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Synthesis and Characterization of MnO_2, Mn_3O_4, NiO and Cd Doped ZnO Nanoparticles *via* a PEG Assisted Route

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MnO_2, Mn_3O_4, NiO and Cd doped ZnO nano structures have been synthesized by PEG assisted process. The effect of amount of polymer, calcination and temperature on the formation of these nano structures has been investigated. It is observed that these factors play vital role on the growth of nanostructures. The products were characterized by X-ray diffraction (XRD), IR, optical absorption measurement (UV/VIS), scanning electron microscopy (SEM) and EDAX.

Key Words: Polymer, Nanoparticles, PEG400, Assisted route.

INTRODUCTION

MnO_2, Mn_3O_4, NiO and Cd doped ZnO nanostructures have attracted much interest due to their unique properties. Manganese dioxide has many important applications, such as ionic and molecular sieves[1,2], catalysts[3] and cathode material for rechargeable batteries[4]. Mn_3O_4 used as a starting material in the production of soft ferrites[5]. Nanostructure NiO behaves as *p* type semiconductor and with a uniform size and well dispersion and desirable for many application in designing ceramics[6], magnetic[7], electrochromic and heterogeneous catalytic material[8]. The doping of ZnO nanostructures with cadmium offers an effective method to enhance and control its electrical and optical properties[9]. Generally, long chain polymers help the growth of nanostructures but their practical usage is limited. It is feasible that short chain polymers can also promote the formation of nanostructures; therefore we can use short chain polymers to selectively control synthesis of nanostructures. In the present work, a short chain polymer poly ethylene glycol (PEG400) has been used for formation of nanoparticles hydroxides. Then the obtained nanopowders were calcinated in different temperatures to obtain nanostructure oxides. This method develops a new route to synthesis of nanometal oxides.

EXPERIMENTAL

All the chemicals were of analytical grade and were used without any purification. For the synthesis of manganese oxides, $MnSO_4$ was dissolved in distilled water to form 0.5 M solution. the obtained precursor solution (4 mL) was added to 100 mL conical flask containing mixed solution of 50 mL distilled water, 2.8 g NaOH and different quantities of PEG 400 and well blended by stirring for 10 min subsequently, the mixed solution were placed for certain time at room temperature (Table-1). White crystalline products were collected,

TABLE-1
EXPERIMENTAL CONDITIONS AND CORRESPONDING PRODUCTS

	No of experiment	PEG volume (mL)	Reaction time (day)	Furnace temperature (ºC)	Furnace (h)
Nickel oxide	1	10	4	400	2
Nickel oxide	2	10	7	400	2
Nickel oxide	3	20	4	400	2
Nickel oxide	4	10	4	600	2
Manganese oxide	5	10	4	250	4
Manganese oxide	6	20	4	250	4
Manganese oxide	7	10	6	250	4
Manganese oxide	8	10	4	250	1
Manganese oxide	9	10	4	400	1

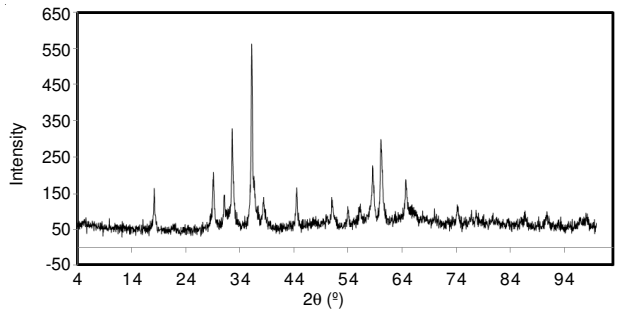
washed with distilled water and ethanol several times and dried at 60 ºC in a vacuum oven for 10 h. The hydroxide nanoparticles formed were heated in furnace for certain time (Table-1) to obtain MnO_2 and Mn_3O_4 nanoparticles. Similar procedure is used for preparation of NiO nanoparticles using ($NiCl_2 \cdot 6H_2O$). For the synthesis of Cd doped ZnO, 2 mL of 0.86 M solution of $Zn(CH_3COOH)_2 \cdot 2H_2O$ was added to conical flask containing 2 mL of 0.75 M solution of $Cd(CH_3COOH)_2 \cdot 2H_2O$, 50 mL distilled water, 2.8 g NaOH and 10 mL PEG (Mw = 400). After mixing well for 1 h with magnetic stirring in 70 ºC, the mixed solution was placed at room temperature for 4 days. The white crystalline product was collected and washed with ethanol and water several times and placed in vacuum oven for 12 h at 60 ºC, then placed in furnace for 1 h at 400 ºC.

All the samples were characterized by X-ray diffraction (XRD) with K_α (λ = 1.5418 Å) incident radiation. XRD patterns were recorded from 20-80º (2θ) with a scanning step of 0.03º. The optical absorption was recorded on a Perkin-Elmer, Lambda UV-VIS by dispersing nano powders in anhydrous alcohol and using anhydrous alcohol as the reference. IR spectra were obtained using KBr discs (4000-500 cm^{-1}) on Bruker Tensor 27 FTIR spectrophotometer. The SEM pictures were carried on Philips XL30. Energy dispersive spectrometry (EDAX) was employed to perform the elemental analyses of the nanostructures materials.

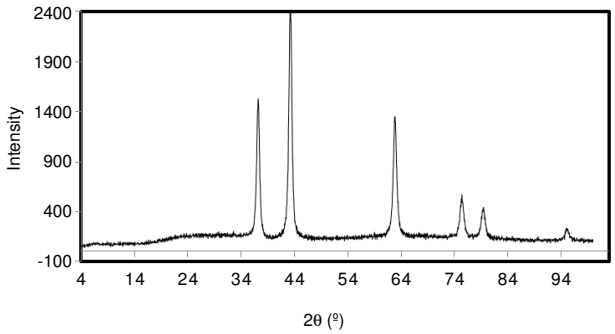
RESULTS AND DISCUSSION

X-Ray diffraction patterns (XRD) of the products: The XRD pattern of as-obtained nanoparticles of Mn_3O_4, NiO and Cd doped ZnO are shown in Fig. 1(a-c).

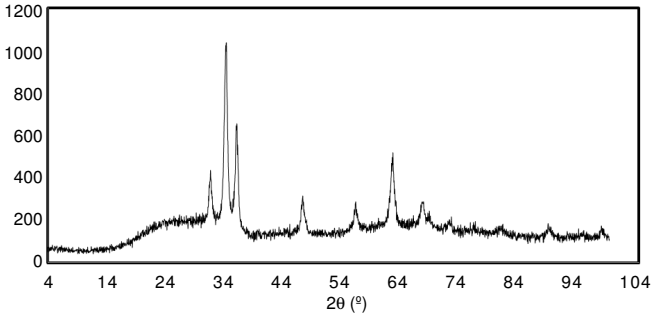
Fig. 1a shows typical XRD pattern of Mn_3O_4 prepared at 400 ºC 1 h, sharp and intense peaks prove the synthesis of good quality crystalline Mn_3O_4 (JCPDS Card No. 24-0743).



(a)



(b)



(c)

Fig. 1. Typical XRD pattern (a) Mn_3O_4, (b) NiO and (c) Cd doped ZnO nanoparticles

Fig. 1b shows typical XRD pattern of NiO nanoparticles prepared with 20 mL polymer. Peaks at 2θ = 32.327, 43.160, 62.90, 75.44, 79.43 correspond to (111), (200), (220), (311), (222) Brags reflection planes of cubic NiO, respectively (JCPDS Card No. 78-0643). Employing the Scherrer equation, the sizes of nanoparticles is 22.2 nm.

Fig. 1c shows typical XRD pattern of Cd doped ZnO. Peaks at 2θ = 31.8, 34.4, 36.23, 47.5, 56.5, 62.7, 69.1 correspond to (100), (002), (101), (102), (110), (103),(201) Brags reflection planes of wortzitte ZnO.

Morphologies of the nonoparticles: Typical SEM images of as obtained nanoparticles are shown in Figs. 2-4 as well as EDAX pattern for detail illustration. Fig. 2a shows the SEM image of the as obtained nano wire of MnO_2 with diameters ranging 43-54 nm and Fig. 2b shows the SEM image of Mn_2O_3 with diameters ranging 34 nm. The EDAX Fig. 2c image of MnO_2 showed that components of the crystals are Mn and O.

Fig. 3 shows the SEM image of the as obtained nano spherical of NiO with diameters ranging 22.2 nm (calculated from Scherrer equation). The EDAX image of NiO showed that components of the crystals are Ni and O.

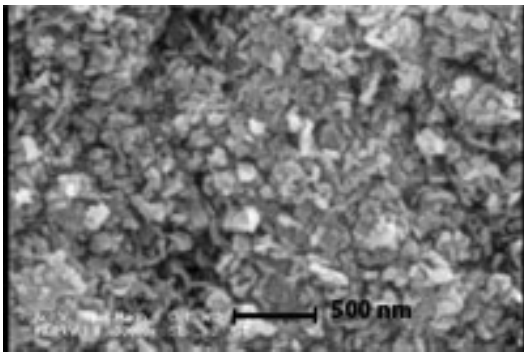
Fig. 4 shows the SEM image of the as obtained nano spherical of Cd doped ZnO, with diameters ranging 52 nm. The EDAX image of it showed that the synthesized sample is pure and have zinc and cadmium element.

FT-IR and electronic specra: In the IR spectra of nano MnO_2 there is resolved shoulder at 636 cm^{-1} due to vibration of Mn-O[10] and in nano Mn_3O_4 there are shoulders at 511 and 622 cm^{-1} which indicated structure of Mn_3O_4[11]. UV-VIS absorption spectrum of MnO_2 and Mn_3O_4 nano structures showed both of the synthesised MnO_2 (362 nm) and Mn_3O_4 (420 nm) have blue shift compared to balk sample[12,13].

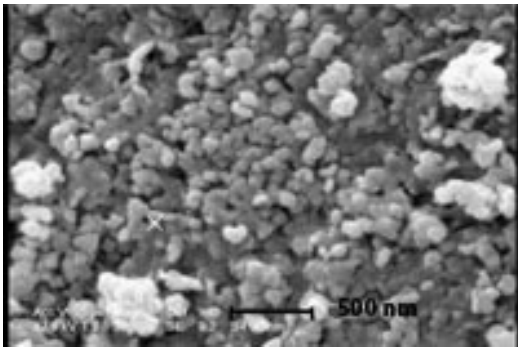
In the FT-IR spectrum of NiO nano structure. There is resolved shoulder at 450 nm due to vibration of Ni-O[14]. UV-VIS absorption spectrum of NiO nanostructures shows maximum absoption at 345 nm and has blue shift compared with the balk sample[14].

In the FT-IR spectrum of Cd doped there are shoulders at 427 cm^{-1} due to the vibration of Cd-O and shoulders at 558 and 917 cm^{-1} due to Zn-O vibration. In its UV-VIS spectra a maximum peak at 397 and 375 nm due to zinc oxide which has red shift and shows cadmium is doped to ZnO[15].

Possible formation mechanism: PEG with uniform and ordered chain structure is adsorbed at the surface of metal



(a)



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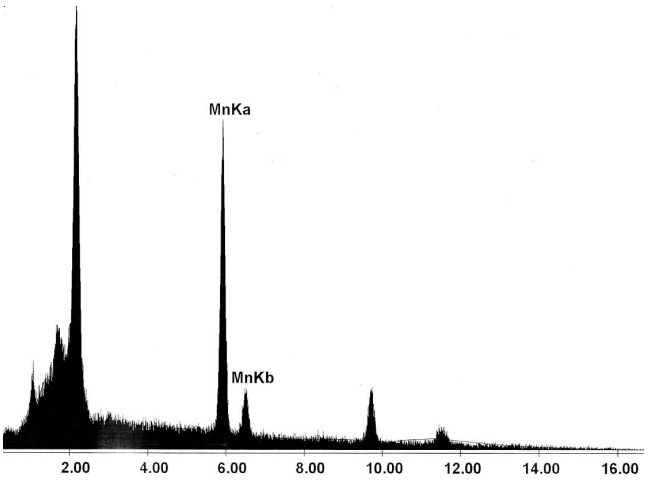
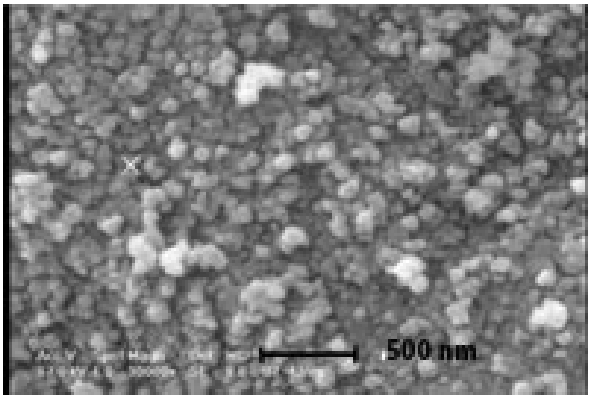


(c)

Fig. 2. (a) SEM image of the MnO_2; (b) SEM image of the Mn_2O_3 and EDAX spectra of the MnO_2



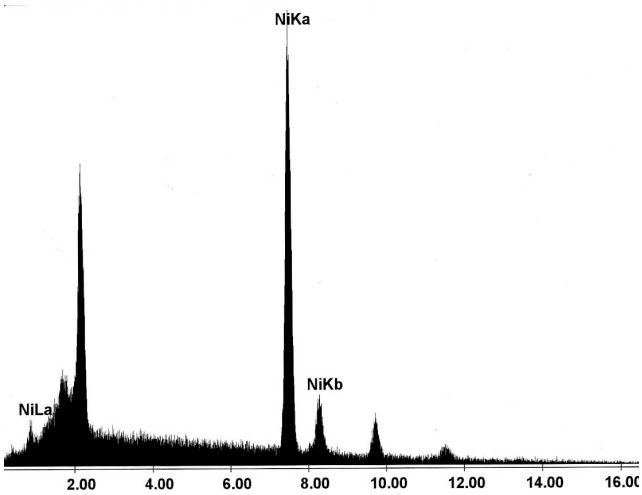
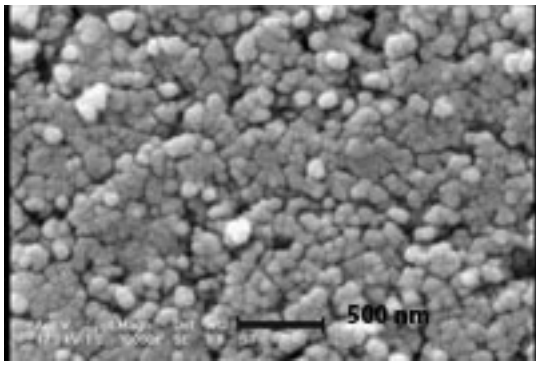


Fig 3. SEM image of the NiO and its EDAX spectra



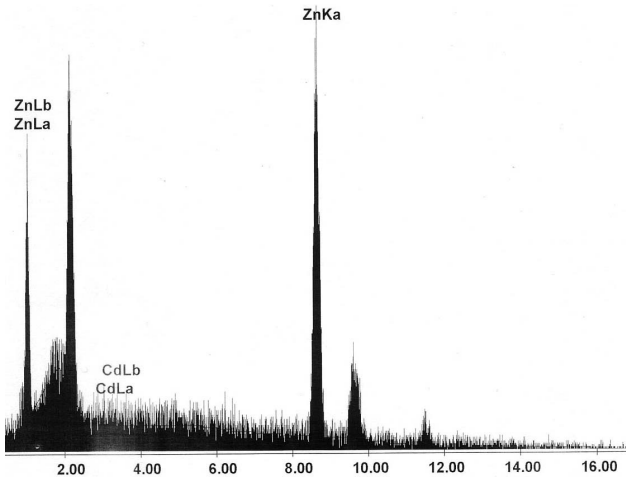


Fig. 4. SEM image of the Cd doped ZnO and its EDAX spectra

oxide colloid[16]. From the view of kinetics of colloid growth, if the colloid adsorbs the polymer on some area of its surface, the growth rate of the colloid in some certain direction will be confined. In the present work, PEG400 can efficiently adsorb the surfaces of metal hydroxide colloids[17] therefore it is thought that the formation of metal hydroxides nanostructures is due to the adsorption of PEG400 leading the growth of the metal oxide crystal nanoparticles. In order to investigate the effect of length of PEG on the kinetics of growth of a metal oxide nanostructure, experiments have been done with PEG200 and PEG6000 under the same conditions. In both case no nanoparticles formed.

Conclusion

This study demonstrated a new method for synthesis of nano metal oxide by short chain polymer PEG400. PEG400 plays a vital role in the growth of nano crystals. Therefore first addition of PEG400 to the solution of NaOH then to the aqua solution of manganese acetate or nickel choloride or blend of zinc acetate and cadmium acetate will modify the growth kinetics of the growing cells, which finally lead to the anisotropic grows of the crystals and forms nanostructures. This method needs no complicated procedure. The reaction times and dosage of PEG are important factors in determining the size of nano metal oxides.

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