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Research Article

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Chemically Synthesized ZnO Nanostructure: Effect of Polyethylene Glycol (PEG) Surfactants

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Abstract: ZnO nano-particles is synthesized using hydrated zinc chloride ($ZnCl_2.2H_2O$) as main raw components. It is calcined at different temperatures (i.e., 200 ºC, 400 ˚C, 600 ºC and 800 ºC). Synthesized ZnO is characterized by XRD, SEM/EDS, HRTEM, UV Visible, and Band Gap. XRD result showed pure wurtzite-structure and is crystalline nature. Both XRD results and SAED obtained from pattern HRTEM studies are indicated similar information of the ZnO nanomaterials. Both FESEM and HRTEM techniques are used to observe surface morphology of ZnO nanomaterials. Such analyses are directed to the thermo-chemical reaction of prepared nanostructures. FESEM analysis showed different nano-sized structures of synthesized ZnO. Different nanostructures of ZnO are found in HRTEM images. EDS results of synthesized ZnO is showed to find Zn and oxygen elements. UV Visible and band gap are indicated.

Keywords: Synthesis, ZnO, Growth technique, XRD, FESEM, HRTEM, Band gap

1. Introduction

In the metal oxide family, ZnO has potential and is extensively used in different technological applications in optical and electronic sectors. These sectors are electronic devices, piezoelectricity, gas sensing device, photocatalysis, solar cells, etc [1-5]. Therefore, it is a multi-functionality material. Electronic property of ZnO is directly depends band gap. ZnO has ~3.3 eV (direct band gap). Binding energy (BE) of ZnO has ~60 meV. It is observed at room temperature. Due to the above excellent properties, ZnO is used in optoelectronic sectors [1]. Optoelectronic performance of ZnO can be regulated by different factors. These factors are growth conditions, introducing types of dopants, and reducing grain dimensions [6]. Such behavior i.e., optoelectronic properties of ZnO is strongly influenced by thin films and nanostructures based ZnO materials [7, 8]. Particularly, grown detached ZnO nanorods are tested for gas sensors. In ZnO nano rods, sensing behaviour is increased due to high aspect ratio [9]. ZnO coated nanoparticles have used potentially in electroluminescence application [10]. ZnO nanomaterial is found application in dye-sensitized solar cell (DSSC). These nanomaterials are also used in photovoltaics [11]. Mou et al have studied ZnO nanomaterials (nanobullets and nanoflakes) in DSSC systems [12]. With and without dopant based ZnO thin films are used in room-temperature ferromagnetism (RTFM) [13]. For the potential applications, synthesis route plays key role. For ZnO synthesis, thermal decomposition, co-precipitation, combustion, and sol-gel techniques, etc are adoteds [14-17].

Various processes are used to prepare different ZnO nanostructured. High-temperature process is also required to get high crystallinity. This may help to form more than one phase. Present scenario demands to synthesis ZnO nanomaterials having spherical size with narrow distribution. Accordingly, microwave plasma assisted spray (MPAS) method is adopted [18, 19]. This is because numerous advantages [20].

In the current research work, ZnO nanomaterials are synthesized from $ZnCl_2.H_2O$ predecessor. It is calcined by different temperature and is made by thermal-chemical process. A ZnO nanomaterial is characterized through XRD, HRTEM, FESEM, FTIR, and UV-Visible.

2. Experimental Section

2.1. Chemicals and Materials

Hydrated Znic chloride ($ZnCl_2.H_2O$) is purchased from Loba Chemicals, Assay= 97 %.

Ammonium hydroxide (NH_4OH) and different grade of polyethylene glycol (PEG) are procured from Merck India. Hydrated Znic chloride, Ammonium hydroxide, and polyethylene glycol are lab scale. During synthesis, distilled water is used.

2.2. Synthesis of ZnO Nanomaterials

2.2.1 Synthesis of ZnO Nanomaterials (Without Using PEG Surfactant)

Typically, chemical synthesis process, room temperature ZnO synthesis procedure is slightly modified [21]. It is followed two steps.

In step 1, $Zn(OH)_2$ is prepared from hydrated $ZnCl_2.2H_2O$. 0.2 M solution of hydrated zinc chloride ($ZnCl_2.2H_2O$) is added to ammonium hydroxide (NH_4OH) solution. Solution is stirred continuously to 20-30 min. Zinc hydroxide is formed, which is white precipitate.

In step 2, Zinc hydroxide is crushed and thereafter, grinded zinc hydroxide is calcined (at 400 ºC) to form ZnO powder. Color of ZnO powder is appears to be slight yellow color. Schematically is depicted synthesized nano-sized ZnO powder particle in Figure 1 (Flow chart).

2.2.2 Synthesis of ZnO Nanostructured Materials Presence of 200 Grade Polyethylene Glycol (PEG) Surfactant

In the synthesis process, ZnO powder is prepared at room temperature and synthesis procedure is reported earlier [21]. It is followed two steps process.

Step 1 Synthesis of $Zn(OH)_2$

Hydrated $ZnCl_2.2H_2O$ is taken as starting components during the synthesis of $Zn(OH)_2$. At first, $ZnCl_2.2H_2O$ solution (0.2 molar) is made. 2mL of PEG 200 is put on hydrated zinc chloride solution. Ammonium hydroxide (NH_4OH) solution is added drop wise to above solution and then, is stirred continuously to 20-30 min. White color precipitate is prepared.

Step 2 Preparation of ZnO powder

$Zn(OH)_2$ is crushed in motar with pastel.

Crushed $Zn(OH)_2$ is calcined (at 400 ºC) to make ZnO powder. ZnO powder after calcination is appears to be slight yellow color. Total synthesis procedure of calcined ZnO powder is indicated in Figure 2. Such ZnO powder is used in different characterizations.

Similarly, Synthesis of ZnO Nanostructure using other grades of polyethylene glycol (PEG) surfactant (i.e., PEG 400, PEG 600, PEG 800, and PEG 2000) is prepared.

2.3. Characterization Techniques

HRTEM (High resolution transmission electron microscope) test method is employed to analyse bulk topography, structure, element detection of prepared ZnO samples by drop-casting method. In ethanol, prepared ZnO dispersed using electrical vibrator. Then, it is put on carbon coated copper grids and kept overnight (i.e., 12 h) for drying of ethanol. Measurements are performed by JEM-2100 HRTEM, JEOL, and Japan. During HRTEM measurement, 200 kV (i.e., an accelerating voltage) is fixed.

FESEM (Field emission scanning electron microscope) analyses are employed to observe surface topography of prepared ZnO materials. FESEM analyses are made with Carl Zeiss Supra 40 instruments. During the measurement, operating voltage is kept at 30 kV. Elemental analyses are done in the same experiment.

XRD (X-ray diffraction) experiment is performed to study sample structure. Phillips PW-1710 advance wide-angle X-ray diffractometer and Phillips PW-1729 X-ray generator instrument is used to do the experiment. Cu Kα radiation is used.

FTIR (Fourier transformation infra-red) spectra are recorded on a Thermo Nicolt Nexus 870 spectrophotometer. Spectra are taken in the range of 400-4000 cm^{-1}. Scan rate, resolution, etc are kept constant.

UV-Vis (Ultra Violet) spectra are noted (Micropack UV-VIS-NIR, DH 2000). Powdered samples are used as test samples. UV-Vis spectra data are helped to determine optical band gap.

Figure 1. Flow chart of chemically synthesized ZnO nanostructures

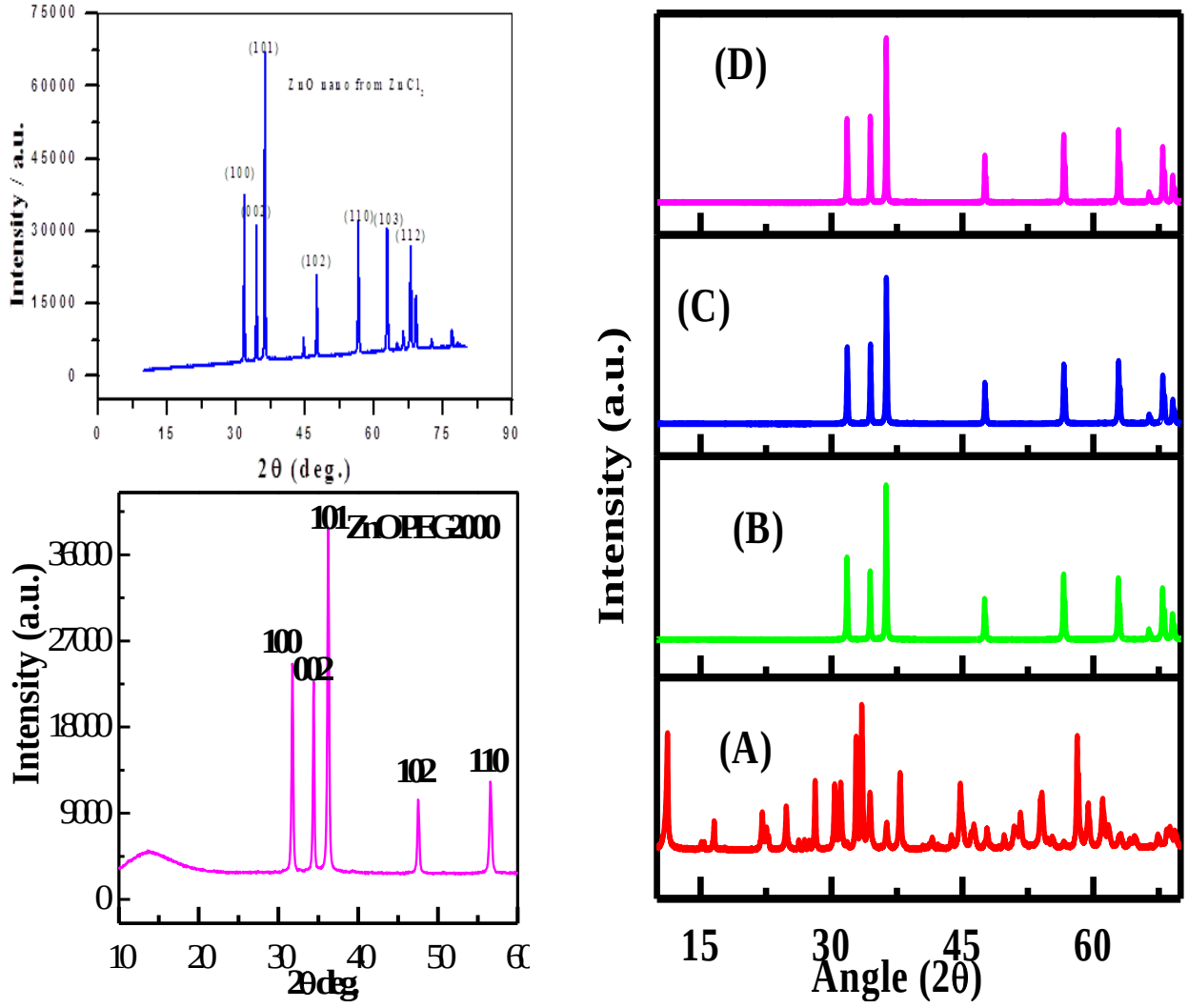

Figure 2. XRD parrten of without (top left corner) and with PEG based ZnO samples (A: ZnO PEG 200, B: ZnO PEG 400, C: ZnO PEG 600, D: ZnO PEG 800, ZnO PEG 2000)

Figure 1 show XRD patterns of ZnO nanomaterials with different grade polyethylene glycol (PEG) surfactant and without assist surfactant. Left side top corner (Figure 1) indicate ZnO nanoparticle. It is prepared without using PEG surfactant. Diffracted peaks fit well and are wurtzite crystal structure [22, 23]. Left side bottom corner (Figure 1) specifies ZnO and is prepared by chemical method using PEG 2000 surfactant. There is marked difference in intensity of ZnO nanomaterials (without and with-PEG surfactants). It is observed from Figure 1 that there is decrease of intensity of ZnO nanomaterials with assist PEG surfactants. This is indicating decrease of crystallinity [22, 23].

FESEM images of without and with polyethylene glycol surfactant assisted ZnO nanomaterials are shown in Figure 3. FESEM image of without surfactant assisted ZnO (Figure.3A) shows particles-like. Average particle size is estimated to be 0.2 µm. FESEM image of 300 grade polyethylene glycol (PEG) surfactant assisted ZnO nanomaterial (Figure.3B) displays cluster-like morphology. Figure 3C indicates FESEM image of ZnO nanomaterial assisted by 400 PEG surfactants. Small capsule-like morphology is observed (Figure.3C). FESEM image of 600 grades PEG surfactant assisted ZnO nanomaterial (Figure.3D) looks-like particles and range of particle size is 0.1-0.2 µm. FESEM image of 2000 grade polyethylene glycol surfactant assisted ZnO nanomaterial (Figure.3E) shows capsule-type morphology. Different type of surface

Figure 4 displays HRTEM images of ZnO nanomaterials (made with PEG surfactants) and ZnO nanomaterials without PEG surfactant. From Figure. 4, it is observed that each prepared nanomaterial looks – like particle with different diameter. Diameter of particle is to be 90 to 150 nm. It is spread non-homogeneously in the background.

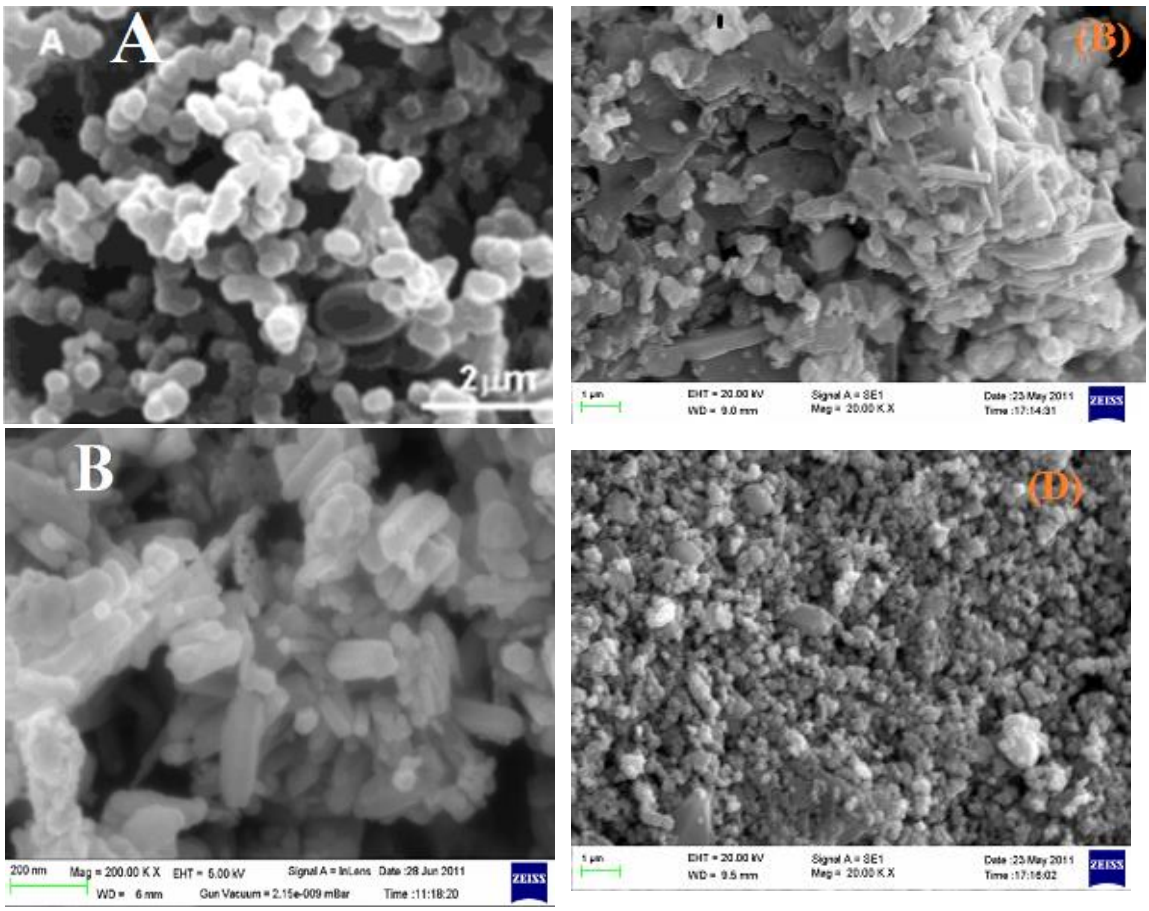

Figure 3. FESEM images of ZnO nanoparticles (A), ZnO nanoparticles with PEG 300 (B), ZnO nanoparticles with PEG 400 (C), and ZnO nanoparticles with PEG 600 (D)

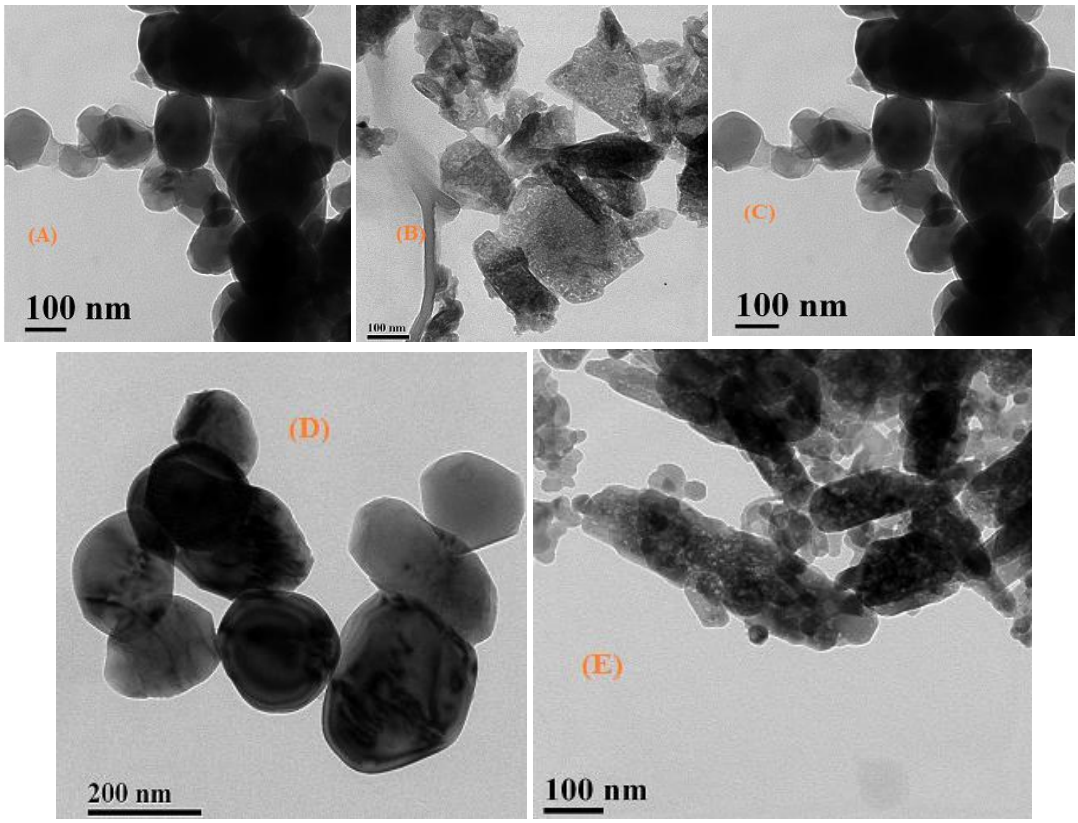

Figure 4. HRTEM images of ZnO nanoparticles (A), ZnO nanoparticles with PEG 300 (B), ZnO nanoparticles with PEG 400 (C), and ZnO nanoparticles with PEG 600 (D), and ZnO nanoparticles with PEG 2000 (E)

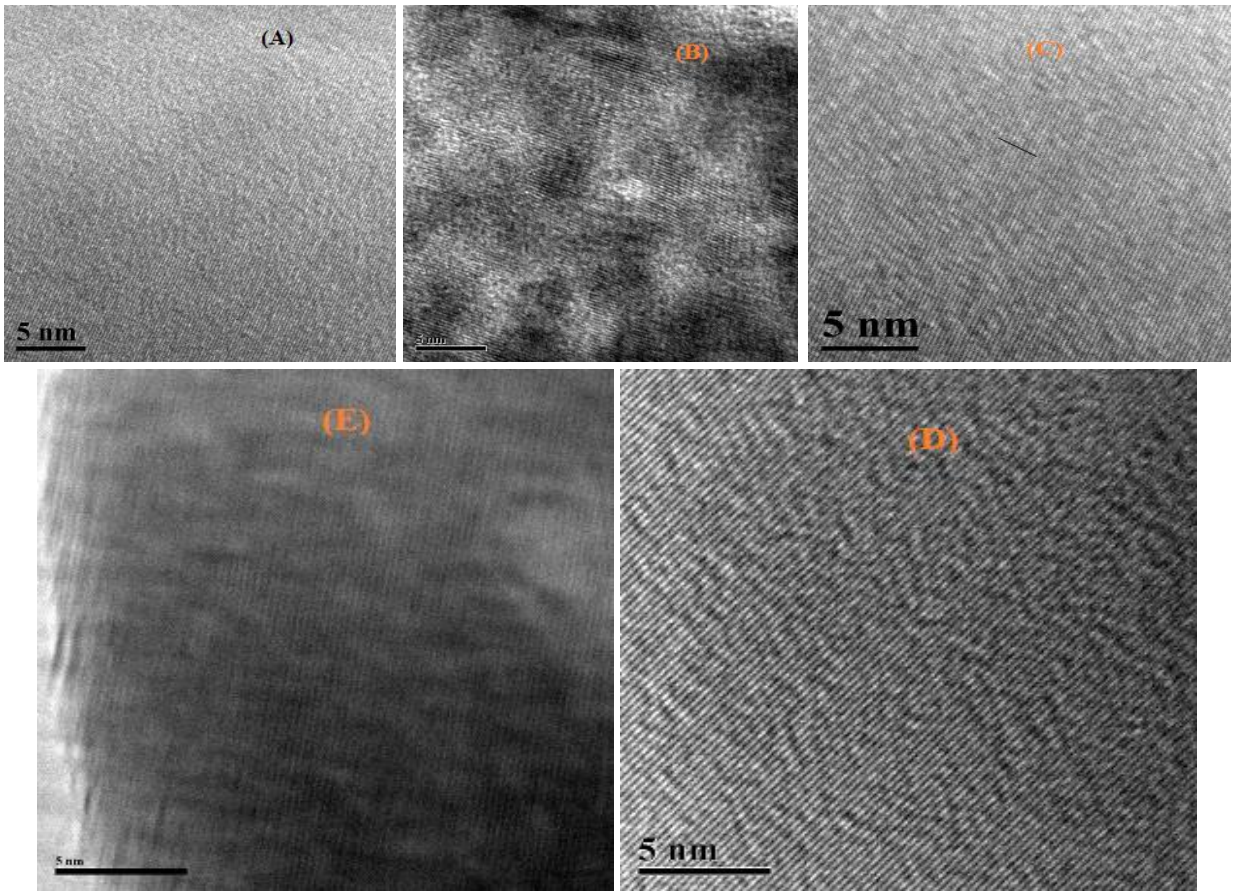

Figure 5. HRTEM images of ZnO nanoparticles (A), ZnO nanoparticles with PEG 300 (B), ZnO nanoparticles with PEG 400 (C), and ZnO nanoparticles with PEG 600 (D), and ZnO nanoparticles with PEG 2000 (E)

Table 1. EDS analyses of ZnO nanoparticles with PEG 300 (A), ZnO nanoparticles with PEG 400 (B), and ZnO nanoparticles with PEG 600 (C), and ZnO nanoparticles with PEG 2000 (D)

S.No.	Sample ID	Elements present in samples (weight in percent)				
		Cu	Zn	O	Cl	Density (g/cc)
1	ZnO (PEG 300)	74.87	22.57	0.16	2.41	8.36 g/cm^3
2	ZnO (PEG 400)	76.71	23.12	0.16	---	8.52 g/cm^3
3	ZnO (PEG 600)	53.94	43.97	2.09	---	8.00 g/cm^3
4	ZnO(PEG 2000)	50.48	45.74	3.78	---	7.84 g/cm^3

It is further revealed in Lattice fringes of prepared ZnO nanomaterials, which is shown in Figure**. 5.** It is suggested crystallized nature of materials.

EDS study of prepared surface assisted ZnO nanomaterials is done during HRTEM analysis and is shown in Figure 6. Table 1 indicates elements present in atomic weight percentage in the sample [21].

Surfactant assisted ZnO is then, characterized by UV Visible spectroscopy. It is measured between 300–800 nm. Figure. 7 displays superimposed UV Visible spectra of surfactant assisted ZnO nanomaterials. Figure 7 shows peak at 369 nm. It is assigned as an excitonic absorption peak. Size of nanomaterials is become more and more. There is a decrease in absorbance.

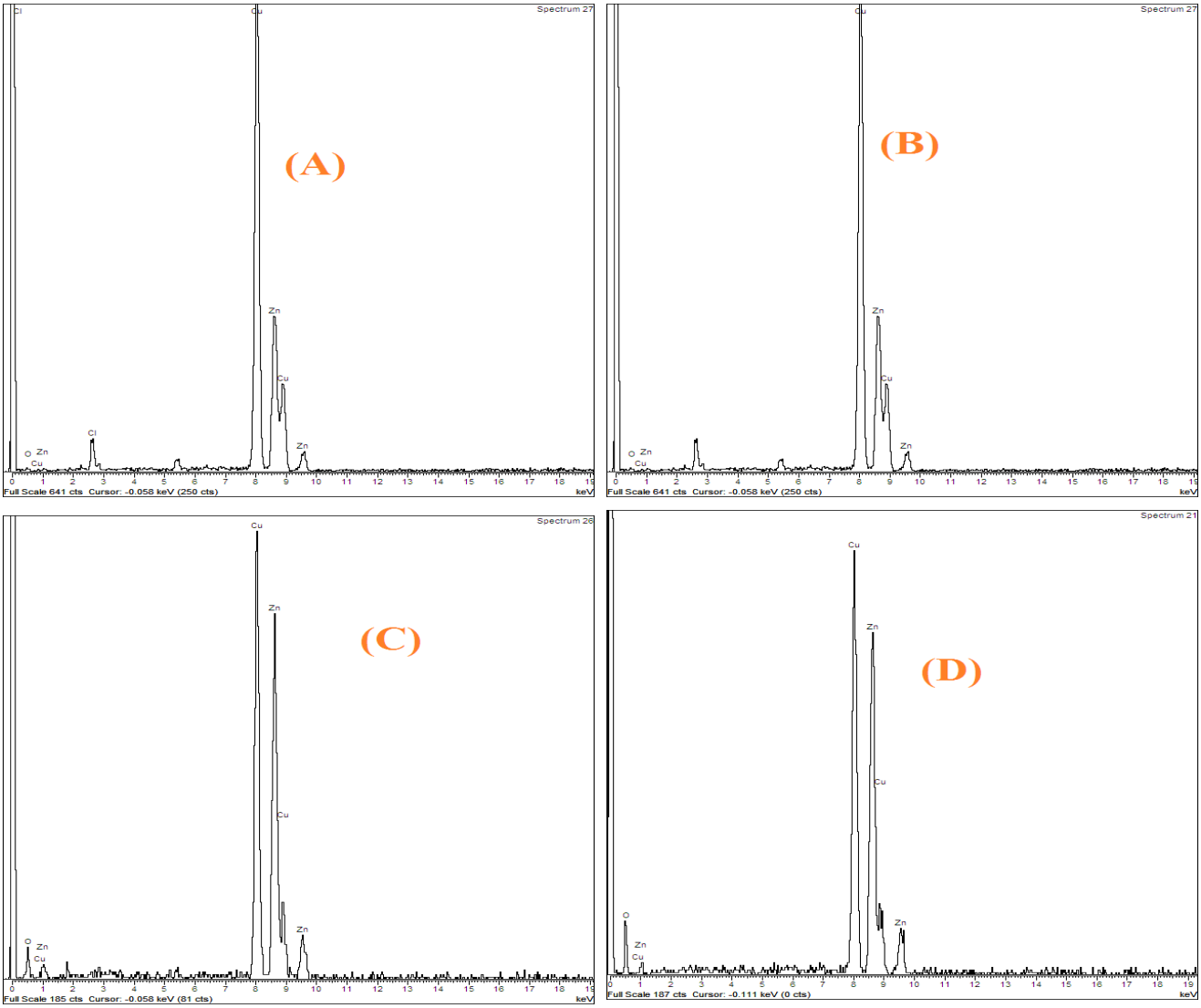

Figure 6. Elemental analysis of ZnO nanoparticles with PEG 300 (A), ZnO nanoparticles with PEG 400 (B), and ZnO nanoparticles with PEG 600 (C), and ZnO nanoparticles with PEG 2000 (D)

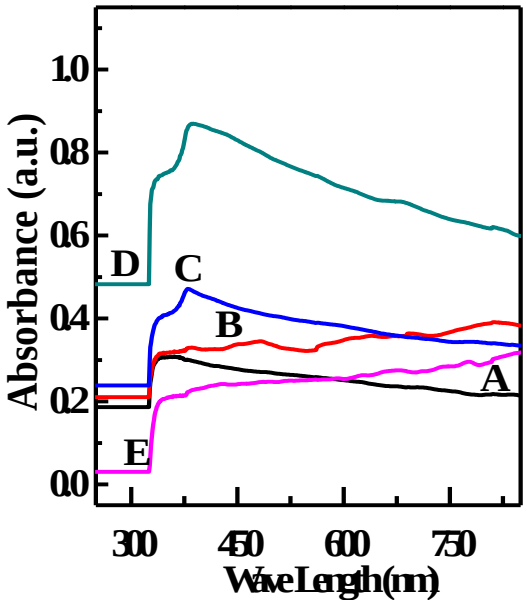

Figure 7. UV-Visible spectra of as-prepared ZnO nanomaterials [A-$Zn(OH)_2$, B-PEG 200 assisted ZnO, C- PEG 400 assisted ZnO, D- PEG 600 assisted ZnO, and E- PEG 800 assisted ZnO]

This type of behaviour is observed in many semiconducting materials. There is development of electric fields within the crystal and inelastic scattering of charge carriers by phonons [24, 25].

3. Conclusions

In the current work, of ZnO nano materials are synthesized by chemical method using $ZnCl_2.2H_2O$. Prepared surfactant assisted ZnO nanomaterials are tested by different characterization techniques. XRD analysis of ZnO nanomaterial indicated wurtzite structure. FESEM image(s) of the prepared nanomaterials showed particles with different sized. In EDS analyses, Znic and oxygen is found. This indicate the purity. For electronic transition study, UV-Visible analyses are done.

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Does this article screened for similarity?

Yes

Conflict of interest

The Author declares that there is no conflict of interest anywhere.