Visible light photocatalysis of methylene blue using cobalt substituted cubic NiO nanoparticles

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Abstract. This study reports the facile co-precipitation synthesis of pure and cobalt substituted NiO nanoparticles. The cubic crystalline structure of the synthesized NiO nanoparticles was confirmed through X-ray diffraction. Structural behaviour, morphological, elemental composition and optical properties of the prepared nanoparticles are investigated by Fourier transform infrared spectroscopy, scanning electron microscopy-energy dispersive spectrum, transmission electron microscopy and UV-Vis spectroscopy. The optical band gap is determined using UV spectra and is observed to decrease with an increase in cobalt ion concentration. Furthermore, methylene blue dye solution has been used to investigate the photocatalytic ability of the synthesized nanoparticles in the presence of sunlight. It is found that percentage degradation in dye concentration increases with irradiation time and also with the increase in the concentration of doping of cobalt in NiO. The dye solution is found to degrade to 94% within 50 min in the presence of solar radiation and the $\text{Ni}_{0.6}\text{Co}_{0.4}\text{O}$ sample.

Keywords. NiO; UV-Vis spectroscopy; photocatalysis.

1. Introduction

The advances in technology and industrialization impose a global threat to human life and the environment. Good quality of water is a precious resource which is necessary for sustaining all forms of life but the number of factors has led to pollution of water. Organic dyes disposed from textile industries constitute a major water pollutant. The release of this coloured wastewater in the environment through a chemical reaction taking place can produce harmful byproducts which may be eutrophic. The polluted water needs to be treated in order to improve its quality which has led to a number of studies being carried out by researchers in this regard. The colour removal has been extensively studied using different methods such as coagulation [1], ultra-filtration [2], nano-filtration, flocculation, reverse osmosis, activated carbon [3], etc. However, these methods are inefficient having operational problems such as generation of sludge, which leads to disposal problems and require further separation techniques adding more cost to the entire process. An alternative to this, an advanced oxidation process (AOP) is used which starts with the generation of strong hydroxyl radicals, which can completely degrade the pollutant into less toxic or harmless products (CO_2 and H_2O) [4–6]. The main supremacy of the AOP is that there is no consumption of chemicals, no sludge production and no strict lab conditions are required [7]. The widely used AOP includes photolysis, fenton method, photofenton, ozonolysis, sonolysis and photocatalysis [8]. Out of these AOP processes, photocatalysis uses visible and ultraviolet (UV) radiation from sunlight and in the presence

of suitable catalysts degrades the organic pollutants present in wastewater through a chemical reaction.

During the past decade, metal oxide nanoparticles have been studied as efficient photocatalysts and have been used to degrade synthetic dyes under different conditions [9,10]. The main features to be effective photocatalysts are stability, non-toxicity, suitable morphology, appropriate band gap and reusability [10]. Nickel oxide (NiO) nanoparticles have been effectively used as photocatalysts [4]. NiO is a stable p-type semiconductor metal oxide having tendency to absorb UV radiations due to its wide band gap and therefore a small portion of the solar spectrum is absorbed by this material [11]. NiO nanoparticles find potential applications in gas sensors [12–15], fuel cells [16], electrochromic films [17,18] and heterogeneous catalytic materials. To date, different methods have been employed to synthesize NiO nanoparticles, namely, thermal decomposition [19], hydrothermal [20], pulsed-laser ablation [21], solvothermal [22], anodic arc plasma method [23], sol-gel [24] and chemical co-precipitation methods [25]. The synthesis route and conditions may affect various properties of these nanoparticles. In addition to the synthesis route, doping with other metal ions has also been employed to improve the physicochemical properties of nanomaterials which is essential for their various applications [26].

Motahari *et al* [27] synthesized NiO nanostructures by the thermal decomposition method for the photocatalyst application and reported that NiO nanoparticles act as highly efficient photocatalysts towards degradation of Rhodamine B under UV radiation. Gnanasekaran *et al* [28] reported the synthesis of metal oxide nanoparticles (CeO_2 , NiO, ZnO, etc.)

by the precipitation method and degradation of textile dyes using these metal oxide nanoparticles. In the present work, firstly $\text{Ni}_{1-x}\text{Co}_x\text{O}$ ($x = 0, 0.1, 0.2$ and 0.4) cubic nanostructures were synthesized by the chemical co-precipitation method which is simpler as compared to other methods and is a facile method of synthesis without requiring any expensive equipment. Surface morphologies and structural features of the samples were characterized by X-ray powder diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, ultraviolet–visible (UV–Vis) spectroscopy, scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) and transmission electron microscopy (TEM). These nanostructures were then utilized to degrade methylene blue (MB) dye through photocatalysis in the presence of sunlight.

2. Experimental

2.1 Materials

All the chemicals and reagents used in our work were purchased from Merck and were used as received without further purification. Double distilled water was used throughout the synthesis process. The reagents used were analar grade nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), cobalt(II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), NaOH flakes and MB dye (Fisher Scientific).

2.2 Synthesis of nanoparticles

$\text{Ni}_{1-x}\text{Co}_x\text{O}$ ($x = 0, 0.1, 0.2$ and 0.4) nanoparticles were synthesized by the chemical precipitation method [29]. In this procedure, homogeneous solutions of the required amount of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were prepared by dissolving them in double distilled water using a magnetic stirrer. Both of these solutions were then mixed using a stirrer and the pH of the solution was increased through dropwise addition of NaOH with continuous stirring for 30 min. The light green precipitates obtained were then aged under ambient conditions for 24 h. Then, the resulting green precipitates were centrifuged for 10 min at 4000 rpm and washed several times with distilled water to remove the impurities and then dried overnight at 70°C . Finally, the obtained products were pulverized using a mortar-pestle and annealed at 400°C for 4 h to obtain the desired nanoparticles. The prepared samples were named as pure and cobalt substituted NiO nanoparticles.

2.3 Characterization

XRD was carried out on an X-ray diffractometer (Rigaku Ultima-IV) for the determination of the crystalline nature of the prepared samples. Spectra were recorded in the 2θ range of 20 – 80° with a scanning speed of 2° min^{-1} using $\text{CuK}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) as the X-ray source. Room temperature FTIR spectra were recorded on an FTIR spectrophotometer

(Perkin Elmer Frontier) in the wavenumber range of 4000 – 400 cm^{-1} . The standard KBr pellet technique was employed to carry out IR measurements [30]. Morphological and elemental composition analyses of all samples were carried out on a scanning electron microscope-energy dispersive spectrometer (SIGMA-ZEISS SIGMA 5.05) at an acceleration voltage of 5 kV. Transmission electron microscopy (TECHNAI) at an acceleration voltage of 200 kV was performed to gain an insight into the morphology of nanoparticles. The optical behaviour was investigated by recording UV–Vis spectra on a UV–Vis spectrophotometer (Shimadzu UV-2450). Then the band gap energy of the prepared nanoparticles was derived from the absorbance spectra.

2.4 Photocatalytic activity

The photocatalytic activity of the prepared pure and cobalt substituted nickel oxide nanoparticles was assessed by degradation of aqueous solution of MB dye under sunlight. MB dye solution with 5 ppm concentration was prepared using double distilled water. One milligram of prepared sample $\text{Ni}_{1-x}\text{Co}_x\text{O}$ was added to 100 ml of MB dye solution. The solution was made basic by increasing the pH through dropwise addition of NaOH. Before switching to irradiation, the mixture was stirred in dark for 30 min in order to maintain the adsorption–desorption equilibrium between the catalyst and aqueous MB dye solution. The dye solution containing catalyst was then exposed to sunlight under continuous stirring. Aliquots were collected at a regular time interval and were analysed to determine the residual amount of MB dye after irradiation by using a UV–Vis spectrophotometer. The percentage degradation was calculated by using the following formula [31]:

$$\% \text{ Degradation} = \frac{(A_0 - A_t)}{A_0} \times 100,$$

where A_0 is the initial absorbance of the MB solution which reached absorbency balance and A_t is the absorbance of the dye solution at irradiation time (t).

3. Results and discussion

3.1 X-ray diffraction

The room temperature XRD profiles of the synthesized pure and co-substituted NiO nanoparticles are shown in figure 1. As can be seen, each plot exhibits peaks at $\sim 37.26, 43.26, 62.86, 75.44$ and 79.42° which can be perfectly indexed to (111), (200), (220), (311) and (222) crystal planes of NiO respectively (JCPDS card no. 47-1049). The diffraction pattern indicates the formation of the FCC structure of pure NiO and co-substituted NiO nanoparticles [32]. The relative intensity ordering of each peak also resembles with the standard XRD profile (JCPDS card no. 47-1049) of the

Figure 1. XRD pattern of $\text{Ni}_{1-x}\text{Co}_x\text{O}$ nanoparticles.

cubic NiO structure. The intensity and sharpness of peaks mark good crystallinity of the synthesized composition and a little broadening in peaks indicates that particles are in the nanometre range. The broadening of XRD peaks provides a suitable method to measure the average crystallite size. The highest intense peak (200) is considered to find the average crystallite size, D using the Debye–Scherrer formula [33]:

$$D = \frac{k\lambda}{\beta \cos \theta}.$$

Here k is the Debye constant equals to 0.9, λ is the wavelength of Cu-K α radiation, β is the full-width at half-maximum intensity lines in radians and θ is the Bragg's [49] angle of the highly intense peak. The estimated values of the crystallite size are reported in table 1. The lattice parameter ' a ' was calculated from the relation:

$$d^2 = \frac{a^2}{(h^2 + k^2 + l^2)}.$$

Here d is the interplanar spacing, while h , k and l are the miller indices. The obtained values for the lattice constant

are also presented in table 1. No peak of cobalt is observed at lower content of cobalt in the NiO lattice indicating that Co^{2+} ions are incorporated into the lattice site of Ni^{2+} ions in the NiO matrix. As the ionic radii of Ni^{2+} (0.55 Å) and Co^{2+} (0.58 Å) are close to each other, therefore Co^{2+} can enter the lattice sites of Ni^{2+} via substitutional doping [34]. A small shift towards the lower angle (see the inset in figure 1) is observed with the enhanced substitution of cobalt, which might be due to occupancy of Co^{2+} ions at Ni sites leading to an increase in the lattice constant in NiO nanoparticles. As evident from table 1, the average crystallite size of pure NiO nanoparticles is 24 nm which is observed to increase with an increase in the concentration of cobalt. A small difference in the ionic radii of Ni^{2+} and Co^{2+} leads to an increase in the size of the lattice of substituted NiO nanoparticles and hence causing a microstructural disorderness [35]. With the addition of cobalt ions, the peak intensity decreases which might be due to an increase in microstrain caused by disorder in the crystalline structure. At higher concentration of cobalt, peaks corresponding to cobalt oxide appear (marked asterisk) at ~ 31.32 , 36.88 , 59.26 and 65.16° which are indexed to (220), (311), (511) and (440) crystal planes respectively (JCPDS card no. 01-074-2120) forming composites of NiO and Co_3O_4 [36,37].

3.2 FTIR spectroscopy

FTIR spectroscopy is an essential tool to study the functional groups present in the synthesized sample. The infrared vibrations of one component are independent of the presence of other components. The FTIR spectra of all prepared $\text{Ni}_{1-x}\text{Co}_x\text{O}$ ($x = 0, 0.1, 0.2$ and 0.4) are depicted in figure 2. As can be seen, all compositions exhibit strong and weak absorption bands/shoulders at ~ 3846 , ~ 3736 , ~ 3445 , ~ 2923 , ~ 2854 , ~ 2361 , ~ 1737 , ~ 1638 , ~ 1453 , ~ 1386 , ~ 1217 , ~ 1162 , ~ 1114 , ~ 1034 , ~ 667 , ~ 558 and $\sim 438 \text{ cm}^{-1}$ [38,39]. The absorption bands appeared around ~ 3846 , ~ 3736 , ~ 2923 and ~ 2854 represent characteristic vibrations of aliphatic C–H groups [39]. The wide band at 3428 cm^{-1} can be attributed to the O–H stretching vibrations [38] and the weak band at 1638 cm^{-1} is assigned to the H–O–H bending vibrations [24] in hydroxyl groups which might be due to the employment of the KBr pellet technique as KBr

Table 1. The crystallite size ' D ', lattice parameter ' a ', cut-off wavelength ($\lambda_{\text{cut-off}}$), optical band gap (E_g) and Urbach energy (E_U) of pure and Co-substituted NiO nanoparticles.

Sample	Average crystallite size D (nm)	Lattice parameter a (Å)	Cut-off wavelength $\lambda_{\text{cut-off}}$ (nm)	Band gap E_g (eV)	Urbach energy E_U (eV)
NiO	24	4.1742	317	3.91	0.34
$\text{Ni}_{0.9}\text{Co}_{0.1}\text{O}$	38	4.1760	361	3.89	0.38
$\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}$	47	4.1778	370	3.66	1.04
$\text{Ni}_{0.6}\text{Co}_{0.4}\text{O}$	37	4.1778	425	3.10	2.58

Figure 2. FTIR spectra of $\text{Ni}_{1-x}\text{Co}_x\text{O}$ nanoparticles.

is highly hygroscopic. The bands at ~ 2361 and $\sim 1737\text{ cm}^{-1}$ are assigned to the stretching vibrations of $\text{C}=\text{O}$ due to the absorption of CO_2 from the atmosphere [40–42]. The band at $\sim 1450\text{ cm}^{-1}$ contributes to $\text{C}-\text{H}$ scissoring [43]. Moving further, the band appeared at 1386 cm^{-1} is primarily due to the symmetric stretching vibrations of $\text{O}-\text{C}=\text{O}$ groups. The peak at 1217 cm^{-1} may be assigned to vibrations on account of $\text{C}-\text{H}$ wagging. The next small kink at $\sim 1162\text{ cm}^{-1}$ can be attributed to the $\text{C}-\text{O}$ stretching vibrations. A faint shoulder at 1114 cm^{-1} may be assigned to in and out plane deformations in $\text{C}-\text{H}$ bonds. The band around $\sim 1034\text{ cm}^{-1}$ is due to the asymmetric stretching of the resonance interaction between vibration modes of oxide ions in the nanoparticles [41]. The vibrations of nickel species are usually active in the wavenumber range of $700\text{--}400\text{ cm}^{-1}$. A close observation of this region resulted in yielding two absorption bands at ~ 667 and $\sim 438\text{ cm}^{-1}$ and shoulder at around $\sim 558\text{ cm}^{-1}$ which can be easily deconvoluted to obtain Gaussian absorption bands. The first weak but well defined absorption band at $\sim 667\text{ cm}^{-1}$ can be attributed to the $\text{Ni}-\text{O}-\text{H}$ vibrations due to the formation of nickel hydroxide units. The weak shoulder around 558 cm^{-1} may be ascribed to the bond bending vibrations of $\text{Ni}-\text{O}$ units whereas the last band at $\sim 438\text{ cm}^{-1}$ is due to the stretching vibrations of $\text{Ni}-\text{O}$ units. The position of stretching vibrations of $\text{Ni}-\text{O}$ units confirmed the formation of nanoparticles [44]. The peak due to $\text{Ni}-\text{O}-\text{H}$ vibrations exhibits a loss in intensity on the initial incorporation of cobalt in the NiO lattice indicating that the formation of nickel hydroxide units is less favourable but further addition of cobalt content leads to an enhancement in the intensity of this peak again. The $\text{Ni}-\text{O}$ peaks exhibit a very small red shift indicating a vibrational distortion due to the presence of cobalt species in NiO units as the atomic mass of cobalt is higher than that of nickel [45].

3.3 SEM-EDS and TEM

In order to obtain insight information of morphology, distribution and shape of the prepared nanoparticles, SEM is performed. Figure 3a–d show the morphology of $\text{Ni}_{1-x}\text{Co}_x\text{O}$ ($x = 0, 0.1, 0.2$ and 0.4) nanoparticles annealed at 400°C . Inspection of these images reveals that particles are non-spherical in shape and are agglomerated. The agglomeration is due to the nano-dimension of particles [35]. The addition of Co^{2+} ions improves the morphology with suitable concentration but as the concentration is increased from $x = 0.2$ to 0.4 , particles aggregate. We can say that insertion of cobalt ions leads to a change in the shape as compared to pure NiO nanoparticles. Thus the morphology can be tuned by varying the amounts of doping into the lattice. Qualitative elemental composition was measured by EDS. The EDS spectra as shown in figure 4 clearly validate that the synthesized nanoparticles are made up of Ni , O and Co ions only. The presence of the peak corresponding to carbon may be due to the use of grid during analysis [40]. No other peaks corresponding to any type of salt impurity are present which confirms the high purity of the synthesized nanoparticles. Figure 5 depicts the TEM images of $\text{Ni}_{1-x}\text{Co}_x\text{O}$ ($x = 0, 0.1, 0.2$ and 0.4) nanoparticles with different concentrations of cobalt. All the prepared samples show the non-spherical structure of the synthesized nanoparticles.

3.4 UV-Vis spectra

The optical absorption spectra of $\text{Ni}_{1-x}\text{Co}_x\text{O}$ ($x = 0, 0.1, 0.2$ and 0.4) nanoparticles are recorded by using double distilled water as a solvent and are shown in figure 6a. The absorption edge of these spectra can be used to obtain the band gap of nanoparticles because the absorption edge arises due to the electronic transitions from the valence band (VB) to the conduction band (CB) [46]. The cut-off wavelength ($\lambda_{\text{cut-off}}$) has been evaluated by x -axis intercept of the absorption edge and the obtained values are reported in table 1. A small red shift in $\lambda_{\text{cut-off}}$ is evident from table 1 for cobalt substituted nanoparticles in comparison with the pure NiO nanoparticles. This shift indicates a decrease in the band gap as $\lambda_{\text{cut-off}}$ usually exhibits an inverse relation with the optical band gap. The band gap is an important factor to decide the photocatalytic activity of nanomaterials [47]. The optical band gap E_g can be calculated using the Tauc's method, by extrapolating the linear portion of the curve to the zero absorption edge [48]:

$$(\alpha h\nu) = B(h\nu - E_g)^n.$$

Here α is the absorption coefficient, $h\nu$ is the energy of photon, E_g is the optical band gap, B is the material constant, n is $1/3$, $1/2$, 2 and 3 for direct forbidden, direct allowed, indirect allowed and indirect forbidden transitions, respectively [46]. NiO is considered to be a material with a direct band gap energy, hence $n = 1/2$ for direct allowed transitions [48]. The respective Tauc's plot is shown in figure 6b and the

Figure 3. SEM images of $\text{Ni}_{1-x}\text{Co}_x\text{O}$ nanoparticles (the inset shows the magnified image of the selected area).

Figure 4. EDS spectra of $\text{Ni}_{1-x}\text{Co}_x\text{O}$ for (a) $x=0$ and (b) $x=0.4$ (the inset shows the image of the area selected for EDS).

Figure 5. TEM images of pure and cobalt substituted NiO nanoparticles.

Figure 6. (a) Absorbance spectra of $\text{Ni}_{1-x}\text{Co}_x\text{O}$ nanoparticles and (b) Tauc's plot for $\text{Ni}_{1-x}\text{Co}_x\text{O}$ nanoparticles.

Figure 7. Urbach plot of $\text{Ni}_{1-x}\text{Co}_x\text{O}$ nanoparticles.

obtained values of the band gap are listed in table 1. As can be seen, the optical band gap for pure NiO is 3.91 eV which is in agreement with the literature [38] and it is decreasing with an increase in cobalt concentration. These compositional trends in E_g can be understood from the corresponding compositional variations in the crystallite size (D) and due to the incorporation of cobalt. A little variation in D usually leads to marked broadening of the absorption edge which might be due to the fact that the lower crystallite size leads to higher number of defects whereby creating additional energy levels of defects. Therefore, a part of energy is absorbed by the photon and is transferred to excite it in the energy level of the defect instead of the CB, which ultimately leads to an increase in the optical band gap. Moreover, the optical band gap of cobalt oxide is usually less than that of NiO which might force the composition containing the highest cobalt content to exhibit a synergic effect between the crystallite size and cobalt substitution. These results are firmly corroborated by the corresponding compositional trends in $\lambda_{\text{cut-off}}$.

The band tail energy or Urbach energy (E_U), which characterizes the width of the localized states, is calculated using the formula [48]:

$$\alpha = \alpha_0 \exp\left(\frac{h\nu}{E_U}\right),$$

where α_0 is the constant. The above equation can be utilized to draw the Urbach plot ($\ln \alpha$ vs. $h\nu$). Figure 7 shows the Urbach plots of the prepared nanoparticles. The Urbach energy is evaluated from reciprocal of the slope of the linear portion of the absorption edge to study the disorder for all compositions and the obtained values are listed in table 1. One can clearly observe from table 1 that compositional trends in E_U are in synchronization with the cut-off wavelength which

Figure 8. UV-Vis spectroscopic variation of MB dye solution without any photocatalysts.

validates the effect of Co incorporation in the NiO structure as concluded from E_g .

3.5 Photocatalytic activity of $\text{Ni}_{1-x}\text{Co}_x\text{O}$ nanoparticles

In the absence of pure NiO and Co-doped NiO photocatalysts, the sunlight photolysis of aqueous MB dye solution was tested. It was found that MB dye cannot be easily degraded by sunlight photolysis shown in figure 8. The typical absorption spectra of MB under solar light radiation in the presence of $\text{Ni}_{0.9}\text{Co}_{0.1}\text{O}$ and $\text{Ni}_{0.6}\text{Co}_{0.4}\text{O}$ nanoparticles are shown in figure 9. It can be clearly observed that the MB absorption band at 664 nm decreases gradually with time and almost flattens after 50 min of irradiation time indicating the photodegradation of MB (see the inset in figure 9). The percentage degradation as function of time was calculated for each photodegradation by considering the maximum absorbance at 664 nm as the reference. The reaction kinetics is determined by plotting $\ln C_0/C_t$ vs. irradiation time (t) for the photocatalytic decolourization process. Figure 10 typically shows the effect of cobalt concentration doped in NiO nanoparticles at a fixed concentration of cobalt ions ($x = 0.1$ and 0.4) on photocatalytic decolourization kinetics of MB dye solution. Reaction kinetics gives enough information about the reaction rates. The result showed that the photocatalytic decolourization of MB dye obeys apparently pseudo-first order kinetics and the rate expression is given by [4]:

$$\ln \frac{C_0}{C_t} = kt,$$

where C_0 is the initial concentration of MB dye, C_t is the concentration at time t and k is the pseudo-first order rate constant. The rate constant, k was found to be 0.044 and 0.059 min^{-1} in the case of $\text{Ni}_{0.9}\text{Co}_{0.1}\text{O}$ and $\text{Ni}_{0.6}\text{Co}_{0.4}\text{O}$ nanoparticles,

Figure 9. UV-Vis spectroscopic variation of MB dye solution in the presence of (a) $\text{Ni}_{0.9}\text{Co}_{0.1}\text{O}$ and (b) $\text{Ni}_{0.6}\text{Co}_{0.4}\text{O}$ nanoparticles.

Figure 10. Variation of MB concentration $\ln C_0/C$ with time over $\text{Ni}_{0.9}\text{Co}_{0.1}\text{O}$ and $\text{Ni}_{0.6}\text{Co}_{0.4}\text{O}$ nanoparticles as catalysts.

respectively. The obtained correlation coefficient (R^2) is 0.976 and 0.979 for $\text{Ni}_{0.9}\text{Co}_{0.1}\text{O}$ and $\text{Ni}_{0.6}\text{Co}_{0.4}\text{O}$ nanoparticles, respectively. While without any photocatalysts, the rate constant and correlation coefficient were found to be 0.0168 min^{-1} and 0.988. It was found that higher cobalt ion content results in an enhanced degradation rate. This is because cobalt substitution has a direct influence on the optical band gap of NiO nanoparticles promoting the photocatalytic activity. An in-depth review of the literature has been carried out to find decolourization of MB using different materials as photocatalysts and the typical comparison with the present study is reported in table 2. As can be seen, the materials synthesized in present work are performing well towards the photocatalytic degradation of MB. Figure 11 shows the degradation efficiencies for cobalt substituted NiO

Table 2. A comparison with the literature for decolourization of MB.

Photocatalyst material	Light source	Time (min)	% Degradation	References
Mn doped NiO nanoparticles	UV light	210	92	[3]
TiO_2	UV light	250	100	[6]
NiO–ZnO nanocomposite	UV light	80	72	[52]
ZnO nanoparticles	UV light	120	90	[53]
NiO nanoparticles	Sunlight	120	94	[54]
ZnO nanoparticles	UV light	60	>90	[55]
WO_3 –GO nanocomposite	Sunlight	70	94	[42]
Au/ZnO– CeO_2 nanohybrid	N. M.	8	100	[56]
$\text{Ni}_{0.9}\text{Co}_{0.1}\text{O}$	Sunlight	50	~89	T. W.
$\text{Ni}_{0.6}\text{Co}_{0.4}\text{O}$	Sunlight	50	~94	T. W.

T. W. → This work.

Figure 11. Percentage degradation of MB dye solution as a function of irradiation time (min) in the presence of nanoparticles as catalysts.

Figure 12. Mechanism for the dye degradation process in the presence of the catalyst.

nanoparticles as catalysts. It is clearly evident that better degradation is achieved in the presence of $Ni_{0.6}Co_{0.4}O$ indicating that the doping of cobalt ions enhances the photocatalytic activity of NiO nanoparticles. From the optical properties, it can be inferred that there is a decrease in the band gap on

increasing the concentration of cobalt doping. As sunlight radiation is used to excite the nanoparticles, the photocatalytic activity increases with the decrease in the optical band gap [50]. As the band gap is decreased, generation of the e^-/h^+ pair is enhanced, thus the photocatalytic process is

accelerated. The photodegradation mechanism of MB dye solution using $\text{Ni}_{1-x}\text{Co}_x\text{O}$ nanoparticles is shown in figure 12 which can be deduced as: when $\text{Ni}_{1-x}\text{Co}_x\text{O}$ nanoparticles are exposed to sunlight, the electrons present in the VB acquire enough energy so as to get excited to the CB leaving holes behind in the VB. These holes and electrons are now available for the oxidation and reduction processes, respectively. The electrons present in the CB are transferred to adsorbed oxygen (O_2) on the surface of nanoparticles to give oxygen (O^{2-}) radicals. The photocatalytic performance of nanoparticles as evident from figure 10 increases with an increase in the substitution of cobalt. It may be due to the fact that doping of cobalt in NiO accelerates the transfer of the electron in the CB to the dissolved oxygen. As a result of this, chances of recombination of electrons–holes get reduced leading to advancement in the photocatalysis process. The photogenerated holes will abstract electrons from H_2O to produce hydroxyl ($\bullet\text{OH}$) radicals. The hydroxyl radical is an efficient oxidant for the partial or complete degradation of organic chemicals [51]. These hydroxyl radicals facilitate the oxidation of MB dye molecules adsorbed on the surface of nanoparticles leading to the decolourization of MB dye.

4. Conclusion

The pure ($x = 0$) and cobalt substituted ($x = 0.1, 0.2$ and 0.4) $\text{Ni}_{1-x}\text{Co}_x\text{O}$ nanoparticles were synthesized successfully by the chemical co-precipitation method. The XRD analysis revealed the FCC structure of the prepared nanoparticles. The presence of all functional groups was observed by FTIR analysis. The SEM micrographs affirm the non-spherical morphology of the synthesized nanoparticles. Compositional analysis (EDS) ascertained the existence of Ni, O and Co in the synthesized nanoparticles. The purity of nanoparticles is confirmed by the absence of impurity peaks in EDS spectra. TEM images showed an irregular shape of nanoparticles with different nanosizes. The analysis of the optical properties using UV–Vis spectroscopy indicated a decrease in the optical band gap with an enhanced substitution of cobalt ions. The photocatalytic activity of the synthesized nanoparticles under solar light irradiation revealed that MB dye can be almost degraded in 50 min in the presence of the $\text{Ni}_{0.6}\text{Co}_{0.4}\text{O}$ sample.

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