International Journal of Veterinary Sciences and Animal Husbandry

ISSN: 2456-2912
VET 2023; SP-8(4): 67-70

www.veterinarypaper.com
Received: 03-04-2023
Accepted: 07-05-2023

Somveer
Ph. D Scholar, Dairy Engineering, ICAR-National Dairy Research Institute, Karnal, Haryana, India

F Magdaline Eljeeva Emerald
Principal Scientist, Dairy Engineering, ICAR-National Dairy Research Institute, Karnal, Haryana, India

Kumari M
Teaching Associate, Dairy Engineering, CoDS&T, RAJUVAS, Bikaner, Rajasthan, India

Shivananda
Ph. D Scholar, Dairy Engineering, ICAR-National Dairy Research Institute, Karnal, Haryana, India

Corresponding Author:
Somveer
Ph. D Scholar, Dairy Engineering, ICAR-National Dairy Research Institute, Karnal, Haryana, India

Storage study to examine the changes in optical properties of ZnO nanoparticles

Somveer, F Magdaline Eljeeva Emerald, Kumari M and Shivananda

Abstract
Ensuring the optimum storage conditions for nanoparticles (NPs) is crucial for their successful utilization and shelf-life determination. In this research, freshly synthesized zinc oxide (ZnO) NPs were subjected to a 6-months storage study under air-tight conditions at room temperature and pressure to investigate the effects of storage period and conditions on their properties. UV-visible spectroscopy was employed to characterize the ZnO NPs for changes in purity, stability, agglomeration, and optical properties. A maximum absorption peak at 381 nm in the UV-visible spectra confirmed the presence of ZnO NPs. Absence of major peaks in the range of 300-450 nm affirmed the purity of ZnO NPs, indicating the absence of impurities. A red-shift in the UV-visible spectra indicated agglomeration of NPs over the storage period. A significant 29.8% reduction in the energy band gap value was observed in stored ZnO NPs compared to freshly synthesized ones (3.25 eV). This reduction in the energy band gap value inferences an increase in the size due to the agglomeration of NPs during storage.

Keywords: Nanoparticles, UV-visible spectroscopy, energy band gap, agglomeration, LSPR

1. Introduction
Metallic nanoparticles are now widely used in almost every field of science and engineering to solve a number of global problems, such as infectious diseases, food packaging, climate change, agriculture, and environmental pollution because of their extraordinary physical and chemical characteristics (Morphology, size, shape, dispersibility, etc.) (Nguyen *et al*., 2022) [6]. Metal oxide nanomaterials, more especially ZnO-NPs, are a class of extremely useful and functional inorganic chemicals. They have special physical and chemical properties, which justifies this. These nanoparticles have great photostability, a high electrochemical coupling coefficient, a broad radiation absorption spectrum, and exceptional chemical stability. They have the chemical formula ZnO, which specifies their molecular composition (Agnieszka and Jesionowski, 2014) [1]. Zinc oxide nanoparticles are semiconducting metal oxide nanoparticles that have a wide range of uses in solar selective materials, sensors, catalysis, and other fields (Jamdagni *et al.,* 2018) [3]. The ZnO NPs are generally characterized for their purity, stability, optical properties using UV-visible spectroscopy.

2. Methodology
2.1 Procurement and storage
Freshly prepared ZnO nanoparticles were taken. The ZnO NPs were stored at optimum conditions in airtight plastic bottle at room temperature and pressure (Figure 1). The following study was aimed to investigate any change in optical energy absorbance, absorption coefficient and energy band gap over a storage period of 6 months

2.2 Sample preparation for UV-Visible spectroscopy
A high-shear homogenizer operating at 10,000 rpm for 10 minutes was used to dissolve 5 mg of ZnO NPs in 250 mL of Milli-Q water to provide the initial solutions for UV-visible spectroscopy analysis. A precise 3 mL of this homogenised stock solution was taken, and Milli-Q water was used to dilute it to a volume of 10 mL. The UV-visible double beam spectrophotometer (Model: UV 3600, Shimadzu, Kyoto, Japan) was used to analyse the UV-visible absorption spectrum and peak absorption wavelength from this standard solution after it was thoroughly stirred.

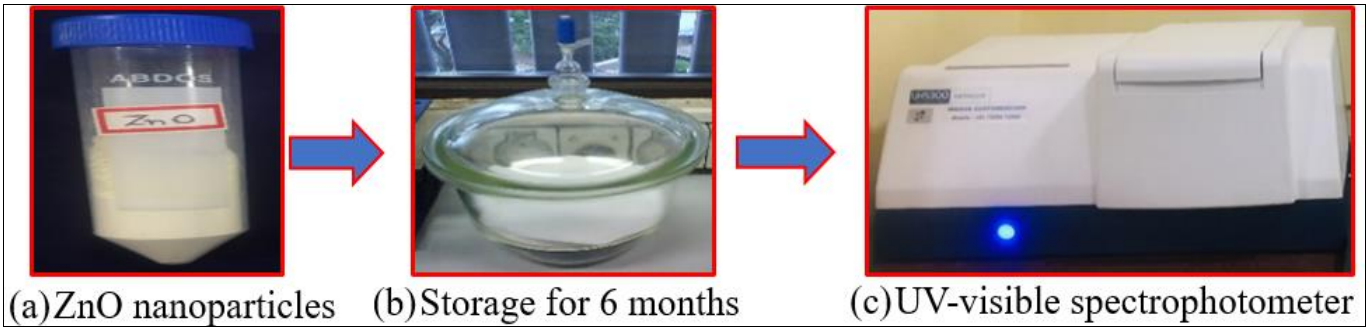

Fig 1: Storage and UV-visible spectroscopy characterization for ZnO nanoparticles

2.3 Equations and formulas for analysis

The frequency (v) and wavelength (λ) of the radiation causing an electronic transition are related to the energy absorbed (E) as expressed in equation 1.

$$\Delta E = h\nu = \frac{hc}{\lambda} \quad (1)$$

Where, 'h' is Plank's constant (6.62610^{-34} Js), 'c' is velocity of light (3×10^{8} m/s), 'λ' is wavelength of light (nm), and 'ΔE' is the amount of energy absorbed during electronic transition in a molecule. Energy band gap (E_g) was calculated using the Tauc equation, and the Tauc relation was expressed in terms of photon frequency (v), absorption coefficient (α), and Planck's constant (h) (6.62610^{-34} Js) in equation 2.

$$\alpha h\upsilon = B(h\upsilon - E_g)^n \quad (2)$$

Where, 'B' is equation constant, 'n' is the factor that depends on electron transmission. For direct energy band gap, the value of 'n' is 2, while for indirect energy band gap, 'n' is ½. The absorption coefficient (α) was determined using the following equation 3.

$$\alpha = 2.303\frac{a}{t} \quad (3)$$

Where, 'a' is absorbance (a.u.) and 't' is the thickness of cuvette (10^{-2} m). The energy band gap was computed from equation 4.

$$E_g = \frac{hc}{\lambda} \quad (4)$$

The above-mentioned parameters were calculated and discussed in next section.

3. Results and Discussion

The UV-visible absorption spectra of ZnO NPs, which confirms their presence is illustrated in figure 2. The absorption band between 300-800 nm with a maximum edge at 381 nm indicates the presence of ZnO NPs after storage period of 6 months. Additionally, the absorption peak from 300-450 nm further confirms the presence of ZnO NPs, while the absence of any other major peak in the UV-visible spectra confirms the purity of NPs even after 6 months of their synthesis. The obtained results were in accordance with the findings of Ali *et al.* (2019) [2]. Mohammadi and Ghasemi (2018) [5] observed absorption peak at 378 nm for freshly synthesised ZnO NPs using green synthesis approach. Mahmood *et al.* (2022) [4] noted that UV-visible absorption spectra peak for ZnO NPs was at 376 nm.

In present study, a little red shift in UV-visible spectra was noticed for ZnO NPs after their storage at room conditions for 6 months. The observed red shift in the UV-visible spectra after 6 months of storage of ZnO NPs is probably caused by aggregation or particle growth. Over time, smaller nanoparticles can come together to form larger clusters, resulting in agglomeration or coalescence of NPs. As a result, the localized surface plasmon resonance (LSPR) of the NPs undergoes a red shift in the UV-visible spectra, leading to a shift towards longer wavelengths. This can also be attributed to their lower band gap energy compared to smaller nanoparticles. The band gap energy of the nanoparticles is directly related to their size, and as they aggregate and increase in size, the wavelength required for absorption also increases (Ali *et al.*, 2019) [2]. Another potential reason for the red shift is the oxidation of the NPs. When exposed to air and various environmental factors, the NPs can undergo surface oxidation, which alters their optical characteristics. This oxidation is associated with a shift in the LSPR peak towards longer wavelengths, resulting in a red shift in the UV-visible spectra.

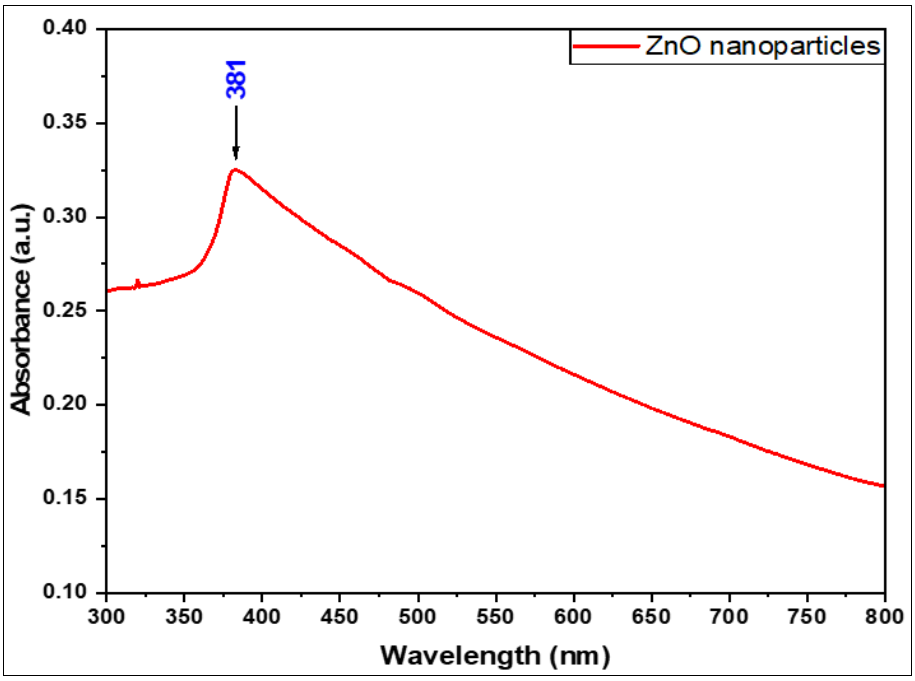

Fig 2: UV-visible Spectrum of ZnO Nanoparticles after 6 months storage study

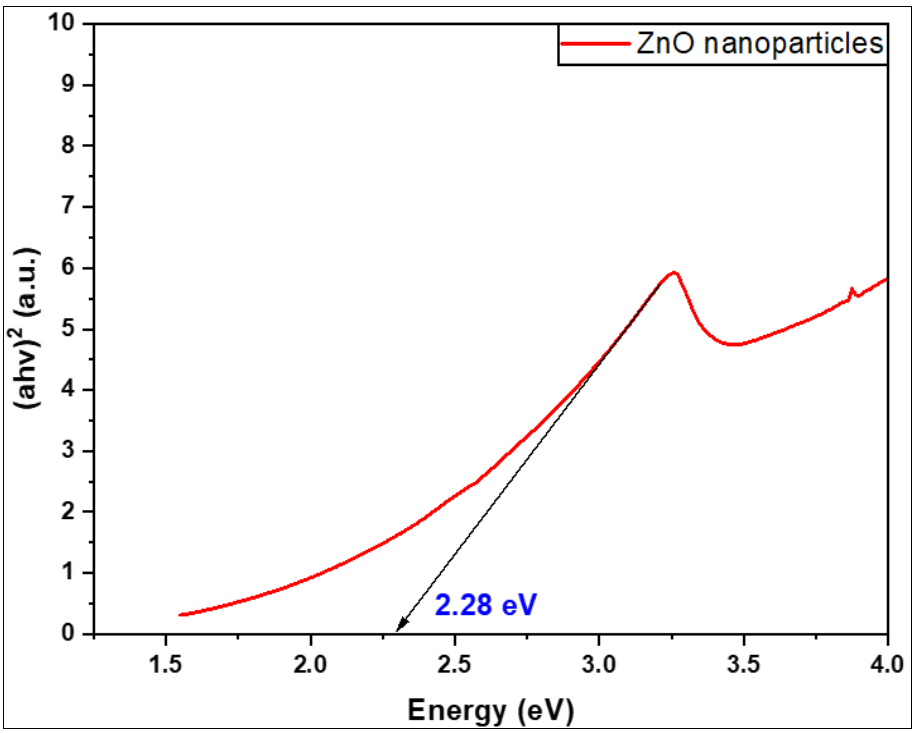

Fig 3: Tauc Plot of ZnO Nanoparticles after 6 months storage study

Figure 3 depicts the Tauc plot, which illustrates the relationship between the square of the absorption coefficient multiplied by the incident photon energy $[(\alpha h\nu)^2]$ and the incident photon energy($h\nu$). A linear regression analysis was conducted to determine the linear portion of the squared absorption coefficient $[(\alpha h\nu)^2]$, which was then adjusted to zero. By employing Equation 2, the energy band gap of ZnO nanoparticles was calculated to be 2.28 eV. The obtained value of energy band gap of ZnO NPs after storage was lower than the value obtained by Yuwono *et al.* (2016) [9] for freshly synthesised ZnO NPs (3.25 eV). Wang *et al.* ((2009) [8] and Schmidt-Mende and MacManus-Driscoll (2007) [7] also observed the energy band gap of 3.3 eV for ZnO NPs. In the present study, the obtained results from UV-visible spectra and the calculated energy band gap value are in good agreement with each other. The reduction in energy band gap and red-shift in UV-visible spectra indicate towards agglomeration of ZnO NPs during storage period.

4. Conclusive remarks and future aspects

Nowadays, storage of NPs at optimum conditions has become need of the hour for their proper utilization and shelf-life determination. So, to determine the effects of storage period and conditions on the properties of NPs, the freshly synthesised ZNO NPs were taken and kept for storage study of 6 months under air-tight conditions at room temperature and pressure. After this, the ZnO NPs were characterized for any change in their purity, stability, agglomeration and optical properties using UV-visible spectroscopy. The key findings of the present study are listed below:

1. The maximum absorption peak obtained at 381 nm in the UV-visible spectra confirmed the presence of ZnO NPs in the sample.
2. The absence of any other major peak in the range of 300-450 nm indicated the absence of impurity and affirmed the purity of ZnO NPs.
3. The maximum absorption peak showed a red-shift in the UV-visible absorption spectra, which was due to the agglomeration of NPs over the time of storage.
4. The energy band gap of ZnO NPs was obtained as 2.28 eV, using Tauc relation (Eq. 2).
5. There was 29.8% reduction in energy band gap value of stored ZnO NPs when compared with the freshly synthesised ZnO NPs (3.25 eV) (Yuwono *et al.*, 2016) [9].
6. This reduction in energy band gap value could be due to increase of size of NPs during storage period.
7. The red shift obtained by UV-visible absorption spectra and the value obtained for energy band gap (2.28 eV) supported each other and showed agglomeration of NPs, leaded to their increased size, when compared with the literature studies.

The findings of present study can be forwarded by analyzing the stored ZnO NPs for particle size using SEM-EDS. All the possible changes in structure, composition, size etc. for stored NPs should be studied well so as to design proper storage conditions for their enhanced shelf-life and fields of applications.

Acknowledgment
The authors acknowledge the support from the Department of Dairy Engineering, ICAR-National Dairy Research Institute, Karnal (Haryana) and the facilities provided at CeNSE, Indian Institute of Science, Bengaluru, funded by Ministry of Education (MoE), Ministry of electronics and Information technology (MeitY) and Nano-mission, Department of Science and technology (DST), Govt. of India.

References

1. Agnieszka K.-R, Jesionowski T. Zinc Oxide-From Synthesis to Application: A Review. Materials. 2014;7:2833-2881.
2. Ali S, Khan T, Khan M, Khan R, Hussain S. Morphological structural and energy storage based study of MoS_2/ZnO nanocomposite. Materials Research Express. 2019;6(12):125087.
3. Jamdagni P, Khatri P, Rana JS. Green synthesis of zinc oxide nanoparticles using flower extract of Nyctanthes arbor-tristis and their antifungal activity. Journal of King Saud University-Science. 2018;30(2):168-175.
4. Mahmood A, Munir T, Fakhar-e-Alam M, Atif M, Shahzad K, Alimgeer KS, *et al*. Analyses of structural and electrical properties of aluminium doped ZnO-NPs by experimental and mathematical approaches. Journal of King Saud University-Science. 2022;34(2):10-17.
5. Mohammadi FM, Ghasemi N. Influence of temperature and concentration on biosynthesis and characterization of zinc oxide nanoparticles using cherry extract. Journal of Nanostructure in Chemistry. 2018;8(1):93-102.
6. Nguyen NTT, Nguyen LM, Nguyen TTT, Tran UP, Nguyen DTC, Van Tran T. A critical review on the bio-mediated green synthesis and multiple applications of magnesium oxide nanoparticles. Chemosphere, 2022, 137301.
7. Schmidt-Mende L, MacManus-Driscoll JL. ZnO-nanostructures, defects, and devices. Materials Today. 2007;10(5):40-48.
8. Wang XC, Chen XM, Yang BH. Microstructure and optical properties of polycrystalline ZnO films sputtered under different oxygen flow rates. Journal of Alloys and Compounds. 2009;488(1):232-237.
9. Yuwono AH, Kurniawan D, Sofyan NBI, Ramahdita G, Sholehah A. Effect of pressure in post-hydrothermal treatment on the nanostructural characteristics of ZnO nanoparticles. International Journal of Technology. 2016;7(3):424-430.