



Bio-Encapsulated CdSe/ZnSe Composite Nanorods

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ABSTRACT

The high-quality of bio-encapsulated CdSe/ZnSe composite nanorods has been developed by using environmentally friendlier amino acid solvents L-cystine and CTAB. The crystallographic properties of CdSe/ZnSe systems were investigated by XRD pattern, which are indicating both CdSe and ZnSe nanocomposite hetrostructures are in wurtzite hexagonal phase. Energy dispersive X-ray analysis (EDA) confirms the elemental compositions of the two components are rich. The SEM/TEM photographs confirm the presence of nanorods (NRs), the obtained NRs have diameter in the range of 50-70 nm and the length is in the range of 150-175 nm. The photoluminescence (537 nm) and absorption (524 nm) spectral study support the existence of predominant nanorods. The lattice plane can be indexed with the wurtzite (hexagonal) structure and calculated interplanar distance is around 0.338 nm. The XRD and UV/PL characteristic studies confirm quantum confinement effect by the blue shift. The narrow photoluminescence were observed at 537 nm in the prepared nanorods. The mechanism of formation of the nanorods were investigated and discussed on the basis of experimental results.

1. Introduction

Inorganic nanocrystals with certain geometries exhibit unique shape dependent phenomena and subsequent utilization of them as building blocks for the key components of nanodevices is of huge interest. Architecture of these nanocrystals can be simply classified by their dimensionalities: zero-dimensional (0D) quantum dots which including spheres, cubes and tetrahedrons. One-dimensional (1D) are nanorods and nanowires, two dimensional (2D) are nanodiscs and plates and other advanced shapes such as rod-based multipods and nanostars. The 1D semiconductor nanostructures are considered to be critical building blocks for nanoscale electronic and optoelectronic devices fabrication. To improve performance of the nanodevices, it is important that the efficiency of 1D semiconductor nanostructures be increased [1].

Recently, studies on the shape control of nanocrystals have been highly focused on 1D system. Since 1D rod growth is the fundamental step of anisotropic shape control, it may be possible to have further control of nano-building blocks. To generate 1D nanocrystals, researchers have explored one step *in situ* methods similar to those of the well-studied spherical nanocrystals. For example, the 1D colloidal rod based system of CdSe has been successfully demonstrated by Peng et al [2] and Alivisatos and co-workers [3]. The use of binary capping molecules such as TOPO and hexylphosphonic acid (HPA) was effective for the generation of shape anisotropy in CdSe along with the nature of its intrinsic hexagonal structure. Tang and co-workers [4] demonstrated the formation of CdTe nanowires via crystal dipole-induced self-assembly of CdTe nanospheres.

In principle, ZnSe is a very good candidate of shell materials having a wider bandgap (2.72 eV) than that of CdSe (1.74 eV) and the band alignment is of type-I, ie, both holes and electrons are confined in CdSe core [5]. The preparation of "core\shell" systems requires careful selection of both core and shell materials with the goal to optimize the passivation and to minimize structural defects induced by positive mismatch of their lattice parameters [6].

Presently, hetrostructured nanocrystals (NCs) exhibiting photoinduced charge separation have become the subject of an increasing number of investigations due to their potential use in photovoltaic applications. Spatial separation of electrons and holes in these materials is achieved via a staggered alignment of band edges at the boundary of nanocrystalline

domain that form the composite nano objects [7]. Various II-VI semiconductors have been investigated as nanocomposite material for CdSe/ZnSe nanorods to improve the product yield and chemical stability. However, CdSe/ZnSe and CdSe/CdS are mostly obtained through TOP/TOPO system in which reagents are injected into a hot coordinating solvent like TOPO at high temperature (200-400 °C). The process needs to be operated under nitrogen atmosphere or in a glove-box because the positive reagents used in those systems are hazardous.

To overcome this problem, an attempt has been made in the present study to prepare CdSe/ZnSe nanocrystals in aqueous solution. The aim of present work is to synthesize water soluble L-cystine and CTAB capped CdSe/ZnSe nanorods through a straightforward simple step process by using safe and low-cost organic/inorganic precursors and without using TOPO/TOP. L-cystine is an important source of sulfide in human metabolism. The protein containing Cystine, such as metallothionein will bind metals such as cadmium, lead and mercury tightly. It is observed, the mixture (CTAB and L-cystine) focuses the size distribution during particle growth so that, no post preparative size-selective precipitation is required. The prepared CdSe nanocrystals surface can be passivated with ZnSe nanocrystals from the crude solution by growing organic surface modification with alkylamines. The high quality CdSe/ZnSe hetrostructure nanocomposite was successfully prepared by simple and versatile hydrothermal approach and it was characterised by X-ray diffraction, SEM/ Transmission electron microscopy (TEM) and UV-visible absorptions and photoluminescence (PL) spectroscopy.

2. Experimental Methods

2.1 Synthesis of CdSe/ZnSe

Cadmium nitrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) with sodium selenite (Na_2SeO_3) and zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) with sodium selenite were used for the synthesis of CdSe and ZnSe respectively. The used precursors are analytical reagent grade (Merck, India, purity $\geq 98\%$). The synthesis procedure of CdSe is already reported by the author [8], similarly ZnSe was prepared as follows. 2.9747 g of zinc nitrate (0.01 mol) was dissolved in 20 mL of direct Milli-Q water and 0.86 g of sodium selenite (Na_2SeO_3) was dissolved in 15 mL of hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$). To synthesis CdSe/ZnSe composite, 3.208 g of L-cystine was dissolved in water then mixed slowly with ZnSe containing solution and 0.46 g of CTAB was dissolved in water and mixed with CdSe solution. Both the solutions were

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mixed and transferred into a teflon-coated autoclave. The autoclave was sealed and heated at 200 °C for a reaction time of 4 hrs. After that it was allowed to cool to room temperature. The obtained dark red CdSe/ZnSe precipitate was separated by centrifuge and its impurities were removed by repeated washing with water, ethanol and methanol. The synthesized nanocomposite was annealed at 120 °C.

2.2 Characterization Techniques

Powder X-ray diffraction (PXRD) pattern was recorded on model Rich Seifer rotation anode X-ray diffractometer with Ni-filtered $\text{CuK}\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$). Transmission electron microscopy (TEM) images, high-resolution transmission electron microscopy (HRTEM) images and selected-area electron diffraction (SAED) patterns were taken at 200 KV with JEOL- JEM 2010 electron microscope. Scanning electron microscopy (SEM) images were taken with a Hitachi-S 4700 microscope with an accelerating voltage of 15 KV. UV-Vis absorption spectra and photoluminescence (PL) spectra were recorded by using Varian Cary 5E spectrophotometer and Jobinyvon Fluorolog-3-11 spectrofluorometer respectively. In the PL study, a 450W Xenon lamp was used as the excitation source and a photomultiplier tube with a resolution of 0.2 nm acted as the detector.

3. Results and Discussion

3.1 Powder X-Ray Diffraction

The crystallographic properties of CdSe/ZnSe systems were investigated by XRD pattern shown in Fig. 1. The major diffracted planes (002), (100), (200) and (103) are indicating both CdSe and ZnSe nanocomposite heterostructures are in wurtzite hexagonal phase. This has been verified with JCPDS file numbers of CdSe (77-2307) and ZnSe (89-2940). A hump in the lower angle region shows correspond the character of nanocrystalline structure. The broad diffraction spectral feature indicates the nanometric dimensions of CdSe/ZnSe. The broadening of the diffraction spectrum could also be expected for a highly crystalline with variations in the lattice space induced by the lattice mismatch [9]. This explanation is consistent with the observation of structural disorder of some of the particles in the periphery region. This shows composite formation which is confirmed in the UV-Vis absorption spectrum and PL studies. The hydrothermally as grown CdSe/ZnSe nanocrystals have hexagonal (wurtzite) phase and their crystalline is very high with a negligible content of the amorphous phase and the broad diffraction peaks which originate from the overlapping of multiple peaks and their fine size.

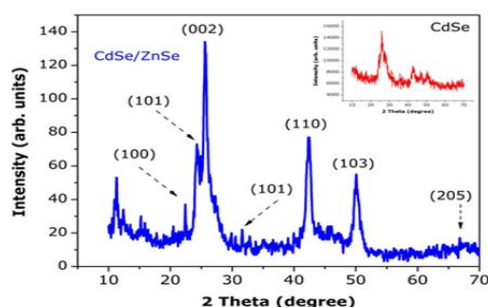


Fig. 1 Powder XRD pattern of nanocomposite

3.2 Energy Dispersive X-Ray Spectrometry (EDX)

The EDX was used to examine the local atomic composition of the heterostructures. The resulting EDX lines-scan Fig. 2 confirms the presence of Zn at either end of branched-rod heterostructures. Selenium (Se) is present at the center of the rod and Cd is present throughout the rod. Similarly the results of extended rods confirm the end growth of thinner CdSe extensions on ZnSe rods. While spherical size particles are sufficiently small, the spatial resolution of the EDX data was limited by the drift of the instrument so that it remains uncertain about the composition of the interface.

3.3 Scanning Electron Microscopy (SEM)

The SEM images of water soluble CTAB, L-Cystine capped/reagent of CdSe/ZnSe nanorods is shown in Fig. 3a and b. The hydrothermal synthesis temperature along with the capping reagent can influence the nanoparticle size and morphology. At lower temperature (200 °C) spherical nanocomposite is initially formed. A close observation of the SEM image of CdSe/ZnSe suggests that the surface of nanorods is relatively

smooth and this may be attributed to the relatively high reaction time/temperature employed. It reveals that L-cystine plays an important role in controlling the size and nano-dispersion of the CdSe/ZnSe nanocrystal. The absence of agglomerates is attributed to the role of CTAB. In the shape evolution of CdSe/ZnSe, the capping agent CTAB/ L-cystine gets adsorbed at different planes of the incipient CdSe/ZnSe. The nucleation not only prevents the particles from agglomeration, but also influences the growth of rod-like morphology.

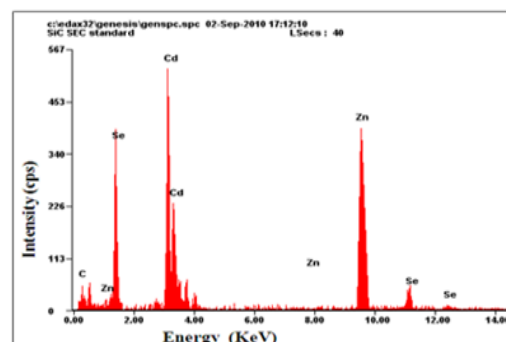


Fig. 2 EDX line scanning spectrum of CdSe/ZnSe

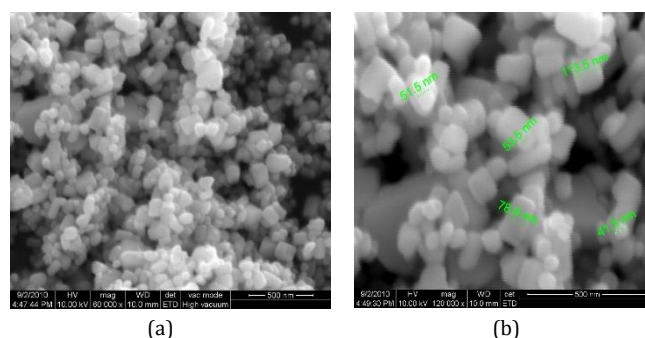


Fig. 3 SEM image of CdSe/ZnSe nanorods

3.4 Transmission Electron Microscopic Analysis (TEM)

The TEM analysis allows visualizing particles at nanosize regime with high degree of accuracy. It offers better understanding about passivation of CdSe/ZnSe nanocomposite growth aspects and helps to analyze the actual size of the particles, shape and growth pattern.

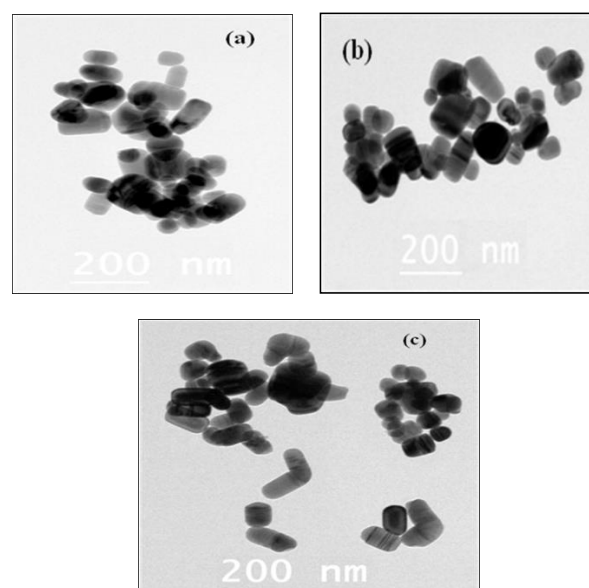


Fig. 4 TEM images of growing CdSe/ZnSe nanorods

The TEM photograph Fig. 4a-c shows the presence of nanorods with a major population of prolonged nanorods as well as a minor population of spherical shape nanoparticles. The obtained nanorods have diameter in the range 50-70 nm and the length is in the range of 150-175 nm whereas the spherical shape nanocomposites are achieved within 40-50 nm diameters. The PL ($\lambda_{em} \sim 537 \text{ nm}$) and absorption ($\lambda_{abs} 524 \text{ nm}$) spectral

study support the existence of predominant nanorods. At the same time, the minor population of spherical nanoparticles is observed in the ensemble with the help of minor peak at 520 nm as shown in Fig. 4b and such similar rods are also seen in the TEM images. It is clearly seen when the time of growth increases, the spherical shape of the nanocomposite grow towards rod-like morphologies. The UV and PL studies also reveal the formation of nanorods and spherical nanocomposite. The obtained nanocrystals belong to CdSe/ZnSe composite structure. It is observed from the TEM images (Fig. 4a and b) that the CdSe/ZnSe nanorods synthesized in this work are in good shape with less pronounced stacking faults and very less agglomeration in the synthesis condition at 200 °C for 4 hrs. So we can conclude that the reaction time and temperature are more important in the formation of nanorods.

The SAED pattern of CdSe/ZnSe nanorods in the Fig. 5 shows a superimposed pattern of single crystalline composite material. The crystallinity of composite NC is confirmed by the clear lattice fringes Fig. 6 and the intermediate lattice spacing between those of CdSe and ZnSe, as indicated by SAED and X-ray diffraction patterns. The lattice fringes persist throughout the entire nanocrystal and it is an indication of epitaxial growth.

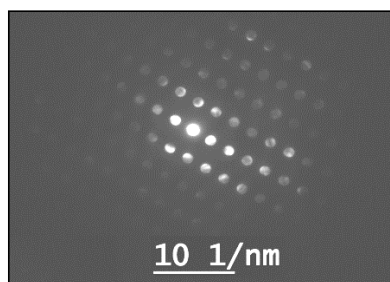


Fig. 5 SAED pattern of nanocomposite

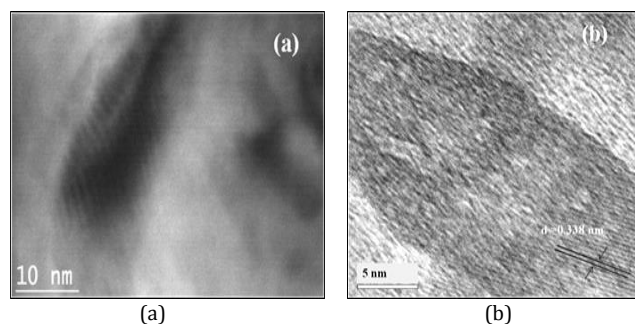


Fig. 6 HRTEM images of as-prepared CdSe/ZnSe nanorods

HRTEM (Fig. 6a and b) of linear junctions found in extended rods reveals continuations of anisotropic wurtzite growth of the semiconductor. At these junctions, the small diameter allows dislocation-free epitaxial growth despite of fair large lattice mismatches. Further the figure shows the lattice fringes of a single nanorod and clearly visible lattice plane endorses the formation of well crystallized single crystal CdSe/ZnSe nanorods. This lattice plane can be indexed with wurtzite structure and the calculated interplanar distance is around 0.338 nm.

In the search for a reactive, water-soluble and readily available ligand for CdSe nanorods, the possibility of using CTAB and L-cystine has been explored in this work. Moreover, the synthesis of CdSe/ZnSe composite nanorods was successfully achieved via a simple hydrothermal technique. It is worth mentioning that water-based synthesis with thiols as the capping agent has attracted significant attention for applications in biological imaging. Additionally the organic solvent and water are cheap, nontoxic, inflammable and readily available. Compared to the other thiols, we suggest that L-cystine and CTAB proves the better surface passivation of the CdSe/ZnSe crystalline lattice under laboratory conditions. It is noted that thiol-capped NC containing amino groups can be easily used for the conjugation of two binary metals. The organic surfactant (CTAB) adsorbed by the coating of nanorods is essential to disperse and stabilize them in the solvent which could prevent their further agglomeration and oxidation [10]. The nanorods and spherical nanoparticles are in the wurtzite structure, elongated along the unique *c*-axis. Invariably, such nano crystals contain statistical distributions of stacking faults. In CdSe/CdS and CdSe/ZnSe [11] stacking faults are clearly evident with dislocations and agglomeration free CdSe/ZnSe nanorods.

Twin rotational faults also appear in CdSe/ZnSe, with the twin boundaries. Our approach is to synthesize heterostructures of CdSe/ZnSe nanorods through quasi 1D dimensional arrangement of components with

unique functionality. Representative heterostructures reported here incorporate either type-I or type-II interfaces to define the nature of the interactions between components. These stacking faults are the predominant forms of disorder in bulk II/VI materials [12]. However in the present case, very less stacking faults are occurred. In the case of CdSe/ZnSe, electrons and holes are separated by a barrier in extensions of rods and spherical nanocomposite. The coupling of these rods is tunable by changing the length of the original rod or by extensions or selecting a different material to vary the barrier height.

3.5 UV-Vis Absorption Spectroscopy

In the UV-Vis absorption spectral study, red shift in frequency indicates the formation of core/shell structure while blue shift indicates the formation of composite material [13, 14]. The effect of passivation on the optical properties of CdSe was explored with ZnSe on the overgrowth of CdSe. The true changes in the optical properties were observed in the as prepared CdSe nanocrystals and the composite CdSe/ZnSe samples. Room temperature absorption spectra of pure CdSe nanocrystals and CdSe/ZnSe nanocomposite are shown in Fig. 7. The spectra display a similar absorption edges but there is difference in their observed wavelengths.

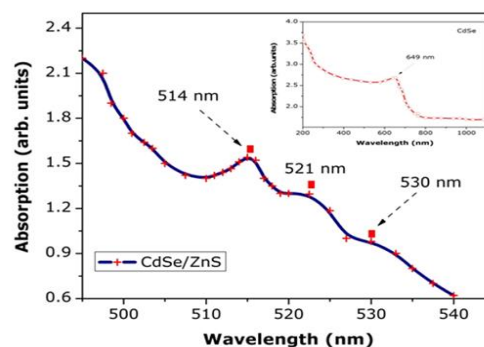


Fig. 7 Absorption spectra of pure CdSe and CdSe/ZnSe nanocomposite

The absorption cut-off frequency (λ_{abs}) of CdSe is 700 nm and for CdSe/ZnSe is 524 nm. The increase in the frequency shift indicates the quantum-confinement in the CdSe/ZnSe rods. The blue shift confirms that the formed material is a nanocomposite. The presence of ZnSe on the CdSe surface decreases the exciton energy which is consistent with relaxation of quantum-confinement in the CdSe rods. It may be suggested that some portion of the low-energy optical transitions are localized in the ZnSe layer [15].

3.6 Photoluminescence Study

It is well known that ZnSe is a wider band gap semiconductor compared to CdSe nanocrystal. CdSe nanocrystal has been widely used commercially as a phosphor in luminescent devices due to its emission in the visible range. Room temperature photoluminescence (PL) spectrum of the CdSe/ZnSe nanocomposite was measured using the excitation wavelength of 350 nm. Generally, it is known that the optical properties of particle depend on many factors such as particle size, shape and crystal surface state. Defect surfaces normally act as site for non-radioactive recombination of electron-hole pairs. So the higher crystallinity with lower concentration of defect will benefit the emission intensities. The results of the present work reveal that the defect is related to the emission of synthesized nanocomposite and is evident from the recorded PL spectrum of CdSe/ZnSe. It is well known that due to their very small diameter, the nanocrystals have a very high ratio of surface to volume that makes them susceptible to various surface defects. Moreover, the particle size, shape and surface of the crystallites have significant role in the emission properties.

Incorporation of overcoated nanocrystals results in a remarkable enhancement of the photoluminescence properties of the materials. The PL spectra (Fig. 8a and b) is now dominated by an intense band-edge emission. The width of the emission band is comparable to those for the initial nanocrystals. The PL spectrum shows a strong emission peak which lies in the visible region (537 nm) and another relatively weak emission peak in the visible region centered around 520 nm. Further the effect of capping ligand on CdSe/ZnSe nanoparticles is to be investigated. Comparing the PL spectra of pure CdSe and composite CdSe/ZnSe nanocrystals, it is to be noted that the PL spectra of both pure and composite nanocrystals are quite broad. The peak becomes blue shifted 700, 537 nm for pure CdSe and CTAB, L-cystine capped composite nanorods respectively [8, 13]. Usually in the absence of the capping ligand, uncontrolled nucleations and growth of the particles result in the

formation of defect states. This is the reason for using capping ligand like CTAB, L-cystine during the synthesis of CdSe/ZnSe nanocrystals.

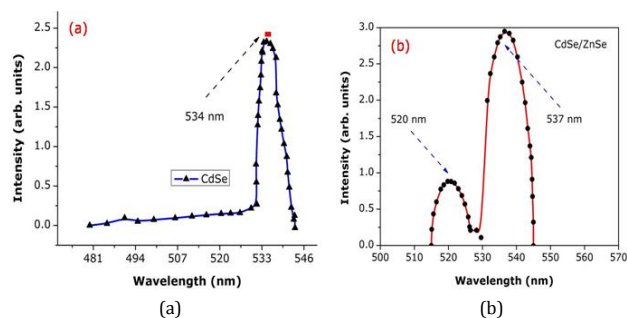


Fig. 8 Photoluminescence spectra of pure CdSe and CdSe/ZnSe

The sharp absorption features ($\lambda_{\text{abs}} \sim 524$ nm) and the narrow PL emission $\lambda_{\text{emi}} \sim 537$ nm indicates band-edge emission. The fact that the PL emission maximum lies close to its absorption-onset indicates that the PL emission arises as a result of direct recombination between LUMO and HOMO charge carriers [16]. This implies the efficient passivate interaction between water interfaces L-cystine /CTAB molecules with CdSe/ZnSe metal interface significantly modify the relaxation process of photon energies absorbed by nanocrystals (i.e blocking of the non-radiative relaxation pathway and facilitation of the radiative relaxation process).

As previously mentioned [17, 18] these temporal emission changes in NC photoluminescence spectral features indicate that the L-cystine and CTAB molecules significantly modify the relaxation processes of photon energies absorbed by nanocrystals. It has been previously reported that thiol groups have a stronger affinity for adsorption to NC surfaces and that coordination of the thiol functional group generally causes strong quenching of photoluminescence quantum yields in contrast to amine functional groups which typically have relatively lower binding affinities and only enhance photoluminescence emission intensities until a certain amine concentrations, where upon abrupt quenching is observed [19].

Therefore defects in the overlayer and at the CdSe/ZnSe interface should be the effective recombination centers for the photo excitation. Thus it is likely that the observed band-edge photoluminescence originates from the small fraction of particles with a defect-free over layer.

4. Conclusion

A bio-encapsulated CdSe/ZnSe composite nanorod was successfully synthesized by employing cheaper chemicals and easy process, and with better control over the morphology and crystalline quality. The wurtzite-hexagonal morphology is verified by powder XRD and transmission electron microscopy. From the SEM/TEM analysis the absence of agglomeration and 1D shape evolution of nanocomposite by using CTAB and L-cystine respectively. A CdSe nanorod overcoated with a layer of ZnSe has much narrower band-edge luminescence and higher quantum yields with respect to CdSe. It has been demonstrated that the energy of the band-edge luminescence can be readily tuned by adding the ZnSe overlayer. The EDA confirms the presence of Cd, Zn, Se metal in the as prepared nanorods. This study opens up new avenues for research to find suitable experimental conditions and the possibilities of using different

reaction mechanisms to bring out better control over the size/morphology of the semiconducting nanoparticles. This new class of alloyed semiconducting nanorods has the potential nanomaterials to be applied to solid-state lighting technologies and molecular bio-imaging etc.

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