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Sonochemical Synthesis and Characterization of $NiMoO_4$ Nanorods

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$NiMoO_4$ nanorods have been successfully synthesized by sonochemical method process by using $Ni(CH_3COO)_2.4H_2O$ and $(NH_4)_6Mo_7O_{24}.4H_2O$ as starting materials. Some parameters including ultrasonic power, stirring effect and effect of high pressure and temperature were investigated to reach optimum condition. The as synthesized nanostructures were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), photoluminescence (PL) spectroscopy and energy dispersive X-ray microanalysis (EDX). Facile preparation and separation are important features of this route. This work has provided a general, simple, and effective method to control the composition and morphology of $NiMoO_4$ in aqueous solution, which will be important for inorganic synthesis methodology.

Keywords: Nanorods; $NiMoO_4$; Ultrasonic; Electron microscopy

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1. INTRODUCTION

Metal molybdate is one of the most important family of inorganic materials which has attracted increasing attention due to their interesting application in various field such as industrial catalysts for partial oxidation of hydrocarbons and precursors in the synthesis of hydrodesulfurization (HDS) catalyst [1], humidity sensors [2], scintillator materials [3], magnetic and electrochemical (Li storage) properties [4]. Among the molybdate materials, the polymorphic $NiMoO_4$ is the best choice specifically for alkane dehydrogenation [5]. The numerous investigations on the synthesis routs of nickel molybdate have been carried out, including hydrothermal rout [6], citrate complex route [7], solid state synthesis at high temperature [8] and sol-gel method [9]. However these approaches usually require high pressure or heat-treating at temperatures higher than 180 °C for several hours. These problems can be avoided by applying sonochemical method.

In recent years, sonochemical methods have been extensively explored to synthesize various nanostructures, including rods, wires, tubes, particle, and porous spheres [10-12]. During sonication, ultrasonic sounds waves radiate which lead to short required time and low temperature to carry out chemical reaction [11]. The sound wave radiations are effective on the morphology and size of the samples, as well. There has not been any report for precipitation of $NiMoO_4$ using only ultrasonic process, so far. In this work, the low temperature synthesis of nanostructures of $NiMoO_4$ with the different geometrical configuration was reported via ultrasound waves applying the temperature of below 93 °C in less than 35 minutes. The effect of different synthetic conditions on the morphologies and size of the final products were investigated.

2. SYNTHESIS AND CHARACTERIZATION

2.1 Method of Sample Manufacturing and Analysis

$NiMoO_4.nH_2O$ was synthesized via sonochemical method. Appropriate amounts of $Ni(CH_3COO)_2.4H_2O$ and $(NH_4)_6Mo_7O_{24}.4H_2O$ were used as the Ni and Mo sources. In a typical synthesis .058 g $(NH_4)_6Mo_7O_{24}.4H_2O$ and .1g of $Ni(CH_3COO)_2.4H_2O$ was dissolved in 30 ml distilled water separately. Then $Ni(CH_3COO)_2.4H_2O$ was heated at 70 °C for 15 min and finally the $(NH_4)_6Mo_7O_{24}.4H_2O$ solution was added drop wise to this solution and final solution was heated at 70 °C for 30 min under stirring. During these processes no sample was observed. Then solution temperature was increased to 90 °C and finally treated with ultrasonic irradiation with different power. The yellow green product was filtered, washed with distilled water and ethanol several times and dried in vacuum in less than 60 °C. The as synthesized $NiMoO_4$ nanostructures were characterized by SEM, PL, EDS, and XRD analyses.

3. RESULTS AND DISCUSSION

The XRD patterns of samples No 1, No 3, have depicted in Fig. 1. As can be seen, the XRD pattern of as prepared $NiMoO_4$ are very similar except that a slight difference is observed for the peaks between 30 and 35. The pattern agree well with the reported pattern for nickel molybdate (JCPDS No 13–0128).

In the EDX spectrum of $NiMoO_4$ obtained from sample No 3 (Fig. 2), Ni (56.08 %) and Mo (43.92 %) elements are detected.

The nature of the optical transitions of molybdates is still unclear, but by analogy with the tungstate crystals, the bands could be interpreted luminescence spectrometer with an excitation slit as the radiative recombination of the electron-hole pairs localized at the $[MoO_4]^{2-}$ group [13] on the basis of previous reflectivity measurements [14] and the current knowledge of their electronic structure [15]. Fig. 3 shows a typical photoluminescence (PL) spectrum (λ_{exc} = 457 nm) of $NiMoO_4$ nanostructures (sample No 3) that was measured using a Perkin-Elmer LS-55 width of 5 nm and an emission slit width of 5 nm. A sharp peak at

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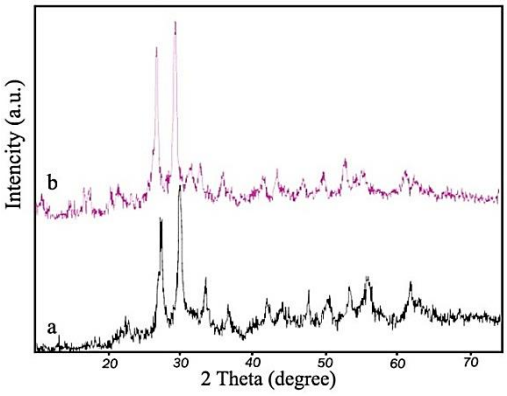

Fig. 1 – XRD pattern of as prepared samples at: (a) without ultrasound (sample No1), (b) power of ultrasound 75 W (sample No 3)

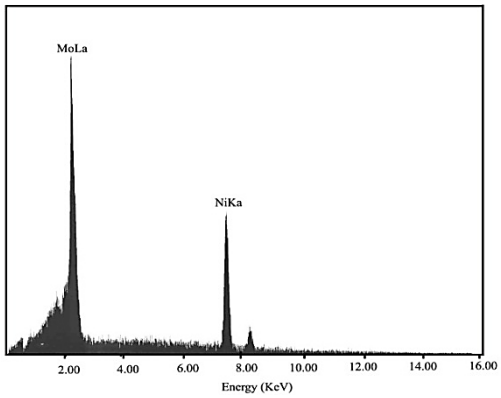

Fig. 2 – EDX pattern of the as-prepared samples (sample No 2)

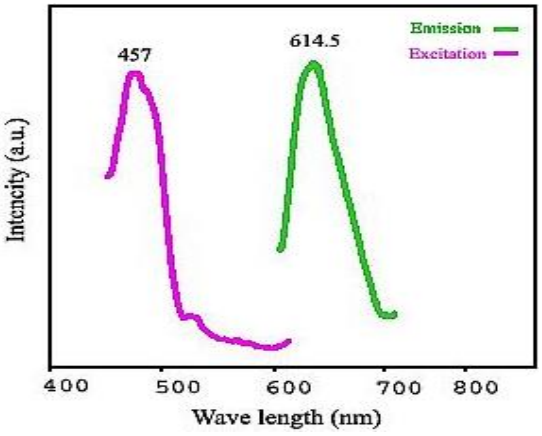

Fig. 3 – The room-temperature photoluminescence spectrum of the nanostructure $NiMoO_4$. (sample No 3)

614.5 nm was observed and band gap of sample was calculated about 2.018 eV that showed 1.9 eV blue shift (band gap of bulk types of $NiMoO_4$ = .2 eV) [16] which suggest that the nanoparticles behave within the quantum confined regime.

Fig. 4a shows SEM images of samples which obtained with no ultrasonic irradiation. These samples were obtained by heating the reaction component at 90 °C for 30 min under stirring (sample No 1). It is clear that these products have irregular morphology and long size distribution. By applying ultrasonic irradiation with different power under stirring at 90 °C for 30 min, it is obvious that the morphology is changed and $NiMoO_4$ nanorods are obtained. Ultrasonic irradiation creates bubbles which produces high temperature and energy after decomposition. This process provides appropriates amounts of energy for formation of $NiMoO_4$ nanorods. Careful observations to the images

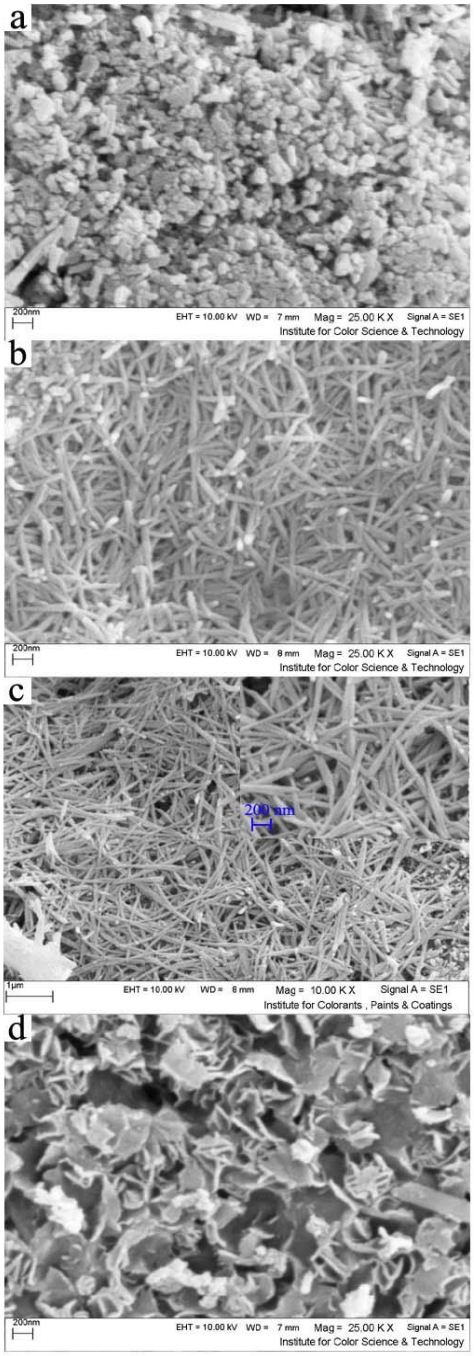

Fig. 4 – SEM images of: (a) sample No 1, (b) sample No 2, (c) sample No 3, (d) sample No 4.

suggest that by varying ultrasonic power from 45 W (Fig. 4b) to75 W (Fig. 4c) the morphology and homogeneity of samples is changed. When the power was set at 45 W (sample No 2) nanorods were agglomerated and fused to each other. By increasing the power to 75 W (sample No 3) the aggregated nanorods were se-parated

well and nanorods length increased which may be due to an increase in diffusion rate of bubbles innucleation region and affecting reactants concentration [17].

These results indicate that sonication is favorable to produce $NiMoO_4$ nanorods with uniform shape. By using ultrasound irradiation, the formed bubbles collapse asymmetrically, resulting in the generation of high speed microjets with very high velocity [18]. Due to the very high velocity of microjets, the chance of collision between the primary nanoparticles increases [19]. These processes are schematically presented in scheme 1.

Scheme 1 – Increasing of nanorods length by increasing ultrasonic power (from left to right without ultrasound, 45 W, and 75 W).

As mentioned above reaction was done under stirring. To investigate stirring effect on samples morphology these reactions was performed at the same condition as discussed above but without stirring (sample No 4). As can be seen in Fig 4d, new shapes of samples obtained which differs from those obtained under stirring. These shapes are like sheets which their arrangement represents flower-like structures. Also, there are some nanorods with the length of about 1-2 μm with these results it can be concluded that ultrasonic irradiation under stirring is necessary for the formation of $NiMoO_4$ nanorods. It is believed that stirring affects bubbles distribution in reaction medium and local concentration of reactants which finally leads to formation of nanorods.

After obtaining optimum conditions for the synthesis of $NiMoO_4$ nanorods, to investigate the effect of high pressure and temperature on morphology of the products, the nanorods were transferred to a stainless steel autoclave and heated at 90 °C for 10 h (Fig. 5). These are observed that initial nanorods show a morphology transition from rode to sheet under hydrothermal condition and form tangled nanosheets. Which deserve further works for obtaining more interesting morphologies useful for special applications.

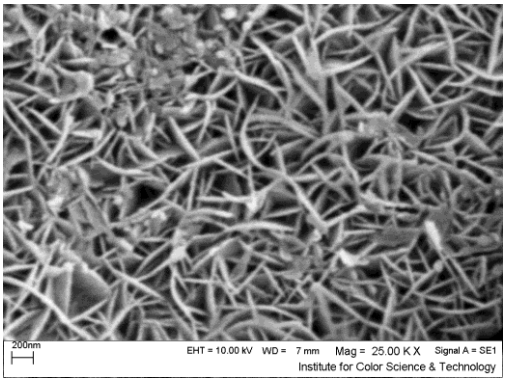

Fig. 5 – SEM images of samples obtained under hydrothermal condition: 90 °C for 10 h

4. CONCLUSIONS

Among various methods reported for synthesis of $NiMoO_4$ which lead to formation of nanorods and nanopraticles of $NiMoO_4$, we have performed some series of expriment and different morphology of $NiMoO_4$ were obtained. The current method is facile and employes non toxic materials.The results described here suggested that $NiMoO_4$ nanostructures can be obtained by the reaction between $Ni(CH_3COO)_2.4H_2O$ and $(NH_4)_6Mo_7O_{24}.4H_2O$ under low temperature and ultrasound irradiation. Ultrasonic was used for the first time in the synthesis of $NiMoO_4$ nanostructures and the significantly lower reaction time was required in comparison with other conventional method. The advantage of using ultrasound radiation in low temperature is that it the high yield of reaction.

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