Semi-conducting Ni/Zn nano-hybrids’ driven efficient electro-catalytic performance: fabrication, characterization, and electrochemical features’ elucidation

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ABSTRACT
The current work reports the synthesis, analytical evaluation, and electrochemical performance investigation of green bio-factories’ triggered mixed metal oxides’ nano-hybrids comprising of nickel (Ni) and zinc (Zn) for the first time. Modified sol–gel synthetic route used for the synthesis of NiO/ZnO green nano-hybrids ([NiO/ZnO]-GNH) is devoid of utilization of any chemical-reducing agents. Efficient [NiO/ZnO]-GNH electro-catalysts were characterized for various aspects using Fourier transform infra-red spectroscopy (FT-IR), gas chromatography and mass spectrometry (GC-MS), energy-dispersive X-ray spectroscopy (EDX), field emission scanning electron micrographs (FE-SEM), UV-Visible spectrophotometry (UV-Vis), and X-ray photoelectron spectroscopy (XPS). Oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) steps of water splitting reactions were evaluated via linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) via fabrication of modified Ni-foam electrode through decoration of [NiO/ZnO]-GNH. The as-synthesized [NiO/ZnO]-GNH promises electro-catalytic performance with a small over-potential of 0.42 V and 264 mV for OER and HER, respectively, for the achievement of a current density of 10 mA/cm². Results of the current work can be extended to the practical scale adoption of the fabricated electro-catalysts through optimized investigation and economical evaluation for the consolidation of environmental sustainability and green energy production.

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Introduction
Indiscriminate utilization of fossil fuels i.e. coal, oil, and natural gas for varied activities is associated with the emission of toxic gases e.g. SOx, CO2, NOx, CH4, etc., into environmental compartments leading to numerous ecologically periling consequences. Environmentally deteriorating events of global warming, climatic change, acid rain, and threats to biodiversity are some of these consequences. In addition to this, fossil fuels are the finite reserves which would diminish on a specific time scale due to over-utilization. Therefore, renewable sources of energy as an alternate to these non-renewable reserves need to be urgently explored and employed. Such infinite energy sources signify not only a safe and cleaner option to conventional fossil fuels but also marked by abundance and replenishment through natural and anthropogenic processes. Critically
elevating concerns of climate change as a result of burning of fossil fuels and increasing energy demand have motivated the researchers in consideration of infinite and clean energy alternatives. Electrochemical water splitting has been taken as an alternative approach to produce clean energy fuel by using renewable energy sources. A high performance efficient catalyst is required to promote the slow kinetics of water splitting in terms of hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Pt and Ru/ Ir-centered catalysts are known as the most favorable electro-catalysts for OER and HER, respectively, but their high cost and scarcity limit their application at commercial scale. Accordingly, investigations have been done to produce low-cost, abundant, and durable electro-catalysts for efficient OER and HER performance. Transition metal chalcogenides, carbides, phosphides, oxides, and hydroxides synthesized by physical or chemical routes have been extensively studied for both HER and OER studies in alkaline or acidic electrolytes (1) and gave remarkable performance. However, this strategy results in toxicity, pollution, and long hours to synthesize the material due to complex synthesis procedures and involvement of toxic chemical reagents (2).

Hydrogen (H₂) is a noteworthy green fuel having an inherent capability of substitution of vanishing hydrocarbons (3). H₂ as a fuel is a cleaner option with a renewable nature and possesses a remarkable energy content of 122 kJ/g obtained from various resources, including naturally existing and bio-resources. Energy yield gained from H₂ fuel is proved superior to that of hydrocarbon-based fuels up to 2.75 times, which is also devoid of emission of toxic gases including CO₂ and other gases into environment. Rather, the major combustion product obtained upon H₂ utilization is water; this product can be recycled to obtain even more H₂. This approach strengthens the concept of sustainability and green energy policy, for which it has attracted greater attention in the form of fuel cell electricity production, and also, fuel used for transportation and combustion purposes (4). However, the fact that there are no natural reserves for H₂ gas as in the case of fossil fuels cannot be neglected, and the conventional methods employed for its generation are not viable from an economic perspective. In the current era, H₂ generation is accomplished via non-renewable resources. Fossil fuels accounts for 98% generation of H₂; followed by natural gas or steam restructuring of hydrocarbons accounting for ~40%. ~30, 18, 4, and 1% of H₂ generation is attributed to oil, coal, water electrolytic procedures, and biomass, respectively (5). In such a scenario, the development of green modes aimed at green H₂ production would secure the future needs in addition to satisfying current energy crises. Novel and efficient materials in this regard can be potential candidates for green production of H₂ in a cost-effective, energy in exhaustive, and environment-friendly manner (6).

A p-type semiconductor oxide, nickel oxide (NiO), is known for its favorable characteristics, such as conductivity and transparency, possessing a structure similar to rock salt (NaCl). Ni is an abundantly available material having low cost which makes it a good candidate for utilization as a catalyst (7). NiO has been investigated for its potential to be used in various applications e.g. ultraviolet detectors, photovoltaic solar cells, light emitting diodes (LEDs), displays, photodetectors, and electrochromic devices etc. Furthermore, NiO is an efficient hole transport layer (HTL), catalyst for hydrogen evolution reaction (HER), and oxygen evolution reaction (OER), photo-cathode besides carrier selective contact. In addition to HER, Ni and its associated oxides are used for cracking of hydrocarbons, CO₂, and O₂ generation procedures (8). Zinc oxide (ZnO) has been another remarkable metal oxide used for catalysis applications for many years due to its stable, environmentally benign, comparatively abundant nature, and economic viability. ZnO is also very flexible in terms of band gap tailoring via different techniques. Many research studies reports fabrication of ZnO nanoparticles (NPs) with varied morphologies used in different applications (9,10). Various synthetic modes have been employed for metal oxides e.g. chemical bath deposition, co-precipitation, and hydrothermal methods. Of them, hydrothermal route has been the frequently used method (11).

Nano-composite hybrid of NiO/ZnO has been fabricated and used in different applications by virtue of their favorable opto-electronic, mechanical, catalytic, thermal, and mechanical characteristics. Mixing semiconductor metal oxide, having nano-dimensions and varied band gaps in the form of nanocomposites, has been shown to express impressive physicochemical aspects. In this regard, NiO/ZnO nanocomposite has gained prominence due to their intrinsic semiconductor characteristics i.e. NiO is p-type, while ZnO is n-type material with approximately 3.6 and 3.37 eV of direct band gap, respectively (12,13). Therefore, NiO/ZnO nano-hybrids express outstandingly new properties. Furthermore, as binary metal oxides, they show excellent electrochemical performance in terms of high extent of redox behavior and electrochemical conductivity as compared to single phase metal or metal oxides. Mixing of n-type and p-type metallic oxides at nanometer scale gives rise to the formation of a p-n junction giving rise to interesting characteristics for
nano-technological applications. The conventional methods used for the synthesis of single metal oxides have been utilized for metal oxide nano-hybrids e.g. homogeneous precipitation, sol–gel, solvo-thermal, hydrothermal, electro-spinning etc. (14,15). An array of these chemical and physical methods adopted for the fabrication of nano-materials used in different applications is known for some practical scale limitations. For instance, chemical routes are based on using synthetic toxic compounds which are not only released into environment but also remain there for an infinite time due to their persistent nature. In the similar manner, physical routes used complicated reaction conditions e.g. elevated temperature and pressure. Such problems render physicochemical synthetic modes unfit for utilization at commercial scale due to economic, environmental, and operational concerns. Biogenic synthetic route, on the other hand, is in complete harmony with the rules of green chemistry and sustainability. Green nano-materials are fabricated using nature’s biological factories i.e. plants, microbes etc. Bio-molecules from plants and microbes are used as reducing and stabilizing agents for nanomaterial fabrication. Nanomaterials synthesized via biogenic route signify a facile, economical, non-toxic, and bio-compatible agents for different applications i.e. electro-catalysts (16), super-capacitors (17), antimicrobial agents (18), and photo-catalysts (19) etc.

Adoption of a greener route is advantageous over other physical and chemical methods in terms of sustainability and production of good quality nanoscale materials having sound economic viability. Metallic and metal oxide NPs have been synthesized via a chemical route by using strong bases as reducing agents e.g. sodium borohydride or hydrazine or sodium hydroxide, which reduces the metallic ions from salt solution. Additionally, capping agents are added for the stabilization of the NPs. Such synthetic chemicals are not only toxic to the environment but also hostile for human and other life forms. On the contrary, biogenic synthesis done through nature’s bio-factories signifies a completely benign route (20–23). Although the production of composites can be achieved through heating of the precursor salts, such methods are not good for the production of large-sized particles having an elevated extent of agglomeration. For instance, in the previous studies done with chalcogenides, agglomerated particles were reported despite utilization of chemical ligands like dithiocarbamtes (24–26). Therefore, utilization of bio-derived reducing agents is a sustainable option for the production of stabilized nanoparticles having negligible agglomeration (27,28) and for this reason, greener nanomaterials are gaining a focus of the scientific community. Opto-electronic and other features of nanomaterials synthesized via the greener route can be easily tuned by changing reaction conditions for utilization in a diverse range of applications ranging from photovoltaics to biomedical devices. Greener synthesis of NPs is associated with the comparatively easier separation of the synthesized NPs from reaction media via centrifugation. The selection of biological agent for green NPs synthesis is usually dependent on the type of the reducing phyto-constituents having a higher potential of reduction and stabilization (29). *Olea ferruginea* Royle belonging to Oleaceae family has been granted with a unique mix of phytochemicals, possessing reducing and stabilizing power. This plant is underutilized in terms of biogenic nanoparticle synthesis, but has been used as an important ethno-medicinal agent for curing different ailments. Leaf and bark parts of this plant are rich sources of phenols (30). Trees of *Olea ferruginea* Royle are known for covering 8 million hectares of land, especially in Mediterranean countries (31). Therefore, the diet of inhabitants residing such areas is usually based on *Olea* fruits and oils. *Olea ferruginea* Royle leaves comprise of oleuropein and oleacin, which are cherished for their remediative roles in hypoglycemic and hypotensive activity, respectively.

Investigations in great detail have been done on the exploration of the water splitting potential of different transition metal oxides. However, ZnO has attracted a special attention by virtue of facile synthetic procedures, comparatively lower cost, higher availability extent, and ecologically non-toxicity. In the current era, many researchers attempted to enhance the water splitting potential of ZnO by modifying it through composite, alloying, doping etc. with other metals. Furthermore, development of different types of nanoscale materials, such as nanorods, nanoflowers, nanowires etc., has been done for obtaining a maximized extent of water splitting. For instance, in a recent report by Pavlenko et al. (32), ZnO NPs were modified by the formation of n-Si/TiO2/ZnO and an enhancement in the photocurrents was obtained owing to the presence of the barrier effects (32). In another study, ZnO nanorods were synthesized having a nucleation regulated vertical orientation. Such ZnO nanorods expressed a commendable water splitting potential (33). Yoo et al. (34) reported an impressive hydrogen evolution for ZnO particles fabricated using a precipitation route reaching up to 1092.5 μmolg⁻¹ h⁻¹. In terms of doping ZnO for performance enhancement, Co-doped ZnO nanorods having a coating of metal – organic framework with profound transparent functionalization was proved to be an efficient photo-anode for water splitting. Such an enhanced performance is attributable of the
improvement in the light absorption brought in ZnO nanorods via Co doping. In addition to this, molecular organic framework improved the transferal aspects, stability, and separation of the charged species (35). Similarly, doping of ZnO with Fe synthesized via aerosol-assisted chemical vapor deposition (AACVD) has also been reported to be effective in water splitting (36). Nanocomposite of ZnO-NiO has been synthesized recently through the chemical method and used for sulfasalazine photodegradation (37). All these reports are indicative of the great potential of ZnO and its modified versions as an efficient material for water splitting, but no reports are available on the water splitting investigation of NiO/ZnO green nano-hybrids [NiO/ZnO]-GNH. Also, to the best of our knowledge, no study has been reported based on the utilization of secondary metabolites of Olea ferruginea Royle leaves for the synthesis of NiO/ZnO nano-hybrids as efficient electro-catalysts for green energy production via OER and HER. Therefore, the current work has, for the first time, undertaken the synthesis of mix metal oxides based on [NiO/ZnO]-GNH using biological assets of Olea ferruginea Royle leaves. The synthesized [NiO/ZnO]-GNH was analyzed for different characteristics using different analytical tools i.e. Fourier transform infra-red spectroscopy (FT-IR), gas chromatography and mass spectrometry (GC-MS), X-ray diffraction (XRD), Energy-dispersive X-ray spectroscopy (EDX), field emission scanning electron microscope (FE-SEM), UV-Visible spectrophotometry (UV-Vis), and X-ray photoelectron spectroscopy (XPS). Furthermore, the electro-catalytic role of [NiO/ZnO]-GNH was also evaluated by investigating OER and HER explored via linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) by fabricating on Ni-foam as a working electrode. The catalyst expressed remarkable efficiency toward OER as compared to HER. Therefore, by conforming the phyto-synthesis approach, pure cubic-shaped [NiO/ZnO]-GNH based electro-catalyst materials have been synthesized.

Methods

Chemicals and reagents

Metal salts i.e. nickel (II) acetate tetrahydrate (Ni(CH3CO2).2·4H2O), zinc acetate (ZnO(CH3COO)2), and other reagents i.e. ethanol (C2H5OH), polyvinylidene difluoride (PVDF) [−(C2H2F2)n−], N-methyl pyrrolidinone (NMP) [C5H9NO], potassium hydroxide (KOH), sodium hydroxide (NaOH), and potassium bromide (KBr) were purchased from Merck chemicals Ltd. Germany. Acetylene black was procured from VWR Chemicals BDH, United Kingdom, and used as received. Entire experimentation was done with deionized water (DI) and the apparatus was sterilized with C2H5OH. Reducing cum stabilizing agents were extracted from foliar extracts of Olea ferruginea Royle sampled from Rawalakot region (33.8584° N, 73.7810° E) located in Azad Kashmir (33.9259° N, 73.7810° E). Sampled leaves were shade dried, extracted with DI, and stored at 4°C for utilization as reducing agents and characterization.

[NiO/ZnO]-GNH electro-catalyst synthesis

Biomimetic synthesis of [NiO/ZnO]-GNH electro-catalysts was synthesized using biological agents as reducing agents by adoption of the conventional sol–gel route without utilization of chemical reducing agents. The generalized path adopted in the current work has been shown in Figure 1. 20 mM of metal salts i.e. Ni(CH3-CO2)2·(4H2O) and ZnO(CH3COO)2 stock solution were prepared separately inside 250 mL beakers using DI. Leaf extract of Olea ferruginea Royle was prepared by mixing 2 g of plant powder and 100 mL of DI. Plant powder mixed in DI was boiled at 40°C for 20 min, centrifuged, and cooled down for 1 h. Metal salt solutions of Ni(CH3CO2)2·(4H2O) and ZnO(CH3COO)2 were mixed and stirred for 20 min for gaining homogeneity. It was followed by the addition of 10 mL of Olea ferruginea Royle leaf extract in a dropwise manner. The reaction mixture, containing metal salts and leaf extract, was stirred for 1 h at 80°C. pH of this mixed metallic oxide complex solution was regulated at 8 through the addition of NaOH drops. Formation of biomimetic [NiO/ZnO]-GNH electro-catalysts was indicated physically by the conversion of the metal complex solution to a dark brownish gel. The obtained gel was washed twice with DI and C2H5OH. Washed gel was further purified by the expulsion of any organic residuals by drying at 95°C inside the hot air oven (UN110, Memmert, Germany) followed by calcination at 450°C in the furnace (D550, Ney Vulcan, U. S. A.). Finally the obtained mixed metal oxide nano-hybrid was stored in properly labeled eppendorfs for utilization in electro-catalytic experiments.

Characterization

Biomimetic synthesized [NiO/ZnO]-GNH electro-catalysts were evaluated for chemical and physical peculiarities using a myriad of characterization techniques. The presence of organic functional groups and molecular arrangements in Olea ferruginea Royle foliar extract was analyzed using FT-IR (8400, Shimadzu,
Japan), secondary metabolites in the leaf extract were analyzed via GC-MS (QP5050, Shimadzu, Kyoto, Japan). [NiO/ZnO]-GNH electro-catalysts were also analyzed for chemical composition using FT-IR, scanning range in the case of both leaf extract and synthesized nano-hybrid was varied from 4000 to 400 cm$^{-1}$. Crystal specifications and lattice parameters of [NiO/ZnO]-GNH electro-catalysts were analyzed by XRD (Bruker Advanced X-ray Solutions D9, U. K.). Morphological and elemental composition of the synthesized nano-hybrids were examined using FE-SEM (Quanta 250-FEG, Thermo Fisher Scientific, U.S.A.) and EDX (Bruker, U.S.A), respectively. Optical feature exploration and band gap measurement were done using (UV–Vis, spectrophotometer 1602, Biomedical services, Spain). Surface characteristics of green nano-hybrid were analyzed using via XPS (Lucideon, U.K.).

[Nio/ZnO]-GNH electrode preparation

[NiO/ZnO]-GNH modified electrode was fabricated by mixing [NiO/ZnO]-GNH (80 wt. %), acetylene black (10 wt. %), and PVDF (10 wt. %) using NMP in background. The reaction mixture was homogenously mixed and the resultant slurry was applied on Ni-foam in the form of a uniform deposition under vacuum for 12 h at 60° C. [NiO/ZnO]-GNH mass loading was weighed in an accurate manner by means weighing Ni-foam mass prior to and after the preparation of the modified electrode using analytical balance.

Electrochemical measurements

The electrochemical performance of [NiO/ZnO]-GNH synthesized using biomolecules of Olea ferruginea Royle foliar extract was studied using an electrochemical work-station (Princeton Applied Research, U.S.A.) having conventional electrode configuration. The standard assemblage used a counter electrode made up of graphite rod, reference electrode comprising of saturated calomel electrode (SCE), and the working electrode was the modified [NiO/ZnO]-GNH electrode prepared on Ni-foam. The electrochemical assemblage was immersed in an electrolyte solution having 1 M KOH. Examination for electro-catalytic functionality of [NiO/ZnO]-GNH included LSV and EIS. LSV investigations were done at 1 mV/s rate with potential conversion to RHE in accordance with Nernst equation. Measurements for EIS were recorded by applying 10 mV of alternating current (AC) amplitude with the frequency range varying from 0.05 Hz to 10 kHz.

Results and discussion

Secondary metabolite exploration

Olea ferruginea Royle leaf extract was analyzed for the detection of organic functional groups and secondary metabolites via FT-IR and GC-MS spectroscopic techniques. FT-IR, UV-Vis, and GC-MS chromatograms of Olea ferruginea Royle leaf extract have been presented in (Supplementary Figure S1) and (Supplementary Tables S1 and S2). UV-Vis spectrophotometric analysis was done in the range of 200–800 nm. Prominent peaks of phyto-compounds found in Olea ferruginea Royle leaf extract have been distinguished, as shown in (Supplementary Figure S1(b) in the ultra-violet and visible region. Phenolic components were indicated by the UV-Vis detectors in the UV-Visible region which is attributable to the expression of conjugated benzene-based systems known for the absorption of the light, preferably in the UV region (38,39). In Supplementary Figure S1(a), the absorption peak appearing at 271 nm
corresponds to the phenolic components comparable to flavonoids comprising of benzene ring with conjugated association at A site. In general, the absorbance detected between 200 and 520 nm is due to phenols and flavonoids in addition to flavones and flavonols showing the presence of these compounds in *Olea ferruginea* Royle leaf extract.

Molecular arrangements and organic functional groups explored via FT-IR in the scanning range of 4000–400 cm$^{-1}$ expressed varied phyto-metabolites in the powder of *Olea ferruginea* Royle leaf extract. FT-IR spectrum illustrated the vibration of phyto-compounds at different frequencies i.e. 3382.28, 2922.25, 1645.33, 1424.40, 1321.43, 1094.39, 1018.05, 666.40, and 797.11 cm$^{-1}$ as expressed in Supplementary Table S2. Vibration detected at 3382.28 cm$^{-1}$ is representative of the O–H stretching corresponding to the presence of alcohols and phenols in the extract. The frequencies at 2922.25 and 1645.33 cm$^{-1}$ represent the C–H stretch and –C=C– stretch suggesting alkanes and alkynes, respectively. The peak at 1404.22 cm$^{-1}$ is associated with C-C stretch (ring) representing the presence of aromatic compounds in the *Olea ferruginea* Royle leaf extract. Nitro-compounds were also indicated by the FT-IR pattern showing N-O symmetric stretch observed at 1424.40 cm$^{-1}$. Minor vibration, at frequencies 1094.39 and 1018.05 cm$^{-1}$, was attributed to alkyl halides having C–H wag (–CH$_2$X) bond. Besides these compounds, aromatic amines, ethers, alcohols, esters, carboxylic acids, aliphatic amines, and alkynes were also indicated. Comparatively minor vibration was observed at 797.56 and 666.40 cm$^{-1}$ expressing the presence of =C–H bend and C–Cl stretch, respectively. Hence in conformity with the UV–Vis analysis, results of FT-IR corroborated the presence of phenolic compounds, alcohols, carbohydrates, alkane, alkenes, amines and aromatics exhibiting phenols, flavonoids, and alkaloids in the plant extract. GC-MS profiling was used for exploring the exact secondary metabolites present in *Olea ferruginea* Royle leaf extract. Supplementary Table S2 is expressive of the presence of varied secondary metabolites present in the methanolic extract detected at variegated retention times. Some of the conspicuous secondary metabolites i.e. 1-cyclohexylethylamine, cathinone, propanedioic acid, benzenemethanol, and 3-azabicyclo nonane are in shown Supplementary Figure S1(c).

The possible mechanism for the biological entity-based reduction of [NiO/ZnO]-GNH derived from *Olea ferruginea* Royle leaf extract has been depicted in Figure 2. A number of secondary phyto-metabolites are involved in the reduction cum stabilization of the metallic salts (40). Despite voluminous research studies done on the biogenic synthesis of NPs, the exact definition of mechanistic route, through which reduction and stabilization is done, has remained an open area of investigation for scientific researchers. Therefore, this mechanism is yet to be comprehended through further research. However, the involvement of biological molecules, especially alkaloids, phenolic compounds, terpenoids, and flavonoids in reduction, capping, and stabilization of biogenic NPs from metallic salts, can be associated with the presence of certain functional groups that develop a linkage with the metallic ions. As expressed from the GC-MS analysis, secondary phyto-metabolites, such as 1-cyclohexylethylamine, cathinone, propanedioic acid, benzenemethanol, and 3-azabicyclo nonane, found in the *Olea ferruginea* Royle leaf extract are responsible for the reduction of the metallic salts. Possibly, these compounds when interacted with metallic salt inside a reaction mixture, they caused the consequent alteration of the metallic salts through oxidation reaction through free radicals. Subsequently, electrostatic interaction was developed between the newly produced free radical and metallic precursor (18,19).

**[NiO/ZnO]-GNH analysis**

Transformation of reaction mixture stabilized by *Olea ferruginea* Royle leaf extract pointed the formation of [NiO/ZnO]-GNH. Reaction mixture changed from light brown
to blackish brown within 15 min expressing the complexation of the metallic particles followed by the consequent reduction and stabilization as observed in the case of other green nanomaterials also (16–19). Synthesized [NiO/ZnO]-GNH were analyzed for compositional, structural, morphological, elemental, and optical analysis via sophisticated techniques. Figure 3 (a) shows the FT-IR spectra of biomimetic [NiO/ZnO]-GNH stabilized via *Olea ferruginea* Royle leaf extract phyto-compounds. 450°C calcined [NiO/ZnO]-GNH expressed the presence of varied functional groups. FT-IR spectrum expressed the presence of metal oxide (M-O) bond below 700 cm$^{-1}$. Calcined [NiO/ZnO]-GNH powder exhibited prominent vibration at 522 cm$^{-1}$ shown in Figure 3 (a inset) corresponding to the M-O indicating formation of the metal oxide (41,42). The sharp and broad absorption peaks at 2038.0, 1374, and 1104 cm$^{-1}$ were associated with aromatic C–H stretch or due to O-H stretching; this type of vibration shows the characteristics of much hydrated compounds or adsorbed water molecules (43). In comparison with the *Olea ferruginea* Royle spectra, a number of peaks disappeared in spectra obtained for [NiO/ZnO]-GNH i.e. 2922, 1424, and 1321 cm$^{-1}$ referred to the presence of alkanes, alcohols, phenols, and aromatic compounds which are mainly playing the part in the reduction of metal ions (43). The role of phyto-compounds responsible for the reduction and stabilization of [NiO/ZnO]-GNH was further confirmed by GC-MS. GC-MS spectrum shown in Figure 3(b) expressed different compounds with corresponding retention time and peaks shown in Table 1. A detailed account of the corresponding compounds has been presented in (Supplementary Table S2). The identified capping agents are benzenemethanol and decanoic acid in good agreement with compounds predicted by FT-IR analysis shown in Figure 3(a). The presence of these compounds has also been confirmed in the methanolic extract of *Olea ferruginea* Royle. FT-IR and GC-MS results are suggestive of the reducing and stabilizing role of phyto-capping agents present in *Olea ferruginea* Royle (44).

Crystalline features and phase purity of *Olea ferruginea* Royle derived biomimetic [NiO/ZnO]-GNH were investigated via XRD shown in Figure 3(c). XRD pattern for [NiO/ZnO]-GNH expressed comparative peak intensities and location of constituent NiO and ZnO in conformity with JCPDS card no. 00-044-1159 and card no. 00-005-0664, respectively. NiO exhibited a rhombohedral
crystal structure with miller indices at (101), (012), (104), (113), and (202) represented by (\(\phi\)). But, ZnO presented a hexagonal structure having hkl index (100), (002), (102), and (110) corresponds to 31.75\(^{\circ}\), 35.44\(^{\circ}\), 47.54\(^{\circ}\), and 56.55\(^{\circ}\) peak position, respectively. Average crystallite size (\(D\)) was calculated using Debye Scherrer’s relation shown by Equation (1):

\[
D = \frac{0.9 \times \lambda}{\beta \cos \theta}
\]

where \(\lambda\) is referred to the wavelength and \(\beta\) is representative of full width at half maximum intensity of the respective peak. Average crystallite sizes obtained by Equation (1) indicated NiO and ZnO to be of 7.84 and 9.07 nm, respectively. Crystallite sizes are indicative of the fact that they can be further reduced for biomimetic [NiO/ZnO]-GNH by means of optimized calcination.

The absence of any additional supplementary peaks confirms the remarkable purity and crystallinity of the synthesized [NiO/ZnO]-GNH by means of optimized calcination. The presence of carbon depicts the involvement of organic compounds present in Olea ferruginea Royle that acted as bio-factories for the conversion of metallic oxides to their nanoscale hybrids with a commendable crystallinity pattern.

Figure 4 expresses the FE-SEM micrographs of Olea ferruginea Royle-derived biomimetic [NiO/ZnO]-GNH recorded at different magnifications. Exploration of morphological details of nanomaterials is essential for comprehending the potential of these materials in different applications. [NiO/ZnO]-GNH expressed to be of cubic shape possessing resemblance with leaf having well-defined configuration with minimal agglomeration. Negligible agglomeration is ascribable to the profound role of secondary metabolites of Olea ferruginea Royle leaves responsible for reduction and stabilization of [NiO/ZnO]-GNH (46). Synthesized [NiO/ZnO]-GNH were also evaluated for surficial characteristics via X-ray photoelectron spectroscopy by using Kratos Axis Ultra XPS instrument, supplied with a monochromatic X-ray source (1486.6 eV). [NiO/ZnO]-GNH powder was pressed onto a double-sided, conducting graphite tape. The built-in charge neutralizer in the instrument was used to minimize charging of the sample. XPS spectra obtained for

| Retention time | Area (%) | Height (%) | Formula weight (g/mol) | Formula | Compound name       | Structure |
|---------------|----------|------------|------------------------|---------|---------------------|-----------|
| 12.8          | 1.01     | 1.84       | 171                    | C\(_{11}\)H\(_{25}\)N | 1-Methyldecylamine | [image]   |
| 25.6          | 2.58     | 4.06       | 243                    | C\(_{19}\)H\(_{41}\)N | 2-aminononadecane  | [image]   |
| 28.50         | 36.84    | 4.8        | 172                    | C\(_{10}\)H\(_{20}\)O\(_{2}\) | Decanoic acid | [image]   |

Table 1. Secondary metabolites found in the foliar extract of Olea ferruginea Royle used for the reduction and stabilization of biomimetic [NiO/ZnO]-GNH.
[NiO/ZnO]-GNH have been arranged on the scale of binding energy in association with aliphatic C–C/C–H at 284.8 eV (47) and binding energies are quoted to ±0.1 eV shown in Figure 5 (a–d). Narrow core level spectra for Ni 2p, Zn 2p, C 1s, and Ni 1s are shown in Figure 5(a). The Ni 2p spectrum consists of 5 peaks: a multiplet split Ni 2p3/2 peaks at 853.9 and 855.7 eV, the Ni 2p3/2 satellite at 861.0 eV, a broad multiplet split Ni 2p1/2 peak centered around 872.2 eV, and the corresponding 2p1/2 satellite at 879.8 eV. The Ni 2p3/2 peak has been fitted with multiplet peaks for NiO using the parameters determined by Biesinger and co-workers (48). Results expressed a considerably good fit to the data obtained from experiments and confirmed the presence of NiO at the surface. The Zn 2p spectrum in Figure 5(b) showed a doublet with peaks at 1021.9 and 1044.8 eV binding energies corresponding to the Zn-2p3/2 and Zn-2p1/2 spin-orbit split peak, respectively. The binding energies obtained for these peaks are consistent with ZnO (49,50).

The manifestation of various kinds of organic functional groups at the surface of the powders is indicated by the C 1s spectrum in Figure 5(c). The C 1s spectrum is fitted at 284.8, 286.4, and 288.5 eV corresponding to aliphatic C–C/H, C–OH, and O–C=O, respectively. We note that there will be a contribution to the C 1s peak from adventitious C since the samples are exposed to atmosphere prior to analysis, but the relative proportion of organic oxygen containing species is somewhat higher than would be expected for adventitious carbon, suggesting the presence of adsorbed plant extracts at the surface. We also note that there may be contributions to the 284.8 eV from aromatic plant compounds but that the binding energy of these components at 285 eV is too close to the aliphatic/adventitious C to meaningfully fit a peak here. The high-resolution O 1s spectrum shown in Figure 5(d) dominated by a relatively narrow peak at a binding energy of 529.4 eV will arise from the lattice oxygen of the Ni and Zn oxides (48,49). To the high binding energy side of the lattice oxygen peak there is a broad peak which can be fitted at binding energies of 530.9, 531.9 and 533.3 eV. The first of these arises from the formation of Ni hydroxides at the surface (48), but will also contain contributions from defects in the oxide lattice as well as surface hydroxides on the ZnO material (49,50). The peaks at 531.9 and 533.3 eV are consistent with the presence of organic oxygen species (51) in agreement with the C 1s spectra and offer further evidence of the presence of the plant extract at the surface of the powders and adsorbed water. XPS spectra (Figure 5(a–d)) have been recorded from a powder sample of the NiO/ZnO material. The Ni 2p3/2 spectrum in (a) is fitted with multiplet split features for NiO. All fitted peaks are 70:30 Gaussian: Lorentzian mixed peaks. A Shirley background is used for all peaks except Zn 2p where the negative slope for the Zn 2p3/2 peak is not consistent with a Shirley background.

**Band gap energy**

Synthesized [NiO/ZnO]-GNH were observed for optical characteristics via UV–Vis spectrophotometry in the...
range of 200–800 nm as shown in Figure 6(a). Prominent absorptive behavior has been observed at 343.19 nm. Previous research studies done on single metal oxides i.e. NiO and ZnO have also expressed nearly similar absorptive patterns. For instance, in a report by El-Kemary et al. (52) on NiO NPs, lambda maximum obtained was ~330 nm. Another report indicated the maximum absorption for NiO to be ranging between 190 and 237 nm (53). Similarly, ZnO has also expressed maximum absorption at 350 and 385 nm in previous reports (54,55). The absorption has been attributed to [NiO/ZnO]-GNH charge transfer transition, indicating the blue shift along with bathochromic shift, which suggested the involvement of phyto-capping agents of Olea ferruginea Royle e.g. phenols and alcohols which are involved in the synthesis of [NiO/ZnO]-GNH. The band energy of fabricated biomimetic [NiO/ZnO]-GNH was calculated utilizing absorption characteristics by via Tauc’s plot presented in Figure 6. Equation (2) shows the relationship used for finding band gaps for [NiO/ZnO]-GNH

\[ a\nu = (\hbar\nu - E_g)\hat{\alpha}(n) \]  

(2)

where \( \alpha \) is expressive of the absorptive coefficient, \( \hbar \nu \) is indicative of the incident photon energy, and \( E_g \) refers to the optical band gap energy. The corresponding band gap energy was decreased to 2.18 eV for phyto-capped [NiO/ZnO]-GNH, as marked in Figure 6(b). Thus, the band gap changed by a combination of mixed material and produced synergic effect in catalytic charge carrier properties of electro-catalyst.

Interestingly, the results are indicative of the reduction in the band gap of the synthesized nano-hybrid in comparison to the standard band gaps of the constituent materials i.e. ZnO (3.37 eV) and NiO (3.6 eV). The dependence of optical aspects of any material is largely associated with the structural properties. Such alleviated band gaps can be attributed to the increment in the crystallite size as a result of nano-hybrid formation. However, the currently obtained band gaps are in agreement with the previously obtained reports. In a report by Singh et al. (56), ZnO yielded 2.81 eV of energy band gap (56). ZnO has been ranked as a semiconductor having a wider band gap in the UV region and thus its energy harvesting is limited to this region only. Such challenge can be resolved via doping of the ZnO with other metallic oxides having considerably narrower band gaps which will cause an augmentation in the sensitization process (57). Ahmad and Jaffri (58) fabricated photo-catalysts having greater efficiency with composition of silver-doped ZnO nanostructures and obtained a band gap of 2.81 eV. They attributed the reduction in the band gap to the to the oxygen vacancy leading to the facilitation of the transferal of the electronic species between valence band (VB) and conduction band (CB) (58,59). Also, in the case of NiO, the obtained results expressed conformity with Hosny (60), who synthesized nanoscale NiO and obtained diverse band gaps i.e. 2.45, 2.82, 2.93, and 3.12 eV by alteration of the experimental conditions and suggested their NiO to be commendable agents for utilization in the solar cell applications for the harvesting of the solar radiations. In another report, a band gap of 0.85 eV for NiO was indicated (61). In terms of considering studies based on the modification of NiO host material with dopants such as iron (Fe), an alleviation of band gap was obtained from 3.48 eV to 2.86 eV, possibly associated with the involvement of the dopant material in causing structural disfiguration of the host material. Additionally, such reduction in size can be associated with the interplay of the Burstein-Moss effect (62,63). In addition to doping-based investigations, Hussain et al. (64) obtained band gap energies of 2.1 and 1.9 eV for pristine NiO NPs and nanocomposites of NiO and carbon nanotubes (CNTs), respectively (64).

Figure 6. Optical features of biomimetic NiO/ZnO nano-hybrids: (a) UV-Vis absorption spectrum, and (b) Tauc’s plot of energy vs. \( a\nu^2 \).
Figure 7. Measurements for OER electro-catalytic performance of NiO/ZnO nano-hybrids (a) LSV polarization curves, (b) Tafel slope, (c) Nyquist plot at various over-potentials, and (d) deviation of impedance as a function of frequency recorded at several over-potentials.

Figure 8. Measurements for HER electro-catalytic performance of NiO/ZnO nano-hybrids (a) LSV polarization curves, (b) Tafel slope, (c) Nyquist plot at various over-potentials, and (d) deviation of impedance as a function of frequency recorded at several over-potentials.
**Electrochemical investigation**

Solar- and wind energy-driven renewable forms of energy express a diffusive and intermittent nature owing to the variations in the diurnal and seasonal patterns, thus indicating the urgency to develop materials which could store the converted energy for a longer span of time (65). The quest is ongoing for the robust, economically viable, and functional electro-catalysts in terms of water splitting i.e. OER/HER for turning the lab-based investigations of future renewable energy designs and sustainable energy storage into practicality (66). Nevertheless, the issues of slower kinetics and elevated energy barriers associated with the OER/HER cannot be overlooked and they need an improvement and efforts for optimization. Interestingly, the derivation of H₂ over a larger scale from water can be done through cheaper and non-precious electro-catalysts; therefore, the major challenge remains in the designing of the catalytic materials in a rational manner, which is not only beneficial for environment but also sustainable. For the validation of the electrochemical performance of fabricated biomimetic [NiO/ZnO]-GNH, the synthesized material was subjected to LSV and EIS for studying the charge transfer properties. The OER and HER behaviors of [NiO/ZnO]-GNH/Ni-foam catalyst were examined in 1 M KOH solution at observed at a sweeping rate of 1 mV/s shown in Figure 7(a). The anodic current demonstrated the redox type behavior of the fabricated biomimetic [NiO/ZnO]-GNH. A current density greater than 1.6 V significantly demonstrated the catalytic oxidation of H₂O approving the surface favorability of the synthesized green material as an OER catalyst (44). In the present investigation, [NiO/ZnO]-GNH expressed an onset potential of 1.65 V vs. RHE and an over-potential of 0.44 V making it a promising [NiO/ZnO]-GNH/Ni-foam electro-catalyst via facile synthesis route and possibly be due to the involvement of carbon containing phyto-capping agents found in *Olea ferruginea* Royle foliar extracts. Electro-oxidation mechanism occurred on the surface of the modified electrode which is significant by the appearance of a redox peak at 1.4 V and then changing of potential with increasing current density (67). Currently obtained results for green nano-hybrid are in conformity with the previous studies done with the NPs of the mixed metal oxides such as cobalt and iron yielding a 10 mA cm⁻² of the current density and 1.53 V (versus RHE) of an operational over-potential. OER activity has been found lower in the case of using lower dopant concentrations for transforming metallic oxide NPs owing to the insufficiency in the active interfacial zones. However, previous studies have confirmed the saturation of the interfacial sites of the electro-catalysts with higher dopant concentrations (68). In another recent report by Elayappan et al. (69), mixed metal oxide modified by incorporation of the 3D nitrogen-doped graphene/CNT conductive matrix (NCGC) analyzed for OER activity expressed good performance with 10 and 100 mA cm⁻² of current density with over-potentials of 290 and 490 mV, respectively (69). Zha et al. (70) obtained an improved electrochemical for FeNi₃ alloy/oxide which was entrenched in nitrogen-doped porous nanofibers (FeNIO/NCF) with driving 10 mA cm⁻² of a current density and an over-potential of 260 mV with a Tafel slope of 67 mV dec⁻¹ (70). Comparison with such physicochemically synthesized nanomaterials, the currently obtained results for green nano-hybrid are indicative of the auspiciousness of bio-based electro-catalysts. [NiO/ZnO]-GNH/Ni-foam electro-catalyst’s surface expressed capacitive behavior which was possibly attributed to organic capping agents suggesting electrochemically active nature of the electrode (71,72).

The Tafel slope obtained for [NiO/ZnO]-GNH/Ni-foam catalyst is expressive of the suitability of the synthesized material for oxygen evolution. Tafel slope was examined from the linear part of the curve potential (RHE) and current density as shown in Figure 7(b) which is indicative of the remarkable OER commotion. 80 mV/dec of the value was obtained for Tafel slope. It has been evaluated from the lower Tafel value that [NiO/ZnO]-GNH was deposited well on Ni-foam exhibiting good OER performance. [NiO/ZnO]-GNH/Ni-foam show enhanced charge transfer characteristics which might be due to carbon containing functional groups revealed from EDX. Using electrochemical impedance measurements the charge transferability of as-synthesized electrode material was assessed. EIS characteristics were demonstrated by Nyquist plot referring to the basic real and fictional impedance discrepancy as a function of frequency at 0–100 frequency range, as shown in Figure 7(c). EIS examination was done for the investigation of the internal resistance and charge transfer resistance. The Nyquist plot shows small semicircle from 0 to 0.6 at varied potentials. The Nyquist plot is also indicative of charge transferal resistance characteristics representative of the ionic and charge between [NiO/ZnO]-GNH/Ni-foam catalyst and electrolyte interfacial region. It has been observed that with increasing potential the semicircle arc goes on decreasing with increasing potential. Such results are indicative of the fact that Rₑ alleviated with an enhancement in the potential expressing auspicious electrochemical transfer in terms of hastening of the charge transferal between electrolyte and [NiO/ZnO]-GNH/Ni-foam catalyst. The previous reports for physicochemically
synthesized nanomaterials are indicative of the improved OER performance achieved with FeCoNiO@IrPt NPs-based catalyst in comparison with FeCoNiO and Ir expressing a current density of 10 mA cm\(^{-2}\) at over-potential of 240 mV. In addition to this, the poly-elemental FeCoNiO@IrPt NPs catalyst expressed a good Tafel slope i.e. 34 mV dec\(^{-1}\) than that of FeCoNiO (83 mV dec\(^{-1}\)) and Ir NPs (59 mV dec\(^{-1}\)) expressive of the commendable OER kinetics (73). Another study reports the utilization of polymeric waste for the fabrication of ZnO functionalized with the nitrogen-doped mesoporous carbon (ZnO@NMC) via a solvo-thermal route. For such a ZnO@NMC nanocomposite, Ubaidullah et al. (74) reported the enhanced OER and HER.

At higher potential the semicircle arch is smaller which becomes larger with decreasing potential and then disappears making the plot nearly vertical representing \(Z_w\) at angle between 45° and 90° pertaining to Z real axis representing Warburg impedance (75). The smaller Warburg impedance means electrolyte charge transfer diffusion is easier. Thus the extension of plot toward low-frequency region on 0, 0.4, and 0.45 V indicated the increase of diffusion control reaction (76,77).

In the same way, the charge transfer resistance (\(R_{ct}\)) value decreased significantly with increasing potential exhibiting an increase in charge carriers because of minimum interfacial resistance enhancing the electro-current response toward water oxidation (78). Impedance and frequency dependence plot of [NiO/ZnO]-GNH/Ni-foam catalyst was inscribed for understanding the mechanism of charge-transfer resistance, as shown in Figure 7(d) at different voltages ranging from 0 to 0.6 V. It was observed that impedance was shifting toward a minor frequency region with an augmenting voltage, revealing fast electronic conduction of [NiO/ZnO]-GNH/Ni-foam catalyst. In Figure 7(d), it can be seen that at lower voltage frequency increases with impedance but at 0.5 V the frequency moving toward a low-frequency region and then at 0.55, 0.6 V it goes down the impedance or nearly become zero indicating the fast charge transfer in consistence with the lower \(R_{ct}\) value. The involvement of mixed metal oxide and carbon-based organic phyto compounds resulted in decreased recombination life time which prominently enhanced the electrochemical performance.

In addition to the comprehension of [NiO/ZnO]-GNH/Ni-foam catalyst, the synthesized green material was also tested for HER with a variegated potential (V, RHE), expressed in Figure 8(a–d). Polarization curve obtained for [NiO/ZnO]-GNH/Ni-foam catalyst was indicative of an over-potential of 262 mV at ~10 mA/cm\(^2\). The Tafel slope of [NiO/ZnO]-GNH/Ni-foam catalyst is considerably larger for HER expressed in Figure 8(b). Protonic adsorptive interaction developed at the active sites on the [NiO/ZnO]-GNH/Ni-foam catalyst is responsible for constraining the rate of hydrogen evolution causing surficial poisoning and consequent dysfunctionality of the modified [NiO/ZnO]-GNH/Ni-foam catalyst. Protonic (H\(^+\)) adsorption, occurring on the active site, is reflected in the form of higher value obtained for Tafel slope signifying rate-limiting step i.e. Volmer step (48). Results of HER [NiO/ZnO]-GNH/Ni-foam catalyst are proceeding at a comparatively slower speed showing the favorability of the synthesized material as an OER catalyst in comparison to HER. The EIS examination toward HER is shown in Figure 8(c) as Bode plot. The impedance frequency plot shows a better response in terms of catalytic performance at different potentials spanning over a range of 0.036–0.34 V (vs. RHE). At higher voltage, the impedance curve decreases, which represents good charge transfer behavior with least resistance. The best response was observed at higher voltages. In a recent nanocomposite-based study by Uma et al. (79), HER was estimated for pristine ZnO and ZnO/α-Fe₂O₃ nanocomposites. The studies were indicative of the higher HER activity obtained for nanocomposite owing to the easier charge transferal between the electro-catalyst and water molecules. The impedance value decreases with the increase of voltage at high-frequency region in comparison with the semicircle of Nyquist plot (Figure 8(d)). Smaller-sized semi-circle is obtained in the higher frequency region and augments with alleviation in voltage, expressive of the minimal resistance and enhanced diffusive efficiencies. Although the HER performance of [NiO/ZnO]-GNH/Ni-foam catalyst is not satisfactory as compared to OER, but it can be improved by tuning the morphology and working conditions of the electro catalyst. In a study by Elayappan et al. (69), NCGC electro-catalyst was found to be producing 74 mF cm\(^{-2}\) of double layer capacitance indicating the presence of higher extent of the active sites and thus gave rise to enhanced HER and OER electro-catalytic reactions (69).

**Conclusion**

A simple and sustainable approach has been adopted for the preparation of mixed metal oxide as an efficient electro-catalytic material. Modified sol–gel synthesis was adopted for the fabrication of [NiO/ZnO] green nano-hybrid which is reduced and stabilized by the secondary metabolites of *Olea ferruginea* Royle leaf extracts. Spectroscopic and chromatographic analysis confirmed the involvement of organic capping agent’s role in synthesis mechanism in the pure formation of NiO/ZnO nanoparticles. Synthesized nano-hybrid was
decorated on Ni-foam to study the electrochemical functionality toward water oxidation by LSV and EIS. The bioactive semiconducting material expressed excellent electro-catalytic properties with lower over potential and smaller Tafel slope of 80 mV/dec possibly by involving carbon-based organic phyto-metabolites. The biomimetic approach for synthesis of mixed oxides is a step toward generation of cheap and cost-effective electrode material for sustainable energy generation applications in complete conformity with the principles of green chemistry and cleaner production.

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