

# Effect of Benzalkonium Chloride on Properties of Zinc Oxide Nanoparticles Synthesized through Sol-Gel Technique



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## ABSTRACT

In the present study, to synthesize controllable sized metal oxide particles, benzalkonium chloride (BAK) as cationic surfactant was added to zinc oxide (ZnO) nanostructures synthesis at room temperature using sol-gel method. The effect of cationic surfactant BAK concentrations, on the optical properties, size, and morphology of ZnO nanoparticles synthesized through sol-gel method was studied. The characterization of ZnO nanostructures was occurred using transmission electron microscopy (TEM), X-ray diffraction (XRD), ultraviolet-visible near infrared (UV-Vis) spectrophotometer, Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). ZnO nanostructures shape and size were revealed by SEM and TEM. The hexagonal (wurtzite structure) of ZnO was confirmed by an X-ray diffractogram. The bandgap energy of the prepared ZnO samples was determined by UV-Vis spectrophotometer. FTIR analyzed the presence of functional groups.

**Index Terms:** Benzalkonium Chloride, Cationic Surfactants, Sol-Gel Method, Zinc Oxide, Nanostructures

## 1. INTRODUCTION

In an experimentally accessible size range, one of the few oxides that show quantum confinement effects is zinc oxide (ZnO), which is a semiconductor with a wide bandgap of 3.4 eV and a large exciton binding energy of 60 MeV at room temperature. What makes ZnO favorable is its qualities such as low-temperature process, transparency, and high carrier mobility in addition to cost savings. As well as ZnO properties, size-dependent optical absorption is also a valuable tool. Therefore, to quantum size ZnO particles, sol-gel preparation method can be used [1]. In

many particle synthetic processes, especially surfactant-free chemical reactions, as particles start to generate, aggregation immediately occurs. This agglomeration for nanostructured materials does cause a problem in the many chemical and pharmaceutical products. The direct mutual attraction between particles through chemical bonding or Van der Waals forces, simply leads to aggregation as represented in conventional studies [2]. Although this agglomeration can be counted onto prevent toxicity of nanoparticles, especially in cosmetic products as ZnO is widely used such as sunscreen or industrial factories like paint factories [3]. Nanoparticles recently considered to be dangerous, both medically and environmentally [4]. In fact, it has the ability to make the particles very reactive or catalytic because it has a high surface [5]. They are also capable of harming cell membranes in organisms and biological systems [6]. However, if the particles are larger in size, they are unlikely to harm the cell nucleus and other internal cellular components due to the particle agglomeration [7].

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Lung inflammatory and systemic activity can be noticed in experimental animals when they inhaled ultrafine particles unlike an equal mass of larger particles, which may also affect adult human subjects [8].

Due to its bulky bi-tailed structure, which is insoluble, benzalkonium chloride (BAK) particles tend to agglomerate, which caused the increase in the particle size [9].

Several physical and chemical methods could be taken under consideration to synthesize ZnO nanostructures. Chemical vapor deposition (CVD), metal-organic CVD and molecular beam epitaxy, pyrolysis, vapor-liquid-solid growth, and vapor-solid processes such as thermal reduction, are considered physical methods. At the same time, to have a very large scale production, there are chemical methods that are very simple yet effective such as precipitation, sol-gel, and solvothermal processes. Unlike general methods, these methods do not require high temperatures and sophisticated instruments [10]. In this work, there must be a controllable grain size of particles as a result, to approach that goal, it's better to use the sol-gel method, especially when we adjust the experimental conditions such as concentration, temperature, pH, and reaction time. In addition, this method is simple yet reproducible and does not cost much, not to mention its reliability of stoichiometry control, which makes it a totally suitable process for industrial production of ZnO [11].

## 2. EXPERIMENTAL

### 2.1. Preparation of ZnO Nanoparticles

ZnO nanocrystals were prepared by adding 100.0 mL of 0.5 mol/l NaOH solution dropwise slowly into 250.0 mL of 0.1 mol/l  $Zn(Ac)_2$  distilled water using distilled water under vigorous stirring and closed vessel to produce the  $Zn(OH)_2$  precipitate, then an appropriate amount of  $NH_4HCO_3$  (0.8 g) powder was added to adjust pH value of the solution. After stirring for 30 min, a semitransparent zinc carbonate hydroxide colloid was obtained. After 30 min, the colloid was centrifuged and dried at 80°C. Thus, the precursor of a small crystallite of  $Zn_5(CO_3)_2(OH)_6$  with white color was formed then calcined at 450°C for 2 h. The sample was washed by deionized water, and finally, the product was dried at 70°C to obtain the white colored sample of ZnO nanoparticle.

### 2.2. Preparations of ZnO Nanoparticles with BAK

The procedure was repeated as in 2.1 with addition BAK (95% purity Sigma-Aldrich) ( $1 \times 10^{-5}$  M below,  $5 \times 10^{-5}$  M

at,  $15 \times 10^{-5}$  M above) critical micelle concentration (CMC), respectively. The CMC value of BAK was taken from literature data [12]. Although this time, the precursor was calcined at 550°C for 5 h to obtain the sample, as shown in Fig. 1. Finally, the product was dried at 70°C to obtain the white-colored sample of ZnO.

## 3. RESULTS AND DISCUSSION

The CMC value of BAK was taken from literature data and it was 0.04 mM [12].

### 3.1. Analysis of Fourier Transformed Infrared (FTIR)

Fig. 2a shows the FTIR spectrum of prepared ZnO nanoparticles without BAK. Furthermore, Fig. 2b-d shows

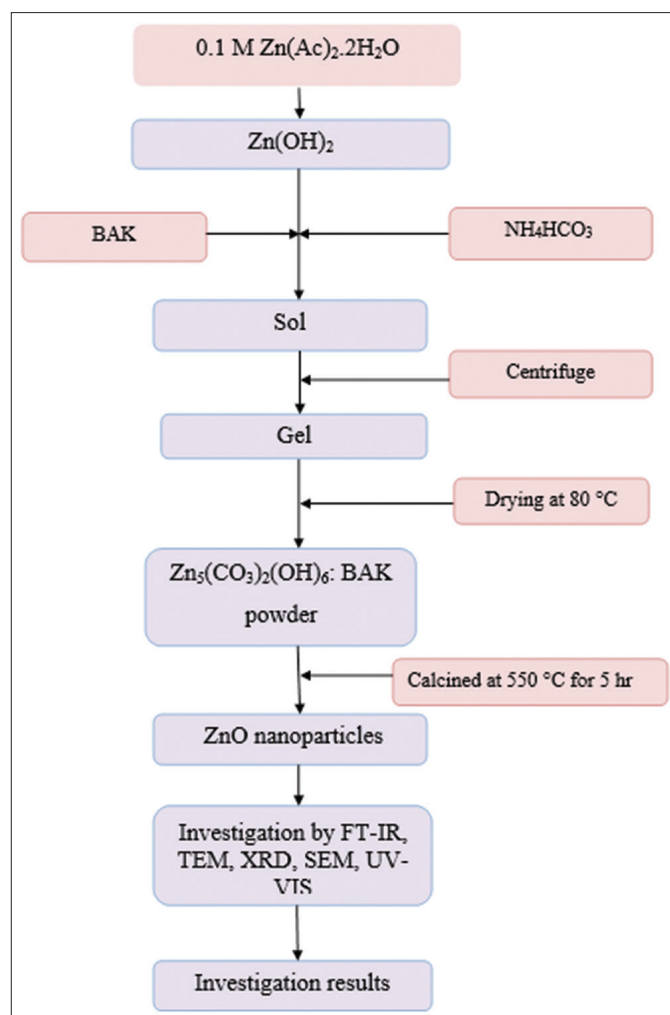
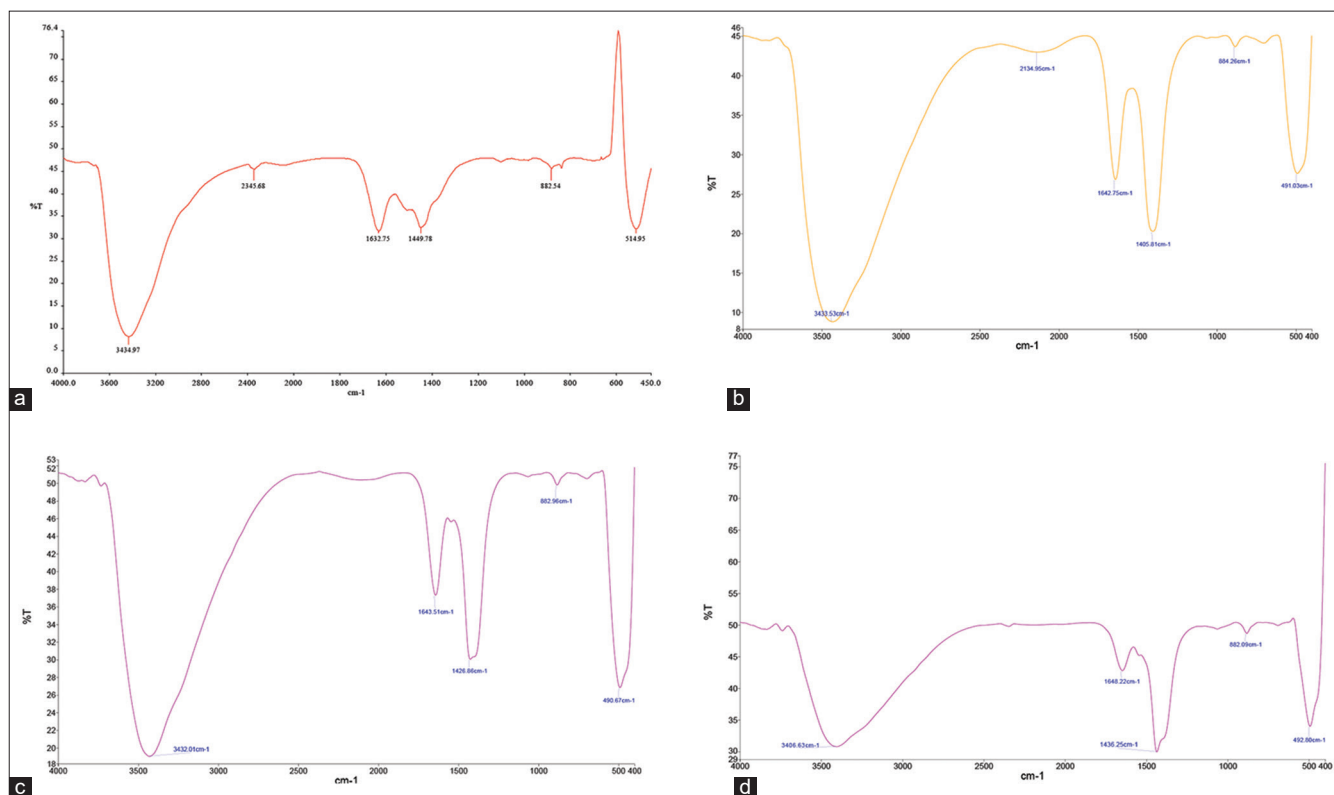


Fig. 1. Preparation of benzalkonium chloride with benzalkonium chloride surfactant.



**Fig. 2.** Combined Fourier transformed infrared spectra of zinc oxide nanoparticles without and with benzalkonium chloride (BAK) surfactant (a) without surfactant, (b) with BAK below critical micelle concentration (CMC), (c) with benzalkonium chloride at CMC, (d) with BAK above CMC.

the FT-IR spectra of prepared ZnO particles in the presence of BAK (below CMC, at CMC, and after CMC), respectively. The broad absorption band centered above 3000 cm<sup>-1</sup> is attributable to the band O–H stretching vibrations of water molecules on ZnO, and the band near 1630 cm<sup>-1</sup> is assigned to the covalent bond in H–O–H bending vibrations mode which were also presented due to the adsorption of humidity in the air when FT-IR sample disks were prepared in an open air.

The spectrums near 1450 cm<sup>-1</sup> indicate the existence of C–O. However, for ZnO samples with BAK surfactant, the calcination temperature was raised at 550°C for 5 h and is not blue shifted. The difference in the calcination temperatures and the time could explain the difference among the figures.

### 3.2. Analysis of Scanning Electron Microscope (SEM)

The morphology of the prepared ZnO samples was determined by SEM analysis, as shown in Figs. 3-6. ZnO samples with BAK that is calcined at 550°C for 5 h, do not reveal uniform morphology. The structure of BAK

is bulky and bi-tailed which is insoluble; the particles tend to agglomerate, which caused the increase in the particle size [9]. The particle size of ZnO sample was taken by line intersecting method; the result revealed that the prepared ZnO sample without BAK in Fig. 3 was in the range of 80–85 nm which smaller than the prepared samples in the presence of BAK Figs. 4-6, respectively.

Although SEM is not an accurate technique to determine the particle size, according to particle size distributions of ZnO nanoparticles based on SEM images, ZnO particles without surfactant reveal an average size of 86 nm, as shown in Fig. 7. However, the results for ZnO samples with BAK revealed a bigger average size of 125 nm for ZnO with BAK below CMC point, 145 nm for ZnO with BAK at CMC point, and 212 nm for ZnO with BAK above CMC point. These samples are not nanosized, as shown in Figs. 8-10. The actual reason is due to BAK's bulky structure which contains 25 carbon atoms in the tail that cause the agglomeration; as a result of this led to an increase in the size of the particles [9].

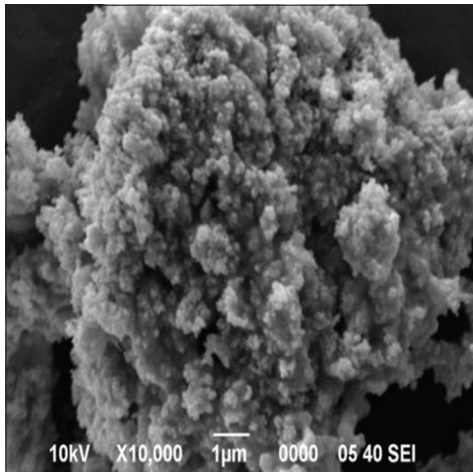


Fig. 3. SEM analysis of ZnO without surfactant.

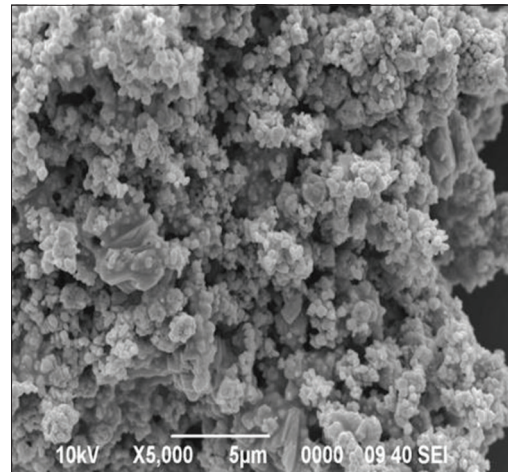


Fig. 6. SEM analysis of ZnO with benzalkonium chloride surfactant above critical micelle concentration.

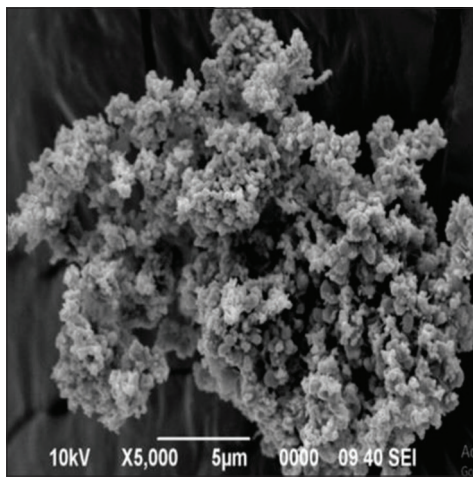


Fig. 4. SEM analysis of ZnO with benzalkonium chloride surfactant below critical micelle concentration.

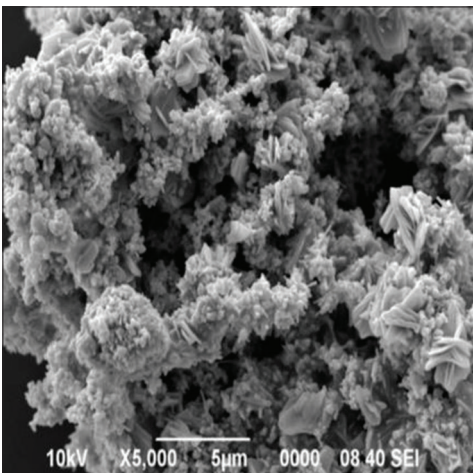


Fig. 5. SEM analysis of ZnO with benzalkonium chloride surfactant at critical micelle concentration.

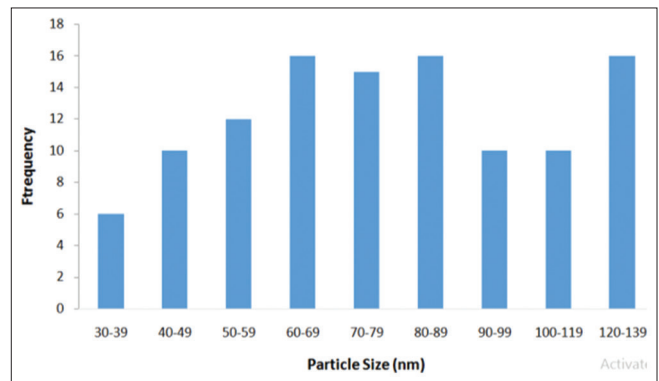


Fig. 7. The particle size distribution of ZnO without surfactant.

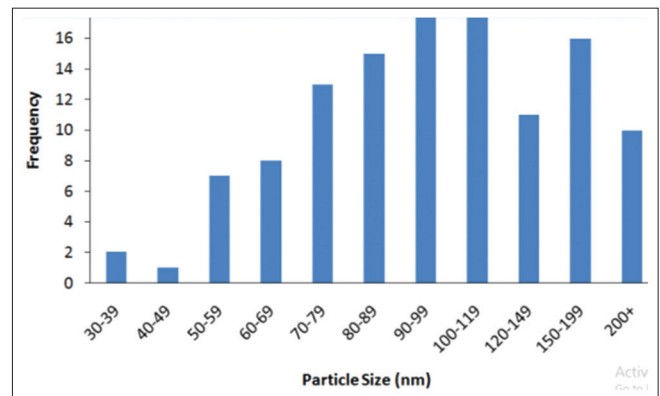


Fig. 8. The particle size distribution of ZnO with benzalkonium chloride surfactant below critical micelle concentration.

### 3.3. Analysis of Ultraviolet–Visible Near Infrared (UV-Vis-NIR) Spectroscopy

Figs. 11-14 illustrate the  $\alpha h\nu^2$  versus  $h\nu$  plot used for the estimation of the bandgap of ZnO nanoparticles calcined

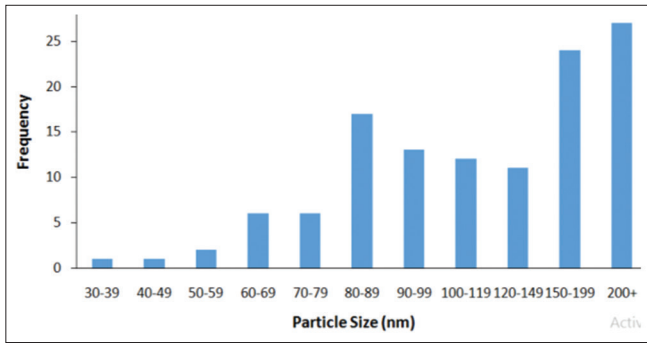


Fig. 9. The particle size distribution of ZnO with benzalkonium chloride surfactant at critical micelle concentration.

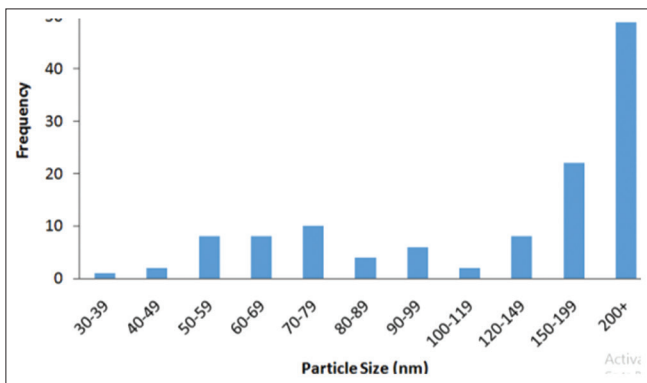


Fig. 10. The particle size distribution of ZnO with benzalkonium chloride surfactant above critical micelle concentration.

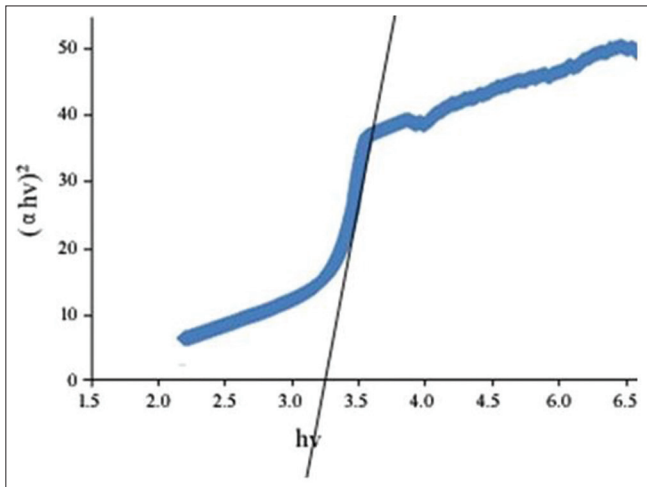


Fig. 11. Analysis of (UVVis-NIR) Spectroscopy of ZnO without surfactant.

at 550°C by extrapolating the graph to X-axis so as to calculate the bandgap of the samples. The bandgap is found to be 3.26 eV, 3.27 eV, 3.24 eV, and 3.21 eV for the samples prepared without surfactant and BAK individually at different concentrations (below, at, and after), respectively.

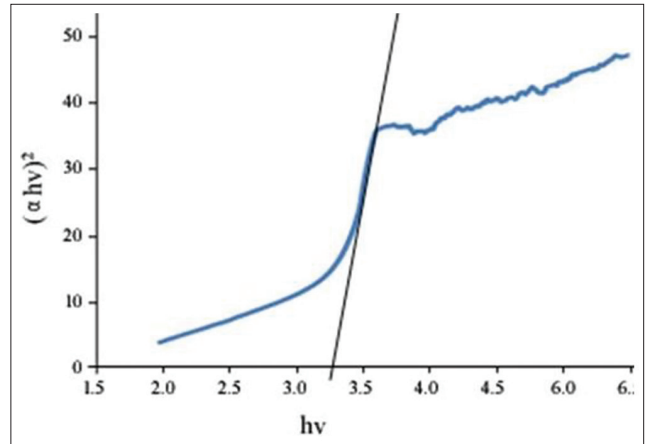


Fig. 12. Analysis of (UVVis-NIR) Spectroscopy of ZnO with benzalkonium chloride below critical micelle concentration.

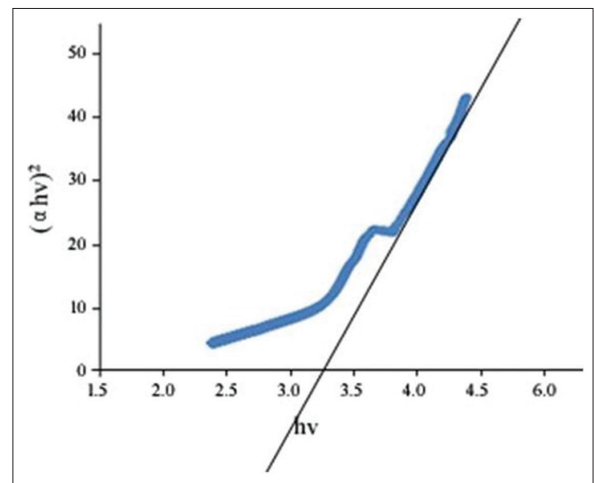


Fig. 13. Analysis of (UVVis-NIR) Spectroscopy of ZnO with benzalkonium chloride at critical micelle concentration.

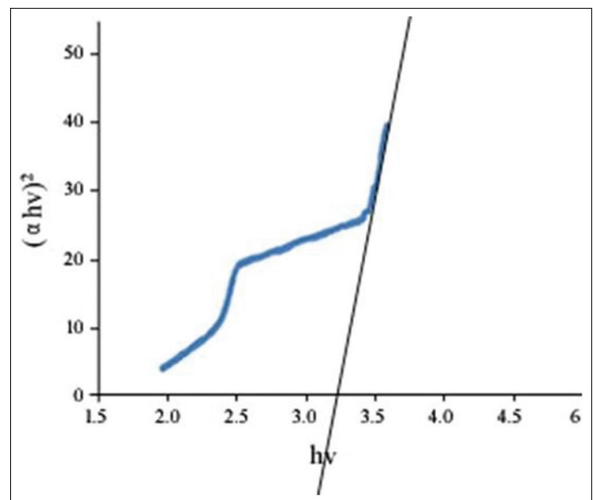


Fig. 14. Analysis of (UVVis-NIR) Spectroscopy of ZnO with benzalkonium chloride above critical micelle concentration.

The bandgap decreases in the presence of BAK surfactant because of its bulky structure which contains 25 carbon atoms in the tails that cause agglomeration [9]. Although the results show two curves, which apparently means impurities presence.

Table 1 reveals a comparison of bandgap energy for each sample:

### 3.4. Analysis of X-ray Diffractometer (XRD)

Fig. 15 shows the XRD patterns of the ZnO nanoparticles calcined at 450°C for 2 h. A study of standard data JCPDS 76-0704 confirms that all the synthesized materials are hexagonal ZnO phase (wurtzite structure). The XRD pattern for the ZnO nanoparticle prepared without surfactant calcined at 450°C for 2 h is shown in Fig. 15. The three highest spectrums were assigned as 100, 002, and 101 matched planes for 2θ values of 31.769, 34.422, and 36.254°, respectively. The calculated average size of the most intense three diffraction spectrums was 76.9 nm.

The XRD pattern of the ZnO nanoparticle prepared with BAK surfactant below CMC calcined at 550°C for 5 h is shown in Fig. 16. The three highest spectrums were assigned

as (100), (002), and (101) matched planes for 2θ values of 31.769, 34.422, and 36.254°, respectively. The structure of synthesized material is hexagonal ZnO (wurtzite structure), according to standard data JCPDS 76-0704. The calculated average size of the most intense three diffraction spectrums was 116.4 nm. Moreover, the structure was hexagonal as the others. On the other hand, Fig. 17 shows the XRD pattern of the ZnO nanoparticle prepared with BAK surfactant at CMC calcined at 550°C for 5 h. The three highest spectrums were assigned as (100), (002), and (101) matched planes for 2θ values of 31.769, 34.422, and 36.254°, respectively. The calculated average size of the most intense three diffraction spectrums was 130.0 nm.

The XRD pattern for the ZnO nanoparticle prepared with BAK surfactant above CMC calcined at 550°C for 5 h is shown in Fig. 18. The three highest spectrums were assigned as (100), (002), and (101) matched planes for 2θ values of 31.769, 34.422, and 36.254°, respectively. The calculated average size of the most intense three diffraction spectrums was 240.0 nm. As its obvious, the particle size of ZnO samples in the presence of BAK increased due to the bulky and hydrophobic bi-tailed structure of BAK. The tail of BAK contains 25 carbon atoms, which cause agglomeration and lead to increase in the particle size [9].

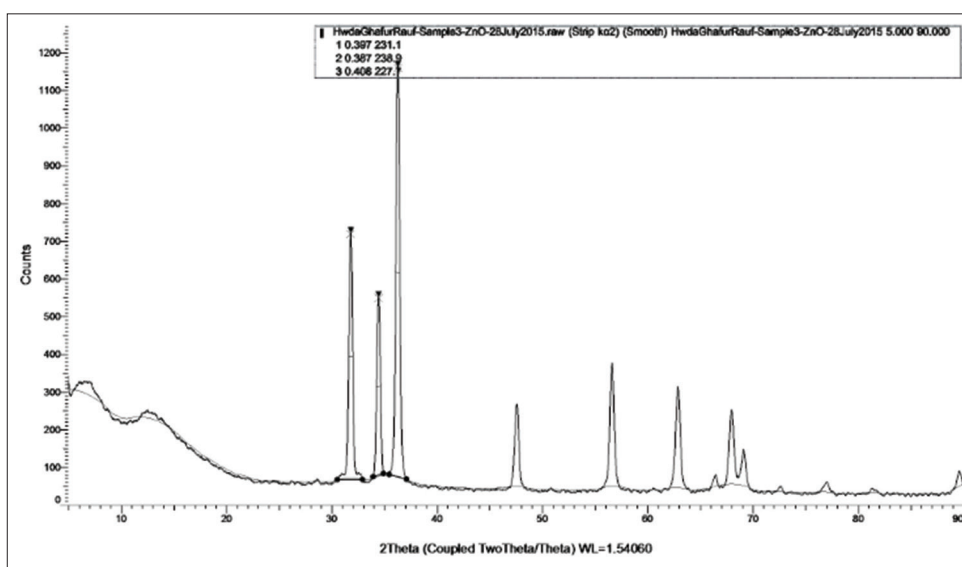
**TABLE 1: Bandgap energy for each sample.**

Status	Bandgap for ZnO: Benzalkonium chloride
Below CMC	3.27 eV
At CMC	3.24 eV
Above CMC	3.21 eV

CMC: Critical micelle concentration, ZnO: Zinc oxide

### 3.5. Analysis of Transmission Electron Microscopy (TEM)

TEM was used to determine the average particle size. The results that obtained by TEM image and TEM particle



**Fig. 15.** XRD diffractogram of zinc oxide nanoparticles without surfactant.

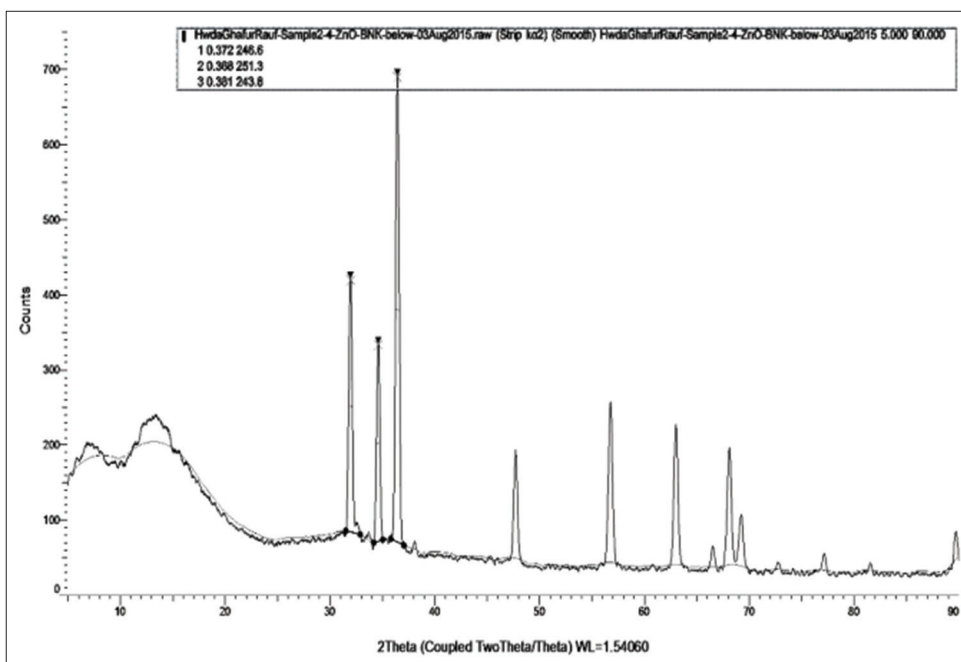


Fig. 16. XRD diffractogram of zinc oxide nanoparticles with benzalkonium chloride Surfactant below critical micelle concentration.

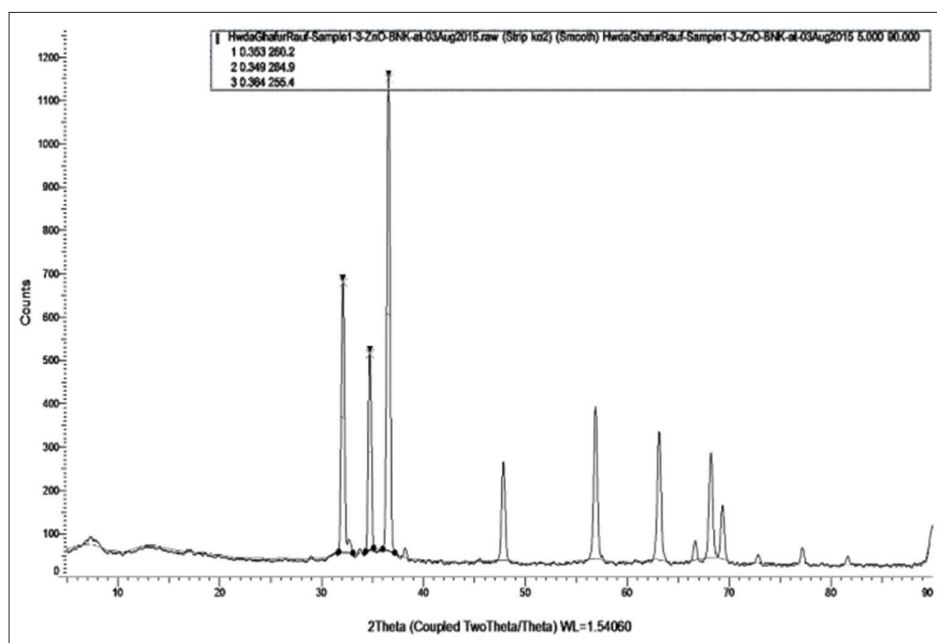
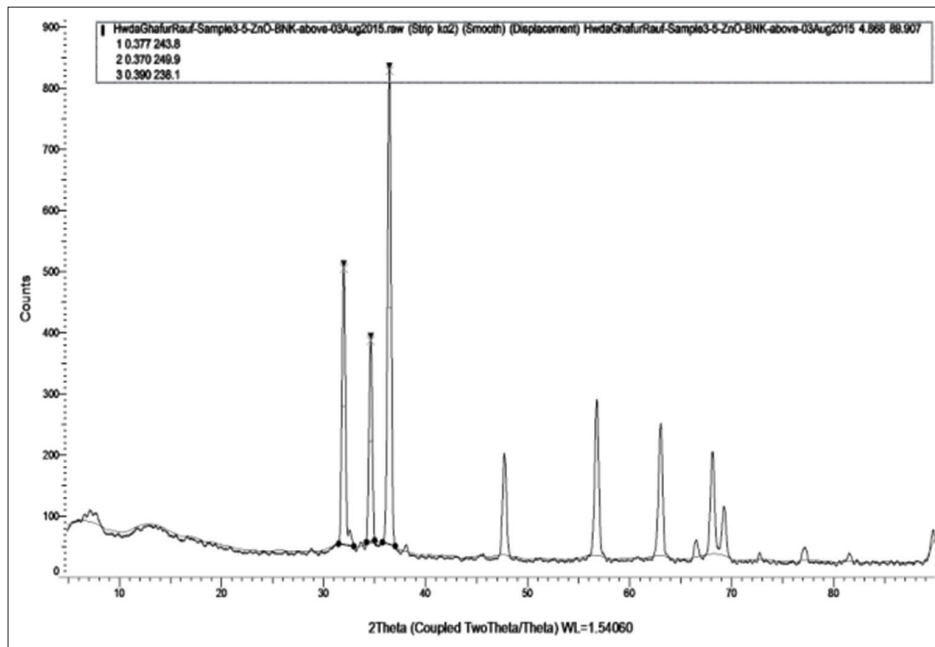


Fig. 17. XRD diffractogram of zinc oxide nanoparticles with benzalkonium chloride surfactant at critical micelle concentration.

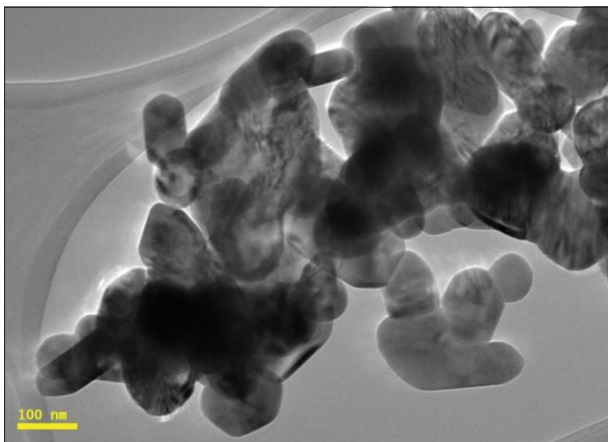
size distribution of the ZnO sample without surfactant were 66 nm, 100 nm for ZnO with BAK below CMC, and 140 nm for ZnO with BAK at CMC, as shown in Figs. 19-24, respectively. As it is been mentioned in the previous investigations, the particle size of ZnO samples in the presence of BAK increased due to the bulky and bi-tailed

structure of BAK. The tail of BAK contains 25 carbon atoms, which causes agglomeration and lead to an increase in the particle size [9].

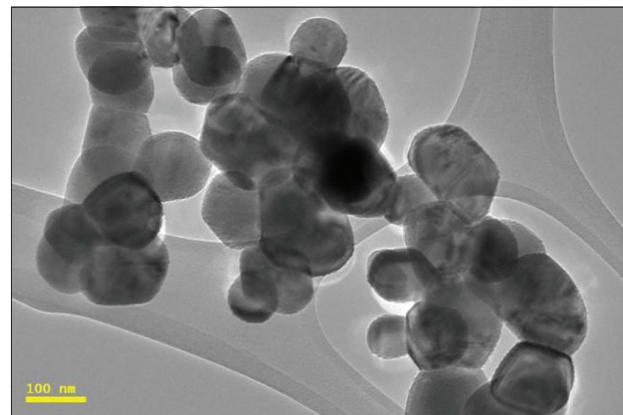
The calculated particle sizes for each sample from XRD, TEM, and SEM are depicted in Table 2.



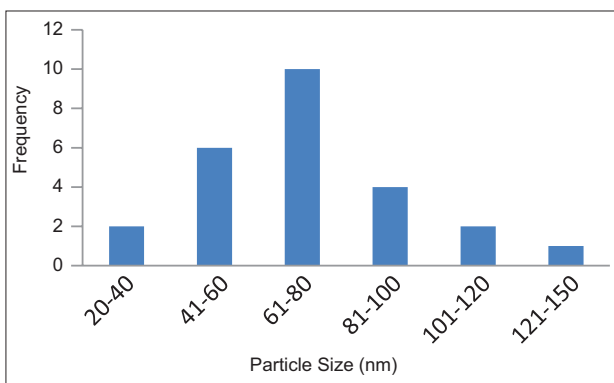
**Fig. 18.** XRD diffractogram of zinc oxide nanoparticles with benzalkonium chloride surfactant above critical micelle concentration.



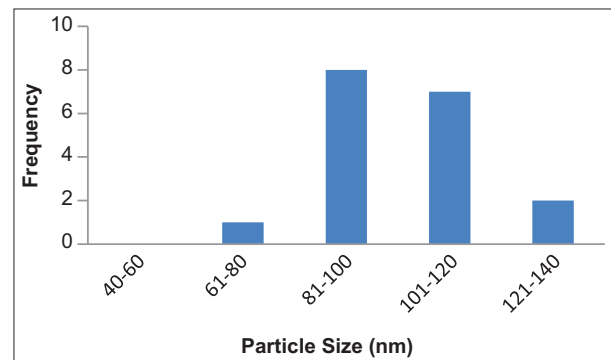
**Fig. 19.** TEM analysis of ZnO without surfactant.



**Fig. 21.** TEM analysis of ZnO with benzalkonium chloride below critical micelle concentration.



**Fig. 20.** Particle size distribution of ZnO based on TEM without surfactant.



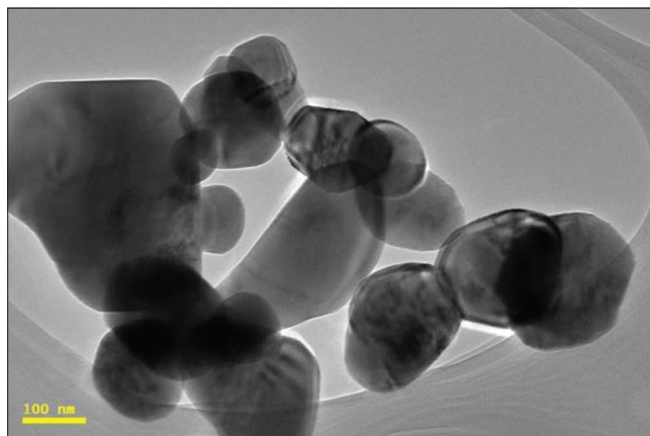
**Fig. 22.** Particle size distribution of ZnO based on TEM with benzalkonium chloride below critical micelle concentration.



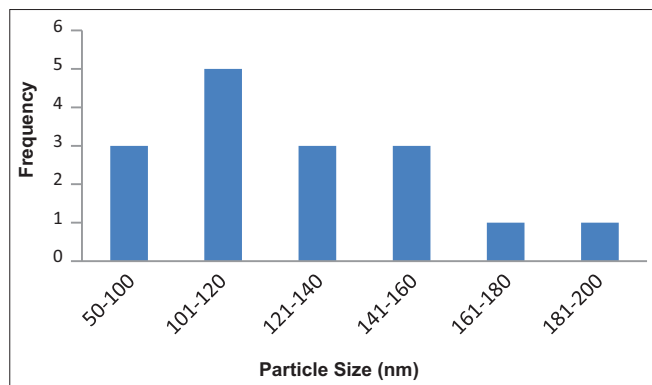
**TABLE 2: Calculated particle sizes for each sample from XRD, TEM, and SEM in different conditions.**

Status	Temperature°C	Average particle size from XRD nm	Average particle size from TEM nm	Average particle size from SEM nm
ZnO without surfactant	500	76.9	66	87
ZnO with BAK below CMC	500	116.4	100	125
ZnO with BAK at CMC	500	130	140	145
ZnO with BAK above CMC BAK	500	240	-	212

BAK: Benzalkonium chloride, ZnO: Zinc oxide, CMC: Critical micelle concentration, TEM: Transmission electron microscopy, SEM: Scanning electron microscope



**Fig. 23.** TEM analysis of ZnO with benzalkonium chloride at critical micelle concentration.



**Fig. 24.** Particle size distribution of ZnO based on TEM with benzalkonium chloride at critical micelle concentration.

## 4. CONCLUSION

In this paper, sol-gel method was used to synthesize ZnO with controllable particles. Afterward, three samples of ZnO nanoparticles were synthesized with and without surfactant, to study the influence of BAK as cationic surfactants on properties of ZnO nanoparticles such as particle size, morphology, and bandgap energy [2]. Although this agglomeration can be counted on to prevent toxicity

of nanoparticles, especially in cosmetic products as zinc oxide is widely used such as sunscreen or industrial factories like paint factories [3]. Nanoparticles recently conceded to be dangerous, both medically and environmentally [4]. In fact, It has the ability to make the particles very reactive or catalytic because it has a high surface [5]. They are also capable of harming cell membranes in organisms and biological systems [6]. However, if the particles are larger in size, they are unlikely to harm the cell nucleus and other internal cellular components due to the particle agglomeration [7].

Lung inflammatory and systemic activity can be noticed in experimental animals when they inhaled ultrafine particles unlike an equal mass of larger particles, which they may also affect adult human subjects [8].

TEM, SEM, FTIR spectroscopy, X-ray diffraction (XRD), and UV-visible spectroscopy were used to characterize the structure, morphology, and size of the synthesized ZnO nanoparticles. The surfactants create their own interface and form micelles at CMC [13]. Under these conditions, there would be micelle formation in the bulk phase and surfactant-coated nanoparticles formed start to decrease by increasing surfactant concentration beyond the CMC point [14].

Moreover, with the addition of BAK surfactant, the particle size of all the samples starts to increase due to the bulky hydrophobic part and carbon number in the structure of BAK which is for both tails is 25, which causes agglomeration [9].

The XRD patterns of the ZnO nanoparticles; based on the study of standard data JCPDS 76-0704 confirm that all the samples of synthesized ZnO are hexagonal (wurtzite structure). On the other hand, UV-Vis-NIR result revealed that the bandgap value for ZnO without any surfactant was 3.26 eV while with BAK at the same point was 3.24 eV.

## 5. ACKNOWLEDGMENTS

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## 6. FUNDING

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## 7. COMPETING INTEREST

The authors declare that they have no competing interest.

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