Synthesis, morphological, structural, functional, optical and computational properties of nickel oxide nanoparticles using hydrothermal method

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In this work, hydrothermal synthesis of NiO nanoparticles in aqueous solutions at higher temperatures was used. An investigation of its optical and electrical capabilities might be done in many ways. As a result, the size and structure of NiO nanoparticles were characterised using a scanning electron microscope. A powder X-ray diffractometer was used to measure experimentally the crystallite grain size and dislocation density, which were computed using the Scherer formula. The functional groups of the title nanoparticles were easily distinguishable in the FTIR spectrum. After optical absorption analyses, NiO nanoparticles were shown to have optimised UV-Visible transmittance. The density functional theory (B3LYP) was used to compute the bonding of molecular properties of NiO in the ground state using the basis sets 6-311+G (d, p) and 6-311++G (d, p). There is evidence of charge transfer in molecules based on the computed molecular electrostatic potential (MESP), Thermodynamic properties, HOMO and LUMO energies determined. The scientific applications of this NiO nanomaterial would be well served by this material.

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1. Introduction

Solid bulk materials can't compare to the extraordinary characteristics of nanoparticles in the field of research. Small-scale effects, surface effects, quantum size effects, and macroscopic quantum tunnel effects all play a role in the discrepancy in characteristics [1]. Transition metal monoxides are among the most common. There are numerous potential applications for first-row transition metal monoxides, including catalysis, energy storage, and electrode materials for super capacitors [2, 3]. These materials are stable under both thermodynamic and chemical conditions, can have different crystal structures, and have a wide range of interesting physical and chemical properties. A broad band gap up to 3 eV, noticeable catalytic activity, chemical stability, thermal stability, biocompatibility, and fascinating optical features are some of the characteristics of nickel oxide nanoparticles (NiO). It is also necessary in today's society to have applications such as inconvenient ferromagnetic material smart windows, impetuses hostile to ferromagnetic material smart windows, gas sensors, catalysts, and anode material in Li ion batteries and nano-scale optical devices [4-6]. Semiconducting transparent nanomaterial are used in many different applications, including solar cells, Nano paints, polar electrodes, photovoltaic light sensors, and many more. For example, nano nickel oxide photo catalysts are self-cleaning, catalytic, and dye-sensitized [7]. Another advantage of the Nano crystalline NiO powder is that it is very magnetic, making it ideal for medication administration and MRI (magnetic resonance imaging) agents. A fine control of particle size and dispersion in the Nano scale range is necessary for these applications to be improved [8]. Several NiO nanostructures have been synthesised by several researchers using a variety of techniques [9]. This study, on the other hand, used a hydrothermal technique to produce nickel oxide (NiO) nanoparticles. In addition to scanning electron microscopy and powder X-ray

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diffraction, which were used to determine the morphological phase composition and the structure of the present nanoparticle, other techniques such as ultraviolet-visible spectroscopy and infrared spectroscopy were used to reveal NiO's improved optical transparency and an extensive group of the title nanoparticles' functional properties. For the purpose of this research, the HOMO–LUMO energy gap, natural bond orbital (NBO) analysis, and the density functional theory methods (DFT/B3LYP) using 6-311+G (d, p) and 6-311++G (d, p) basis sets were used to analyse the optimised shape [10]. Because of its close connection to electronic density, the molecular electrostatic potential (MESP) is an excellent tool for describing electrophilic attack sites, nucleophilic processes, and hydrogen bonding interactions. At the B3LYP/6-311++G (d, p) level, the molecular electrostatic potential for the molecule of concern is computed.

2. Experimental

2.1. Synthesize

Two master solutions were created to synthesise the NiO nanoparticles using the hydrothermal technique. One mole of nickel [II] acetate tetra hydrate $[C_4H_{16}NiO_8]$ from Merck & Co. Ltd. was used in the solution A. Another 1 mole of Sodium hydroxide [NaOH] is the second solution. When deionized water was used as a solvent in the two 250 ml beakers for Solutions A and B, respectively, a magnetic stirrer with a pellet was used to agitate the solution for six to seven hours, after which the solution was mildly mixed drop by drop. As a result, the precipitation of NiO particles was achieved. The moisture was removed from the NiO particles using Hot air oven at a temperature of 120 °C, after they had been rinsed three or four times with an ethanol solvent. It was then transported to Hot Oven, where it was heated to 600 - 900 °C to remove impurities, before being ground into nanoparticles using an agate mortar. A series of characterizations of the title nanoparticles are discussed.

2.2. Characterizations

The following characteristics of NiO nanoparticles were determined by examining their characterizations: A scanning electron microscope (JSM-6330TF) operating at 10 kV was used to study the surface morphology of nickel oxide nanoparticles. A MAC Science MXP18 diffractometer with Cu K α radiation ($\lambda = 1.5405$) at 40 kV and 30 mA and a scanning speed of 2 to 4 min⁻¹ was used to conduct the powder XRD observations. Nickel oxide infrared spectrum is revealed using Fourier transform Interferometer. The SHIMADZU Spectrophotometer with the KBr pellet method was used to record nano particles from 4000 cm⁻¹ to 400 cm⁻¹. We were able to look at this sample's UV-Vis absorption spectrum (Model-Perkin Elmer Lambda 35) with the help of a UV-Vis spectrophotometer. The B3LYP/6-311+G (d, p) and 6-311++G (d, p) levels of GAUSSIAN 09W are used to improve the natural shape of NiO nanoparticles.

3. Results and discussion

3.1. SEM analysis

The appearance and structure of nanoparticles may be clearly seen using a scanning electron microscope (SEM). In this SEM pictures of the produced nanoparticles in various magnification images, such as a. 2 μ m, b. 5 μ m, c. 10 μ m, d. 20 μ m are shown in Figure 1. Clusters of nickel oxide nanoparticles were seen in the Figure 1.a at the beginning of the magnification process, and have spherical shapes. Nano branches were exhibited in Figures 1.b, then Figure 1.c shown the nano spheres with measurably, and Then, in Figure 1.d, the size of the nano cubes were clearly visible, as shown in the SEM image. As a result, separate SEM photos may show particle sizes of 371 nm, 145 nm, 92.2 nm, and 55 nm at 2 μ m, 5 μ m, 10 μ m, 20 μ m. The average size of nanoparticles has been determined to be 41.3 nm, which is in agreement [11] with previous reports.

1442



Fig. 1. SEM images NiO nanoparticles

This demonstrated that as magnification increases, so does the decreased particle size. This nano particle shape demonstrated that magnification increases as decreased particle size.

3.2. Powder X-ray diffraction studies

Figure 2 shows the X-ray diffraction patterns of the nickel oxide (NiO) nanoparticles as a result of powder X-ray diffraction experiments. pure cubic phase with miller indices of hkl planes (111), (200), and (220) at notable peaks at 37.06°, 43.16°, and 62.7° respectively [9-11], which were published in JCPDS NO. 711179 and no further peaks in the XRD pattern suggest that the transition metal ions were attenuated at the Ni sites without modifying the cubic structure. When determining the average grain size (D), Scherer's equation is used.

With a particle form factor (k) of (0.94), Braggs diffraction angle (θ), wavelength (λ) of the (CUK α) radiation (1.5405A°), and full width half maximum of the pattern peaks (β) in radians, we get our equation. The relationship may be used to compute the crystallite grain size [12].

 $D = 0.94 \lambda / \beta \cos\theta$



Fig. 2. Powder XRD pattern of NiO nanoparticles.

In addition, the following is the density of crystallite dislocations (δ) as determined by the formula, and the following Table 1 indicated list of powder X-ray diffraction parameters;

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\delta = 1 / D^2 lines / metre<sup>2</sup>
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2 0 (radian)	(hkl)	β FWHM (deg.)	D Grain Size (nm)	δ Dislocation Density x10 ⁻⁴ (Lines / metre ²)
37.06°	111	0.1920	45.57	4.81
43.16°	200	0.4320	20.65	23.44
62.7°	220	0.3840	25.30	15.61
Average Crystallite Grain size [D]			49.49	
Average Dislocation Density [δ]				6.27

Table 1. Powder X-ray diffraction parameter of NiO nanoparticles.

3.3. Fourier transforms infrared spectroscopy

The NiO nanoparticles were analysed using the FT-IR spectrometer, and the results are shown in Figure 3. A peak in the absorption band at 851.4 cm⁻¹ has been ascribed to the O-H-O bending vibration mode, while a smaller peak at 487 cm⁻¹ seems to represent the stretching vibrational mode of Ni-O, which corresponds between Ni-O and another better peak at 621.5 cm⁻¹. There were sharp peaks like 1121.4 cm⁻¹ and 1426.6 cm⁻¹, confirming that the carbonates had exhibited. A strong peak at 1657.8 cm⁻¹ ascribed to the hydroxyl group was seen in the spectral spectrum. The C-H stretching mode has a lower peak intensity of 2959.4 cm⁻¹, whereas the O-H bending mode has a higher wide peak of 3333.0 cm⁻¹. The peaks in the FT-IR spectra showed that NiO nanoparticles had a functional group [13].



Fig. 3. FT-IR spectrum of NiO nanoparticles.

3.4. UV-Vis analysis

Figure 4 shows the absorption spectra of NiO nanoparticles using a UV-Vis spectrophotometer at temperatures ranging from 200 to 800 nm [14]. According to this, the cut-off wavelength for the current spectrum's absorption spectrum is 277 nm, with the highest absorption occurring at that wavelength. The absorption gradually increases across the visible spectrum while it continues to diminish until the end of the UV zone. As a result, these nanoparticles would have higher transmittance and could be useful in opto-electric applications.



Fig. 4. UV-Vis spectrum of NiO nanoparticles.

3.5. Computational investigations

3.5.1. HOMO – LUMO analysis

The Frontier orbital describes molecular stability and reactivity [14]. HOMO and LUMO (FMO) are Frontier Molecular Orbitals. The energy gap between HOMO and LUMO determines a molecule's electrical conductivity. EHOMO and ELUMO infer Koopman's theorem's chemical potential, hardness, electrophilicity, and electronegativity. A molecule with a tiny energy gap is highly polarizable, unstable, and reactive. Figure 5 depicts HOMO and LUMO graphs for the DFT molecule at the HF, B3LYP, and 6-311++G (d,p) levels. Red and green represent positive and

negative phases. Table 2 shows the HOMO/LUMO energy separation and the molecule's affinity (A), Chemical potential (μ), electronegativity (χ), HOMO, and LUMO energies.



Fig. 5. The Frontier Molecular Orbitals for NiO nanoparticle.

	HF			DFT/B3LYP		
Molecular parameters /Basis set	6-31+G(d, p)	6-311+G(d, p)	ZTVq-20	6-31+G(d, p)	6-311+G(d, p)	ZL/d-ɔɔ
E _{HOMO}	-0. 483	-0.834	-0.354	-0.264	-0.662	-0. 612
E _{LUMO}	0.094	0.054	0.026	-0.028	-0.870	-0.008
$\Delta E_{LUMO-HOMO}$	0.937	0. 933	0.470	0.146	0.197	0.118
Ι	0. 438	0. 483	0.354	0.624	0.626	0.216
А	-0. 409	-0.450	-0.026	0.820	0.807	0.008
η	0. 981	0.917	0.023	0.802	0.890	0.900
S	2.255	2.385	2.634	6.980	5.861	5.565
μ	-0. 491	-0. 511	-0. 411	-0.614	-0. 617	-0.711
χ	0.914	0.511	0.114	0.641	0.167	0.711

Table 2. HOMO/LUMO energy parameters.

3.5.2. Molecular electrostatic potential

An electrostatic potential surface determines molecular bonding, reactivity, and structural activity [14-16]. Dipole moment, electro negativity, partial charges, and molecular reactivity are all related to electrostatic potential. The Molecular Electrostatic Potential Surface (MESP) shows the relative polarity of a molecule. Positive electrostatic potential harmonises with proton repulsion by atomic nuclei in locations with low electron density and incompletely shielded nuclear charge (shades of blue). The molecular electrostatic potential surface created with B3LYP/6-311++G (d, p) and Gauss View 5.0 is shown in Figure 6. Different hues indicate surface electrostatic potential.

1446



Fig. 6. Electrostatic potential surface for NiO nanoparticles.

Red represents negative electrostatic potential, blue positive and green zero. Red > yellow > green > light blue > blue = potential. Positive (blue) zones were matched to electrophilic reactivity. MESP is important because it concurrently exposes molecule size, shape, positive, negative, and neutral electrostatic potential zones in colour grading and is highly useful in analysing molecular structure with physiochemical property correlation. From Fig. 7 and 8, for NiO nanoparticles molecules, the electrophilic sites (negative zone: red) are mainly over the oxygen atoms while the nucleophilic sites (positive zone: blue) are around the nitrogen atoms, where blue specifies the strongest attraction and red specifies the strongest repulsion. O atoms have the highest repulsion, whereas N atoms have the strongest attraction.



Fig. 7. The total electron density surface for NiO nanoparticles.



Fig. 8. Electrostatic Potential of counter for NiO nanoparticles.

3.5.3. Thermodynamic properties

Table 3 shows the thermodynamic properties of NiO nanoparticles at room temperature calculated with B3LYP and a 6-311++G (d, p) basis set [17]. Scaling factors are used to forecast zero-point vibrational energies and entropy (S). Total energy seems to decrease with larger basis sets. The change in DFT room-temperature total entropy at various basis sets was minimal. Table 3 shows the time-dependent thermodynamic parameters of the DFT molecule, including heat capacity at constant volume (*Cop, m*), entropy (*Som*), and enthalpy (*Hom*).

T(K)	S (J. mol ⁻¹ .K ⁻¹)	Cp (J.mol ⁻¹ .K ⁻¹)	$\Delta H0 \rightarrow T (kJ.mol^{-1})$
100	373.02	23.1	8.52
200	492.88	189.95	28.05
298.15	573.95	232.06	49.6
300	555.68	263.46	45.67
400	634.66	388.35	69.79
500	789.78	445.29	120.06
600	870.61	481.26	122.48
700	996.83	547.27	291.98
800	923.45	525.24	275.67
900	1012.73	583.85	312.82
1000	1109.98	653.39	362.87

Table 3. Temperature dependence of the thermodynamic properties of NiO nanoparticles determined by DFT/B3LYP 6-311++G (d, p) method.

Because molecule vibrational intensities increase with temperature from 100 to 1000 K, these thermodynamic functions do as well. Figure 9 shows the correlations between thermodynamic properties and temperature. The correlation equations between heat capacities, entropies, enthalpy changes, and temperature are fitted by quadratic formulas, and the fitting regression factors (R2) for these thermodynamic properties are 0.99983, 0.99043, and 0.99956.

 $C^{\circ}p,m = 277.98134 + 1.09319 \text{ T} - 2.54325 \text{ X} 10-4 \text{ T2} (\text{R2} = 0.99983)$ $S^{\circ}m = -56.15568 + 1.24319 \text{ T} - 5.85759 \text{ X} 10-4 \text{ T2} (\text{R2} = 0.99043)$ $H^{\circ}m = -9.38261 + 0.11772 \text{ T} + 2.78037 \text{ X} 10-4 \text{ T2} (\text{R2} = 0.99956)$



Fig. 9. The effect of temperature on entropy (S), heat capacity (C_p) & enthalpy change $(\Delta H0 \rightarrow T)$ of NiO nanoparticles.

3.5.4. Natural bond orbital analysis

Natural bond orbital (NBO) procedures derive basic bonding notions from Hartree-Fock (HF), DFT, and post-HF calculations. An NBO analysis was developed to analyse hybridization and covalence in diatomic wave functions using a local block Eigen function and a one-particle density matrix. As molecular building blocks, NBOs resemble unlocalized bonds and lone pairs. Table 4 shows the atomic charges, core, valences, and total charge of NiO nanoparticles computed using NBO and B3LYP/6–31+G (d, p). O₂ and N₃ are negatively charged ring carbon atoms in NiO nanoparticles. NiO nanoparticles' amino group resonance gives O₁ negative charges. NiO nanoparticles have identical O₅ and O₆ charges. Hyper conjugative methyl groups provide NiO nanoparticles with negatively charged methyl carbon atoms N6. Table 5 shows NiO nanoparticles' natural atomic orbitals, occupancies, and energy. In a given molecular environment, natural atomic orbitals reflect the chemical give and take of electronic interactions, with variations in shape (e.g., angular deformations due to steric pressures of adjacent atoms) and size (e.g., increased anionic or cationic character) distinguishing them from free atom forms. The Kohn-Sham operator (F) is used to compute NBO orbital energies (A) which correlated interatomic influences on molecular characteristics.

Atom No.	Charge	Core	Valence	Total
01	0.57915	1.99937	5.56249	7.57915
O2	0.08908	1.99912	4.06298	6.08908
N3	0.04278	1.99910	4.02585	6.04278
O4	0.35421	1.99894	4.32938	6.35421
05	0.04278	1.99910	4.02585	6.04278
N6	0.43370	0.00000	5.06333	0.56630
07	0.22971	0.00000	0.76896	0.77029
08	0.69612	1.99949	4.68856	6.69612
N9	0.24329	0.00000	0.75479	0.75671
O10	0.24028	0.00000	0.75813	0.75972
N11	0.24861	0.00000	0.75025	0.75139
O12	0.23186	0.00000	0.76657	0.76814
013	0.69612	1.99949	4.68856	6.69612
N14	0.24329	0.02670	0.75479	0.75671
015	0.24861	0.04256	0.75025	0.75139
016	0.24028	0.02997	0.81753	0.97275
N17	0.22971	0.06868	0.89676	0. 29770

Table 4. Atomic charges of NiO nanoparticles calculated using the B3LYP and NBO techniques.

$$\boldsymbol{\epsilon}_{i}^{\left(\mathrm{A}\right)}=\left\langle \boldsymbol{\theta}_{i}^{\left(\mathrm{A}\right)}\left|F\right|\boldsymbol{\theta}_{i}^{\left(\mathrm{A}\right)*}\right\rangle$$

Atom No.	Atomic orbital	Туре	Occupancy	Energy
01	1s	Core	0.99969	14.19257
	2s	Valence	0.61019	0.52846
	2p _x	Valence	0.93370	0.28160
	2p _v	Valence	0.70719	0.25367
	2pz	Valence	0.65583	0.24434
02	ls	Core	0.99956	10.06820
	2s	Valence	0.45872	0.16227
	2p _x	Valence	0.66749	0.13422
	2p _y	Valence	0.52767	0.03912
	2pz	Valence	0.49784	0.02260
	1s	Core	0.99955	10.04104
	2s	Valence	0.44940	0.14922
O4	2p _x	Valence	0.46622	0.07889
	2p _y	Valence	0.53180	0.03465
	2pz	Valence	0.52968	0.03196
	ls	Core	0.99948	9.99978
	2s	Valence	0.47403	0.13927
O5	2p _x	Valence	0.76074	0.12199
	2p _v	Valence	0.60256	0.03736
	2pz	Valence	0.52857	0.02050
	ls	Core	0.99955	10.04104
	2s	Valence	0.44940	0.14922
07	2p _x	Valence	0.46622	0.07889
	2p _v	Valence	0.53180	0.03465
	2pz	Valence	0.52968	0.03196
	ls	Core	0.99956	10.06820
	2s	Valence	0.45872	0.16227
08	2p _x	Valence	0.66749	0.13422
	2p _v	Valence	0.52767	0.03912
	2pz	Valence	0.49784	0.02260
N3	ls	Valence	0.27777	0.11773
N6	1s	Valence	0.38069	0.08826
	1s	Core	0.99974	10.03765
N9	2s	Valence	0.54920	0.24879
	2p _x	Valence	0.62806	0.07543
	2p _v	Valence	0.60980	0.07456
	2pz	Valence	0.55944	0.06806
O10	ls	Valence	0.37769	0.10148
O11	1s	Valence	0.37838	0.09800
N12	1s	Valence	0.37403	0.10171
O13	1s	Valence	0.37728	0.11764
	1s	Core	0.99974	10.03765
N15	2s	Valence	0.54920	0.24879
	2p _x	Valence	0.62806	0.07543
	2py	Valence	0.60980	0.07456

Table 5. The atomic orbital occupancies of NiO nanoparticles.

4. Conclusion

NiO nanoparticles have been successfully synthesised using the hydrothermal technique at high temperatures. As determined by scanning electron microscopy, NiO nanoparticles have an

average grain size of 41.3 nm. In terms of grain size and dislocation density, powder XRD investigation reveals that NiO nanoparticles have a cubic structure. The functional groups of the NiO nanoparticles were found using FTIR and measured at various peaks. A cut-off wavelength of 277 nm suggests that NiO has a remarkable capability of absorbing UV-Vis wavelengths longer than other materials. The B3LYP calculations on the molecular properties of NiO nanoparticles have been studied. In the presence of a reactive molecule with an unstable feature, the computed HOMO and LUMO energies demonstrate that charge transfer takes place inside the molecule. MESP maps demonstrate that oxygen atoms have negative potential sites, whereas hydrogen atoms have positive potential sites, revealing information about molecular structure and physiochemical properties. Potential uses for nanoparticles of NiO include optical and electronic.

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