Photocatalytic Activity of Nickel Oxide

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**Abstract**

In this work, synthesis of nickel oxide (NiO) using nickel acetate as a starting material by sol-gel method and then deposited as collide on glass slides to form thin layers of NiO by spin-coating technique with high photo-catalytic activity using as self cleaning coating. These films of NiO were annealed at different temperature 450 °C, 550 °C. The structural, morphological, spectral and optical properties of prepared NiO thin films were measured by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Ultraviolet spectroscopy (UV-visible) respectively. These results; it was shown that the crystallinity of NiO films evolves gradually as the temperature of the annealing films increases. Depended on the (SEM) and (AFM) result in the average grain size is a range of (15–30) nm. The films achieved a higher optical transparency of thin films synthesis it was annealing at 550 °C temperature. Finally, photo-catalytic test were studies by using potassium permanganate (K\textsubscript{2}MnO\textsubscript{4}) as a model of pollutant with two methods for achieved the effect of annealing temperature of NiO thin films on the photo-catalytic test and effect the grain size and weight of NiO nanopowder for photo-degradation percentage under exposure to UV-Visible source irradiation.

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**1. Introduction**

In the previous decades, the efficiency of photo-catalytic activity to degradation the organic pollutants by semiconductor metal-oxide such as NiO nanoparticle has drew the public attention due to the fact is NiO have high transparency considered as a p-type semiconductor with a broadband gap around of \(~(3.2 \text{eV}–4 \text{eV})\).\textsuperscript{1} NiO thin films With high photo-catalytic activity, low cost in the synthesis and low toxicity, high stability in physical and chemical properties, especially, strong ability of high decomposing organic contamination into harmless types such as (CO\textsubscript{2}, H\textsubscript{2}O, etc.).\textsuperscript{2–7} Nickel oxide (NiO) nanoparticles can be synthesis by a different process, such as the sol-gel method, microwave, and hydrothermal method, chemical co-precipitation method, reflux method, thermochemical route, etc.\textsuperscript{8–11} The mechanism of Photo-catalysis process to degradation the organic contamination is (the acceleration of a photo-reaction by the presence of a catalyst involvement of light in the photo-catalysis activity process).\textsuperscript{12} A catalyst material does not change in itself and is not consumed during the chemical reactions. Semiconductor metal-Oxide photo-catalysis process describes a process when a semiconductor particulate such as (NiO, TiO\textsubscript{2}, ZnO, WO\textsubscript{3}, etc.) is

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activated by exposure to UV-visible light appropriate to its band gap energy to catalyze a redox reaction at its surface. The primary criterion for an efficient metal-oxide semiconductor photo-catalysis activity method is that the redox potential of the charge couple, i.e., (e− + h+), lies within the band gap domain of the photo-catalyst process. In a typical sol–gel process, a colloidal suspension or a sol is formed due to hydrolysis and polymerization reactions of the precursors, which, upon completion of the polymerization and loss of solvent, leads to the transition from the liquid sol into a solid gel phase.13-15 There are some studies have tried to exploit nickel oxide (NiO) nano particles for the ability of efficiently and effectively of using solar cells light or visible light to photo-degradation the pollutant.16

The present work, an investigation has been achieved to prepared NiO thin films by sol–gel process as simple, ease, stability and mass production method. NiO nanoparticles with high photo-catalysis activity characteristics to be used as self-cleaning transparent nano-coating for solar cells to prevent the deposition of dust and air pollutants on the solar cells in the street, thus reducing their efficiency over time. The morphology, structure and topography characterization of NiO thin films before and after annealed at different temperature. The fabricated nanostructures were examined as photo-catalyst for degradation of potassium permanganate (K_MnO_4) dye as the pollutant dye model in Solar cell panels in the future.

2. Experiment work

2.1. Nickel oxide (NiO) sol-preparation

NiO solution was synthesis depend on the sol–gel technique and deposition by a spin-coating method for obtained thin films17 by using the following material prepared the NiO sol:

Nickel acetate [Ni(CH₃COO)₂·4H₂O] using as starting material supply by Sigma Aldrich with purity 98%, 2-Methoxethanol (C₃H₇HO) as a solvent material supply by Fluka with purity 99.5%, mono-ethanolamine [MEA] (C₂H₇NO) supply by Sigma Aldrich with purity 98% as a catalyst material. The prepared process was achieved according to the following procedure:

Nickel acetate of 0.122 gm was dissolved in 80 ml of 2-Methoxethanol for 15 min at room temperature, then a drops wise of MEA added to this mixture and stirring at 60 °C for 2-h to obtain a transparent and homogenous green color solution. The molar ratio of MEA to nickel acetate was to be 1:1. The prepared solution of NiO was cooling down at room temperature for one day. Before deposition NiO as thin films, firstly the glass substrates cleaned with methanol supply by J.T. Baker (Netherlands) and acetone supply by Hayman (UK) with purity 98% for 10 min and drying it by using ultrasonic bath then deposition it on to glass substrates as thin films by spin coating as shown in Fig. 1.

2.2. Photo-catalytic activity test

The effect of photo-catalytic activity test on manufacture NiO thin films were obtained through the photo-degradation of potassium permanganate (K_MnO_4) dye supply by Fluka (with purity 98%) using as a model of dye pollutant because it is a common chemical, cheap and available in laboratories. The concentration of 0.5[M] Potassium permanganate (K_MnO_4) was dissolved in the distilled water, and then they were taken and put in a Petri-dish. Variation preparation of these thin films of NiO sample groups was put in this solution. Finally, the samples were exposure to UV-Visible light sources around the range (300–800) nm to study the efficiency of photo-degradation for pollutant dye (K_MnO_4).

The photo-degradation percentage (DP %) was measured based on the hydrogen peroxide (H₂O₂) titration method according to the following equation.18

\[
(Dp)\text{K}_\text{MnO}_4 = \frac{V_2 - V_1}{V_0} \times 100
\]

where \((V_o)\) the added volume of Hydrogen peroxide (H₂O₂) supply by Merck (with purity 98%) to reaching yellowing color and \((V_1)\) represented to the volume of (H₂O₂) which was added to the potassium permanganate (K_MnO_4) solution after the UV-Lamp irradiation.

2.3. Characterization

Nickel oxide (NiO) films were characterized of their nature surface morphological and the behavior crystallinity under different conditions of depositing measurements using X-ray diffraction have been made according to the ASTM (American Society of Testing and Materials) cards, using XRD-6000 Shimadzu X-ray diffractometer of 1.54 Å from Cu-κα. The average thicknesses of the modification films were obtained by using an optical method (laser light interference) were equal to 120 nm. The topographical features of the top surface for NiO coatings have been carried out by using Tescan VEGA 3SB Scanning Electron Microscope (SEM) with Accelerating Voltage: 200 V to 30 kV and the magnification power continuous from 6–100000 X and (AFM) microscope using (SPM) microscope in non-contact mode, made by (DME Co.), Dual scope, and model (DS95–200E). Photo-catalytic activity and effect of photo-degradation percentage (DP%) about particle size and weight of nickel oxide (NiO) nano powder was obtained by using potassium permanganate (K_MnO_4) dye as a model of pollutant exposure to UV-Lamp sources they were illuminated with wavelength range of (300–800) nm.
The observed indexed x-ray pattern was attributed the characteristic peaks of the plane (111), (200), (220) and (311) respectively, the data of the XRD diffraction are in good agreement with (JCPDS-files-NO.711179). No secondary pattern peaks were obtained from X-ray diffraction analyses such as [Ni(OH)2] were obtained. This is special important because these index peaks date were reported about achieved sol-gel technique using another products to modification nickel oxide thin films.\(^{19,20}\) The nearly sharper peak detected at (43.3') for the sample film annealed at 450 °C and the pattern peaks for the films become more sharply when we raised the sintered temperature around (37.1'), (43.3'),(63.1') and (75.2') films of annealing temperature 550 °C. The average crystallite size (D) is calculated using the Sherrer equation.\(^{21}\)

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

where (k) is constant is equal to (0.94), (\(\theta\)) is Braggs diffraction angle in degree, (\(\lambda\)) is the wavelength of (CuK\(\alpha\)) radiation = 1.54 Å, (\(\beta\)) the full-width half maximum of pattern peaks in radians.

### 4. Photo-catalytic activity properties

#### 4.1. Effect of NiO thin films at different annealing temperature on photo-catalytic activity

The glass substrates of nickel oxide films were investigate the photo-catalytic activity characteristics depended on the performance of photo-degradation the potassium permanganate (KMnO\(_4\)). This experimental was achieved by examined the annealing films under UV-Lamp source. The relationship between the absorbance decay of (KMnO\(_4\)) versus UV-irradiation time in minutes was represented at Fig. 3. Through the details are shown in Fig. 3b the absorbance for the sample film annealed at 550 °C which was considered the optimized film for the group of thin films reaches to zero at 550 °C at wavelength before the other films of NiO. The behavior of this film comparison with other thin films because of having good cubic crystallinity surface morphology and small spherical size less than50 nm. This result indicated that the integrality and regularity of NiO crystal structure have critical influences on the photo-degradation rate because the photo-generated electron-hole pair was produced less on the surface of the catalyst which has a poor crystallinity and an imperfect crystal structure. Although the largest surface area and the strongest UV absorption of NiO catalyst can partially compensate for the loss of photo-generated

### Table 1 – Analysis XRD-peaks for the NiO sample films.

<table>
<thead>
<tr>
<th>Annealed temperature</th>
<th>(\theta/2) (degree)</th>
<th>planes</th>
<th>(\beta) (FWHM) (degree)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C450(^{\circ})</td>
<td>37.1(^{\circ})</td>
<td>(111)</td>
<td>0.9371</td>
<td>15.85</td>
</tr>
<tr>
<td></td>
<td>43.3(^{\circ})</td>
<td>(200)</td>
<td>0.5233</td>
<td>18.11</td>
</tr>
<tr>
<td></td>
<td>63.1(^{\circ})</td>
<td>(220)</td>
<td>0.6919</td>
<td>13.26</td>
</tr>
<tr>
<td>C550(^{\circ})</td>
<td>75.2(^{\circ})</td>
<td>(311)</td>
<td>0.8566</td>
<td>16.22</td>
</tr>
<tr>
<td></td>
<td>37.1(^{\circ})</td>
<td>(111)</td>
<td>0.6336</td>
<td>12.69</td>
</tr>
<tr>
<td></td>
<td>43.3(^{\circ})</td>
<td>(200)</td>
<td>0.5901</td>
<td>24.69</td>
</tr>
<tr>
<td></td>
<td>63.1(^{\circ})</td>
<td>(220)</td>
<td>0.2355</td>
<td>21.50</td>
</tr>
<tr>
<td></td>
<td>75.2(^{\circ})</td>
<td>(311)</td>
<td>0.3339</td>
<td>19.00</td>
</tr>
</tbody>
</table>

Fig. 2 – XRD-diffraction of annealing nickel oxide films at variation temperatures. (a) 450 °C, (b) 550 °C.

### 3. Results and discussion

#### 3.1. Structural characterizations

##### 3.1.1. X-ray diffraction (XRD)

The X-ray diffraction pattern for the optimized films of NiO was achieved in Fig. 2 and Table 1. The XRD diffraction peaks of NiO thin films dried at 180 °C for 15 minutes and annealed at 450 °C,550 °C at 30 min and collected from (2-Theta) of range (20°–80°). X-ray diffractometer is specially developed to investigate the crystal surface structure and the crystallinity of NiO annealing films. These sample films were a pure cubic structure having the bunsenite phase.
electron-hole pair. Therefore, under the condition of catalyst with a perfect crystal structure, the NiO sample which has a small particle size (<50 nm), high annealing temperature, and strong UV absorption exhibits a high photocatalytic activity in the photo-degradation of (KMnO₄) dye because these characters are beneficial for the catalyst to capture photons efficiently and generate electron–hole pairs in large quantities. This shows for us the principles of photo-catalytic when raising the annealing films temperature the absorbance decay decreasing and rapidly reaching to zero value, Finally, the photo-catalytic activity increasing this result we obtained is in good agreement with.²²–²⁶

4.2. **Effect of nickel oxide nano-powder weight**

The effect of NiO nano powder weight has been achieved by measuring the photo-degradation percentage (DP%) of potassium permanganate (KMnO₄). Fig. 4a shows the result when the UV-Lamp irradiation exposure time increase the degradation percentage (DP%) of the potassium permanganate solution increases and reaching the saturation state after one hour at a (DP%) of (50%) for 0.02 g of NiO nano powder with particle size (40 nm), while when increasing the weight of NiO nano powder four times to be 0.08 g the (DP%) reaching (100%) at the same time of exposure to UV-Lamp. When the grain size

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**Fig. 3** – The photo-catalytic activity of nickel oxide (NiO) annealed at (a) 450 °C, (b) 550 °C.

**Fig. 4** – (a) Degradation percentage versus UV-Lamp time in min for (0.02 g and 0.08 g) of NiO nano powder (40 nm). (b) Degradation percentage versus UV-Lamp time in min for (0.02 g and 0.08 g) of NiO nano powder (20 nm). (c) Degradation percentage versus UV-Lamp time in min for (0.02 g) of NiO nano powder with (20 nm and 40 nm) particle size. (d) Degradation percentage versus UV-Lamp time in min for (0.08 g) of NiO nano powder with (20 nm and 40 nm) particle size.
of NiO nano powder was reduced to (20 nm) the (DP%) reached to (100%) after 30 min of UV-Lamp exposure of the weight of (0.08 gm) and grain size (20 nm), While it was reached (100%) of (DP%) after one hour of exposure to UV-Lamp using the grain size (20 nm) and weight 0.02 gm this result shows at Fig. 4b.

4.3. **Effect of size of NiO nano powder on the photo-degradation percentage**

The effect of particle size on the degradation percentage (DP%) when using the small weight (0.02 g) of NiO nano powder was achieved in Fig. 4c shows the sample of grain size (40 nm) have a weak degradation percentage (DP%) in comparison with NiO nano powder of grain size (20 nm) for the using the same weight of NiO nano powder, while when increasing the weight to (0.08 gm) of NiO nano powder the sample of grain size (20 nm) reached rapidly to (100%) of (DP%) after 30 min of UV-Lamp irradiation, while it reached to (100%) of (DP%) after 60 min of UV-Lamp at grain size (40 nm) shows in Fig. 4d. From this result, we chose the good sample to be effective for photo-degradation application when having a large weight and small particle size of NiO nano powder.
5. Morphological properties of nickel oxide thin films

5.1. Scan Electron Microscopy (SEM) analysis

The morphological surface changes of the synthesized NiO films at variation annealing temperatures were achieved by using Scanning Electron Microscopy.

Fig. 5a shows the SEM surface profile image for the film annealed at 450 °C the grain size of the nickel oxide (NiO) nanoparticle is (15)nm. The image appeared that the surface of this film sample was homogenous nanostructured and the Nano particles are uniformly distributed. When increase in the annealing temperature of more than 450 °C we noticed the Nano particles grain size is become bigger from (15–30) nm with a spherical shape and randomly distribution that observed at Fig. 5b. The crystalline size of NiO films are in good agreement with XRD analysis and with.27

5.2. Atomic force microscopy (AFM) analysis

In order to examine the surface morphologies and roughness characterization for the sample groups of NiO thin films annealed at a different temperature, Atomic force microscopy (AFM) technique has been used. The result of these samples presented in Fig. 6 shows the two-dimensional (2D) and three-dimensional (3D) image. Fig. 6a indicates that; the formations of these films consist of fine agglomerations and non-uniform particle size but, at Fig. 6b the film of nickel oxide (NiO) annealed at 550 °C shows the increasing in grain size with increase the annealing temperature and dense nanoparticles with uniform grain size. The value of the root means square (RMS) used to determine the roughness of nickel oxide (NiO) films. The roughness (RMS) of the sample films is equal to (8.52 nm), (9.75 nm) respectively. The roughness of the surface films for samples is a criterion of it is crystallinity.28

The roughness is important factor measured to evaluation the efficiency of photo-catalytic activity in semi-conductors nano particles that we noticed at.28 The value of roughness more it increases means the surface of the sample has got the crystallinity structure that we have achieved at XRD patterns. From the result, we evaluate the sample of nickel oxide (NiO) thin films annealed at 550 °C and have a roughness (9.75 nm) have a very good photo-catalytic efficiency surface more than other samples (Table 2).

6. Conclusion

The nickel oxide nano-catalytic was synthesis successfully by spin coating technique with the sol–gel method. The morphology surface result achieved by (SEM) and (AFM) reveal the average grain size around (15–30) nm and the roughness coefficient at the range about ~(8–12) nm this raising in value related with the thermal annealing increasing. The photo-catalytic activity shows higher efficiency when increasing the thermal annealing films and roughness surface for photo-degradation the dye pollutant. The excellent activity for nickel oxide nano powder appears when the increasing the weight for the same particle size. This test to examine the photo-catalytic activity revealed that the NiO act as photo-degradation for dye pollutant.

Table 2 – The roughness value increase with annealing temperature increase.

<table>
<thead>
<tr>
<th>Roughness (RMS)</th>
<th>Annealed temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.52 nm</td>
<td>450 °C</td>
</tr>
<tr>
<td>9.75 nm</td>
<td>550 °C</td>
</tr>
</tbody>
</table>

Conflicts of interest

Compliance with ethical standards

Conflict of interest the authors declare that they have no conflict of interest.

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