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Potato extract as reducing agent and stabiliser in a facile green one-step synthesis of ZnO nanoparticles


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A facile green recipe was developed to synthesise highly pure, safe and durable zinc oxide nanoparticles (ZnO Nps) using homemade starch-rich potato extract. The ZnO Nps were synthesised using zinc nitrate and potato extract, and the whole reaction is carried out for 30 min at 80 °C. In the synthesis, starch-rich potato extract acted as the reducing agent and as a stabilising layer on freshly formed ZnO Nps. Hexagonal (wurtzite) shaped ZnO Nps with size about 20 ± 1.2 nm were synthesised and characterised using X-ray diffraction, transition electron microscope and scanning microscopy analyses. Fourier transform infrared spectral analysis indicated that highly pure ZnO nanopowders were obtained at higher temperatures. The use of environmentally benign and renewable material as the respective reducing and protecting agents, starch-rich potato extract, as well as a gentle solvent medium (H2O), offered a simple and quite efficient procedure for the synthesis of ZnO Nps in neutral medium with promising potential for biological and biomedical applications.

Keywords: nanostructures; green synthesis, ZnO; crystal structure; potato extract

1. Introduction

Green nanotechnology as a novel branch of nanoscience has grown to be an important research field in all areas including biological, water purification and medicinal application.[1] It involves the application of green chemistry principles to the design of nanoscale products, the development of nanomaterial production methods and the application of nanomaterials.[2] This approach aims to develop an understanding of the properties of nanomaterials, including those related to toxicity and ecotoxicity, and to design nanoscale materials that can be incorporated into high-performance products that pose little hazard to human health or the environment. It strives to discover synthesis/production methods that eliminate the need for harmful reagents and enhance the efficiency of these methods, while providing the necessary volume of pure material in an economically viable manner. In this connection, the prospect of exploiting natural
resources for metal nanoparticles (Nps) synthesis has become to be a competent and environmentally benign approach.[3] Green synthesis of Nps is an eco-friendly approach which might pave the way for researchers across the globe to explore the potential of different herbs in order to synthesise Nps.[4] Metal and metal oxide Nps have been of great interest due to their distinctive features such as catalytic, optical, magnetic and electrical properties.[5,6] In particular, zinc oxide (ZnO) Nps is an important semiconductor with band-gap energy of 3.37 eV at room temperature and has a very large excitation binding energy of about 60 meV.[7] Moreover, great interest has focused on the synthesis of ZnO spheres because of their potential applications in paints, ceramics gas sensing, cosmetics, drug delivery, catalysis, chemical storage, microcapsule reactors and photoelectric materials.[8,9] Evidently, conventional chemical and physical methods used to synthesise ZnO Nps are expensive and often lead to questions of environmental risk because of involving the use of toxic, hazardous and non-friendly chemicals.[10,11] Accordingly, there is an urgent need to develop environment-friendly procedures for synthesising ZnO Nps.[12,13] Recently, green approaches using natural sources such as micro-organisms, plants or plant extracts for nanoparticle synthesis were suggested as valuable alternatives to chemical methods.[14–20] Among them, plant extracts have shown large prospects in nanoparticle synthesis.[21–24]

The potato is a tuberous crop which is best known for its carbohydrate contents. The predominant form of this carbohydrate is starch. Starch is a natural polymer that is abundant, renewable, inexpensive and widely available. Starch can be obtained by hydrolysis of starch-rich materials. Boiling the fresh vegetables gives large amounts of starch and glucose by hydrolysis. It contains two types of biopolymers: amylose (normally 20%) and amylopectin (80%) (Figure 1). These poly-hydroxylated macromolecules present interesting dynamic supramolecular associations facilitated by inter- and intramolecular hydrogen bonding resulting in molecular-level capsules, which can act as templates for nanoparticle growth.[8,25] So, following our previous studies on green synthesis of Nps, [26–28] herein, we report a facile, green, low-cost and homemade method for preparing stable ZnO Nps by starch-rich potato extract, without any additives such as reducing agent, acids and organic solvents. To the best of our knowledge, green approach using potato extract is used for the first time as a reducing as well as capping agent for the synthesis of highly pure ZnO Nps. The morphology, phase and structure of synthesised products were investigated by the standard characterisation techniques.

Figure 1. (a) Light spectroscopy of the as-prepared starch-rich potato extract; starch subunits structures: (b) amylopectin (80%) and (c) amylose (20%).
2. Experimental

2.1. Materials
Zinc nitrate (Zn(NO$_3$)$_2$.6H$_2$O) (99.99%, w/w) and ammonia (NH$_3$) were of analytical grade and purchased from Merck (Darmstadt, Germany). Deionised (DI) water is used for rinsing and for makeup of all aqueous solutions.

2.2. Preparation of the potato extract
Fresh potatoes were provided from local supermarket. The potatoes were washed several times with water to remove the dust particles and then sun dried to remove the residual moisture. Then 13 g of washed dried fine cut potato pieces were placed in 500 mL glass beaker along with 300 mL of DI water. The mixture was then boiled to 85 °C for 30 minutes until the colour of the aqueous solution changes from watery to milky. After cooling to room temperature, the liquid solution was centrifuged to remove insoluble parts and the supernatant was stored in plastic bottles and kept in a refrigerator in order to be used for further experiments (Figure 1).

2.3. Preparation of zinc oxide nanoparticles
For the synthesis ZnO Nps, 50 ml of potato extract liquid solution was taken and boiled to 80 °C using a stirrer-heater. Three grams of zinc nitrate was added to the solution as the temperatures reached 85 °C. Heating treatment was required to expand the starch molecules, which in return accelerates the reduction process by resulted electron-donator groups.[22] The pH of the mixture solution was then adjusted to 6.5—7.5 by gradual addition of ammonia (ca. 4 ml), and a milk-like solution was formed. It is found that at strongly alkaline condition, the more abundance OH ions in the solution, make complex with Zn$^{2+}$ cations which promoted the molecules Zn(OH)$_2$ and (Zn[OH]$_4^{2-}$), which could restrain the production of ZnO Nps.[29] Moreover, in alkaline solution at higher pH, enhanced growth of ZnO Nps was significant when compared to those obtained at lower pH.[30—32] The solution was stirred for an additional 25 min at 85 °C, and the resulting precipitate was centrifuged, washed with DI water and dried at 50 °C. The as-prepared powder was then collected in a ceramic crucible and heated in an air heated furnace at 500 °C for 10 min to obtain starch-free pure ZnO Nps. The ZnO nanopowder can be stored at room temperature.

2.4. Characterisation of ZnO Nps
X-ray diffraction (XRD) was performed on a Xpret Pro-Philips diffractometer with CuK$_\alpha$ ($\lambda = 1.5405$ Å) radiation at a scanning speed of 2 min from 10 to 80 (2$\theta$). The morphology and size of the synthesised ZnO Nps were probed on Leo 912 AB transition electron microscope (TEM) at an accelerating voltage of 120 kV. Infrared spectra were recorded on Fourier transform infrared spectroscopy (FTIR, Brucker Tensor 27) spectrometer using a KBr wafer. Properties of nanocomposite are characterised by scanning electron microscopy (SEM) operating at 26 kV.
3. Results and discussion

3.1. XRD analysis

Figure 2 represents the XRD pattern of as-synthesised ZnO nanoparticles as well as samples calcined at 500 °C and 10 min. The crystallinity of the ZnO Nps was confirmed by the reflections observed at typical 2θ values of 31.92° (100), 34.59° (002), 36.40° (101), 47.69° (102), 56.73° (110), 63.00° (103), 66.49° (200), 68.07° (112) and 69.21° (201) (Figure 2 and Figure S1). All of the diffraction peaks of the uncalcined and the calcined zinc oxide nanopowders match well with those of the standard ZnO XRD pattern (JCPDS cards no. 89-0510). These results coincide with literature XRD pattern for hexagonal wurtzite ZnO.[8,9] Moreover, no impurity peak was observed in XRD graph indicating that ZnO Nps prepared by proposed method is highly pure. In contrast to the uncalcined ZnO Nps (Figure 2a), crystal plane peaks of the ZnO Nps calcined at 500 °C for 10 min obviously became sharper indicating the improved crystallinity of the ZnO Nps (Figure 2(b)).[8] These results are consistent with FTIR findings (Figure 3). According to the Scherrer formula,[33] the average crystallite size of ZnO according to the most intensive diffraction peak at 2θ = 36.40° (101) was 20 ± 1.2 nm.

3.2. FTIR analysis

Figure 3 presents the infrared spectra of the starch-rich potato extract, as-prepared- and calcined ZnO Nps. The wide band observed at 3282 cm⁻¹ can be attributed to the O–H stretching, in addition, its width was ascribed to the formation of inter and intramolecular hydrogen bonds. The band at 1636 cm⁻¹ was ascribed to chemisorbed and/or physisorbed

![Figure 2. XRD patterns of the synthesised ZnO nanoparticles by potato extract (a) uncalcined and (b) calcined at 500 °C for 10 min.](image-url)
water on the particle surface,[34] while the bands at 1355 cm$^{-1}$ was attributed to the angular deformation of C–H. The two peaks at 1000 cm$^{-1}$ and 1050 cm$^{-1}$ were ascribed to C–O ether bond of glucose ring of starch and the C–O bond of the C–O–H group shows stretching at 1240 cm$^{-1}$ (Figure 3(a)).[35,36] These results indicate that similar

Figure 3. FTIR spectra of various samples: (a) starch-rich potato extract, (b) uncalcined ZnO powders and (c) ZnO Nps calcined at 500°C for 10 min.
characteristic adsorption peaks of the organic compounds along with new inorganic material (Zn–O) could obviously be observed in the spectrum of the uncalcined ZnO powders (Figure 3(b)). Due to relative weak interaction between starch molecules and nanoparticles, the main characteristic peaks existed in ZnO samples in Figure 3(a) and 3(b) disappeared after calcination at 500 °C for 10 min which indicated that approximately all the organic molecules from the as-prepared ZnO Nps were removed. This is agreement with the reported results in the literatures.[8,37] Finally, the absorption bands at 485 cm\(^{-1}\) in Figure 3(b) and 3(c) were attributed to the stretching vibrations of Zn–O, which confirms the formation of ZnO Nps (Figure S2).[8]

3.3. SEM and TEM observations
A typical SEM image of uncalcined ZnO Nps formed is displayed in Figure 4. The ZnO Nps were well distributed in the starch matrix. From Figure 4(a) and 4(b), it can be seen that relatively spherical ZnO Nps with diameters ranging from 100 to 300 nm were obtained at 85 °C within 30 min. Moreover, TEM image confirmed the nanostructure and hexagonal (wurtzite) shape of ZnO Nps with the size being less than 50 nm (Figure 5 and Figure S3).[9] SEM imaging further revealed that these ZnO Nps are smaller in size but they were agglomerated resulting from sample preparation. These results illustrate the synthesis of ZnO Nps through reduction of Zn ions inside the starch-rich potato extract template.[22]

3.4. Mechanism of ZnO nanoparticles formation
The notion ‘green’ is appended to the synthesis procedure reported here mainly due to the application of starch-rich potato extract as natural medium. Starch consists of amylose and amylopectin which are structurally linear and branched molecules, respectively (Figure 1). The extensive number of hydroxyl groups present in starch can facilitate the complexation of Zn ions to the molecular matrix, while the aldehyde terminals helped in reduction of the Zn (II) ions to Zn (0) nanoparticles.[22] In addition to this criterion for the use of starch in the solution mixture, there are several key advantages to the use of this renewable material as the protecting agent. First, it is possible to form a dispersion of

![Figure 4. SEM images with (a) low magnification (28.89×) and (b) high magnification (45.96×) of the ZnO Nps obtained after calcination at 500 °C for 10 min.](image-url)
starch in H₂O, and so one can completely avoid the use of organic solvents. Second, the binding interaction between starch and the metal nanoparticles is relatively weak as compared to the interaction between the nanoparticles and typical thiol-based protecting groups.[38] This implies that the protection should be easily reversible at relatively higher temperatures, enabling the separation of these particles (see Figure 3). Taking advantage of multifunctional (reducing and capping) capabilities of starch-rich potato extract, a simplified mechanism of organic phase synthesis of ZnO Nps via green approach, was illustrated in Scheme 1. The process for using starch-rich extract was similar to our report

![Figure 5. TEM image of the ZnO Nps obtained after calcination at 500 °C for 10 min.](image)

Scheme 1. Proposed mechanism of green synthesis of pure ZnO nanoparticles using starch-rich potato extract as both reducing and stabilising agent.
on starch-stabilised ZnO Nps.[26] Due to its long alkyl chain, starch easily dissolves the ZnO Nps and prevents their aggregation in distilled water. Thus, it shows a high dispersing ability in promoting the dispersion of modified-ZnO Nps which leads to an increase in the monodispersity and decreases the mean size (20 ± 1.2 nm) of ZnO Nps (Figures 2 and 5).[26] A corresponding mechanism was reported for silver and gold nanoparticles using chitosan and starch–glucose biopolymer ligands.[39–41] However, the most intriguing result with the best quality ZnO Nps comes from the presence of heat (500 °C), giving a sharp peaks in XRD pattern, clean spectrum in FTIR and high-crystalline particles in TEM, respectively (Figures 2, 3 and 5).

4. Conclusions

In summary, we reported a novel green one-step synthesis of ZnO nanoparticles reduced and stabilised via homemade starch-rich potato extract. The uncalcined powders were composed of starch and ZnO crystals, while with increasing calcination temperature and time (500 °C, 10 min), by the removal of the starch molecules, highly pure and durable ZnO Nps were obtained. According to XRD and TEM results, the pure green ZnO Nps were formed in hexagonal (wurtzite) structure and had diameters of about 20 ± 1.2 nm. However, SEM images revealed the presence of some aggregation of smaller particles. The advantages of this approach are: (a) neutral pH; (b) fast reaction times (30 min); (c) natural aqueous medium potential for large-scale production of durable ZnO Nps and (d) no hazardous chemicals involved. In this study, synthesis of ZnO Nps in neutral aqueous solution at gentle temperature offers a green and non-toxic procedure which is attractive for biological and medically related applications. Our homemade recipe will extend using extracts from natural starch-rich food sources such as potato, rice, corn and other grains sources for eco-friendly nanoparticles preparation.

Disclosure statement

No potential conflict of interest was reported by the authors.

Supplemental data

Supplemental data for this article can be accessed here.

References


