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Original Research

Green Synthesis of NiO Nanoparticles Using the Shell Waste of *Prunus dulcis*: their Characterization and Electrochemical Studies

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Abstract

Nickel oxide (NiO) nanoparticles (NPs) were successfully synthesized by utilizing the waste shell powder of *Prunus dulcis* (almond) through a simple, environmentally sound, cheap, and novel green approach. The almond shell powder was used as a stabilizing and reducing agent for the synthesis of NiO nanoparticles from $NiNO_3.6H_2O$ solution at 60 ºC and pH 12. FTIR studies verified the synthesis of NiO NPs by the appearance of a characteristic vibrational peak at 611.97cm^{-1} whereas an absorption peak at 267 nm appeared in the UV-Visible spectrum. However, the XRD and SEM analyses have shown the amorphous nature of synthesized NiO NPs. The cyclic voltammetry (CV) curve of NPs clearly indicated the redox reaction and the reversible behavior of NiO NPs. The galvanostatic charge discharge (GCD) curves have shown a higher charging time as compared to the discharging time.

Keywords: Biosynthesis, NiO, almond shell powder, cyclic voltammetry, GCD

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Introduction

Nanotechnology plays an important role in different disciplines of life [1], including water treatment [2], biomedical services [3], drug delivery [4], photo-electrochemical applications, catalysis [5], cosmetics [6], optics [7], etc. Currently, the green synthetic methodology is a fast-growing approach that involves the use of numerous organisms or plants for the synthesis of NPs [8]. Biocompatibility, cost effectiveness, and many other factors are driving the green production of NiO NPs [9]. Moreover, this method is rapid, more secure, eco-friendly, sustainable, and is associated with many ecological benefits [10, 11]. NiO-NPs were reported earlier owing to their clinical and catalytic applications, enzyme inhibition, remediation, antioxidant, anticancer, cytotoxic, antifungal, and antibacterial properties [12]. They are highly reactive and eco-friendly and are employed in magnetic separations [13], automatic catalytic converters, magnetic fluids, propellants, and sintering additives, fast separations [13], and the absorption of inorganic pollutants and harmful dyes [14]. They are used in optoelectronic devices as catalysts for benzyl alcohol oxidation [15]. Because of their smaller size (4.5 nm diameter) and large surface area, NiO NPs have shown good electrical activity and were reported as an electrode material in super capacitors [16]. Nickel nanoparticles (NPs) have the potential to be used in a variety of fields, such as biomedicine [17], magnetism [18], electronics [19], and energy technology [20]. They are used to catalyze a variety of organic reactions, such as the reduction of aldehydes and ketones [21], the hydrogenation of olefins [22], the synthesis of stilbenes from alcohol through Witting-type olefination [23], the alkylation of methyl ketone [24], and also for photocatalytic hydrogen evaluation by using an aqueous methanol solution [25]. NiO NPs capped with biomolecules like glucose demonstrate significantly increased biocompatibility, making them useful as biosensors and heat nonmediators for cancer hyperthermia [26].

Currently, plant-mediated synthesis of NPs has attracted the attention of researchers due to its cost-effectiveness, sustainability, and useful applications [27, 28]. Plants have been considered important sources for green syntehsis due to their easy availability [29] and useful phytochemical ingredients [30, 31]. The almond (also known as *Prunus dulcis*, *Prunus amygdalus,* or *Amygdalus communis)* is a tiny deciduous tree that relates to the Rosaceae subfamily *Prunoideae* and bears an almond-like fruit [32]. Kernel, hull, and shell are three components of almonds [33]. The edible portion of the nut is the kernel. Almond shells are totally contained in about ¾ portion of total almond fruit. The shell is the central portion of the external kernel and hull. Hemi-cellulose, cellulose, and starch make up the majority of the almond shell; the ratio between these components determines the strength of the shell [34]. After the use of the kernel (edible portion) of an almond, its shell (not edible) is discarded as waste material.

The primary goal of this research is to utilize the waste shell material of *Prunus dulcis* (almond) for the synthesis of nickel oxide nanoparticles through a green route. The synthesized NPs have been characterized by XRD, FTIR, UV-Visible, and SEM analyses, and they were also subjected to electrochemical studies by cyclic voltammetry and galvanostatic charge-discharge (GCD) testing.

Materials and Methods

Nickel (II) nitrate 6-hydrate, sodium hydroxide, and methanol were used in this study; they were purchased from Sigma Aldrich and were used without further purification. The powder extract of *Prunus dulcis* shell (a waste material) was used as a reducing agent. A Bruker AXS, D8 Advance X-ray diffractometer (XRD) instrument was used to analyze the structural information of JSM-6480LV. The synthesized NPs were tested for their optical properties by using a UV-Visible Spectrophotometer (UVD-3500, Lambod, Inc., UAS, Double Beam). The functional group analysis was performed with an FT-IR Spectrometer (Cary 630, Agilent Technology, USA). The electrochemical applications of NiO NPs were determined from Cyclic Voltammetry (CV) by Potentiostate/Galvonostate of model CS300.

Green Synthesis of Ni Nanoparticles by Using *Prunus dulcis* Shell Powder Extract

Preparation of Plant Extract

Prunus dulcis (almond) with shells (Fig. 1a) were purchased from a local market in Lahore, Punjab, Pakistan, in August 2022. The *Prunus dulcis* shells (Fig. 1b) were washed with distilled water to remove dirt and contaminants and dried at 80ºC for 4 hours, then the almond shells were ground by a steel grinder into a homogenized almond shell powder (Fig. 1c). 30 g of *Prunus dulcis* shell powder was soaked in 100mL of 40% methanol. The solution was stirred for 24 hours at ambient temperature. The extract was filtered, centrifuged to remove any impurities, and refrigerated at 4ºC for its usage within a week.

Procedure for the Synthesis of Ni Nanoparticles

30 mL of 5% nickel (II) nitrate hexa-hydrate was taken in a 250 mL beaker. Then 30 mL of almond shell extract was added to it, and the pH of the solution was maintained at 12 by adding a drop-wise NaOH solution (0.1 N). The solution was stirred for 2 hours at 60ºC, cooled, and centrifuged at 2000 rpm for 15 minutes at ambient temperature. The color of the solution was changed from dark green to light green, confirming the

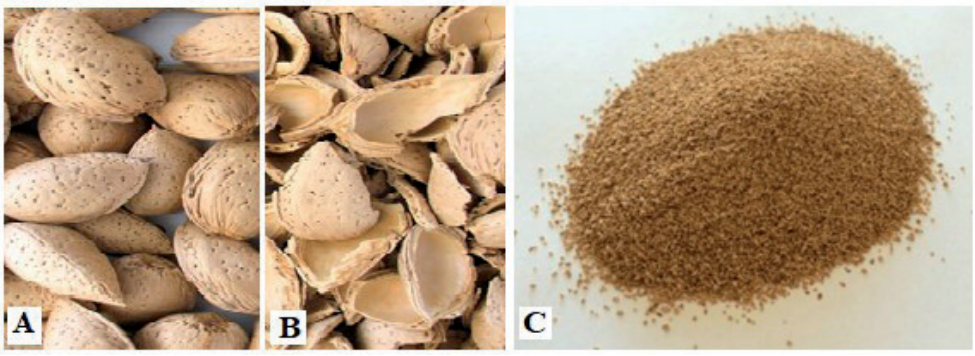

Fig. 1. a) *Prunus dulcis* (almond with shells) b) Broken shells of *Prunus dulcis* after separation of its seeds (nuts) c) Fine powder of *Prunus dulcis* shells.

synthesis of NiO NPs. The solution was finally filtered, and the obtained nanoparticles (residue) were dried in an oven at 100ºC; finally, they were stored for analysis and further usage.

Results and Discussion

FT-IR Spectroscopy

The FTIR spectrum of the synthesized nanomaterials was recorded in the range of 4000-500 cm^{-1}; the obtained spectrum has been shown in Fig. 2. The different peaks could be interpreted as representatives of the vibrational modes of the nanoparticle. The spectrum has shown a very clear Ni-O vibrational stretch of medium intensity at 611.97 cm^{-1}. The C-O bond stretching band was reflected by the large absorption peak at 1344.25 cm^{-1}, whereas a peak at 1625.97 cm^{-1} existed due to the C=O group of the carbonyl group. The stretching bands at a frequency of 3368.37 cm^{-1} were attributed to the presence of O-H groups. The simultaneous existence of C-O, C=O, and O-H peaks evidently depicts the presence of carboxylic acid moieties on the surface of the synthesized NPs. It commonly occurs in plant-mediated NP synthesis, where the plant material acts as a coating on the surface of NPs and also prevents their agglomeration.

UV-Visible Spectroscopy

UV-Visible spectroscopy is a very important tool for the verification of NiO-NPs. The formation of synthesized NPs can be verified by measuring the highest absorption peak and analyzing the collective oscillations of conduction band electrons in response to the electromagnetic pulses. UV-Visible spectroscopy (Fig. 3) has shown a maximum absorption band at 267 nm, which verified the presence of NiO NPs (Ikuhara al., 2012).

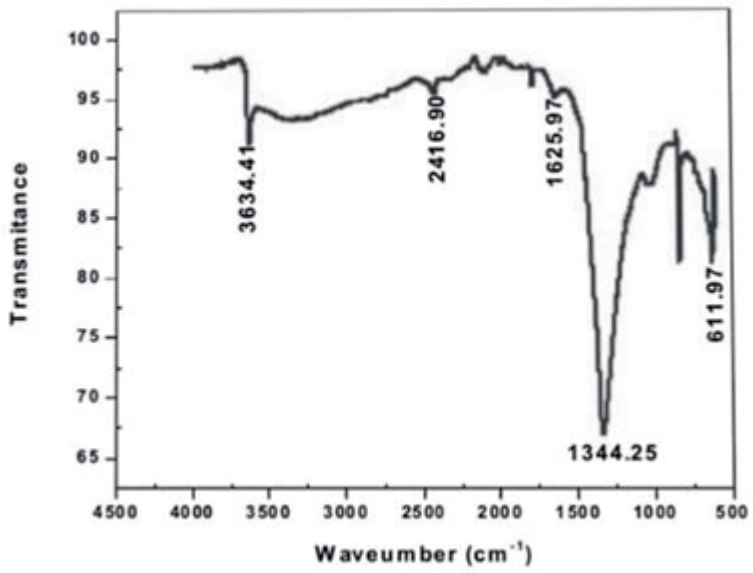

Fig. 2. FTIR spectrum of the synthesized NPs.

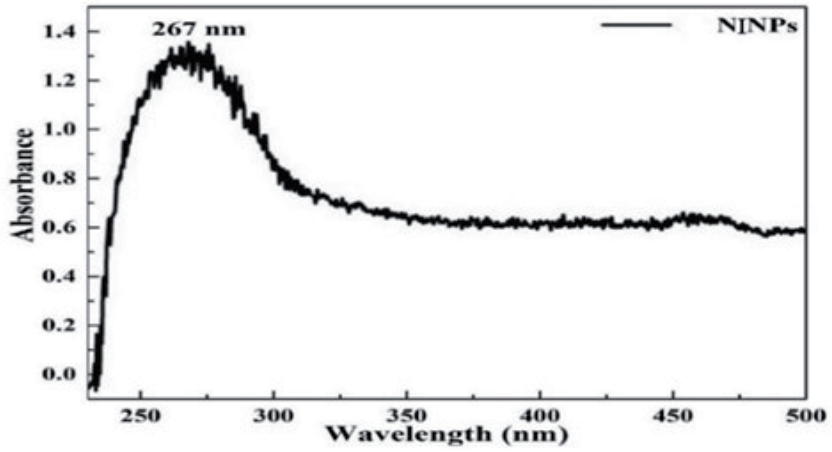

Fig. 3. UV-Visible spectrum of NiO NPs.

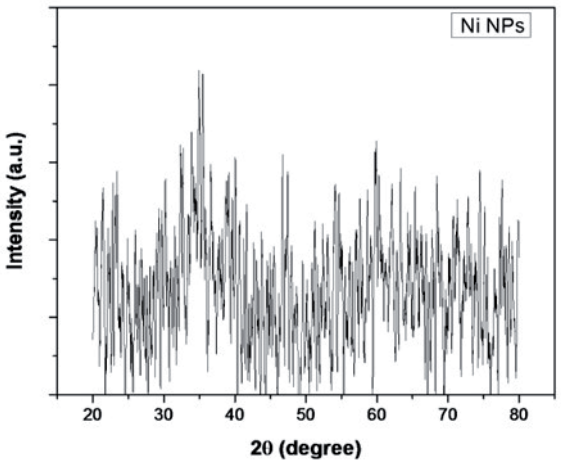

Fig. 4. XRD picture of synthesized NiO NPs.

Structural Studies

X-ray powder diffraction (XRD) is typically employed for characterizing crystalline materials and can yield data on the dimensions of their unit cells. Analyzing X-ray diffraction (XRD) data carefully can provide valuable information and also assist in correlating microscopic findings with the bulk sample because XRD patterns seem different for specimens of nanomaterials having varying shapes and sizes. The XRD spectra of the synthesized NPs were recorded between 2θ values of 10 and 80º; the respective patterns are shown in Fig. 4. The XRD patterns have shown no distinct peak for NiO nanoparticles, demonstrating the amorphous nature of the synthesized material. So, it was not possible to determine the crystallite size due to its amorphous nature, which is also verified from the SEM images (next section). Here, almond shell powder acts as a stabilizer or capping agent, demonstrating the amorphous behavior of nickel nanoparticles. This might be due to the low-temperature synthesis method (ImranDin, 2016).

SEM Analysis

A scanning electron microscope (SEM) was used to investigate the morphology of synthesized NPs. The obtained SEM images of NiO NPs at 50 µm and 100 µm are shown in Fig. 5.

The SEM results completely support the findings of the XRD analysis, as discussed in the last section. Since XRD studies confirmed the amorphous nature of synthesized NiO-NPs, it was not possible to determine

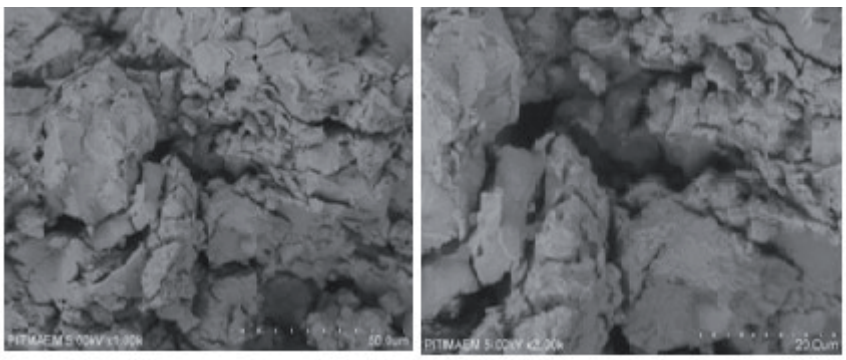

Fig. 5. SEM images of NiO-NPs at 50 µm (Left) and 100 µm (Right).

their morphology and size. The results indicated that nickel nanoparticles are amorphous in nature.

Electrochemical Studies of NiO NPs

Cyclic Voltammetry

The kinetic irreversibility of the redox reaction causes an asymmetry between the oxidation and reduction peaks throughout the anodic and cathodic scans. The cyclic volta-gram of the synthesized NPs is shown in Fig. 6. As with the cathodic scan, the Ni^{2+} in the KOH electrolyte is oxidized to Ni^{3+} during the scanning of the anode from –1.000-1.000 V. In the presence of an electrical field, ions migrate across the electrolytic solution to the NiO electrode. Since the electrolyte does not transport electrons, it prevents the transfer of charge-neutralizing electrons across the electrolyte. In this way, electrons from an external circuit infiltrate into the electrode material, where they mix with surface-bound ions. Therefore, the electrochemical reaction takes place close to the NiO electrode's surface.

The observed redox potential of NiO NPs was 0.0892 V at a scan rate of 100 mVs^{-1}, whereas the redox current was found to be 1.0284 mA.

Galvanostatic Charge and Discharge (GCD)

The GCD curve (Fig. 7) showed the charging and discharging peaks of NiO NPs. The charging capacitance is 13.924, 61.32, 18.95, 2.411, and 7.620 at an applied current of 1,2,3,4, and 5A. Moreover, the discharging capacitance is 1.369, 0.746, 0.746, 2.614, 1.169, and 2.260 at the applied current. The GCD curve

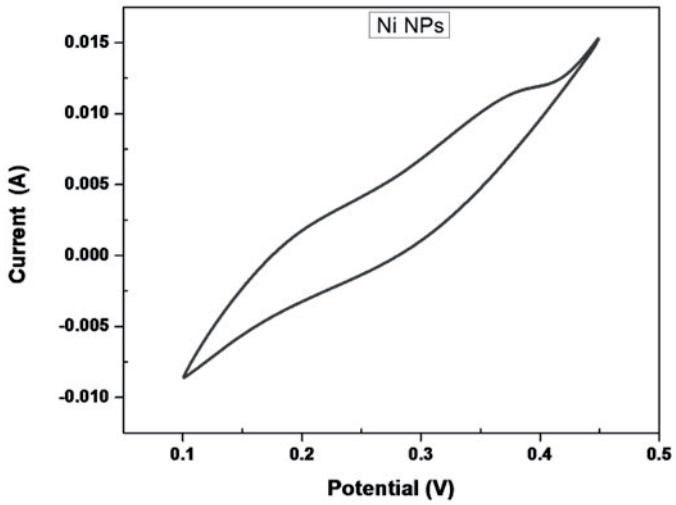

Fig. 6. Cyclic Volta-gram of the synthesized Ni-O NPs.

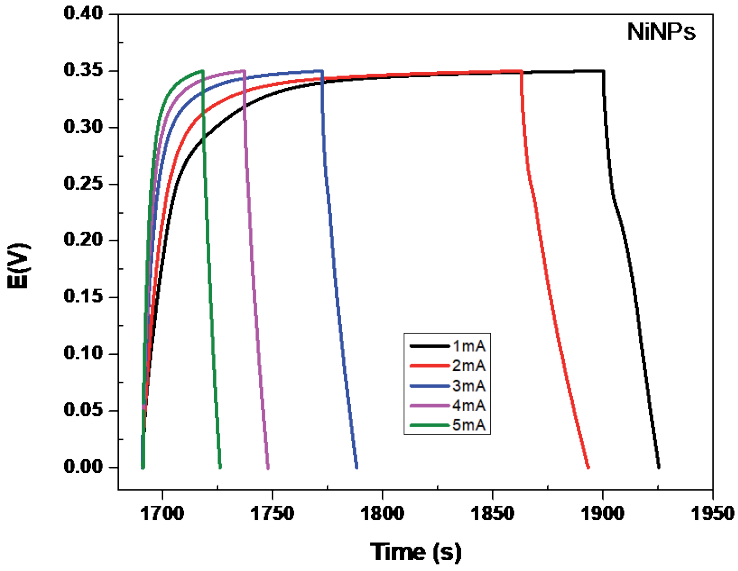

Fig. 7. GCD curve of the synthesized Ni-O NPs.

showed that charging time is greater than discharging, which demonstrated that NPs are good irreversible materials.

Conclusion

Nickel oxide (NiO) nanoparticles were successfully synthesized by treating $NiNO_3.6H_2O$ with the waste shell powder of *Prunus dulcis* (almond) and using a simple, environmentally sound, cheap, and novel green approach. FTIR and UV-Visible spectroscopies verified the formation of Ni-O nanoparticles. However, XRD and SEM analyses demonstrated the amorphous nature of NPs. There was a coating of carboxylic acid moieties on the surface of the NPs. The electrochemical studies were performed by cyclic voltammetry and GCD. Cyclic voltammetry has shown the redox nature of the synthesized NiO NPs. The charging time of the synthesized nickel oxide NPs was higher as compared to the discharging time.

Acknowledgments

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Conflict of Interest

The authors declare no conflict of interest

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