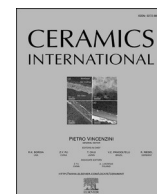




Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

X-ray diffraction (XRD) profile analysis and optical properties of Klockmannite copper selenide nanoparticles synthesized via microwave assisted technique

Ibrahim Garba Shitu^{a,*}, Kamil Kayode Katibi^{b,c}, Lawan Sani Taura^a, Aminu Muhammad^{a,d}, Idris Muhammad Chiromawa^a, Suleiman Bashir Adamu^{a,e}, Sani Garba Durumin Iya^a

^a Department of Physics, Faculty of Science, Sule Lamido University, Jigawa State, Kafin Hausa, 700271, Nigeria

^b Department of Biological and Agricultural Engineering, Faculty of Engineering, Universiti Putra Malaysia, Serdang, Selangor, 43400, Malaysia

^c Department of Agricultural and Biological Engineering, Faculty of Engineering and Technology, Kwara State University, Malete, 23431, Nigeria

^d Institute of Nano Optoelectronics Research and Technology (INOR), Universiti Sains Malaysia, Malaysia

^e Department of Physics, Faculty of Science, Universiti Putra Malaysia, 43400, Serdang, Selangor Darul Ehsan, Malaysia

ARTICLE INFO

Keywords:

CuSe Nanoparticles
Crystallite-size
Optical properties
Structural properties
Williamson-Hall
Halder-wagner

ABSTRACT

In this study, copper selenide (CuSe) nanoparticles (NPs) were prepared using the microwave irradiation technique. The effect of the irradiation time on the structural properties of CuSe NPs was investigated. The XRD results confirms the formation of the hexagonal (Klockmannite) structure of CuSe NPs. Different X-ray diffraction profile analysis techniques comprising strain-size plot (SSP), Scherer's method (S-M), Monshi-Scherer's method (MSM), Halder-Wagner (H-W) technique, and Williamson-Hall technique (WHM) were employed to examine the effect of irradiation time on the particle size as well as intrinsic strain of CuSe NPs using XRD peak broadening analysis. Uniform deformation model, uniform stress deformation model, as well as uniform energy density deformation model of Williamson-Hall technique were used to calculate the average crystallites size of CuSe NPs. Essential physical variables involving stress and energy density were also computed. Also, field emission scanning electron microscope (FESEM) in addition to atomic force microscopy (AFM) were further used to determine the mean particle size of CuSe NPs depending on varying irradiation time. The obtained results were found to be in agreement and comparable with the results of XRD profile analysis methods. Raman spectroscopy revealed three vibrational bands which are ascribed to the CuSe vibrational modes. Furthermore, the optical characteristics of the synthesized CuSe NPs were also investigated. The result obtained revealed a decrease in the optical bandgap from 2.43 to 2.71 eV with increase in irradiation time. Photoluminescence study revealed two peaks at 530, and 610 nm respectively. Therefore, it can be deduced that inclusion of intrinsic strain play an important role on the estimation of CuSe NPs size and microstrain of CuSe NPs synthesized via microwave assisted synthesis technique.

1. Introduction

Semiconductor nanomaterials have received a lot of attention in the field of nanotechnology owing to their unique properties and possible applications in things like transistors, light emitters, optical devices, solar cells, and optoelectronics [1–3]. These nanoparticles have distinct electronic and optical properties and have been extensively researched for a variety of applications. Copper selenide nanoparticle has sparked

considerable interest among semiconductor nanoparticles due to its unique electronic and optical properties. Being a p-type semiconductor with a bandgap ranging from 1.2 to 2.4 eV [4]. CuSe NPs can be synthesized through various techniques such as solvothermal [3–5], hydrothermal [5,6], chemical deposition [7,8], gamma irradiation [9], sol-gel [10], solid-state [9,10], etc. However, most of these synthesis techniques are quite expensive, complex, and require a high temperature to provide the necessary energy for their synthesis to be completed.

* Corresponding author. Department of Physics, Faculty of Natural and Applied Sciences, Sule Lamido University, Kafin-Hausa, Jigawa State, Nigeria.

E-mail addresses: ibrahim.garbashitu@slu.edu.ng (I.G. Shitu), kamil.katibi@kwasu.edu.ng (K.K. Katibi), lstaure@yahoo.com (L.S. Taura), aminumuhammad1427@gmail.com (A. Muhammad), idrismc@yahoo.com (I.M. Chiromawa), sulbash@gmail.com (S.B. Adamu), d.iya4real@yahoo.com (S.G. Durumin Iya).

<https://doi.org/10.1016/j.ceramint.2022.12.086>

Received 24 September 2022; Received in revised form 26 November 2022; Accepted 11 December 2022

Available online 16 December 2022

0272-8842/© 2022 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

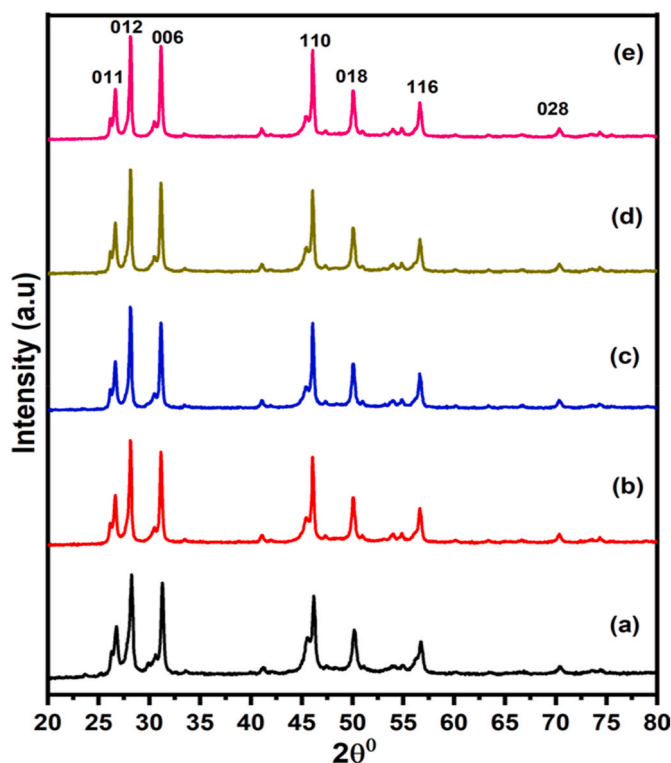


Fig. 1. X-ray diffraction patterns of prepared CuSe NPs at varying irradiation time: (a) 10 min (b) 15 min (c) 20 min (d) 25 min (e) 30 min.

Microwave-assisted synthesis is regarded as an alternative to the aforementioned challenges due to its numerous advantages over the remaining synthesis methods, including low cost, shorter processing time, higher yield, high purity, and small particle size distribution, etc. It also has a high degree of control over the morphology as well as particle size of the final products [10,11].

Numerous techniques for estimating the crystallite nature of semiconductor nanomaterials have been reported. These methods include field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM), transmission electron microscopy (TEM), and the well-known XRD profiling based on Scherer's technique to compute the crystallite size distribution of semiconductor nanomaterials [12]. Most studies nowadays employ the famous Debye-Scherrer's formula to determine the mean crystallite size by considering the most intense peaks of the XRD spectra without taking into consideration the remaining peaks and the intrinsic strain impact on the broadening of the XRD peaks. Generally, the broadening of the XRD peaks is the combined effect of intrinsic lattice strain associated with the NPs due to the crystal imperfection and smaller crystallite size. The broadening of the XRD peaks as a result of the lattice strain might be attributed to grain boundaries, dislocation densities, point defects, stacking faults, and contact or sinter stress. The synergistic effect of the lattice strain and the crystallite size in the XRD peaks is owing to the peak width, peak intensity, peak intensity, and the peak position (2θ). The crystallite size together with the lattice strain of many semiconductor nanomaterials have been analysed using X-ray diffraction peak broadening analysis. Various techniques including Scherer's method [13], Monshi-Scherer's method (modified Scherer's method) [14], Halder-Wagner method [15], Williamson-Hall method [16], have been used for the computation of average crystallites size together with intrinsic strain of semiconductor nanomaterials. An X-ray diffraction peak profiling is identified to be a simple and effective approach to compute the crystallite size as well as lattice strain of nanomaterials. Thus, the size of the nanoparticles and the value of the lattice strain can be estimated from the XRD peak profile analysis, including additional elastic features such as energy density and

stress, which are closely associated with lattice strain [17].

In this work, X-ray diffraction peak profile analysis was conducted on CuSe NPs produced using microwave-assisted synthesis method at different irradiation time. Different methods of peak profiling approaches were used to investigate the average crystallite size and lattice strain of CuSe NPs. Besides the atomic force microscopy, the emission scanning electron microscope were also used to determine the particle sizes and morphological properties. The mean particle sizes obtained from these techniques are found to be comparable with those obtained using X-ray diffraction peak profile analysis. Moreover, the optical properties of CuSe NPs for different irradiation times was also investigated.

2. Materials and method

2.1. Materials

As starting materials used in this research are sodium selenide (Na_2SeO_3 , purity $\geq 99\%$ Sigma Aldrich) and copper (II) chloride 2-hydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, Purity $\geq 99\%$ HmBG chemicals) salts. Besides them, hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, Purity $\geq 80\%$ Sigma Aldrich) salt was also used. Deionized water was applied as solvent. All chemicals were used with no purification and are of analytical grade.

2.2. Method

CuSe NPs was synthesized using microwave-assisted synthesis approach. Firstly, 0.3069g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.3457g of Na_2SeO_3 with 3 ml Of hydrazine hydride ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) were dissolved in two different beakers containing 50 ml of deionized water under constant stirring at 500 rpm for a period of 10 min. After that, the solutions were then mixed and further stirred constantly for additional 5 min to attain a uniform mixture. The solution was later irradiated at the microwave power of 380 W for 10 min of irradiation time using microwave oven (Electrolux Microwave Oven ELE-EMM 2001S, 700W), and black precipitate was obtained. The resultant precipitate was ultrasonicated for a period of 5 min, and then centrifuged at 280 rpm employing deionized water, followed by ethanol for five times. The final product was oven-dried at 60°C overnight. This procedure was repeated for 15, 20, 25, and 30 min of irradiation time to investigate the effect of the irradiation time on the final on the particle size and microstrain of the final product.

2.3. Characterization

Powder X-ray diffraction (PXRD) patterns were characterized using an X-ray diffractometer (X'pert Pro, Panalytical) $\text{CuK}\alpha$ radiation ($\lambda = 0.154187 \text{ nm}$) measured (20° to 80°) range of 2θ angle. X'pert High-Score Plus software was used to analysed the XRD patterns obtained. Alpha 300R Laser Raman Spectrometer and were used to further characterized all the samples obtained. The surface morphology of the samples were analysed via Bruker dimension edge atomic force microscopy (AFM) using ScanAsyst peak force tapping mode. FEI Nova SEM230 was also utilized to analysed morphology of the prepared samples operating at 10.0 kV accelerating voltage with 5.2 nm working distance. A spectrophotometer (Shimadzu-UV3600) and fluoromax3 spectrophotometer were used to examine the samples' optical and photoluminescence properties of the all the samples obtained.

3. Results and discussion

3.1. Reaction mechanism

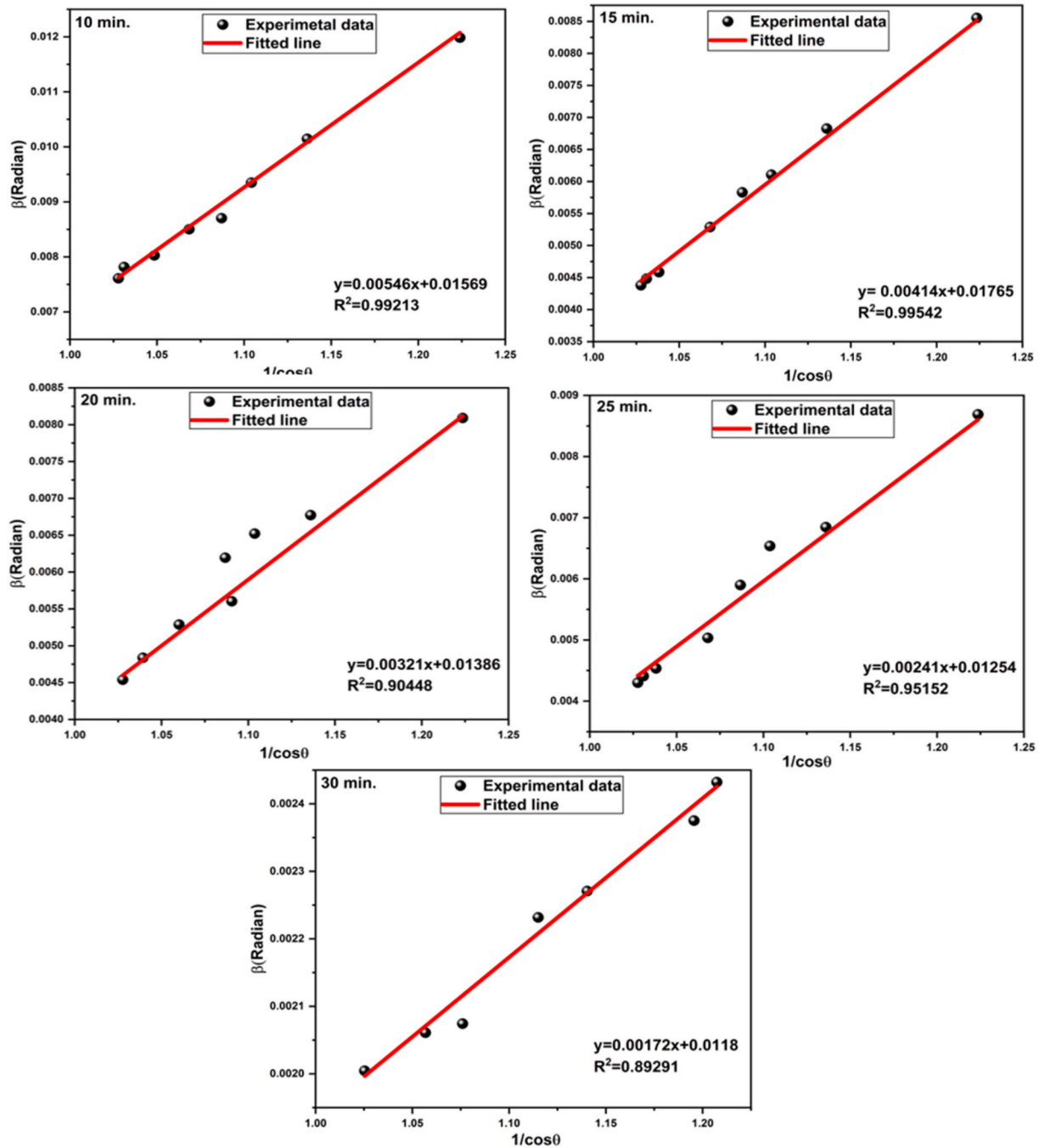
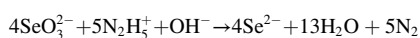
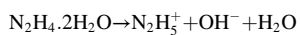
The mechanism for the reaction to produce the CuSe NPs is described below [18]:



Table 1

Characteristics of CuSe NPs synthesized at varying irradiation time.

Sample Designation	Crystallite Size (nm)	Dislocation Density (δ) $\times 10^{-3}$ (nm) ⁻²	Volume of NP (V) (nm ³)	Unit Cell Volume (n) (nm ³)	Bond Length (L) (nm)	Young Modulus (GPa)
10 min.	26.52	2.40	10.95	47.09	0.190	37.90
15 min.	34.64	2.31	11.21	48.21	0.190	26.60
20 min.	45.10	2.10	12.00	51.70	0.190	21.45
25 min.	60.08	1.90	12.73	54.78	0.190	31.10
30 min.	84.17	1.12	17.92	77.11	0.190	34.20

**Fig. 2.** Scherer's method Plots of CuSe NPs synthesized at varying irradiation time.

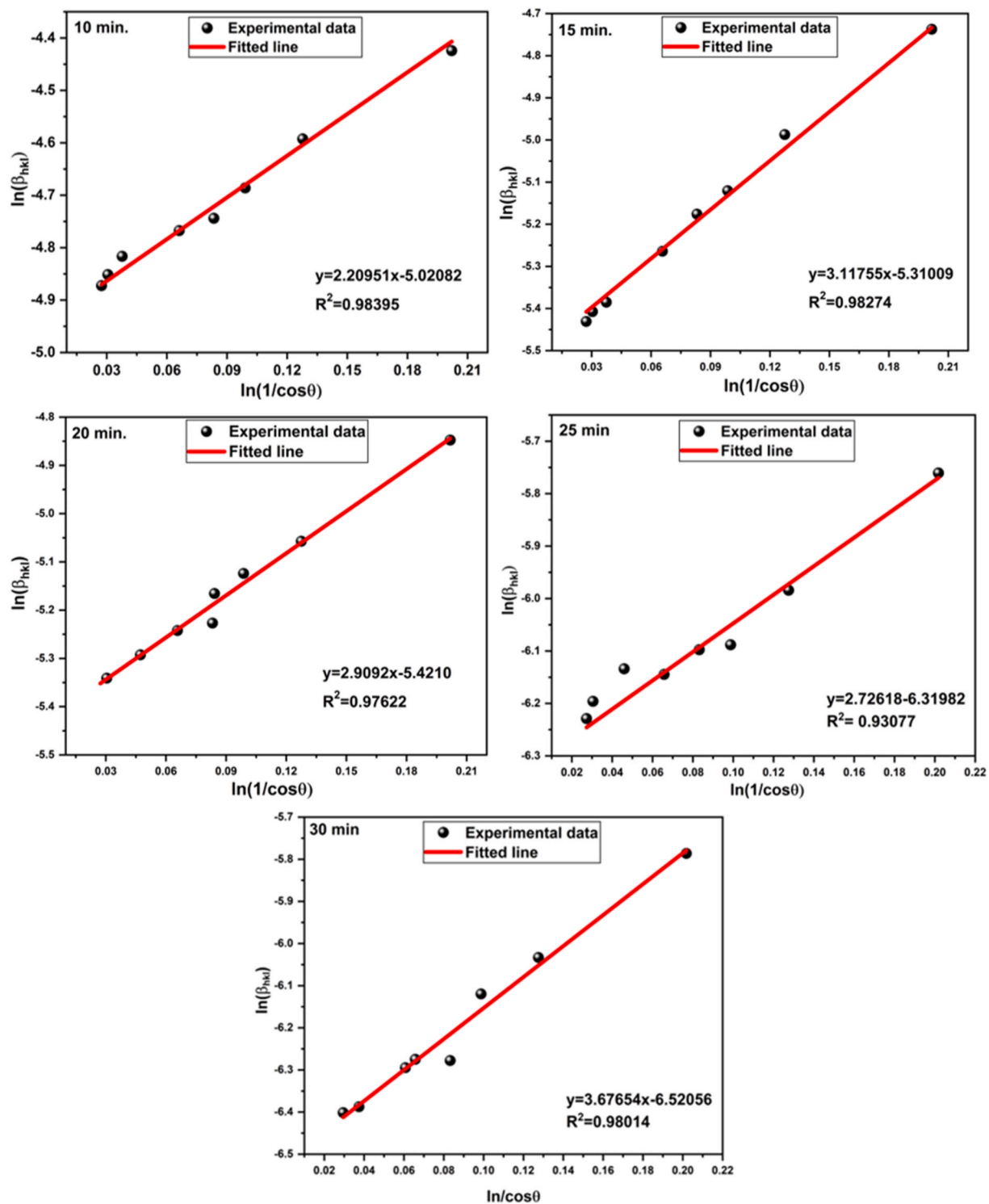


Fig. 3. Monshi-Scherer's Plots of CuSe NPs prepared at varying irradiation time.

SeO_3^{2-} ion was obtained when sodium selenide was added to de-ionised water and was reduced to Se^{2-} ion in the presence of hydrazine hydrate. The Se^{2-} ion will then react with Cu^{2+} ion to form the final product of CuSe NPs.

3.2. Analysis of phase and diffraction pattern of CuSe NPs

Fig. 1 illustrates the X-ray diffraction patterns of copper selenide (CuSe) NPs at varying irradiation time using microwave-assisted

synthesis technique. All the XRD patterns exhibits a crystalline structure of a single-phase CuSe NPs with diffraction peaks at 2θ values of 26.75° , 28.20° , 31.50° , 45.47° , 50.25° , 56.85° , 71.20° corresponding to (011), (012), (006), (110), (018), (116) and (028) the reflection planes. These hkl reflection planes are found to be fitting with the hexagonal (Klockmannite) structure of CuSe, which corresponds to ICSD Data File: 98-004-5640.

Observably the full width at half the maximum (FWHM) decreases with the increase in irradiation time based on the XRD patterns (Fig. 1).

Table 2

Estimated crystallites sizes of CuSe NPs obtained from SM, MSM, H-W, and SSP methods.

Sample Designation	Scherer's Method (SM)		Monshi-Scherer Method (MSM)		Halder-Wagner Method (H-W)		Size-Strain Plot Method (SSP)	
	Size (D) (nm)	Strain (ϵ) $\times 10^{-3}$	Size (D) (nm)	Strain (ϵ) $\times 10^{-3}$	Size (D) (nm)	Strain (ϵ) $\times 10^{-3}$	Size (D) (nm)	Strain (ϵ) $\times 10^{-3}$
10 min.	26.52	1.57	21.94	5.02	21.59	7.30	20.02	1.10
15 min.	34.64	1.77	29.30	5.31	32.01	1.50	34.89	1.10
20 min.	45.10	1.39	32.74	5.42	33.48	1.40	36.38	8.46
25 min.	60.08	1.25	80.42	6.31	73.86	1.40	74.25	1.32
30 min.	84.17	1.18	96.83	6.52	99.80	1.30	100.54	8.31

The FWHM is strongly correspond to the size of the crystallite sample. The narrower the FWHM of the XRD peak, the bigger the size of the crystallite and vice versa. The increase in the sharpness and narrowing of the XRD peaks with a rise in irradiation time is characterized by an enhancement in the crystallinity and the crystallite size of as-synthesized CuSe NPs.

3.3. Sherrer's method

The XRD peak broadening occurs due to three main factors, namely: crystallite size, lattice strain, and instrumental effects [19]. The broadening due to instrumental effects is normally removed from the experimental data using a standard material (silicon). The equation relating to the XRD peak broadening as well as the crystallite size has been derived by Scherrer and is given as [19–21].

$$D = \frac{K\lambda}{\beta_{hkl} \cos \theta} \quad (6)$$

Thus λ depicts the X-ray wavelength of the Cu-K α radiation (1.54187 Å), k represent the shape factor (0.94), θ is the diffraction angle while β_{hkl} denote the peak width at half highest (FWHM) [22,23]. The mean crystallite size can be calculated using the well-known Scherrer's equation (6). The mean crystallite sizes of the CuSe NPs were computed to be 19.20, 28.40, 30.30, 73.10, 102.40 nm according to the applied irradiation of time 10, 15, 20, 25, and 30 min, respectively. Moreover, the crystallite size (D) can be used to calculate the vacancies and the proportion of defects in the NPs (dislocation density) using equation (7):

$$S = \frac{1}{D^2} \quad (7)$$

Table 1 lists the dislocation density (S) values for the samples of CuSe NPs synthesized at various reaction time. As presented in Table 1, the S values vary as the reaction time changes, indicating that the lattice defect increased as particle size decreased. Moreover, the volume of the NPs, the quantity of unit cells detected in the particle as well as the volume of the unit cell, can be computed using XRD data analysis. The volume of nanoparticles can be determined using equation (8) [24]:

$$V = \left(\frac{4}{3}\right)\pi\left(D/2\right)^3 \quad (8)$$

where D is the mean crystallite size of CuSe NPs, V is the volume of nanoparticles.

Also, CuSe unit cell volume (hexagonal) can be determined from the relation $v = 3a^2c/2$. The number of unit cells contained in the CuSe NPs can be calculated from the proportion V/v using equation (9) [25]:

$$n = 1.621 \left(D^3/a^2c\right) \quad (9)$$

where D denote the mean crystallite size, a as well as c represent the lattice parameters of the as-synthesized CuSe NPs. Table 1 shows the number of unit cells in a particle for CuSe NPs samples synthesized at various irradiation time. The bond length describe a typical separation between the nuclei of fused atoms in a molecule. Bond dissociation energy and bond strength both have an inverse relationship with bond

length [26]. The bond lengths in the solid phase are measured using XRD. The Cu–Se bond length (L) was estimated using equation (10) [27]:

$$L = \sqrt{\frac{a^2}{3} + \left(\frac{1}{2} - u\right)^2 c^2} \quad (10)$$

where a is a lattice parameter and u is representing the positional variable in the hexagonal structure in addition to representing the distance between each atom and the one before it lies along the 'c' axis. In this case, "u" is described by the following equation (11):

$$u = \frac{a^2}{3c^2} + 0.25 \quad (11)$$

The mean crystallite size (D) of CuSe NPs can be determined using Sherrer's plots method. Now, by plotting the Scherrer plot, which is a graph of β_{hkl} against $1/\cos \theta$ for CuSe NPs, the average crystallite size was estimated from the slope of the graph as depicted in Fig. 2. The average estimated crystallite sizes 26.52, 34.64, 45.10, 60.08, and 84.17 nm of the NPs obtained applying 10, 15, 20, 25, and 30 min respectively are given in Table 1. The average crystallite is noticed to increase with the increase in irradiation period. The growing in crystallite size with the increasing in irradiation time is attributed to the Ostwald refining process whereby smaller crystallites combine and contributes to the evolution of larger ones with the increase in irradiation time [28]. Additionally, the relationship between the crystallite size and irradiation time may also be ascribed to the stable growth and nucleation of CuSe NPs at longer irradiation time [29].

3.4. Modified Scherrer's method (Monshi-Sherrer's method)

Monshi and his co-workers in 2012 introduced some adjustments to the use of the well-known Scherrer's formula for computing crystallite size as well as lattice strain of nanostructures. Sherrer's formula systematically shows an increase in the crystallite size when the distance of the diffracted planes values (d) decreases while 2θ values rise as well. This phenomenon occurred because $\beta \cos \theta$ cannot be kept constant [30]. More so, Monshi-Sherrer's equation (modified Sherrer's formula) has the merit of reducing the errors to obtain better and accurate results of the crystallites size as well as lattice strain from the XRD diffraction planes. The modified Sherrer's formula is given in equation (7) [31]:

$$\ln \beta = \ln \left(\frac{K\lambda}{D}\right) + \ln \left(\frac{1}{\cos \theta}\right) \quad (12)$$

Therefore, plotting a graph of $\ln \beta$ (β in radian) on the y-axis along with $\ln \left(\frac{1}{\cos \theta}\right)$ on the x-axis gives a linear plot for all the selected peaks of the XRD pattern. After establishing the fitted linear plots, the crystallite size (D) can be determined from the intercept of the graph. The plots of the modified Scherrer's method of CuSe nanoparticle synthesized at different irradiation times together with their respective equation of the linear least square approach found from the linear regression data plots given in Fig. 3. According to the modified Sherrer's method, for calculating the crystallite size (D) of CuSe nanoparticle, equation (13) is simply employed.

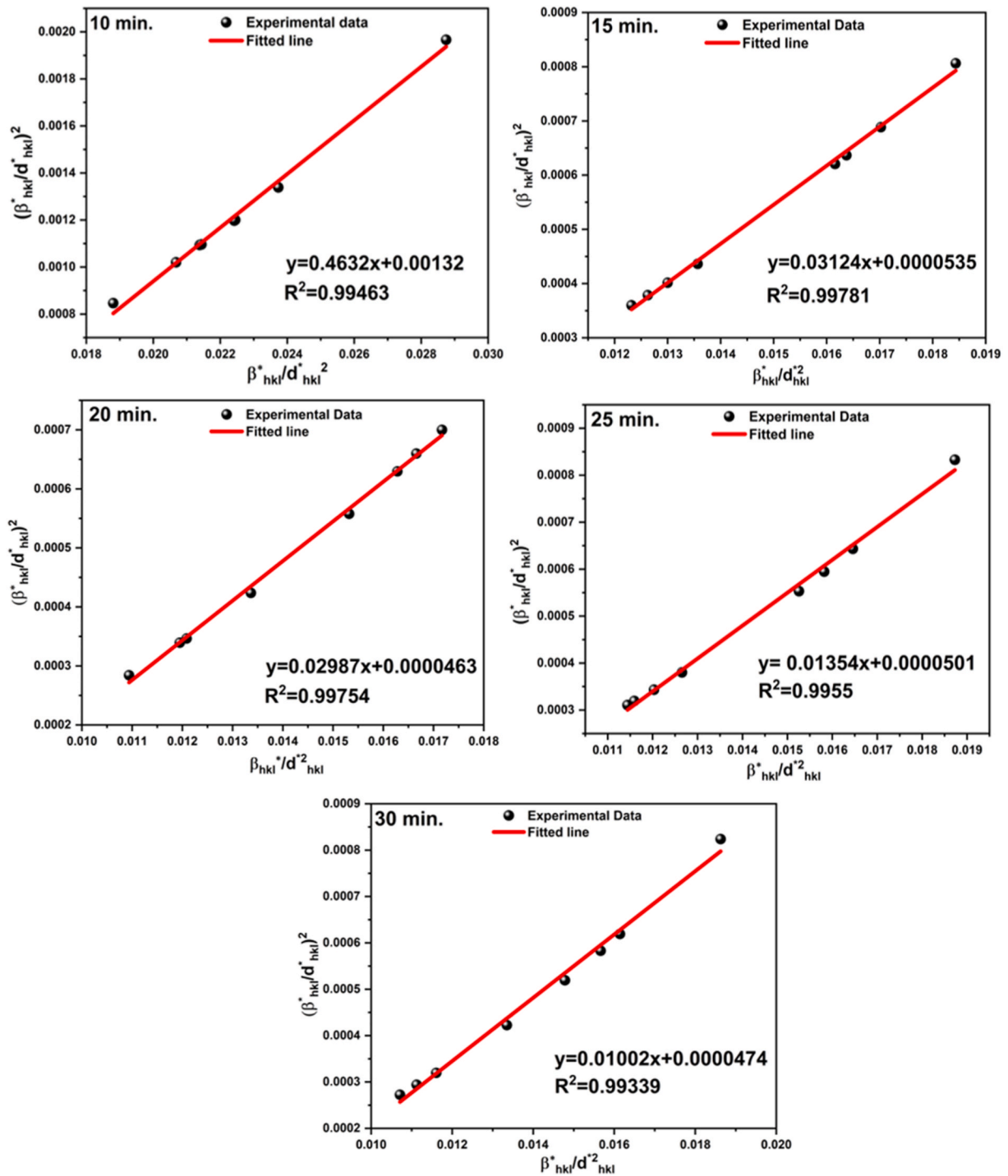


Fig. 4. Halder-Wagner Plots of CuSe NPs synthesized at varying irradiation time.

$$\frac{K\lambda}{D} = e^{(\text{intercept})} \quad (13)$$

Therefore, the estimated microstructural properties of CuSe NPs prepared applying different irradiation times are summarized in Table 2. The crystallites size of CuSe NPs prepared at varying irradiation time were computed as 21.94, 29.30, 32.74, 80.42, and 96.83 nm corresponding to 10, 15, 20, 25, as well as 30 min of irradiation time. Therefore, the obtained average crystallite size results employing modified Scherer's method suits well with crystallite size obtained based on both Scherer's formula and Scherer's plots method. Hence, it can be suggested that, Monshi-Scherer method is suitable for estimating the

crystallites size of CuSe NPs prepared at varying irradiation period using microwave assisted technique.

3.5. Halder-Wagner method (H-W)

In the strain-size plot technique, the XRD diffraction peak broadening owing to the size is presumed as a Lorentzian function, while the broadening caused by strain is assumed as a Gaussian function. But the XRD peak is neither Gaussian nor Lorentzian function, As the XRD pattern suit well with the Gaussian function, without matching, its tail falls off too speedily, and the tails of the XRD peaks profile suit well with

Table 3

Estimated crystallite size of CuSe NPs using Williamson-Hall models.

Sample Designation	Scherer's Method		Williamson-Hall Models							
			UDM Model		UDSM Model			UDEM Model		
	Size (D) (nm)	Strain (ϵ) $\times$ 10^{-3}	Size (D) (nm)	Strain (ϵ) $\times$ 10^{-3}	Size (D) (nm)	Strain (ϵ) $\times$ 10^{-3}	Stress (σ) (MPa)	Size (D) (nm)	Stress (σ) (MPa)	Energy Density (u) (kJm ⁻³)
10 min.	26.52	1.57	22.98	3.20	18.92	0.22	95.48	21.74	377.66	69.52
15 min.	34.64	1.77	31.40	7.30	34.47	0.23	88.40	29.66	138.48	93.48
20 min.	45.10	1.39	33.82	1.2	35.83	0.02	10.82	29.30	64.51	20.29
25 min.	60.08	1.25	72.02	1.86	67.33	1.80	11.48	74.24	16.35	13.03
30 min.	84.17	1.18	99.83	1.55	99.83	1.82	11.32	116.74	43.33	91.52

the Lorentzian function well on the side, Which does not suit with the XRD peak region [32]. However, the Halder-Wagner method is used to overcome these difficulties. This method work on the assumption that the broadening of XRD peaks is symmetrically the Voigt function, since the Voigt function combines both Gaussian as well as Lorentzian functions [33]. Thus, the overall width at half the highest of the physical profile can be described as per the Halder-Wagner technique for the Voigt function as indicated in equation (14):

$$\beta_{hkl}^2 = \beta_L \beta_{hkl} + \beta_G^2 \quad (14)$$

where β_L and β_G are the FWHM of the Gaussian as well as Lorentzian function respectively. This technique exhibits the potential that it provides the peaks more weight both at the mid as well as low angle range, where the diffracting peaks shows much less overlap. The computation together with the values of the lattice distance, (d_{hkl}), between (hkl) planes is an important step in this method. Therefore, according to the Halder-Wagner technique, the relation between the crystallite sizes along with the lattice strain is given by the formula in equation (15):

$$\left(\frac{\beta_{hkl}^*}{d_{hkl}}\right)^2 = \frac{1}{D} \frac{\beta_{hkl}^*}{d_{hkl}^2} + \left(\frac{\epsilon}{2}\right)^2 \quad (15)$$

where $\beta_{hkl}^* = \beta_{hkl} \cos \theta$ and $d_{hkl}^* = 2d_{hkl} \sin \theta$.

By plotting a graph of $\left(\frac{\beta_{hkl}^*}{d_{hkl}}\right)^2$ being the Y-axis while $\frac{\beta_{hkl}^*}{d_{hkl}^2}$ represent X-axis for all the XRD pattern, a linear plot will be obtained. Fig. 4 shows the Halder-Wagner plots together with the linear least square equations found from the plotted linear regression. Also, the mean crystallite size was computed from the slope of the plotted straight line, whereas the intrinsic strain of CuSe nanoparticle is obtained from the intercept value. From the plot, the mean particle size as well as microstrain of CuSe NPs prepared at varying irradiation period of 10, 15, 20, 25, and 30 min are computed as 21.59, 32.01, 33.48, 73.86, and 99.80 nm, and 7.3×10^{-3} , 1.5×10^{-3} , 1.4×10^{-3} , 1.4×10^{-3} , and 1.3×10^{-3} , respectively. The average crystallite size together with the microstrain attained using the Halder-Wagner approach are in tandem with the model obtained from Scherrer's technique, and Monshi-Scherer's method. Table 3 gives the microstructural parameters of all the samples.

3.6. Strain-size plot (SSP) technique

The broadening of peaks is considered by the Williamson-Hall technique based on the diffraction angle (2θ), which is presumed to be an overall impact of the expansion arises from the smaller crystallite size along with intrinsic strain of the nanocrystal [34]. But in some models, they only give out with the peak profile analysis. One such method is the Strain-size plot (SSP) which considers the XRD peak profile as the amalgamation of both Gaussian as well as Lorentzian function, where the size induced XRD peak broadening is considered as a Lorentzian function while the strain-stimulated broadening is regarded as the Gaussian function. Therefore, the overall peak broadening in the strain-size plot method (SSP) can be related in equation (16) [35]:

$$\beta_{hkl} = \beta_L + \beta_G \quad (16)$$

where β_G and β_L are Lorentzian and Gaussian Peak broadening, respectively. Moreover, the SSP technique always gives a superior output for an isotropic enlargement, as it offers greater relevance to low angle reflections, where there is better accuracy compared with higher angles. This is due to lower quality of the XRD data at higher angles as well as peaks are usually greatly overlapped at greater diffraction angles [36]. Therefore, the SSP computation was done using equation (17) as follows:

$$(d_{hkl} \beta_{hkl} \cos \theta)^2 = \frac{K\lambda}{D} (d_{hkl}^2 \beta_{hkl} \cos \theta) + \frac{\epsilon^2}{4} \quad (17)$$

where d_{hkl} represent lattice separation between the lattice plane (hkl) of the hexagonal crystal structure. The lattice separation between the diffraction planes (hkl) can be calculated using the equation express as:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \left(\frac{l^2}{c^2} \right) \quad (18)$$

$$d_{hkl}^2 = \left(\frac{a^2}{h^2 + k^2 + l^2} \right) \quad (19)$$

Therefore, Fig. 5 revealed a plot of $(d_{hkl} \beta_{hkl} \cos \theta)^2$ on y-axis while $(d_{hkl}^2 \beta_{hkl} \cos \theta)$ on the x-axis. Using the intercept as well as the slope from the linearly fitted data, the mean crystallite size as well as the intrinsic strain of CuSe NPs is obtained. As shown in Table 2, the estimated crystallite size and microstrain corresponding to 10, 15, 20, 25, and 30 min irradiation time were found to be 20.02, 34.89, 36.38, 74.25, and 100.54 nm, and 1.10×10^{-3} , 1.10×10^{-3} , 8.46×10^{-3} , 1.32×10^{-3} , and 8.31×10^{-3} , respectively.

3.7. Williamson-Hall method

Sherrer's formula only takes into account the impact of crystallite size on the expansion of XRD peak nevertheless does not take into consideration the intrinsic strain closely related to the microstructure of the crystal, which is created by the point defect, triple junction, grain boundary, together with the stacking faults in the nanocrystals [37]. There are several techniques, including the Williamson Hall technique, the Warren-Averbach technique, etc., that consider the effect of the XRD peak broadening induced by the strain likewise can be used to compute the intrinsic strain together with the crystallite size of a crystal structure [38]. Williamson-Hall method has proven to be one of the simplest method among these methods. Physical line expansion of the XRD peak appears due to the combined effect of size in addition to intrinsic strain induce on the nanocrystals as well as the overall broadening can be express as:

$$\beta_{hkl} = (\beta_{size} + \beta_{strain}) \quad (20)$$

where β_{size} and β_{strain} are the XRD peak broadening (FWHM) because of the size as well as intrinsic strain of the nanocrystal. In this work, the

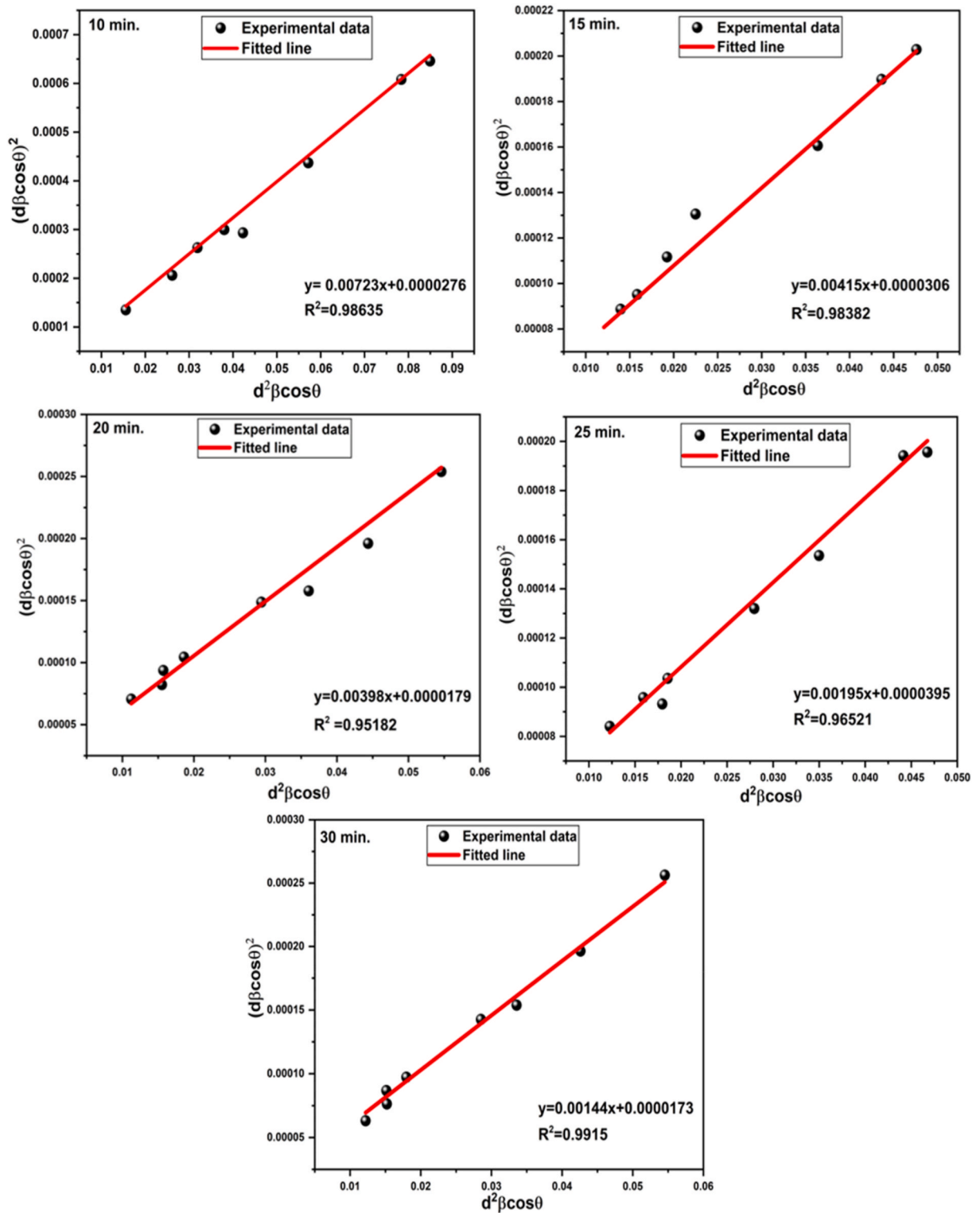


Fig. 5. Size-strain Plots (SSP) of CuSe NPs prepared at different irradiation time.

mean crystallite size as well as intrinsic strain was computed using different Williamson-Hall models such as USDM, UDM, as well as USDEM, which are utilized in detail in the subsequent sections.

3.7.1. Uniform deformation model (UDM)

In this model, uniform strain is considered in the crystallographic directions, which is associated with the nanocrystals owing to imperfections of the crystal. Besides, UDM considers the strain to be isotropic

[32]. This intrinsic strain impacts the line broadening of the XRD peaks and the broadening of peaks caused by the strain can be described as:

$$\beta_{\text{strain}} = 4\varepsilon \sin \theta \quad (21)$$

Therefore, the total peak broadening caused by strain as well as size in all the diffraction planes (hkl) of the XRD peaks is express:

$$\beta_{\text{hkl}} = (\beta_{\text{size}} - \beta_{\text{strain}}) \quad (22)$$

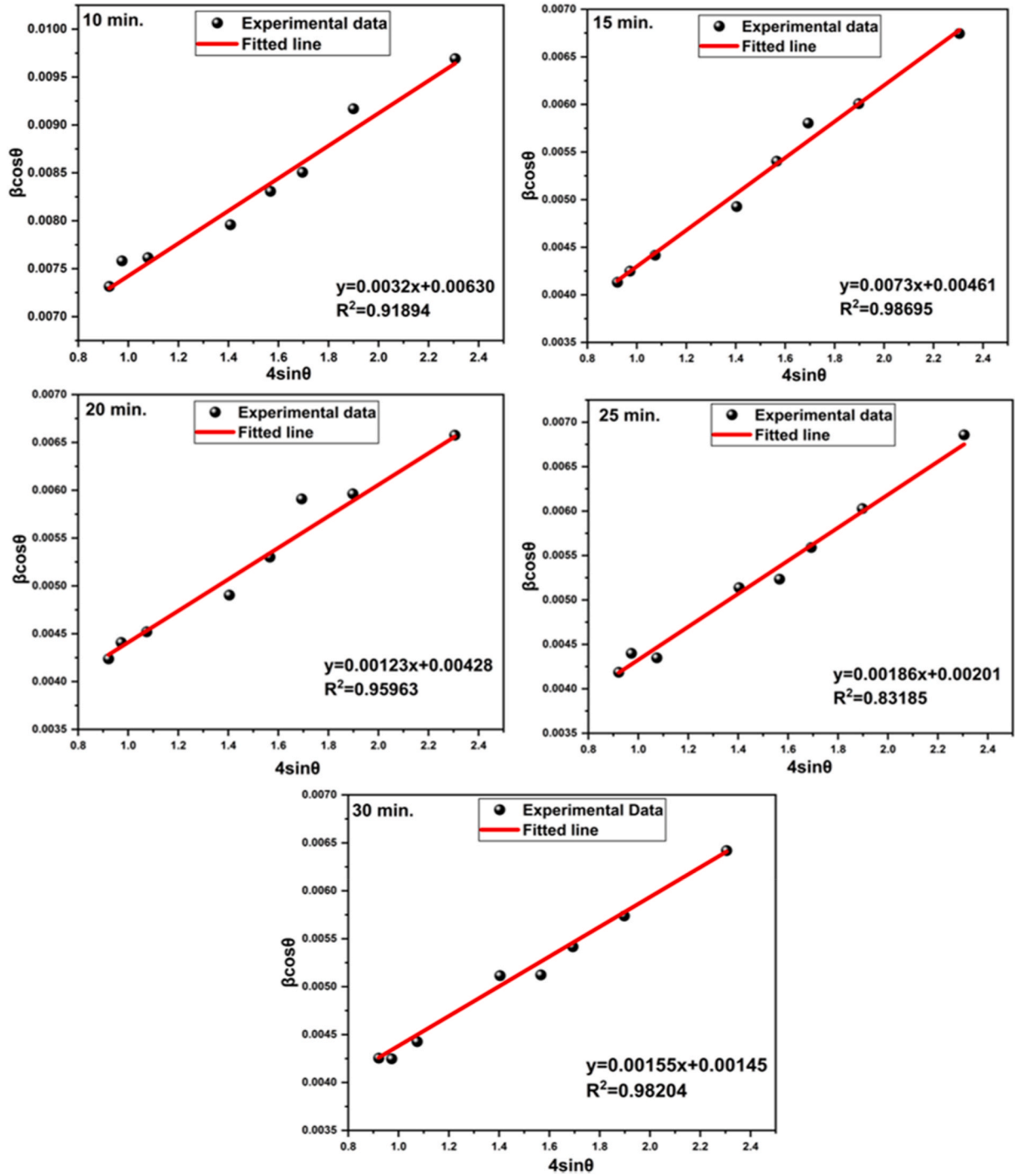


Fig. 6. UDM Plots of CuSe NPs prepared at varying irradiation time.

where β_{hkl} is the FWHM of the diffraction planes (hkl) of all or some selected peaks in the XRD spectra, $\beta_{size} = \frac{k\lambda}{D \cdot \cos \theta}$ and $\beta_{strain} = 4\epsilon \sin \theta$. Therefore, the formula for the uniform deformation model is express as:

$$\beta_{hkl} = \frac{k\lambda}{D \cdot \cos \theta} + 4\epsilon \sin \theta \quad (23)$$

Rearranging equation (13) yields:

$$\beta_{hkl} \cos \theta = \frac{k\lambda}{D} + 4\epsilon \sin \theta \quad (24)$$

Equation (24) is a straight-line equation which describes the even deformation model (UDM). Fig. 8 reveals the plots of equation (14) with

($4 \sin \theta$) along the x-axis together with ($\beta_{hkl} \cos \theta$) along the y-axis which corresponds to all major diffraction peaks of CuSe NPs. The slope and the intercept of the linearly fitted graph provides the intrinsic strain and the mean crystallite size of CuSe NPs prepared at varying irradiation periods. The existence of the lattice strain is principally caused by the enlargement or contraction of the lattices in nanocrystals is because of the size confinement effect, hence, the atomic composition is slightly altered when compared with its bulk counterpart. Moreover, several defects are also created in the lattice structure, owing to the size confinement, which also leads to the strain in the lattice. Fig. 6 shows the UDM plots of CuSe NPs synthesized at varying irradiation time.

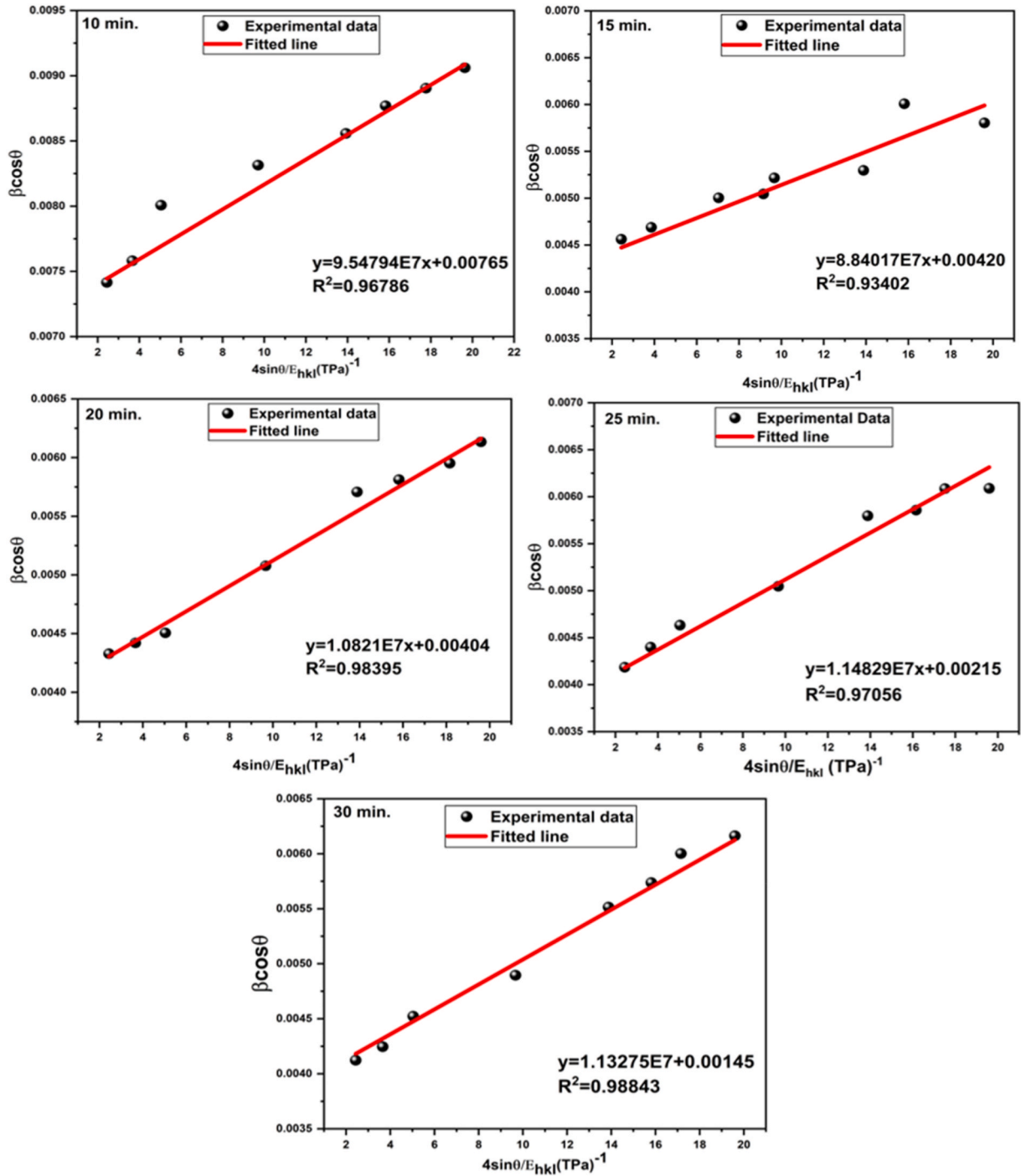


Fig. 7. USDM Plots of CuSe NPs prepared at varying irradiation time.

3.7.2. Uniform stress deformation model (USDM)

The USDM is also one of the Williamson-Hall models which is used for computing the crystallite size as well as microstrain of a crystal. In the UDM model, it is considered that the sample is uniform and isotropic, but in the USDM model, the crystal is considered to be anisotropic [24]. Thus, the Williamson-Hall equation is modified by introducing an anisotropic term. The adjusted model is regarded as the even stress deformation model (USDM), where the lattice stress deformation is considered homogenous in all the diffraction planes of the crystal lattices [39].

According to Hook's law, stress as well as strain are linearly proportional to each other, the linear proportionality relationship between

them is expressed as $\sigma = E_{hkl} \epsilon$, where σ represent the stress of the crystal, ϵ denote the anisotropic strain, while E signifies the Young modulus. It is a well-known fact that the stress is linearly relative to strain with constant of proportionality, E . The crystallites turn away from this linear proportionality by increasing the strain [40]. As a result, the Williamson-Hall equation can be altered by replacing the value of ϵ ($\epsilon = \frac{\sigma}{E_{hkl}}$) in Equation (19) above. The modified Williamson-Hall equation which takes into consideration uniform stress in all the lattice planes (hkl) can be express as:

$$\beta_{hkl} \cos \theta = \frac{k\lambda}{D} + 4\sigma \frac{\sin \theta}{E_{hkl}} \quad (25)$$

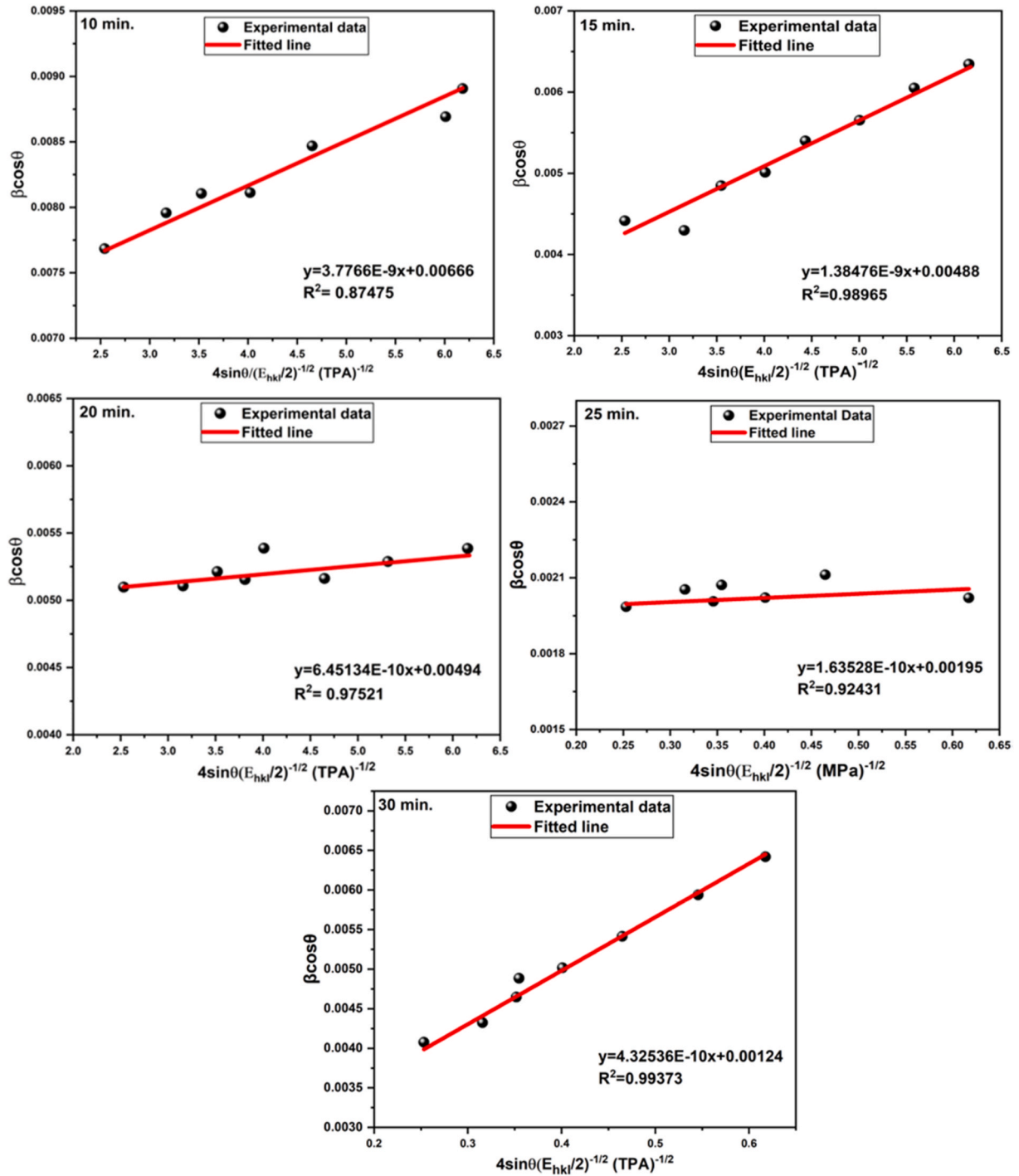


Fig. 8. UDED Plots of CuSe NPs prepared at different irradiation time.

Equation (25) is referred to as the even stress deformation model (USDM). Plotting a graph of $(\beta_{hkl} \cos \theta)$ as y-axis and $4 \frac{\sin \theta}{E_{hkl}}$ as x-axis, the uniform stress and the crystallite size (D) can be determined from the slope and intercept of the linearly fitted graph as demonstrated in Figure (6). More so, the intrinsic strain can also be determined from the value of the stress and the Young modulus (E_{hkl}) of CuSe NPs for all the crystallographic directions. For hexagonal structures, the Young modulus is determined from the following formula [32]:

$$E_{hkl} = \frac{\left[h^2 + \frac{(h+2k)^2}{3} + \left(\frac{a}{c} \right)^2 \right]^2}{S_{11} \left(h^2 + \frac{(h+2k)^2}{3} \right)^2 + S_{33} \left(\frac{a}{c} \right)^4 + (2S_{13} + S_{44}) \left(h^2 + \frac{(h+2k)^2}{3} \right) \left(\frac{a}{c} \right)^2} \quad (26)$$

where hkl, are indexes of the XRD planes, a and c are the lattice parameter of the hexagonal structure of CuSe NPs (these data can be obtained from phase file by X-pert HighScore software). S_{11} , S_{13} , S_{33} , as well as S_{44} are the elastic compliances of CuSe are obtained from the elastic stiffness constants C_{11} , C_{13} , C_{33} , as well as C_{44} and are express as follows [41]:

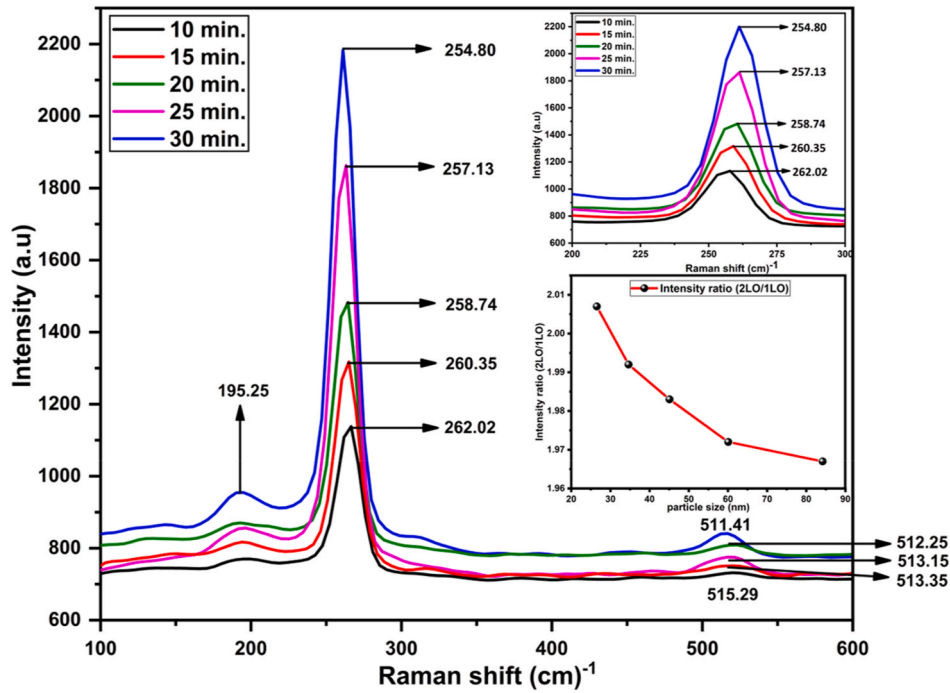


Fig. 9. Raman spectra of CuSe NPs synthesized at varying irradiation time.

Table 4

Raman vibrational band of CuSe NPs at varying irradiation time.

Sample designation	LO (cm ⁻¹)	2LO (cm ⁻¹)	FWHM (nm)	Intensity (1LO) (a. u)	Intensity (2LO) (a. u)	2LO/1LO (a. u)
10 min.	262.02	515.29	20.06	1128.67	730.25	0.65
15 min.	260.35	513.35	18.89	1303.26	757.64	0.58
20 min.	258.74	513.15	18.60	1475.08	779.47	0.53
25 min.	257.13	512.25	18.35	1854.45	801.30	0.43
30 min.	254.80	511.41	18.13	2187.16	842.16	0.39

$$S_{11} = \frac{1}{2} \left[\frac{C_{33}}{C_{33}(C_{11}+C_{12}) - 2(C_{13})^2} + \frac{1}{(C_{11}-C_{12})} \right] \quad (27)$$

$$S_{13} = \left[\frac{-C_{13}}{C_{33}(C_{11}+C_{12}) - 2(C_{13})^2} \right] \quad (28)$$

$$S_{33} = \left[\frac{C_{11}+C_{12}}{C_{33}(C_{11}+C_{12}) - 2(C_{13})^2} \right] \quad (29)$$

$$S_{44} = \frac{1}{C_{44}} \quad (30)$$

The values of the elastic stiffness constants C_{11} , C_{13} , C_{33} , as well as C_{44} are 109, 25, 117, and 14 GPa. The elastic compliance, S_{11} , S_{13} , S_{33} , as well as S_{44} are computed from elastic stiffness constant using equation 27–30 and their computed values are 20×10^{-12} , -2.1×10^{-12} , 9.0×10^{-12} , and $69.3 \times 10^{-12} \text{ m}^2\text{N}^{-1}$ respectively. In addition, using these compliances, the Young modulus for all the crystallographic directions (011), (012), (006), (110), (018), (116) and (028) are computed as 37.90, 26.60, 11.10, 10.10, 31.10, 8.64, 12.00, and 14.43 GPa respectively. The average value of the young modulus of CuSe has been further calculated using equation (16) to be ~ 19.00 GPa which is comparable with the Bulk Young modulus of CuSe (20.514 GPa)

Using equation (25), a plot of $(\beta_{hkl} \cos \theta)$ as the y-axis and $4 \frac{\sin \theta}{E_{hkl}}$ as x-axis which corresponds with the XRD peaks is demonstrated in Fig. 7.

From the slope as well as intercept of the straight-line graph, the stress as well as the mean crystallite size of CuSe NPs prepared at varying irradiation time could be obtained.

3.7.3. Uniform deformation energy density model (UEDM)

UEDM is also one of the Williamson-Hall models for evaluating the microstructural properties of a crystal. In the UDM model, it is presumed that the crystal is isotropic, whereas according to Hooke's law, linear proportionality between stress as well as strain is assumed for the USDM model [42]. However, in real crystals, the linear relationship between strain as well as stress and the isotropic nature of the crystals are not considered. This is due to the existence of dislocations, agglomerations, and defects that ultimately create imperfections in most of the crystals [43]. For this purpose, the Uniform Deformation Energy Density Model (UEDM) model was also utilized. This model take into consideration uniform anisotropic strain across all diffraction planes, as well as the density deformation energy is responsible for the uniform anisotropy of the strain [44]:

Therefore, the energy density in accordance with Hooke's law is related to strain as:

$$u = \epsilon^2 \frac{E_{hkl}}{2} \quad (31)$$

Also, we know that stress is linearly related to strain $\sigma = \epsilon E_{hkl}$. Thus, the strain can be expressed in response to energy density as:

$$\epsilon = \sigma \sqrt{\frac{2u}{E_{hkl}}} \quad (32)$$

where E_{hkl} is modulus of elasticity (Young modulus) for all crystallographic directions.

Now, substitution equation (32) into (25) above, by rearranging we get:

$$\beta_{hkl} \cos \theta = \frac{k\lambda}{D} + 4\sigma \sin \theta \sqrt{\frac{2u}{E_{hkl}}} \quad (33)$$

Equation (33) is an equation of a straight-line equation and is considered as the uniform deformation energy density model (UEDM).

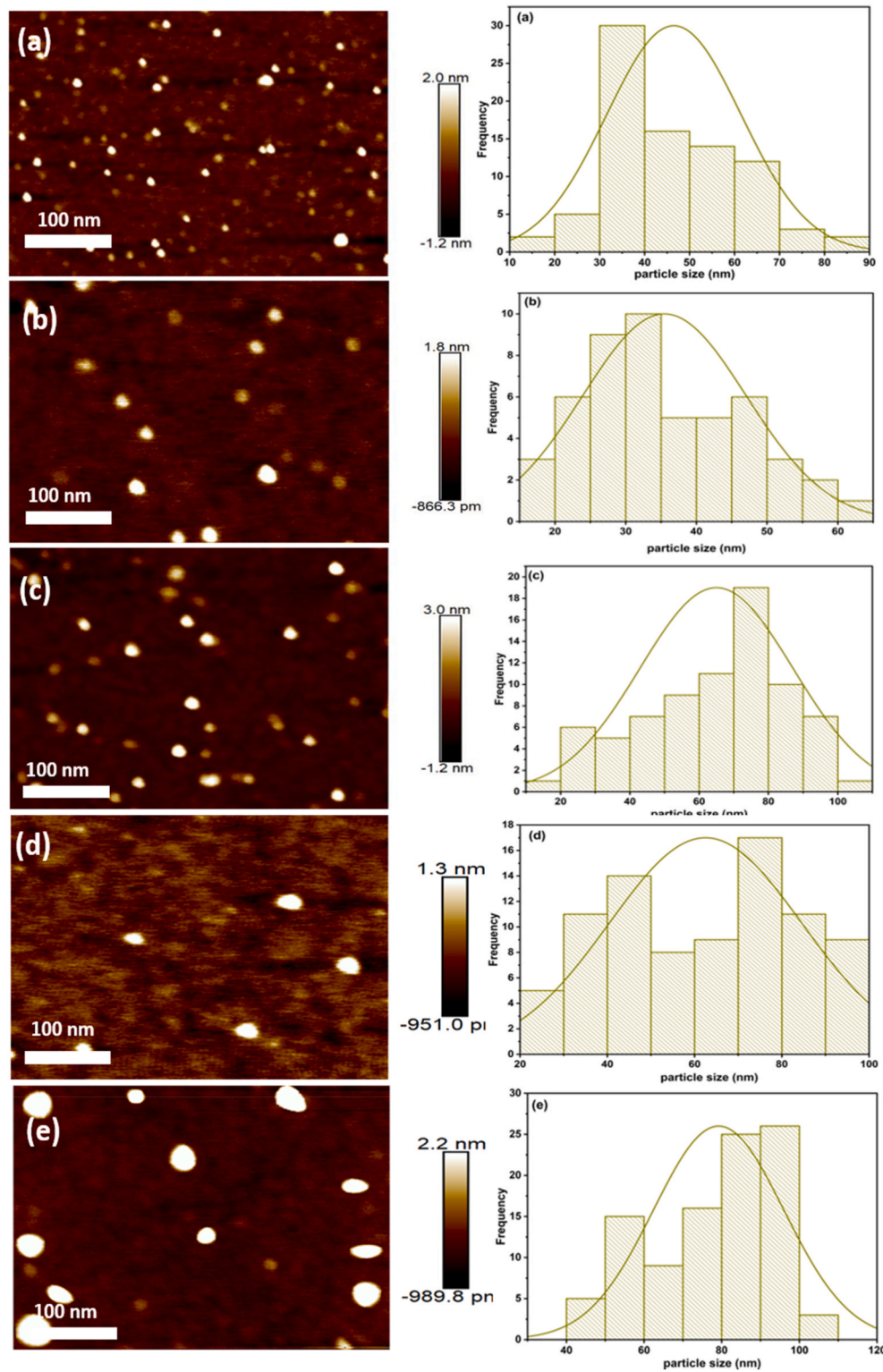


Fig. 10. AFM images and size distribution histograms of CuSe NPs synthesized at varying irradiation time (a) 10 min (b) 15 min (c) 20 min (d) 25 min (e) 30 min.

Therefore, as shown in Fig. 8, a plot of a graph of $(\beta_{hkl} \cos \theta)$ as y-axis and $(4 \sin \theta \sqrt{\frac{2u}{E_{hkl}}})$ as x-axis gives a straight line graph and from the slope as well as intercept of the linearly fitted graph, the energy density (u) as well as the mean crystallite size (D) of CuSe NPs prepared at various irradiation time can be obtained.

3.7.3.1. Raman spectroscopy (RS). Analysis of Raman scattering data

can be used to investigate the crystalline or nanocrystalline nature of a material. Raman spectroscopy is a quick and easy way to examine the vibrational properties of crystalline and amorphous semiconductors [3]. The principle behind RS in semiconductor nanomaterials is on the basis of the inelastic interface of incidence photons with lattice vibrations or phonons, that are responsive to external or internal perturbations. The variation in the Raman line-shape variables (asymmetry, position, peak as well as complete width at half maxima or FWHM) is beneficial in

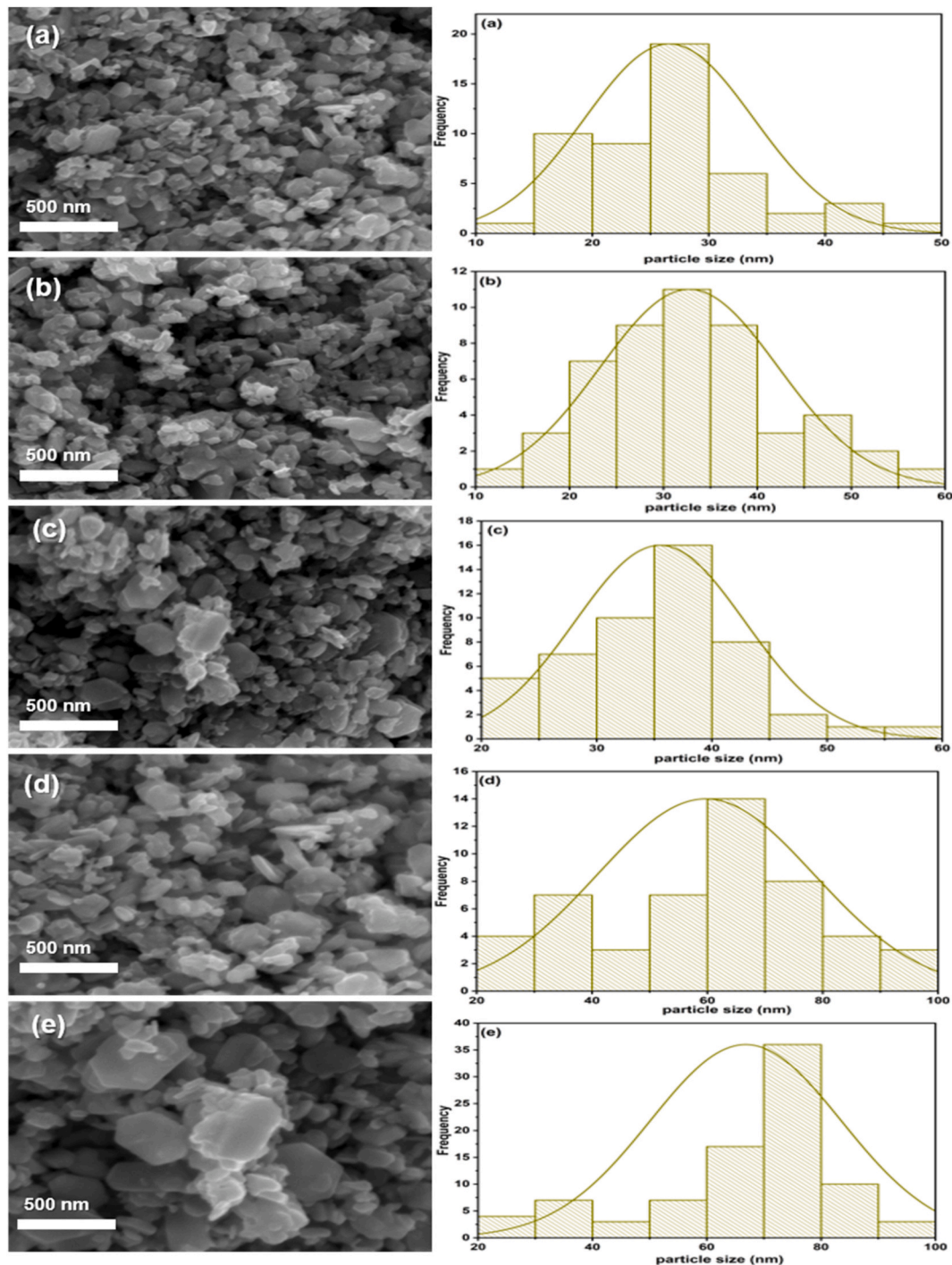


Fig. 11. FESEM image and size distribution of CuSe NPs synthesized at varying of irradiation time (a) 10 min (b) 15 min (c) 20 min (d) 25 min (e) 30 min.

estimating the shape, size, as well as size distribution of nanostructures, because photon broadening and softening of Raman lines are associated with the size of nanostructures. Fig. 9 shows the RS of CuSe NPs synthesized at varying irradiation time under 532 nm excitation wavelength, recorded over a wavenumber range of (100–600 cm^{-1}). All the five samples show a strong and intense peak centred at 262.02, 260.35, 258.74, 257.13, and 254.80 cm^{-1} proportionate to 10, 15, 20, 25, as well as 30 min. The slight shift in the main Raman peaks was observed and it is attributed to the first longitudinal (1LO) phonon mode and corresponds to the Raman vibrational peak of CuSe NPs [45]. The intensity of the principal Raman (1LO) peak is seen to rise with increase in irradiation time. The exciton-longitudinal optic (LO) phonon coupling

strength, calculated using the ratio of the intensity of the second longitudinal (2LO) to the first overtone (1LO) phonon frequency, increases with the particle size as demonstrated in the inset of Fig. 8. The large value of 2LO/1LO ratio indicates that the intensity of electron-photon combination is declining as size of CuSe NPs increases. In the present work, it was noticed that the strength of electron-phonon coupling is decreasing gradually with the increase in CuSe NPs size. For each particle size, the principal Raman peak at (1LO) reveals a visible asymmetry towards lower wavenumber number. The asymmetrical properties continue expanding upon reducing the particle size from 21.59 to 102.40 nm. Moreover, the full width at half maximum (FWHM) of the principal Raman peak is observed to be decreasing as the size of CuSe NPs

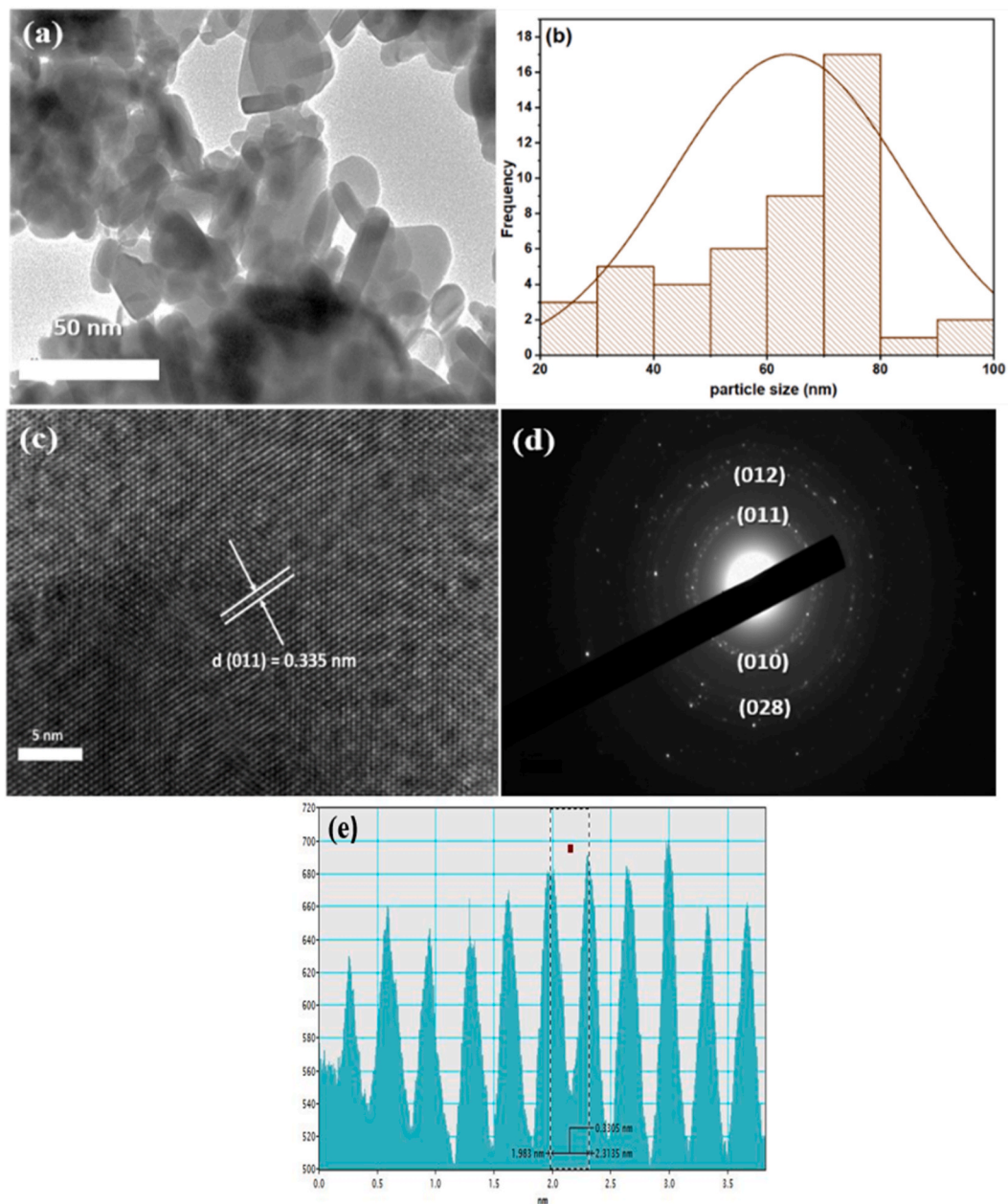


Fig. 12. CuSe NPs synthesized at 25 min of irradiation time (a) TEM image (b) size distribution histogram (c) HRTEM image (d) SAED image (e) SEAD pattern image.

is increased. The shrinking of the Raman peak is as a result of the increase in the particle size of the synthesized CuSe NPs as the irradiation time is increased. Hence, there is a direct relationship between the intensity of electron-phonon coupling and the particle size of CuSe NPs. A relatively weak peaks in the region of wavenumber 511.41, 512.25, 513.15, 513.35, and 515.29 cm^{-1} represents the first overtone peaks (2LO). This fits well with the previous report that the overtone (2LO) peak is typically located twice or triple the central peak frequency. Additionally, a shallow peak at wavenumber 195.25 cm^{-1} corresponds to the transverse optical (TO) phonon mode of CuSe [46]. Table 4 present the Raman results.

4. Morphological analysis

4.1. Atomic force microscopy (AFM)

The morphological surface as well as texture of CuSe NPs synthesized

via microwave irradiation time was characterized using AFM. Fig. 10 shows 2D AFM micrograph along with the size distribution histogram of CuSe NP synthesized at varying irradiation time. The average particle size of CuSe NPs synthesized at irradiation period of 5, 10, 15, 20, and 25 min were found to be 21.98, 38.46, 50.12, 66.35, 102.10 nm. The mean particle size acquired by AFM analysis is observed to be comparable with the mean crystallite size from XRD profile analysis methods used in this study. Therefore, it can be concluded that the mean particle size of CuSe NPs synthesized at varying irradiation time is in agreement with the crystallite size obtained utilizing various XRD profile analysis methods.

4.2. Field emission scanning electron microscopy (FESEM)

FESEM was employed to characterize the surface morphology of CuSe NPs synthesized through microwave-assisted technique. Fig. 11 reveals the FESEM micrographs and the size distribution histogram of

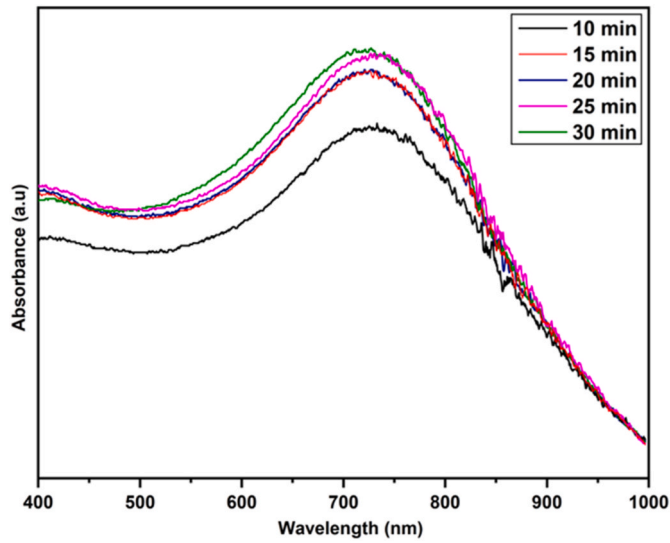


Fig. 13. Optical absorption spectra of CuSe NPs synthesized at varying microwave power.

CuSe NPs prepared at varying irradiation period. The average particle size of CuSe NPs at irradiation time of 5, 10, 15, 20, and 25 min calculated by considering 100 particles is estimated to be 28.25, 36.11, 49.56, 73.20, and 99.45 nm respectively. The particle size estimated is compatible with the mean crystallite size obtained using the X-diffraction profile analysis methods used for determining the mean crystallite size used in this study. Therefore, from the FESEM result, it can be concluded that the mean particle size of CuSe NPs were found to be in tandem with the crystallite size estimate using XRD profile analysis methods.

4.3. Transmission electron microscopy (TEM)

Fig. 12 reveals the TEM images of CuSe NPs synthesis at 25 min of irradiation time, size distribution histogram, selected area electron diffraction (SEAD) of CuSe NPs synthesized at 25 min of irradiation time, and the SEAD image. As demonstrated in Fig. 6 (a & b), the obtained average particle size was 78.55 nm. In addition, from the corresponding SAED pattern as depicted in Fig. 6 (c), the interplanar d-spacing corresponding to the diffraction rings from inside and outside were found to be $d(011) = 0.34647$, $d(012) = 0.317218$, $d(010) = 3.4127$, $d(028) = 0.133772$. The interplanar d-spacing obtained from SAED measurement is found to be consistent with that of the XRD analysis. However, some of the lattice planes also shows weak signals on the pattern, which is based on the inhomogeneous nature of the as-synthesized CuSe samples.

5. Analysis of optical properties

5.1. Diffuse reflectance spectroscopy (DRS)

To examine the effect of irradiation time on the optical characteristics of CuSe NPs, UV–visible absorption spectroscopy was conducted on all the prepared samples. Fig. 13 reveals the absorption spectra at ambient temperature of all the samples in the wavelength range of (250–800 nm). As revealed in Fig. 13, all the samples demonstrate a broad absorption ranging from (450–700 nm) as determined from the absorption spectra. The optical bandgap of CuSe nanoparticle is obtained using the absorption spectra. The optical band gap energy was obtained using the Kubelka Munk formula given as [47]:

$$[F(R) \cdot hv]^2 = A(hv - E_g) \quad (34)$$

where:

$$F(R) = \frac{K}{S} = \frac{(1 - R)^2}{2R} \quad (35)$$

and $F(R)$ represent the Kubelka-Munk function, R denotes diffuse

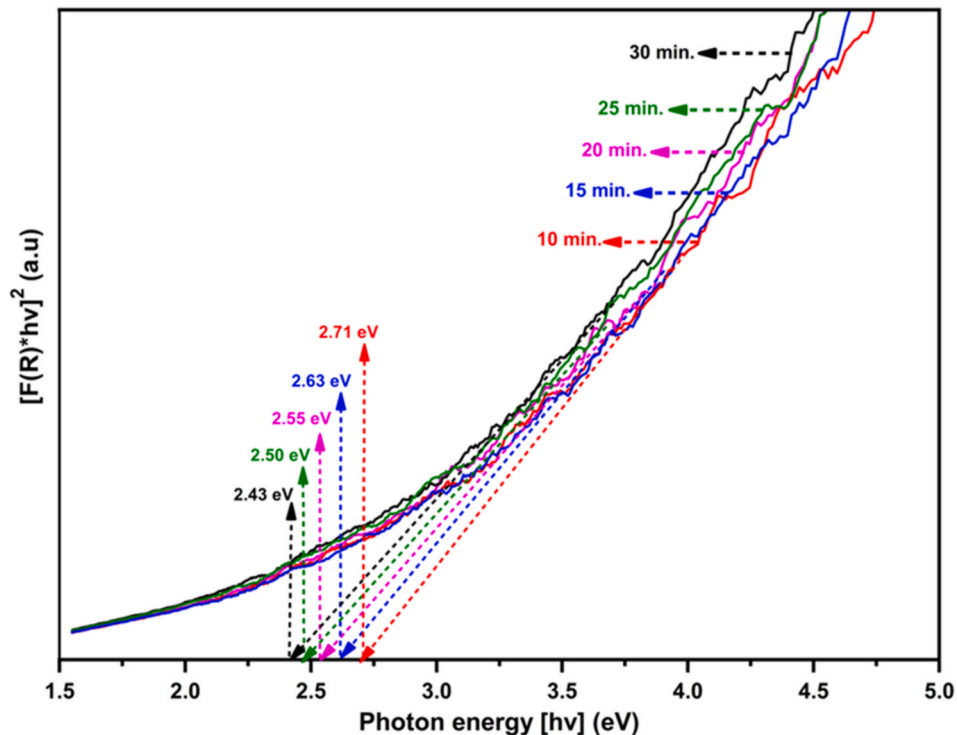


Fig. 14. Optical bandgap of CuSe NPs prepared at varying irradiation time.

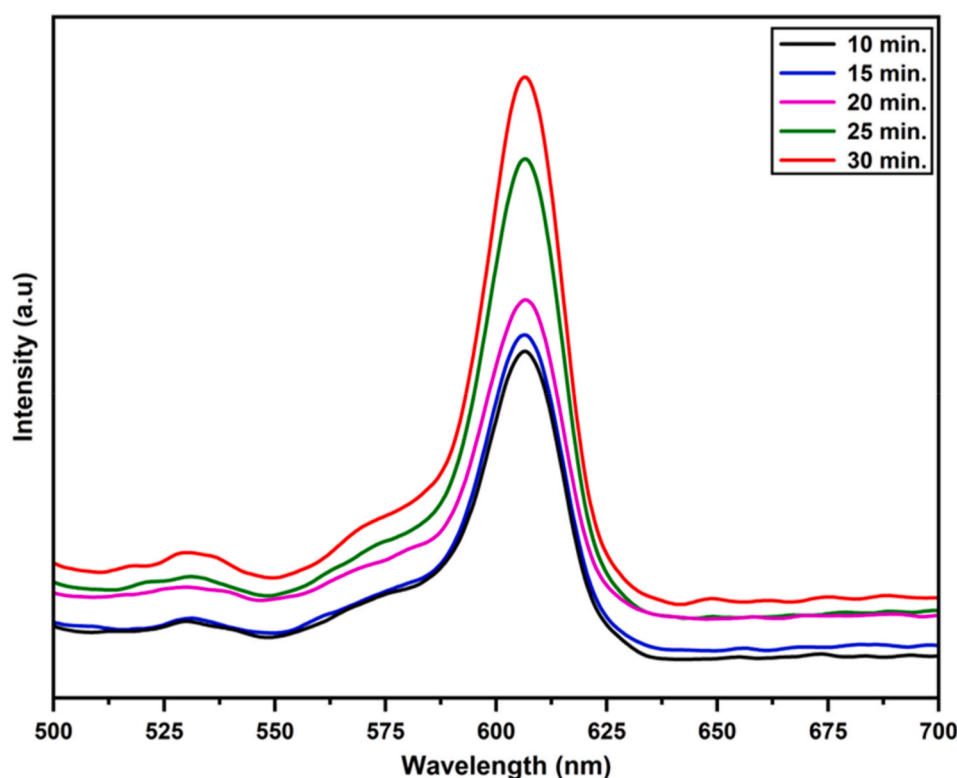


Fig. 15. Photoluminescence (PL) spectra for CuSe NPs synthesis at varying irradiation time.

reflectance found by dividing the reflectance from the test sample to that of the standard sample, i.e., $R = R_{\text{sample}}/R_{\text{standard}}$, $h\nu$ is the photon energy from the light source, A signifies a constant reliant on the probability of transition, while E_g and R are the bandgap [48]. Fig. 14 shows the optical band gaps of CuSe NPs synthesized at different microwave power. The optical band gap declined from 2.50 to 2.10 eV. The reduction in the optical band gap along with the rise in microwave power is caused by the expansion in particle size of the as-synthesized CuSe NPs.

5.2. Photoluminescence spectroscopy (PL)

Fig. 15 illustrates the PL spectra of the as-prepared CuSe NPs under room temperature at varying irradiation time under 400 nm excitation in the range of (500–700 nm) wavelength. It can be noticed that two peaks are overserved, a shallow green emission at 530 nm as well as 610 nm (intense orange emission). The first peak is related to the defects associated with the sample. This anomaly might be caused by occurrence of copper vacancies, interstitials and antisites related defects of the as-prepared sample [49]. The second peak correlated with the sample emission when an electron is being excited from the balance band to the conduction band. The optical band gap obtained from the PL spectra for the as-synthesized CuSe NPs at various microwave power condition was found to be 2.03 eV. The resultant optical band gap is in agreement with that of previous works [50].

6. Conclusion

Copper selenide NPs was successfully manufactured via microwave assisted synthesis procedure. The influence of microwave power condition on the optical and structural properties were investigated. The XRD result indicated that a crystalline phase of hexagonal (Klockmannite) structure was obtained. The crystallite size were found to expand from 45.14 to 123.85 nm with the increase in irradiation time. The estimated crystallites size obtained using various XRD profile

analysis methods were found to be comparable with the estimated crystallite size is found to be comparable with the famous Scherer's method and also consistent with the particle size determined from the FESEM and AFM analysis. Three Raman vibration bands which suits well with the vibrational modes of CuSe were observed from the Raman spectrum. The energy band gap increases from 2.43 to 2.71 eV with a rise in irradiation time. A strong orange emission (610 nm) and a weak green emission (530 nm) were detected from the PL spectroscopy. Hence, it can be concluded that inclusion of intrinsic strain has a substantial influence on the estimation of CuSe NPs size. Therefore, this study reported a facile synthesis route that is eco-friendly, inexpensive and time saving to synthesize semiconductor nanomaterials that could be utilized for optoelectronics and solar cell applications.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors would like to acknowledge the support from the Malaysian Ministry of Higher Education for their financial support through Geran Putra (GPIPS/2018/9664400), (GP/2018/9618700). (FRGS/1/2018/STG07/UPM/02/5) and Tertiary Education Trust Fund (TETFund).

References

- [1] I.G. Shitu, Z.A. Talib, J.Y.C. Liew, M.M.A. Kechick, H. Baqiah, H.K. Lee, A. Muhammad, Facile microwave-assisted synthesis and characterization of CuSe nanosheets: effect of EDTA concentration, *J. Mater. Sci. Mater. Electron.* 31 (16) (2020) 13549–13560.
- [2] I.G. Shitu, Z.A. Talib, J.L.Y. Chi, M.M.A. Kechick, H. Baqiah, Influence of tartaric acid concentration on structural and optical properties of CuSe nanoparticles synthesized via microwave assisted method, *Results Phys.* 17 (2020), 103041.

- [3] I.G. Shitu, Z.A. Talib, J.Y.C. Liew, M.M.A. Kechick, H. Baqiah, H.K. Lee, A. Muhammad, Facile microwave-assisted synthesis and characterization of CuSe nanosheets: effect of EDTA concentration, *J. Mater. Sci. Mater. Electron.* 31 (16) (2020) 13549–13560.
- [4] K. Tyagi, B. Gahtori, S. Bathula, S. Auluck, A. Dhar, Band structure and transport studies of copper selenide: an efficient thermoelectric material, *Appl. Phys. Lett.* 105 (17) (2014), 173905.
- [5] R.A. Hussain, I. Hussain, Copper selenide thin films from growth to applications, *Solid State Sci.* 100 (2020), 106101.
- [6] W.D. Liu, X.L. Shi, R. Moshwan, L. Yang, Z.G. Chen, J. Zou, Solvothermal synthesis of high-purity porous Cu₁ 7Se approaching low lattice thermal conductivity, *Chem. Eng. J.* 375 (2019), 121996.
- [7] F. Kong, J. Bai, P. Bi, X. Liu, Z. Wang, R. Xiong, Size effect enhanced thermoelectric properties of nanoscale Cu₂-xSe, *Ceram. Int.* 45 (7) (2019) 8866–8872.
- [8] A. Sobhani, M. Salavati-Niasari, A new simple route for the preparation of nanosized copper selenides under different conditions, *Ceram. Int.* 40 (6) (2014) 8173–8182.
- [9] A. Abedini, A.R. Daud, M.A. Abdul Hamid, N. Kamil Othman, E. Saion, A review on radiation-induced nucleation and growth of colloidal metallic nanoparticles, *Nanoscale Res. Lett.* 8 (1) (2013) 1–10.
- [10] H. Kaur, J. Kaur, L. Singh, Influence of different deposition potential on the structural and optical properties of copper selenide nanowires, *Superlattice. Microsc.* 97 (2016) 85–93.
- [11] J. Li, G. Liu, X. Wu, G. He, Z. Yang, J. Li, Reaction mechanism in mechanochemical synthesis of Cu₂-xSe, *Ceram. Int.* 44 (18) (2018) 22172–22175.
- [12] H. Wasly, X-ray analysis for determination the crystallite size and lattice strain in zno nanoparticles, *J. Al-Azhar Univ. Eng. Sect.* 13 (49) (2018) 1312–1320.
- [13] M. Bodke, U. Gawai, A. Patil, B. Dole, Estimation of accurate size, lattice strain using Williamson-Hall models, SSP and TEM of Al doped ZnO nanocrystals, *Matériaux Tech.* 106 (6) (2018) 602.
- [14] A. Monshi, M.R. Foroughi, M.R. Monshi, Modified Scherrer equation to estimate more accurately nano-crystallite size using XRD, *World J. Nano Sci. Eng.* 2 (154) (2012) 160, 2012.
- [15] A.A. Al-Tabbakh, N. Karatepe, A.B. Al-Zubaidi, A. Benchaabane, N.B. Mahmood, Crystallite size and lattice strain of lithiated spinel material for rechargeable battery by X-ray diffraction peak-broadening analysis, *Int. J. Energy Res.* 43 (5) (2019) 1903–1911.
- [16] K.V. Chandekar, K.M. Kant, Size-strain analysis and elastic properties of CoFe₂O₄ nanoplatelets by hydrothermal method, *J. Mol. Struct.* 1154 (2018) 418–427.
- [17] S.G. Pandya, J.P. Corbett, W.M. Jadwisieniczak, M.E. Kordes, Structural characterization and X-ray analysis by Williamson-Hall method for erbium doped aluminum nitride nanoparticles, synthesized using inert gas condensation technique, *Phys. E Low-dimens. Syst. Nanostruct.* 79 (2016) 98–102.
- [18] M. Chen, L. Gao, Synthesis and characterization of cadmium selenide nanorods via surfactant-assisted hydrothermal method, *J. Am. Ceram. Soc.* 88 (6) (2005) 1643–1646.
- [19] S. Devesa, A.P. Rooney, M.P. Graça, D. Cooper, L.C. Costa, Williamson-hall analysis in estimation of crystallite size and lattice strain in Bi₁ 34Fe₀ 66Nb₁ 34O₆ 35 prepared by the sol-gel method, *Mater. Sci. Eng., B* 263 (2021), 114830.
- [20] A.A. Akl, A.S. Hassanien, Microstructure characterization of Al-Mg alloys by X-ray diffraction line profile analysis, *Int. J.* 2 (11) (2014) 1–9.
- [21] Shitu, I. G., Talib, Z. A., Chi, J. L. Y., Mustapha, M., Kechik, A., & Baqiah, H. Influence of Microwave Power on Structural and Optical Properties of CuSe Nanoparticles Synthesized via Microwave Assisted Technique.
- [22] I.G. Shitu, J.Y.C. Liew, Z.A. Talib, H. Baqiah, M.M. Awang Kechik, M. Ahmad Kamarudin, I.I. Lakin, Influence of irradiation time on the structural and optical characteristics of CuSe nanoparticles synthesized via microwave-assisted technique, *ACS Omega* 6 (16) (2021) 10698–10708.
- [23] A. Muhammad, Z. Hassan, S.M. Mohammad, S. Rajamanickam, I.G. Shitu, Fabrication of ultra-violet photodetector with enhanced optoelectronic parameters using low-cost F-doped ZnO nanostructures, *Sensor Actuator Phys.* 332 (2021), 113092.
- [24] A. El-Sadek, H.S. Wasly, K.M. Batoo, X-ray peak profile analysis and optical properties of CdS nanoparticles synthesized via the hydrothermal method, *Appl. Phys. A* 125 (4) (2019) 1–17.
- [25] B. Güzeldir, M. Sağlam, Using different chemical methods for deposition of copper selenide thin films and comparison of their characterization, *Spectrochim. Acta Mol. Biomol. Spectrosc.* 150 (2015) 111–119.
- [26] M. Rabiei, A. Palevicius, A. Monshi, S. Nasiri, A. Vilkauskas, G. Janusas, Comparing methods for calculating nano crystal size of natural hydroxyapatite using X-ray diffraction, *Nanomaterials* 10 (9) (2020) 1627.
- [27] P. Muhammed Shafi, A. Chandra Bose, Impact of crystalline defects and size on X-ray line broadening: a phenomenological approach for tetragonal SnO₂ nanocrystals, *AIP Adv.* 5 (5) (2015), 057137.
- [28] H. Rojas-Chávez, H. Cruz-Martínez, E. Flores-Rojas, J.M. Juárez-García, J. L. González-Domínguez, N. Daneu, J. Santoyo-Salazar, The mechanochemical synthesis of PbTe nanostructures: following the Ostwald ripening effect during milling, *Phys. Chem. Chem. Phys.* 20 (42) (2018) 27082–27092.
- [29] A. Monshi, M.R. Foroughi, M.R. Monshi, Modified Scherrer equation to estimate more accurately nano-crystallite size using XRD, *World J. Nano Sci. Eng.* 2 (154) (2012) 160, 2012.
- [30] P. Kumar, G.K. Rao, The effect of precursor concentration and post-deposition annealing on the optical and micro-structural properties of SILAR deposited SnO₂ films, *Mater. Res. Express* 7 (1) (2020), 016428.
- [31] A. Khandan, E. Karamian, M. Bonakdarchian, Mechanochemical synthesis evaluation of nanocrystalline bone-derived bioceramic powder using for bone tissue engineering, *Dent. Hypotheses* 5 (4) (2014) 155.
- [32] D. Nath, F. Singh, R. Das, X-ray diffraction analysis by Williamson-Hall, Halder-Wagner and size-strain plot methods of CdSe nanoparticles-a comparative study, *Mater. Chem. Phys.* 239 (2020), 122021.
- [33] Z.Y. Aydın, S. Abacı, Synthesis and characterization of Cu₃Se₂ nanofilms by an underpotential deposition based electrochemical codeposition technique, *Solid State Sci.* 74 (2017) 74–87.
- [34] B. Rajesh Kumar, B. Hymavathi, X-ray peak profile analysis of solid-state sintered alumina doped zinc oxide ceramics by Williamson-Hall and size-strain plot methods, *J. Asian Ceram. Soc.* 5 (2) (2017) 94–103.
- [35] H. Irfan, K.M. Racik, S. Anand, Microstructural evaluation of CoAl₂O₄ nanoparticles by Williamson-Hall and size-strain plot methods, *J. Asian Ceram. Soc.* 6 (1) (2018) 54–62.
- [36] S. Ilyas, B. Abdullah, D. Tahir, X-ray diffraction analysis of nanocomposite Fe₃O₄/activated carbon by Williamson-Hall and size-strain plot methods, *Nano Struct. Nano-Objects* 20 (2019), 100396.
- [37] P. Garg, R. Rai, B.K. Singh, Structural characterization of “as-deposited” cesium iodide films studied by X-ray diffraction and transmission electron microscopy techniques, *Nucl. Instrum. Methods Phys. Res. Sect. A Accel. Spectrom. Detect. Assoc. Equip.* 736 (2014) 128–134.
- [38] P.C. Dey, S. Sarkar, R. Das, X-ray diffraction study of the elastic properties of jagged spherical CdS nanocrystals, *Mater. Sci.* 38 (2) (2020) 271–278.
- [39] R. Sivakami, S. Dhanuskodij, R. Karvembu, Estimation of lattice strain in nanocrystalline RuO₂ by Williamson-Hall and size-strain plot methods, *Spectrochim. Acta Mol. Biomol. Spectrosc.* 152 (2016) 43–50.
- [40] A.H. Abed, Z.T. Khodair, T.M. Al-Saadi, T.A. Al-Dhahir, Study the evaluation of Williamson-Hall (WH) strain distribution in silver nanoparticles prepared by sol-gel method, in: *AIP Conference Proceedings*, 2123, AIP Publishing LLC, 2019, July, 020019. No. 1.
- [41] M. Rabiei, A. Palevicius, A. Dashti, S. Nasiri, A. Monshi, A. Vilkauskas, G. Janusas, Measurement Modulus of elasticity related to the atomic density of planes in unit cell of crystal lattices, *Materials* 13 (19) (2020) 4380.
- [42] Y.T. Prabhu, K.V. Rao, V.S.S. Kumar, B.S. Kumari, X-ray analysis by Williamson-Hall and size-strain plot methods of ZnO nanoparticles with fuel variation, *World J. Nano Sci. Eng.* (2014), 2014.
- [43] T.M.K. Thandavan, S.M.A. Gani, C.S. Wong, R.M. Nor, Evaluation of Williamson-Hall strain and stress distribution in ZnO nanowires prepared using aliphatic alcohol, *J. Nondestruct. Eval.* 34 (2) (2015) 1–9.
- [44] K. Maniammal, G. Madhu, V. Biju, X-ray diffraction line profile analysis of nanostructured nickel oxide: shape factor and convolution of crystallite size and microstrain contributions, *Phys. E Low-dimens. Syst. Nanostruct.* 85 (2017) 214–222.
- [45] N.S. Babu, M.A. Khadar, Deposition of nanocrystal thin films of Cu₂Se and their optical and electrical characterization, *Appl. Surf. Sci.* 474 (2019) 34–41.
- [46] L. Li, J. Gong, C. Liu, Y. Tian, M. Han, Q. Wang, J. Bao, Vertically oriented and interpenetrating CuSe nanosheet films with open channels for flexible all-solid-state supercapacitors, *ACS Omega* 2 (3) (2017) 1089–1096.
- [47] S. Akir, A. Barras, Y. Coffinier, M. Bououdina, R. Boukherroub, A.D. Omrani, Eco-friendly synthesis of ZnO nanoparticles with different morphologies and their visible light photocatalytic performance for the degradation of Rhodamine B, *Ceram. Int.* 42 (8) (2016) 10259–10265.
- [48] I.G. Shitu, Z.A. Talib, J.L.Y. Chi, M.M.A. Kechick, H. Baqiah, Influence of tartaric acid concentration on structural and optical properties of CuSe nanoparticles synthesized via microwave assisted method, *Results Phys.* 17 (2020), 103041.
- [49] K.S. Urmila, T.A. Namitha, B. Pradeep, Characterization of Defects Levels and Their Influence on the Photoconductivity of P-type CuInSe₂ Thin Films, *Int. J. Res. Rev.* 8 (2015) 10–15.
- [50] Y. Gu, Y. Su, D. Chen, H. Geng, Z. Li, L. Zhang, Y. Zhang, Hydrothermal synthesis of hexagonal CuSe nanoflakes with excellent sunlight-driven photocatalytic activity, *CrystEngComm* 16 (39) (2014) 9185–9190.