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Synthesis of Cr₂O₃ nanopowders by microwave-induced solid-state decomposition method: A simple and rapid synthetic route

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Abstract : Chromium (III) oxide (Cr_2O_3) nanopowders with 27 nm in size were synthesized through microwave-induced solid-state decomposition of nitrato (2,3:8,9-diphenanthrene-5,6:11,12-dibenzo-1,4,7,10 tetraazacyclododecane) chromium(III), $[CrL](NO_3)_3$ where $(L=C_{40}H_{28}N_4)$, as new precursor in the presence of CuO powder as strong microwave absorber within a very short reaction time of 10 min. The product was identified by X-ray diffraction (XRD), Fourier-transformed infrared spectroscopy (FT-IR), Field emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDX). The microstructures and morphology Cr_2O_3 powders was quasi-spherical shape. The XRD pat-

INTRODUCTION

Nowadays the chromium (III) oxide (Cr_2O_3) as an important functional oxide is the subject of scientific investigation due to unique properties such as thermo dynamical stability, resistance to chemical attack, high melting point temperature (2435 °C) and high hardness^[1,2]. These excellent properties make Cr_2O_3 suit-

tern of product showed only the peaks corresponding to chromic (III) oxide. The rhombohedral system and space group R-3c (No. 167) can be considered by using the X-ray powder diffraction data. Microwave-induced combustion method is an easy and, safe, low-cost, suitable for high purity production and energy efficient method has been reported for the preparation of Cr_2O_3 nanopowder. This method is an economical method for the preparation of Cr_2O_3 nanopowder with respect to energy, time and simplicity. **© Global Scientific Inc.**

Keywords : Nanopowder; Cr_2O_3 ; Solid-state; Decomposition; Microwave; XRD.

able for different applications in green pigments^[3], heterogeneous catalysts^[4,5], coating materials for thermal protection^[6], important refractory material^[1], wear resistance fields^[7] and so on. There have been many techniques to obtain Cr_2O_3 nanoparticles, including microwave plasma^[8], hydrothermal reduction^[9,10], laser-induced deposition^[11], decomposition of chromium (III) nitrate solution^[12], gas condensation^[13] sonochemical reaction^[14], mechanochemical processing^[15], and so

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Synthesis of 2,3:8,9-diphenanthrene-5,6:11,12dibenzo-1,4,7,10-tetraazacyclododecane ligand (L)

on[16-20]. In recent years, microwave-assisted combustion method attracted wide interests in diversified fields due to its inherent advantages, such as rapid and green methodology^[21], and has unique effects including rapid volumetric heating, high reaction rate, short reaction time, enhanced reaction selectivity, environmental friendliness, energy saving^[22], homogeneous thermal transmission^[23], and the ability to produce different morphologies with narrow size distribution particles with high purity^[24]. The reason that this method gained importance over the conventional heating methods is interaction microwaves with the reactants at the molecular level, where this electromagnetic energy is transferred and converted to heat by rapid kinetics through the motion of the molecules^[25]. It demonstrates that many functional of metal oxides with novel structures and properties have been synthesized by microwave assisted method such as preparation of cadmium oxide (CdO) nanospheres^[26], nickel oxide (NiO) nanoparticles^[27], zinc oxide (ZnO) nanoparticles^[28], cellulose/CuO nanocomposites^[29]. In this paper chromium (III) oxide (Cr₂O₃) nanopowders were synthesized through solid-state decomposition of nitrato (2,3:8,9-diphenanthrene-5,6:11,12-dibenzo-1,4,7,10-tetraazacyclododecane) chromium (III) [Cr L](NO₃)₃ where (L= $C_{40}H_{28}N_4$) precursor with the assistance of microwave heating. The product was identified by X-ray diffraction (XRD), Fourier-transformed infrared spectroscopy (FT-IR), Field emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDX). The advantage of our approach is that this method is simple, safe, low-cost, fast and energy efficient and suitable for high purity industrial production. Specifically, wide variety of metal ox- $(NO_3)_3$ ide particles could be prepared by this method no need any additional template agents like surfactants.

EXPERIMENTAL

Materials

Chromium (III) nitrate nonahydrate, hydrochloric acid, *o*-phenylenediamine, 9,10-phenathrenequinone alsomethanol and acetonitrile were used as solvents. All the reagents used were purchased from either Merck or Fluka Company as received, were used without further any purification.

The symmetrical Schiff base ligand (2,3:8,9diphenanthrene-5,6:11,12-dibenzo-1,4,7,10-tetraazacyclododecane) (L= $C_{40}H_{28}N_4$) was prepared according to previously published methods^[30]. After addition methanolic solution of o-phenylenediamine to methanolic solution of 9,10phenanthrenequinone at the presence of hydrochloric acid, the mixture was boiled under reflux for 5 h when a greenish compound was precipitated. The product was filtered off, washed with methanol, and dried in vacuo. The mentioned ligand was studied by the melting temperature (melting point: 182–7 °C) and the ¹H NMR spectrum that shows six types of signals integrating for four protons in the phenanthrene ring and two in the phenyl rings of condensed o-phenylenediamine. The chemical shifts (δ) and coupling constant (J) values are at 9.31 ppm (4H, d, J = 8.04 Hz), 8.83 ppm (4H, d, J = 7.32), 8.37 ppm (4H, m), 8.01 ppm (4H, m) and 7.91 (4H, t, J = 7.32) and 7.84 ppm (4H, t, J = 7.32) Hz) which can be assigned to the phenanthrene and phenyl ring protons. The IR spectrum of the free ligand shows bands at 1590 cm⁻¹ region, 1450–1400, 1100– 1090 and 760-720 cm⁻¹ regions respectively that assigned to C=N and aromatic rings vibrations. The absence of band characteristic of $v_{(C=0)}$, aromatic primary amine bands $v_{(N-H)}$ expected to appear in free 9,10-phenanthrenequinone and o-phenylenediamine, respectively, confirms the formation of the proposed macrocyclic framework.

Synthesis of chromium (III) complexe [CrL] (NO₃)₃

For the synthesis of nitrato (2,3:8,9-diphenanthrene-5,6:11,12-dibenzo-1,4,7,10-tetraazacyclododecane) chromium (III), [CrL] (NO₃)₃ to a solution of ligand (L) (0.01 mol; 0.560 g) in acetonitrile (25 ml) was added dropwise acetonitrile solution (25 ml) of Cr(NO₃)₂·9H₂O (0.01 mol). After 3 h at 50 °C giving colored product. The product was filtered off, washed with acetonitrile, and dried under vacuum at room temperature.

Synthesis of Cr₂O₃ nanopowders

For the synthesis of Cr₂O₃ nanopowders, the

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 $[CrL](NO_3)_2$ where $(L=C_{40}H_{28}N_4)$ precursor powder (1 g) was taken in a small porcelain crucible and was placed in the middle of another larger porcelain crucible filled with CuO powder as a secondary microwave absorber. This assembly was then exposed to microwaves in a domestic microwave-oven (LGintellowave, 900 W, 2.45 GHz) operated at the power level of 900W in air for 10 min. After the CuO powder reaches to the point of spontaneous combustion, it became fully red hot and followed with the evolution of gases by decomposition of precursor powder. At the same time, various gases such as CO₂, NO₂ and water vapor were produced and this gas evolution breakdown the pellet of precursor powder to a fine powder during irradiation time of 10 min. The schematic diagram for preparation of Cr₂O₃ nanopowders shows in Figure 1.

Characterization of the Cr₂O₃ nanopowder

The product was characterized by a Rigaku D-max C III, X-ray diffractometer (X'Pert-Pro system, Philips) using Ni-filtered Cu K α radiation (λ = 0.154056 nm). Diffraction angles (2 θ) were 10–80°. Infrared spectra were recorded on a Schimadzu system FT-IR 8400 spectrophotometer using KBr pellets. Field emission scanning electron microscope (FESEM) and energydispersive X-ray spectroscopy (EDX) images were taken on a Hitachi s4160/Japan and oxford instrument /England respectively.

RESULTS AND DISCUSSION

A schematic diagram of preparation of Cr_2O_3 nanopowders through microwave-induced solid-state decomposition of nitrato (2,3:8,9-diphenanthrene-5,6:11,12-dibenzo-1,4,7,10 tetraazacyclododecane) chromium (III), $[CrL](NO_3)_3$ where $(L=C_{40}H_{28}N_4)$, is presented in Figure 1. XRD pattern $(10^{\circ} < 2\theta < 80^{\circ})$ of the decomposition product of the [CrL](NO₃)₃ complex is shown in Figure 2. The XRD pattern of the decomposed sample reveals broad diffraction peaks with 20 values at 24.6054°, 33.7127°, 36.3090°, 41.6062°, 50.3247°, 54.9545°, 63.5892°, 65.2016°, 73.1116° and 76.9737° that are assigned to the crystal planes of (0 1 2), (104), (1 1 0), (113), (0 2 4), (1 1 6), (214), (3 0 0), (1 0 10) and (0 2 10) of crystalline Cr₂O₃, respectively, consistent with the literature values (JCPDS Card No. 84-0312). This result confirms that the formation of the Cr_2O_2 phase, also this spectrum confirms that no peak attributable to possible impurities that the final product is highly pure. All of the reflection peaks of this XRD pattern can be indexed well to rhombohedral phase of Cr_2O_2 (space group: R-3c (No. 167) with calculated cell parameters $a = 4.9507^{\circ}A$ and $c = 13.5656^{\circ}A$. The crystallite sizes of the as-synthesized Cr_2O_3 , D_{XRD} , were calculated from the major diffraction peaks of the base of (104), (110) using the Scherer formula D=0.9 λ



Figure 1 : Schematic diagram for preparation of Cr₂O₃ nanopowders

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/ $\beta \cos \theta$ where λ is the X-ray wavelength Cu K_a, used in XRD (1.5418AÏ), θ is the Bragg angle and β is the pure diffraction broadening of a peak at halfheight, that is broad due to the crystallite dimensions. The size of the crystallite was estimated from Debye– Scherer equation 27 nm.

The decomposition product was characterized by

Fourier-transform infrared spectroscopy (FT-IR). The FT-IR spectra its product is shown in Figure 3. FT-spectra of the sample were examined to confirm the nature of decomposition product. In the FT-IR spectrum of the product the large domain located between 500 and 700 cm⁻¹ are related to the vibration band of the metal–oxide links the vibration band at 551 cm⁻¹ characterizes the



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84-0312; Cr2 O3			1	

Figure 2 : The XRD pattern of Cr₂O₃ nanopowder.



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Figure 4 : The FESEM images of Cr₂O₃ nanopowders

Cr–O distortion vibration and the band at 618 cm^{-1} identifies the chromium oxide as the Cr₂O₃ phase^[31]. Also, the weak broad bands at 3000–3600 cm⁻¹ is corresponded to the stretching and bending vibrations of the water molecules absorbed by the sample or KBr.

In this spectrum strong intensity absorption band at 1590 cm⁻¹ assigned to C=N stretching mode of the ligand, vibrations 1450–1400, 1100–1090 and 760–720 cm⁻¹ regions of aromatic rings and the strong band in the region 460–440 cm⁻¹ be due to $v_{(Cr-N)}$ vibrations have been eliminated that confirm the formation of the proposed Cr₂O₃ phase^[30,32]. Figure 4 shows the FESEM images of the as synthesized Cr₂O₃ powders. This Figure gives an overall view of the product, re-

vealing the surface morphology of the Cr_2O_3 powders. The microstructures and morphology Cr_2O_3 powders was quasi-spherical shape. Lower magnification reveals that the product consists of loosely aggregated grains less than 50 nm in size (Figure 4a). Higher magnification confirms that the grains are composed of extremely fine particles and are essentially secondary agglomerates of primary particles (Figure 4b). One can observe that nano-sized particles started to become evident within the grains and agglomerates.

The Cr_2O_3 nanopowder was also tested by EDX analysis. The EDX analysis of the Cr_2O_3 nanopowder confirms that the sample contains only Cr and O elements (Figure 5). The experimental atomic percentages

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Figure 5 : EDX spectrum of the Cr₂O₃ nanopowders.

of Cr and O are found to be 37.58% and 64.35%, respectively. The atomic ratio of Cr/O is approximately 2:3, which further confirms pure Cr_2O_3 phase was synthesized in perfect agreement with the XRD data.

CONCLUSION

In this study pure Cr_2O_3 nanopowders with quasispherical shape and 27 nm in size have been successfully synthesized through the decomposition of the of nitrato (2,3:8,9-diphenanthrene-5,6:11,12-dibenzo-1,4,7,10 tetraazacyclododecane) chromium (II), [CrL](NO₃)₃ where (L=C₄₀H₂₈N₄), as new precursor under microwave heating in the presence of CuO as the secondary heater. Microwave-induced combustion is an easy and, safe, low-cost, suitable for high purity production and energy efficient method has been reported for the preparation of Cr_2O_3 nanopowder. Also reaction time is reduced to few minutes, in contrast to few hours in conventional methods. This method is an economical method for the preparation of Cr_2O_3 nanopowder with respect to energy, time and simplicity.

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REFERENCES

- P.Gibot, L.Vidal; J.Eur.Ceram.Soc., 30, 911-915 (2010).
- H.Ma, Y.Xu, Z.Rong, X.Cheng, S.Gao, X.Zhang, H.Zhao, L.Huo; Sens.Actuators, B, 174, 325-331 (2012).
- [3] T.Brock, M.Groteklaes, P.Mischke; 'European Coating Handbook', Vincentz Verla, Hanover, Germany, 133 (2000).
- [4] M.Yoshida, K.Takanabe, K.Maeda, A.Ishikawa, J.Kubota, Y.Sakata, Y.Ikezawa, K.Domen; J.Phys. Chem.B, 113, 10151-10157 (2009).
- [5] B.M.Abu-Zied; Appl.Catal.A: Gen., 198, 139-153 (2000).
- [6] P.Berdhal; Trans.Am.Soc.Mech.Eng.J.Heat Transfer, 117, 355-358 (1995).
- [7] H.Kitsunai, K.Hokkirigawa, N.Tsumaki, K.Kato; Wear, 151, 279-289 (1991).
- [8] D.Vollath, D.V.Szabo, J.O.Willis; Mater.Lett., 29, 271-279 (1996).
- [9] M.D.Lima, R.Bonadimann, M.J.de Andrade, J.C.Toniolo, C.P.Bergmann; J.Eur.Ceram.Soc., 26(7), 1213-1220 (2006).
- [10] Z.Gui, R.Fan, W.Mo, X.Chen, L.Yang, U.Hu; Mater. Res.Bull., 38, 169-176 (2003).
- [11] Z.C.Zhong, R.H.Cheng, Jocelyn. Bosley, P.A.Dowben, D.J.Sellmyer; Appl.Surf.Sci., 181, 169-200 (2001).
- [12] L.D.Zhang, C.M.Mo, W.L.Cai, GChen; Nanostruct. Mater., 9, 563-566 (1997).
- [13] U.Balachandran; Nanostruct.Mater., 5(5), 505-512 (1995).
- [14] N.Arul Dash, Y.Koltypin, A.Gedanken; Chem. Mater., 9, 3159-3163 (1997).

- [15] T.Tsuzuki, P.G.McCormick; Acta Mater., 48(11), 2795-2801 (2000).
- [16] M.A.Wolfowich, H.Rotter, M.V.Landau, E.Korin, A.I.Erenburg, D.Mogilyansky, D.E.Gartstein; J.Non-Cryst.Solids, 318, 95-111 (2003).
- [17] M.Ocana; J.Eur.Ceram. Soc., 21, 931-939 (2001).
- [18] L.Znaidi, C.Pommier; Eur.J.Solid State Inorg. Chem., 35(6-7), 405-417 (1998).
- [19] A.Kawabata, M.Yoshinaka, K.Hirota, O.Yamaguchi; J.Am.Ceram. Soc., 78, 2271-2273 (1995).
- [20] D.W.Kim, S.I.Shin, J.D.Lee, S.G.Oh; Mater.Lett., 58, 1894-1898 (2004).
- [21] V.Polshettiwar, M.N.Nadagouda, R.S.Varma; Aust.J.Chem., 62, 16-26 (2009).
- [22] Y.J.Zhu, W.W.Wang, R.J.Qi, X.L.Hu; Angew. Chem.Int.Ed., 43, 1410-1414 (2004).
- [23] H.Cheng, J.Cheng, Y.Zhang, Q.M.Wang; J.Cryst. Growth, 299, 34-40 (2007).
- [24] Z.Zhu, N.Wei, H.Liu, Z.He; Adv.Powder Technol., 22, 422-426 (2011).
- [25] K.Aslan, C.D.Geddes; Plasmonics, 3, 89-101 (2008).
- [26] N.Clament Sagaya Selvam, R.Thinesh Kumar, K.Yogeenth, L.John Kennedy, G.Sekaran, J.Judith Vijaya; Powder Technol., 211, 250-255 (2011).
- [27] C.H.Jung, S.Jalota, S.B.Bhaduri; Mater.Lett., 59, 2426-2432 (2005).
- [28] J.Ma, J.Liu, Y.Bao, Z.Zhu, X.Wang, J.Zhang; Ceram.Int., 39, 2803-2810 (2013).
- [29] M.G.Ma, S.J.Qing, S.M.Li, J.F.Zhu, L.H.Fu, R.C.Sun; Carbohydr.Polym., 91, 162-168 (2013).
- [30] M.Shakir, Y.Azim, H.T.N.Chishti, S.Parveen; Spectrochim.Acta, Part A, 65, 490-496 (2006).
- [31] Y.Murakami, A.Sawata, Y.Tsuru; J.Mater.Sci., 34, 951-955 (1999).
- [32] V.B.Rana, D.P.Singh, P.Singh, M.P.Teotia; Transit. Met.Chem., 7, 174-177 (1982).