Characterization of ZnO Nanoparticles Prepared from Green Synthesis Using Euphorbia Petiolata Leaves

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Abstract: This investigation is one of the early studies for preparation of zinc oxide (ZnO) nanoparticles from green synthesis utilizing Euphorbia petiolata leaves, which are collected from Kurdistan region in Iraq, as a reducing and stabilizing agent throughout an easy and green synthesis method. The chemical interaction of Euphorbia petiolata leaves extract with the aqueous mixture of zinc nitrate and the oxidation through galvanizing process professionally produced the reduction of the zinc ions and creation of zinc oxide nanoparticles. The steadiness, cleanliness and crystalline nature of green synthesized nanoparticles were verified by means of UV-vis spectroscopy, EDAX and XRD procedures. UV-vis spectroscopy of prepared zinc colloidal solution displayed absorption maxima at 360 nm. XRD analysis revealed that Zn nanoparticles approve the hexagonal-wurtzite construction with a typical particle size of 55-60 nm. Likewise, the pattern of promising process result in creation of nanoparticles was explained. The important advantages of this process are: short reaction-time, fast, distinct stage, environmentally friendly synthesis of the ZnO nanoparticles, removal of harmful ingredients, and reproducibility of the process.

Keywords: Green Synthesis Nanoparticles, ZnO Nanoparticles, Euphorbia Petiolate

1. Introduction

The research field of nanotechnology is one of the greatest energetic investigations in recent materials science. Recently, green synthesis of metal oxide nanoparticles is a remarkable subject of the nanoscience (Kharissova, Dias, Kharisov, Pérez, & Pérez, 2013). Therefore, nanomaterials have been receiving cumulative consideration as a result of their prospective requests in numerous different fields for instance coatings, catalysts, sensors, magnetic data storage, solar energy procedures, Ferro fluids, cell classification, extraordinary drug transfer arrangements, etc. (Nasrollahzadeh, Sajjadi, Maham, Sajadi, & Barzinjy, 2018; Byrappa, Ohara, & Adschiri, 2008; Nagarajan, 2008; Lohse & Murphy, 2012). Nanomaterials can be categorized into a collection transitional between molecules and bulk materials with sizes of the order of $10^{-9}$ m (nm). This leads to having physical and chemical characteristics dissimilar from that of molecules and bulk materials despite the fact the constituents are equivalent (Sattler, 2016).
Nanoparticles (NPs) are generally well-defined along with their dimension. Bulk materials, in general, possess permanent physical properties regardless to their dimension. Conversely, NPs might possess the identical physical characteristics than that of bulk materials. Quantum dots are denoted as nanoparticles in the situation of semiconductors which possess quantum confinement characteristics. Nano-clusters, on the other hand, are similarly nanoparticles whose dimension ranges between 1 and 10 nm with a thin dimension circulation which continuously display the consequence of the quantum confinement. Generally, semiconductors possess a nonzero, tiny, band gap (Naito, Yokoyama, Hosokawa, & Nogi, 2018).

The semiconductor materials display the similar physical characterization regardless of their dimensions above a specific value entitled the edge value for that material. Below this edge the band-gap of the semiconductor materials increases with decreasing their sizes. For instance, in ZnO quantum particle thin films, the band gap rises with a reduction of the particle dimensions, and the improvement of the band-gap is important when the particle dimensions are smaller than 3 nm (Bergman & McHale, 2016).

The reduction in dimensions improves the surface area compared with the volume. This causes an upsurge in surface particles, which has a durable effect on the electrical and magnetic characteristics of the materials (McFarland, 2018). Throughout the past three decades, the synthesis of II-VI semiconductor NPs has accomplished a massive progress, to the point where the available material associated with the subject matter has become almost uncontrollable (Schmid, 2011). Recently, II-VI semiconductor NPs have been extensively studied for their applications in displays, high-density storage devices, photovoltaics, biological labels, etc. (Kumar & Nann, 2006; Tomashyk, 2015). Zinc oxide NPs possess extraordinary catalytic competence, robust adsorption capability, great isoelectric point, bio-compatibility, and fast electron transfer kinetics for bio-sensing drives (Ansari, Alhoshan, Alsalhi, & Aldwayyan, 2010; Yang, 2015).

Enhancing the emission properties of the wide band gap for the II-VI semiconductor materials is one of the desired properties. This is due to the growing request for high illumination light sources operating in the UV region. ZnO has a wide band-gap among the II-VI semiconductor materials. Accordingly, ZnO is one of the greatest talented nominees for the UV-emitter requests as a result of its wide band gap of ~3.37 eV, at room temperature, and an extraordinary exciton-binding-energy of 60 meV (Janotti & Van de Walle, 2009). An equivalents system to ZnO is GaN, a wide band gap of GaN is ~3.4 eV, at room temperature. GaN is extensively utilized for green, blue, UV, and white light emitting equipment (Wang et al., 2014). Nevertheless, ZnO has numerous essential compensations beyond GaN, for instance a greater free excitonic binding energy 60 meV when linked to GaN which is ranging between 21-25 meV.

An additional remarkable consequence is size quantization in semiconducting NPs. As the dimensions of the semiconductor particles are reduced to lengths (<5 nm) analogous to an exciton length, the energy gap between the valence and the conduction band rises. Accordingly, the optical absorption displays a blue shift. For instance, semiconducting ZnO NPs display a blue shift in the optical spectra as a result of quantum size consequence (Zeng et al., 2010). ZnO exists in three phases: hexagonal wurtzite, cubic zinc blende and cubic rock-salt. The wurtzite configuration, shown in the Figure 1, is the further steadiest phase of ZnO in ambient circumstances. Other II-VI semiconductors, such as ZnS, present in both hexagonal-wurtzite and the cubic zinc-blende structure,
Figure 1: Hexagonal wurtzite structure of ZnO

Euphorbia petiolata Banks and Sol is a natural but to some extent uncommon member of the type of Euphorbia from Kurdistan Region in Iraq, essentially found in the Azerbaijan region of Iran (Pahlevani & Akhani, 2011). This type is conventionally utilized for treating verruca, dermatitis, and fungal contaminations. Previous phytochemical investigations on this species showed the attendance of ingenane-type diterpenes and triterpenes (Jassbi, 2006). The intention of the current investigation is to produce ZnO nanoparticles by means of a straightforward solution-based green method using Euphorbia petiolata leaves. Thus, according to the initiated results, the main differences that distinguish the ZnO nanoparticles preparation from the previous studies are simplicity of preparation and sensible cost. Moreover, the produced NPs propose a possible request as an adsorbent in the removal of heavy metals from aqueous solutions.

2. Experimental Procedures

2.1 Preparation of Euphorbia Petiolata Leaves Extract

High pureness substances, zinc nitrate, were obtained from the Merck and Aldrich chemical companies. 100 g of dried powder Euphorbia petiolata leaves was simmered in 1 L double deionized water for 1 hour at 80 °C. After that the aqueous extract was clarified and kept in fridge for supplementary usage.

2.2 Preparation of ZnO Nanoparticles Using the Extraction of Euphorbia Petiolata Leaves

Euphorbia petiolata leaves Banks Sol. was collected in Kurdistan region in Iraq. The preparation and characterization has been done locally in Soran Research center. 40 mL of Euphorbia petiolata leaves extract was added to 65 mL zinc nitrate (>1M) drop wise underneath reflux-condition at 85 °C for 2 hours till fluctuating the color resulting in the surface plasmin resonance consequence, as checked by UV-vis method, and creation of some snowy sedimentation. The sedimentation was totally alienated by means of centrifugation at 7500 rpm and acquired powder cleaned with methanol and deionized water to remove possible sedimentation. Lastly simulated-annealing followed out on the Bunsen burner flame at ~500 °C for ~1 hour as shown in Figure 2.
The attained NPs were characterized utilizing UV-Vis, XRD, SEM and EDAX analysis. Besides, the potential procedure for the creation of green synthesized NPs is reproducible. X-ray diffraction (XRD) measurements were carried out using a PAN analytical X’ Pert PRO (Cu Kα = 1.5406 Å). The scanning rate was 1 °/min in the 2θ range from 20 to 80°. UV-visible spectral analysis was recorded on a double-beam spectrophotometer (Super Aqua spectrophotometer) to ensure the formation of NPs. Morphology and particle dispersion was investigated by fast emission scanning electron microscopy (FE-SEM) (Quanta 4500). The chemical composition of the prepared nanostructures was measured by EDAX (Energy Dispersive X-ray Spectroscopy) performed in SEM.

3. Results and Discussion

The optical feature of synthesized ZnO nanoparticles was investigated by UV-v spectroscopy and presented in Figure 3. The absorption peak observed at 360 nm confirms the creation of ZnO nanoparticles using the biosynthesis method (Kavitha, John, Gopinath, & Philip, 2013). The peak at 250 nm corresponds to the extract of Euphorbia petiolata leaves. Additionally, the robust absorption band appeared at 360 nm which can be allocated to the fundamental band-gap absorption of ZnO as a result of the electron transitions from the valence-band to the conduction-band (Zak, Majid, Mahmoudian, Darroudi, & Yousefi, 2013).

It can be noted that for the plant extract, both signals at 220 nm and 250 nm are for phenol and flavonoids systems, as shown in the Figure 3. Since the application of UV-vis signals as fingerprint and specification of flavonoids, these absorbent bonds revealed the presence of antioxidant flavonoids in plant extract (Sghaier et al., 2011). Existence of massive OH groups’ in phenol and flavonoids is the accountable for reducing zinc nitrate into ZnO nanoparticles. Former investigators
stated that C=O, C=O–C and C=C groups of heterocyclic complexes might have as a chemical-stabilizer (Bala et al., 2015).

Figure 3: UV-Vis spectrum of Euphorbia petiolata leaves extract (black line) and green synthesized ZnO nanoparticles after 2 hours (red line)

The UV-Vis band of green synthesized ZnO nanoparticles categorized the impact of surface plasmon resonance as a result of the substantial fluctuations in the absorbance maxima, 360 nm, which point out to the interaction of phytochemicals with zinc ions inside the plant extract and alters the color of the chemical-reaction, as shown in Figure 4. Moreover, according to the additional UV-vis results the green NPs display an appropriate steadiness even after two weeks as a result of the adsorption of antioxidant phytochemicals on the Nano-surface and defend it from breakdown and distortion procedures. The energy band gap of ZnO nanoparticles can be computed by means of the following equation,

\[ E = \frac{hc}{\lambda} \]  

where, \( h \) is planks constant \((6.626 \times 10^{-34} \text{J.s})\), \( c \) is the speed of light \((3 \times 10^8 \text{ m/s})\) and \( \lambda \) is the wavelength \((360\text{nm})\) which can be obtained from the Figure 3. The energy band gap of ZnO can be found utilizing equation 1 to be 3.45 eV. Similar results have been obtained by Senthilkumar et al. (2017). The robust absorption of the ZnO nanoparticles in the UV province demonstrates the applicability of this material in numerous medicinal uses for instance sunscreen glasses or as antibacterial in creams (Suresh, Nethravathi, Rajanaika, Nagabhushana, & Sharma, 2015). Prepared ZnO nanoparticles by this method can also be used in water purification which is our recent project and many promising results have been found that lead to several high impact publications.
In the current investigation, phenols and flavonoids in the aqueous leaf extract connect the surface of zinc in zinc nitrate to stimulate the creation of ZnO nanoparticles and similarly govern the dimension. The –OH groups from the phenol and flavonoid complexes can behave as a covering agent. Phenols and flavonoids are subordinate metabolites that nearly exist in all medical plants. They have been described to attend as a bio-reductants of metal ions in aqueous media and display an extensive range of organic actions comprising antioxidant and anti-carcinogenic action (Yuvakkumar, Suresh, Nathanael, Sundrarajan, & Hong, 2014).

As shown in the Figure 2, the creation of ZnO nanoparticles as a white-crystalline powder is for plummeting enactment of antioxidant-phenolic of the plant extract as shown in the Figure 2. Indeed after creation of Zn nanoparticles, due to their big surface area they initiate the nucleation process and additional Zn ions adsorb on the nano-surface then they convert to nano state undergo the plant plummeting potential (Shen et al., 2014). This procedure lasts to raise the nano-layers and form a mass of Zn nanostructures over the growing mechanism (Gholipour, Dinh, Béland, & Do, 2015). Lastly under annealing temperature at ~500°C the mass of Zn nanoparticles oxidized and produce the crystalline ZnO nanoparticles. Figure 5 displays the X-ray diffraction configuration of ZnO nanoparticles prepared by the green synthesized technique and it approves the hexagonal-wurtzite construction. From the X-ray diffraction configuration the dominant reflection planes are (100), (002), (101), (102), (110), (103), (200), (112), (201) and (202) correlated with scattering angles 31.6º, 34.3º, 36.3º, 47.5º, 56.5º, 62.8º, 66.4º, 67.7º, 69.1º, 76.8º respectively. The obtained peaks equivalents with the JCPDS: No.36-1451 indicates that the ZnO is a pure crystalline possessing hexagonal-wurtzite construction (Jamdagni, Khatri, & Rana, 2018). It can be noticed that, the sharpened and tight scattering peaks are good indicators to prove the purity and crystallinity feature of the material. The dominant deflection peak detected at the plane (101) and the crystalline dimension can be computed by means of Scherrer’s equation,

$$D = \frac{0.94\lambda}{\beta \cos \theta}$$

where, D is the crystalline dimension, λ is the X-ray wavelength, equals to 1.5406 Å, β is the full width half maximum of the peak, ~ 0.003, from the Origin Pro9. Therefore, the average crystalline size of the ZnO nanoparticles can be calculated ca.60 nm. Similar results have been obtained by

![Figure 4: Manifestation mechanism of ZnO nanoparticles](image-url)
Senthilkumar et al. (2017). Unlike our plant, Senthilkumar and coworkers (Senthilkumar et al., 2017) utilized Tectona Grand leaf extract as an effective bioactive for ZnO nanoparticles preparation.

Figure 5: Precipitate XRD configuration of ZnO nanoparticles

Figure 6 shows the diverse enlargement of the surface morphology and features of the produced ZnO nanoparticles. In general, the produced ZnO nanoparticles were described as uniform, conglomerate and dividable from having any other overlooking phases. In the current investigation, it can be seen from FE-SEM graph that identical dissemination and to some extent ZnO nanoparticles are sphere-shaped. The size of the particle was found to be 55 nm, which is comparable with our previous calculation using Scherrer’s equation.

Figure 6: Different magnification of SEM micrographs of green synthesized ZnO nanoparticles

Analogous outcomes have been acquired by Senthilkumar et al. (2017). Figure 7 displays the dissemination of two elements, O and Zn, in ZnO nanoparticle products. The disseminations of these two elements are regular with the distribution of ZnO nanoparticles. The dissemination concentration of O is smaller than that of Zn. The Zn concentration in the elemental distribution of ZnO is greater.
than that of the mapping results found by Senthilkumar et al. (2017). The results pointed toward that the main components of ZnO is Zn. The content of O is few, but uniformly dispersed on the surface of ZnO nanoparticles. Further support regarding these contents can be found also in the Figure 8.

Figure 7: Corresponding mapping images for O and Zn in ZnO nanoparticles

Figure 8 illustrates the EDAX analysis of ZnO nanoparticles which is produced by means of bio-reduction technique. The EDAX study assured the existence of the zinc and oxygen. The presence of Au in EDAX analysis is a result of using gold coating in order to get better SEM images. Along with the EDAX, X-ray diffraction and SEM micrographs, one can approve that ZnO nanoparticles were precisely produced using green synthesized technique. Besides, the obtained results from EDAX and X-ray diffraction study support the pureness of bio-synthesized ZnO nanoparticles.

Figure 8: EDAX analysis of green synthesized ZnO nanoparticles using the extract of Euphorbia petiolata
4. Conclusions

In this study, a proficient bioactive ZnO nanoparticle by means of the extract of Euphorbia petiolata leaf extract testified for the first time. All utilized techniques including UV-vis, X-ray diffraction, SEM micrographs and EDAX analysis intensely proved that this method is extraordinary technique for producing ZnO nanoparticles. Thus, the essential advantages of this procedure are short reaction-time, fast, distinct stage, environmentally friendly synthesis of the ZnO nanoparticles, removal of harmful ingredients, and reproducibility of the process. The crystalline structure and the hexagonal structure of the synthesized ZnO nanoparticles were established by X-ray diffraction investigation. The formation of ZnO nanoparticles was specified through the observation of color alteration and likewise it was exposed by a peak perceived at 360 nm in UV–vis spectrum. The size of the particle was found from SEM images, ~ 55 nm, and comparable with the Scherrer’s results. Since this method is very cheap therefore it can be stated that the ZnO nanoparticles synthesized through this research can be a prospective candidate for numerous medicinal and water purification applications.

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References


