DOI: http://dx.doi.org/10.22104/jpst.2016.401 Journal of Particle Science and Technology 2 (2016) 69-77

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jpst.irost.ir

Journal of
Particle Science and Technology

IROST

Synthesis of pure monoclinic zirconia nanoparticles using ultrasound cavitation technique-

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HIGHLIGHTS

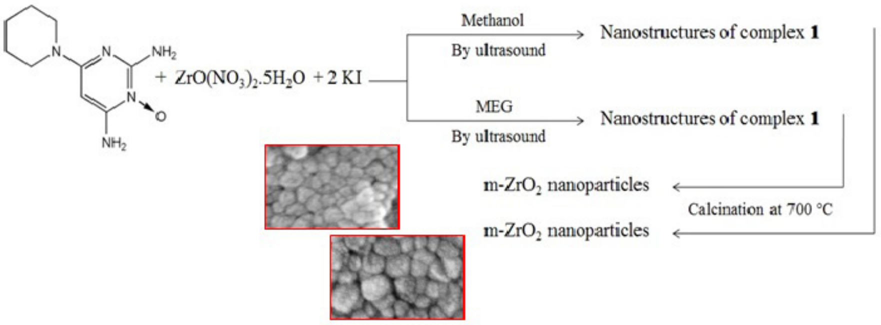
- The sonochemical synthesis and characterization of a nano-sized zirconium(IV)-minoxidil complex have been investigated in two different solvents.
- The pure monoclinic zirconia nanoparticles were readily synthesized from thermal decomposition of the complex as a precursor in both solvents.
- The average particles size of zirconia were significantly reduced when monoethylene glycol was used as solvent.
- The sonochemical method can be successfully applied as an efficient method for the preparation of nano-scale materials.

ARTICLE INFO

Article history:
Received 30 August 2016
Received in revised form
23 November 2016
Accepted 03 December 2016

Keywords:
Zirconia nanoparticles
Monoclinic
Zr(IV) complex
Sonochemical method
Thermal decomposition

GRAPHICAL ABSTRACT



ABSTRACT

In the current study, synthesis and characterization of a new nano-structured zirconium(IV)-minoxidil complex (1), where minoxidil, ($C_9H_{15}N_5O$; 6-(1-Piperidinyl)-2,4-pyrimidinediamine 3-oxide), have been investigated in two different solvents. The compound 1 has been synthesized by sonochemical method in the presence of methanol and monoethylene glycol (MEG) as solvents and characterized by scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) spectroscopy and elemental analysis. The thermal stability of the compound 1 has been studied by thermal gravimetric (TG) and differential thermal analyses (DTA). Pure monoclinic (m) zirconia (ZrO_2) nanoparticles were readily synthesized from thermal decomposition of the compound 1 as a new precursor in both solvents. The products were characterized by FT-IR, XRD, and SEM to exhibit the phase and morphology. The results showed that, pure zirconia was produced with particle size of 53 nm and the crystal system was monoclinic when methanol was used as solvent in complexation process. While the particles size of zirconia with the same structure were significantly reduced to 25 nm, using MEG as solvent. This study demonstrates that the coordination compounds may be suitable precursors for the simple one-pot preparation of nano-scale metal oxides with different morphologies.

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1. Introduction

Macroscopic properties of materials strongly depend on both the size and morphologies of the microscopic particles they are made up from. This is especially true for materials with morphological features smaller than a micron in at least one dimension, which are commonly called nano-scale materials, or simply nanomaterials [1]. During the last two decades, the rational design and syntheses of novel coordination supramolecular compounds, which involves self-assembly of organic ligands with appropriate functional groups and metal ions with specific directionality and functionality, have made considerable progress in the field of supramolecular chemistry and crystal engineering [2–4]. The considerable interest is driven by the impact on basic structural chemistry as well as by possible applications in a number of fields such as catalysis, molecular adsorption, luminescence, magnetism, nonlinear optics, and molecular sensing that are not found in mononuclear compounds [5]. By decreasing the size of coordination supramolecular compounds as polymers in nano-size, surface area would be increased. Hence making coordination supramolecular compounds in any form in nano-scale is certainly a major step forward toward the technological applications of these new materials [6]. Due to their possessing combination of unique properties such as excellent refractoriness and chemical resistance, good mechanical strength, high ionic conductivity, low thermal conductivity at high temperature along with relatively high thermal expansion coefficient and good thermal stability, ultrafine zirconia particles have attracted much interest recently [7]. Based on the above mentioned properties, they have found a broad industrial applications including: fuel-cell technology [8], as a catalyst or catalyst support [9], oxygen sensor [10], protective coating for optical mirrors and filters [11], nanoelectronic devices, thermal-barrier coatings [12], ceramic biomaterial [13], and thermo luminescence UV dosimeter [14]. Zirconia exhibits several crystalline modifications at different temperatures: monoclinic, tetragonal, and cubic. At very high temperatures (>2370 °C) the material has a cubic structure. At intermediate temperatures (1150–2370 °C) it has a tetragonal structure. At lower temperatures (below 1150 °C) the material transforms to the monoclinic structure which is a thermodynamically stable phase [15].

A variety of zirconium complexes have been prepared successfully and modified [16,17]. These precursors could be good candidates for the synthesis of cursors could be good candidates for the synthesis of ZrO_2 nanoparticles with different morphologies. So far, few studies has been taken place on using Zr(IV) supramolecules as precursor. We have been investigated the synthesis of monoclinic and tetragonal ZrO_2 nanoparticles from thermal decomposition of the $[ZrO(dmph)I_2]$, as a new precursor in methanol and monoethylene glycol as solvents, respectively [17]. Also, our group worked on the synthesis of pure tetragonal ZrO_2 nanoparticles from isophthalic acid-zirconium(IV) complex by thermal decomposition at 700 °C for 4 h [18]. Salavati-Niasari et al. have been reported the synthesis of single-phase cubic ZrO_2 nanoparticles from bis-aqua tris-salicylaldehydato zirconium(IV) nitrate; $[Zr(sal)_3(H_2O)_2](NO_3)$, as the new precursor [19]. This paper describes a facile and environmentally friendly synthetic sonochemical preparation of nano-sized Zr(IV) complex in the presence of methanol and separately in MEG as solvents, and its use as a new precursor for the preparation of pure m-ZrO_2 nanoparticles. To the best of our knowledge, this is the first report on the synthesis of a Zr(IV) complex with minoxidil as a ligand via sonochemical method and production of ZrO_2 nanoparticles with the same crystal systems by Zr(IV) complex as precursor. The results revealed that in comparison with traditional synthetic techniques, such as solvent diffusion, hydrothermal and solvothermal methods, the ultrasonic synthesis is a simple, efficient, low cost, and environmentally friendly approach to nano-scale coordination supramolecular compounds [20]. Sonochemical method can lead to homogeneous nucleation and a substantial reduction in crystallization time compared with conventional oven heating when nanomaterials are prepared [21]. These extreme conditions permit access to a range of chemical reaction spaces normally not accessible, for example many coordination supramolecular compounds have been synthesized via the sonochemical method, such as: La(III)-LH_2 [22], Zr(IV)-Neocuproine [17], Cu(I)-Neocuproine [1], Zr(IV)-LH_2 [23], Zr(IV)-Isophthalic acid [18], Cd(II)-Thioacetamide [24], Pb(II)-Minoxidil [25], Zn(II)-LH2 [26], and Pb(II)-LH_2 [27].

Minoxidil, ($C_9H_{15}N_5O$; 6-(1-Piperidinyl)-2,4-pyrimidinediamine 3-oxide), has been exploited as an anti-alopecia agent since the late 1980s. It has become one of the most popular anti-alopecia medicaments in the world with a market exceeding $100 million per year in the 1980s–1990s in the United States alone. In 1995 the world market was $125 million [28]. A review of the literature shows that very few metal complexes of minoxidil have been reported. After making a coordination polymer of minoxidil and Pb(II) in presence of KI [29], it was considered interesting to investigate the influence of the bromide counter ion (Br^-) in the polymerization process due to the expected structural diversity [25].

2. Experimental

2.1. Materials and physical measurements

All reagents and solvents were purchased from Merck Chemical Co. and used without further purification. Melting points were measured with a Branstead Electrothermal 9100 apparatus. FT-IR spectra were recorded on a Bruker tensor 27 spectrophotometer in the range 400–4000 cm^{-1} using the KBr disk technique. Elemental analyses (carbon, hydrogen, and nitrogen) were performed using a Heraeus CHN-O- Rapid analyzer. A multiwave ultrasonic generator (UP400S, Hielscher), equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 20 KHz with a maximum power output of 600 W, was used for ultrasonic irradiation. The ultrasonic generator automatically adjusts the power level. Thermogravimetric analysis (TGA) and differential thermal analyses (DTA) of the title compound were performed on a computer-controlled PL-STA 1500 apparatus. Powder sample of 1 was loaded into alumina pans and heated with a ramp rate of 10 °C/min from room temperature to 600 °C under argon atmosphere. X-ray powder diffraction (XRD) measurements were performed using an X'pert diffractometer of Philips Company with graphite monochromatic Cu Kα (λ= 1.5418 Å) radiation at room temperature in the 2 θ range of 20-90 °. The samples were characterized by a scanning electron microscope (Philips XL30) with gold coating.

2.2. Synthesis of nano-structured zirconium(IV)-minoxidil complex (1) by the sonochemical method

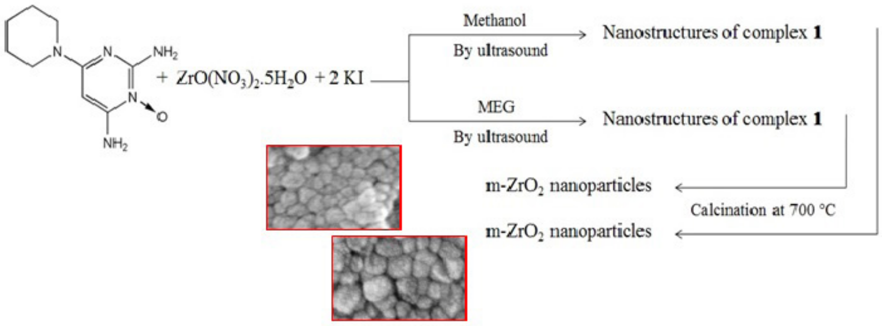
0.23 g (1 mmol) of zirconyl nitrate pentahydrate, $ZrO(NO_3)_2.5H_2O$, and 0.34 g (2 mmol) of potassium iodide (KI) were dissolved in 10 ml methanol. Then, 0.21 g (1 mmol) of minoxidil was dissolved in 10 ml methanol and both of solutions were mixed together and sonicated for 1 hour in an ultrasound vessel to obtain a homogeneous mixture with the rated output power of 600 W and frequency of 25 KHz. After 1 hour a bright yellow precipitate was formed. It was isolated by centrifugation (4000 rpm, 15 min), washed with water and acetone to remove residual impurities and finally dried in air (yield: 0.51 g, 65%). dec. p. ~280°C. Elemental analysis, found (%): Zr, 0.68; C, 13.91; H, 2.75; N, 11.48. FT-IR (cm-1) selected bands observed were: 3319(b), 2933(w), 2852(w), 1637(b), 1383(s), 1279(w), 1251(s), 1231(w), 1125(s), 1023(s), 981(s), 954(w), 825(w), 773(s), 670(w), and 507(s). The experiment was repeated by using MEG as the solvent. The resulting yellow powder of complex 1, (0.53 g) was obtained in 68% yield. dec. p. ~245°C. Elemental analysis, found (%): Zr, 0.56; C, 16.46; H, 4.20; N, 3.06. FT-IR (cm-1) selected bands observed were: 3470(b), 2940(w), 2375(w), 1625(w), 1540(s), 1375(w), 1340(s), 1280(w), 1140(w), 1070(s), 1035(w), 825(w), 810(w), 760(w), 655(w), 625(w), and 490(s).

2.3. Synthesis of ZrO_2 nanoparticles by thermal decomposition of compound 1

For synthesis of zirconia nanoparticles, the compound 1 were calcinated at 700 °C for 4 hour, under atmospheric air. The final products were collected and washed with water and acetone several times, dried in air, and kept for further characterization. The FT-IR spectra and powder XRD diffraction shows that the calcination was completed and the entire organic compound were decomposed. Also, the XRD patterns show the products using both precursors are m-ZrO_2.

3. Results and discussion

Reaction of minoxidil as ligand with zirconyl nitrate pentahydrate and potassium iodide under ultrasonic irradiation in methanol and separately in MEG as solvents, led to the formation of a nano-structured zirconium(IV)-minoxidil complex (1), in 65% and 68% yields, respectively. Scheme 1 gives an overview of the method used for the synthesis of compound 1 nanostructure. The FT-IR spectra for the free minoxidil ligand, Zr(IV) complex in methanol and monoethylene glycol and the as-prepared ZrO_2 nanoparticles in the frequency range from 400-4000 cm^{-1}, are compared in Figs. 1 and 2, respectively. By comparing the FT-IR spectra of minoxidil (Fig. 1a) and the Zr(IV) complex (Figs. 1b and 2a), it was found that minoxidil has been coordinated to Zr^{4+} ion, and forming new complex (1). The only difference among these characteristic peaks is either the peak intensity or a slight shift in the peak position. All distinct absorption peaks of minoxidil are illustrated in Table 1,



Scheme 1. Schematic diagram illustrating the formation of complex 1 and ZrO_2 nanopowders.

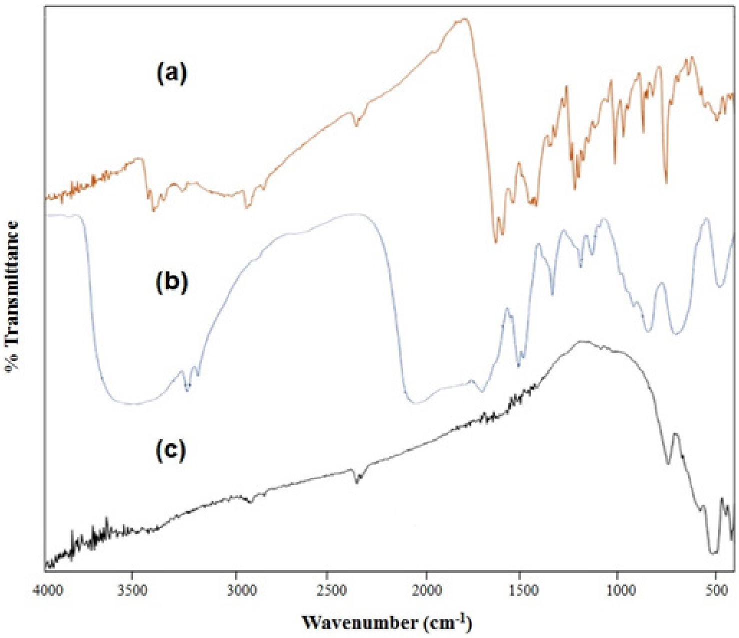


Fig. 1. FT-IR spectra of (a) minoxidil ligand, (b) nanoparticles of compound 1 synthesized by sonochemical method (using methanol), and (c) m-ZrO_2 nanoparticles.

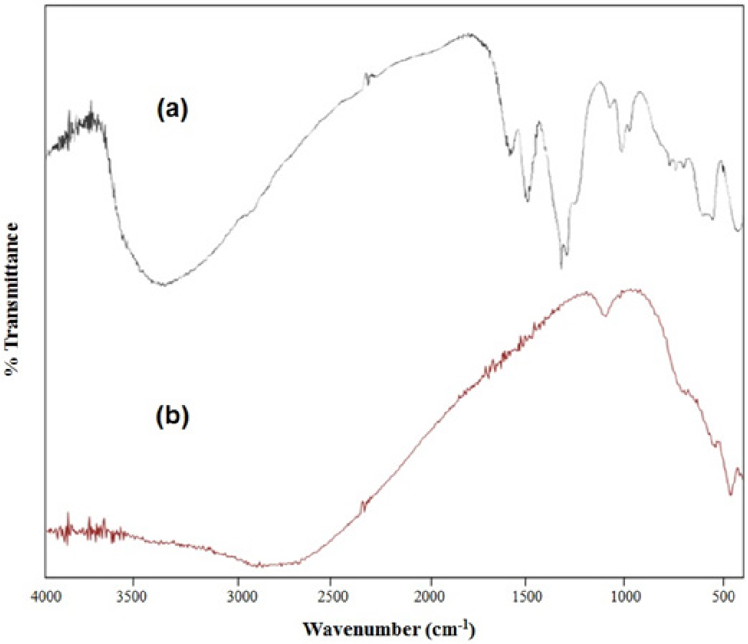


Fig. 2. FT-IR spectra of (a) nanoparticles of compound 1 synthesized by sonochemical method (using MEG), and (b) m-ZrO_2 nanoparticles.

Table 1.
FT-IR absorption peaks of minoxidil [30].

Wavenumber observed (cm^{-1})	Group identified
3432	N-H stretch
3289	H-bonded N-H
2950	Aromatic and aliphatic C-H stretch
1642	Aromatic C-H stretch
1560	Aromatic O-C stretch
1375	N-H bending
1232	Aromatic C-N stretch

and every absorption peak was assigned to corresponding vibration [30]. It is well known that the FT-IR spectra are very useful in determining the crystal phase for ZrO_2 [31]. The extended spectrum in the 400–4000 cm-1 region signified a structure with the surface of the sample containing H_2O molecules. As can be seen from Figs. 1c and 2b, all above bands disappeared when the compound 1 was calcinated. The band at 420-750 cm^{-1} is attributed to the vibration of Zr-O-Zr bond. The presence of adsorbed water molecule in zirconia samples is shown by the bands at around 2600-2000 and 1600-1000 cm-1 as stretching and bending frequencies, respectively.

To examine the thermal stability of the compound 1 nanostructure that obtained via sonochemical method (using methanol), thermal gravimetric (TG) and differential thermal analyses (DTA) were carried out between 20 and 600 °C in air (Fig. 3). As shown in Fig. 3, three weight loss steps were obtained in the TG curve. According to the TG curve, the first weight loss observed at 165 °C was attributed to removal of coordinated methanol, the second weight loss shown at 506 °C corresponds to removal of minoxidil and iodine atoms. At high temperature (up to 506 °C), the decomposition of the complex occurs to ultimately give solid that appears to be zirconia. Mass loss calculations of the end residue and the XRD pattern of the final decomposition product (Fig. 5a) show the formation of m-ZrO_2. There was no organic residue left after 506 °C, as confirmed by the FT-IR spectrum of the residual mass. The DTA curve displays two distinct exothermic peaks at 309 °C and 405 °C for the complex (Fig. 3).

The morphology and size of compound 1 nanostructure which prepared by sonochemical method in methanol and MEG were characterized by SEM and is shown in Fig. 4. Typical SEM images as shown in Figs. 4a and 4b, demonstrate nanoparticles with size about 66 nm and low uniformity. After using MEG as a solvent, the particles size decreased to about 29 nm (Figs. 4c and 4d). Furthermore, this micrograph reveals agglomerated particles with a homogeneous distribution. Also, quasi-spherical shaped morphology has been observed for the nanoparticles.

The XRD patterns shown in Figs. 5a and 5b are corresponding to the zirconia obtained by calcination of the compound 1 synthesized in methanol and separately in MEG at 700 °C for 4 hour, respectively. Fig. 5a shows all diffraction peaks which can be readily indexed to crystalline monoclinic phase ZrO_2 (space group P2/c) which is consistent to the values in the literature (JCPDS no. 001-0750). Compared with the standard diffraction pattern, no peaks of impurities were detected, indicating high purity of the product. In addition, the intense and sharp diffraction peaks suggest the crystallinity of the product. When MEG used as solvent, the same phase was formed under identical conditions, as shown in Fig. 5b. All the reflection peaks in this pattern could be readily indexed to crystalline monoclinic phase ZrO_2 with the same space group (JCPDS no. 007-0343), no characteristic peaks of impurities were detected.

In order to further investigation, the crystallite size (Dc) of products were calculated from the major diffraction peak of the corresponding zirconia using the Debye–Scherrer formula (1).

$$D_c = \frac{0.89\lambda}{\beta \cos\theta} \qquad (1)$$

In Eq. (1), λ is the wavelength of X-ray (1.5418 Å) for Cu Kα radiation, β the full width at half maximum, FWHM of prominent intensity peak (using the 100% relative intensity peak), and θ the peak position. The average crystallite size (Dc) and lattice parameters for two samples are reported in Table 2. As seen from Table 2, the average size of zirconia prepared in MEG is smaller than the one obtained using methanol. Also, average size of the products is in good agreement with the SEM images. Figs. 5 (a,b) and (c,d) show the SEM photographs of ZrO_2 nanoparticles in methanol and MEG, respectively. It represents that the obtained nanoparticles have hexagonal shape with uniform dimensions. As a result, when MEG has been used as solvent, ZrO_2 particles sizes decreased of about 53 nm to 25 nm.

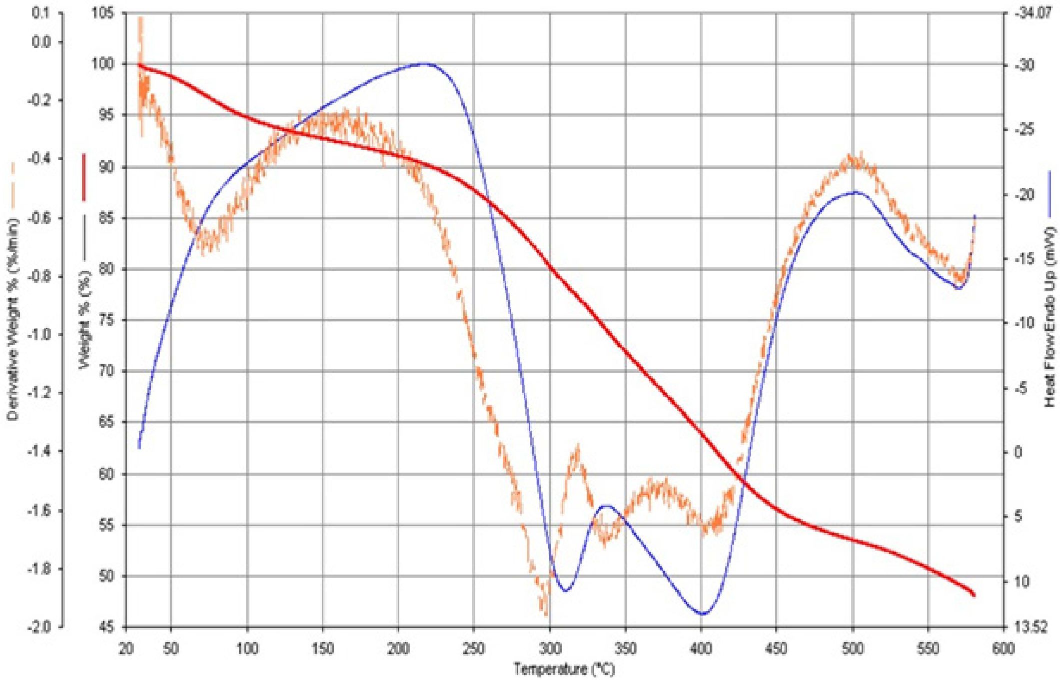


Fig. 3. TGA and DTA diagrams of the compound 1 nanoparticles synthesized by sonochemical method (using methanol).

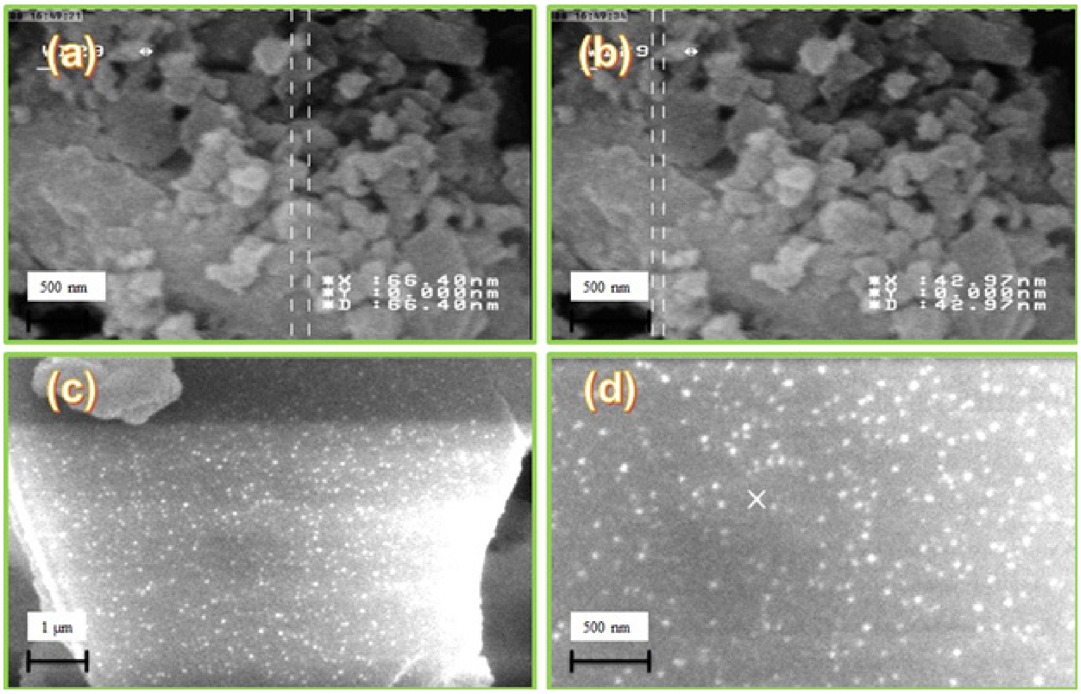


Fig. 4. SEM images of the compound 1 nanoparticles synthesized by sonochemical method in (a, b) methanol as solvent, and (c, d) MEG as solvent.

4. Conclusions

In this work we have successfully demonstrated the synthesis of nano-structured zirconium(IV)-minoxidil complex (1) in methanol and MEG as solvents by sonochemical method. To proceed, pure monoclinic zirconia nanoparticles were synthesized from calcination othe compound 1 at 700 °C. The XRD pattern indicates that the well-crystallized zirconia nanoparticles can be easily obtained under the current synthetic conditions. The results reveal that, when MEG was used as solvent, the produced m-ZrO_2 showed smaller particles size. In overall we can concluded that using nano-structured supramolecular

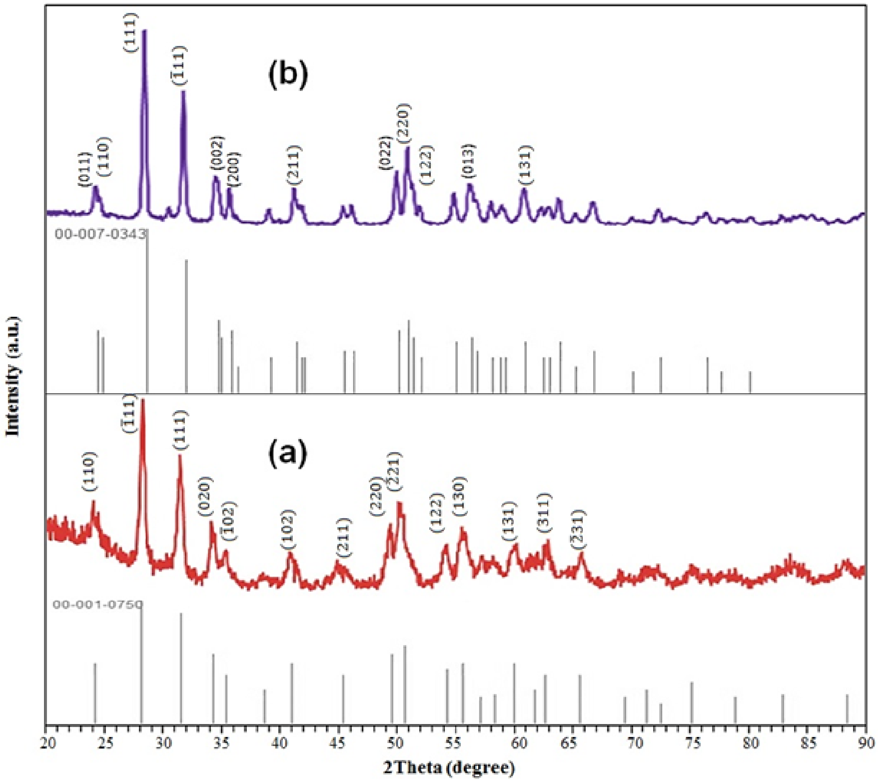


Fig. 5. XRD patterns of m-ZrO_2 nanoparticles synthesized by thermal decomposition of compound 1 in (a) methanol as solvent, and (b) MEG as solvent.

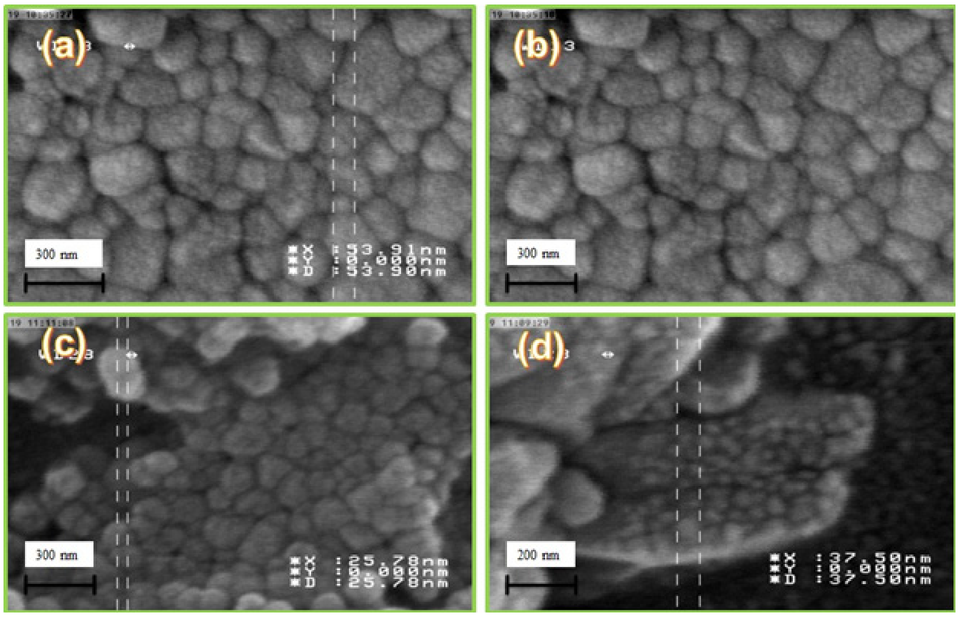


Fig. 6. SEM images of ZrO_2 nanoparticles in (a, b) methanol as solvent, and (c, d) MEG as solvent.

Table 2.

Lattice parameters and particle size of ZrO_2 nanoparticles synthesized by thermal decomposition of compound 1 at 700 °C

Name of the compound	Crystal structure	Solvent	Lattice parameters			Cell volume	Average size (nm)	
			a(Å)	b(Å)	c(Å)		XRD	SEM
zirconia	Monoclinic	Methanol	5.21	5.26	5.37	145.29	76	53
zirconia	Monoclinic	MEG	5.14	5.20	5.31	140.30	59	25

compounds can be appropriate precursors for production of nano-sized metal oxide materials with different and interesting morphologies. The study also establishes that sonochemical method can be successfully applied as an efficient method for the preparation of nano-scale materials.

Acknowledgment

The authors would like to express gratitude for support by Iranian Research Organization for Science and Technology (IROST), University of Damghan, and Nanotechnology Initiative Council.

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