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Preparation of Spherical Shaped Nanocrystalline Composites Based on $Ni(OH)_2$ and Mn_3O_4

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Abstract

Spherical shaped nanocrystalline composites based on $Ni(OH)_2$ and Mn3O4, $(Mn_3O_4)x(Ni(OH)_2)_{1-x}$ (with x having the values 0.0, 0.25, 0.50, 0.75 and 1.0), have been prepared by a simple solvothermal method using a domestic microwave oven and characterized. The chemical composition, morphology, crystallite sizes and phase purity were determined by X-ray powder diffraction, scanning electron microscopic, transmission electron microscopic and thermal analyses. Results obtained in the present study indicate that the composites formed are with good crystallinity, homogeneity, reduced crystallite size and high phase purity. The present study encourages the direct formation of coupled semiconductor systems by a relatively simple and low-cost synthetic procedure described.

Keywords: Composites, Nanoparticles, X-ray diffraction, Electron microscopy, Thermal analysis.

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I.INTRODUCTION

Mn_3O4 and $Ni(OH)_2$ nanocrystals with different crystallite shapes exhibit different characteristics. Therefore controlled synthesis and application of Mn_3O_4 and $Ni(OH)_2$ nanoparticles have been extensively studied over the past several years. [1,2] Use of multiple components (hybrid nanomaterials) offers a higher degree of flexibility for altering and controlling properties and functionalities of nanomaterials. For many emerging technologies, hybrid nanomaterials with improved optical, electronic and magnetic properties are needed. For example, $CdCO_3$-InO_3 nanocomposite is used as a sensor material. [3]

A preliminary experiment made by us indicates that Mn_3O_4 and α-$Ni(OH)_2$ nanocrystals can be prepared (instead of the other phases of manganese and nickel oxides including MnO and NiO) from manganese acetate and urea, nickel acetate and urea respectively in the ambient conditions with ethylene glycol as the solvent. This, in addition to the importance of these manganese and nickel oxide nanocrystals, prompted us to consider these nanocyrstals for our present study. In view of formidable challenges that lie in the synthesis of two-component nanocomposites, we attempted to prepare Mn_3O_4-$Ni(OH)_2$ nanocrystalline powders with different combinations of Mn_3O_4 and $Ni(OH)_2$ by using Solvothermal method using a domestic microwave oven. [4,5] A total of five samples were prepared and characterized chemically and structurally by using suitable standard methods. The results obtained are reported herein and discussed.

2. Experimental Procedure

Analytical Reagent (AR) grade chemicals were used without further purification. Manganese acetate tetrahydrate and nickel acetate tetrahydrate taken together in the required composition and urea in 1: 3 molecular ratio were mixed and dissolved in ethylene glycol and kept in a domestic microwave oven (operated with a frequency of 2.45 GHz and power 800 W) and heated till the solvent got evaporated. The colloidal precipitate obtained was cooled to room temperature naturally and washed several times first with double distilled water and then with acetone to remove the excessive reactants and byproducts or organic impurities present, if any. Finally, the products were filtered and dried in atmospheric air and collected as the yield.

X-ray powder diffraction (XRD) data were obtained using an automated diffractometer (X`PERT PRO PANanalytical) with CuKα radiation (λ=1.54056 Å). The average grain (crystallite) size, D, was estimated from the peak width using the Scherrer`s formula: [6]

$$D = K\lambda / (\beta\cos\theta),$$

where λ is the X-ray wavelength, β is the full width at half maximum of a diffraction peak, θ is the Bragg angle, and K is the Scherrer's constant (0.96). Scanning electron microscopic (SEM) images were recorded using a Hitachi scanning electron microscope (model S-3400). Transmission electron microscopic (TEM) images were recorded for three samples $(Ni(OH)_2$, Mn_3O_4 and $(Mn_3O_4)_{0.5}(Ni(OH)_2)_{0.5})$ using a Philips-TEM instrument. Thermal (TGA, DTA and DSC) analyses were carried out for three samples $(Ni(OH)_2$, Mn_3O_4 and $(Mn_3O_4)_{0.5}(Ni(OH)_2)_{0.5})$ using the TA instruments (Q600 SDT).

3. Results and Discussion

The prepared nanocrystals can be represented as $(Mn_3O_4)x(Ni(OH)_2)1\text{-}x$ with x having the values 0.0$(Ni(OH)_2)$,

0.25, 0.50, 0.75 and 1.0 (Mn_3O_4). Figure 1 shows the photograph of samples prepared (A) and the XRD patterns recorded (B) in the present study. All the prominent diffraction peaks of Mn_3O_4 could be indexed to the tetragonal structure of Mn_3O_4 with lattice parameters a = b = 5.76 Å and c = 9.46 Å which agree with that reported (JCPDS File No. 897111) for Mn_3O_4 crystal. Similarly, all the diffraction peaks of $Ni(OH)_2$ could be readily indexed to the hexagonal structure of $Ni(OH)_2$ with lattice parameters a = b = 4.66 Å and c = 7.25 Å which agree with that reported (JCPDS File No. 894837) for $Ni(OH)_2$ crystal. The strong and sharp diffraction peaks suggest that as-synthesized products are well-crystalline.

It can be seen from Figure 1(B) that the diffraction peaks gradually shift to lower angles from tetragonal Mn_3O_4 to hexagonal α-$Ni(OH)_2$ with the increase of Ni content. Also, the number of peaks gets reduced. The continuous peak-shift may rule out the phase separation or separated nucleation of Mn_3O_4 and $Ni(OH)_2$ nanocrystals, and the $(Mn_3O_4)_x(Ni(OH)_2)_{1-x}$ (x = 0.0, 0.25, 0.50, 0.75 and 1.0; end members are obtained in the form of Mn_3O_4 and $Ni(OH)_2$ nanocrystals instead of MnO and NiO nanocrystals) nanocomposites are probably a kind of alloyed structure. The average crystallite sizes observed for $(Mn_3O_4)x(Ni(OH)_2)_{1-x}$ (x = 0.0, 0.25, 0.50, 0.75 and 1.0) are respectively 1.7, 4.0, 8.9, 15.2 and 14.5 nm. The size nearly decreases when the Ni content is increased. Also, in some patterns, weak peaks not related to the material considered also appear which indicates the presence of trace amount of $MnCO_3$ in the corresponding samples. In the case of Mn3O4, the peaks (not indexed) corresponding to 2θ values 24.16, 41.43 and 49.79 are due to that. Similarly, in the case of $(Mn_3O_4)_{0.75}(Ni(OH)_2)_{0.25}$, the peaks corresponding to 2θ values 24.24, 41.37 and 49.71 are due to that. The pattern observed in the present study for Mn_3O_4 nanocrystal is similar to that reported by Regmi et al.[7] for Mn_3O_4 nanocrystal prepared by the co-precipitation method. A comparison of these two patterns may indicate that the sample prepared in the present study is with more phase purity.

The SEM and TEM images observed are shown in Figure 2. The SEM and TEM images indicate that the nanocrystals prepared are agglomerative and spherical in shape. Also, the morphology is found to be nearly homogeneous. Changes in images observed for the nanocomposites with those of end members indicate that they are mixed ones.

Selected particle sizes are 14.53, 7.79 and 13.80 nm (marked in the TEM images, Figure 2(B)) respectively for the Mn_3O_4, $Ni(OH)_2$ and $(Mn_3O4)_{0.5}(Ni(OH)_2)_{0.5}$ nanocrystals. The spherical shaped morphology observed may allow us to consider as valid the average particle sizes estimated from XRD data by using the Scherrer's formula.

Figure 3 shows the simultaneous thermogravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetric (DSC) curves for $Ni(OH)_2$, Mn_3O_4 and $(Mn_3O_4)_{0.5}(Ni(OH)_2)_{0.5}$ nanocrystals. Figures 3(a) and 3(b) show two and one major weight losses respectively in the TGA curves and corresponding endothermic peaks in the DTA and DSC curves for the $Ni(OH)_2$ and Mn_3O_4 nanocrystals. Figure 3(c) shows a continuous weight loss in the TGA curve and corresponding endothermic peak in the DTA and DSC curves for the $(Mn_3O_4)_{0.5}(Ni(OH)_2)_{0.5}$ nanocrystal. TGA, DTA and DSC curves observed for the $(Mn_3O_4)_{0.5}(Ni(OH)_2)_{0.5}$ nanocrystal indicate that the nanocomposite formed is constituted by both $Ni(OH)_2$ and Mn_3O_4.

The first major weight loss (about 9 % below 100 °C) observed for $Ni(OH)_2$ (see Figure 3(a)) can be attributed to the liberation of adsorbed water molecules. The second major weight loss (about 20 % at ~ 273 °C) observed can be attributed to the decomposition of Ni(OH)2 to NiO as per the reaction equation,

$$Ni(OH)_2 \rightarrow NiO + H_2O.$$

This indicates that the as-prepared sample is a pure nanophase of $Ni(OH)_2$. This also indicates that it may be possible for us to prepare the pure nanophase of NiO by the same simple method adopted in the present study for the preparation of $Ni(OH)_2$ nanocrystal but with an addition of annealing for a required time at about 300 °C .

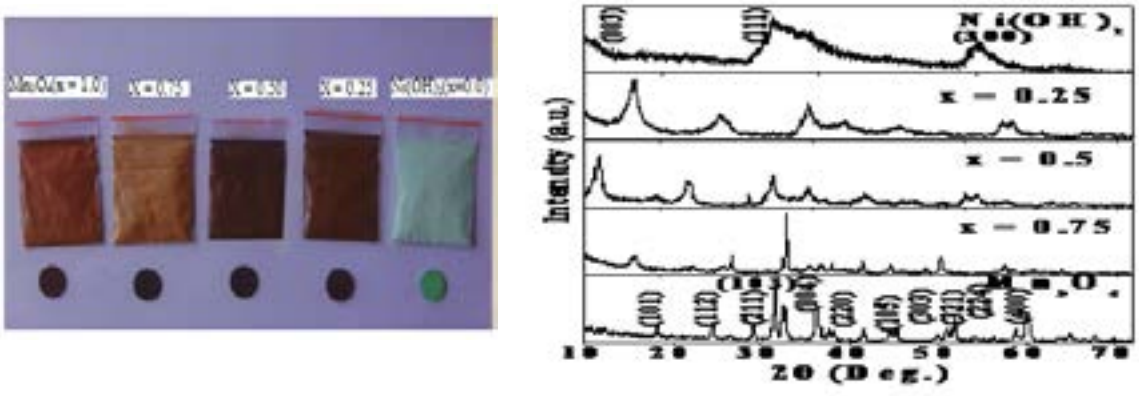
The weight loss of about 17.03 % at ~367 °C observed for the Mn^3O^4 (see Figure 3(b)) can be attributed to the decomposition of $MnCO^3$ to Mn^3O^4 by absorbing oxygen from the atmosphere and with the liberation of carbon dioxide as per the reaction equation,

$$6MnCO_3 + O_2 \rightarrow 2Mn_3O_4 + 6CO_2 .$$

This result is consistent with the presence of small amount of $MnCO_3$ observed through the XRD analysis. The endothermic peaks observed in the DTA and DSC analyses endorse the above result. This indicates that the nanophase of Mn_3O_4 with very high purity and homogeneity may be obtained by annealing the as-prepared sample at about 400 °C for a required time. A small loss of weight and less intense endothermic peak observed at about 40 °C in the TGA and DSC curves respectively indicate the liberation of adsorbed water molecules. [8]

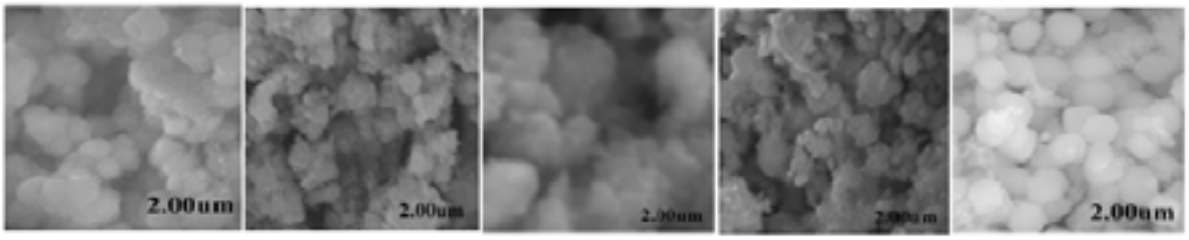
5. Conclusions

Spherical shaped nanocrystalline composites based on $Ni(OH)_2$ and Mn_3O_4 have been prepared by a simple solvothermal method using a domestic microwave oven and characterized by the suitable standard methods. Results obtained through XRD, SEM, TEM and TGA/DTA/DSC analyses indicate that the $(Mn_3O_4)_x(Ni(OH)_2)_{1-x}$ nanocrystals prepared are with good crystallinity, homogeneity, reasonably reduced grain size and high phase purity. In effect, the present study indicates that forming two-component nanocomposites may be considered as a formation of coupled semiconductor systems by a relatively simple and low-cost synthetic procedure.



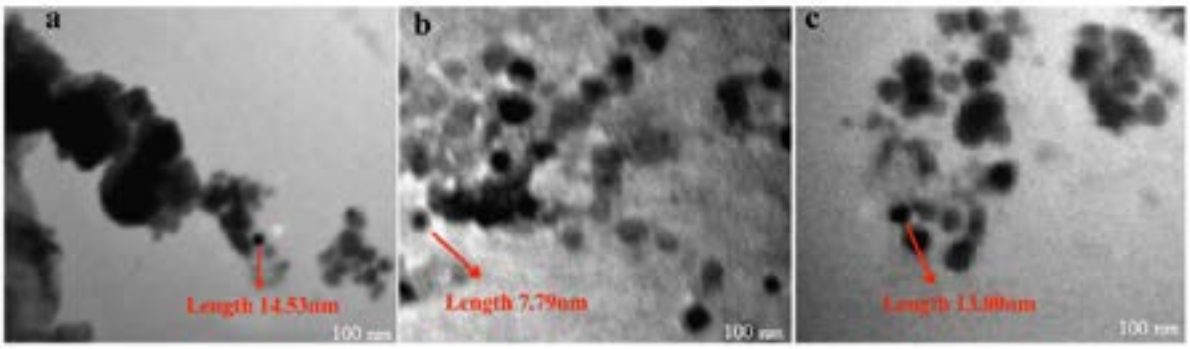
(A) (B)

Figure 1. (A)Photograph of the samples prepared; (B) The XRD patterns observed.



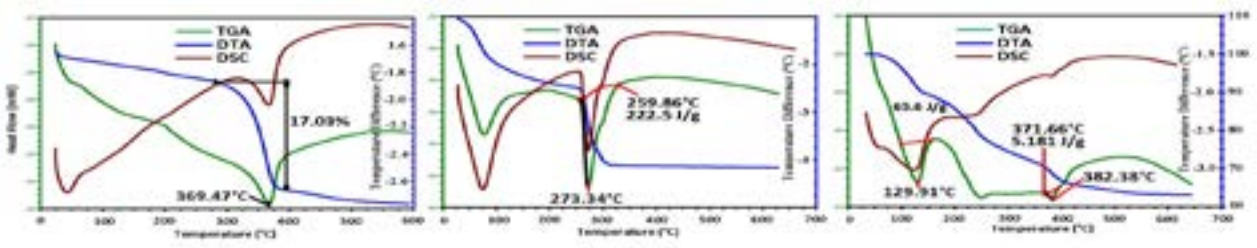
(a) For $Ni(OH)_2$ (b) For x = 0.25 (c) For x = 0.5 (d) For x = 0.75 (e) For Mn_3O_4

(A)



(B)

Figure 2. (A)The SEM images observed for $(Mn_3O_4)_x(Ni(OH)_2)_{1-x}$ nanocrystals; (B) The TEM images observed for (a) Mn_3O_4, (b) $Ni(OH)_2$ and (c) $(Mn_3O_4)_{0.5}(Ni(OH)_2)_{0.5}$ nanocrystals.



(a) For $Ni(OH)_2$ (b) For Mn_3O_4 (c) For $(Mn_3O_4)_{0.5}(Ni(OH)_2)_{0.5}$

Figure 3. The TGA, DTA and DSC curves observed for: (a) $Ni(OH)_2$, (b) Mn_3O_4 and (c) $(Mn_3O_4)_{0.5}(Ni(OH)_2)_{0.5}$ nanocrystals.

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