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A Facile One-Pot Synthesis of MSe (M = Cd or Zn) Nanoparticles Using Biopolymer as Passivating Agent

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1. Introduction

In recent years, semiconductor quantum dots (QDs) sometimes also referred to as nanoparticles (NPs) or nanocrystals (NCs) have attracted much attention for many potential applications due to their unique physical and chemical properties such as size-dependent band gap, size dependent excitonic emission, enhanced nonlinear optical properties and size-dependent electronic properties attributed to quantum size-effect and enormously high specific surface area. Hence they are different from those of the corresponding bulk materials and contain a relatively large percentage of surface atoms which makes them extremely active (Alivastos, 1996; Bruchez et al., 1998). They have been extensively studied over the past decade and are useful in many wider areas of applications hence, they have become an important class of material for the photonic, electronic, biological and other technological industries in the 21st century (Bruchez et al., 1998; Chan & Nie, 1998; Coe et al., 2003; Murphy, 2002). The applicative utility of QDs as seen in various field are: medicine - for diagnostics, drug delivery and tissue engineering, chemistry and environment -for catalysis and filtration, energy - for reduction of energy consumption, increasing the efficiency of energy production, the use of more environmentally friendly energy systems, recycling of batteries, information and communication - novel semiconductor devices, novel optoelectronic devices, displays, quantum computers, heavy industry- aerospace, refineries, vehicle manufacturers to mention a few. Compared with conventional organic fluorophores, QDs exhibit bright fluorescence, narrow emission, broad UV excitation, high quantum yield and high photostability (Coastal -Fernandez et al., 2006; Ozkan, 2004; Derfus et al., 2004).

Among all semiconductor NPs, metal selenides have been the focus of great attention due to their importance in various applications such as thermoelectric cooling materials, optical filters and sensors, optical recording materials, solar cells, superionic materials, laser materials and biological labels. Many synthetic methods have been developed for the preparation of relatively monodispersed selenide nanoparticles (Murray et al., 1993; Korgel

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and Monbouquette, 1996; Trindade and O'Brien, 1996; Pileni, 1997). These methods have proved to be effective in the preparation of high quality selenide nanoparticles, using low molecular weight stabilizers such as thiols (Rockenberger et al., 1997), ethylhexanoate (Diaz et al., 1999), polyphosphate (Spanhel et al., 1987) and trioctylphosphine oxide (Murray et al., 1993; Trindade and O'Brien, 1996, 1997; Malik et al., 2001). However the synthesis usually involve high temperature, sophisticated equipment, complicated processes or complex reagents which are not environmentally friendly and rigorous conditions such as injection of hazardous metal alkyls, which are toxic, volatile, low boiling point materials, explosive at elevated temperature and pyrophoric. Therefore standard airless techniques are required to protect reaction reagents and the as-synthesised nanoparticles from oxidation, a major source of their cytotoxicity (Guo et al., 2007; Austin et al., 2004; Gaunt et al., 2005). As a result of these concerns on toxicity coupled with rigorous conditions involved in the preparation of these materials, the search for greener, sustainable and environmentally benign methods is still ongoing.

Apart from those that utilized highly toxic H_2Se (Trindade et al., 2001) or N, N-dimethylselenourea (Rogach et al., 2000) as selenium source, the solution reaction growth techniques appear to be the cheapest and most convenient approaches (Wang et al., 1999; Li et al., 2007; Ma et al., 2002a, 2002b; Yang and Xiang, 2005). However in solution, bare nanoparticles are thermodynamically unstable and always tend to aggregate, losing their peculiar properties. As a result of this, passivation of the surface is necessary in order to prevent uncontrolled growth and agglomeration of the nanoparticles. Most of the suitable capping agents used as stabilisers to modify the surface include thiols, ethylhexanoate, polyphosphate, trioctylphosphine oxide (TOPO), polyesters, starburst dendrimers and amino-derivatised polysaccharides. Among all these materials used as stabilisers, polymers, by far usually provide an excellent steric hindrance effect with robust stability against the environmental variation on the NPs. In addition, through hybridization with polymer, NPs are envisaged to inherit good compatibility, excellent capability and the high engineering performance which are sought after in most technical applications of the NPs (Abouraddy et al., 2007). Therefore polymer-inorganic nanocomposites have attracted much attention. It has been well established that solutions of polymeric materials contain size-confined, nanosized pools of inter - and intramolecular origin, which can be used for the synthesis of nanoparticles (Raveendran et al., 2003). In nanoparticles synthesis, linear as well as dendritic polymers have been used successfully. The Polyhydroxylated macromolecules in the polymer present interesting dynamic supramolecular associations facilitated by inter and intramolecular hydrogen bonding resulting in molecular level capsules, which can act as templates for nanoparticle growth. Thus these nanocomposites combine advantageous properties of polymers with properties of semiconductor nanoparticles. In general, the role of the polymers is to encapsulate the nanoparticles and enable better exploitation of their characteristic properties. However, it should be noted that polymers do not only serve as good host materials, they can also be used to modify the surface and/or to control the growth of nanoparticles. Surface modification could be of great importance for possible use of semiconductor nanoparticles in biomedical applications and diagnostics. In addition, biopolymers have been proved to be good controlled environments for the growth of metallic and semiconductor nanoparticles (Bozanic et al., 2009). A biopolymer such as starch is inexpensive, hydrophilic, nontoxic, biocompatible, biodegradable, is readily available from agriculture as the major component of carbohydrates and can be easily modified and

transformed into other products (Mondal et al., 2004; Dragunki & Pawlicka 2001; Fang et al., 2005; Patel et al., 2010; Dzulkefly et al., 2007). It has a wide range of potential applications because it is abundant, renewable, safe and economic. Starch based materials have been used as substituent for petroleum-based plastic material especially in packaging industries and thus offer an alternative solution to the disposal and biodegradability problem of petroleum based materials (Fang et al., 2005; Patel et al., 2010; Dzulkefly et al., 2007). In addition, its biodegradable nature may also help in reducing cytotoxicity problems of QDs materials and hence extend their application to food and pharmaceutical products. Other polymers such as polyvinylpyrrolidone (PVP) and polyvinyl alcohol (PVA) are good choices as stabilizers because they can interact with metal ions by complex or ion-pair formation and can be designed to improve certain physical properties of semiconductor nanoparticles (Colvin et al., 1994; Dabbousi et al., 1996; Selim et al., 2005). In addition, the high viscosity of the polymer solution would be helpful in controlling the growth of selenide nanoparticles and thus prevent particles from aggregating hence no additional stabilizer would be needed. Furthermore, these polymers have high aqueous solubility and from an applications point of view, the polymer matrix would protect the selenide against photo-oxidation, a major factor responsible for the cytotoxicity of the quantum dots.

Most of the works on polymer-inorganic nanocomposites containing chalcogenide quantum dots have been concentrated on sulphide because of the accessibility of sulphide sources in wet chemical control synthetic methods, while for the preparation of polymer selenide nanocomposites there were some difficulties. Polymer-selenide nanocomposites are usually prepared via a two-stage process. This involves the synthesis of selenide nanocrystals and polymer separately, followed by the dispersion of the selenide nanoparticles into the polymer matrix. Though well dispersed polymer nanocomposites have been successfully prepared using these methods, as mentioned earlier, the preparation of the selenide nanocrystals usually involves sophisticated equipment, complex or toxic reagents which are not environmentally friendly and rigorous conditions in order to protect reaction reagents and the as-prepared material from oxidation. Therefore in order to develop technologies that can be used to improve or protect the environment, it is desirable to design and use greener methods to synthesise nanomaterials. As described by Murphy and Dahi (Murphy, 2008; Dahi et al., 2007) "green" synthesis involves the use of less toxic starting materials, limited reagents, fewer synthetic steps, reduced amounts of by-products and waste, low reaction temperature and if possible, the use of water as a solvent. Another drawback in the preparation of selenide nanocomposites is the dispersion process which is tedious, time-consuming, involving wastage of ancillary materials used in the reactions and reduction in the optical properties of the final nanocomposite hence, direct synthesis of the polymer selenide nanocomposites using a one - pot synthesis without the use of additional stabiliser will be a better alternative route.

Based on these two considerations, there has been few reports on the synthesis of polymer selenide nanocomposites. Yang et al., (2002) used the redox reaction of selenite and tellurite salts with cadmium nitrate to produce CdSe and CdTe nanowires in an autoclave, through a poly vinyl alcohol (PVA) assisted ethylenediamine solvothermal method at 160 - 180 °C. The PVA used in the process was favourable for the formation of nanowires by promoting the oriented attachment growth under solvothermal conditions. The as-synthesised CdSe and CdTe nanowires are mostly in cubic zinc - blende phase, growing along (111) zone axis direction. By varying the current density and temperature of the solution, Sarangi and Sahu

(2004) used cathodic electrodeposition techniques to produce nanocrystalline CdSe semiconductor thin films of different crystalline sizes. Using sodium selenosulphate as the selenium source, Li et al. (2007) reported the synthesis of spherical cubic structured CdSe nanoparticles with starch as capping agent. Ma and co-workers also reported a series of polyvinyl alcohol (PVA)-selenide nanocomposites via a one step solution growth technique at room temperature and ambient pressure (Ma et al., 2002a, 2002b). Though this technique is simple and its flexibility allows the use of different passivating agents such as starch, PVA, polyvinyl pyrrolidone (PVP) (Yang and Xiang, 2005) and tartaric acid (Behboudnia and Azizianekalandaragh, 2007), the preparation of sodium selenosulphate used as the selenide source requires a longer reaction time and must be stored in the dark at 60 °C due to its instability at room temperature. Recently we have reported a facile, safe and inexpensive synthesis of nearly monodispersed organically soluble CdSe nanoparticles using selenide ion produced via reduction of selenium powder in water as the selenium source (Oluwafemi & Revaprasadu, 2008, 2009; Oluwafemi et al., 2010). Based on the modification of this technique, we have also reported for the first time, a series of water soluble selenide nanoparticles using cysteine, ascorbic acid, methionine and starch as passivating agents (Oluwafemi & Revaprasadu, 2007, 2009; Oluwafemi et al., 2008, 2010; Oluwafemi, 2009; Oluwafemi and Adeyemi, 2010). In this chapter, we will give a review of the starch work and adaptation of this synthetic route to other polymers. An entire 'green' chemistry is explored in this synthetic procedure without further purification steps or adjustments of the reaction environment. The hydroxyl groups of the polymers are expected to facilitate the complexation of the metal ion, solubilisation in water and conjugation site for further functionalisation of the as-synthesised nanoparticles hence no additional stabilisers are required. By varying the reaction time and Cd:Se ratio, the temporal evolution of the optical properties, shape and growth of the as-synthesised NPs were monitored. It is believed that the insight gained from this green synthetic approach will enable an economically viable and environmentally benign method for the synthesis of functionalised water soluble nanoparticles for large scale production and commercialisation.

This chapter is organised as follows: Following this introduction as section 1, a brief description of the synthesis and characterisation techniques used for the as-synthesised polymer capped selenide nanoparticles is given as section 2. In section 3, the mechanism of the reaction, results and discussion of the different selenide nanocomposites obtained using different polymers are given. Section 4, the last section gives a summary of the whole process, followed by references. Acknowledgements are cited before references.

2. Methodology

2.1 Synthesis

2.1.1 Synthesis of the precursor solution

Selenium precursor stock solution was prepared by adding 0.32 mmol of selenium powder to 20 mL deionised water in a three-necked flask. Sodium borohydride (0.81 mmol) was carefully added to this mixture and the flask was immediately purged with nitrogen gas to create an inert environment. The mixture was then stirred for 2 h, at room temperature. The entire selenium dissolves in water giving rise to a colourless selenium solution. The cadmium solution was prepared by adding 0.32 mmol of CdCl₂ powder in 20 mL of deionised water. The zinc solution was prepared by dissolving 0.32 mmol ZnCl₂ in 20 mL of

deionised water. The starch solution was prepared by dissolving 0.05 % wt of soluble starch in 20 mL of deionised water under constant stirring at room temperature. The PVA solution was prepared by adding 6.0 g of PVA into 50 mL of deionised water and heated at 90 °C for 1 h under constant stirring to obtain a viscous transparent solution. The PVP solution was prepared by dissolving 1.0 g of PVP in 20 mL of deionised water under constant stirring at room temperature.

2.1.2 Synthesis of polymer capped MSe nanoparticles

The synthetic approach is very simple and does not require any special set up. In a typical room temperature reaction, 1.0 mL aqueous solution of cadmium chloride was added to 20 mL aqueous solution of soluble starch in a 50 mL one-necked round-bottom flask with constant stirring at room temperature. The pH of the solution was adjusted from 6 to 11 using 0.1 M ammonia solution. This was followed by a slow addition of 1.0 mL colourless selenide ion stock solution. The mixture was further stirred for 2 h and aged for 18 h. The resultant solution was filtered and extracted with acetone to obtain a red precipitate of CdSe nanoparticles. The precipitate was washed several times and dried at room temperature to give a material which readily dispersed in water. The same procedure was repeated for the synthesis of PVA and PVP - capped CdSe nanoparticles by replacing the starch solution with the PVA and PVP polymers while the synthesis of elongated nanoparticles was achieved by changing the Cd:Se precursor ratio from 1:1 to 1:2. The synthesis of polymer capped ZnSe nanoparticles also follows the same procedure except that ZnCl₂ solution was used instead of CdCl₂ solution.

2.2 Characterisations

A Perkin Elmer Lambda 20 UV-vis Spectrophotometer was used to carry out optical measurements in the 200-1100 nm wavelength range at room temperature. Samples were placed in quartz cuvettes of 1 cm path length. Room temperature photoluminescence (PL) spectra were recorded on a Perkin Elmer LS 55 luminescence spectrometer with Xenon lamp over a range 400 – 800 nm. The samples were placed in quartz cuvettes of 1 cm path length. Fourier transform infrared (FT-IR) analysis was carried out using a Perkin Elmer spectrum FTIR Spectrometer with the universal ATR sampling accessory. A Philips CM120 BIOTWIV transmission electron microscope sample viewed at 80k was used for the transmission electron microscopic (TEM) analysis while a JEOL 2100 TEM operating at 200 KV was used for the high resolution transmission electron microscopic (HRTEM) measurements. Samples for the analysis were prepared by putting an aliquot solution of the water soluble nanocrystalline material onto an amorphous carbon substrate supported on a copper grid and then allowing the solvent to evaporate at room temperature. XRD measurements of the samples were performed using a Bruker aXS D8 Advance diffractometer with Cu K α radiation (λ = 1.5406 Å) operated at 40 kV and 40 mA.

3. Results and discussion

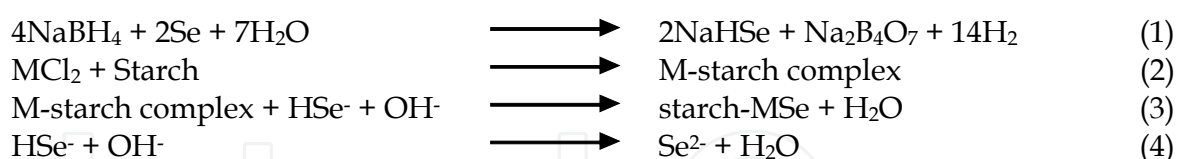
3.1 Starch-capped MSe nanoparticles

Starch is an inexpensive, hydrophilic, nontoxic, biocompatible and totally biodegradable polymer. It is a mixture of two main components: amylose formed by the α -1,4 glycosidic

bonds between D-glucose units and amylopectin, a highly branched water-soluble macromolecule consisting of both α -1,4 and α -1,6 glycosidic bonds (Raveendran *et al.*, 2003). The large number of hydroxyl groups present in glucose monomers can facilitate the complexation of metallic ions to the starch matrix, while nano-supramolecular structures formed by intermolecular and intramolecular hydrogen bonding can act as templates for nanoparticle growth. Thus making starch a good candidate for passivating QDs. Using starch as passivating agent also comes with other advantages which can help in achieving green synthesis of nanoparticles. These includes (i) the high dispersity of starch in water hence, one can completely avoid the use of organic solvents, (ii) the relatively weak binding interaction between starch and nanoparticles compared to the interaction between the nanoparticles and typical thiol-based protecting groups which makes the separation of these particles feasible and (iii) integration of starch-protected nanoparticles readily into systems relevant for pharmaceutical and biomedical applications (Mondal *et al.*, 2004; Dragunki & Pawlicka, 2001; Fang *et al.*, 2005; Patel *et al.*, 2010; Dzulkefly *et al.*, 2007 ; Raveendran *et al.*, 2003). Few authors (Li *et al.*, 2007, Taubert and Wegner, 2002; Raveendran *et al.*, 2003; Wei *et al.*, 2004) have reported the synthesis of inorganic nanoparticles using starch as capping agent. Most of these syntheses are either based on surface modification of the organically soluble nanoparticles prepared using a selenium source that is usually complexed to toxic organic material like trioctylphosphine oxide (TOP) before hot injection or the use of selenosulphate for direct synthesis in aqueous solution. Our work was the first reported 'green' room temperature one - pot synthesis of MSe (M= Cd or Zn) nanoparticles under a mild and environmentally benign conditions using starch as a passivating agent at room temperature (Oluwafemi, 2009; Oluwafemi and Adeyemi, 2010).

3.1.1 Reaction mechanisms

The overall chemical reaction involved in the process is represented by the following equations:



Scheme 1. Proposed chemical reactions involved in the formation of starch capped MSe nanoparticles

We propose a series of equations to represent the whole process of the formation of starch capped MSe nanoparticles at room temperature based on this synthetic route. The whole process is a redox reaction with selenium acting as the oxidant and MSe as the reduction product, while NaBH_4 acts as the reducing agent and $\text{Na}_2\text{B}_4\text{O}_7$ should be the oxidation product. In the experiments, at room temperature, Se is reduced to NaHSe , while the NaBH_4 is oxidised to $\text{Na}_2\text{B}_4\text{O}_7$. MCl_2 reacts with the starch to form the starch-metal complex. Finally the starch-metal complex reacts with Se^{2-} to form starch-capped MSe NPs. Scheme 1 shows the proposed chemical reactions involved in the formation of starch-capped MSe nanoparticles. Equation 1 is the reduction process of selenium powder in aqueous solution at room temperature under an inert atmosphere, for the formation of highly active hydrogen selenide ions. Equation 2 demonstrates that the metal chloride reacts with the starch to generate starch-

metal ion solution. In aqueous solution, starch adopts a right-handed helical conformation in which the ubiquitous hydroxyl groups are expected to facilitate the complexation of metal ions to the molecular matrix. Equation 3 is the reaction of starch-metal ion complex with the active HSe⁻ ions under alkaline medium to produce starch capped metal selenide nanoparticles. When hydrogen selenide ion solution was added to the starch - metal ion solution, it gradually released selenide ions (Se²⁻) upon hydrolytic decomposition in alkaline media (Equation 4). The released selenide ions then react with metal ion to form seed particles (nucleation). The hydroxyl groups of the starch act as the coordination site for the release of the metal ions and hence control the chemical reaction rate of M²⁺ and Se²⁻ to produce MSe. These hydroxyl groups also act as passivating centres for stabilisation and solubility of the as-synthesized nanoparticles in water, while the free aldehyde group on one end of a starch polymer could also act as conjugation site for further functionalization which makes it easier for its biological applications (Raveendran et al., 2003; Mishra et al., 2009; Rodriguez et al., 2008).

3.1.2 Starch capped CdSe nanoparticles

3.1.2.1 Structural analysis

The TEM image of the as-synthesised material at 1:1 precursor molar ratio (Figure 1) showed the presence of monodispersed spherical particles together with elongated particles of low aspect ratios [Oluwafemi, 2009]. The mean particle diameter was calculated to be 4.3 nm with standard deviation (σ) of 0.414 nm. The image also showed different patterns of how the dot particles arranged themselves into elongated ones. Different patterns such as tripods (I), sinusoidal (II) and S-shaped (III) were clearly visible. These different arrangement patterns clearly indicate the mechanism for the formation of one dimensional (1D) nanostructures i.e self-reorganisation occurring via adhesions between the spherical nanoparticles as a result of dipole-dipole interactions between the highly charged surfaces of II-VI semiconductor nanocrystals (Adam and Peng, 2001, 2002; Peng, 2003, Lee et al., 2002, 2003; Wang et al., 2006). The TEM image of the as-synthesised material at 1:2 precursor molar ratio consists of nanorods and nanowires of very high aspect ratio, together with interspersed monodispersed spherical particles (Figure 2). The presence of interspersed spherical particles supports the fact that the formation of elongated nanocrystals, is possibly due to self assembly between the spherical nanoparticles. The increase in the diameter of the interspersed particles at 1:2 (5.5 nm) and its broad size distribution ($\sigma = 1.629$ nm) further confirmed adhesion between the nanoparticles with different sizes. This morphology mutation indicates that, under this synthetic route, the final shape of the CdSe nanocrystals can be determined by controlling the precursor ratio. We proposed that at 0.5:1 (Cd:Se) molar ratio, high selenium monomer concentration in the precursor solution promote anisotropic growth of the pre-existing particles by supplying the reaction with high kinetic drive and the slowest growth rate. The high kinetic drive in conjunction with the reaction temperature, which also provides the reaction system with low thermal energy (KT) and slower reaction rate, enhanced interaction between the existing spherical particles in the product solution, resulting in the formation of elongated particles. In addition, the presence of excess Se increases the Se dangling sites on the surface of CdSe nanoparticles. This makes the spherical particles thermodynamically less stable and increases the energy of the dipole-dipole attraction between the nanocrystals thus, enables the formation of 1D CdSe nanostructures. That is, under this condition, some of the nanocrystals can act as “adhesives” for the adhesion of two or more quantum dots to give the elongated particles. A

similar observation has been reported for organically-capped nanocrystals (Tang et al., 2002; Wang et al., 2006; Deng et al., 2006). At lower initial precursor concentration (1:1), thermodynamically stable, isotropic quasi-spherical growth was observed. These results indicate that, the molar ratio of precursor plays an important role in the shape-control of CdSe nanocrystals and, the shape evolution from spherical to rod was the result of the reaction system shifting from thermodynamically-driven to kinetics-driven control.

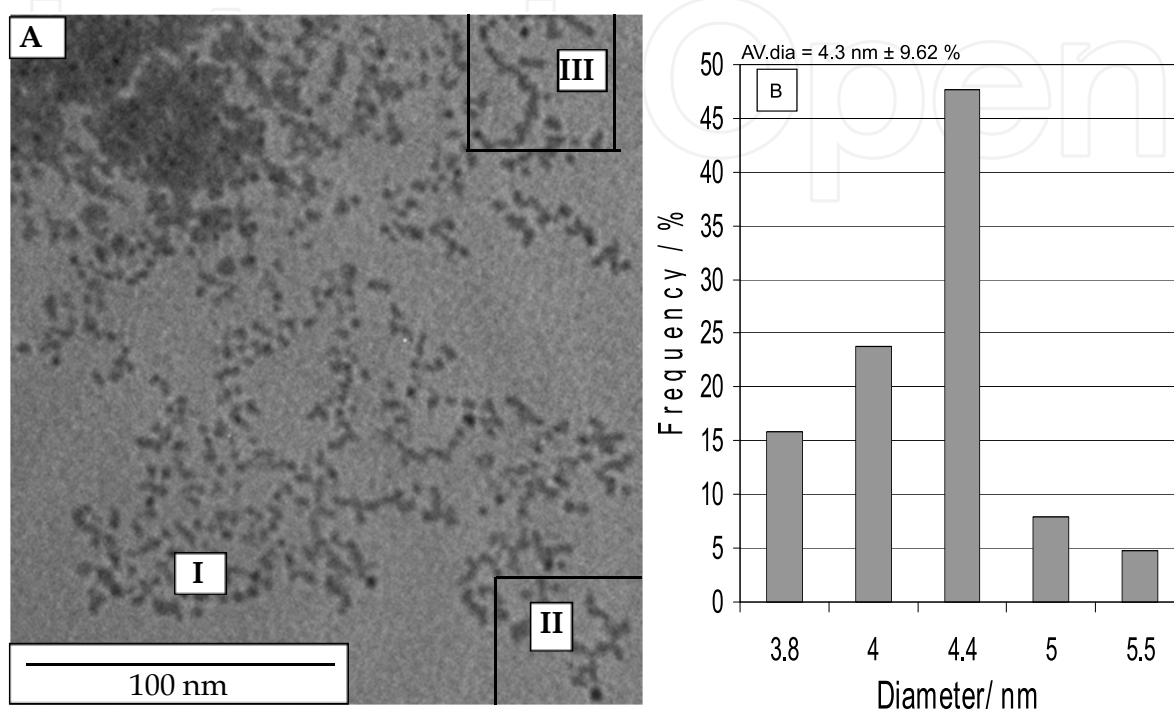


Fig. 1. (a) The TEM image and (b) particle size distribution of starch-capped CdSe nanoparticles at 1:1 precursor molar ratio.

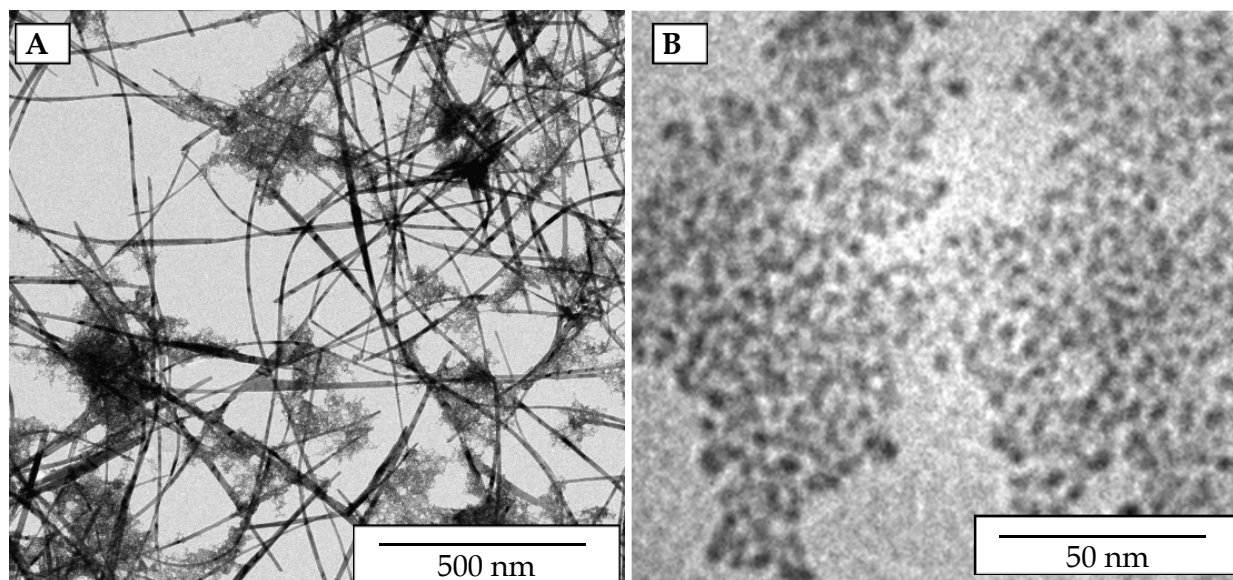


Fig. 2. The TEM images of starch-capped CdSe nanoparticles at 0.5:1 precursor molar ratio showing (A) nanowires with interspersed spherical particles and (B) a fraction of the interspersed spherical particles at low magnification.

The XRD patterns of the starch-capped CdSe nanoparticles at the two molar ratios exhibited predominantly wurtzite crystal structure with distinct diffraction peaks corresponding to the (002), (101), (102), (110), (103), and (112) crystalline planes of hexagonal CdSe (International centre for data diffraction PDF 2). Although the cubic zinc-blende and the hexagonal wurtzite phases could produce similar X-ray powder diffraction (XRD) results in nanocrystals (NCs), the XRD pattern showed unambiguous evidence that the particles are of a wurtzite structure: the (102) and (103) diffraction peaks characteristic of hexagonal-wurtzite CdSe structure, which are usually observed between 35° - 37° and 45° - 47° 2θ values respectively, were clearly seen (Oluwafemi, 2009). The sharp X-ray diffraction patterns suggest that the diffraction is predominantly due to the presence of elongated particles of a very high aspect ratio. This also accounts for the slight shift of the diffraction peaks to higher 2θ values. The sharp diffraction at 1:1 molar ratio was attributed to the self-assembly of the dot particles as indicated by the different arrangement pattern. Generally in thermodynamic terms, it is notable that cubic zinc - blende is the most stable form at lower temperatures (Li et al., 2007; Ma et al., 2002a, 2000b; Yang & Xiang, 2005), while wurtzite is more stable at high temperatures (Murray et al., 1993; Trindade & O'Brien, 1996, 1997; Malik et al., 2001). In the present study, hexagonal wurtzite phase was obtained at room temperature. The invariability of the crystal structure at the two molar ratios indicates that wurtzite is the sole stable resultant phase for this aqueous phase synthesis at room temperature. This shows that temperature is not the factor responsible for the crystal phase in the present case. The high Se:Cd ratio and the nature of the capping agent might induce the change in shape and phase of the CdSe nanocrystals under this synthetic method.

3.1.2.2 Optical analysis

The absorption spectra at 1:2 and 1:1 molar ratios showed an absorption shoulder at 602 nm and 558 nm with an absorption edge at 670 nm (1.85 eV) and 652 nm (1.90 eV) respectively. The broadness of the absorption shoulder was attributed to the self-assembly of the dot particles and the formation of elongated particles. Estimation of the particle diameters using the effective mass approximation (EMA) model (Brus, 1984): 5.59 nm (1:2) and 4.70 nm (1:1) are in agreement with the particle diameter calculated using the TEM. The slight red-shift observed in the absorption spectrum of the elongated particles, as compared to the spherical particles was attributed to the fact that, during the formation of elongated particles through adhesion of the dot particles, the band-gap of elongated particles depended more sensitively on their width than on their length although both parameters were responsible for the variation of band-gap (Wang et al., 2006). These particles emitted in the blue region. The position of the absorption and emission spectra of these particles appeared atypical, as the emission peaks were blue-shifted from the absorption band edges. This suggested that the emission originated from a higher energy state than the band gap, in total contrast to other reports of CdSe nanomaterials. However similar observation has been reported recently for aqueous synthesis of cysteine-capped CdTe by Green *et al.*, (2007).

3.1.3 Starch capped ZnSe nanoparticles

3.1.3.1 Structural analysis

The XRD pattern of the as-prepared ZnSe nanoparticles (Figure 3) exhibited predominantly wurtzite crystal structure with distinct diffraction peaks corresponding to the crystalline planes of hexagonal ZnSe and lattice constant of 0.397 nm, which was

consistent with the JCPDS card for ZnSe (JCPDS no 89-2840). The mean particle diameter as calculated from the line width of the diffraction peak using Debye-Scherrer equation was 3.50 nm. As expected, the XRD peaks of the ZnSe NCs were considerably broadened compared to those of the bulk CdSe due to the nanocrystalline nature of the particles. The stronger and narrower (002) peak in the diffraction pattern indicated that the nanoparticles were elongated along the *c*-axis. The formation of hexagonal ZnSe NCs at room temperature further showed that this synthetic route and the capping agent might be responsible for the formation of hexagonal-wurtzite phase. Similar observation was made for the organically soluble CdSe NCs produced using this synthetic route and hexadecylamine as the capping agent (Oluwafemi and Revaprasadu, 2008; Oluwafemi et al., 2010). The mechanism behind this still needs to be elucidated.

The TEM images of the starch-capped ZnSe nanoparticles showed that the particles were well dispersed, small and spherical in shape. The particles are in the range 2.3 to 4.2 nm with mean particle diameter of 3.3 nm and standard deviation (σ) of 0.562 nm indicating broad size distribution. The TEM diameter is in accordance with the XRD result. The broad size distribution was attributed to the aggregation of the smaller particles which are thermodynamically unstable in the solution as a result of their high surface energy which makes them very reactive (Wei et al., 2004; Lee et al., 2002, 2003).

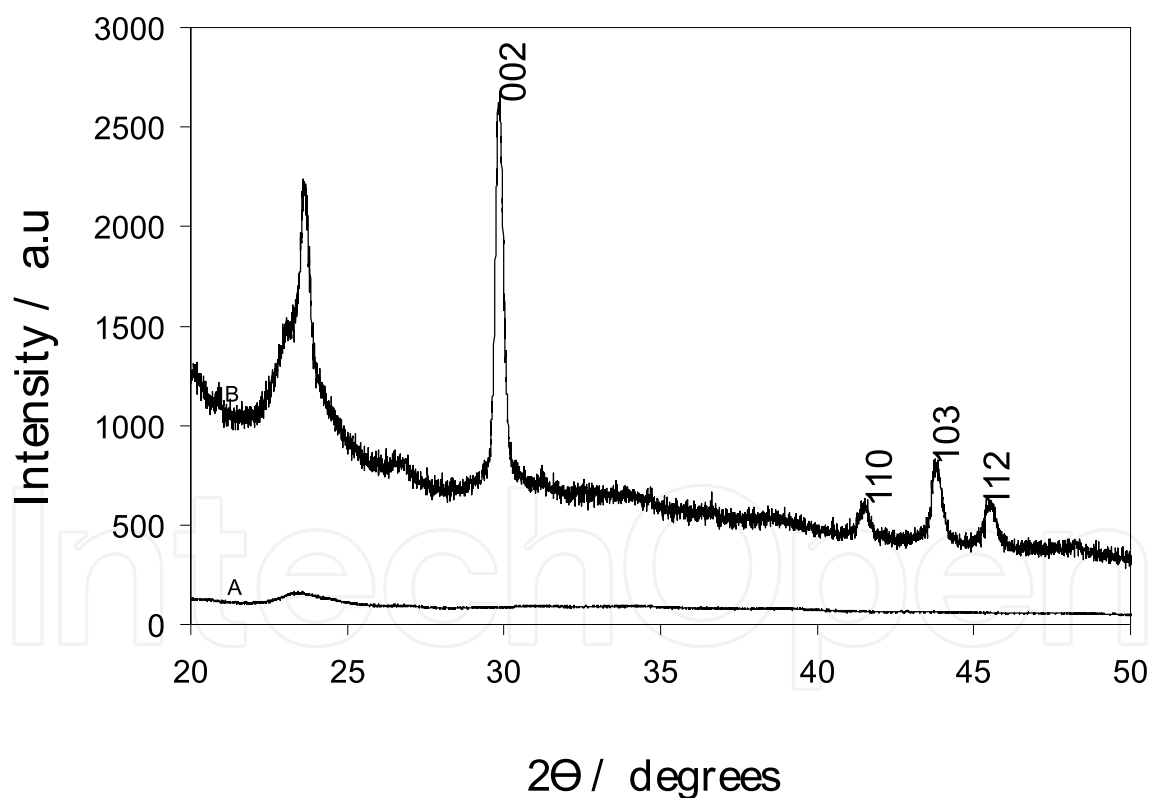


Fig. 3. XRD patterns of (a) pure starch and (b) starch -capped ZnSe nanoparticles.

3.1.3.2 Optical analysis

The absorption spectrum consists of an absorption shoulder at 282 nm (4.40 eV) signifying the monodispersity of the particles and an absorption edge at 303 nm (4.09 eV) which was blue shifted from the bulk band gap of 460 nm (2.70 eV) for bulk ZnSe. This shifting from

the bulk band gap was attributed to strong quantum confinement and also signified small particle size. The emission spectrum was broad and showed a trap state emission with maximum at 408 nm which was red-shifted in relation to its absorption maximum. The emission curve was not smooth/symmetrical suggesting the presence of surface defects which was attributed to the smaller size of the particles. As the particle size decreases, the surface to volume ratio increases, thereby increasing the number of surface atoms and energy. This increased the density of the surface defects and resulted in ineffective passivation of the surface states (Xiong et al., 2007; Qu & Peng, 2002). The surface chemistry of the as-synthesised material was investigated using FT-IR spectroscopy. The spectra showed a strong band at 3298 cm^{-1} attributed to the O-H stretching of starch and its width was ascribed to the formation of inter and intramolecular hydrogen bond. The asymmetric stretching of C-H band was at 2921 cm^{-1} while the band at 1630 cm^{-1} was attributed to tightly bound water present in the starch. The two characteristic bands at the fingerprint region of spectra at 1146 cm^{-1} and 1075 cm^{-1} were attributed to the C-O, C-C stretching and C-O-H bending of starch respectively while the band at 1330 was attributed to the angular deformation of C-H. The prominent band at 992 was attributed to the skeletal mode vibration of α 1,4-glycosidic linkage (C-O-C) while the band at 757 was attributed C-C stretching. All these characteristic bands confirmed the capping of the particles by starch.

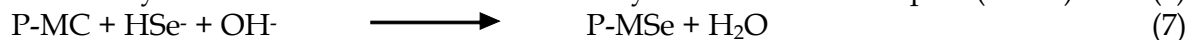
3.2 PVA and PVP-capped MSe nanoparticles

PVA and PVP are good choices as stabilizers because they can interact with metal ions by complex or ion-pair formation and can be designed to improve certain physical properties of semiconductor nanoparticles (Colvin et al., 1994; Dabbousi et al., 1996; Selim et al., 2005). In addition, the high viscosity of the polymer solution would be helpful in controlling the growth of selenide nanoparticles and thus prevent particles from aggregating hence no additional stabilizer would be needed. Furthermore, these polymers have high aqueous solubility and from an applications point of view, the polymer matrix would protect the selenide against photo-oxidation. Most of the direct aqueous synthesis for the polymer selenide nanocomposite usually involves the use of selenosulphate as the source of selenium. Ma and co-workers had reported a series of polyvinyl alcohol (PVA)-selenide nanocomposites using this technique (Ma et al., 2002a, 2002b). They observed that, the particle size can be determined to some extent by the experimental conditions such as pH, concentration of the free ions and reaction temperature. They indicated that under weakly basic conditions (pH \sim 10), sodium selenosulphate gradually released Se^{2-} upon hydrolytic decomposition, while in the acidic system, it decomposed quickly to produce selenium and no crystalline selenides were obtained. In all, their reactions complex ions play a significant role of controlling the release of free metal ions, which can then steadily combine with Se^{2-} to form nanocrystalline selenides. Otherwise, free metal ions with a high concentration would have rapidly combined with Se^{2-} , hence difficulties in controlling the nucleation and growth of the selenide nanocrystallites. In another development, Badr and Mahmoud (2005) using this technique prepared different sizes of PVA-capped CdSe NCs by varying the Cd:Se ratio. The optical properties showed that the particle size decreases with increasing cadmium ratio. The complexation between the polymer and the CdSe NPs as well as the conductivity of the PVA was also found to increase with decreasing particle size. This complexation leads to decrease in the

intermolecular interaction between the PVA chains and thus decrease in the degree of PVA crystallinity. A similar observation has also been reported by Ma and co-workers (Ma et al., 2002b). Using selenosulphate, Yang and Xiang (2005) also reported the synthesis of PVP-capped CdSe nanoparticles. However, the reaction takes place in the presence of thioglycerol which acts as both complexant and catalyst for the decomposition of selenosulphate. In the absence of the complexant, no UV-vis absorption peak and PL emission peak was observed. The mechanism of the direct reaction between cadmium ion and selenosulphate in aqueous solution to form CdSe had been investigated by Yochelis and Hodes (Yochelis & Hodes, 2004). They discovered that CdSe were formed as a disordered phase surrounding the CdSO₃ produced via reaction between the Cd precursor and sodium selenosulphate in the presence of excess sodium sulphite. These amorphous CdSe then break off from CdSO₃ crystals to form nanocrystals of CdSe. In this section, we report the synthesis of PVA and PVP-capped MSe nanoparticles using selenide ion produced via reduction of selenium powder at room temperature. However as far as we know, our work will be the first reported 'green' room temperature one pot synthesis of PVA and PVP capped MSe (M= Cd or Zn) nanoparticles under a mild and environmental benign synthetic route.

3.2.1 Reaction mechanisms

The overall chemical reaction involved in the process is represented by the following equations:



Scheme 2. Proposed chemical reactions involved in the formation of polymer capped MSe nanoparticles

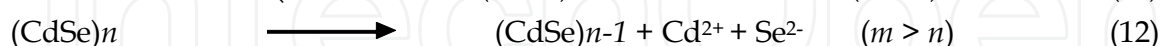
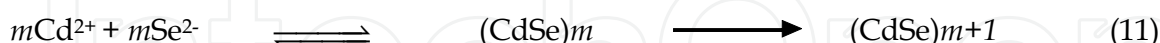
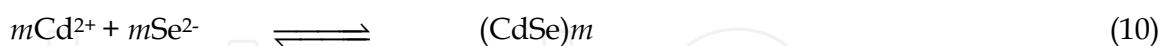
As discussed earlier the whole process is a redox reaction. Selenium is reduced using sodium borohydride to give selenide ions. In the above reaction, the metal ion reacts with the polymer (PVP or PVA) solution to form the polymer-metal ion solution. Addition of the selenide ion solution to the polymer-metal ion solutions resulted in instantaneous change in the colour of the solutions from colourless to orange (PVA) and orange red (PVP). This indicates the formation of CdSe nanoparticles. The addition of the selenide solution to the polymer - metal ion solution resulted in gradual release of selenide ion (Se²⁻) upon hydrolytic decomposition in alkaline media (equation 4). The released selenide ions then react with metal ion to form seed particles (nucleation).



The growth of the nanoparticles could have occurred either by the growth of CdSe on the seeds (growth from supersaturated solution) or by the process of Ostwald ripening whereby larger seed grow at the expense of the smaller ones.

In this reaction, the complexation of the metal ion by the polymer is expected to play a significant role in the formation of the nanocrystalline selenides. During the reaction, the

complex ion controls the gradual release of the free metal ion which can then steadily combine with Se^{2-} to produce CdSe nanocrystals. This gradual release controls the nucleation and growth process. In addition, the high viscosity of the polymer solution would be helpful in preventing the particles from aggregating hence no additional stabilizer would be needed.



3.2.2 PVA- capped CdSe nanoparticles

3.2.2.1 Optical analysis

The absorption and emission spectra of PVA-capped CdSe nanoparticles are shown in Figure 4. The absorption band edges are all blue-shifted in relation to the bulk band gap (indicating quantum confinement effects) and appeared at the same position without any significant shift throughout the reaction time. The absorption spectra consist of an absorption band edge at 648 nm (1.91 eV) and excitonic shoulder at 299 nm and 315 nm signifying the monodispersity of the particles. The particle sizes as estimated using the effective mass approximation (EMA) model (Brus, 1984), is 4.57 nm. The appearance of the absorption features at the same position is an indication that the growth of the nanoparticles ceases after 1 hr. This shows that the generation of the CdSe particles reaches a homeostatic state after 1 hr, suggesting that the polymer matrix confines the growth of particles and prevents further growth or aggregation. The emission spectra (Figure 1 insert) show that the emission line width becomes narrower as the reaction time increases indicating that, extending the reaction further only results in better passivation of the as-synthesised CdSe nanoparticles. This shows that, there is optimal surface structure reconstruction of the nanocrystals with increasing reaction time which can be attributed to the effective passivation of the surface trapping states that are normally associated with semiconductor nanoparticles. All the absorption spectra showed the presence of two bands in the UV region located at 269 nm and 278 nm. These bands are attributed to the $n-\pi^*$ excited transition of CdSe-PVA nanocomposite confirming the interaction/complexation between the polymer and the CdSe (Selim et al., 2005). All the particles emit in the blue region without any significant change in the emission maxima, which is at 406 nm. The observed blue shift in the emission spectra in relation to the absorption suggested that the emission originated from a higher energy state than the band gap (Green et al., 2007). This can be attributed to the shrinkage of the CdSe emitting core due to the interaction between the CdSe particles and the polymer. Similar observation has been reported by (Akamatsu *et al.*, (2005), for CdTe particles and was attributed to the particle reacting with the thiol transferring agent. This atypical trend in the position of the absorption and emission spectra of these particles was also reported earlier for the starch - capped CdSe nanoparticles under this synthetic route (Oluwafemi, 2009). It also suggests that the bigger particle size calculated from the absorption spectroscopy might be a contribution from both the capping group at the surface of the emitting CdSe core and the emitting CdSe core.

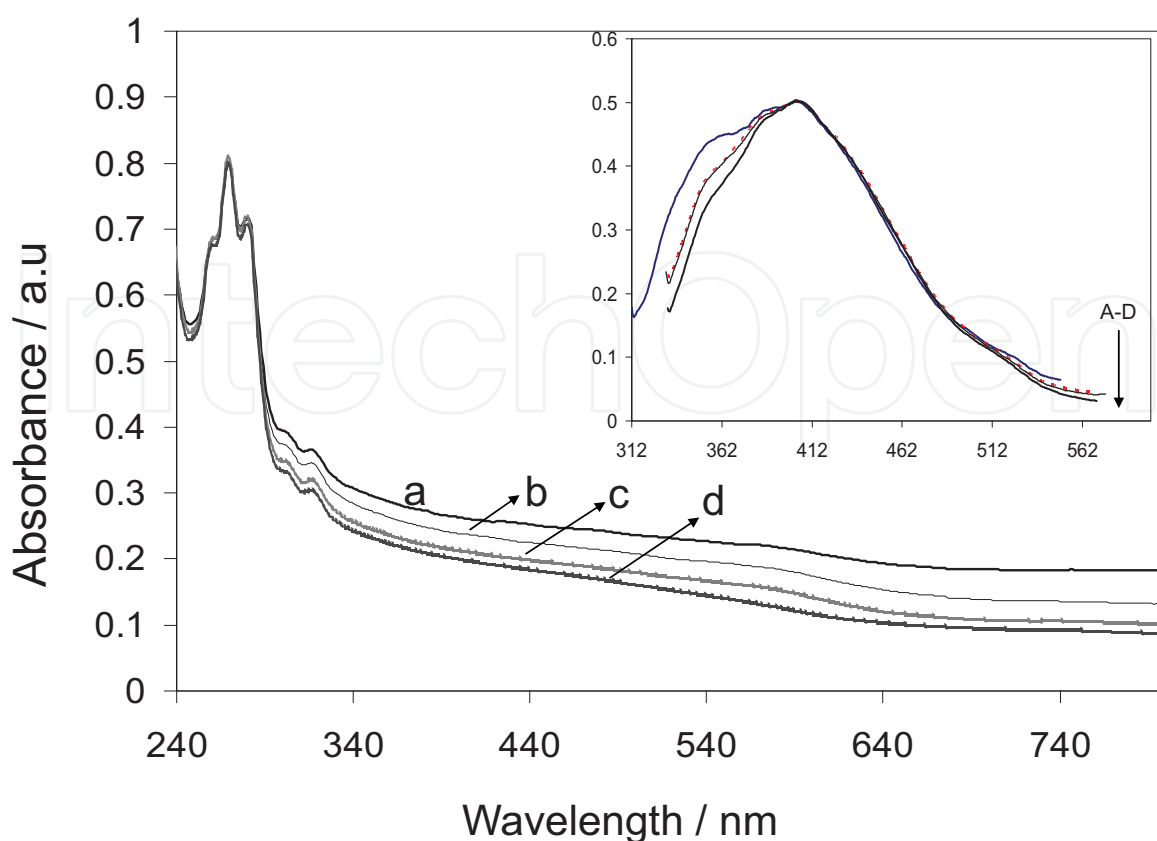


Fig. 4. Absorption and photoluminescence (inlet) spectra of PVA-capped CdSe nanoparticles at (a) 1 hr, (b) 3 hrs, (c) 5 hrs and (d) 24 hrs reaction times.

3.2.2.2 Structural analysis

A typical representative of the TEM image is shown in Figure 5A. The image shows well-defined, monodispersed, spherical particles. The particles are in the range of 3.80 to 5.0 nm with mean particle diameter of 4.51 nm. The relative standard deviation of the size of the nanoparticles shown in Figure 5A (insert) is 0.37 nm (8 %) indicating a narrow size distribution. These particle sizes suggest that, there is possibility for the adhesion of the smaller nanoparticles (seed particles) produced at the beginning of the reaction before complete passivation by the polymer. These smaller particles possess high surface to volume ratio and are therefore very reactive. The surface chemistry of the as-synthesised materials investigated using FTIR spectroscopy confirmed the interaction of the particles with PVA as shown in figure 5B. The spectrum exhibits bands characteristic of stretching and bending vibrations of O-H, C-H, C=C and C-O groups. The strong bands observed at 3229-3365 cm^{-1} corresponding to the O-H stretching frequency indicates the presence of hydroxyl groups (Sweeting, 1968). The broad weak band observed at 2159 cm^{-1} has been assigned to the combination frequency of C-H with C-C (Raju et al., 2007). The bands observed at 1634 cm^{-1} and 1411 cm^{-1} have been assigned to the C=C stretching mode and bending modes of CH_2 group respectively. The weak broad band at 1103 cm^{-1} is attributed to the stretching mode of C=O group. The absence of non bonded -OH stretching band at $\nu = 3600\text{--}3650\text{ cm}^{-1}$ and the decrease in the intensity of the O-H stretching vibration peak at $\nu = 3229\text{--}3365\text{ cm}^{-1}$ in the PVA - CdSe spectrum further confirm the complexation of PVA chains CdSe nanoparticles.

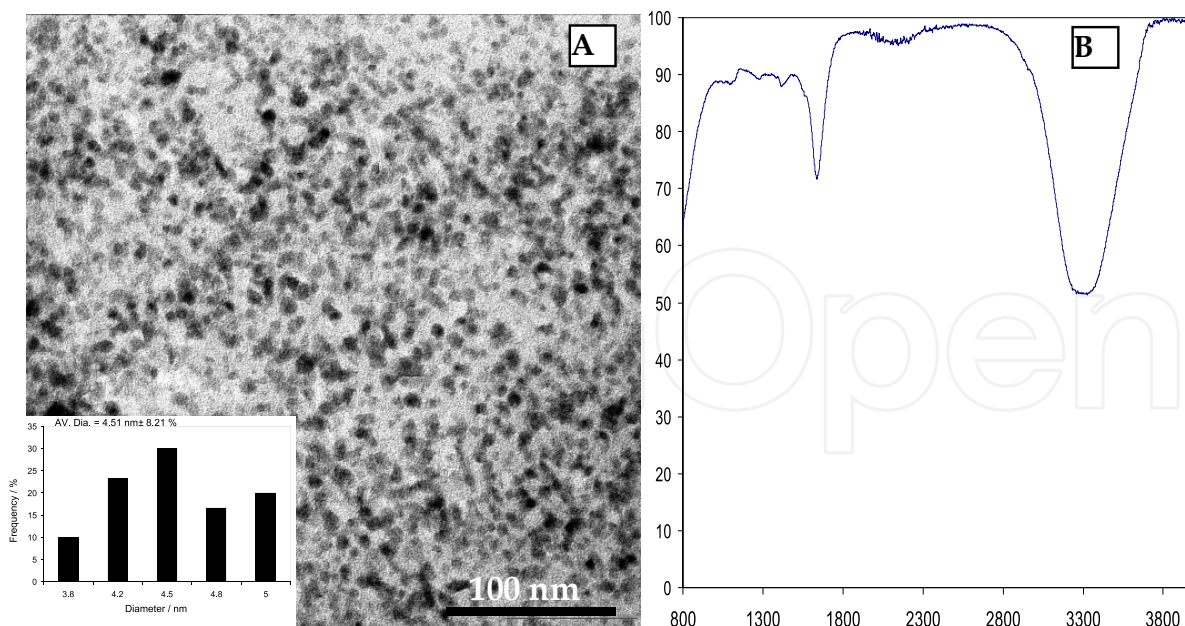


Fig. 5. The TEM image (A), particle size distribution (inset) and FTIR spectra (B) of PVA - capped nanoparticles at 5 hrs reaction time.

3.2.3 PVP- capped CdSe nanoparticles

The addition of the colourless selenide ion solution to the PVP-metal ion solutions resulted in instantaneous change in the colour of the solutions from colourless to orange red. The orange red seed particles (after 1-h reaction) showed an absorption shoulder at about 546 nm and the band gap (E_g) calculated was 2.27 eV. This absorption edge was significantly blue-shifted (167 nm) compared to bulk CdSe ($E_g = 1.74$ eV) indicating quantum effect. As the reaction times increases, the samples showed an absorption band edge at about 566 nm ($E_g(556) = 2.19$ eV) at 3 h with increased intensity in the colour of the solution. This increase in the band edge suggests the growth process via Ostwald ripening whereby larger seeds grew at the expense of the smaller ones. The absorption band edge remained at the same position at 5 h and for the rest of the reaction indicating that the polymer matrix confined the growth of the particles and the generation of CdSe particles reached a homeostatic state. Since the absorption edge was an index of particle size, smaller particles have larger band gaps and absorb at shorter wavelengths (Brus, 1983). The particles emit in the blue region and the emission line width is narrow, signifying particles with narrow size distributions. The emission maxima appeared at the same position through out the reaction time and are blue shifted in relation to the absorption band edge. This blue shift in the emission spectra in relation to the absorption has been attributed to emission from a higher energy state than the band gap (Green et al., 2007) due to the shrinkage of the CdSe emitting as a result of the interaction between the CdSe particles and the polymer. Since this atypical trend in the position of the absorption and emission spectra was reported for all the polymer capped CdSe nanoparticles under this synthetic route, it will be good to study the reaction earlier, i.e. before 1 hr, in order to gain better understanding of the reaction process.

The TEM image of the PVP capped CdSe at 5 hr in figure 6A showed small, spherical particles with some aggregation. The aggregation is due to the oriented attachment between the spherical nanoparticles as a result of dipole-dipole interactions between the highly

charged surfaces of seed particles of nanocrystals. The particle sizes are in the range 3.5 to 5.8 nm with mean particle diameter of 4.49 nm. The HRTEM image in figure 6B shows clearly the lattice fringes, indicating the crystalline nature of the as-synthesised material. There are also discontinuities in the lattice fringes which are due to dislocations and stacking faults which further confirm oriented attachment growth among the nanoparticles.

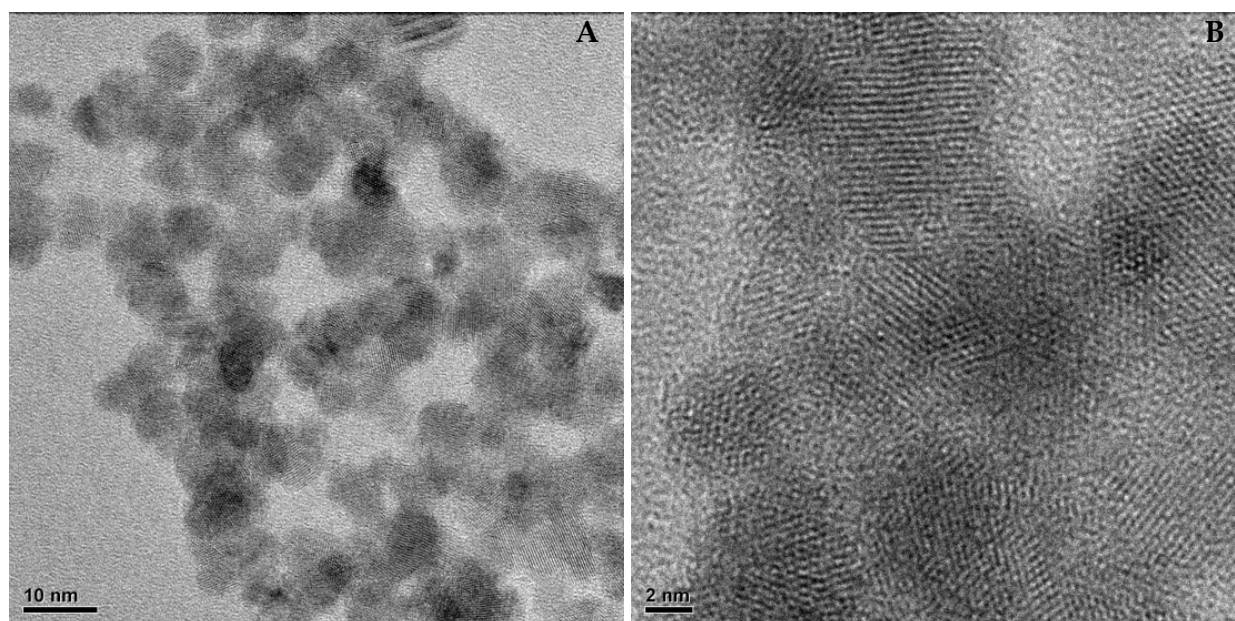


Fig. 6. Typical representative of the TEM image (A), and HRTEM image (B) of PVP-capped nanoparticles.

3.2.4 PVP-capped ZnSe nanoparticles

The absorption and emission spectra of PVP-capped ZnSe nanoparticles at different reaction times are shown in Figures 7 and 8. The absorption band-edges and emission maxima are slightly blue-shifted from the bulk band gap. The absorption spectra are characterised by tailing band-edges with no distinctive excitonic feature at lower reaction times (1–3 hrs) indicating the presence of large particles. As the reaction progressed, a distinctive excitonic shoulder appeared in the spectra, without any changes in the absorption band-edges of the particles at 5 and 24 h. The emission spectra of the particles showed band-edge luminescence. The emission maxima appeared at the same position as the reaction time increased for the first 3 hrs and decreased slightly as the reaction time increased. The emission maxima appeared at 446 nm (1 and 3 h), 435 nm (5 h) and 427 nm (24 h). The blue shift in the emission spectra and the appearance of the distinct excitonic shoulder at 5 and 24 h indicates the presence of smaller particles. This type of atypical optical spectra as the reaction time increases has been reported recently and was attributed to digestive ripening (Green et al, 2007). According to Green *et al.*, digestive ripening is essentially the opposite of Ostwald ripening. It usually involves the breaking of particles into smaller fragments or digestion of a layer at a time. Several factors such as ligands (Prasad et al.2002), solvent (Hines & Scholes, 2003) and surfactant (Green et al., 2007; Samia et al., 2005), have been reported as the driving force for this mode of particle growth. The digestive ripening reported here is possibly a contribution from both the ligand and reaction medium. Another possible explanation for this atypical optical spectrum, like the CdSe NPs discussed earlier,

could be shrinkage of the ZnSe core as the reaction time increases which could be due to the interaction between the ZnSe particles and the polymer.

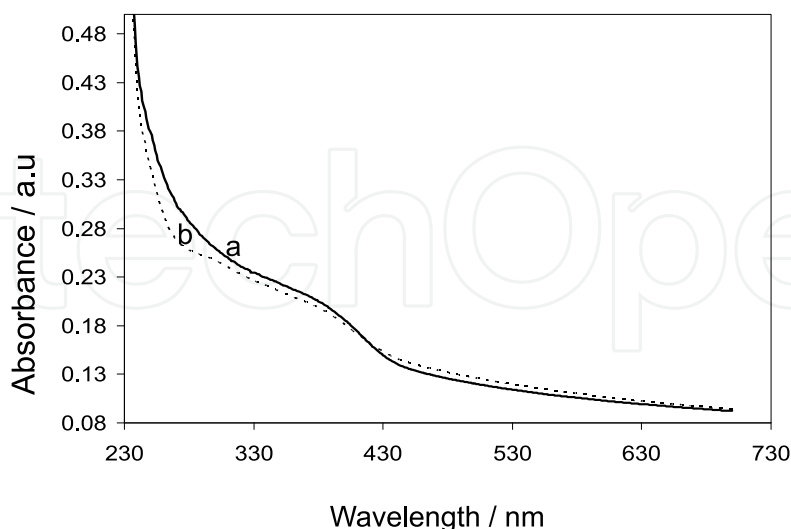


Fig. 7. Absorption spectra of PVP-capped ZnSe nanoparticles at (a) 5 h, (b) 24 h and Fig. 5 the photoluminescence (PL) at (a) 1 h, (b) 3 h, (c) 5 h and (d) 24 h reaction times

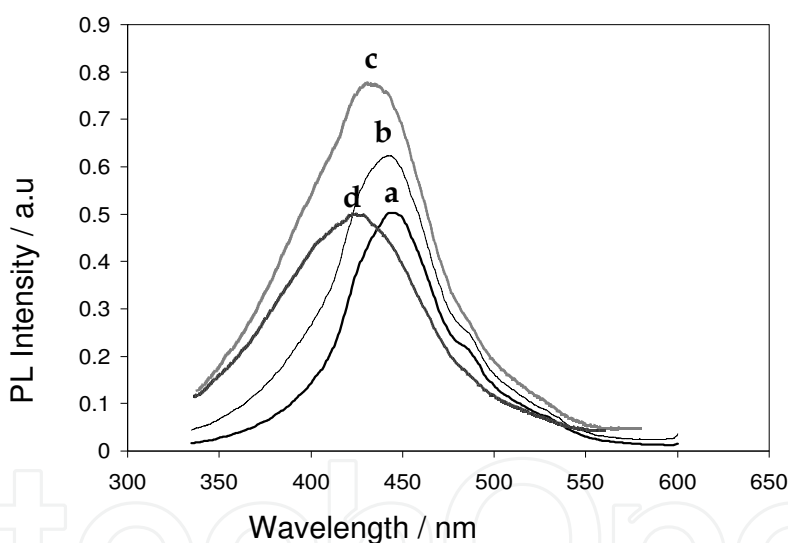


Fig. 8. The photoluminescence (PL) spectra of spectra of PVP-capped ZnSe nanoparticles at (a) 1 h, (b) 3 h, (c) 5 h and (d) 24 h reaction times

4. Conclusion

We have reported a simple, 'green', bench top, economical and environmentally benign room temperature synthesis of MSe (M=Cd or Zn) nanoparticles using starch, PVA and PVP as passivating agents. The whole process is a redox reaction with selenium acting as the oxidant and MSe as the reduction product. An entire "green" chemistry was explored in this synthetic procedure and it is reproducible. The optical spectroscopy showed that all the particles are blue shifted from the bulk band gap clearly due to quantum confinement. Starch capped CdSe nanoparticles showed the presence of monodispersed spherical

particles together with elongated particles of low aspect ratios at 1:1 precursor molar ratio. Different arrangement patterns such as tripods, sinusoidal and S-shaped were also clearly visible. These arrangement patterns clearly indicate the mechanism for the formation of one dimensional (1D) nanostructure under this aqueous route. At 1:2 precursor molar ratio, nanorods and nanowires of very high aspect ratio were produced indicating that, under this synthetic route, the final shape of the CdSe nanocrystals can be determined by controlling the precursor ratio. The XRD patterns of the starch-capped CdSe nanoparticles at the two molar ratios exhibited predominantly hexagonal wurtzite crystal structure, in contrast to the cubic zinc-blende structure normally obtained at lower temperature. Well dispersed, small and spherical particles with wurtzite crystal structure were observed for the starch capped ZnSe nanoparticles. The absorption spectra of the PVA and PVP-capped CdSe nanoparticles showed that the growth of the particles reach a homeostatic state after 1 h and 3 h respectively, suggesting that, the polymer matrix confines the growth of particles. FTIR spectroscopic analysis confirmed the capping/interaction of the nanoparticles surface by/with the polymers. All the as-synthesised CdSe nanoparticles under this synthetic route emitted at lower wavelength compared to the absorption wavelength suggesting that, the emission originated from a higher energy state than the band gap. This has been attributed to the shrinkage of the CdSe emitting core due to the interaction between the CdSe particles and the polymers. More work is still required for better understanding of the whole process. Compared to the exiting methods, the solution route reported here is a relatively simple, "green", low-cost technique, one - pot and reproducible. We believe that the knowledge gained from this study will enable an easy greener approach that would be more promising for practical production and will open the way for direct synthesis of highly luminescent water-soluble CdSe nanoparticles using different biomolecules for large scale productions.

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6. References

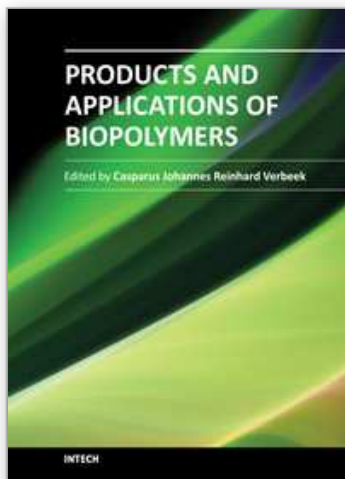
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It is interesting to consider that biopolymers are by no means new to this world. It is only because of our fascination with petrochemical products that these wonderful materials have been neglected for so long. Today we face a different challenge. Environmental pressure is pushing away from synthetic or petro-chemically derived products, while economic factors are pulling back from often more expensive "green" options. This book presents two aspects of biopolymers; potential products and some applications of biopolymers covering the current relevance of biopolymers.

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