Influence of laser energy on synthesizes of CdO/Nps in liquid environment

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Abstract. CdO NPs were prepared using laser ablation method in Ethanol using Nd:YAG laser at different energies (171, 201 and 263 mJ/pulse). The optical, structural and morphological properties were inspected using uv-vis spectrophotometer, XRD and AFM, respectively. The results showed that when increasing the laser energy, the band gap energy increases from 2.53 to 2.85 eV. The CdO Nps are proven to be pure and of a crystalline structure. The morphological studies indicated that the size of synthesized NPs is highly dependent on the laser energy. As the energy increases, the average diameter of prepared NPs decreased from 80.18nm to 67.68 nm.

Keywords: PLAL, CdO, NPs, Ethanol.

1. Introduction

Nanomaterial has became an important subject of research, due to its remarkable properties that differ from their bulk material [1]. The different properties are attributed to their small size that ranges between 1-100 nm, which causes a change in their physical and chemical properties [2]. The reason why nanomaterial properties are different from their conventional form is they have a new quantum effects, and larger surface to volume ratio [3].

Among metal oxides nanoparticles, cadmium oxide nanoparticle has proven to be one of the most important materials for various applications [4]. CdO is a vital n-type semiconductor [5] that has a direct and indirect energy gap of 2.5, 1.98 eV, respectively [6]; it expresses a high transparency in the region between 300 to 700 nm, and it's widely employed as a transparent conductive oxide in optoelectronic devices such as solar cells [7]. Thanks to these features, CdO NPs are chosen in many optoelectronic applications like gas sensors, photocatalytic activities, biosensors, photodiodes, photo detectors and solar cells [8–14].

Several methods and techniques are available to synthesis CdO nanoparticles, such as sol-gel [15], Cyclic Voltammetry Technique [6], chemical bath deposition [4], chemical method [16], R.F. magnetron sputtering [17], pulsed laser deposition PLD [12], spray pyrolysis[18], Heat Treatment Technique [19], Thermal Evaporation [20] and precipitation method [21]. However, these techniques have their limitations like raw material cost and expensive components, time consuming, complicated procedures and chemically contaminated surfaces [22–24]. To overcome these disadvantages, pulsed laser ablation in liquid environment PLAL can be used; this method provides nanomaterial of the same chemical composition of the target material, this provides the ability to produce nanomaterial of desired chemical components. Also, the shape and size of the resulted nanomaterial can be easily...
controlled by changing the laser ablating parameters. Furthermore, PLAL have the ability to synthesize nanomaterial with no chemical contamination in one step without the need to further purification processes [25, 26]. Several studies were published in the past decade discussing synthesizing CdO Nps by PLAL [5, 25–27]. However, best to our knowledge, CdO NPs prepared by PLAL in ethanol at different energies is yet to be investigated.

In this paper, for the first time, we experimentally demonstrate a simple way to synthesis CdO NPs by Pulsed Laser Ablation in ethanol, and study the effect of energy change on the optical, structural and morphological properties of the resulted nanoparticles.

2. Experimental part

2.1 materials
In this work we used:
1- Pure CdO powder (99%) was purchased from BDH chemicals Ltd Poole, England.
2- Pure Ethanol (99.9%) was purchased from SOLVOCHEM, UK.

2.2 Experimental setup
A 2g of CdO powder was pressed into a circular pellet with a diameter of 16mm, 3mm high using hydraulic compressor under the pressure of 10Tons. The CdO pellet was placed in the bottom of a glass vessel containing 2.5ml of Ethanol, which was irradiated with the fundamental radiation of Q-switched Nd:YAG laser (Model HF -301, Huafei technology, China) at different energies for 200 pulses. Table 1 lists the laser parameters used in this work. The laser beam was focused on the pellet surface using a lens that has a focal length of 120mm, the depth of Ethanol layer above the pellet was about 10mm as shown in figure 1. The vessel was rotated during the laser irradiating process so that the nanoparticles produced would not shield the laser radiation from hitting the target surface.

| Table 1. Nd:YAG laser properties |
|----------------------------------|
| E (mJ/pulse) | Freq. (Hz) | λ (nm) | Pulse duration (nm) | Spot size (mm) |
|----------------|-----------|-------|---------------------|----------------|
| 171, 201, 263 | 1         | 1064  | 10                  | 2.2            |

Figure 1. Experimental representation of PLAL technique.

The resulted liquid was deposited on glass slides using drop casting method at temperature about 65°C. the glass slides were previously cleaned with de-ionised water in ultrasonic bath for 30 minutes, and then submerged in methanol for another 10 minutes, and finally were air dried to prevent impurities and surface contaminations.

2.3 measuring technique
The optical properties of the samples were measured using SP-8001 UV/Visible Spectrophotometer, Metertech, Taiwan. The crystalline structure of prepared samples were examined using XRD (D2 phaser, Bruker, Karlsruhe, Germany) operating with CuKa1 radiation at wavelength= 0.154060 nm, generated at 30 KV and 10 mA; for 20 values between -3º to 160º. The surface morphology of CdO NPs was imaged by atomic force microscope (AFM) (CSPM- Scanning probe microscope).

3. Results and discussion

3.1 Optical properties

During the laser ablation process, it was noticed that the color of the Ethanol had changed from transparent to a yellowish brown, which gives the expectation of CdO/NPs formation.

Figure 2.a shows the absorption as a function of wavelength. It's shown that maximum absorption appears to be at 320 nm. As the laser energy increase, more particles are ablated from the target surface, which produces a higher concentration of CdO/NPs suspended in Ethanol that leads to increase the absorption spectrum. Furthermore, gives it a darker color as shown in figure 2.b.

The optical band gap of CdO/NPs is estimated graphically using Tauc's law for direct transitions [26 , 28- 29]as shown in equation (1):

\[ (\alpha h\nu)^2 = A^2 (h\nu - E_g) \]  

Where, \( E_g \) is the optical energy gap, \( \alpha \) is the absorption coefficient, \( h\nu \) is the photon energy of incident light and \( A \) is a constant. The band gap is influenced by the laser energy, as seen in figure 3, as laser energy increase the band gap shifts towards higher energy. At low laser energy, larger NPs are produced and the band gap is estimated to be 2.53 eV for 171 mJ/ pulse. However, by increasing the laser energy to 201, 263 mJ/pulse, the band gap energy increases to 2.6, 2.85 eV respectively. The band gap energy of all prepared samples was higher than 2.2 eV of bulk CdO. This can be attributed to the shift of absorption to lower wavelength caused by the decrease in particle size led by the quantum confinement effect [3].
3.2 structural properties

XRD patterns for CdO NPs prepared at 171, 201, 263 mJ that are deposited on a glass substrate are shown in figure 4. The XRD patterns exhibit peaks centered at $2\theta = 33.0^\circ, 38.28^\circ, 55.25^\circ, 65.9^\circ$ and $69.28^\circ$ which corresponds to (111), (200), (220), (311) and (222) planes that agrees with the faced cubic structure (fcc) of pure CdO (JCPDS No. 05-0640) which was close to what was obtained from previous studies [16,26,30]. From figure 4, we notice that the crystalline structure is more crystallized and secondary peaks becomes present as the laser energy increase. Furthermore, there are no other impurity peaks present, implying that the prepared NPs are pure at all energies. The broadened XRD patterns refer to reduction in the size of synthesized CdO NPs. The interplaner spacing (standard $d$ value) was calculated using Bragg formula [31] and compared with standard JCPDS card and listed in table 2 along with the crystalline size value of synthesized samples, which are calculated according to Scherrer's equation [32-33]. From table 2, the FWHM of (111) peak is slightly increasing in both width and height, indicating an enhancement in the CdO crystalline formation. The calculated crystalline size in table 2 decreases for the main peak as laser energy increase.
### Table 2. The crystalline size of CdO NPs prepared at different energies.

| E= 171 mJ/ Pulse | 2θ (deg.) | (hkl) | d\text{hl} | d\text{hl} | FWHM (deg.) | Crystalline size (nm) |
|-------------------|-----------|-------|-----------|-----------|-------------|----------------------|
|                   | 33        | 111   | 2.712     | 2.7122    | 0.181       | 79.88                |
|                   | 38.2      | 200   | 2.349     | 2.3541    | 0.215       | 68.24                |
|                   | 55.25     | 220   | 1.661     | 1.4306    | 0.269       | 58.17                |

| E= 201 mJ/Pulse | 2θ (deg.) | (hkl) | d\text{hl} | d\text{hl} | FWHM (deg.) | Crystalline size (nm) |
|-----------------|-----------|-------|-----------|-----------|-------------|----------------------|
|                 | 33        | 111   | 2.712     | 2.7122    | 0.206       | 70.19                |
|                 | 38.2      | 200   | 2.349     | 2.3541    | 0.224       | 65.50                |
|                 | 55.25     | 220   | 1.661     | 1.6613    | 0.271       | 57.74                |
|                 | 65.9      | 311   | 1.416     | 1.4162    | 0.372       | 44.41                |

| E= 263 mJ/ Pulse | 2θ (deg.) | (hkl) | d\text{hl} | d\text{hl} | FWHM (deg.) | Crystalline size (nm) |
|------------------|-----------|-------|-----------|-----------|-------------|----------------------|
|                  | 33        | 111   | 2.712     | 2.7122    | 0.216       | 66.94                |
|                  | 38.2      | 200   | 2.349     | 2.3541    | 0.227       | 64.63                |
|                  | 55.25     | 220   | 1.661     | 1.6613    | 0.384       | 40.75                |
|                  | 65.9      | 311   | 1.416     | 1.4162    | 0.322       | 51.31                |
|                  | 69.28     | 222   | 1.355     | 1.3552    | 0.385       | 43.77                |

3.3 Morphological properties

The surface morphology and size distribution of the synthesized CdO NPs at different energies are illustrated in figure 5. As shown from these figures, the morphology and size of CdO NPs are varied when increasing the laser energy.

Laser pulse interacts with the surface of the target submerged in Ethanol, which in turns effects the properties of the generated plasma in the interaction region between laser pulse and the target's surface. The size and morphology of NPs is strongly dependant on the characteristics of the induced plasma. At low laser energies, low temperature plasma is produced and large NPs are created. On the other hand, when increasing the laser energy, larger kinetic energy is generated from the high temperature plasma, which leads to increase the number of collisions between the larger formed NPs causing it to reduce in size. These results agrees with the previously published papers reported by A.F.M.Y. Haider [34], E. Solati [35], D. Dorranian [36] and A. HAHN [37]. The average diameter of CdO NPs prepared under different energies is listed in table 3.

### Table 3. The average diameter and roughness of CdO NPs prepared under different laser energies.

| Laser energy(mJ/pulse) | Average diameter (nm) | Roughness (nm) |
|------------------------|-----------------------|----------------|
| 171                    | 80.18                 | 3.85           |
| 201                    | 77.94                 | 3.21           |
| 263                    | 67.68                 | 2.15           |
Figure 5. 3D AFM images and size distribution of CdO NPs prepared at different laser energies (a) 171 mJ/pulse, (b) 201 mJ/pulse and (c) 263 mJ/pulse.

4. Conclusion
Cadmium oxide nanoparticles have successfully been prepared using laser ablation technique in Ethanol at different laser energies (171, 201 and 263 mJ/pulse). When increasing the laser energy, blue shift occurs in the absorption spectrum towards the UV region, and the energy gap increase due to quantum confinement effect caused by the small size of NPs. The high intensity of XRD peaks indicated the resulted Nps are of a crystalline structure with high purity. AFM images showed that the particle size is influenced by the laser energy, the higher the energy the lower the average diameter of the synthesized NPs.

5. References
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