Int. J. Electrochem. Sci., 8 **(2013)** xx - yy

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Synthesis and Characterization of CdO Nanoparticles Starting from Organometalic Dmphen-CdI_2 complex

A.S. Aldwayyan[1], F.M. Al-Jekhedab[2], M. Al-Noaimi[3], B. Hammouti[4,], T. B. Hadda[5], M. Suleiman[6], I. Warad[6*]*

[1]Department of Physics and Astronomy, College of Science, King Saud University, PO Box 2455, Riyadh 11451, Saudi Arabia.
[2] The National Center for Nanotechnology Research (NCNR), King Abdulaziz City for Science and Technology, PO Box 6086, Riyadh 11442, Saudi Arabia,
[3]Department of Chemistry, Hashemite University, P.O. Box 150459, Zarqa-13115-Jordan,
[4]LCAE-URAC18, Faculty of Sciences, University Mohammed Premier, Oujda-60000, Morocco,
[5]Laboratoire LCM, Faculty of Sciences, University Mohammed Premier, Oujda-60000, Morocco
[6]Department of Chemistry, AN-Najah National University, Nablus, Palestinian Territories
[*]E-mail: warad@najah.edu

Received: 29 May 2013 / *Accepted:* 1 xxx 2013 / *Published:* 1 xxx 2013

Cadmium oxide (CdO) nanoparticles were prepared starting from organometallic *cis*-[dmphen-CdI_2] complex (dmphen = 2,9-Dimethyl-1,10-phenanthroline) through one step calcination process at 800 ^oC, the thermal behavior of the complex during calcination was recorded by TGA/DTA. The obtained product are analyzed by FT-IR, UV-visible, X-ray diffractometer (XRD), EDS, SEM and TEM, the average size of CdO nanoparticles found to be 50 nm.

Keywords: CdO Nanoparticles, XRD, UV-visible, EDS, SEM, TEM, TGA/DTA, FT-IR.

1. INTRODUCTION

Nanoparticles have attracted great interest recently due to their unique physical and chemical properties, which are different from those of either the bulk materials or single atoms [1].

In recent years, many researchers have focused on cadmium oxide (CdO) due to their applications in several areas of research, specifically in optoelectronic and other applications, including solar cells [2, 3], phototransistors [4], photodiodes [5], transparent electrodes and gas sensors [6]. Reduction in the dimensionality of such materials from the three dimensional bulk phases to the zero-dimensional nanoparticles can lead to enhanced non-linearity, determined by the quantum size

effects and other mesoscopic effects. Because of these interesting possibilities, there has been some effort to prepare nanoparticles of CdO. Liu et al. [7] synthesized CdO nanoneedles by chemical vapour deposition. CdO nanowires have been synthesized by decomposing $CdCO_3$ in a KNO_3 salt flux [8]. Zou et al. [9] have prepared CdO nanoparticles by the micro-emulsion method employing AOT reverse micelles. There is also a report of stearate coated CdO nanoparticles of 5–10 nm size range, obtained by the micro-emulsion method starting from an aqueous solution of a cadmium salt and stearic acid in xylene [10].Wu et al. [11] prepared a nanometer-sized CdO organosol from an aqueous solution of $Cd(NO_3)_2$, in the presence of a surfactant and toluene as solvent.

Some workers try to modify the synthesis procedure for CdO with the aim to improve chemical and physical properties of this material. Such examples of this are: Gulino et al. [12] that investigated the formation of CdO thin films by thermal decomposition of cadmium hexafluoroacetylacetonate dehydrate [$Cd(C_5F_6HO_2)_2.H_2O$]. The $Cd(C_5F_6HO_2)_2.CH_3OCH_2OCH_3$ complex was precursor in the preparation of thin CdO films [13]. The thermal decomposition of cadmium itaconate monohydrate ($C_5H_4O_4Cd.H_2O$) in N_2, H_2 or air was also investigated [14]. Uplane et al. [15] reported the preparation of CdO thin films onto the hot glass substrate at 400 °C by spray pyrolysis of the aqueous cadmium acetate solution.

2. EXPERIMENTAL PART

2.1. Apparatus

All the chemical reagents was from Riedel-Dehaenag (Germany), and used as received. The obtained nanoparticles were examined by a Brucker D/MAX 2500 X-ray diffractometer with Cu K radiation (λ = 1.54 Å), and the operation voltage and current were maintained at 40 kV and 250 mA, respectively. The transmission electron microscopy was (TEM, 1001 JEOL Japan). The scanning electron microscopy (SEM, JSM-6360 ASEM, JEOL Japan). And the IR spectra for samples were recorded by using (Perkin Elmer Spectrum 1000 FT-IR Spectrometer). Samples were measured and recorded using a TU-1901 double-beam UV–visible spectrophotometer was dispersed in toluene solution

2.2. Chemicals and Solutions

Cadmium iodide, 2,9-dimethyl-1,10-phenanthroline ligand, dichloromethane (99.0%), Ethanol (99.5%), were purchased from Fluka.

2.3. Preparation of the dmphen-CdI_2 complex

A mixture of 2,9-dimethyl-1,10-phenanthroline (50.0 mg, 0.24 mmol) in dichloromethane (5 ml) and CdI_2 (65.4 mg, 0.24 mmol) in methanol (10 mL) was placed in a round bottom flask and stirred for 4 h at room temperature. The solution was concentrated to about 1 mL under reduced pressure. Addition of

40 mL of n-hexane caused the precipitation of white powder, which was filtered and then dried under vacuum to 108 mg (yield 94% based on Cd).

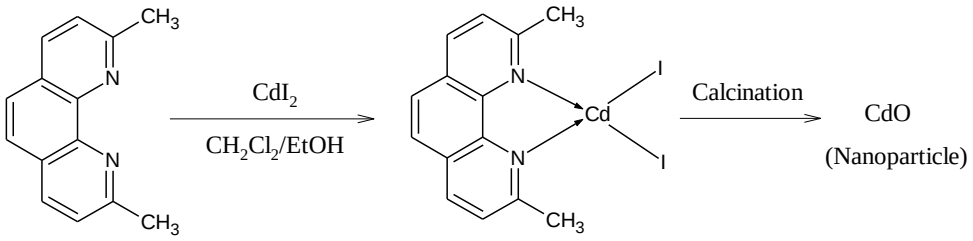
2.3. Preparation of CdO nanoparticles

0.5g dmphen-CdI_2 was calcinated directly at 800 ^oC for 120 min, the calcinations process was stopped upon no organic function group vibrations was detected by IR, white powder CdO was formed at the end of the process.

3. RESULTS AND DISCUSSION

3.1. Synthesis of dmphen-CdI_2 complex and CdO

The *cis*-[dmphen-CdI_2] as mononuclear complex was prepared by use of a modification of our literature method [16, 17]. The complex was isolated in good yield from a simple, 3 h, RT reaction of one equivalent of dmphen ligand with CdI_2 under gentle, stirred, open atmosphere conditions, using mixture of dichloromethane and ethanol as solvent (Scheme 1). The white powder complex product is soluble in chlorinated solvents, for example chloroform and dichloromethane, and insoluble in alcohols, water, ethers, and n-hexane.



Scheme 1. Synthesis of the desired dmphen-CdI_2 complex and CdO nanoparticle .

CdO nanoparticle was prepared for the first way through direct calcinations of *cis*-[dmphen-CdI_2] complex at 400 ^oC for 120 min.

3.2. Thermal Properties of cis-[dmphen-CdI_2] complex and CdO nanoparticle (TGA/DTA)

To follow up the thermal decomposition of the *cis*-[dmphen-CdI_2] complex to form the CdO nanoparticle, identify the thermal behavior and determine the crystalline conditions, Differential Thermal Analysis (DTA) and Thermal Gravimetric Analysis (TGA) were carried out. The thermal decomposition study was investigated in the 25–1000 ^oC temperature range under open atmosphere at a heating rate of 10 ^oC/min. typical thermal TGA and DTA curves are given in Figure 1. There is no weight loss in the range 0–320 ^oC, which indicates the absence of coordinated or uncoordinated water

molecules. Such complexes undergo three-step decomposition with weight loss experimentally 73%, the coordinated iodide and 1,10-phenanthroline ligands have been de-structured from the complex. Three exothermic DTA peaks at 420, 590 and 670 ^{o}C were recorded. The DTA patterns is the signature of the good crystallization of such complexes, the exothermic peaks reaction indicated that the complexes thermally decomposed for formation of Cadimium-oxide phase through oxidation decomposition process. The final residue was analyzed as CdO which revealed thermal stability from 700 to 1000 ^{o}C.

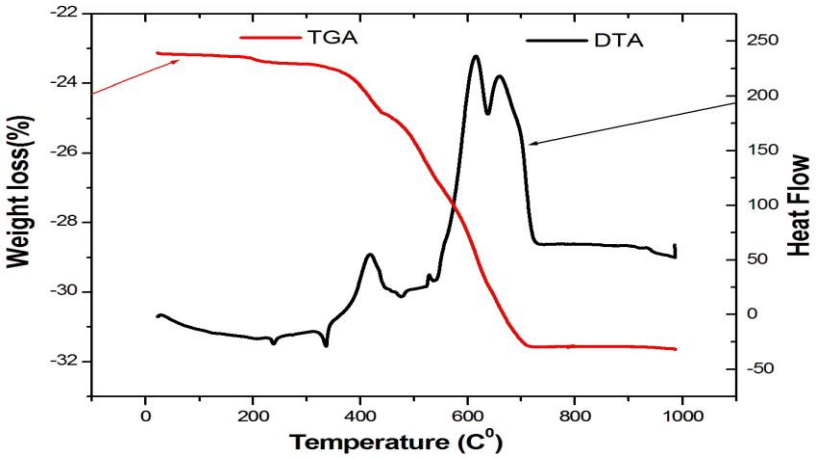


Figure 1. TGA and DTA curves of dmphen-CdI_2 complex.

3.3. FT-IR investigation

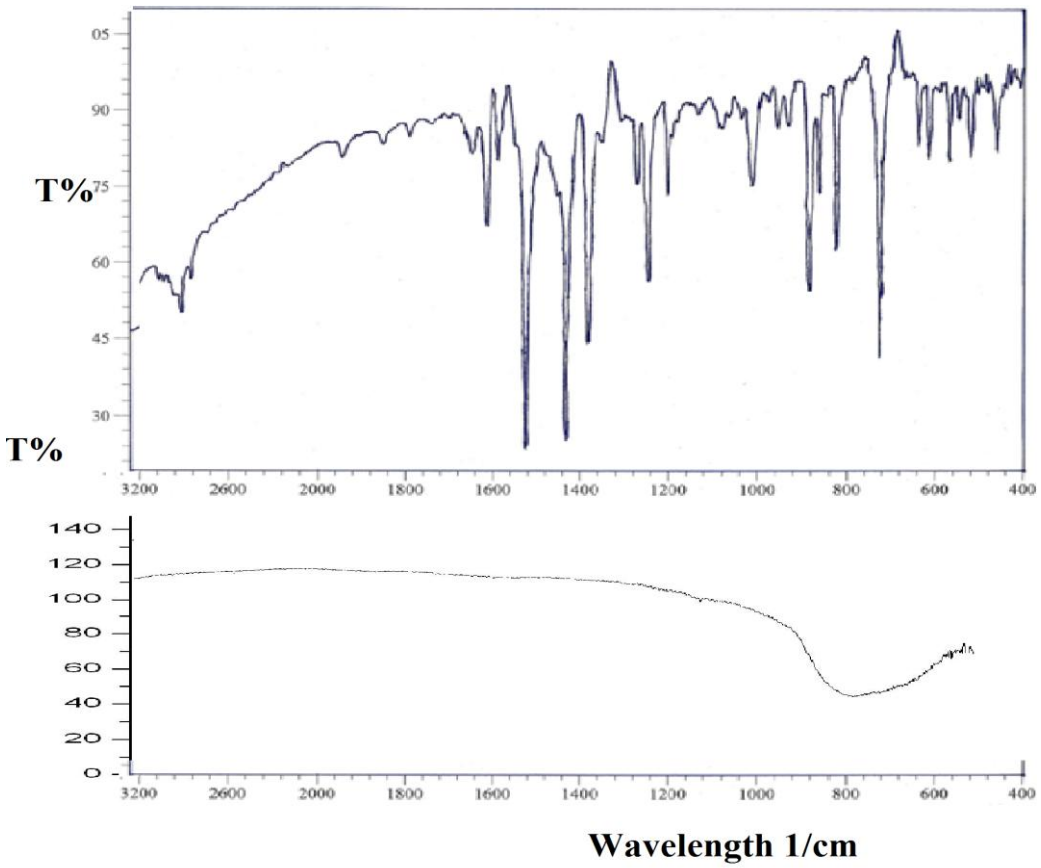


Figure 2. IR spectra of dmphen-CdI_2 complex up and CdO nanoparticles (dmphen-CdI_2 after calcinations at 600 ^oC) down

Figure 2 shows the IR spectra for these samples: the starting complex dmphen-CdI_2 and the product CdO nanoparticle. IR spectra of the dmphen-CdI_2 complex contained four characteristic absorption peaks at 3090, 2890, 820, and 290 cm^{-1}, which can be assigned to, Ph–CH, Me–CH, Cd–N and Cd–Cl stretching vibrations, respectively. All other functional group vibrations appeared at their expected positions. After calcinations of dmphen-CdI_2 at $400C^0$ for 120 min only, Fig. 2 shows all the vibration of the organic function groups were disappeared and only one broad sign at 750- 500 cm^{-1} belongs to CdO bond, it could be useful in understanding the bonding between the Cd-O atoms, the formed CdO phase is characterized by an intense and very broad IR band with poorly resolved shoulder at 550 and 480cm^{-1} which characteristic of CdO.[18].

3.4.UV–visible absorption spectra for CdO nanoparticles

The UV–visible absorption spectra of CdO nanoparticles are shown in Figure 3 although the wavelength of our spectrometer is limited by the light source, the absorption band of the CdO nanoparticles have been shows a blue shift due to the quantum confinement of the exactions present in the sample compare with bulk CdO particles. This optical phenomenon indicates that these nanoparticles show the quantum size effect [19, 20].

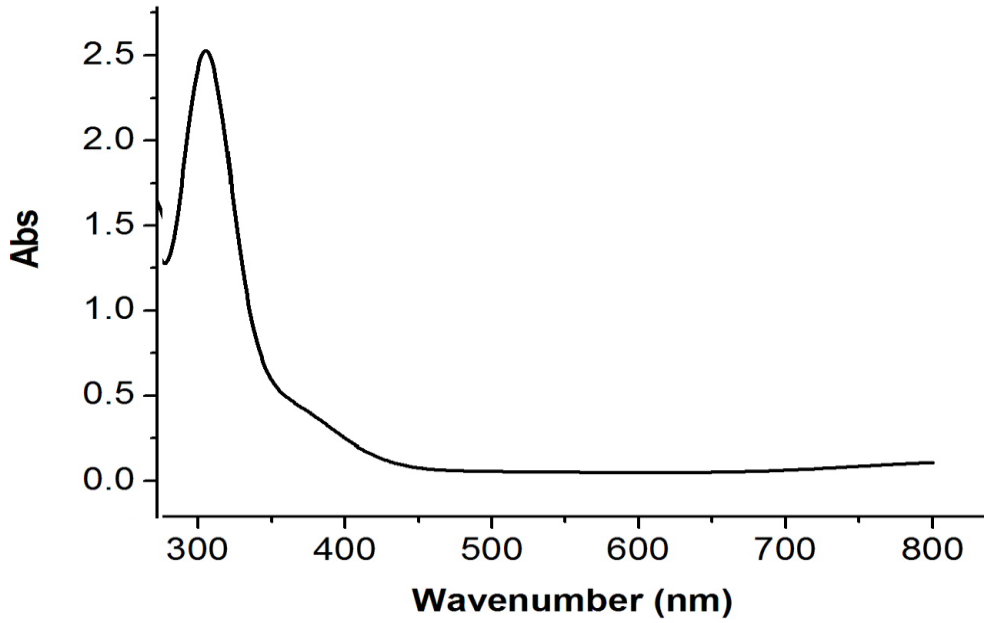


Figure 3. UV-Absorption spectra for CdO nanoparticles

3.5. XRD pattern for CdO nanoparticles

The XRD patterns of the CdO nanostructure showed diffraction peaks absorbed at 2θ values (Fig. 4). The prominent peaks were used to calculate the grain size via the Scherrer equation expressed as follows:

$$\mathbf{D = (094\ \lambda)/(\beta\ \cos\theta)}$$

Where λ is the wavelength (λ = 1.542 Å) (CuKα), β is the full width at half maximum (FWHM) of the line, and θ is the diffraction angle. The grain size estimated using the relative intensity peak (220) for CdO nanoparticles was found to be 48 nm and increase in sharpness of XRD peaks indicates that particles are in crystalline nature. The (111), (200), (220), (311) and (222) 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 [21].

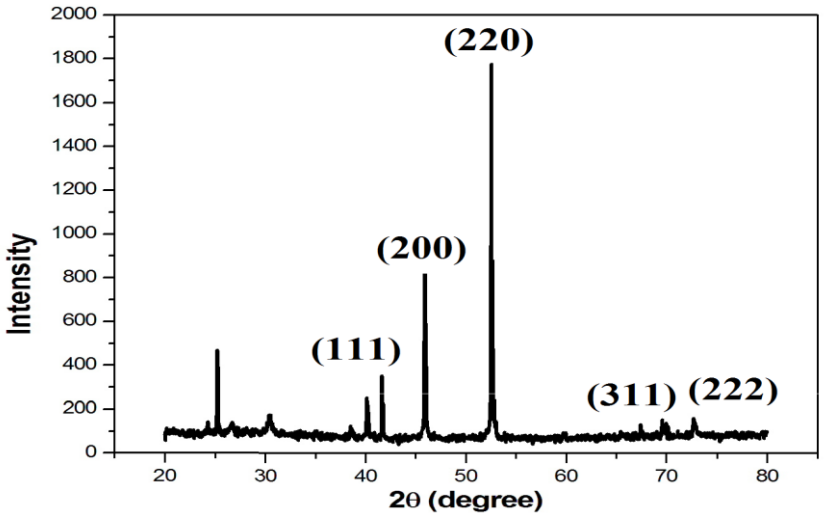


Figure 4. XRD pattern for CdO nanoparticles

3.6. EDS measurement

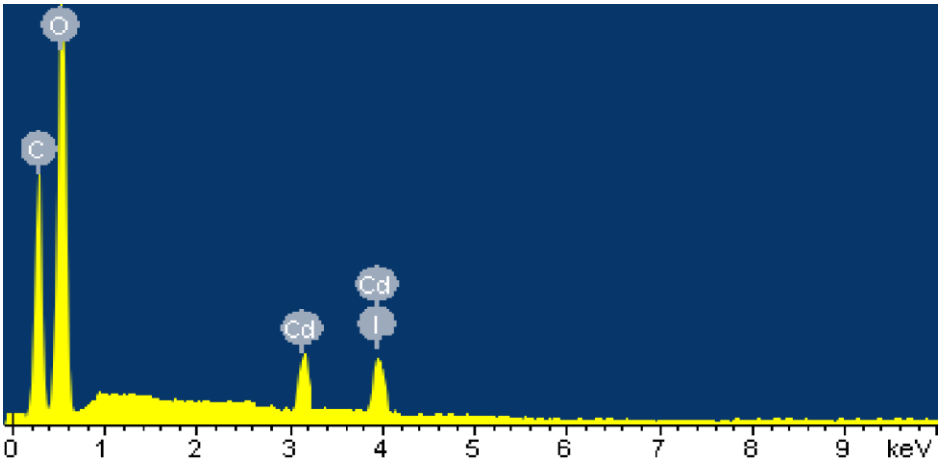


Figure 5. EDX spectrum of CdO nanostructure, the atomic percentages of Cd and O, 15 and 85%.

To identify and differentiate the chemical composition of the desired nanomaterial. It was subjected to EDS measurement as in Figure 5, which found to have signs belong their composition; they contain signs of carbon at 0.2 eV, oxygen at 0.6 eV, and cadmium sign at 3.2 and 3.9 eV.

3.7. Scanning Electron Microscopy (SEM) measurement

The SEM image of the CdO nanoparticles corresponding to the XRD pattern in Fig.4 is shown in Fig. 6, it is clear that the prepared CdO nanoparticles have regular spherical shape and uniform size, with an average size of 50 nm and one can see some coalesced nanoparticles with a size of about 100 nm.

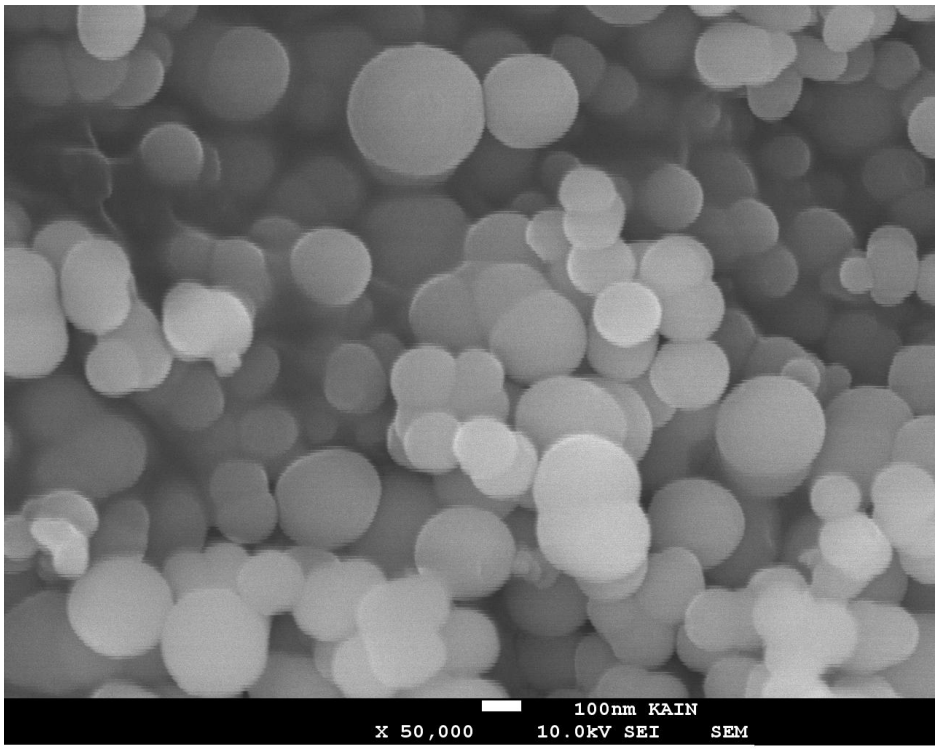


Figure 6. SEM image of CdO nanoparticles of an average diameter of 40-100 nm.

3.8. Transmission Electron Microscopy measurement (TEM)

The TEM image of the CdO nanoparticles corresponding to the same sample of XRD pattern in Figure 4 and SEM in Figure 6, the particle size distribution was shown in Figure 7. 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, not unlike those reported by Dong et al. [10].

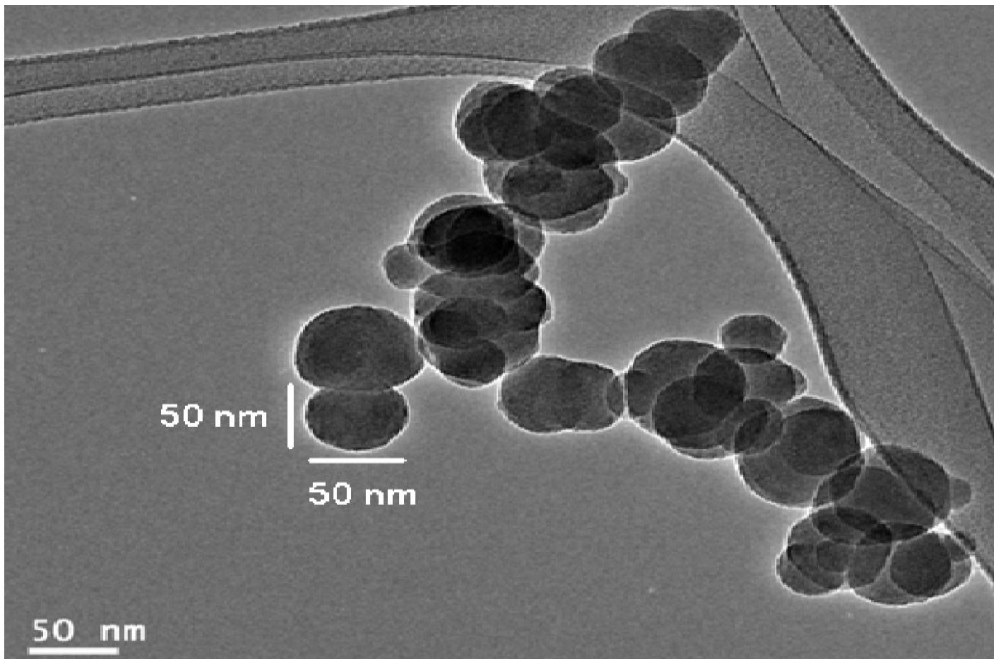


Figure 7. TEM image of CdO nanoparticles of an average diameter of 50 nm.

4. CONCLUSION

This report has shown the synthesis of CdO nanoparticles using organometallic dmphen-CdI_2 complex through one step calcinations process at 800 ^{o}C. From XRD, SEM and TEM data obtained of the nanoparticle size were ~ 50 nm. Advantage of this method is convenient for synthesis of CdO nanoparticles in normal laboratory conditions and low cost.

ACKNOWLEDGEMENTS
The project was supported by King Saud University, Deanship of Scientific Research, College of Science Research Center.

References

1. V.S. Muralidharan, and A. Subramania, *Nanoscience and technology*, Crc Press, New Delhi, (2009) 542.
2. C. Sravani, K.T.R. Reddy, O.M. Hussain, and P.J. Reddy, *J. Solar. Energy. Soc. India* 1 (1996) 6.
3. L.M. Su, N. Grote, and F. Schmitt, *Electron. Lett.* 20 (1984) 716.
4. R. Kondo, H. Okimura, and Y. Sakai, *Jpn. J. Appl. Phys.* 10 (1971) 1547.
5. F.A. Benko, and F.P. Koffyberg, *Solid State Commun.* 57 (1986) 901.
6. A. Shiori Jpn. Patent No. 7 (1997) 909.
7. Y. Liu, C. Yin, W. Wang, Y. Zhan, and G. Wang, *J. Mater. Sci. Lett.* 21 (2001) 137
8. X. Liu, C. Li, S. Han, J. Han, and C. Zhou, *Appl. Phys. Lett.* 82 (2003) 1950.
9. B.S. Zou, V.V. Volkov, and Z.L. Wang, *Chem. Mater.* 11 (1999) 3037.
10. W. Dong, and C. Zhu, *Opt. Mater.* 22 (2003) 227.
11. X. Wu, R. Wang, B. Zou, L. Wang, S. Liu, and J. Xu, *J. Mater. Res.*13 (1998) 604.

12. A. Gulino, F. Castelli, P. Dapporto, P. Rossi, and I. Fragala, *Chem. Mater.* 14 (2002) 704.
13. A. Gulino, P. Dapporto, P. Rossi, and I. Fragala, *Chem. Mater.*14 (2002) 1441.
14. M.A. Mohamed, S.A. Halawy, *J. Anal. Appl. Pyrolysis* 65 (2002) 287.
15. M.D. Uplane, P. N. Kshirsagar, B.J. Lokhande, and C.H. Bhosale, *Mater. Chem.* 64 (2000) 75.
16. I. Warad, A. Boshaala, S.I. Al-Resayes, S.S. Al-Deyab, M. Rzaigui, *Acta Cryst.* E67 (2011) 1846.
17. I. Warad, A. Boshaala, S.I. Al-Resayes, S.S. Al-Deyab, and M. Rzaigui, *Acta Cryst.* E67 (2011) 1650.
18. K.M. Abd El-Salaam, and E.A. Hassan, *Surf. Technol,* 16 (1982) 121.
19. X.R. Ye, C. Daraio, C. Wang, and J.B. Talbot, *J. Nanoscience and Nanotechnology,* 6 (2006) 852
20. Z. Guo-hua, L. Ming-fang, and L. Ming-Li *CEJC,* 5 (2007) 1114.
21. H.P. Klug, and L.E. Alexander, X-ray *Diffraction Procedures for Polycrystalline and Amorphous Materials,* Wiley, New York (1954).
22. M. Pandurangachar, B.E. Kumara Swamy, U. Chandra, O. Gilbert and B.S. Sherigara, *Int.J. Electrochem. Sci,* 4 (2009) 672.
23. Rekha, B.E. Kumara Swamy, R. Deepa V. Krishna, O. Gilbert, U. Chandra, and B.S. Sherigara, *Int. J. Electrochem. Sci.,* 4 (2009) 832.