

Synthesis And Characterization Of Flexible Copper Doped Nickel Oxide-Based Paper Electrode For Perovskite Solar Cell Applications

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ABSTRACT: Perovskite solar cells (PSCs) are engaged in solar cell production as they improve power conversion efficiency. The steadiness and performance of cells are dependent on the hole-transporting materials, one of the vital constituents of the perovskite solar cells. The preeminent hole transporting material is the one that holds high hole mobility, durable air, and mechanical stability and ought to have energy levels that reasonably match with the perovskite layer. As hole materials (HTM) for perovskite solar cells, numerous sorts of semiconductor materials can be utilized. In this research work, Nickel Oxide (NiO) is utilized as a hole transporting material (HTM) because of its unrivaled electrical properties, long-term mechanical and air stability, high hole mobility, and high conductivity. To improve the properties of NiO thin films and to increment the power conversion efficiency of perovskite solar cells, Cu was added into it as a dopant. Cu-doped NiO (Cu:NiO) has a high conductivity compared with undoped NiO. Lignocellulose (LC) fiber is reflected as an extremely abundant, eco-friendly, lightweight natural fiber and a biocompatible polymer. In this work Lignocellulose (LC) fiber is utilized as a substrate. X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Ultraviolet-Visible Spectroscopy (UV-Vi) were completed to portray the integrated material. It was shown that Cu:NiO has improved effectiveness as compared to pure NiO when utilized as HTM in the Perovskite solar cells.

Keywords: Spectroscopy, Conductivity, Scanning, Solar Cell, Power etc.

INTRODUCTION

Starting from the acquaintance of nanotechnology with this world by Richard P. Feynman in his prestigious talk in 1959 citing "There's a lot of room at the bottom" [1], this world has been so anxious to investigate this field increasingly more with progressive changes in it. In the field of nanotechnology, we can modify the properties of a material according to our application by reducing the size because the smaller the size more critical the properties. The field of nanotechnology has extended to almost every aspect of life such as the electronics industry, defense, transport, drug delivery, food and agriculture, biotechnology, textile, and most importantly energy storage applications [2].

We have been idealizing our natural assets, for example, oil, gas, and even coal as never-ending energy sources yet that has never been the situation and because of their wide reach utilization, these assets have now arrived at a lethal degree of lack. Oil and Coal are significant fuels for our energy utilization and their use is delivering a lot of CO₂ to our climate and its level is expanding with every passing day [3].

Non-renewable energy is harvested through sources that will run out or will not be restocked within our lifespan. These sources include fossil fuels like coal, petroleum, etc. The energy resulting from a wide range of resources all of which are renewable such as wind, flowing water, biomass and sunlight, etc. is called renewable energy [4]. From the very outset of humanity, non-renewable energy resources have been utilized for the harvesting of energy. The entire world is looking for a sustainable energy source and numerous specialists are dealing with economical energy improvement.

Green energy is found to be one of the best sustainable sources of energy [5]. Green energy is extracted from natural sources while renewable energy is the one that comes from sources that are being reused again and again. Wind energy, solar energy, and geothermal energy all are kinds of green energy. As this world is in unavoidable peril of energy breakdown, efficient green energy has become a promising solution to fulfill world's increased energy demand. To be a green energy source the material should not deliver any sort of poison which implies that not all sustainable assets are green [6]. Greenhouse gases delivered by green energy sources are extremely low when compared with that released by petroleum products.

Solar energy is viewed as the cleanest type of green energy as it utilizes sunlight which is a characteristic source. Solar innovation has involved man-made fibers as terminal materials particularly glass films, for example, Fluorine-doped tin

oxide (FTO) films and Indium-tin oxide (ITO) films. The adaptability factor is the most significant of all because inflexible designs truly do accompany the expiry date and their storage is an extremely delicate matter. However, the adaptable cathodes take out a wide range of supportability issues. Not just these glass substrates are not eco-friendly materials and cannot be utilized over and over with the same productivity in addition throughout time it has been seen that after some time they likewise become a piece of ecological contamination.

Among natural fibers, the one with prime significance is transparent Nano paper comprised of lignocellulose. Lignocellulose is the dry matter of plants and is the combination of cellulose, lignin, hemicellulose, and tannis. It is a significant part of both woody and non-woody plants and is no question the most plentiful sustainable natural fiber. These materials have high renewability, optoelectronic properties, biodegradability, and light dispersing properties [7]. Normally lignocellulose fibers are integrated into metal oxide sheets like ZnO, and TiO₂ to be utilized as a working cathode and to upgrade their functioning properties [8]. Additionally, the porosity and surface area of the working electrode is likewise expanded by the addition of LC. The incorporation of LC appears to expand the conductivity of metal electrodes by decreasing their band gap.

A mineral of calcium titanium oxide comprising calcium titanate (CaTiO₃) is known to be a perovskite [9]. The wide utilization of Perovskite Solar Cells (PSCs) is a direct result of its property of not only converting visible light into electricity but also transforming ultraviolet light into electricity very efficiently. When presented to sunlight the photons are consumed by the perovskite layer creating excitons. A perovskite solar cell (PSC) contains a compound having a perovskite structure, fundamentally a hybrid organic/inorganic (lead or tin) halide-based material to be utilized as a light overseeing layer [10]. Electrons are conveyed from perovskite to TiO₂ and to be utilized by electron transport material (ETM) at last gathered by fluorine-doped tin oxide (FTO). Because of the distinction in the exciton binding energy of perovskite materials free carriers for example electrons and holes are created by these excitons. The efficiency provided by PSCs is about 22% [11].

Metal oxides are crystalline compounds including an oxide anion and a metal cation. Oxygen in metal oxides possesses the oxidation number of - 2. Transition metal oxides (TMOs) have many surface properties which further give us various chemical properties. Consolidation of lignocellulose (LC) in transition metal oxides generally upgrades their efficiency, current density, and fill factor. Optoelectronic properties, fill factor, photovoltaic properties, work function, and numerous different properties are increased by the utilization of TMO Hole Transport Layers. Transition metal oxides are profoundly utilized in perovskite solar cells as the substrate for electrodes and are widely used as hole transporting material [12].

Nickel oxide, an inorganic hole transport material has been kept under the spotlight for the exploration of perovskite solar cells. NiO is a photocathode in Dye synthesized solar cells (DSSC) and a hole collector in Perovskite solar cells. Nickel oxide is utilized as hole transport material in thin film solar cells. Components like Lithium, Zinc, Magnesium, Copper, and Iron are doped on NiO to upgrade their properties. Doping of Cu is seen to have incremented the conductivity of NiO alongside its optoelectronic properties and different factors generally contributing to the higher productivity of perovskite solar cells.

MATERIALS AND METHODS

Chemicals used in the synthesis method were Nickle Nitrate Hexahydrate (Ni(NO₃)₂·6H₂O), Copper Nitrate Trihydrate (Cu(NO₃)₂·3H₂O), Sodium Hydroxide (NaOH), and Distilled water (H₂O). Apparatuses used during the synthesis of Cu:NiO nanoparticles were Beakers, Burette, Pipette, Magnetic Stirrer, Burette Stand, Petri Dish, Drying Oven, and Weight Machine.

An enormous number of strategies have been utilized in the synthesis of nanoparticles. The Chemical Precipitation technique is one of them and it is one of the most encouraging ones. It is the easiest, least expensive, and most ecological amicable process. It permits adequate precipitation of metal ions. Besides, high surface nanoparticles are incorporated through this method [13]. Another benefit is that it gives generally a higher likelihood of creating pure and homogenous material than other combination procedures. Nanoparticles blended with this strategy have high thermal and mechanical stability.

Synthesis of Cu:NiO nanoparticles

Cu:NiO nanoparticles were prepared using the chemical precipitation method. Ni(NO₃)₂·6H₂O was used as a NiO precursor while Cu(NO₃)₂·3H₂O was used as a Cu precursor. 0.25M solution of Ni(NO₃)₂·6H₂O was prepared in 30 ml of DI water. A dark green solution was obtained. The copper (4%) solution was also prepared in DI water. Both the solutions were magnetically stirred until all the chemical was completely dissolved. After that, both precursor solutions were mixed thoroughly. A 10M NaOH solution was produced and was added dropwise under vigorous stirring. The pH of the solution was continuously measured using a pH meter. As the pH of the solution reached 10 the supply of NaOH was cut off. The solution was allowed to be magnetically stirred for another 10 minutes, the solution turned milky. Now the obtained solution was allowed to settle for about one hour so that the precipitates may settle down. To remove excess water, the solution was centrifuged until the water was completely removed. The resultant paste form was now dried in the oven at 80°C for about 6 hours [14]. Finally, the Cu:NiO powder was obtained.

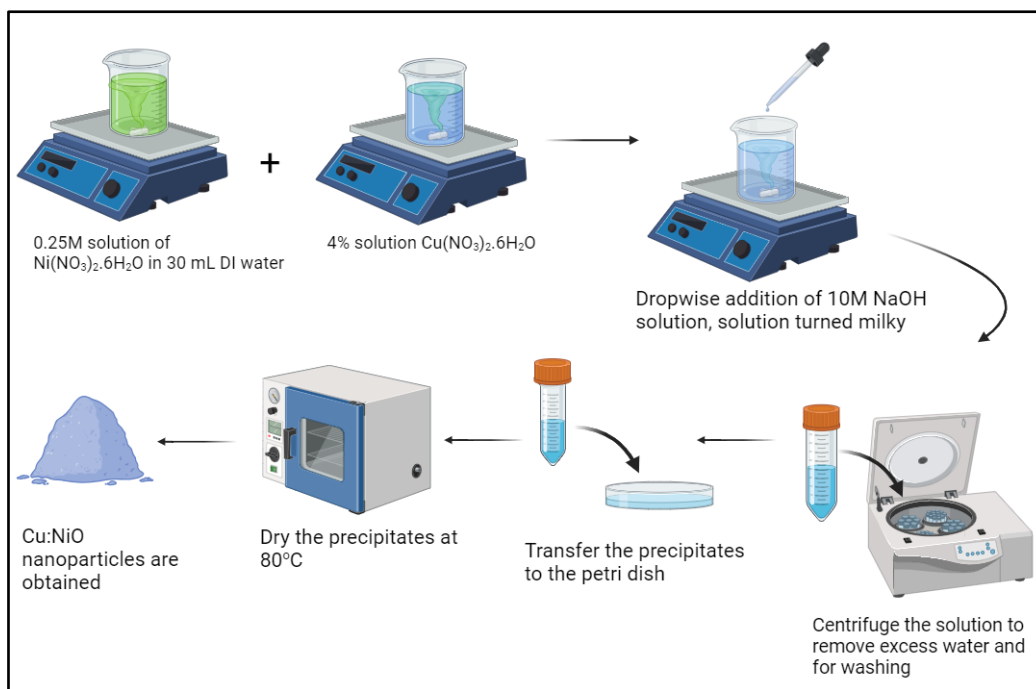


Figure 1: Synthesis of Cu:NiO Nanoparticles

Synthesis of Lignocellulose (LC) sheets

Lignocellulose fibers (LC) were taken from the red carrot source. Approximately 2-3 carrots were taken and crushed. Then this crushed source was blended in a blender along with the 50 ml of de-ionized water. Then this paste was converted into circular sheets by filtering with Buchner Funnel. For drying these sheets were sandwiched between filter paper and were allowed to dry at room temperature for 48 hours. As a result, circular sheets with pale red color were achieved.

Synthesis of Lignocellulose (LC)/ Cu:NiO sheets

1 gram of CU:NiO powder and 0.5 gram of Lignocellulose sheet was weighed using a weighing machine. The ratio of LC to Cu:NiO powder is maintained at 1:2. Lignocellulose sheets and Cu:NiO powder were taken in mortar and pestle with the addition of 50mL de-ionized water and then mixed for some time until it became a thick solution. This solution was converted into circular sheets by vacuum drying. For further drying, these sheets were sandwiched between filter paper and were allowed to dry at room temperature for 48 hours.

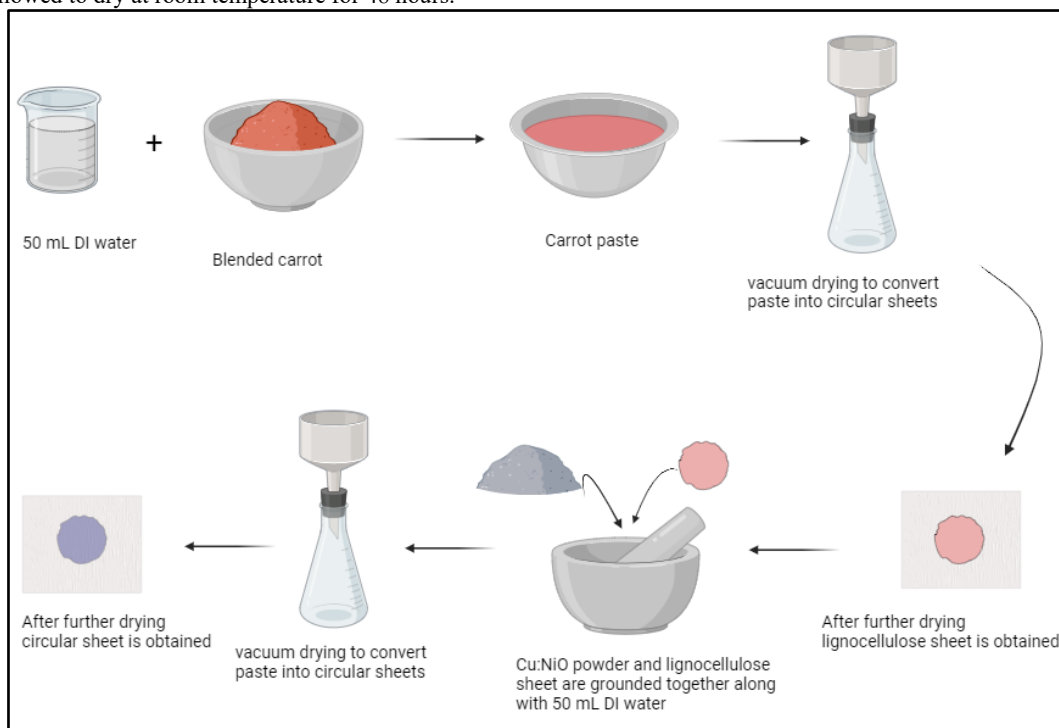


Figure 2: Synthesis of LC/Cu:NiO Sheet

RESULTS AND DISCUSSION

X-Ray Diffraction (XRD)

X-Ray diffraction (XRD) is a technique for inspecting the sub-atomic or molecular conglomerations of crystalline material. It is a non-destructive technique. XRD gives not just phase identification, yet in addition data on how the genuine structure digresses from the ideal structure because of inward stress and imperfections. XRD works by lighting material with incident X-rays and estimating the intensity and angle of scattering of the X-rays radiated by the material. This procedure is essential because every crystal has its own arrangement of d-spacings. Utilizations of XRD have extended to the fields of microelectronics, glass-producing forensic science, geographical applications, and pharmaceuticals as well as corrosion investigation [15]. The XRD pattern was utilized for the primary examination of Cu:NiO. The diffraction peaks showed that Cu:NiO has a face-centered cubic crystal structure (FCC). XRD diffraction peaks of Cu:NiO is displayed in Figure 3.

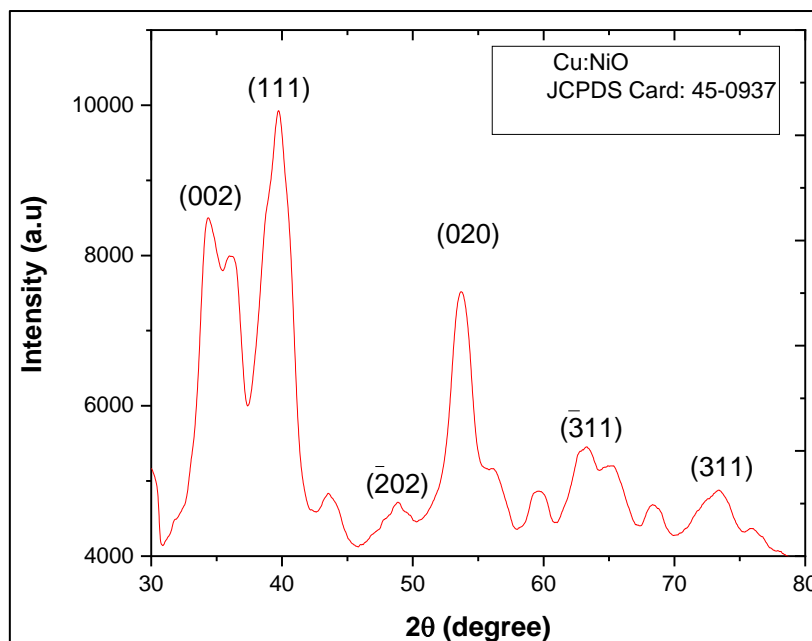


Figure 3: XRD Graph of Cu:NiO

The main diffraction peaks were obtained at $2\theta = 34.33^\circ, 39.7^\circ, 48.7^\circ, 53.7^\circ, 63.2^\circ,$ and 73.4° corresponding to the planes (002), (111), ($\bar{2}02$), (020), ($\bar{3}11$), (311) respectively [16] which are in consent to the standard Cu:NiO diffraction peaks with the JCPDS data card (45-0937). The most intense peak was observed at $2\theta = 39.7^\circ$ corresponding to the plane (111). Despite Cu doping, every peak was like that of NiO and this is because the doping of transition metal oxides frequently declines the intensity of XRD peaks as it were. The ionic radii of Ni^{2+} (0.78 \AA) and Cu^{2+} (0.82 \AA) do not vary by a lot so after doping Cu^{2+} particles effectively replace the Ni^{2+} particles with no adjustment of the crystal structure [17]. Crystallite size was determined using the Scherer formula;

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (3.1)$$

Where K denotes the shape factor which is 0.94 in this case, λ denotes the wavelength (1.5406 \AA), β denotes the full-width half maxima (in radians) and in this case, its value is $\beta = 4.85997$ and θ denotes the angle of an intensity peak. The average crystallite size of the Cu:NiO nanoparticle was calculated to be 2 nm [18]. The interplanar spacing (d) was calculated by using the Bragg formula:

$$n\lambda = 2d\sin\theta \quad (3.2)$$

where λ is the wavelength (1.5406 \AA), θ is the peak position, n is the order of diffraction ($n=1$) and d is interplanar spacing also known as d-spacing. The value of d-spacing was calculated to be 1.9 nm.

Scanning Electron Microscopy (SEM)

SEM is a versatile and powerful tool for surface morphological studies. It is one of the most extensively involved instrumental procedures for the assessment and investigation of micro and nanoparticle imaging interpretation of solid objects. SEM involves electrons for imaging similar to a light microscope that utilizes visible light. Electrons are bombarded onto the sample permitting the interactions to take place. These collaborations give us high-quality data about the sample as it is elemental and various samples interface contrastingly with the beam of electrons [19]. SEM is used for image formation, morphological studies, and compositional analysis as well. Particle size and morphology of LC/Cu:NiO was measured by performing scanning electron microscopy. Following are the images obtained by performing SEM of Cu:NiO;

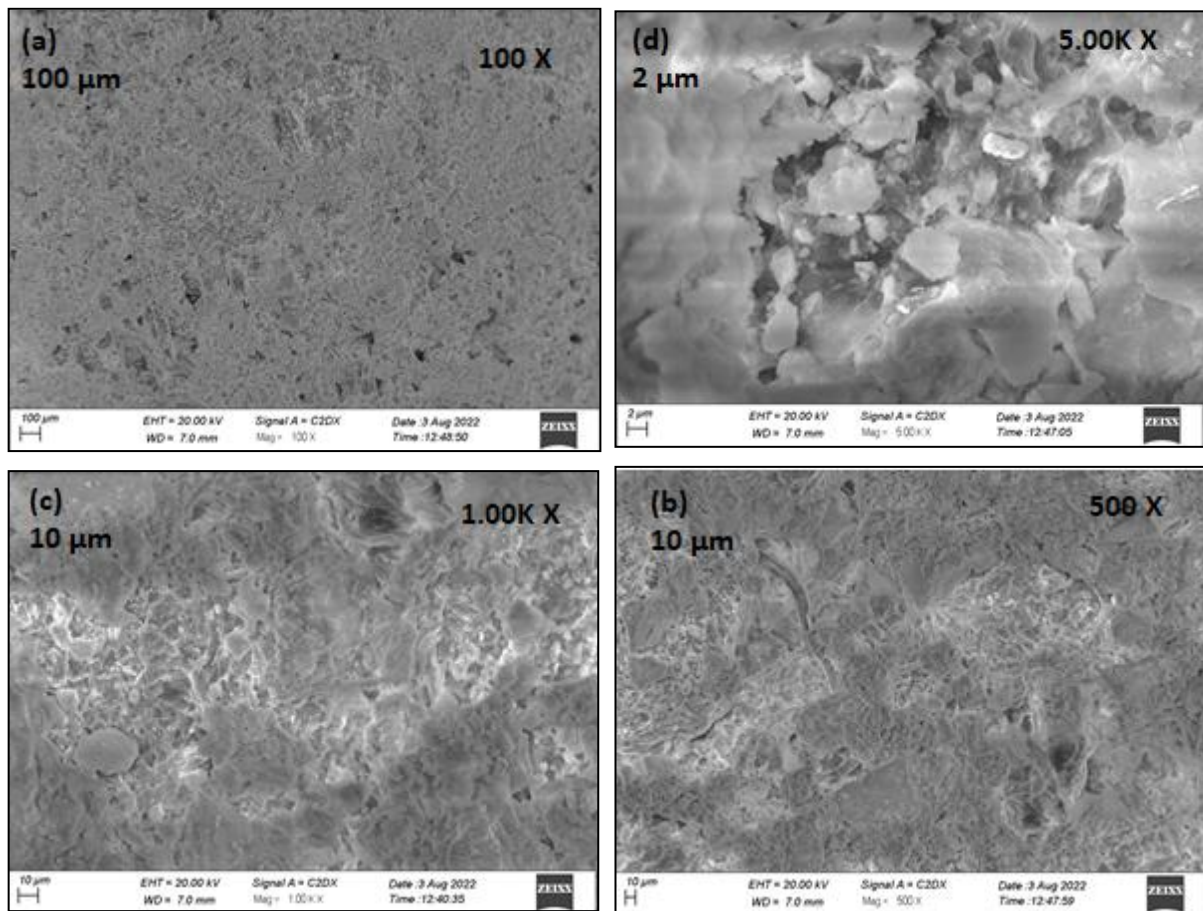


Figure 4: SEM images of LC/Cu:NiO

The average particle size was calculated to be 3.2 nm. The images indicate that the LC/Cu:NiO nanoparticles are porous in nature. The outcomes reflect that more or fewer particles show a spherical shape, but an agglomeration of particles arose. It is obligatory to take into consideration that the presence of some larger nanoparticles may be credited to the circumstance that Cu:NiO nanostructures have high surface energy and tension and have the tendency to form clusters. The agglomeration of nanoparticles happens during the synthesis procedure exclusively due to their high surface area and surface energy. It is additionally gathered that the crystal structure stays unaltered by the doping of copper [20].

Ultraviolet-Visible (UV-Vis) Spectroscopy

UV-Vis spectroscopy is an analytical technique fundamentally measuring the quantity of a particular wavelength of UV or visible light that is absorbed by or transmitted through a sample in contrast to a reference or blank sample [21]. It is likewise an elemental procedure as it is fundamentally impacted by minor changes in the configuration of a sample. As this spectroscopy depends on the utilization of light, one must have a legitimate comprehension of the properties of light before dealing with this procedure. UV-Vis spectroscopy has now stretched out to the fields of drug identification, quality control in the beverage industry, bacterial culturing, and synthetic exploration. A spectrophotometer with a wavelength ranging from 300 nm to 750 nm was utilized to notice the absorbance spectra of our orchestrated material. Figure 5 shows the absorbance spectra of Cu:NiO and LC/Cu:NiO. The most extreme peak for Cu:NiO was seen at 350 nm While the absorbance spectra of LC/Cu:NiO flexible material indicates that the maximum peak for LC/Cu:NiO was at 349.642 nm. As the frequency of Electromagnetic wave decreased the wavelength of peaks also tend to decrease.

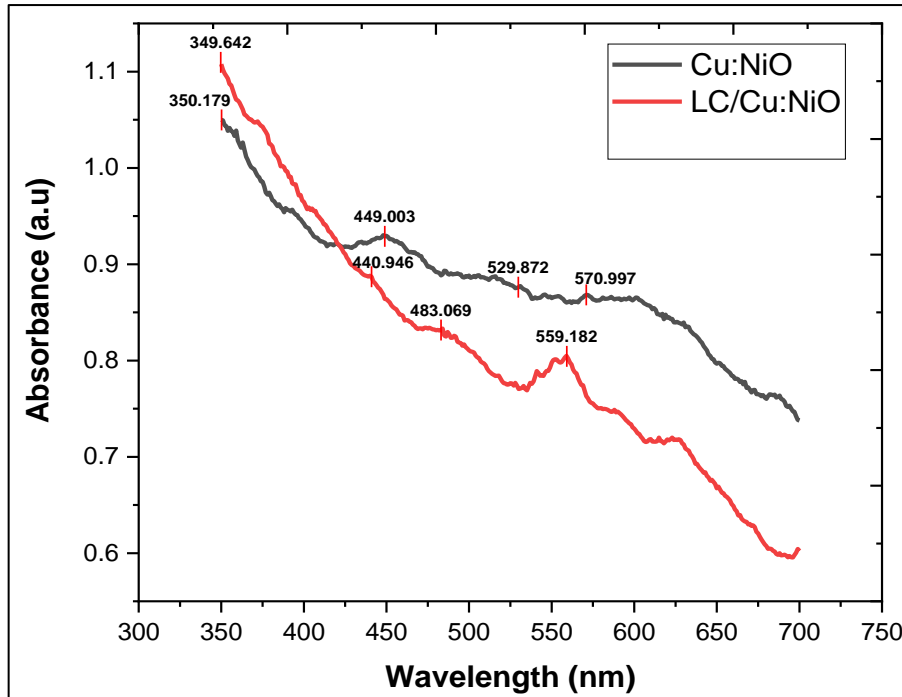


Figure 5: UV Graph of Cu:NiO and LC/Cu:NiO

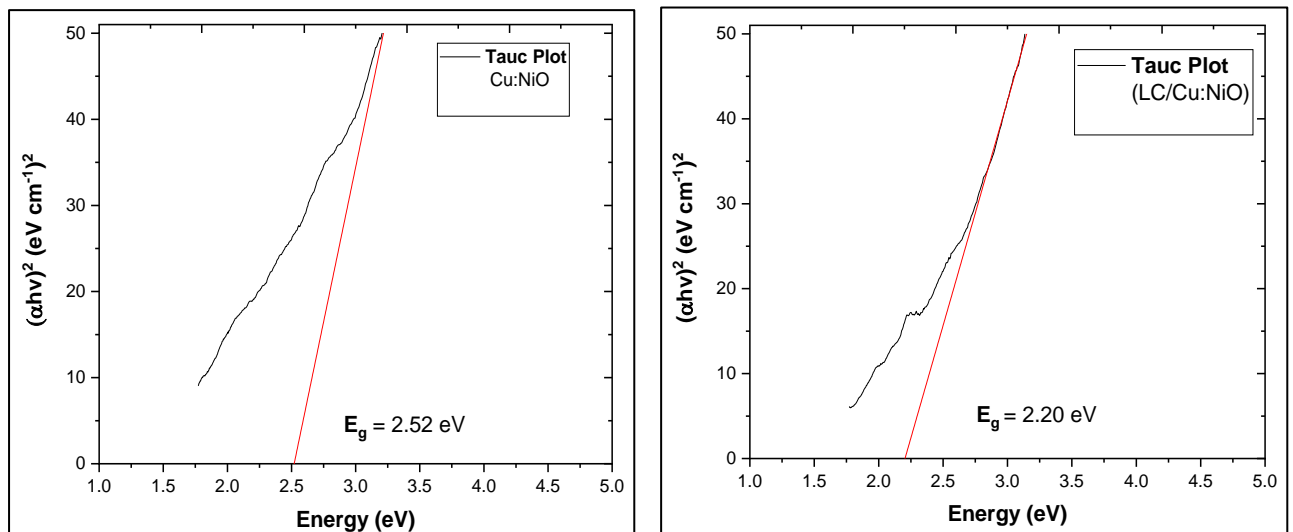
For the calculation of the band gap, Taucplot was used. In this regard, a tangent is drawn which gives us the value of the band gap. The band gap is calculated using the following equation;

$$(\alpha h\nu)^n = K(h\nu - E_g) \quad (3.3)$$

This equation is known as Tauc and Davis-Mott relation and is used to probe the optical band gap of nanoparticles from UV-Vis absorption spectroscopy. In this equation, K is an optical constant for direct transition and its value is $K = 1$, α is the coefficient of absorption, and $h\nu$ is the photon energy from light in electron volt.

The bandgap energy of Cu:NiO was calculated to be 2.52 eV [22] as shown in figure 6. While the bandgap energy of LC/Cu:NiO was as expected decreased as lignocellulose was added to synthesized nanoparticles calculated. The bandgap energy of LC/Cu:NiO was calculated to be 2.20 eV.

Figure 6: Tauc Plot of Cu:NiO and LC/Cu:NiO



CONCLUSION

In this research work, NiO nanoparticles were synthesized utilizing a chemical precipitation technique, and afterward, these nanoparticles were doped with Cu to obtain Cu:NiO nanoparticles which can be utilized as hole transporting material for perovskite solar cells. This material is more reliable than others given its fast hole extraction capability, high conductivity, and mechanical stability. To enhance the conductivity and add adaptability to the electrodes lignocellulose sheets extracted from the carrot source were added as a substrate to synthesize Cu:NiO nanoparticles. Different characterization techniques, for example, XRD, SEM, and UV-Vis spectroscopy were done for the sample examination. Crystallite size of Cu:NiO was affirmed by XRD investigation and was determined to be 2.01 nm. XRD examination additionally affirmed that Cu:NiO has a face-centered cubic crystal structure. The morphology of Cu:NiO was affirmed by SEM examination and it was shown that Cu:NiO is a permeable material. SEM investigations revealed that agglomerations took place on the surface. Moreover, the particle size of Cu:NiO was determined to be 3.231 nm. The UV-Vis examination was done which showed that the most intense peak for Cu:NiO was at 350 nm and for LC/Cu:NiO most intense peak was found at 349.642 nm. To ascertain the band gap Tauc plot strategy was utilized. The bandgap of Cu:NiO came out to be 2.52 eV and that of LC/Cu:NiO was 2.20 eV. It is reasoned that LC/Cu:NiO is a sustainable material for hole transporting layer as it has high porosity and a decreased band gap which improves its conductivity, ultimately prompting the higher effectiveness of Perovskite Solar Cell.

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