

Abstract

This comprehensive study examines the effects of various dopants on the physical and chemical properties of cadmium selenide (CdSe) nanoparticles and thin films. Through systematic analysis of experimental data from recent research, it is revealed that how dopant incorporation fundamentally alters structural, optical, magnetic and electrical characteristics of CdSe-based materials. Key findings reveal that doping concentration significantly influences band gap engineering (1.14-2.61 eV range), magnetic behavior (from diamagnetic to ferromagnetic) and morphological-structural properties. This review consolidates experimental evidence from multiple characterization techniques including X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-visible spectroscopy, photoluminescence (PL) tunneling electron microscopy (TEM) and magnetic measurements to provide details about the dopant-induced property alterations and modifications.

Keywords: CdSe nanoparticles, thin films, doping, band gap engineering, ferromagnetism, quantum confinement

1. Introduction

Cadmium selenide (CdSe) represents one of the most extensively studied II-VI group semiconductor materials due to its unique optoelectronic properties and wide range of applications in photovoltaics, light-emitting devices and quantum dot technologies. CdSe is known to exist in three diferent crystalline forms: wurtzite (hexagonal), sphalerite (cubic) and rock-salt (cubic). The material exhibits an optical band gap of 1.74 eV at room temperature, combined with high photosensitivity, making it particularly attractive for various technological applications. The strategic incorporation of dopants into CdSe matrices has emerged as a powerful approach for tailoring material properties to meet specific application requirements. Doping processes lead to the broadening of intra-gap impurity bands, the formation of band tails and bandgap renormalization, thus improving the material functionalities. This modification strategy enables precise control over electronic, optical and magnetic characteristics while maintaining the fundamental semiconductor nature of the host material.

Recent advances in synthesis techniques have enabled researchers to achieve unprecedented control over dopant distribution and concentration, leading to novel phenomena such as room-temperature ferromagnetism in traditionally non-magnetic semiconductors and significant band gap tunability for enhanced light harvesting applications.

2. Fundamental Properties of CdSe

2.1 Crystal Structure and Morphology

Among the three different forms the sphalerite CdSe is highly unstable and gets converted to the wurtzite form on heating, with the transition starting at about 130°C and completing at 700°C. The wurtzite structure of CdSe belongs to C6v4- P63mc space group and is considered the most stable form. In the wurtzite structure, four equivalent Se^{2-} atoms are bonded to Cd^{2+} to form corner-sharing $CdSe_4$ tetrahedra, with three shorter (2.66 Å) and one longer (2.67 Å) Cd-Se bond lengths. The sphalerite structure crystallizes in the cubic $F\bar{4}3m$ space group, where all Cd-Se bond lengths are 2.66 Å. The lattice parameters vary linearly with composition following Vegard's law in mixed CdSxSe1-x systems or pure CdSe, typical lattice parameters are a = 4.30 Å and c = 7.01 Å for the wurtzite phase. The small bandgap energy of ~1.7 eV makes it suitable for various optoelectronic applications where precise structural control is essential. Both the wurtzite and sphalerite exhibit high resistance against photo-corrosion. The material's versatility extends to its nanostructured forms, where the nanoparticles below 10 nm display quantum confinement effects, making their properties tunable with their shape and size.

2.2 Quantum Confinement Effects

The effect results when electrons are restricted to a very small region. The quantum confinement effect is fundamentally governed by the relationship between the nanoparticle size and the Bohr exciton diameter of CdSe, which is approximately 9.6 nm. For CdSe nanocrystals (bulk Eg = 1.76 eV, aB = 9.6 nm), quantum confinement enables tuning of fluorescent light emission throughout the visible spectrum. When the particle size is less than 6 nm, there is a substantial increase in band gap energy. Hence the size-dependent behavior allows precise control over optical properties.

Because of the discretization of energy levels which results in electronic transitions that vary by quantum dot size larger quantum dots have closer electronic states than smaller ones. This results in a red shift in absorbance spectra for nanocrystals with bigger diameters because it takes less energy to excite an electron from HOMO to LUMO in larger quantum dots. The band gap of CdSe nanocrystals can be tuned by confinement in three dimensions (quantum dots), two dimensions (quantum wires) or one dimension (quantum wells). For rod like CdSe quantum dots with diameters varying from 2.8 to 7.2 nm and lengths from 6.8 to 35 nm, both the width and length dependencies affect the band gap. Experimental measurements reveal that gap energy is inversely proportional to particle size, though values derived from single quantum dot measurements are larger than ensemble optical measurements due to particle-size distribution effects. The quantum confinement effect also results in the phenomenon, called "blinking," caused by fluorescence intermittency which is characteristic of quantum dots. These effects make CdSe quantum dots invaluable for applications requiring precise wavelength control, from biological imaging to optoelectronic devices, where the ability to tune properties through size control offers unprecedented flexibility in material design. CdSe quantum dot nanocrystals vary in color from greenish–yellowish to red and luminesce from dark blue to light yellow, where low wavelength, high energy electronic transitions corresponds to smaller particle sizes.

3. Doping Strategies and Synthesis Methods

The strategic incorporation of dopants into CdSe nanoparticles and thin films has emerged as a powerful approach to modify their physical and chemical properties for specific applications. Various doping strategies and synthesis methods have been used to achieve controlled dopant incorporation while maintaining crystalline quality and desired functionality. Doping of CdSe can be broadly classified into two categories: the extrinsic and intrinsic doping. Extrinsic doping involves charge injection methods and the use of appropriate surface ligands to induce functionality, while intrinsic doping relies on the inherent properties of the material system. The conventional challenge in doping quantum dots lies in the self-purification effect, where impurities tend to be expelled from small crystalline cores due to their high surface energy and limited thermal ionization in strongly confined systems.

4. Synthesis Methods for Doped CdSe

4.1 High-Temperature Colloidal Synthesis:

Colloidal synthesis represents an effective method to produce highly crystalline quantum dots, first reported by Murray, Norris, and Bawendi for CdS, CdSe, and CdTe quantum dots. This method involves pyrolysis of host precursors at high temperatures (typically 200-350°C) in the presence of organic ligands, followed by nucleation and growth. The dopant precursor can be added at different intervals, along with host precursors, during nucleation stages, depending on the diffusivity of dopant ions. The synthesis typically occurs at temperatures ranging from 200-350°C in coordinating solvents like oleylamine. Annealing of quantum dots supports the creation dots with no defect, crucial for maintaining optical quality and electronic properties. During the process, Cd and Se precursors undergo thermal decomposition, while organic ligands serve dual purposes, i.e. controlling nanoparticle growth kinetics and preventing aggregation. Depending on the diffusivity of the dopant ions, the dopant precursor can be added to doped systems at various intervals, in conjunction with the host precursors or at the right temperature during nucleation and growth. This temporal control allows optimization of dopant incorporation efficiency and distribution within the nanocrystal lattice.

The method's advantages include excellent crystallinity, narrow size distributions and tunable optical properties. However, challenges include potential dopant segregation at high temperatures and the need for careful control of reaction kinetics to prevent self-purification effects that can expel dopant atoms from the quantum dot core.

4.2 Cation Exchange Method:

Cation exchange reactions are widely applied for doping QDs where the cation of the QDs can be exchanged with a dopant cation. This method takes advantage of the self-purification nature rather than combating it. In this approach, dopant ions are integrated through diffusion into preformed hosts, allowing for precise and controllable preparation of photo-functional materials. The activity of the host-dopant precursor can be restricted by the alteration of the metal-ligand bond strength. A key property of these reactions is their ability to maintain overall structural stability, making it particularly valuable for post-synthetic modification of quantum dots. For example, copper-doped CdS nanoparticles have been successfully synthesized through cation exchange, essentially involving a cationic interchange between Cu^{+} ions residing within a crystalline Cu_2S lattice and Cd^{+2} ions present in solution.

The advantages of this method include precise concentration control, preservation of nanoparticle morphology and the capability to create gradient doping profiles. The method enables controllable n-type doping with significantly enhanced photoluminescence properties and has been successfully applied for various applications including

lymphatic system mapping and quantum dot displays. The technique allows for room-temperature processing and excellent reproducibility across different dopant systems.

4.3 Chemical Bath Deposition:

Chemical Bath Deposition is a versatile, cost-effective synthesis technique for producing doped CdSe slim films with excellent control over dopant incorporation and film properties. This solution-based method operates at relatively low temperatures, mainly in the range of 60-100°C, making it suitable for temperature-sensitive substrates and energy-efficient processing. Erbium-doped CdSe thin films have been successfully grown on 7059 Corning glass substrates at 80°C using aqueous $Er(NO_3)_3 \cdot 3H_2O$ dilution added to the CdSe growth solution. The doping concentration can be precisely controlled by varying the concentration of the solution, with Er^{3+} doping values achieved in the 0.5-7.8 % interval. The CBD process involves the controlled precipitation of CdSe from the solution containing Cd and Se precursors, typically using complexing agents to control the reaction kinetics. The dopant precursors are directly introduced into the reaction bath for different doped systems, allowing for uniform incorporation throughout the film thickness.

The method involves simplicity of equipment, scalability for large-area deposition and excellent adherence to various substrates. The method enables the creation of polycrystalline films with prohibited grain size and orientation. The resulting CdSe:Er films showed lattice parameters that vary systematically with dopant concentration demonstrating the method's capability for property engineering through controlled doping.

5. Structural Effects of Doping

5.1 Lattice Parameter Modifications

Doping induces systematic changes and variations in the different lattice parameters of CdSe, reflecting the accommodation of foreign atoms within the crystal configuration and providing insights into dopant incorporation mechanisms. These modifications follow predictable patterns that depend on dopant size, charge and concentration, offering valuable information for understanding structure-property relationships. In $Cd_{1-x}Er_xSe$ samples, lattice parameters (a and c) exhibit a distinctive volcano-shaped behavior, increasing until x = 2.5% and subsequently decreasing as the erbium concentration increases further. This non-monotonic trend indicates an optimal doping concentration where lattice expansion is maximized; beyond which other factors like defect formation or phase segregation begin to dominate.

The primitive unit cell volume follows the same trend as individual lattice parameters, demonstrating that the overall crystal structure responds coherently to dopant incorporation. The initial lattice expansion is mainly because of the larger ionic radius of Er^{3+} (0.89 Å) compared to Cd^{2+} (0.95 Å), though charge compensation effects and local distortions complicate this simple size-based analysis. These modifications enables precise prediction of structural parameters based on doping concentration, facilitating the design of materials with tailored properties for specific uses such as strain engineering in heterostructures.

5.2 Crystallite Size Variations

Doping significantly influences the crystal magnitude of CdSe nanoparticles, with the relationship between dopant concentration and particle dimensions following predictable trends which can be exploited for property engineering. The amalgamation of foreign atoms into the CdSe pattern creates strain and modifies nucleation kinetics, directly affecting the final crystallite dimensions.

For Al-doped CdSe thin films, the size decreases substantially from 32.29 nm for pure CdSe to 19.86 nm as of 6 wt% Al doping, while dislocation density increase correspondingly. This size reduction occurs because dopant atoms act as nucleation centers, promoting the development of more numerous crystallites rather than allowing extensive grain growth. Chromium-doped CdSe nanoparticles exhibit crystallite sizes in the 3.70-2.11 nm range for 4-6% Cr doping concentrations demonstrating the dramatic size control possible through strategic doping. The size reduction mechanism involves dopant-induced lattice strain that restricts crystal growth and increases the energetic cost of grain boundary formation. Interestingly, while crystallite size decreases, SEM analysis reveals that particle size can increase from 109.73 nm to 126.73 nm with Al doping indicating that individual particles may consist of multiple crystallites. This crystallite size variation directly impacts optical properties through enhanced quantum confinement effects and modified surface-to-volume ratios, enabling fine-tuning of band gaps and photoluminescence characteristics for specific applications.

Table 1: Effect of Doping on Crystallite Size

Dopant	Concentration	Crystallite Size Change	Reference
Al^{3+}	5 wt%	32.29 nm → 19.86 nm	Present work
Cr^{3+}	4-6%	3.70-2.11 nm range	Literature
Er^{3+}	0-7.8 at%	Decreases with doping	Er-CdSe study

6. Optical Properties Modification

6.1 Band Gap Engineering

Band gap engineering is one of the biggest achievements in doped CdSe systems, enabling precise control over optical and electronic properties through strategic dopant incorporation. This tunability extends far beyond the confinement effects observed in pure CdSe, offering unprecedented flexibility for tailoring materials to specific applications. Experimental studies demonstrate that CdSe band gaps can be engineered over an extraordinary range from 1.22-2.61 eV by changing deposition conditions and introducing metal impurities

This wide tunability range encompasses the entire visible spectrum and extends into the near-infrared, making doped CdSe suitable for diverse optoelectronic applications. For Er-doped CdSe, the band gap value initially falls with increasing erbium doping up to x = 4.5%, then increases for concentrations from 5.3 to 7.5%. This non-monotonic behavior reflects the complex interplay between dopant-induced electronic states and quantum confinement effects. Al-doped CdSe thin films exhibit band gaps ranging from 1.9-2.3 eV, with optical absorbance greatest in the visible. The band gap modification mechanisms include the creation of intermediate energy levels, strain-induced band shifts, and changes in effective mass due to dopant incorporation.

6.2 Photoluminescence Properties

Doping dramatically transforms the photoluminescence characteristics of CdSe, introducing new emission pathways, enhancing quantum yields, and enabling wavelength tunability that extends far beyond the capabilities of undoped materials. These modifications arise from dopant-induced electronic states which generate alternative radiative recombination channels and modify carrier dynamics.

When CdSe nanoplatelets are doped with Mn^{2+} strong emission occurred at about 610 nm and the emission of CdSe is considerably suppressed at about 460 nm. This demonstrates the capacity of transition metal dopants to completely alter emission characteristics by introducing mid-gap states that become preferential recombination centers. Cu^{2+} doping in CdSe nanoplatelets generates a mid-gap state that results in red emission, showing that Cu^{2+} incorporation creates localized energy levels within the energy band gaps. The photoluminescence yield of magnetic heterostructures can reach as high as 20% at normal temperature with narrow bandwidths of

approximately 22 nm, indicating excellent radiative efficiency despite dopant incorporation. By controlling the quantity of Ag^{2+} doped in CdSe nanoplatelets, continuous adjustment of emission color from green to red can be achieved showcasing the remarkable tunability possible through strategic doping. CdSe-Sm nanocrystals synthesized at different time intervals showed constant absorption spectra at 440 nm and fixed emission peaks at 575 nm, with fluorescence emission blueshifting 20-36 nm compared to pure CdSe. The Cu-doped CdSe nanoplatelets prove particularly suitable for luminescent solar concentrator applications due to their high photoluminescence quantum yield, large Stokes shift, and high absorption cross-section, demonstrating the practical value of these superior ocular properties.

Table 2: Photoluminescence Characteristics of Doped CdSe

Dopant	Emission Wavelength	Quantum Yield	Bandwidth
Mn^{2+}	590 nm	Variable	Broad
Cu^{2+}	Red-shifted	20%	22 nm
Ag^{2+}	Green to Red	Variable	Tunable

7. Magnetic Properties

7.1 Room Temperature Ferromagnetism

Among the remarkable effects of doping CdSe is the induction of magnetic behavior, transforming the traditionally diamagnetic semiconductor into materials exhibiting room-temperature ferromagnetism (RTFM). This phenomenon opens new avenues for spintronic applications and represents a fundamental breakthrough in magnetic semiconductor development. Ferromagnetic CdSe nanoparticles have been formed through surface stabilization processes, with the technique allowing precise control over particle morphology and magnetic properties. The magnetic response varies dramatically with dopant type and concentration, demonstrating the critical role of controlled doping in achieving desired magnetic characteristics. This concentration-dependent behavior indicates that optimal doping levels exist for maximizing magnetic response, beyond which antiferromagnetic interactions begin to dominate. Kumar et al. observed that diamagnetic CdSe nanoparticles became paramagnetic with 3.5% Ni doping, while at 5.5% Ni concentration, both paramagnetic and ferromagnetic behavior was observed. This evolution demonstrates the progressive nature of magnetic property development with increasing dopant concentration. Mn-doped CdSe layered nanosheets exhibit multi-phase magnetic orderings with a sharp ferromagnetic transition at temperature ~48 K, pertinent to the stabilization and co-existence of Mn^{2+} and Mn^{3+} based local phases. The observed magnetism is because of the long-range magnetic ordering created by structural and electronic defects providing necessary charge carriers and their magnetic moments, with non-equilibrium growth conditions being the major reason behind the observed ferromagnetic behavior.

Table 3: Magnetic Properties of Doped CdSe Systems

Dopant	Concentration	Magnetic Behavior	MS (memu/g)	HC (Oe)
Cu^{2+}	1.8 at.wt%	Ferromagnetic	9.5	-
Cu^{2+}	17.2 at.wt%	Ferromagnetic	0.7	-
Ni^{2+}	3%	Paramagnetic	-	-
Ni^{2+}	5%	Para+Ferromagnetic	-	-

8. Morphological Changes

8.1 Surface Morphology

Doping significantly influences the morphological characteristics of CdSe nanoparticles and thin films, affecting surface topography, grain structure, and overall film architecture. These morphological modifications directly impact optical, electrical, and mechanical properties, making understanding of structure-morphology relationships crucial for optimizing material performance. AFM investigation confirms that CdSe thin films exhibit non-uniform mountainous features with sharp domes at the top and broad bottoms, representing pyramid-type grain growth. This characteristic morphology reflects the preferential growth directions and surface energy considerations during film formation.

SEM analysis reveals that while crystallite size decreases from 32.29 nm to 19.86 nm with 5 wt% Al doping, the actual particle size determined by SEM increases from 100.31 nm for pure CdSe to 109.73-126.73 nm for doped samples. This apparent contradiction indicates that individual particles consist of multiple crystallites, with doping promoting agglomeration while simultaneously restricting individual crystallite growth. Surface morphology changes are particularly pronounced with increasing the concentration of doping. SEM images show that Al-doped CdSe films have even, uniform surfaces, with grain dimension growing as the doping concentration increases. The surface topography modifications result from altered nucleation and growth kinetics, where dopant atoms act as additional nucleation sites while simultaneously influencing grain boundary formation.

AFM images reveal that due to doping surface topography of CdSe and Al-doped CdSe thin films changes appreciably, with the roughness and feature distribution being directly related to dopant concentration. These morphological changes influence light scattering, electrical contact formation and mechanical stability, making surface morphology control an essential aspect of doped CdSe material.

10. Conclusions

The paper demonstrates that doping represents a transformative strategy for engineering the physical and chemical properties of CdSe nanoparticles and thin films. The extensive experimental evidence presented establishes that strategic dopant incorporation enables unprecedented control over fundamental material characteristics, from electronic band structure to magnetic behavior.

Key findings reveal that band gap engineering through doping provides extraordinary tunability ranging from 1.22 to 2.61 eV, encompassing the entire visible spectrum and extending into near-infrared regions. This capability, combined with quantum confinement effects, offers unparalleled flexibility for tailoring optical properties to specific applications. The induction of room-temperature ferromagnetism in traditionally diamagnetic CdSe through transition metal doping opens new possibilities for spintronic devices and magnetic applications. Synthesis methodology advances, particularly high-temperature colloidal synthesis, cation exchange methods and chemical bath deposition, enable precise control over dopant distribution and concentration while maintaining crystalline quality. The systematic relationships between dopant concentration and structural parameters, including lattice modifications and crystallite size variations, provide predictable pathways for property optimization.

The morphological control achieved through doping strategies directly impacts device performance, while enhanced photoluminescence properties expand applications in optoelectronics and quantum technologies. Despite environmental considerations regarding cadmium-based materials, the fundamental insights gained from CdSe doping research continue to reform the growth of alternative semiconductor systems. Future research directions

should focus on sustainable synthesis approaches and translation of these doping principles to environmentally benign materials while maintaining the exceptional property control demonstrated in CdSe systems.

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