Facile Synthesis and Characterization of Mn_3O_4, Co_3O_4, and NiO

A.D. Khalaji[a,*], M. Soleymanifard[a], M. Jarosova[b] and P. Machek[b]

[a]Department of Chemistry, Faculty of Science, Golestan University, Gorgan, Islamic Republic of Iran

[b]Institute of Physic of the Czech Academy of Sciences, Na Slovance 2, 182 21 Prague, Czech Republic

(Received July 26, 2019; revised version October 30, 2019; in final form November 12, 2019)

Nanoparticles of three transition metal oxides (Mn_3O_4, Co_3O_4, and NiO) were prepared by facile and green method using calcination of mixture of 1 g MCl_2 (M = Mn, Co or Ni) and 1 g polyvinyl alcohol (PVA) in weight ratio 1:1 at 600 °C for 3 h. The resulting products were characterized by the Fourier transform infrared spectroscopy, X-ray diffraction, and transmission electron microscopy. Sharp peaks unambiguously explain all X-ray diffraction patterns which confirms that the transition metal oxide nanoparticles are pure with high degree of crystallinity. However, diffraction peaks in Mn_3O_4 and Co_3O_4 patterns are narrower than those in NiO which indicates that the particle size of these oxides is larger than that one of nickel oxide. This result was confirmed by transmission electron microscopy. The average crystallite size determined for Mn_3O_4 sample is 101 nm, for Co_3O_4 sample it is 76 nm and for NiO sample it is 49 nm.

DOI: 10.12693/APhysPolA.137.1043

PACS/topics: nanoparticles, transition metal oxides, calcination, Mn_3O_4, Co_3O_4, NiO

1. Introduction

In recent years, research on TMO nanoparticles has been often carried out in order to prepare nanoparticles with various morphology, sizes, properties and for various applications [1–5]. To the list of most important and widely used TMO nanoparticles belong nanoparticles of manganese oxide (Mn_3O_4) [6, 7], cobalt oxide (Co_3O_4) [8, 9], and nickel oxide (NiO) [10, 11]. They can be synthesized using various techniques [1–14]. However, advanced equipment which is used for most of these techniques is often very expensive and not eco-friendly.

Synthesis of transition metal oxides (TMO) nanoparticles [3, 5, 12–14] was a part of our ongoing investigation. Here, we report the synthesis and characterization of manganese oxide (Mn_3O_4), cobalt oxide (Co_3O_4), and nickel oxide (NiO) nanoparticles (Fig. 1). The proposed method is simple, cheap, and eco-friendly.

2. Experimental

All input materials ($MnCl_2{\cdot}H_2O$, $CoCl_2{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$, and polyvinyl alcohol) are commercially available from Merck Co. and they were used as received without further purifications.

2.1. Synthesis of Mn_3O_4 nanoparticles

Typically, 1 g of $MnCl_2{\cdot}H_2O$ was dissolved in 5 ml of H_2O. Then 1 g of PVA was added to the prepared solution under vigorous stirring. The mixture was stirred for 0.5 h, then transferred into a crucible and maintained at 80 °C for 3 h to dry it completely. After that, it was annealed at 600 °C in air atmosphere for 3 h. The black product was several times rinsed with deionized water and ethanol and finally it was dried overnight at 65 °C in oven.

2.2. Synthesis of Co_3O_4 nanoparticles

Cobalt oxide (Co_3O_4) nanoparticles were prepared by similar method as manganese oxide (Mn_3O_4) nanoparticles. The difference is that $CoCl_2{\cdot}6H_2O$ was used instead of $MnCl_2{\cdot}H_2O$.

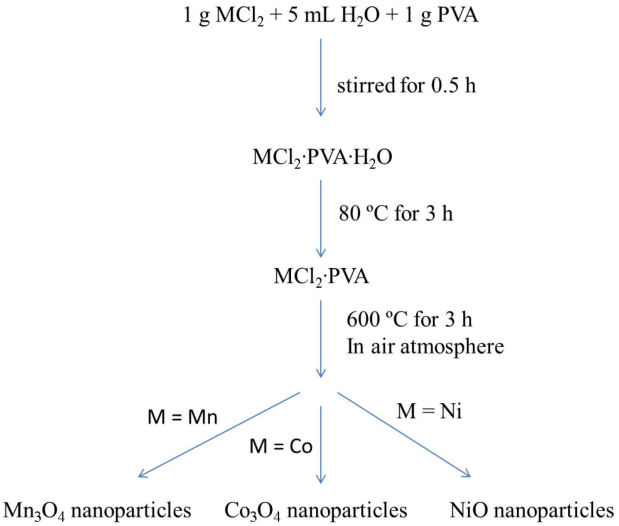

Fig. 1. Preparation procedure of manganese oxide (Mn_3O_4), cobalt oxide (Co_3O_4), and nickel oxide (NiO) nanoparticles.

*corresponding author; e-mail: alidkhalaji@yahoo.com

2.3. Synthesis of NiO nanoparticles

Nickel oxide (NiO) nanoparticles were prepared again by similar routine as manganese oxide (Mn_3O_4) nanoparticles. $NiCl_2 \cdot 6H_2O$ was used instead of $MnCl_2 \cdot H_2O$ in this case.

2.4. Characterization

The Fourier transform infrared (FTIR) spectra were recorded as a KBr disk on an FTIR Perkin–Elmer spectrophotometer. X-ray diffraction (XRD) pattern of the complex was obtained on Empyrean powder diffractometer of PANalytical in the Bragg–Brentano configuration equipped with a flat sample holder and PIXCel3D detector (Cu K_α radiation, $\lambda = 1.5418$ Å). Transmission electron microscopy (TEM) images of nanoparticles were recorded on transmission electron microscope Philips CM120 with a LaB_6 cathode operating at 120 kV and equipped with CCD camera Olympus Veleta.

3. Results and discussion

3.1. FTIR spectra

By the Fourier transform infrared spectroscopy (FTIR) M–O vibration in the metal oxide were analyzed. In the FTIR spectrum of nanoparticles, there are some weak vibrations at about 1600–1630 cm^{-1} and also at 3250–3350 cm^{-1}. The vibrations are assigned to H–O bond that confirms adsorption of water on the surface of nanoparticles [30–35]. Also, there are two sharp peaks at 430 cm^{-1} and 592 cm^{-1} for Mn_3O_4, at 532 cm^{-1} and 628 cm^{-1} for Co_3O_4, and at 421 cm^{-1} for NiO. These peaks confirm occurrence of Mn_3O_4, Co_3O_4, and NiO, respectively [12–14].

3.2. XRD patterns

We used XRD technique for structure and phase analysis of all compounds. Figure 2 shows the XRD patterns of Mn_3O_4, Co_3O_4, and NiO nanoparticles. The clear and sharp diffraction peaks confirmed that the as-prepared compounds are pure with high degree of crystallinity and they were assigned to the standard patterns of Mn_3O_4 (JCPDS file no. 04-005-9818), Co_3O_4 (JCPDS file no. 04-002-0644), and NiO (JCPDS file no. 04-011-8441), respectively. The structure was further refined by the Rietveld fit in crystallographic program Jana2006 [15]. The sizes of crystallites were calculated from XRD patterns (Fig. 2) using fundamental parameter approach [16], integrated in Jana2006 [15], which removes the instrumental part of the diffraction pattern by means of known geometry of the diffractometer. The average crystallite size determined for Mn_3O_4 sample is 101 nm, for Co_3O_4 sample it is 76 nm, and for NiO sample it is 49 nm.

We calculated average crystallite sizes from XRD patterns (Fig. 2) using fundamental parameter approach by Cheary and Coelho [16], which is integrated in crystallographic fitting program Jana2006.

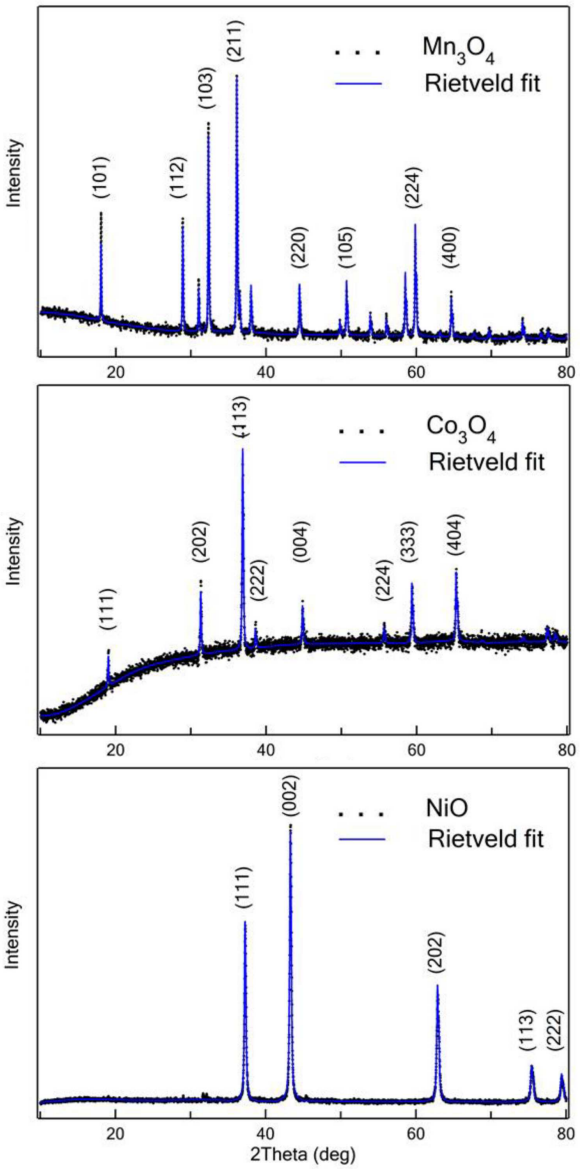

Fig. 2. The XRD patterns of (a) Mn_3O_4, (b) Co_3O_4, and (c) NiO.

3.3. TEM images

TEM images of the synthesized Mn_3O_4, Co_3O_4, and NiO nanoparticles are shown in Fig. 3. The crucial role of used type of metal salt in morphology and size of prepared nanoparticles is approached. A huge clusters of Mn_3O_4 and Co_3O_4 nanoparticles were observed. On the other hand, single particles or clusters of only few particles can be found in NiO sample. The sizes of particles are also different. NiO sample contains predominantly particles with size about tens of nm. Sizes of Mn_3O_4 and Co_3O_4 particles are very difficult to determine from TEM figures due to cluster-formation. However, it is evident that these oxides contain larger particles than NiO and some of them exceed nanoparticle size.

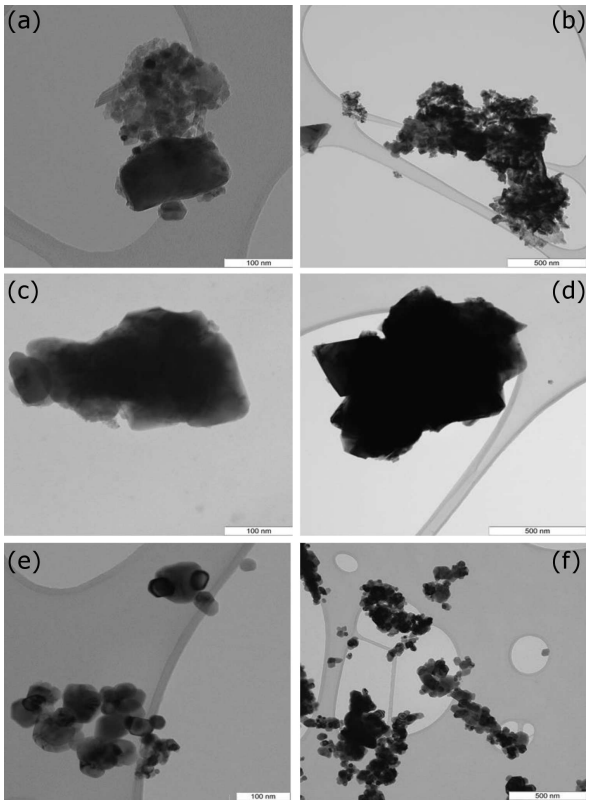

Fig. 3. The TEM images of (a, b) Mn_3O_4, (c, d) Co_3O_4, and (e, f) NiO at different scales.

4. Conclusions

Nanoparticles of transition metal oxides Mn_3O_4, Co_3O_4, and NiO were prepared by cheap, simple, and eco-friendly method and the basic characteristics were performed. According to the XRD and TEM results, the crystallite size of NiO is finer than sizes of Mn_3O_4 and Co_3O_4 particles. This fact confirmed the fundamental role of metal ion precursor in the morphology and crystallite size of nanoparticles. It was shown in this paper that the use of facile and green method is suitable for synthesis of nanoparticles of TMO and that there is well-founded proposal to use this method for preparation other TMO nanoparticles such as CuO and Fe_2O_3.

Acknowledgments

We are grateful to the Golestan University for financial support of this work. XRD and TEM analysis were supported by the project 18-10504S of the Czech Science Foundation using instruments of the ASTRA lab established within the Operation program Prague Competitiveness and project CZ.2.16/3.1.00/2451.

References

[1] S. Tavakpli, M. Kharaziha, S. Ahmadi, *J. Nanostruct.* **9**, 163 (2019).

[2] Z. Rostami, M. Rouhanizadeh, N. Nami, D. Zareyee, *Nanochem. Res.* **3**, 142 (2018).

[3] E. Shahsavani, N. Feizi, A.D. Khalaji, *J. Ultrafine Grained Nanostruct. Mater.* **49**, 48 (2016).

[4] M.J. Mazaheri, M. Ahmadi, M. Sabet, *J. Nanostruct.* **7**, 194 (2017).

[5] A.D. Khalaji, *Chem. Method.* **3**, 635 (2019).

[6] D. Yan, H. Zhang, L. Chen, G. Zhu, Z. Wang, H. Xu, A. Yu, *RSC Adv.* **2**, 23649 (2014).

[7] S. Guo, M. Zhang, G. Zhang, L. Zheng, L. Kang, Z.H. Liu, *Powder Technol.* **228**, 371 (2012).

[8] A. Abbasi, M. Ahmadi Golsefidi, M. Mohammad Beigi, N. Sadri, *J. Nanostruct.* **8**, 89 (2018).

[9] Y. Huang, C. Chen, C. An, C. Xu, Y. Xu, Y. Wang, L. Jiao, H. Yuan, *Electrochim. Acta* **145**, 34 (2014).

[10] C. Wang, Y. Zhao, D. Su, C. Ding, L. Wang, D. Yan, J. Li, H. Jin, *Electrochim. Acta* **231**, 272 (2017).

[11] S.H. Choi, Y.C. Kang, *ACS Appl. Mater. Interfaces* **6**, 2312 (2014).

[12] A.D. Khalaji, S. Izadi, G. Grivani, *Iran. J. Sci. Technol. Trans. Sci.* **43**, 105 (2019).

[13] A.D. Khalaji, *J. Clust. Sci.* **24**, 189 (2013).

[14] A.D. Khalaji, *J. Clust. Sci.* **24**, 209 (2013).

[15] V. Petricek, M. Dusek, L. Palatinus, *Z. Kristallogr.* **229**, 345 (2014).

[16] R.W. Cheary, A.A. Coelho, *J. Appl. Crystallogr.* **31**, 862 (1998).