



Formation of ZnO nanoparticles in the presence of Tannic acid

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ABSTRACT

Zinc Oxide nanoparticles (ZnO NPs) have received abundance attention due to their ability to provide as a good semiconductor and UV absorbance materials. In this research, ZnO NPs are synthesised by hydrothermal method which employed a green synthesis method of which fully assisted by the Tannic Acid (TA). The controllable morphologies and mean sizes of ZnO NPs are observed to increased due to aggregation that occurred due to the influence of acidic medium (TA molecule). The morphological properties are discussed based on the TEM and FESEM images which indicated the average size of 14 nm and 32.7 nm for ZnO NPs and ZnO-TA NPs obtained, respectively. Meanwhile, the optical properties are discussed based on the UV-Vis absorbance spectroscopy results. The UV absorbance performance showed the behavior of absorbance peak at shorter wavelength as the ZnO NPs are capped with TA. The absorbance peak is shifted from UV-A region to UV-C region which indicated the transition from ZnO NPs to ZnO-TA respectively.

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1. Introduction

Zinc Oxide nanoparticle had gained huge attention of interest in contemporary research due to its unique structure and properties. Particularly, the superior performance of ZnO NPs in detecting Ultraviolet (UV) ray had gained a huge potential in development of semiconductor-and LEDs- based materials [1,2]. The ability of ZnO NPs in photonic and electronic material (semiconductor) is due to its large excitonic energy (~60 meV) and wide direct band gap (3.37 eV) which makes it able to be involved in various applications in optoelectronic research and technologies [3–6]. The wide bandgap of ZnO NPs raised up by tiny size group of ZnO NPs (average diameter less than 100 nm) is important to be considered as functional material for effective UV absorber which exhibits optical transparency in the range of 400 to 700 nm wavelengths. Besides, few previously reported research erect the biocompatible ability of ZnO NPs which can be applied without coating together to inhibit microbial growth and is indexed as a

generally recognized as safe (GRAS) material by the U.S. Food and Drug Administration [6–10].

The most common method in synthesizing nanoparticles are wet chemical, hydrothermal, sol-gel and green synthesis method [11,12]. Herein, for the synthesis of ZnO NPs, the hydrothermal method in the presence of stabilizing agent of Sodium Tri-citrate which resembles a green synthesis method with the usage of green reductant chemical, Tannic Acid (TA) were employed. The combination of both hydrothermal and green synthesis method is well accepted through many research due to its beneficial as cost-effective and ecologically method in synthesizing ZnO NPs [12–15]. Basically, the green synthesis method approach is by manipulating reagents from natural resources such as glucose, plant extracts and biodegradable polymers as capping agents [16] and in the present work, TA is used as both the capping agent and second size influencer. TA has been proved to influence the synthesis of metal size [13,17]. The previous study has been shown to produce ZnO NPs excellent properties with sizes in the range of 23 to 48 nm [18–21].

The purpose of this study was to synthesize smaller size (average diameter less than 20 nm) of ZnO NPs in the aid of TA as both

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the size influencer and capping agent. Noted that the formation of ZnO NPs at the initial stage plays a crucial stage in the final product formation. The smaller the size of ZnO NPs obtained, the better the optical properties performance. The novelty of this research is to monitor the influenced of TA to the aggregation level of the as-synthesised ZnO NPs.

2. Materials and characterisation

Materials: All materials were purchased from the commercial market with high purity (95%) and used without further purification. Zinc powder (Zn) and Trisodium Citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) as the starting materials, Tannic Acid ($\text{C}_{76}\text{H}_{52}\text{O}_{46}$) as capping agent and distilled water as dispersing solvent were used to prepare ZnO nanoparticle.

Preparation of ZnO nanoparticles: 0.4 g of ZnO powder is diluted in 100 ml of distilled water in a beaker. After the ZnO powder is completely dissolved, 0.2 g of Trisodium Citrate is added and stirring is continued. As both are dissolved, the mixture is then placed on a heated plate and stirred continuously with a heated temperature of 70 °C for 1 h and 30 min. Upon the process, the beaker is then left cooled in open air, which helps in terminating the regrowth of ZnO NPs. The mixture is then separated into two sample vials with volume of 3 ml which one of the samples remains pure and another sample is then added with 0.4 M tannic acid accordingly before shaken well. The mixture of the solution is then centrifuged to evacuate surfactant and other impurities.

Characterization methods: The optical properties of the ZnO NPs were characterised using a UV–vis spectrometer in the range of 200 to 800 nm, which works at the visible light spectrum that was dispersed in a distilled water base and placed in a small cuvette. Whilst, the morphological structure of the synthesised ZnO NPs is characterized by Transmission electron microscope (TEM) and of Field Emission Scanning Electron Microscope (FESEM).

3. Results and discussion

FESEM and TEM images of as-synthesized ZnO NPs without the TA is shown in Fig. 1. It can be observed that the ZnO NPs diameter range is within 11.2 nm to 16.8 nm. This was confirmed by the nature of the structure shown in FESEM images where the morphology of nanoparticles are in irregular morphology with most of them are in the shape of nano-rod like with the smallest diameter range is less than 20 nm. From the average size distribution plotted in Fig. 2 (a) 25% frequency of ZnO NPs attributed to the measurement of NPs with the size range of 11 nm to 15 nm. Thus, this followed with the second-highest attribution of 16.8% of ZnO NPs size

in range of 6 nm to 10 nm and 16 nm to 20 nm. The Trisodium Citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) which added during the synthesis is to help in stabilizing the ZnO NPs which is then prevent the nanoparticles from aggregated and agglomerated. Meanwhile, it is known from the literature that the ZnO NPs which is coated with citrate have lower wavenumber vibration for Zn–O–Zn bond present [22]. Thus, the citrate ions present prevent the growth of nanoparticles and further halt it from attracted and binding which then caused them to remains in the nano-size structure [23].

To monitor the yield level of ZnO NPs, the NPs are synthesised with the presence of TA with different TA concentration ranging from a very high concentration (pH acidic medium (pH 3)) to a very low concentration. The morphological structure of ZnO NPs capped with TA are shown in Fig. 3. From Fig. 3, the range of ZnO NPs size increases with the average diameter is in between 27.3 nm and 36.4 nm (spherical in shape) which then inclined to attached towards each other. From the size distribution plotted in Fig. 2 (b), most of the ZnO-TA NPs are measured in range of 26 nm to 30 nm and 31 nm to 35 nm which both contributed to the 22.3% of frequency in TEM image characterisation. As observed from Fig. 2, it could be monitored that the binomial of the graph is shifted to the right as TA are added to the ZnO, this indicated that the size of ZnO-TA NPs is slightly bigger as compared to the pure ZnO NPs. This occurred due to aggregation that took place due to the very strong acidic medium of TA. Rapid adjustment of pH caused advance formation of acidic environment which enhanced nanoparticle agglomeration and aggregation [24]. Instead, with further addition of TA, the ZnO NPs synthesised showing great morphological performance with further reductant in nanoparticle size which yield smaller nanoparticle size with the size less than 50 nm as found in previous research [18,25–28]. Generally, the NPS structure is well known to be synthesised at high temperature as it is the optimum temperature to breakdown the ZnO bond and triggered it to smaller nanoparticle size which results into NPs with diameter ranging to 50 nm [20,29]. In the present, the ZnO NPs are synthesised at 70 °C which is merely close to the optimum temperature range of 80 °C to 100 °C.

The UV–Vis spectrum determined the relation of the morphology of ZnO NPs which attributed to the absorbance at different bands that exist at various frequencies. Fig. 4 indicated that the absorbance spectrum by ZnO NPs and ZnO-TA NPs under reaction temperature of 70 °C. As plotted in Fig. 4, the peaks for both pure ZnO NPs and ZnO-TA NPs are observed to be below 400 nm (green region) which indicated the region of UV radiation wavelength. Noted that, the UV radiation is subdivided into UV-A, UV-B and UV-C which having peak within range of 315 nm to 400 nm, 280 nm to 315 nm and 100 nm to 280 nm, respectively [30]. For

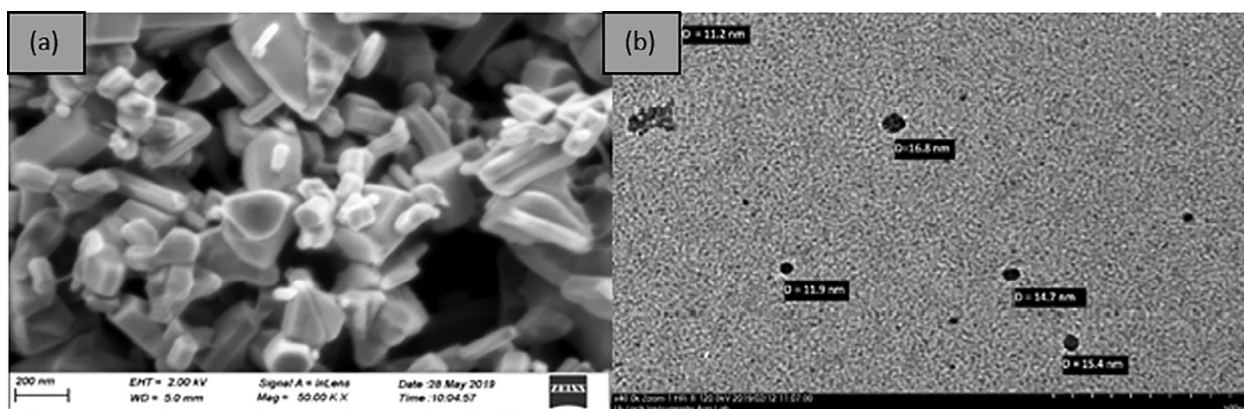


Fig. 1. (a) FESEM and (b) TEM image of ZnO NPs synthesised without TA.

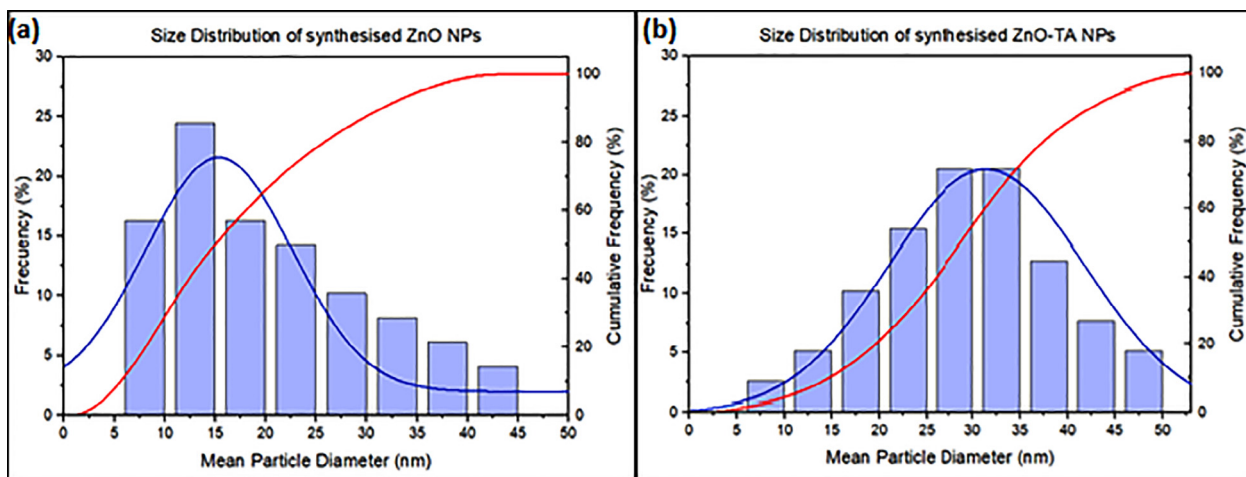


Fig. 2. Particle Size distribution of (a) ZnO NPs and (b) ZnO-TA NPs.

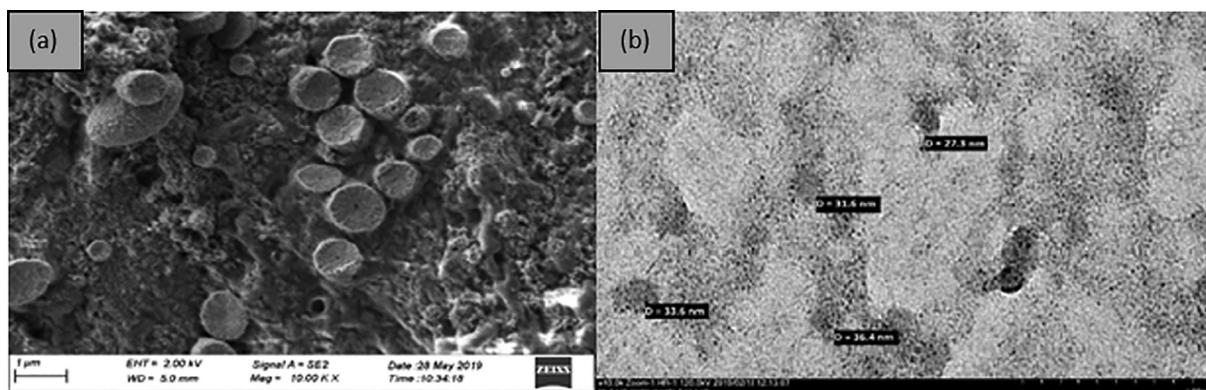


Fig. 3. (a) FESEM and (b) TEM image of ZnO NPs synthesised with presence of TA.

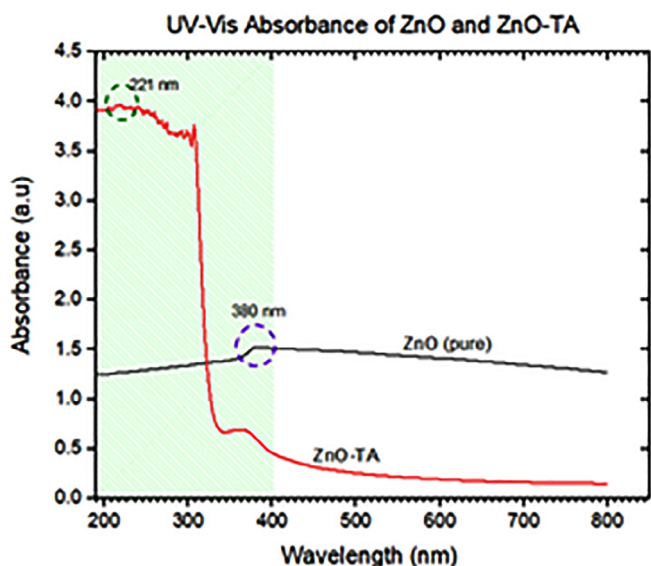


Fig. 4. UV-Vis Absorbance spectrum of ZnO NPs and ZnO-TA NPs.

pure ZnO NPs, the curve indicated the peak absorbance position at 380 nm which signifies to the electron transitions from the valence of intrinsic band-gap of ZnO [31–33]. As TA are capped around the ZnO nanoparticles, the UV absorbance peak is shifted following the

peak absorbance of TA (300 nm). Thus, it results in a peak with shorter wavelength. From the peak (wavelength number) of the curve, the produced ZnO NPs absorbance peaks at UV-A range which majorly known caused the skin damage to human [34]. While from Fig. 4, ZnO-TA NPs having peak absorbance at 221 nm which is proved to be far shifted from pure ZnO NPs. The performance of ZnO NPs is enhanced by capping with TA. The acidity of TA reacts with the ZnO during hydrothermal synthesising which effecting the structure and reactivity of the nanoparticle and shifted the absorbance to shorter wavelength [35,36].

4. Conclusions

In conclusion, the reported study presented that ZnO NPs can be produced through simple hydrothermal method and further addition of high concentration of mild acid TA would result in the aggregation of the as-synthesised ZnO NPs. Both pure ZnO NPs and ZnO-TA NPs showed diameter size smaller that is smaller than 50 nm as compared to other existing literatures works. The pure ZnO NPs resulted in hexagonal morphological structure with the average diameter range of 11 nm to 15 nm while the ZnO-TA NPs formed a nano-sphere morphological structure with the average diameter size range of 26 nm to 34 nm. Instead, The optical performance for ZnO-TA NPs are better as compared to pure ZnO nanoparticles as it able to absorb UV ray at shorter wavelength. Again, the advantages of green synthesis of ZnO with TA is, it was chemical-free and eco-friendly as TA is a harmful mild acid

that was eco-friendly. Thus, TA-ZnO NP is better than ZnO NP because of the better UV absorption.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: This work was fully financially supported by the Internal Grant RDU1703152 and RDU190360 of Universiti Malaysia Pahang, Malaysia.

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