Green synthesis of zinc oxide nanoparticles: a comparison

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Abstract

Green synthesis of nanoparticles by biological systems especially plant extracts has become an emerging field in nanotechnology. In this study, zinc oxide nanoparticles were synthesized using Laurus nobilis L. leaves aqueous extract and two different zinc salts (zinc acetate and zinc nitrate) as precursors. The synthesized nanoparticles were characterized by Ultraviolet–Visible spectroscopy (UV–Vis), Fourier Transform Infrared Spectroscopy (FT-IR), X-Ray Diffraction analysis (XRD), Energy-Dispersive X-ray analysis (EDX) and Scanning Electron Microscopy (SEM). UV–Vis spectra showed typical absorption peaks in around 350 nm due to their large excitation binding energy at room temperature. Chemical bond formations of zinc oxide were confirmed by FT-IR analyses. XRD results revealed the formation of hexagonal wurtzite structure, and SEM analyses showed spherical shape with the average size (21.49, 25.26) nm for the synthesized nanoparticles by zinc acetate and zinc nitrate respectively. EDX analyses confirmed high purity for the synthesized nanoparticles.

Introduction

Nanotechnology is an emerging technology that can bring revolution to different scientific fields. Nanomaterials have wide range applications due to their size and morphology, and have been an important subject in the fields of basic and applied sciences. In the recent years, there has been a great focus on nano-sized semiconductors because of their novel properties which have applications in optoelectronic. Among various nanoparticles, zinc oxide nanoparticles (ZNPs) are versatile semiconductors that display significant optical transparency and luminescent properties in UV–Visible (UV–Vis) regions (1). These nanoparticles have become important in recent years, due to their excellent chemical and thermal stability (2). Various approaches for the preparation of ZNPs have been developed, such as sol–gel, hydrothermal, spray pyrolysis, microwave-assisted techniques, chemical vapor deposition, ultrasonic condition and precipitation methods (3–9). These types of preparations suffer from high energy demand and also involve toxic and hazardous chemicals, which may lead to biological risks. In contrast, biological methods are becoming the most preferred methods as they are often single step, clean, safe and cost effective (10). According to Raveendran et al., biosynthetic routes provide nanoparticles of better defined sizes and morphology as compared to other physicochemical methods (11). Biological systems include natural compounds which play essential and versatile role in the synthesis of nanoparticles and act as capping agents to stabilize them. The literature survey shows that using plants offers important advantages over other biological systems. The plants are easily available and safe to handle and the nanoparticles synthesized by plants extracts are more stable (12).

Green synthesis of ZNPs has been carried out by different plant extracts such as Cassia fistula, Trifolium pratense, Ocimum basilicum and so on (13–24).
Laurus nobilis L. has also been used in the synthesis of nanoparticles (25,26). In our previous work, we synthesized silver nanoparticles by aqueous extract of L. nobilis and the antioxidant activity of the extract and silver nanoparticles were evaluated. In the other reports, different pharmaceutical properties were evaluated for the plant extract (27–30).

Here we report the syntheses of ZNPs by using L. nobilis L. leaves aqueous extract and two different zinc salts (acetate and nitrate) as precursors. The structural properties of the synthesized ZNPs have been confirmed by using UV–Vis, FT-IR (Fourier Transform Infrared Spectroscopy), XRD (X-Ray Diffraction), SEM (Scanning Electron Microscopy) and EDX (Energy-Dispersive X-ray analysis) technics.

Materials and methods

Chemical and instrumental

All the chemicals and solvents were purchased from Merck company (Germany). UV–Visible (UV.1800, Shimadzu, Japan); FT-IR (100 Spectrum, Perkin Elmer, Germany); XRD (EQUINX 3000; Intel, France); FESEM (ZIEMAVP-500, Zeiss, Germany; EDS, Oxford instruments, UK); Ultra sonic (S15H, Germany); Heater-Stirrer (MR Heidolph, Germany); Oven (Memmert 100-800, Germany); Rotary evaporator (4003 Heidolph, Germany); Centrifuge (EBA 20 Hettich, Germany).

Preparation of the extract

Fresh leaves of L. nobilis L. (Family Lauraceae) commonly known as Bay were collected from the sea side area of Roudsar (a city located in the north of Iran) in June 2015. The leaves were washed and left to dry. Then the dried leaves were powdered by a mortar and 20 g of powdered leaves was mixed with 200 mL deionized water and heated at 80°C using a heater-stirrer for 10 min. Then the mixture was filtered and centrifuged to remove the plant residue and impurities and was stored for further uses.

Synthesis and purification of zinc oxide nanoparticles

ZNPs were synthesized by the co-precipitation method reported previously by Singh et al. with some modifications (31). In order to find the optimal method of synthesizing the nanoparticles, we needed to do several trial and error testing. For synthesis of ZNPs by zinc acetate and the plant extract, 25 mL of 0.02 M Zn (OAc)₂.2H₂O solution was mixed with 1 mL of the L. nobilis leaves aqueous extract. The mixture was stirred for 2 h using a magnet stirrer at room temperature. Then 0.02 M NaOH was added drop by drop to reach pH 12. The mixture was stirred for 1 extra hour until a solid product with a light yellow color was obtained. The precipitate was purified by several re-dispersions in deionized water and then centrifuged. The final product was a white color powder material which was dried overnight in an oven at 60°C. In green synthesis of ZNPs by zinc nitrate, 25 mL of 0.05 M Zn(NO₃)₂.6H₂O solution was mixed with 4 mL of L. nobilis leaves aqueous extract and then the reaction was continued as we explained above in the previous method.

Characterization of zinc oxide nanoparticles

The synthesized nanoparticles were characterized by different techniques. For the UV–Vis analysis, 1 mL of the suspension was collected from the purified sample at the end of the reaction and was sonicated at 4000 rpm for 15 min. The UV–Vis spectra was recorded over the 200–800 nm range. FT-IR analysis of the dried ZNPs was carried out by the KBr pellet method and the presence of the various vibrational modes in the synthesized nanoparticles was investigated. The phase structure and material identification of ZNPs were studied by X-ray diffractometer. The SEM technique was employed to visualize the size and morphology of the particles. Energy-dispersive x-ray spectrometer (EDX) was employed to analyze the elemental composition of the synthesized particles.

Results and discussion

UV–Visible spectroscopy

UV–Visible absorption spectrum of synthesized nanoparticles is shown in Figure 1. The distinct peak centered around 350 nm is specific for ZNPs which is due to their large excitation binding energy at room temperature (18). It is well known from absorption spectroscopy that the band gap increases on decreasing particle size. There is also an opposite ratio between band gap and the wavelength of absorption. As we know, the absorption for bulk ZnO occurs around 385 nm. The high blue shift absorption for the synthesized ZNPs in comparison with the bulk ZnO can be due to a high decrease in particle size.

FT-IR analysis

FT-IR studies of L. nobilis leaves aqueous extract and the synthesized ZNPs are given in Figure 2. Infrared studies
were carried out in order to ascertain the purity and nature of the nanoparticles and also the presence of phytochemicals in the extract. The phytochemicals such as alcohols, phenols, amines, carboxylic acids and so on can interact with the zinc surface and aid in the stabilization of ZNPs. The peaks that were observed at 1634 and (600, 450) cm\(^{-1}\) correspond to Zn–O stretching and deformation vibration, respectively. Metal oxides generally give absorption peaks in the regions between 600 and 400 cm\(^{-1}\). The Zn–O frequencies observed for the synthesized ZNPs are in accordance with literature values (32,33). The broad peak observed at about 3300 cm\(^{-1}\) indicates the OH stretching vibrations.

**X-ray diffraction analysis**

XRD pattern of synthesized ZNPs clearly indicates crystalline structure for the synthesized nanoparticles (Figure 3). The sharp diffraction peaks were observed at 2\(\theta\) values 31.46, 34.29, 36.33, 47.51, 56.50, 62.84, 67.79 and 76.83 degrees. These peaks are indexed as (100), (002), (101), (102), (110), (103), (112), and (202) diffraction lattice planes respectively which confirm the hexagonal wurtzite structure for the synthesized nanoparticles. This pattern is in accordance with the standard peaks displayed by the International Centre for Diffraction Data. The average size of ZNPs was calculated from the highest intense peak (101) using the Debye–Scherer equation (1), where \(\omega\) is the X-ray wavelength coming from Cu-K\(\alpha\) (1.540560 Å), \(\beta\) is the full width at half maxima of the diffraction peak in radians, \(\theta\) is the Bragg’s angle in degrees, and \(K\) is the shape factor and its value is equal to 0.9.

\[
D = \frac{K\omega}{\beta \cos \theta}
\]

XRD analyses revealed the average size of (21.49, 25.26 nm) for nanoparticles using zinc acetate and zinc nitrate as precursors respectively. Details of XRD analyses are given in Table 1.

The particle size of the synthesized ZNPs was in close agreement with the previous findings (34,35).

**Scanning electron microscopy**

The shape, structure and size of the synthesized ZNPs were determined by the SEM analyses (Figure 4). The

**Figure 1.** UV–Visible spectrum of the synthesized ZNPs by (A) zinc acetate and *L. nobilis* extract and (B) zinc nitrate and *L. nobilis* extract as precursors.

**Table 1.** Details of XRD analyses for the synthesized ZNPs.

| Sample | d-spacing (Å) | FWHM | Estimated crystallite size (nm) |
|--------|--------------|------|--------------------------------|
| A      | 2.47093      | 0.349| 25.26                          |
| B      | 2.46305      | 0.295| 29.48                          |

*Synthesized ZNPs by L. nobilis leaves aqueous extract and A: zinc acetate; B: zinc nitrate.

\(^{a}\)Full width at half maximum.
micrographs of ZNPs proved that they had nano-sized range, spherical shape and uniform distribution. The SEM results illustrated that using different precursors affected the size and shape of the nanoparticles. As it is seen when using zinc acetate as a precursor, the zinc oxide molecules grow slowly and form small spherical structures and accumulate like bullets. On the other hand, by using zinc nitrate as a precursor, the spherical ZNPs are formed and the nanoparticles grow and accumulate to form flower-shaped bundles. This agglomeration is due to polarity and electrostatic attraction of ZnO nanoparticles. Similar kinds of observations have been documented by Madan et al. (36).

In the previous study on the green synthesis of ZNPs by *L. nobilis* leaves aqueous extract and zinc acetate as precursors, the shapes of the nanoparticles were like flowers (26). While, the ZNPs, which we synthesized by *L. nobilis* aqueous extract and zinc acetate, were like bullets. We also used zinc nitrate to find whether or not the salt could influence the shape and size of the nanoparticles. The nanoparticles were like flower when zinc nitrate was the precursor. The size of the nanoparticles in our study was also smaller (21.49, 25.25 nm) than the previous report (47.27 nm). The method which we used was to some extent different from the previous method, and our results look better in regard to the sizes and shapes of the nanoparticles.

**Energy-dispersive X-ray spectroscopy**

The elemental composition analyses of the ZNPs from the EDX plot of the SEM images are shown in Figure 5. The EDX spectra revealed that the required phase of Zn and O is present in the samples and confirmed high

![Figure 2](image)

**Figure 2.** FT-IR spectra of (A) *L. nobilis* L. aqueous extract; (B) ZnO/extract prepared by zinc nitrate, and (C) ZnO/extract prepared by zinc acetate.

![Figure 3](image)

**Figure 3.** XRD results for the synthesized ZNPs by (A) zinc acetate and *L. nobilis* extract; (B) zinc nitrate and *L. nobilis* extract as precursors.
purity for the synthesized ZNPs. Theoretically, the expected stoichiometric mass percent of Zn and O are 80.3% and 19.7% respectively. The EDX analyses in our study show similar results for both synthesized nanoparticles, while in the previous study, the elemental composition of zinc and oxygen was reported 57.16% and 14.87% respectively (26).

**Conclusion**

In this study, ZNPs was synthesized by *L. nobilis* leaves aqueous extract using two different precursors: zinc acetate and zinc nitrate. UV–Visible spectrum showed a distinct peak around 350 nm, which is specific for ZNPs. The XRD results confirmed the efficiency of the synthesis process, evidencing the production of single crystalline ZNPs with hexagonal wurtzite structure. The average size of ZNPs synthesized by zinc acetate and zinc nitrate was found to be (21.49, 25.26) nm, exhibiting bullets and flower like structures, respectively which were confirmed by XRD and SEM analyses. EDX results confirmed the presence of zinc and oxygen in the synthesized ZNPs. FT-IR studies clearly showed the formation of ZnO and indicated that the plant extract

**Figure 4.** SEM micrographs of ZnO nanoparticles synthesized by (A) zinc acetate and *L. nobilis* L. aqueous extract; zinc nitrate and *L. nobilis* L. aqueous extract as precursors.

**Figure 5.** EDX analyses of ZnO nanoparticles synthesized by (A) zinc acetate and *L. nobilis* L. extract and (B) zinc nitrate and *L. nobilis* L. aqueous extract as precursors.
contains various phytochemicals, which work as capping and stabilizing agent for the synthesized ZNPs. From the analyses of results, it is clear that the precursors have played a vital role in surface morphology and structure of ZNPs. Our results confirm the potential of L. nobilis L. for the synthesis of ZNPs in a simple, fast and eco-friendly way.

Disclosure statement

No potential conflict of interest was reported by the authors.

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References

[1] Cao, B.; Liu, R.; Huang, Z.X.; Ge, S. Mater. Lett. 2011, 65, 160.
[2] Nunes, J.P.; Fernandes, B.; Furtunato, E.; Vilarinho, P.; Martins, R. Thin Solid Films. 1999, 337, 176–179.
[3] Omri, K.; Najeh, I.; Dhafr, R.; El Ghoul, J.; Elmir, L. Microelectron. Eng. 2014, 128, 53–58.
[4] Zak, A.K.; Abrishami, M.E.; Majidi, W.H.; Abd Yosefi, R.; Hosseini, S.M. Ceram. Inter. 2011, 37, 393–398.
[5] Lu, C.H.; Yeh, C.H. Ceram. Inter. 2000, 26, 351–357.
[6] Okuyama, K.; Lenggoro, W.W. Chem. Eng. Sci. 2003, 58, 537–547.
[7] Wu, Y.L.; Liu, S.C. Adv. Mater. 2002, 14, 215–218.
[8] Wei, Y.L.; Chang, P.C. J. Phys. Chem. Solids. 2008, 69, 688–692.
[9] Wang, Y.; Zhang, C.; Bi, S.; Luo, G. Powder Technol. 2010, 202, 130–136.
[10] Geoprinci, G.; Vidhya sri, B.N.; Poonguzhali, U.; Nagendra, N.G.; Renganathan, S. Asian J. Pharm. Clin. Res. 2014, 6, 8–12.
[11] Raveendran, P.; Fu, J.; Wallen, S.L. J. Am. Chem. Soc. 2003, 125, 13940–13941.
[12] Iravani, S. Green Chem. 2011, 13, 2638–2650.
[13] Suresh, D.; Nethravathi, P.C.; Udayabhanu, H.; Rajanaika, H.; Nagabhushana, H.; Sharma, S.C. Mat. Sci. Semicon. Proc. 2015, 31, 446–454.
[14] Dobrucks, R.; Dugazewska, J. Saudi J. Biol. Sci. 2016, 23(4), 517–523.
[15] Abdul Salam, H.; Sivaraj, R.; Vencakesh, R. Mater. Lett. 2014, 131, 16–18.
[16] Suresh, D.; Shobharani, R.M.; Nethravathi, P.C.; Pavan Kumar, M.A.; Nagabhushan, H.; Sharma, S.C. Spectrochim. Acta A. 2015, 141, 128–134.
[17] Vimala, K.; Sundarraj, S.; Paulpandi, M.; Vengatesan, S.; Kannan, S. Process Biochem. 2014, 49, 160–172.
[18] Bhuyan, T.; Mishra, K.; Khanna, M.; Prasad, R.; Varma, A. Mat. Sci. Semicon. Proc. 2015, 32, 55–61.
[19] Elumalai, K.; Velmurugan, S.; Ravi, S.; Kathiravan, V.; Ashokkumar, S. Mat. Sci. Semicon. Proc. 2015, 34, 365–372.
[20] Yuvakkumar, R.; Suresh, J.; Hong, S.H. Adv. Mat. Res. 2014, 952, 137–140.
[21] Yuvakkumar, R.; Suresh, J.; Joseph Nathanael, A.; Sundaramurthy, M.; Hong, S.I. Mater. Eng. C. 2014, 41, 17–27.
[22] Iravani, S. Green Chem. 2011, 13, 2638–2650.
[23] Ramesh, M.; Anbuvannav, M.; Viruthagiri, G. Spectrochim. Acta A. 2015, 136, 864–870.
[24] Ochieng, P.E.; Iwuoha, I.; Onyekwere, J.; Githira, P.; Kamau, G.N. Int. J. Biochem. Phys. 2015, 23, 53–61.
[25] Parthiban, C.; Sundaramurthy, N. IJIRSET. 2015, 4, 10, 9710–9718.
[26] Khalil, M.M.H.; Mahmoud, I.I.; Ahmed, M.O. IJGHC. 2015, 4, 3, 265–276.
[27] Vijayakumar, S.; Vaseeharan, B.; Malaikozhundan, B.; Shobiya, M. Biomed. Pharmacother. 2016, 84, 1213–1222.
[28] Muniz-Marquez, D.B.; Rodriguez, R.; Balagurusamy, N.; Carrillo, M.L.; Belmares, R.; Contreras, J.C.; Nevarez, G.V.; Aguilar, C.N. CYTA J. Food. 2015, 12 (3), 271–276.
[29] Sayyah, M.; Valizadeh, J.; Kamalinejad, M. Phytotherapy Res. 2002, 9(3), 212–216.
[30] Sayyah, M.; Saroukhani, G.; Peirovi, A.; Kamalinejad, M. Phytotherapy Res. 2003, 17(7), 733–736.
[31] Dadaloglu, I; Evrendilek, G.A. J. Agric. Food. Chem. 2004, 52(26), 8255–8260.
[32] Singh, R.P.; Shukla, V.K.; Yadav, R.S.; Sharma, P.K.; Singh, P.K.; Pandey, A.C. Adv. Mater. Lett. 2011, 2, 313–317.
[33] Rao, C.N.R. Chemical Applications of Infrared Spectroscopy; Academic Press: New York and London, 1963; pp. 25–40.
[34] Markova-Deneva, I. J. Uni. Chem. Tech. Metal. 2010, 45, 351–378.
[35] Vijayakumar, S.; Vinoj, G.; Malaikozhundan, B.; Shanthy, S.; Vaseeharan, B. Spectrochim. Acta A Mol. Biomol. Spectrosc. 2015, 137(25), 889–891.
[36] Divya, M.J.; Sowmia, C.; Joona, K.; Dhanya, K.P. Res. J. Pharm. Biol. Chem. Sci. 2013, 4 (2), 1137–1142.