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γ-Ray assisted synthesis of Ni_3Se_2 nanoparticles stabilized by natural polymer

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ABSTRACT

Nickel selenide nanoparticles were synthesized using γ-ray irradiation in the presence of natural polymer, chitosan as capping agent. Chitosan is the deacetylated product of chitin, the second most abundant organic resources after cellulose. The nanoparticles were produced using nickel acetate and selenium dioxide and the as-prepared chitosan stabilized nanoparticles were soluble and stable in aqueous solution. The morphology and structure of the nickel selenide nanoparticles were characterized using transmission electron microscope (TEM) and X-ray diffraction (XRD). Optical properties of the nanoparticles were characterized by UV–Visible spectrophotometer and photoluminescent spectroscopy. The XRD result shows that the nickel selenide conformed to Ni_3Se_2 with crystal structure of rhombohedral. The absorption spectrum of the Ni_3Se_2 nanoparticles covered from around 300–600 nm which makes it a potential photovoltaic and optoelectronic device material. In this report, γ-ray irradiation provided a "green", simple and clean route for the synthesis of chitosan stabilized Ni_3Se_2 nanoparticles. The size and size distribution of the nickel selenide nanoparticles were influenced by the concentration of chitosan and absorbed dose of γ-ray irradiation.

1. Introduction

Metal selenides nanoparticles have attracted great attention due to their interesting and unique optical, luminescent, electrical, magnetic, physical and chemical properties as compared to those of the corresponding bulk material [1]. These materials have found wide varieties of potential applications in photodetectors [2,3], photovoltaic [4], superionic materials [5], sensors [6,7], fluorescence bioimaging [8], laser materials [9–10], catalysts [11] and conductivity fields [12–14].

Conventionally, metal selenides have been synthesized by solid-state reactions [15], self-propagating high temperature synthesis [16–20], solution growth technique [21], electrochemical method [22] and photochemical method [23]. These methods usually need high temperature, high pressure or inert atmosphere protection. Another frequently used method involves the reaction of the H_2Se and metal or its compounds for the preparation of metal selenides. However, the process often involves relatively dangerous and highly toxic gases [24]. Over the past several years, organometallic precursors have also been reported to prepare metal selenides [25], which has to be performed at a relatively high temperature with standard airless environment that generally requires intricate processing. In recent years, solvothermal [26] and hydrothermal [27] synthesis methods are emerging as the effective synthetic technique for metal selenides. Different types of nickel selenides have been synthesized for the past decades. $NiSe_2$ with spherical morphology has been synthesized using solvothermal method [28], Liu et al. [29] obtained $Ni_{0.85}Se$ and $NiSe_2$ using hydrothermal method with sea urchin-like morphology and Zainal et al. [30] have fabricated Ni_3Se_2 thin film with band gap energy of 2.0 eV using electrochemistry method.

The solution reaction growth technique is the cheapest and most convenient approach for the synthesis of metal selenides. However, nanoparticles are not thermodynamically stable in the solution due to their high surface energy. These nanoparticles tend to aggregate to form larger particle and thus, loosing their special properties. In order to avoid aggregation, suitable capping agents or stabilizing agents can be used to passivate the nanoparticles. Many capping agents have been introduced which include organic passivators, such as thiolphenol [31], thiourea [32], mercapto acetate [33] and dodecanethiol [34], which are toxic and will pollute the environment if a great amount of nanoparticles is synthesized [35]. Other commonly used capping agent are surfactants, polymers, copolymers and recently there has been an increasing demand for

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"green" capping agents, for example starch [36], calixarene [37], cyclodextrin [38] and chitosan laurate [39].

γ-Ray assisted synthesis method has gained lot of research interests in the synthesis of metal [40], metal selenides [41], metal sulfides [42,43], polymer [44] and composites nanoparticles [45]. γ-Ray irradiation induced synthesis of nanoparticles is one of the very promising strategies as compared to conventional chemical and photochemical methods because the process is simple and clean. The γ-ray irradiation has harmless feature as the ^{60}Co gamma source is well insulated inside a lead chamber. Furthermore, radiochemical reactions can be carried out without using other chemicals or producing undesired side products.

In this paper, nickel selenide nanoparticles were synthesized using a "green" route with chitosan as a natural polymer capping agent at room temperature under γ-ray irradiation. From the view of "green" synthesis, all the reagents including chemical precursors, reaction medium and capping agents should be environmentally benign. Chitosan is the deacetylated product of chitin, the second most abundant organic resources after cellulose and the manufacturing cost of chitosan is relatively low. Chitosan was selected as the capping/stabilizing agent to prepare nickel selenide nanoparticles which are dispersible in aqueous solution. Several authors have reported the use of chitosan as capping agent for the production of uniform and monodispersed nanoparticles like gold [46], silver [47] and quantum dots [48]. To the author's knowledge, no work has been reported on the γ-ray assisted synthesis of nickel selenide nanoparticles with chitosan as stabilizing agent. The as-prepared nickel selenides nanoparticles were characterized by XRD, TEM, UV–visible absorption spectroscopy and photoluminescence spectra. The results indicated stable and well-dispersed nickel selenide nanoparticles in aqueous solution with fairly narrow size distributions were synthesized.

2. Experiment details

2.1. Chemicals

Nickel acetate trihydrate, 99.0%, selenium dioxide, 98.0% and low molecular weight chitosan were obtained from Sigma–Aldrich. Acetic acid, 99.0%, ethanol, 99.8%, isopropanol, 98% were purchased from Merck. Deionized water by Purelab Prima Elga, with 18.2 MΩ electrical resistivity was used throughout the sample preparations. All the chemicals were of analytical grade and were used without further purification.

2.2. Synthesis procedures

The Ni_3Se_2 nanoparticles were synthesized in an aqueous chitosan solution under γ-ray irradiation. To prepare the solution, 0.08 M concentration of nickel acetate trihydrate and selenium dioxide were added into 100 ml deionized water containing low molecular weight chitosan (concentration of 0.5 wt%, 1.0 wt% and 1.5 wt%) with 1.0% (v/v) of acetic acid. The above mixture formed a clear solution without any chemical reactions or precipitations. Then, 10 ml of isopropanol was added into the solution as hydroxyl free radical removal agent. The solution was deaerated by bubbling with pure nitrogen for 20 min to remove oxygen before it was irradiated in a Co-60 γ-ray source with a dose rate of 4.4 kGy/h for

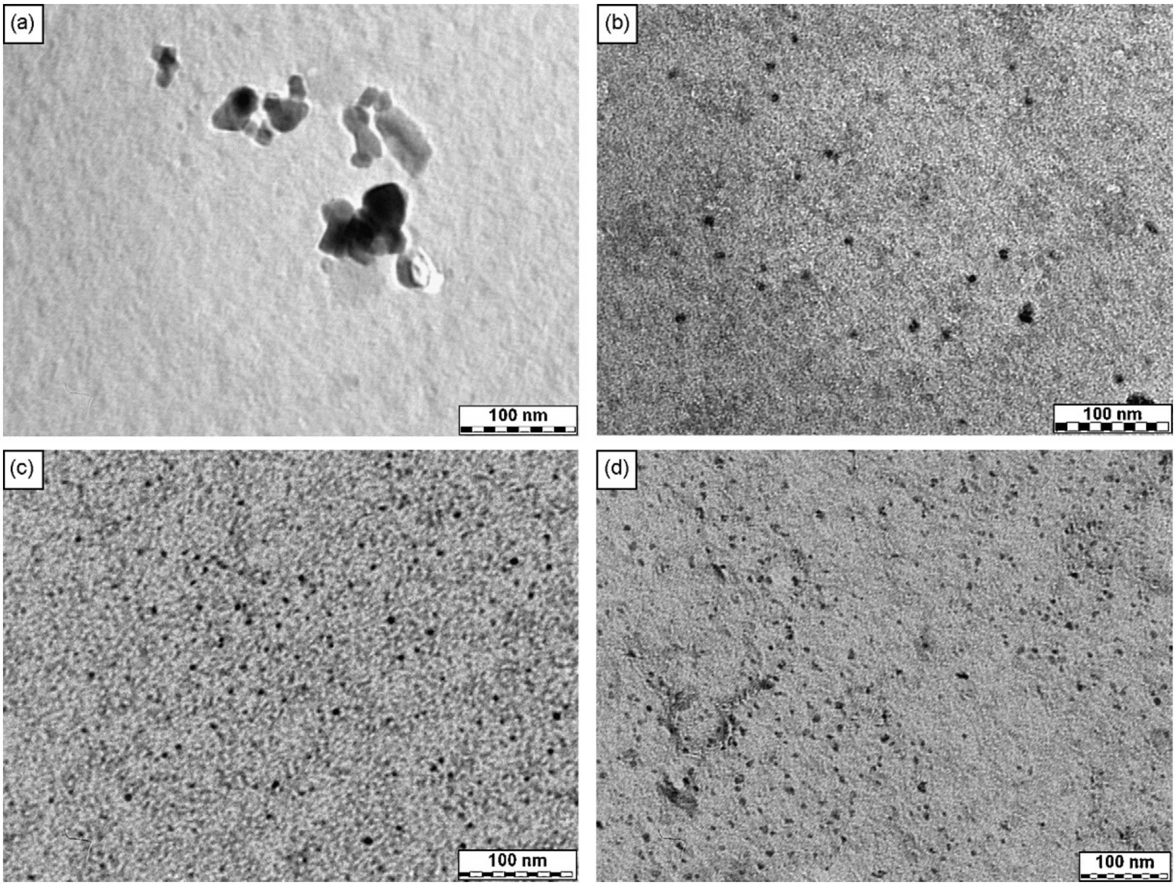

Fig. 1. TEM micrographs for nickel selenide nanoparticles synthesized under γ-ray irradiation without the presence of chitosan (a), 0.5 wt% chitosan (b), 1.0 wt% chitosan (c) and 1.5 wt% chitosan (d). (γ-Ray absorbed dose of 18 kGy, nickel acetate and selenium dioxide concentration of 0.08 M.)

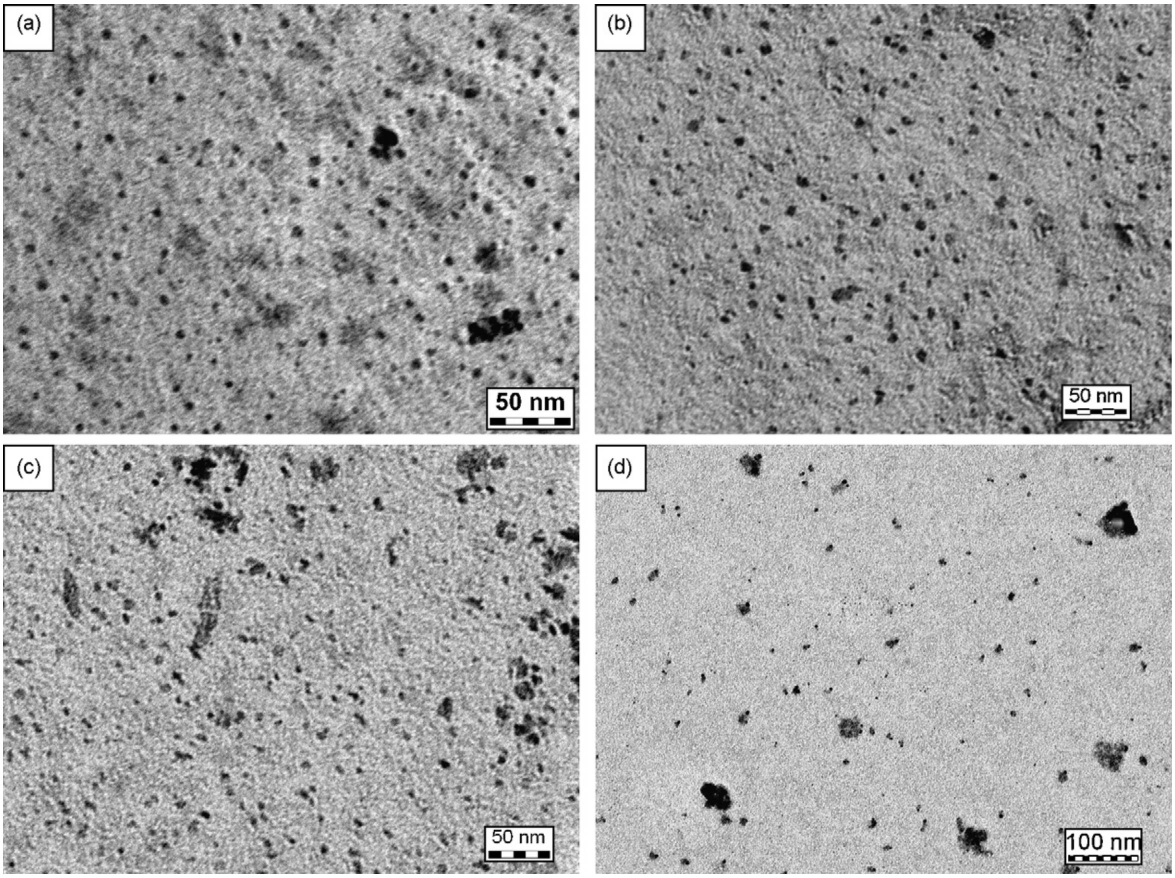

Fig. 2. TEM micrographs for nickel selenide nanoparticles synthesized under γ-ray irradiation absorbed dose of 25 kGy (a), 35 kGy (b), 50 kGy (c) and 80 kGy (d). (1.0 wt% chitosan, nickel acetate and selenium dioxide concentration of 0.08 M.)

total absorbed doses of 18 kGy, 25 kGy, 35 kGy, 50 kGy and 80 kGy, respectively. After irradiation, the synthesized nanoparticles were separated out from solution by centrifugation at 6000 rpm for 5 min. The obtained nanoparticles were dried in a vacuum oven at 50 °C for 1 day before further characterizations.

2.3. Characterizations

Transmission electron microscope, TEM (Philips CM12 operated at 100 kV) was used to view large number of nanoparticles and compiles the statistic of nanoparticles sizes and size distribution. A drop of the nanoparticles solution was cast onto a 300 mesh copper grids coated with a thin amorphous carbon film using a micropipette. The drop casting was allowed to dry in an oven at 40 °C for 1 day. Measurement of the average diameter of the nanoparticles was carried out using I-Solution-DT (version 6.5, IMT) image analysis software with at least 200 nanoparticles being chosen as the sampling data.

The nanoparticles crystalline phase was determine by X-ray diffraction (XRD) using a Philip diffractometer employing a scanning rate of $0.02^\circ\,s^{-1}$ in a 2θ range from 10° to 60° with Cu Kα radiation ($\lambda = 1.5418$ Å). Ultraviolet–visible spectroscopy (UV–visible) was carried out at room temperature using a PerkinElmer Lamda-35 spectrophotometer in the range of

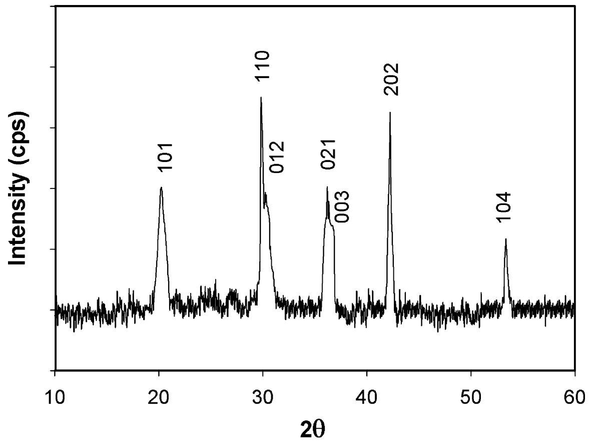

Fig. 3. XRD pattern of Ni_3Se_2 nanoparticles.

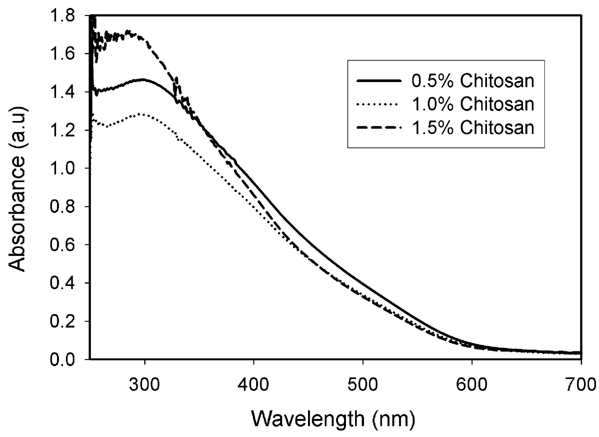

Fig. 4. UV–visible spectra of the synthesized Ni_3Se_2 nanoparticles.

250–800 nm. The photoluminescence emission (PL) spectrum was taken with a PerkinElmer S3 spectrofluorophotometer. All absorption and PL spectra were measured without any post-preparative size separation.

3. Results and discussion

Fig. 1 shows the typical TEM micrographs of the nickel selenide nanoparticles prepared in solutions at different chitosan concentration under γ-radiation absorbed dose of 18 kGy. The nanoparticles produced without the presence of chitosan as stabilizing agent have a large diameter, >15 nm and were poorly dispersed as shown in Fig. 1(a). For chitosan concentrations of 0.5 wt%, 1.0 wt% and 1.5 wt%, the nanoparticles have smaller size, <10 nm and were fairly dispersed dependant on chitosan concentration. During the γ-irradiation, the chitosan chain degrades into smaller fragments. Owing to their interaction with NH_2 and OH groups of the chitosan chain, the nickel selenide nanoparticles formed are enveloped by chitosan fragments, and so the nanoparticles could be kept from agglomerating. The average diameter of the nanoparticles synthesized in the chitosan concentration of 0.5 wt% was 8.5 ± 2.7 nm (Fig. 1b), 1.0 wt% was 5.77 ± 0.96 nm (Fig. 1c) and 1.5 wt% was 5.70 ± 1.2 nm (Fig. 1d). It was found that under higher chitosan concentration, 1 wt% and 1.5 wt% chitosan, the nanoparticles formed are smaller and have narrower size distribution (indicated by lower standard deviation value). This is because the chitosan fragments produced were sufficient to cap the nanoparticles thus resulting in well-dispersed nanoparticles. While for lower chitosan concentration, <0.5 wt% chitosan, the chitosan fragments produced are not enough to effectively stabilize the nanoparticles resulting in agglomeration as can be seen from Fig. 1(b). The optimum chitosan concentration for the synthesis of nickel selenide nanoparticles was 1.0 wt% as the nanoparticles produced has size comparable to 1.5 wt% chitosan and it has the lowest standard deviation.

Another parameter that influenced the diameter of the nickel selenide nanoparticles is the γ-radiation absorbed dose. By increasing the γ-radiation absorbed dose to 25 kGy, 35 kGy, 50 kGy and 80 kGy with 1.0 wt% of chitosan, the diameter of the nanoparticles produced are 6.17 ± 1.3 nm, 7.42 ± 1.6 nm, 7.68 ± 1.94 nm and 12.42 ± 7.17 nm, respectively (Fig. 2a–d). This is due to the nickel selenides nanoparticles continued to grow under longer exposure of γ-radiation resulting in bigger nanoparticles at higher absorbed dose. The size distribution of the nanoparticles also became broader because under prolonged γ-radiation, the chitosan fragments became much shorter and the ability to prevent agglomeration reduced drastically especially under 80 kGy of γ-radiation. The result is consistent with the previous report on the synthesis of silver nanoparticles in chitosan [49] and CdS nanoparticles [43] under γ-radiation.

Fig. 3 showed the XRD pattern of nickel selenide nanocrystals that were obtained in the presence of 1.0 wt% of chitosan, 18 kGy of γ-radiation absorbed dose and 0.08 M concentration of nickel acetate and selenium dioxide. All the peaks at $2\theta = 20.29^\circ$, 29.82°, 30.29°, 36.22°, 36.79°, 42.23° and 53.39° are attributed to (1 0 1), (1 1 0), (0 1 2), (0 2 1), (0 0 3), (2 0 2) and (1 0 4) crystal planes. These 2θ values could be well indexed to Ni_3Se_2 with rhombohedral crystal structure (JCPDS file card no.01-085-0754) and the lattice parameters are a and $b = 6.034$ Å and $c = 7.251$ Å. No characteristic peaks of other molar ratio nickel selenides and impurities were detected. The broadening of the diffraction peaks is due to the finite size of the nanocrystals and indicates that the dimensions of the nanoparticles are very small. The average diameter of the Ni_3Se_2 nanocrystals can be obtained from the full-width half maximum (FWHM) of the diffraction peaks by using the Debye–Scherrer formula [50],

$$D = \frac{0.89\lambda}{B\ \cos\theta} \tag{1}$$

where λ is the X-ray wavelength, 0.89 is the shape factor, D is the average diameter of the crystals, θ is the diffraction angle of the peak and B is the line broadening of the FWHM. The crystallite diameter of the Ni_3Se_2 nanoparticles determined from the Debye–Scherrer formula from the major peak centered at 20.29° was estimated to be about 7.6 nm. The diameter estimated from the XRD result is slightly bigger than the diameter measured from the TEM micrograph (5.77 nm) due to the agglomeration of Ni_3Se_2 during drying of the XRD sample at 50 °C for 24 h.

Fig. 4 shows the UV–visible spectra of the synthesized Ni_3Se_2 nanoparticles prepared by γ-ray assisted method. Samples show the absorption spectrum with an absorption edge near 600 nm. As the concentration of chitosan increased from 0.5 wt% to 1.5 wt%, the absorption edge shifted to lower wavelength which is typical blue shift. This shows that the particles size of the Ni_3Se_2 is smaller when the chitosan concentration increased. These observations are consistent with the result from TEM.

The optical absorption data of the spectra have been analyzed from the following equation in order to determine the optical band gap of the Ni_3Se_2 nanocrystals [51].

$$\alpha h\nu = k(h\nu - E_g)^{n/2} \tag{2}$$

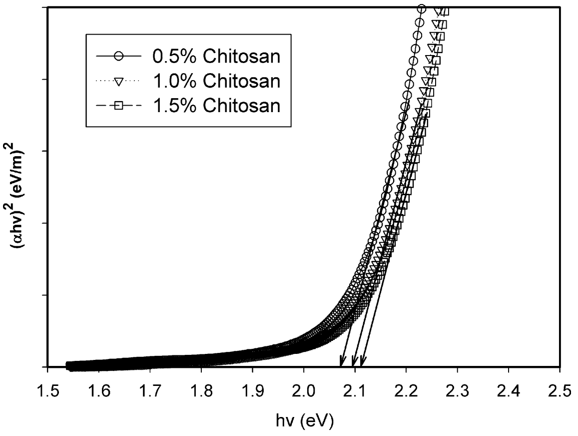

Fig. 5. The curve of $(\alpha h\nu)^2$ against $h\nu$ for the Ni_3Se_2 nanoparticles.

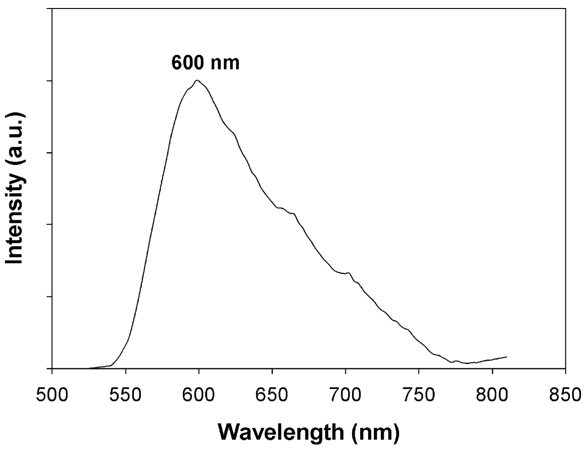

Fig. 6. Photoluminescence spectra for Ni_3Se_2 nanoparticles synthesized under γ-ray irradiation absorbed dose of 18 kGy (1.0 wt% chitosan, nickel acetate and selenium dioxide concentration of 0.08 M).

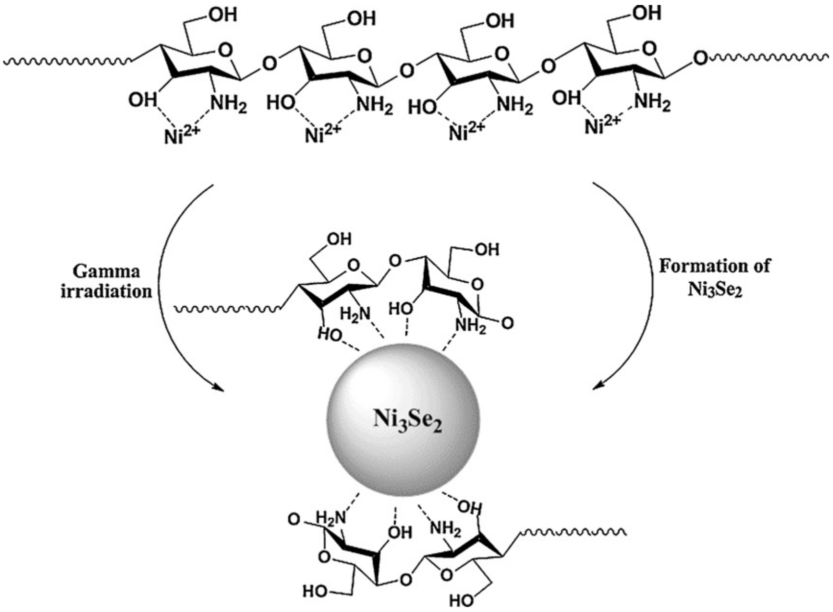

Fig. 7. Schematic capping and stabilizing mechanisms by chitosan in the synthesis of Ni_3Se_2 nanoparticles.

where α is the absorption coefficient, ν is frequency, h is Planck's constant, E_g is the gap energy of the nanoparticles and k equals a constant while n carries the value of either 1 or 4.

The value of absorption coefficient can be calculated by the following equation [52]:

$$\alpha = \frac{1}{t}\frac{-\log I_t/I_o}{\log e} = \frac{1}{t}\frac{A}{\log e} \tag{3}$$

in which t is the thickness of the quartz cell, I_t and I_o are the intensities of transmitted and incident lights, respectively, and A is the absorbance of the samples in UV–visible measurements. If a straight line is obtained for $n = 1$, it indicates a direct electron transition between states of semiconductor, whereas the transition is indirect if a straight line graph is obtained for $n = 4$. The curves of $(\alpha h\nu)^{2/n}$ against $h\nu$ are shown in Fig. 5. It is observed that the plot is linear when the $n = 1$, indicating direct electron transition. The band gap energy of Ni_3Se_2 is estimated from the extrapolation of the curve to the energy axis for zero absorption coefficients. The optical band energies for Ni_3Se_2 produced with 0.5 wt% of chitosan, 1.0 wt% of chitosan and 1.5 wt% of chitosan were 2.07 eV, 2.09 eV and 2.12 eV, respectively. The band gap energy estimated are consistent with value estimated from literature [30].

Fig. 6 shows photoluminescence spectra of Ni_3Se_2 nanoparticles dispersed in aqueous solution. The spectrum shows the emission spectrum with photoluminescence excitation at 260 nm in the range of 550–810 nm and scan rate is set at 50 nm/min. The photoluminescence spectrum has a peak at 600 nm which is an orange emission. The estimated band gap energy from PL spectroscopy is in accordance with the value estimated from UV–visible results which is ~2 eV.

The method used in this work is natural polymer stabilized γ-irradiation route. When H_2O is irradiated by γ-radiation, H_2O decomposes as follows [53]:

$$H_2O \xrightarrow{h\nu} e_{aq}^-, {}^{\bullet}H, {}^{\bullet}OH, H_2, H_2O_2, H_3O^+ \tag{4}$$

In order to remove the very strongly oxidative $^{\bullet}OH$ free radicals produced from the above stoichiometry, hydroxyl free radical removal agent, in this work isopropanol was added.

$$(CH_3)_2CHOH + {}^{\bullet}OH \rightarrow (CH_3)_2CHO^{\bullet} + H_2O \tag{5}$$

The hydrated electron, e_{aq}^- and hydrogen free radical, $^{\bullet}H$ with reduction potentials of −2.77 V and −2.13 V, reduces SeO_2 with the following stoichiometries 6, 7 and 8 and the Se^{2+} ions formed are attracted to Ni^{2+} ions to form NiSe, stoichiometry (9):

$$SeO_2 + H_2O \rightarrow H^+ + HSeO_3{}^- \tag{6}$$

$$HSeO_3{}^- + 6e_{aq}^- + 2H_2O \rightarrow 5OH^- + Se^{2-} \tag{7}$$

$$HSeO_3{}^- + 6H^{\bullet} \rightarrow 3H_2O + H^+ + Se^{2-} \tag{8}$$

$$Ni^{2+} + Se^{2-} \rightarrow NiSe \tag{9}$$

The hydrated electron, e_{aq}^- also reacts with Ni^{2+} ions to form Ni which reacts with NiSe to form Ni_3Se_2 with the following stoichiometry:

$$Ni^{2+} + 2e_{aq}^- \rightarrow Ni \tag{10}$$

$$Ni + 2NiSe \rightarrow Ni_3Se_2 \tag{11}$$

Under γ-irradiation, chitosan is degraded into fragments to form shorter chain of chitosan fragments [49]. The Ni_3Se_2 nanoparticles formed were enveloped by these chitosan fragments due to their interactions with NH_2 and OH groups of the chitosan as shown in Fig. 7. These chitosan fragments coat around the Ni_3Se_2 formed in the solution resulted in the small dimension of the nanoparticles and high solubility in aqueous solution. Fig. 7 shows schematic for the capping and stabilizing mechanisms of the chitosan fragments.

4. Conclusion

In summary, nanocrystalline Ni_3Se_2 had been prepared through reaction between nickel acetate and selenium dioxide solution by γ-irradiation method using chitosan as stabilizing agent. Chitosan, a “green” natural polymer capping agent is very effective in controlling the size of the Ni_3Se_2 nanoparticles. TEM results show that Ni_3Se_2 nanoparticles have spherical morphology and have high degree of dispersion in aqueous solution. The particle diameter was influenced by the concentration of chitosan and γ-radiation absorbed dose. With varying concentrations of chitosan from 0.5 wt% to 1.5 wt%, nanoparticles with diameter in the range of 5.7–8.5 nm were obtained. With higher γ-ray irradiation absorbed dose, the size of the nanoparticles increased and the size distribution became broader. Ni_3Se_2 nanoparticles exhibited an absorption edge and emission peak at 600 nm which is an orange emitter. The γ-ray assisted chitosan stabilizing synthesis method can be used to synthesize other metal selenide nanoparticles.

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