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SYNTHESIS AND OPTICAL PROPERTIES OF SEMICONDUCTOR CORE/SHELL NANOPARTICLES

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ABSTRACT

The core/shell nanoparticles are a new type of material with an inner core and an outer shell made up of two different nano materials. These special types of nanoparticle heterostructure exhibit unique properties arising from the combination of core material and other shell material. The size dependent optical properties of core/shell nanoparticles have been the focus of significant result because of their absorption property, fluorescence efficiency and stability against the photooxidation. The goal of this review work is to explain the synthesis procedures and optical properties of the different types of core/shell nanoparticles.

INTRODUCTION

Semiconductor nano structures have gained much attention because of great scientific and promising technological application for electronic and optoelectronic devices. If a nano particle is covered by another nano structure as a shell layer, then the heterostructure is known as core/shell nanostructure. The optical and electrical properties of such semiconductors are originated from the confinement of the exciton in this core/shell structure. The core/shell nano structures can be classified as Type I and Type II core/shell material depending upon the energy band offset of the heterostructure. If the electron and hole wave functions are confined either in the core or in the shell material then these types of core/shell structures are known as Type I structure. These types of core/shell structures are capable of emitting higher luminescence spectra because of electron and hole recombination. Again, the electron and hole wave function are separated in Type II core/shell nanostructures because of energy band offset. Therefore, Type I core/shell nanostructure is a good candidate for applications in light emitting devices, while Type II core/shell nano structures are promising candidates for photovoltaic or photocatalytic device applications [1-3]. The band-edge alignment can be manipulated to have the Type I or Type II core/shell nanostructures. The optical and electronic properties of core/shell nanostructures are mainly depending upon the size of the core and the thickness of the shell material. With the help of band engineering, one can design the size of core nano particle and can change the thickness of the shell material to tune the relative band offset between the core and the shell so that the core/shell structure may be transformed from Type I to Type II core/shell structures. The destiny of states will be gradually reduced, if a material is transmitted from bulk material into the nano material. The energy of some quantum structure is only continuous in the two dimensional space, when the charge carriers are confined in one dimension by quantum confinement. If the charge carriers are confined in the two dimensional space, then the energy is continuous in one dimension. Again, if the carriers are confined in all three spatial dimensions and energy is completely quantized then the movement of carriers limited in a small box model known as quantum dot. If the core/shell structure is consist of one nano core semiconductor material and surrounded by a layer of nano material with a total diameter less than 10nm then it is considered as core/shell quantum dot. The fluorescence quantum yield, absorption or stability of nanomaterial is greatly improved in comparison to the bare core nanostructures [4-6].

SYNTHESIS OF CORE/SHELL NANOSTRUCTURES

The epitaxial growth of nano shell on a nano particle will give the interesting optical properties in core/shell assembly. The band alignment is not only the sole criterion for the choice of core or shell material. If the core and the shell materials are crystallized in the same structure and exhibited a small lattice mismatch, then it will give the formation of good core/shell structure. If defect states are formed at the interfaces of core/shell materials, then these can be considered as trap states for photogenerated charge carriers and will diminish the fluorescence quantum yield.

The core/shell nano structures are mostly prepared in a two step procedure. The core nano particles are synthesized at first, may be followed by a purification step. In the second step, the shell material is formed on

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the core material by using suitable chemical reaction. In general, the growth temperature of the shell is lower, in order to prevent the nucleation of the shell material and uncontrolled ripening of the core nano particle. Most of the scientist used the one- pot synthesis method without an intermediate purification process for the growth of core/shell nano particles. B.O. Dabbousi et al. have synthesized CdSe/ZnS core/shell nanostructures with core CdSe ranging in the diameter from 2.3 nm to 5.5 nm. The synthesis of the core/shell nanostructure was carried out in room temperature. They have found the narrow edge luminescence spanning in the range of 470 nm to 625 nm in the visible spectrum. The improved photoluminescence quantum yield was carried out by passivated surface non radiative recombination sites. They have used trioctylphosphine oxide (TOPO, 90% pure), trioctylphosphine (TOP, 95% pure), Diethylcadmium (CdMe_2), diethylzinc (ZnEt_2) for the preparation of core/shell nanostructure. Monodisperse CdSe quantum dots were synthesized by the pyrolysis of organometallic precursors, dimethylcadmium, trioctylphosphine selenide in a coordinating solvent of trioctylphosphine oxide (TOPO). These CdSe quantum dots were referred as 'bare' dots and their outer most surface was passivated with organic TOPO/ TOP capping groups. Then they over coated the CdSe particles in TOPO by adding the Zn and S precursors [7].

Alexander Nemchinov et al. have synthesized type II high quality ZnSe/ CdS core/ shell nano crystals. They have followed two step synthesis procedures. The ZnSe core, seeds was prepared in Argon atmosphere by dissolving zinc stearate in octadecane (ODA) solution under constant stirring in a three- necked flask. A selenium stock solution was prepared by dissolving selenium in trioctylphosphine (TOP) and they injected into the reaction chamber. The temperature of the reaction was maintained at 280°C . After completion of the primary reaction, the mixture was allowed to cool to 50°C and 3 ml to 5 ml of hexane was added to the solution to prevent solidification. Again the methanol was added by them for subsequent cleaning of prepared nanocrystals by hexane methanol extraction. In the second step, injection stock solutions were prepared in 1-Octadecene (ODE). Cadmium oxides were dissolved in oleic acid (OA) and ODE in argon atmosphere in preparation of Cadmium solution at 280°C temperatures. The solution was cooled at 60°C . Again sulfur dissolved in ODE was prepared as sulfur solution for the final reaction. They have mixed both precursors together and injected into the reaction vessel containing previously prepared ZnSe nanocrystals for shell formation. Thus ZnSe/CdS core/shell nanostructures were formed. The family of core/shell nano structure has great diversity. The widely used core/ shell materials are only highlighted in this synthesis section. Different core/ shell nanomaterials have different optical properties such as energy band gap, absorption and luminescence spectra [8].

CdSe/ ZnSe core/shell type II nanostructures were prepared by Jia Guo Zhi et al. by using one- pot synthesis procedure. They have confirmed the formation of type II core/ shell heterostructures by employing UV- Vis and PL optical characterization. They have used tellurium powder, CdCl_2 , thioglycolic acid and distilled water for the synthesis method. The Se^{2-} precursors were formed by adding sodium borohydride with selenium powder in distilled water. They have made the molar ratio of $\text{Zn}^{2+}/\text{Cd}^{2+}$ in a mixed solution as 9:1, 8:5 and 1:5 in sequence. Thioglycolic acid was used as stabilized in aqueous solution with N_2 protection for preparation of the water soluble CdSe/ ZnSe core/ shell quantum dots [9].

OPTICAL PROPERTIES OF CORE/SHELL NANOSTRUCTURES

The unique optical properties of core/ shell nano structures have attracted great fundamental interest of the workers. The type I core/ shell quantum structures have some unique advantages in their optical properties over type II core/ shell quantum dots for application in luminescence devices. On the other hand, the optical properties of type II core/ shell structures have identified them as the prominent candidate for a photovoltaic device like a solar cell fabrication. Again, it was found that some core/ shell quantum structures like ZnSe/ CdSe nanocrystals can exhibit either type I or type II behavior with the changing of the core radius and shell thickness. $\text{Au}_x\text{Ag}_y/\text{ZrO}_2$ core/shell nanoparticles were prepared by A.S.Nair et al. [10]. They have shown the HRTEM images of core/shell nanostructures as shown in the Fig.1.

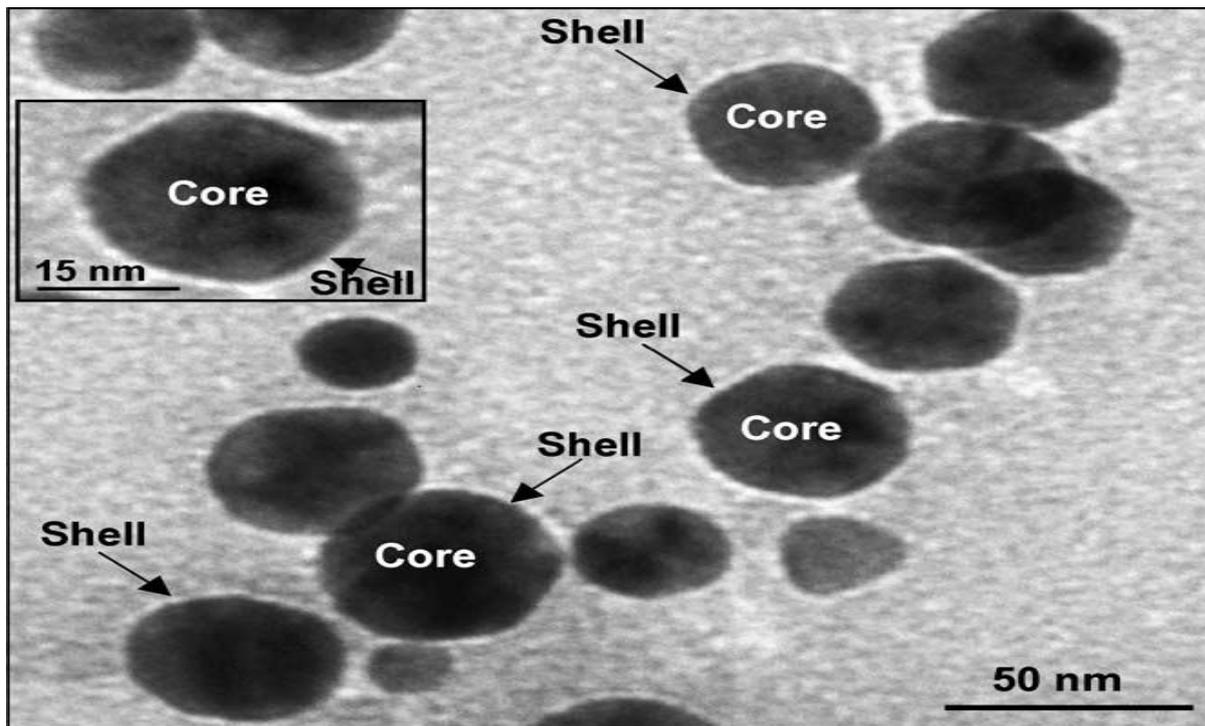


Fig.1. Images of core/shell nanoparticles [Reproduced from Ref.No.10]

Again, beautiful HRTEM images of Cu/silica core/shell nanoparticles were presented by A.V.Nomoev et al. in their work. The inner core material and outer shell material were clearly visualized in these images [11].

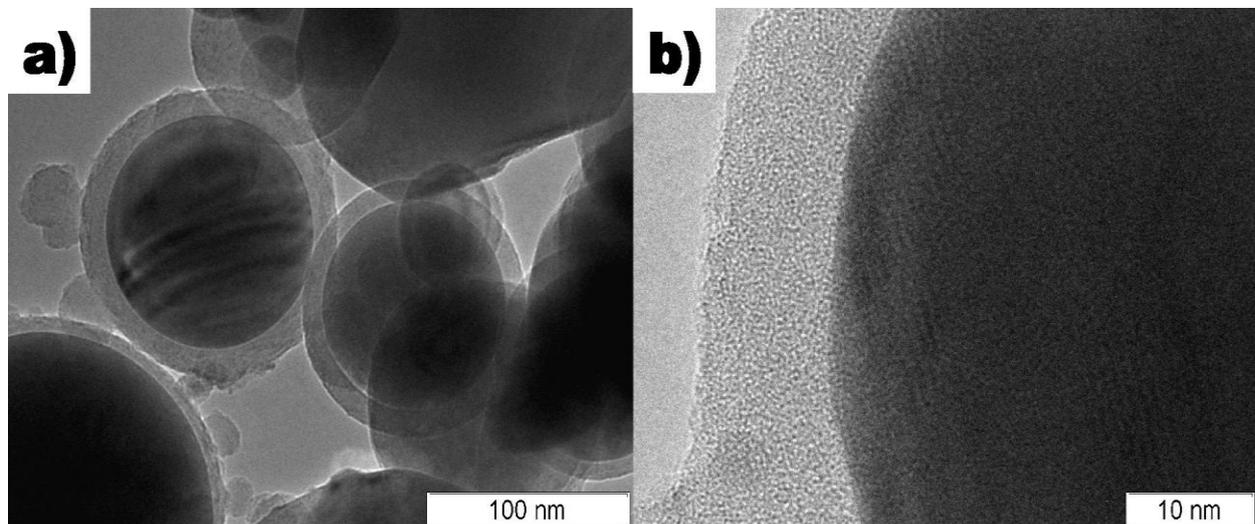


Fig.2. (a) Core/shell nanoparticle in 100 nm range (b) Shell thickness of Core/shell in 10 nm range [Reproduced from Ref.No. 11]

The optical characterization of CdSe/ZnS core/shell nanoparticle was explained by B. O. Dabbousi et al. [7]

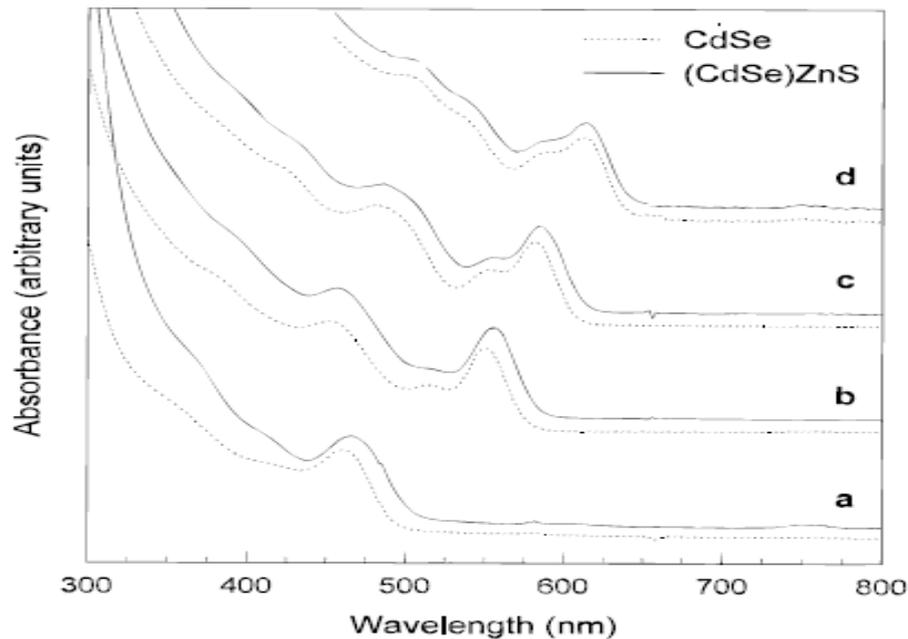


Fig.3. Absorption spectra of bare core CdSe (dashed lines) and CdSe/ZnS core/shell quantum dots with diameters (a) 2.3 nm, (b) 4.2 nm, (c) 5.5 nm. [Reproduced from Ref.No. 7]

They have presented the absorption spectra of CdSe quantum dots and CdSe/ZnS core/shell nanoparticles. A small red shift in the absorption spectra of core/shell was observed by them and it may be due to the partial leakage of exciton into the ZnS matrix. This red shift in the absorption spectra is one of the important characteristics of core/shell structures [7].

In the photoluminescence spectra they have found the higher quantum yield from 30% to 50% for CdSe/ZnS core/shell quantum dots as shown in Fig.4. In core/shell assembly, the presence of ZnS shell suppressed the deep trap emission by passivating most of the vacancies as well as the trap sites on the crystal surface. Therefore the PL intensity was enhanced in this case due to band-edge recombination as shown in Fig.4 [7].

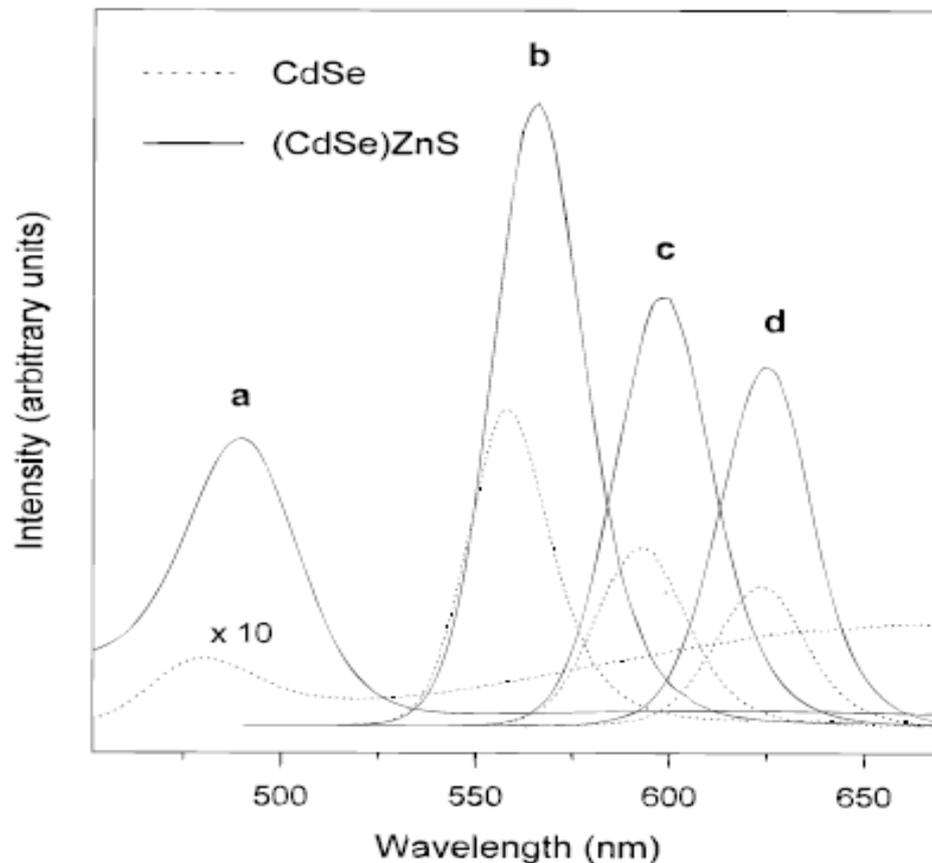


Fig.4. Photoluminescence (PL) spectra of bare core CdSe (dashed lines) and CdSe/ZnS core/shell quantum dots with diameters (a) 2.3 nm, (b) 4.2 nm, (c) 5.5 nm. [Reproduced from Ref. No.7]

The optical properties of nanoparticle can be used as figure print of that particular structure. A red shift of the absorption edge can be generally observed in the absorption spectra of core/shell nanoparticle. The photoluminescence intensity of core/shell structure may be varied depending upon the type of the core/shell heterostructure. The absorption and emission spectra of core/shell nanostructure depend on the energy band gap offsets of core and shell material. In case of type II core/shell structure the excited electrons and holes can be efficiently separated and it will reduce the electron-hole pair recombination. Therefore the PL intensity of type II core/shell heterostructure is generally reduced and they can be used for fabrication of photovoltaic devices. In type I core/shell structure, electron-holes are confined into the core or shell material and it can reduce the interactions of e-h pairs with surface traps. Therefore a significant improvement in emission quantum yield can be obtained in the luminescence spectra [12].

CONCLUSION

Different types of synthesis methods for growth of core/shell structures have been reported in this work. The synthesis of core/shell nanostructure is a big challenge in reality and therefore controlled reaction parameters, optimum conditions for growth mechanism with proper functional materials are required for preparation of core/shell material. The electrons and holes are spatially separated in type II core/shell structure. In case of type I core/shell system, the recombination probability of electron and hole are maximum because of their confinement into the same material. The core/shell nanostructures have potential application for fabrication of most of the optoelectronic devices because of their fascinating optical properties than bare nanoparticle. The fundamental properties of absorption and luminescence spectra of type I and type II nanostructures are well explained in this review work. The improved properties of core/shell nanostructure may be utilized for the development of new kind of optoelectronic devices in near future.



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