Preparation and Study of colloidal CdO nanoparticles by laser ablation in polyvinylpyrrolidone

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Abstract. Nanoparticles NPs of cadmium oxide CdO were generated by laser ablation of a solid target (cadmium) in polyvinylpyrrolidone (PVP) solution. CdO colloidal nanoparticles have been synthesized by laser ablation Nd:YAG (1064 nm, 100 pulses, pulse energy= 400 mJ) when the solid target CdO was immersed in PVP. Structure, topography and optical properties of the CdO nanoparticles NPs have been studied using X-ray diffraction (XRD), atomic force microscope (AFM) and the UV-Vis absorption respectively.

Introduction

Particles with dimensions in the nanometer range made out of II-VI semiconductors are important material for optoelectronic applications [1]. The vast majority of established high –yield method to synthesize nearly mono disperse II-VI semiconductors quantum dot distributions is based on chemical approaches. The most widely used synthetic routes to synthesize CdO and CdTe nanostructures use aqueous solutions facing various functional groups (e.g. polar and unpolar thiols, amines and others) are employed to stabilize the particles[2]. Purely physical production methods which allow the synthesis of uncapped particles were limited to mechanical ball milling processes [3-5] and laser ablation in liquids which used to generate noble metal nanoparticles in suspension is known since 1993 [6-9] and was also applied to several non-metallic systems [9,10]. Also semiconductors nanoparticles were fabricated by other methods, such as deposition on different substrates by pulsed electron deposits technique [11], pulsed laser deposition [12] or pulsed laser ablation in argon gas atmosphere and methanol vapors [13] as well as by laser ablation in liquid environments (usually using long pulse laser sources at high fluence) [14].

The aim of this work focused on the preparation of CdO nanoparticle by PLAL technique in order to study their structural, morphological and optical properties.

Experimental details

Figure 1 shows the experimental setup for laser ablation of cadmium Cd solid target immersed in polyvinylpyrrolidone, which includes the laser source Nd:YAG laser system type HUAFEI, \( \lambda=1064\)nm wavelength with maximum energy per pulse of 400 mJ, pulse width of 9 ns, repetition rate of (1Hz) and beam diameter of 2.3 mm. The laser is applied to a lens of 12 cm focal length to achieve high laser fluence. Cd pure pellet (diameter = 5 mm) was used in this work as a target material for the preparation of CdO nanoparticles. The ablation process was typically done for (1 min) at room temperature. The target and a glass container are rotated by a base rotator during the process.

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X-ray diffractometer (shimadzu – XRD 6000, Shimadzu Company / Japan). with CuKα radiation (λ= 1.5406 Å) in the range of 20°–60° (2θ) at a scanning rate of 0.05°/min. Scanning electron microscope SEM (T-scan Vega III Czech) and transmission electron microscopy TEM (type CM10 pw6020, Philips Germany) were employed to study the structure of nanoparticles, elemental analysis and mapping of the synthesized nanoparticles. Atomic force microscope AFM (AA 3000 scanning probe microscope) was employed to study the morphology of nanoparticles. The absorption of the colloidal nanoparticles solution was measured by using UV–Vis double beam spectrophotometer (CECIL, C. 7200, France). FT-IR spectra were recorded by Perkin Elmer Spectrometer. Photoluminescence spectra were recorded using Shimadzu-5301 spectrophotometer.

Results and discussion

PVP has been applied as a solvent. During laser ablation in PVP, the color of the solvent has been changed to yellow, we expect the formation of CdO particles. The efficiency of particle formation is affected by properties of solution, as shown in Fig. 2.

Fig. 3 illustrate the UV-Vis spectra of PVP solution containing CdO NPs prepared by laser ablation in liquid technique. The spectra shows plasmon resonance peak due to quantum size effect at UV range (300-360) nm, also the transmittance and absorption curves were subdivided into two regions at the visible region. The absorption curve decreases sharply from 360 nm up to 540 nm and after this wavelength tends to saturate. So the CdO NPs have a good transmittance in the visible range, which can be used in solar cell and a smart window.
Fig. 3: UV-Vis transmittance (left) and absorption (right) spectra of nanoparticles colloid fabricated at wavelength CdO ablated with 400 mJ at 1064nm.

Fig. 4 shows the variation of \((\alpha h\nu)^2\) verses \(h\nu\) for direct band gap which have been determined by the extrapolation of linear portion versus the photon energy axis. It can be seen that the value of the energy gap is about 2.8 eV. This optical phenomenon indicates that these nanoparticles show the quantum size effect [15,16].

\[
D = \frac{0.94 \lambda}{\beta \cos(\theta)}
\]

Where \(\lambda\) is the wavelength (\(\lambda = 0.1542\) nm) (CuK\(\alpha\)), \(\beta\) is the full width at half maximum (FWHM) of the line, and \(\theta\) is the diffraction angle. The crystallite size estimated using the relative intensity peak (002) for Cd and (111) for CdO nanoparticles and was found to be around 69 nm and 47 nm respectively, as shown in Table 1. Increase in sharpness of XRD peaks indicates that particles are in crystalline nature. The (200), reflections are clearly seen and closely match the reference patterns for CdO (Joint Committee for Powder Diffraction Studies (JCPDS) File No. 05-0640). The sharp XRD peaks indicate that the particles were of polycrystalline structure, and that the nanostructure grew with a random orientation [18].
The microstrain ($\gamma$) and the dislocation density ($\sigma$) can be calculated by using the following relations [18], see Table (1):

$$\gamma = \frac{\beta \cos \theta}{4} \quad (2)$$

$$\sigma = \frac{1}{D^2} \quad (3)$$

<table>
<thead>
<tr>
<th>2(\Theta) (deg)</th>
<th>FWHM (deg)</th>
<th>d (A)</th>
<th>(hlk) Planes</th>
<th>D (nm)</th>
<th>$\sigma \times 10^{14}$ lines/m$^2$</th>
<th>$\gamma \times 10^{-4}$ lines$^2$/m$^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>29.84</td>
<td>0.11</td>
<td>2.99</td>
<td>Cd (002)</td>
<td>68.84</td>
<td>02.10</td>
<td>05.03</td>
</tr>
<tr>
<td>44.28</td>
<td>0.301</td>
<td>2.04</td>
<td>CdO (200)</td>
<td>47.01</td>
<td>13.70</td>
<td>12.82</td>
</tr>
</tbody>
</table>

Fig. 5: XRD pattern of CdO thin film

Fig. 6 shows the 3D AFM image of the synthesized CdO thin film deposited on glass substrate by drop casing method. The surface of the thin film have a vertically closely packed ball–shaped, homogenous and a good roughness grains of CdO nanostructure within scanning area (2x2)µm. Using special software (4.62 imager), the estimated of average grain was around 88 nm.

Fig. 6: 3DAFM image of synthesized CdO nanoparticles

It is clear from Fig. 7 (SEM image), that the prepared CdO nanoparticles have regular spherical shape and uniform size, with an average size around 52 nm and one can see some coalesced nanoparticles with a size of about 100 nm.
Also, the TEM image of the CdO nanoparticles corresponding to the same sample of XRD pattern in Figure 5 and SEM in Fig. 7, the particle size distribution was shown in Fig. 8. From TEM, the average particle size appears to be around 50 nm. These particles are single crystalline as revealed by the high resolution electron microscope image. The particles are spherical or elliptical in shape.

In Fig. 9 the peak at 1270 cm\(^{-1}\) and comparatively two small peaks confirm the presence of cadmium and oxygen in the sample. In the FTIR spectrum the strong absorption in the range of 1270 to 1641 cm\(^{-1}\) and the other couple of peaks in the range of 553 and 666 cm\(^{-1}\). The weak absorption at 1641 is also found in the FTIR spectrum. The above cadmium reacting with oxygen in the air during the time of preparing CdO NPs. From the FTIR spectrum, it is conclude that the presence of cadmium and oxygen is in the range of 1641 to 1270 cm\(^{-1}\) which is in good agreement with reference [19].
Fig. 9: Shows the Transmittance for CdO Nanoparticles.

Conclusion

The fabrication of CdO NPs in PVP by laser ablation in liquid method was successfully made by this work. CdO NPs have been produced by laser ablation in PVP at (400 mJ) laser energy, 100 pulse and 1064 nm wavelength. From the AFM, SEM and TEM analysis it has been found that the average grain size of CdO hasn’t exceeded 88 nm. Advantage of this method is convenient for synthesis of CdO nanoparticles in normal laboratory conditions and low cost.

References


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