International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.10 No.10, pp 225-231, 2017

Green Synthesis & Characterization of Cadmium Selinium Nanoparticles from soapnuts and study of their fluorescence studies:

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Abstract : Synthesis of Cadmium Selinium Nanoparticles (CdSe-NPs) was accomplished by a green procedure employing aqueous solutions of soapnutsfruit pericarp. The size of nanoparticles obtained are in range of 4–12 nm which is achieved by the reduction of CdSe precursers with the aqueous extract of soapnutsfruit pericarp.The resulted CdSe-NPs are highly crystalline face-centered cubic (fcc) structures. The obtained CdSe-NPs might be stabilized through the interactions of carboxylic groups in the saponins and the carbonyl groups in the flavonoids present in the soapnut shells. TEM, XRD, SEM with EDS were used to study the morphology, distribution, crystallinity and size of the particles. The reports showed that CdSe-NPs formed with Cubic phase. The particles exhibited excellent absorption maximum at 608 nm and produced an emission maximum at 655 nm, upon excitation. This biogenesis is straightforward, amenable for big scale industrial production and technical applications.

Keywords : CdSe-NPs, soapnutsfruit pericarp, excitation, Green synthesis, amenable.

Introduction:

The synthesis of II-VI semiconductor nanoparticles has experienced an enormous development in the past two decades. CdSe, in particular, has been the subject of much basic research into the electronic and optical properties of quantum dots. The amount of literature dealing with this topic is too voluminous to review within the context of this dissertation. As such, we will initially discuss the type of reaction mediums used to prepare the nanocrystals and the results of the effects of experimental parameters on the nanocrystals. We will then focus on the works performed by researchers in their attempts to understand and eventually model the growth kinetics of CdSe nanocrystals. This narrower focus is justified because these are the central topics of this dissertation.

Aqueous-based techniques are always considered to be safe and environmentally friendlytechniques because water is a natural media for all lifes. Historically, the first successful synthesis of colloidal semiconductor nanocrystals was in aqueous solution. Initially, nanocrystalswere formed in homogenous aqueous solution containing appropriate reagents and surfactanttypeor polymer-type stabilizers.[1,2]The charged stabilizers can bind to the surfaces of the nanocrystals and stabilize the particles by steric hindrance and/or electrostatic repulsion.

Besides this monophase synthesis, a bi-phase technique has also been developed. This method isbased on the arrested precipitation of nanocrystals within inverse micelles.[3-5]In this technique, nanometer-sized water droplets (dispersed phase) are stabilized in an organic (continuous phase)solvent by an amphiphilic surfactant. The nanocrystals are generated inside the water droplets(nanoreactor), whose dimensions determine the size of the nanocrystals. At the same time,because these water droplets are dispersed in a continuous phase, they can prevent the newly formed nanocrystals from aggregation. CdS nanocrystals were first obtained by this strategy.[3-5]

Early in stabilizer development, colloidal silica sol[5,6] and short chelating peptides[7] were used.Later, Weller and coworkers pioneered the use of short-chain water soluble thiols, such as 1-thioglycerol, 2-mercaptoethanol, 1,2-dimercapto-3-propanol, thioglycolic acid and cysteamine, as stabilizing agents.[8] The use of these short-chain thiols as capping agents has led to successfulaqueous syntheses group II-VI semiconductor nanocrystals like CdS[8], CdSe[9], CdTe[10,11],HgTe[12], and ZnSe.[13]

The genus *Sapindus* belongs to family *Sapindaceae* possess tremendous medicinal value. Since past, it is used as emetic, tonic, astringent, anthelmintic, for asthma, colic, diarrhea, cholera, tubercular glands and paralysis of limbs. The fruit is commonly used as a remedy for hair problems and also in preparation of shampoos. *Sapindus emarginatus*Vahl family *Sapindaceae* is a medium-sized deciduous tree found in South India. It is commonly called as soap nut tree. Native to South India *Sapindus emarginatus*is found wild or introduced in tropical and sub-tropical regions, particularly the Indo- Malayan region. Traditionally, *Sapindus emarginatus* is used as anti-inflammatory and antiprurutic. It is used to purify the blood. The seed is in intoxicant and the fruit rind has oxytropic action. Its powder is used as nasal insufflations. *S. emarginatus* also showed strong antibacterial activity against the tested bacterial strains.[14] Antifertility and antiandrogenic activities of *S. emarginatus* extract have been reported.[15]High content of saponins has been reported in the pericarp.[16] Two Pisicidaltriterpenoid saponins,[17] acetylated triterpenesaponins, hederagenin, sweet acyclic sesquiterpene glycoside, Mukurozioside IIb[17] have been isolated from the Pericarps of *S. emarginatus*. Flavonoids have been isolated from the pericarp of *Sapindus emarginatus*.[18]These all may act as the reducing agents and by which the present reduction of CdSe ions takes place. It is possible that saponins and proteins/enzymes play a role in the reduction. However, the ingredient responsible for the reduction of CdSe ions needs further study.

Experiment:

Materials:

The reagents used were a Cadmium and Selenium precursor, ammonia forpH adjustment, deionized water as the reaction medium. These reagents were used because they weresuccessfully employed to produce CdSenano crystals in experiments. Cadmium Chloride (Aldrich, 99%), Sodium Selenosulfate (Sigma-Aldrich, 97%), Ammonia (Fisher, 0.1N) were used as received.

Preparation of Seed extract:

Known weight (100 g) of freshly collected, taxonomically authenticated pericarp of *Sapindus emarginatus* (Figure-3) were taken and washed thoroughly in flush of tap water in the laboratory for 10 min in order to remove the dust particles and ringed briefly in sterile distilled water. Then they were taken in 250 ml capacity beaker having 200 mL of organic free water and was placed on boiling steam bath for 15 to 20 min till color of the water changes to dark brown. The extract was cooled to room temperature, gently pressed and filtered firstly through sterile serene cloth. This solution was treated as source extract and was utilized in subsequent procedures.

Synthesis of CdSe nanoparticles and photoluminescence studies:

Firstly, we prepared a solution of 0.5 M sodium selenosulfate (Na_2SeSO_3) by refluxing the aqueous solution containing 1 M Na_2SO_3 and 0.5 M elemental Se under stirring for 5 h.

Secondly, 1mL of 0.1 M $CdCl_2$ aqueous solution was added to the aqueous solution 10 mL filtrate of 30% w/v soapnut shells aqueous extract in beaker with constant stirring. After that 1 mL of $Na_2SeSO_3$was added to resultant mixture and then pH was adjusted to 10-11 using ammonia. Then, the mixture was stirred until the solution become transparent red colour and aged for 12 h. The resultant red transparent solution was extracted into acetone to obtain red precipitate and wash the precipitate for 5 times with acetone and then dried at room temperature for 12 h.

The content was lateron placed on to a rotatory orbital shaker operating at200 rpm, 30 _C for 12 h in dark condition. The formation ofthe particle was monitored by sampling an aliquot (3 ml) ofthe mixture after 12 h, followed by measurement of the UV–vis spectra using a spectrophotometer. In order to find the absorption maximum or kmax, aspectral scanning analysis was carried out by measuring opticaldensity of the content from wavelength, 250–700 nm.

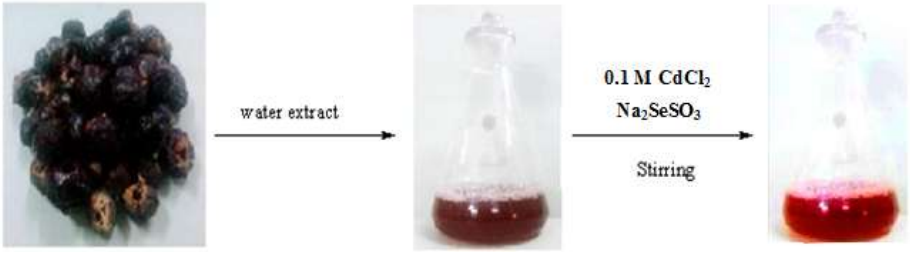


Figure 1: Synthesis of CdSe NP's using soapnuts extract

Sample preparation for transmission electron microscopy (TEM), X-ray diffraction (XRD) and Fourier transformed infra red spectroscopy (FT-IR) study

Transmission electron microscopic (TEM) analysis was performed with Techni 20 (Philips, Holland). A thin film of thesample was prepared on a carbon coated copper grid by droppinga very small amount of the sample on to the grid. Theaqueous solution of QDs was centrifuged at 13,000 rpm for10 min. The pellet thus recovered was subjected to washingby its re-suspension in deionized water followed by centrifugationat 13,000 rpm for 10 min, to remove possible organic contaminationpresent in nanoparticles. Finally, pellet was freeze dried using a lyophilizer(Labconco, Kansas, Missouri). Thepowder of synthesized nanoparticles obtained in this mannerwas subjected to elemental analysis using a scanning electronmicroscope (Philips, Netherlands) equipped with energy dispersiveX-ray spectroscopic system (EDAX-XL-30) operatingat 15–25 kV and X-ray powder diffraction study. XRD datawere collected using a Phillips PW1710 diffractometer with Cu-Ka radiation operating at 40 kV, 35 mA in step scan mode,between 5_ and 75_ and with a counting time of 8 s per step.

Disk of 100 mg KBr containing 1% freeze dried CdS powderserved as material for recording transmission spectra. Spectralscan analysis was carried out at wave number ranging from400 to 4000 cm_1 by using a FT-IR spectrometer (PerkinElmer, Spectrum GX, USA) with a resolution of 0.15 cm_1to evaluate functional groups of the leaf extract that mightbe involved in particleformation process.

Results and discussion:

UV–vis spectroscopy and photoluminescence of CdSe nanoparticles:

Mixing the solution of $CdCl_2$ and Sodium selinosulfide resulted in the formation of CdSe nanoparticles. Initially, at 0 h mixture was light brown which ultimately turned into yellow after12 h. The synthesis of CdSe leading to change in colorcan be attributed to surface plasmon resonance of CdSe nanoparticles. In case of control experiment where seed extract was not added to $CdCl_2$, insoluble yellowish precipitate of CdSe was observed. The spectral analysis of CdSe nanoparticles was performed at 0 h and 12 h. The 0 h spectra however showed an absorbance maximumbut there was significant increase in the absorbance at290 nm after 12 h of incubation period. The optical property synthesized CdSe nanoparticles were evaluated byrecording photoluminescence spectra. Fig. 2 & 3, shows photoluminescence espectra of CdSe nanoparticles synthesized using seed extract. The excitation peak was found at 608 nm while emissionpeak was observed at 655 nm. The excitation peak at 608 nm, very well correlatedwith absorption maxima recorded with a UV–vis spectrophotometer(600 nm).

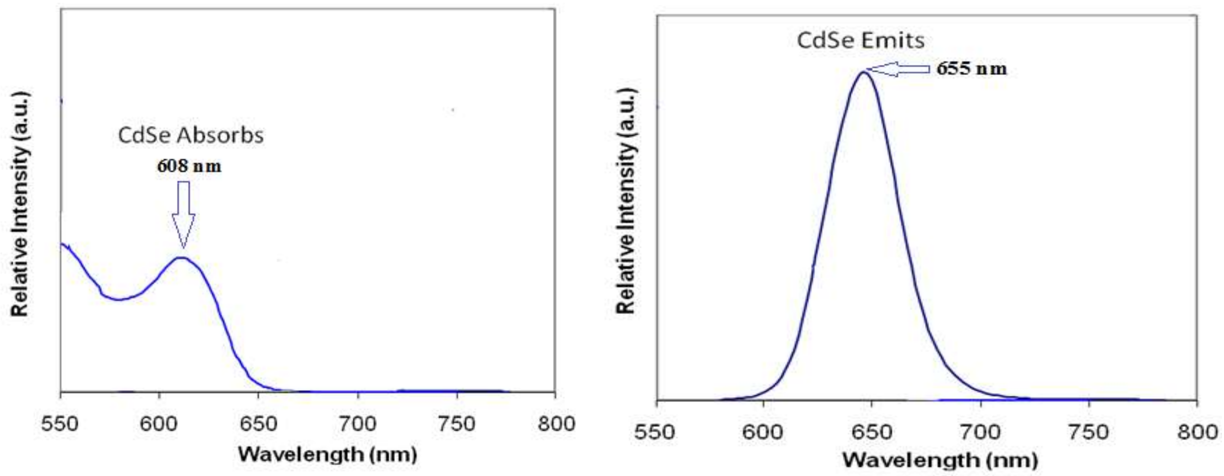


Figure 2 & 3: Absorption spectra and Photoluminescence Spectra of CdSe nanoparticles absorbing at 616 nm and emitting at 608 nm (which was excited at 476 nm).

SEM, TEM, XRD and FT-IR study:

Scanning electron microscopy (SEM) was applied to investigate the size and morphology, which was carried out with a scanning electron micro-analyzer using a JEOL-JSM6700 microscope, operating at 10 A and 15 kV.

The TEM analysis of solution indicated the formation of CdSe nanoparticles. Fig. 4 showed that size of generated particlesusing seed extract ranged from 4 to 12 nm. The formation ofvariable size of particles suggested that seed extract could form polydispersed nanoparticles. Results indicated that particles were crystalline in nature as diffractionring appeared which correspond to diffraction angle of 111,220 and 311, respectively.

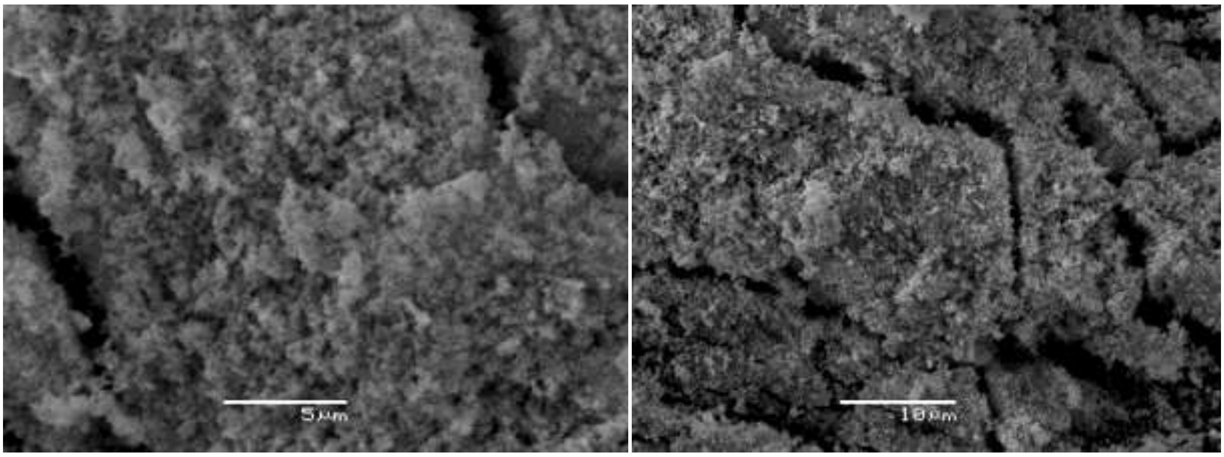
The X-ray diffraction patterns obtained for CdSe nanoparticles synthesized using seed extractis shown in Fig. 3(a). The XRD diffractogram contained three prominent peaks that were clearly distinguishable. All of themcan be perfectly indexed to crystalline CdSe not only in peakposition, but also in their relative intensity. The peaks with2h values of 25.5, 44.4 and 53.6 corresponded to the crystalplanes of 111, 220 and 311 crystalline CdSe, respectively. Sizes of crystallite were estimated using Scherrer's formula, D =Kk/bcosh, where the constant K is taken tobe 0.94, k is the wavelength of X-ray, and b and h are the halfwidth of the peak and half of the Bragg angle, respectively.Using the equation, the crystallite sizes were found to be inthe range of 4–12 nm.

The analysis revealed that apart from Se (41%) and Cd (35%),elements like O (11%), Na (8%), Cl (6%), P (4%), and C (3%)were integral part of synthesized CdSe QDs. FT-IR analysisprovides a presumptive idea of interaction between the functionalgroup of chemical constituents of seed extract and metalions, leading to the formation and stabilization of CdSe nanoparticles.

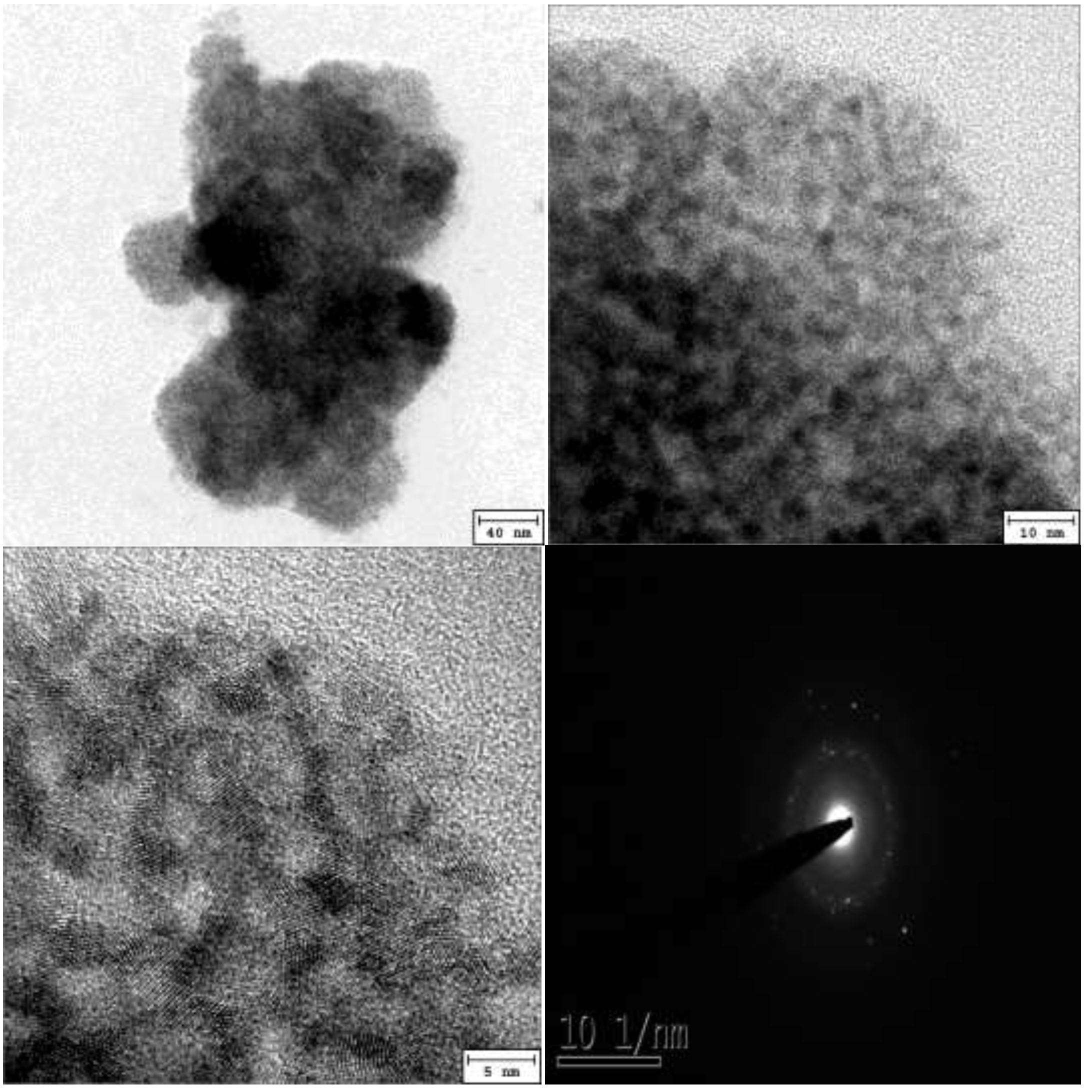
The control FT-IR spectrum is presented in Fig. 5awhile Fig. 5b represents IR spectrum of the seed extract involved in nano CdSe. The shift in peak located around 3427can be assigned to the involvement of OAH (of alcohol) andNAH group in the formation of CdSe nanoparticles. Similarly,shift of peak from 2928 to 2932 in 3200–2800 wave range suggestedthe involvement of CAH (sp3 hybridized) and OAH (ofacid origin) group of plant extract in nanoparticle formation.

The shift of peak 2342–2330 in wavenumber range from2400 to 2100 can be assigned to the presence and involvementof triple bond molecules like alkynes and nitriles in organic mixture.

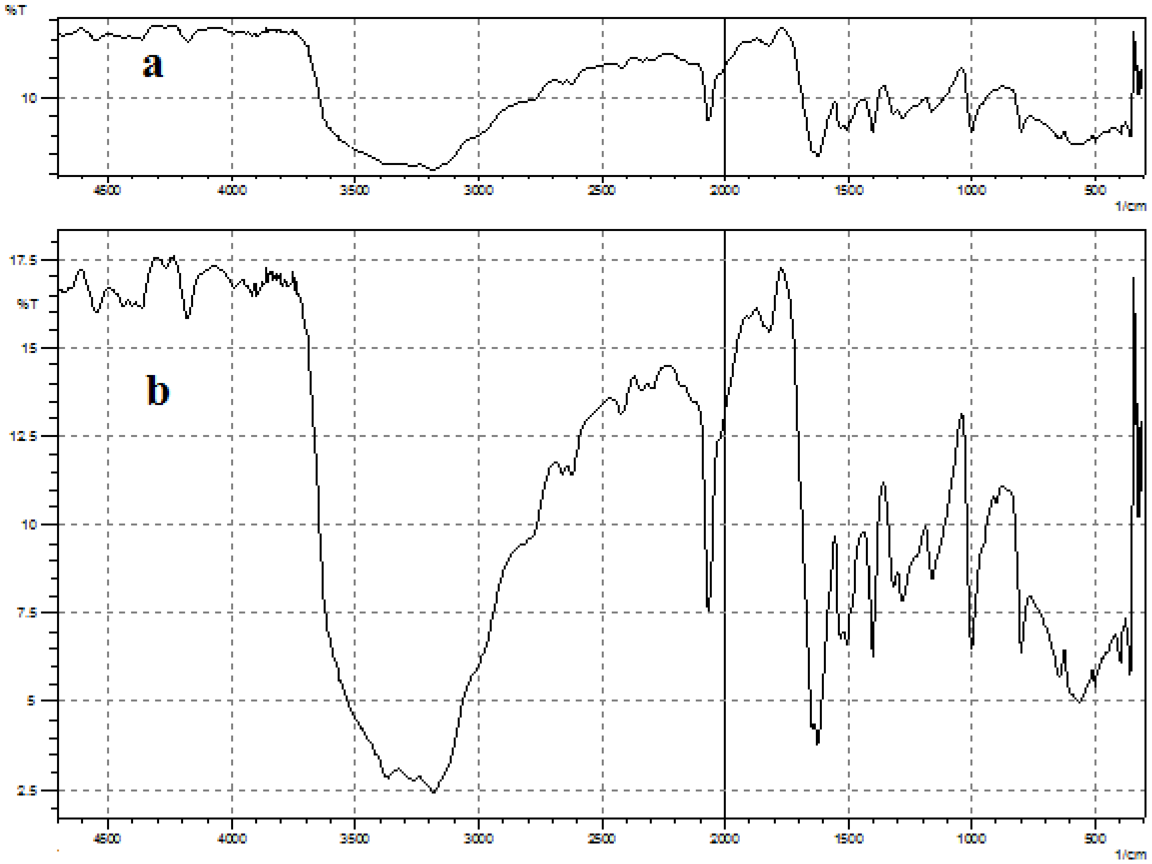
Peaks between finger print regionsi.e. 1500–400 cm^{-1} are due to all manner of bending vibrationswithin the molecules. The peaks around 1300 and 1200 areattributed to the stretching vibration of single bond betweenCAO. The peaks around 1200 and 1000 may be due to stretchingand vibration between NAH.



Scanning electron micrographs of the CdSe nanoparticles used in this work.



Transmission electron micrographs of the CdSe nanoparticles used in this work. (a) The bar marker represents 40 nm, (b) 10 nm & (C) HR-TEM micrograph at 5 nm showing spherical shape of CdSe nanoparticles .



Conclusions

This is a first report, where a seed extract of soapnuts has been used in the synthesis of organic soluble CdSe nanoparticles. Solution containing nanoCdSe showed absorption maximumat 608 nm and produced an emission maximum at 655 nm, upon excitation. TEM, SEAD, XRD and EDAXresults showed the formation of polydispersed, crystalline CdSe nanoparticles. Bio-functionalized CdSe nanoparticles didnot promote cell death as well as genetic damage in humanlymphocytes, whereas chemically synthesized CdSe QD caused significant cell death followed by DNA fragmentation and tailformation. Application of these types of nanoparticles on cancerouscell line and elucidation of exact molecular events are being proposed. Organic soluble nanoCdSe (QDs) synthesized using seed extract can be a suitable candidate for use in biomedicalapplications, since they showed less genotoxic effect than chemically synthesized QDs.

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