Effect of Banana Peels Extract Ratio on The Sustainable Eco-Friendly Synthesis of Zinc Oxide Nanoparticles

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Paper History:

Received: 12th May. 2023

Revised: 31st Oct. 2023

Accepted: 10th Dec. 2023

Abstract

In this work, environmentally friendly zinc oxide nanoparticles was produced using sustainable green technology. With several loading amounts, such as 5%, 10%, 50%, and 100%, the banana peel extract was utilized as a capping agent. This was followed by calcinations at 400 °C for 3 h in a muffle furnace. To evaluate the physical and chemical change of the synthesized nanoparticles, XRD, FTIR, UV-VIS and SEM/EDAX was used. The characterization results reveald that the all the green synthesized ZnO NPs samples strongly supports the well-crystallinity with high phase purity. The average crystallite size of the prepared samples was calculated using Debye-Scherer's formula and the results shows that with an increase in extract amount, the average crystallite size was shrinking. The FTIR result verified the successful chemical reaction between zinc salt and banana peel extract. The UV-VIS results showed the effect of size quantisization phenomena at 100% extract adding. Finally, the SEM images for all the prepared samples confirm the spherical shape.

Keywords: Zinc Oxide Nps, Green Synthesis, Banana Peels, Nano Metal Application, Green Chemistry.

تأثير نسبة مستخلص قشور الموز على التصنيع المستدام الصديق للبيئة لجزيئات أوكسيد الزنك النانوية

أثيل علوش ، فرح مؤيد، سلام محمد

الخلاصة:

في هذا العمل، تم إنتاج جزيئات أوكسيد الزنك النانوية الصديقة للبيئة باستخدام التكنولوجيا الخضراء المستدامة، تم استخدام مستخلص قشور الموز كعامل تغطية بكميات تحميل متعددة، مثل ٥٪، و١٠٪، و٥٠٪، و١٠٠٪. وأعقب ذلك معاملته حراريا عند ٤٠٠ درجة مئوية لمدة ٣ ساعات . و لغرض تقييم التغير الفيزيائي والكيميائي لاكاسيد الزنك النانوية تم استخدام تقنيات متعددة مثل XRD، FTIR، UV-VIS و SEM/EDAX.

كشفت نتائج التشخيص أن جميع عينات اوكسيد الزنك النانوية تدعم بقوة التبلور الجيد و نقاء الطور العالي. كما تم حساب متوسط الحجم البلوري للعينات المحضرة باستخدام صيغة ديباي-شيرر وأظهرت النتائج أنه مع زيادة كمية المستخلص أدى ذلك الى تقلص متوسط حجم البلورات.كما أثبتت نتائج FTIR نجاح التفاعل الكيميائي بين ملح الزنك ومستخلص قشر الموز. بينما أثبتت نتائج UV-VIS تأثير ظاهرة التكميم الحجمي عند إضافة مستخلص الموز ١٠٠٪. وأخيرا، تؤكد صور SEM ان جميع العينات المحضرة كانت تحمل الشكل الكروي.

1. Introduction

The development of banana by-products helps to reduce food waste, create new jobs, and develop sustainable products. The innovation in the development of banana by-products and waste goods is a positive development and it has a potential application including food, feed, biofuel and biomaterials that help us meet the needs of a growing population in a sustainable way.

Banana peels are rich in fibers, phenolic compounds, antioxidant and antibacterial activities. It contain polyphenolic, flavonoids, anthocyanins, tannins, alkaloids and glycosides compounds[1]. The bioactive functional groups of these compounds are used in industries, agriculture, and medical applications, such as dying cotton textiles using banana peel through the interaction between tannin compounds and cellulose cotton fiber [2]. In addition, these neutral wastes have antibacterial activity, antioxidant, anticancer, safe food, and free radical scavenger [3]–[5]. However, discharging dye effluents from various industrial waste dyes such as dyes kinds of stuff, textiles, paint, inks, and cosmetics represents one of the main water contamination problems. The existence of these contaminants in water leads to severe aquatic life problems worldwide [6]. Moreover, the high solubility of the dyes in water makes the theme extremely dangerous to the environment [7]. Up to now, great efforts have been achieved in wastewater treatment, including the preparation of different active materials, i.e., nano metals, and the modification of activation processes to enhance the efficiency of the treatment process using eco-friendly sources like banana peels waste.

Metal oxide nanoparticles have attracted scientific research interest [8]because the metal oxide nanostructure can show a unique chemical property due to its nano size and active surface site density [9], [10]. A wide selection of metal oxide nanoparticles like zinc, copper, titanium, and iron oxides have been prepared for their nano medical, catalytic, solar cells, sensors, and ultraviolet protection, zinc oxide has gotten extensive attention from chemist researchers[11]. Zinc oxide is a semiconductor inorganic substance with three crystalline shapes: zinc blend, wurtzite, and rock salt; the structure of wurtzite has stable tetrahedral geometry with a wide band gap [12].

Various physical and chemical standard methods were used to prepare zinc oxide nanoparticles such as sol-gel, combustion method, polymerization, and microwave-assisted precipitation [13], [14]. However, these preparation methods required toxic and harmful materials with high energy, low yield, and large-size products. [15], [16].

Now a day, researchers have been focused on green preparation for metal nanoparticles derived from plants, bacteria, fungi, and algae. The Plant extracts are easy to prepare and have multiple bioactive functional groups used as reducing and capping factors [17]. In addition, the plant extract is less toxic than chemical substances with low cost and decreases waste in agricultural and industrial fields. Different Plant parts such as roots, leaves, stems, seeds, and fruits have also been used for metal nanoparticle preparation[18].

The current research aims to use a green and eco-friendly preparation method to synthesize zinc oxide nanoparticles using an extract derived from the waste of banana peels. The effect of adding different ratios of peel extract on the prepared zinc oxide nanoparticles was investigated. The crystalline structure with morphology were studied using XRD, SEM, FTIR and diffuse reflection spectra. Bio adsorbents are still under development, but they have the potential to revolutionize the way we treat wastewater and other polluted fluids.

2. Materials and methods

In this work, a capping agent such as banana peel extract was used to investigate its effect on the characteristics of the prepared zinc oxide. Different extract rations were used, i.e. 5%, 10%, 50% and 100%, to determine their effect on the characteristics of the zinc oxide nanoparticles: crystallinity morphology nature.

2.1 Materials

The source of zinc was obtained from Zinc acetate dihydrate as a raw material and purchased from GPR. The sodium hydroxide from Merck. Fresh banana was collected from local market

2.2 The preparation of banana peel extracts:

The fresh banana peels were cut into small pieces. Then, add 50 g of peels with 400 ml of distilled water in a beaker of 500 ml to prepare the banana peel extract. The mixture was allowed to heat for 10 minutes while the colour of the solution was changed from colourless to yellow or little light brown [19]. After that, the mixture was cool until room temperature, followed by filtration to discharge all the unwanted impurities.

2.3 The preparation of zinc oxide nanoparticles

In this step, four glass beakers were used to prepare four types of zinc oxide nanoparticles by changing the amount of banana peels extract added to the solution (5%, 10%, 50% and 100%). For all mixtures, 5 g of zinc acetate dehydrate salt was dissolved in 500 ml of the distilled water and stirred for 5 minutes at room temperature. Next, the peels extract (pH 6.2) with different ratios was added to the four solutions. The pH increased by adding NaOH to 12. The mixture was let for 2 hours to cool with stirring. Filtrated the mixture and washed it with distilled water several times. Finally, the residue was dried in an oven at 80 ℃ for 24 hours, followed by calcination at 400 °C for 3 hrs using a muffle furnace [20].

2.4 Characterization techniques

The characterization of the zinc oxide nanoparticles was performed using different analytical techniques. First, the crystallinity and crystal phase of the samples were characterized using an XRD Philips Goniometer PW 1820 diffractometer. Next, the Fourier transforms infrared spectra measured using Bruker Alpha spectrophotometer. Finally, the reflection spectra of the solid samples were measured by the diffraction spectrophotometer Elmer. Scanning Electron Microscope FEI_Company Inspect S50 (Model) and Energy Dispersive X-Ray Spectroscopy/EDX Bruker Company/ XFlash_6l10/ Model used for surface morphology of zinc oxide nanoparticles.

3. Results and discussion

3.1 The X-ray diffraction

The X-ray diffraction pattern and the crystalline size calculation for the prepared ZnO samples using different ratios of banana peel extracts were performed using XRD techniques, as in Figure (1). All the prepared samples confirm good crystallinity with high intensity. For all samples, the diffraction peaks detected were at (31.75, 34.41, 36.23, 47.16, 56.57, 62.85, 66.34, 67.93, 69.06) the strongest peak was at 36.2, 31.7, 34.4. The diffraction peaks of hexagonal structure were indexed to hexagonal phase (wurtzite structure) which is very close to standard values (JCPDS no. 36-1451). Similar results were detected with [21], [22]. It should be highlighted that no reflection related to any impurities was detected. Furthermore, the high intensity of the diffraction peaks confirms the high crystalline structure and the success of the green preparation of zinc oxide nanoparticles.

The crystallite size (D) of the green synthesized ZnO NPs was calculated by Debye–Scherrer's equation:

$$D=\frac{0.94\,\lambda}{\beta\cos\theta} \quad ----- \quad (1)$$

Where λ is the wavelength *(*1.5406*)*, β the full-width half maximum (FWHM) and θ the diffraction angle.

The average crystallite size for 5%, 10%, and 100% extract ratios was 28.51nm, 21.948 nm, and 17.80, respectively. Therefore, from the above results, the crystalline size was reduced with the increase in extract ratio, which refers to the capping agent's effect on preventing growth and accumulation. On the contrary, the crystallite size was increased to 32.99 nm for a 50 % banana peels extract ratio. Therefore, it could refer to nucleation and a growth process[23].

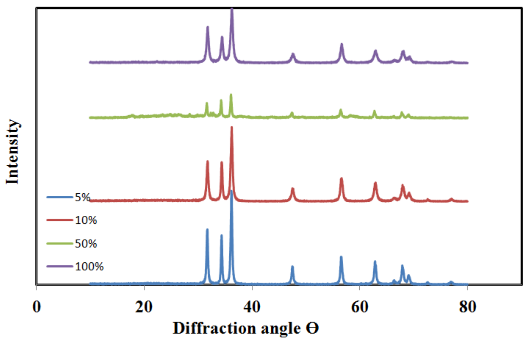

Figure (1): XRD Zinc oxide nano-sized with different ratios of extract.

3.2 Infrared spectroscopy

FTIR spectra for the preparation of znic oxide nanoparticles with different ratios of the banana peel extract were detected and compared to the banana peel extract alone, as in Figure (2a,b). The abroad strong band at 3282.88 cm^{-1} was observed for the spectrum of banana peel extract, and the band at 2904.30 cm^{-1} refers to the stretching vibration mode of the amine group (N-H). In addition, many other peaks were observed for the banana extracts, which distinguish the chemical bonds variety exist in banana extracts such as the bands at 1637.76 cm^{-1}, 1428.8 cm^{-1}, 535.1 cm^{-1} and 492.9 cm^{-1}, which refers to υC=C aromatic, bending vibration band of carboxylic acid(O-H) and aromatics groups respectively. On the other hand, the FTIR spectra detected the disappearance of almost the absorption bands explained, especially for ZnO with 5% and 10% due to the minimum amount of extract added and their volatility after the calcination step. Meanwhile, new absorption bands were detected at 491- 467 cm-1, representing the bond formation between zinc and oxygen [12], [20]. It must be highlighted that the difference in FTIR spectra between the banana peel extract and the green synthesized catalyst was verified by the successful chemical reaction between zinc salt and banana peel extract in the first stage of preparation. Furthermore, the calcination for the prepared powders at 400 º C confirms the complete transformation to zinc oxide as detected by XRD analysis.

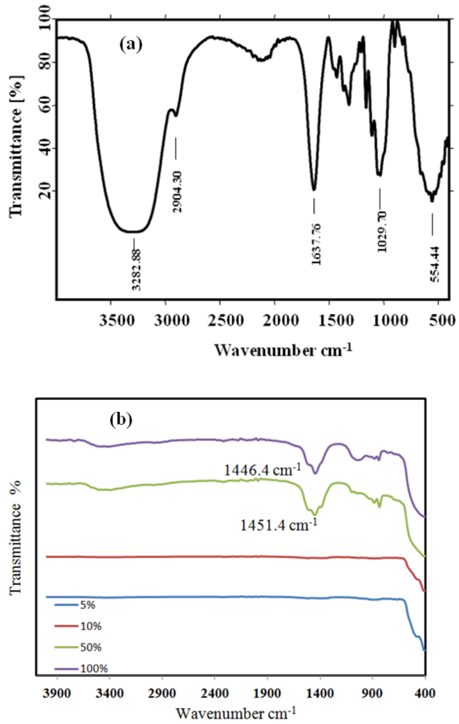

Figure (2): FTIR for (a) Banana peel extract (b)ZnO nanoparticles

3.3. UV Vis diffuse reflectance

The effect of banana peel extract on the optical properties of Zinc oxide nanoparticles was measured by the UV-Vis diffuse reflectance spectra with a wavelength ranging from 200-1200 nm, and the results are shown in Figure (3). The amount ratio of banana peel extract ranging from 5% -100% was added with a fixed amount of zinc acetate.

All the measured samples show sudden reflection spectra in their wavelengths ascribed to the presence of an energy band gap [24]. For example, the sample with 5% peel extract added, the reflection spectrum was 451 nm. As the amount of extract was increased to 10% and 50%, a red shift towards a higher wavelength was noticed at 454 nm and 457 nm, respectively. On the contrary, a blue shift was noticed towards a shorter wavelength of about 445 nm when the extract was increased to 100%. This sudden shifting to a lower wavelength could be ascribed to the size quantization phenomenon [25].

The calculate band gap energy of ZnO (see Figure 4(a,d)) nanoparticles of different extract ratios was calculated by the relationship of Kubelka–Munk function between the square Ln [(Rmax-Rmin)/(R-

Rmin)] versus hv (as abscissa) where hv was calculated according to the equation below[26]

$$h\nu = 1240/(\lambda) \quad \text{-------} \quad (2)$$

The results revealed that the increase of extract amount does not affect the energy gap for 5 and 10% with an energy band gap of 3.41; however, as the extract amount was increased to 50%, the energy band gap was decreased to 3.28 ev. This shifting in band gap energy could be ascribed to the change in particle size that caused the difference between the occupied and the unoccupied levels. However, as the amount of extract was increased to 100%, the band gap energy was increased to 3.34 ev. The increasing in band gap energy was due to the quantum size effect [16], [27].

In our present work, the energy gap values for all the prepared samples were smaller than the band gap energy value of bare zinc oxide of 3.37 ev. The energy gap values may be due to the electronic transfer from the filled valence states to energy levels of defects instead of the electronic transfer between the occupied level and the empty level.

P. Jamdagni, P. Khatri, and J. S. Rana [28] investigated the concentration effect of flower extract on the forming ZnO nanoparticles. The results found that the UV absorption of the samples was increased gradually with an increase in flower extract range (0.25-1) ml. One ml of flower extract in 50 ml of zinc acetate has maximum absorption capacity. However, any increase or decrease above 1 ml led to a decrease nanoparticle synthesis due to the low absorption values [28].

On the other hand, F. M. Mohammadi and N. Ghasemi [29] show that the increase of zinc nitrate metal from (0.005-0.03M) with a fixed amount of cherry extract causes direct biochemical reduction due to the rapid competition between zinc nitrate metal and the fixed concentration of bio-molecules, which capped and stabilized the nanoparticle. That led to less quantities of hexagonal structural of average size equal to 20.7–96.5 nm[29].

3.4. Scanning electron microscopy

Figure (5) represents the SEM images for ZnO nanoparticles using different ratios of banana peel extract. All the images confirm the spherical shape. Similar results were detected with [20]. However, the effects of adding extract were detected throw the SEM images. Figure(5a) with an extract addition of 5%, the spherical shape of ZnO was detected without much agglomeration. However, as the extract ratio was increased, the particles size seems to decrease, as in Figure(5c,d). This result agreed with XRD analysis and UV-Vis diffuse reflectance spectroscopy [23].

The composition of ZnO nanoparticles with different amounts of banana peel extract was analyzed using energy dispersive x-ray spectroscopy (EDX) as in Fig. 6. The spectra indicate the presence of Zn and O with high intensity, and some traces of foreign elements were also detected. However, these small traces did not affect the crystallinity of the ZnO nanoparticles as XRD results detected it since no other phases were detected.

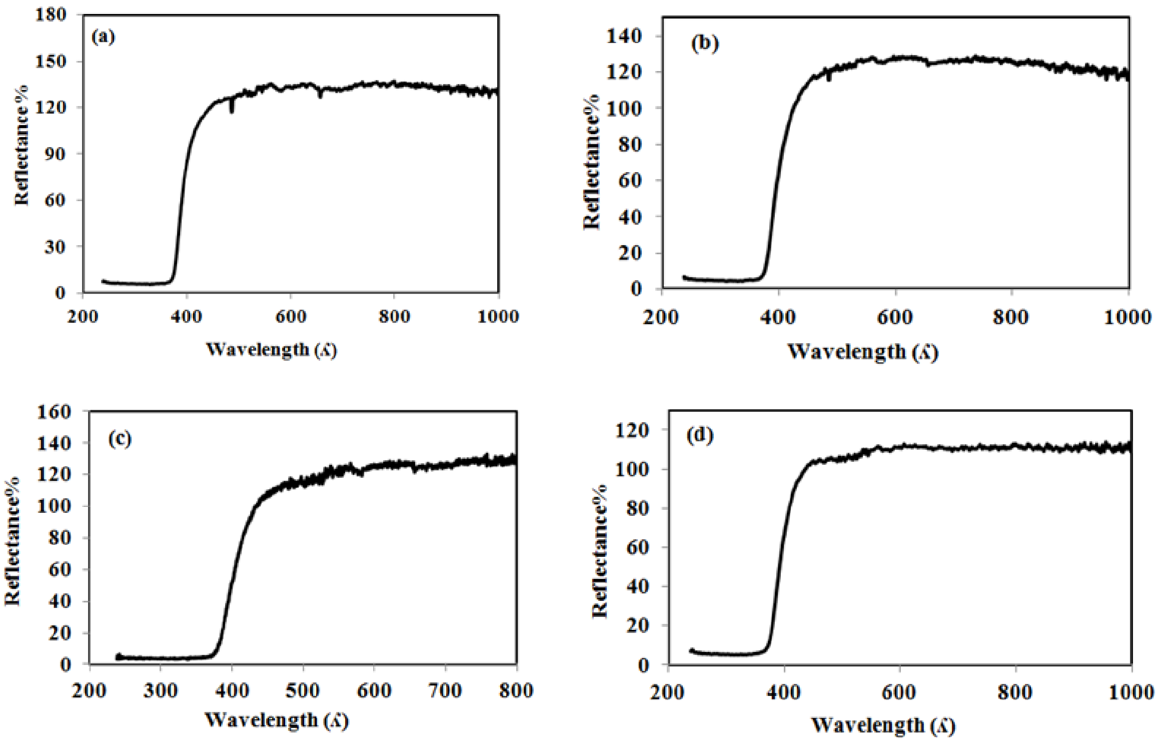

Figure (3): UV-Vis diffuse reflectance spectra for ZnO using banana peel extract of (a) 5%, (b) 10%, (c) 50%, (d) 100%.

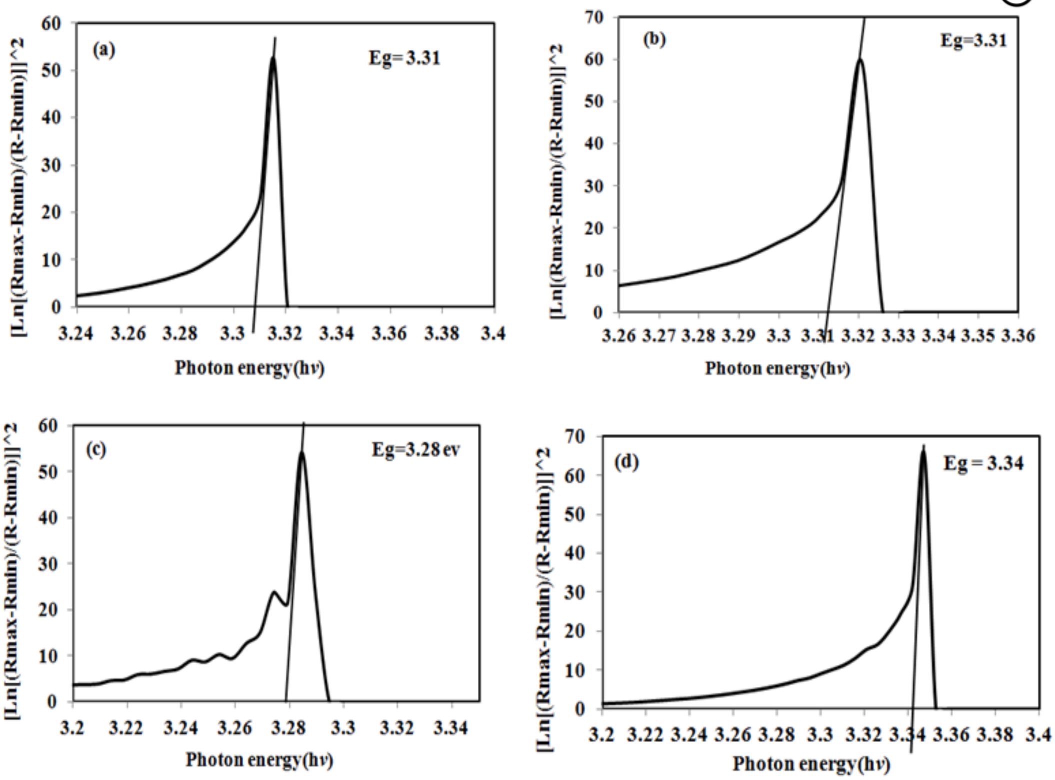

Figure (4): The calculated values for ZnO using banana peel extract of (a) 5%, (b) 10%, (c) 50%, and (d) 100%.

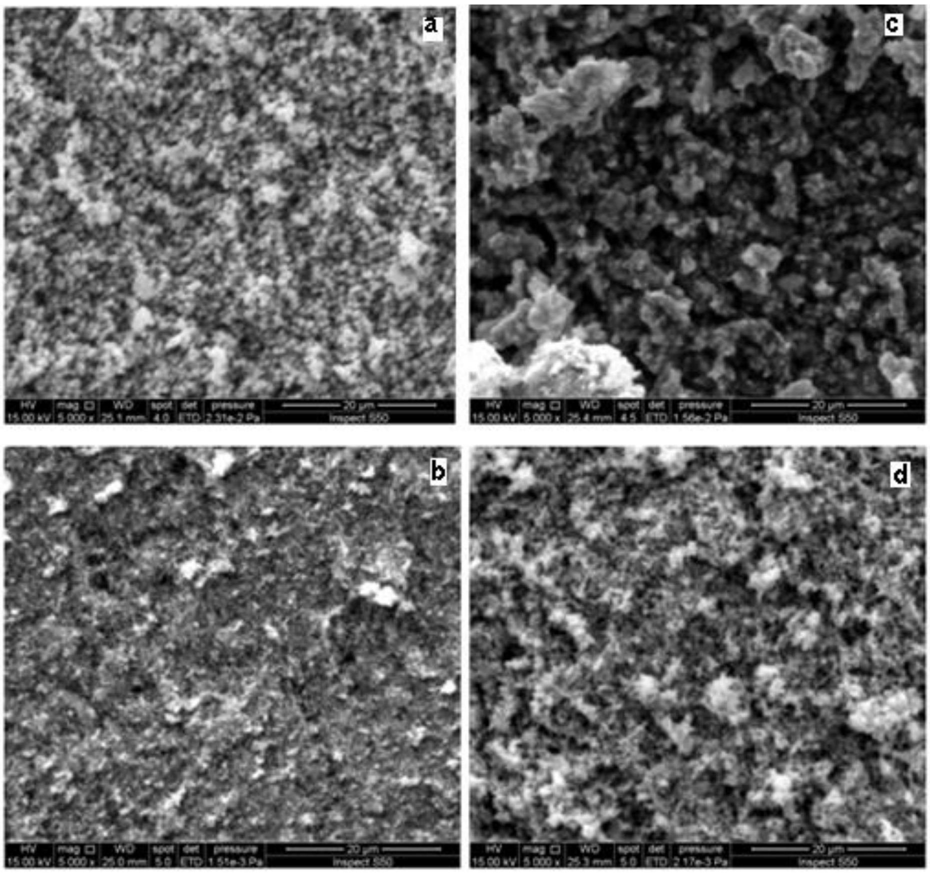

Figure (5): SEM images of ZnO using banana peel extract (a) 5% (b) 10% (c) 50% (d) 100%

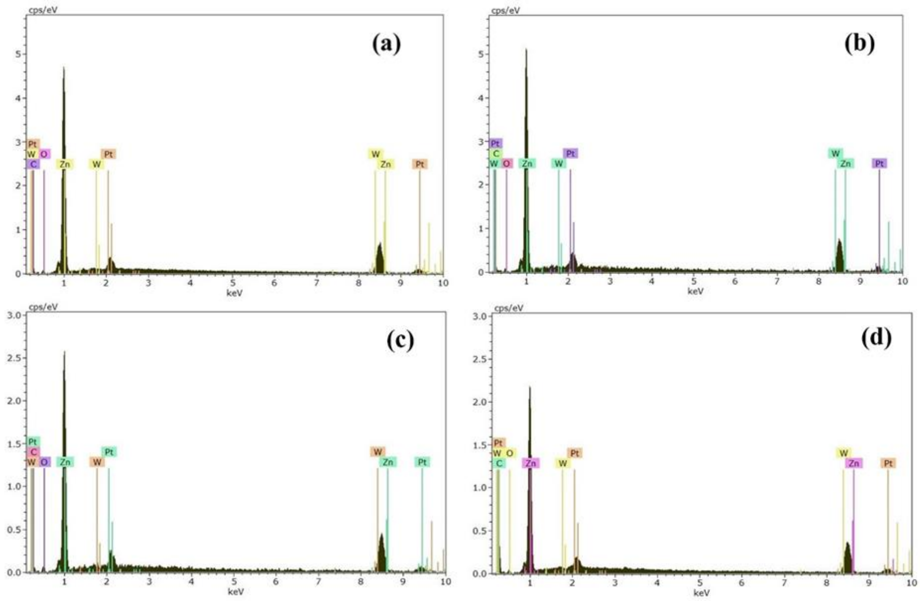

Figure (6): EDX images of ZnO using banana peel extract (a) 5% (b) 10% (c) 50% (d) 100%

4. Conclusion

In this work, the effect of banana peels extract ratio on the synthesize of ZnO nanoparticles was investigated. The XRD results revealed that biosynthesized ZnO nanoparticles have crystalline, hexagonal structure with an average size range from (28.51 to 17.80) nm for 5% and 100%, respectively. Furthermore, the diffuse reflectance spectra results of the prepared zinc oxide nanoparticles showed that there was no change in band gap energy of 3.41 ev for ZnO at 5 and 10% respectively. The FTIR results demonstrate a new absorption band detected at 491-467 cm^{-1}, representing the Zn-O bond. Meanwhile, the calcination for the sustainable ZnO nanoparticles at 400 ^{o} C confirms the complete transformation to zinc oxide. Thus, biosynthesized ZnO NPs was successfully prepared from the banana peels extract which shows direct effect on the physical and chemical characteristic of the ZnO nanoparticles.

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