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Zirconium oxide nanoparticles: Preparation, characterization and optical properties

E. M. Ibrahim, I. S. Ahmed, M. M. Moustafa and A. A. Ali
Chemistry, Dept., Faculty of Science, Benha Univ., Benha, Egypt
esraamokhtar67@yahoo.com

Abstract

Zirconium oxide nanoparticles are prepared using Zirconium oxychloride, ethylene glycol, and tartaric acid via pechini method. The synthesized zirconium oxide nanoparticles are obtained after the calcination at 500 ºC for one hour. The obtained zirconium oxide nanoparticles are characterized using various techniques such as XRD, FTIR, and DRS. The reflectance and optical properties are tested. The band gap and color analysis of the prepared zirconium oxide nanoparticles are investigated.

Keywords: Zirconium oxide nanoparticles, pechini method, DRS and Band gap.

1.Introduction

Crystalline particles with nanostructures have attracted interest of researchers because of their numerous applications and the characteristics that depend on particle size and their relevance to science and industry. In recent year nanoscale semiconductor material particles have established their recent increase in usefulness due to their attractive qualities and their many applications. These nanomaterials exhibited distinct the thermal, structural, and electrical characteristics that contributed their superior scientific appeal in fundamental and applicable fields Sagadevan [1]. There are sever technique have been created for the synthesis of metal oxide with nanostructures for instance: non-hydrolytic sol–gel reaction process [2-4], salt-assisted aerosol decomposition [5], metal alkoxide hydrolysis [6], carbon nanotubes templates [7], mechanochemical processing [8], non-aqueous synthesis [9], alkoxide thermal decomposition [10].

Nanoparticles of metal oxide are a class of materials that is significant for its optical, magnetic, and electronic attributes [11, 12]. Zirconium oxide (ZrO_2) has great importance because it is use in varied workable applications in fuel-cell technology [13] as a catalyst or catalyst support [14], thermal-barrier coatings [15], thermo luminescence UV dosimeter [16], protective coating for optical mirrors and filters [17], oxygen sensor [18], ceramic biomaterial [19], and also used as preservation from metal oxidation and chemical corrosion [20]. ZrO_2 has a wide band gap semiconductor property, so has extremely conductive at high temperature. According to their transformation temperature zirconium oxide can be formed in three crystalline structures like, tetragonal (T), Monoclinic (M) and Cubic (C). Monoclinic form is stable crystalline structure at room temperature; the tetragonal form is generated at 1100-1200 °C, The cubic phase forms only at 2373 °C [21-23]. Zirconium oxide nanoparticle had prepared by different process such as microwave plasma synthesis, chemical vapor synthesis, precipitation from inorganic salt solutions, sol–gel processing, combustion synthesis, laser ablation, ultrasonically assisted hydrothermal synthesis and inert gas condensation [24-26].

Sol gel technique used due to its distinct characteristics and features; this approach can produce high goodness of identical-sized nanoparticles on an industrial scale, so has more industrial use and is more widely used than alternative methods [27, 28], using the sol-gel process can be created high-purity, extremely homogenous composites [29-36]. The lower process temperature of this technology, which makes it possible to produce metal and ceramic nanomaterial at temperatures between 70 and 320°C, is another benefit over conventional methods [37-40]. This paper describes how ZrO_2 nanoparticles was created using pechini method (sol-gel) following by the calcination to increase crystallinity. XRD, FTIR, and DRS are some of the methods used to characterize the obtained zirconium oxide nanoparticles. The reflectance and optical properties of the synthesized zirconium oxide nanoparticles were investigated.

2.Experimental

3.Materials and reagents

The chemicals utilized in this practical work were purchased and used as reached without any further purification. Zirconium oxychloride octahydrate ($ZrOCl_2 \cdot 8H_2O$, 99.5 %) was purchased from Sigma-Aldrich company. Nitric acid (HNO_3, 69%), Tartaric acid (TA: $C_4H_6O_6$ 99 %) and ethylene glycol (EG: $C_2H_6O_2$, 99.8 %) were purchased from El Nasr Pharmaceuticals Chemical Company.

Synthesis of zirconium oxide nanoparticles via pechini method (sol –gel):

0.01 Mole of zirconium oxychloride octahydrate were dissolved in 20 mL distilled water, added 0.5 mL nitric acid at room temperature, and calculated amount of fuels. The obtained solution was preheated at 120 °C on hotplate with magnetic stirring then added 0.05 mole from tartaric acid. After that the temperature was raised at 150°C, 7 ml of ethylene glycol added with continuously magnetic stirring until the viscous gel is formed. Then, the gel ignited at 250 °C on hotplate, producing a white - grey ash powder. The synthesized ash calcined at 500 °C for 1 h to obtain the pure crystalline zirconium oxide nanoparticles as shown in Figure (1). The zirconium oxide nanoparticles synthesized from the sol gel auto-combustion method, named as ZR and ZC for the as-prepared and the calcined at 500/1h, respectively.

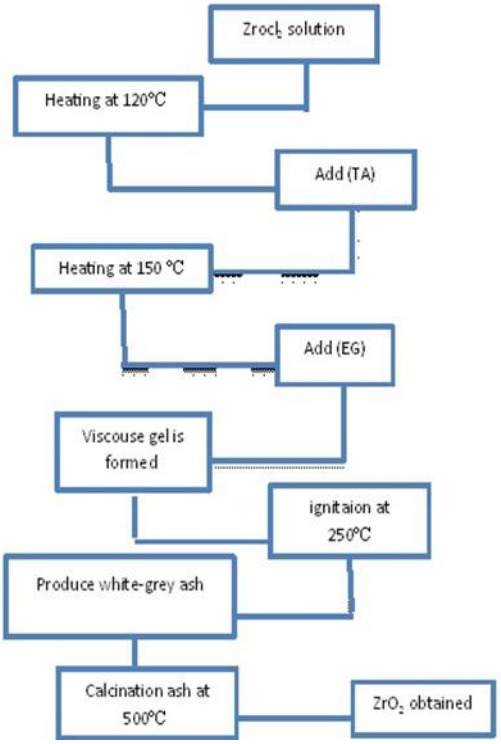

Fig. (1) Schematic flowchart for preparation of zirconium oxide nanoparticles.

Characterization

The X-ray diffraction is employed in order to examine the structural and microstructural characteristics of created nanoparticles. The as-prepared samples were measured using FTIR spectrometer at room temperature from 4000 to 400 cm^{-1}. Calcined sample's diffuse reflectance was investigated in ultraviolet-visible NIR range (200-2500 nm) using Jasco-V670 spectrophotometer and integrating sphere calibrated with barium sulfate as white standard. The CIE-Lab colorimetric method was used for determination of color parameters. CIE LCH is a second method for calculation the color axes. The chroma parameter (C^*) calculated from $C^* = \sqrt{(a^*)^2 + (b^*)^2}$ and the hue angle h^* is determined from $h^* = \tan^{-1}(b^*/a^*)$. . The solar reflectance (SR) is investigated by the following formula (1).

$$SR = \int_{\lambda_1}^{\lambda_2} R(\lambda)I(\lambda)d\lambda \Big/ \int_{\lambda_1}^{\lambda_2} I(\lambda)d\lambda \qquad (1)$$

Where, R(λ) is the experiment reflectance and I(λ) is the standard solar spectrum. The solar reflectance was determined by Japanese Industrial Standards Association (JIS) standard k5602-2008.

4.Results and Discussion

X-ray diffraction (XRD)

Figure (2) exhibits the XRD patterns of the synthesized zirconium oxides nanoparticles (ZC sample) after calcination at 500°C for 1 h. According to XRD lines, two crystalline structures appear due to the reference card No. 2300612 (space group:14:p 121/c1 a=3.5961, b= 3.5961, c= 5.17700, and α =β=γ= 90) of monoclinic structure and card No 1524514 (space group:140:14/mcm a=6.36400, b=6.36400, c=5.51800, α =β=γ= 90) of the tetragonal and the peaks agree with the zirconium oxide nanoparticles. The crystal size (D) of the calcined zirconium oxide nanoparticles (ZC sample) can be determined by using Scherrer formula (2)

$$D = 0.9\lambda/\beta\cos\theta \qquad (2)$$

Where, λ is the wavelength of X-ray (1.5406 A for Cu Kα), θ is the Bragg diffraction angle, and β is the x-ray full width half-maximum height (FWHM) of the XRD peak appearing at the diffraction angle θ. The obtained ZrO_2 average crystallite size (D) was found to be 15.65 nm. Table (1) summed up the position (2θ), d value, FWHM, crystal size at each peak, and (hkl) value for the prepared sample.

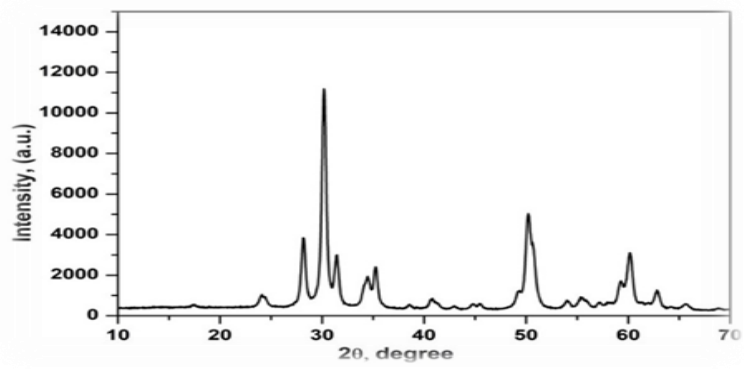

Fig. (2) XRD pattern of the synthesized zirconium oxide nanoparticles (ZC sample) after calcination at 500 for 1 h.

Table (1) The extracted data from XRD pattern of the synthesized ZrO_2 (ZC sample).

No.	2θ, °	d, Å	FWHM, °	Size, Å	Norm. I.	hkl
1.	17.35266	5.10629	0.5216	160.9272	1.42	100
2.	24.1306	3.68516	0.8108	104.6484	7.01	110
3.	28.15578	3.16681	0.4677	182.9164	30.19	11-1
4.	30.16473	2.96032	0.4774	180.0035	100	101
5.	31.40253	2.8464	0.469	183.7893	21.13	111
6.	34.37949	2.60643	0.8923	97.3369	19.59	020
7.	35.23156	2.54532	0.4379	198.8029	12.45	110
8.	38.55124	2.33343	0.4277	205.5107	1.37	021
9.	40.7195	2.21405	0.9173	96.4791	6.26	21-1
10.	42.81344	2.11048	0.5522	161.3928	1.1	102
11.	44.85576	2.01902	1.1703	76.6996	4.17	112
12.	49.09303	1.85421	0.5731	159.1736	6.23	022
13.	50.16286	1.81714	0.9052	101.2093	68.92	220
14.	53.97245	1.69752	0.548	169.8971	2.5	201
15.	55.34757	1.65856	0.6323	148.1797	3.99	013
16.	55.90422	1.64336	0.2848	329.8033	0.86	130
17.	58.10377	1.58627	0.4957	191.4699	0.77	22-2
18.	59.27249	1.55775	0.5724	166.7615	10.95	103
19.	60.14423	1.53724	0.5868	163.3843	24.99	211
20.	62.77174	1.47907	0.5071	191.6661	7.49	311
21.	65.57241	1.42251	0.6863	143.811	2.53	222
22.	68.75054	1.3643	0.6105	164.6654	0.95	212

FT-IR analysis

The FT-IR spectrum of the fabricated zirconium oxide nanoparticle (ZR and ZC samples) is displayed in Figure (3). The vibrational bands that were observed at around 3418.65 cm^{-1} and 1632.47 cm^{-1} are related to the stretching and bending vibrational modes of the water molecules on the surface of zirconium oxide. The weak absorption band at 1300 cm^{-1} is assigned to carbon-oxygen group. The FTIR spectra of the calcined ZC sample revealed a band between 400-750 cm^{-1} associated to the crystalline ZrO_2 nanoparticles.

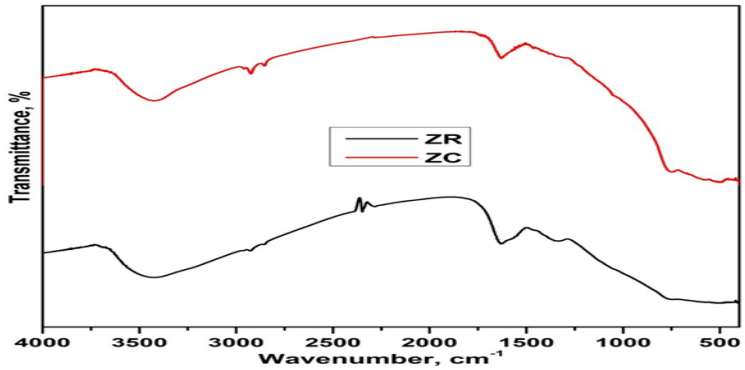

Fig. (3) FTIR spectra of the synthesized zirconium oxide nanoparticles before (ZR sample) and after calcination at 500°C for 1 h (ZC sample).

Optical studies:

The calcined zirconium oxide nanoparticles (ZC sample) are shown in Figure 4(a and b) was examined utilizing diffuse UV-VIS and NIR reflectance. Spectra displayed the measured reflectance between 200-2500 nm. The reflectance edge between 220-280 nm for ZC sample. The absorption coefficients (α) extracted from the experiment reflectance data using Kubelka Munk function as given by equation No (3).

$$F(R) = (K - M) = \alpha = (1 - R)^2/2R \qquad (3)$$

Where, R is the experiment reflectance, F(R) is K-M function, α is absorption coefficients.

The UV-vis-NIR absorption spectra of zirconium oxide nanoparticles (ZC sample) displayed in Figure 5(a and b). The broad absorption band between 250-400 nm as illustrated in Figure 5 (b).

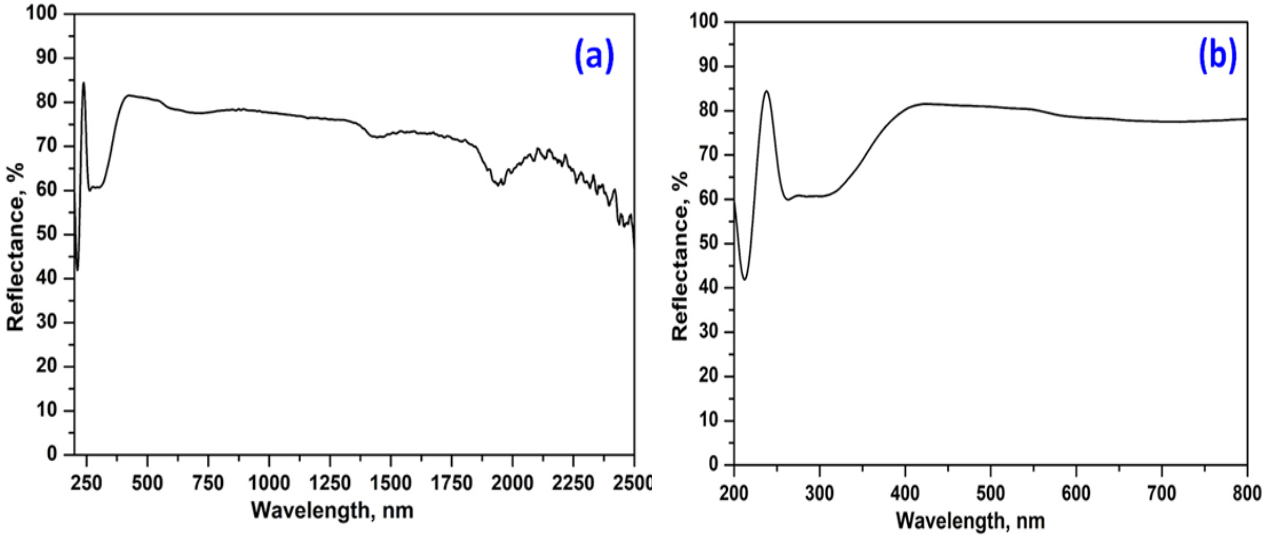

Fig. (4) UV-VIS and NIR diffuse reflectance of the synthesized zirconium oxide nanoparticles (ZC sample).

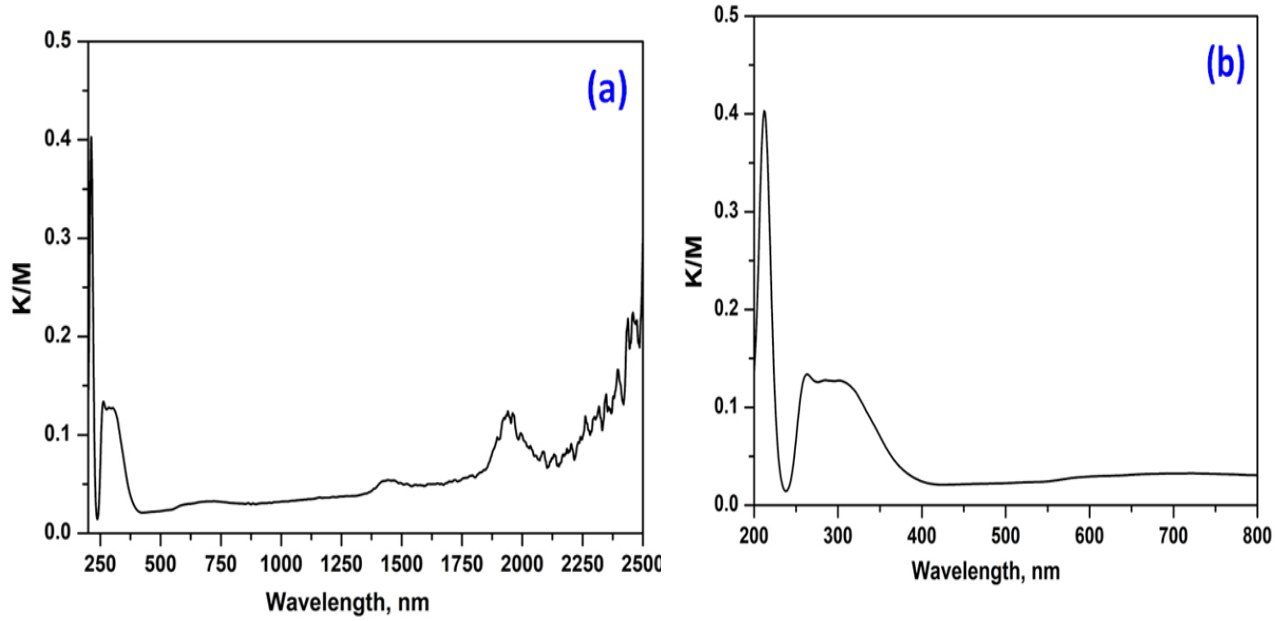

Fig. (5) UV-VIS and NIR absorption spectra of the synthesized zirconium oxide nanoparticles (ZC sample).

The band gap of the produced zirconium oxide nanoparticles (ZC sample) can be calculated using by equation No. (4):

$$(F(R)h\upsilon)^z = A(h\upsilon - E_g) \qquad (4)$$

Where, h and υ are constants, F(R) is Kubelka Munk function, and z is the value between 2 and 1/2 based on the permitted direct and indirect electronic transitions. The band gap calculated to be 3.2/5.4 eV and 2.8/5.1eV for direct and indirect band gap, respectively as shown in Figure (6).

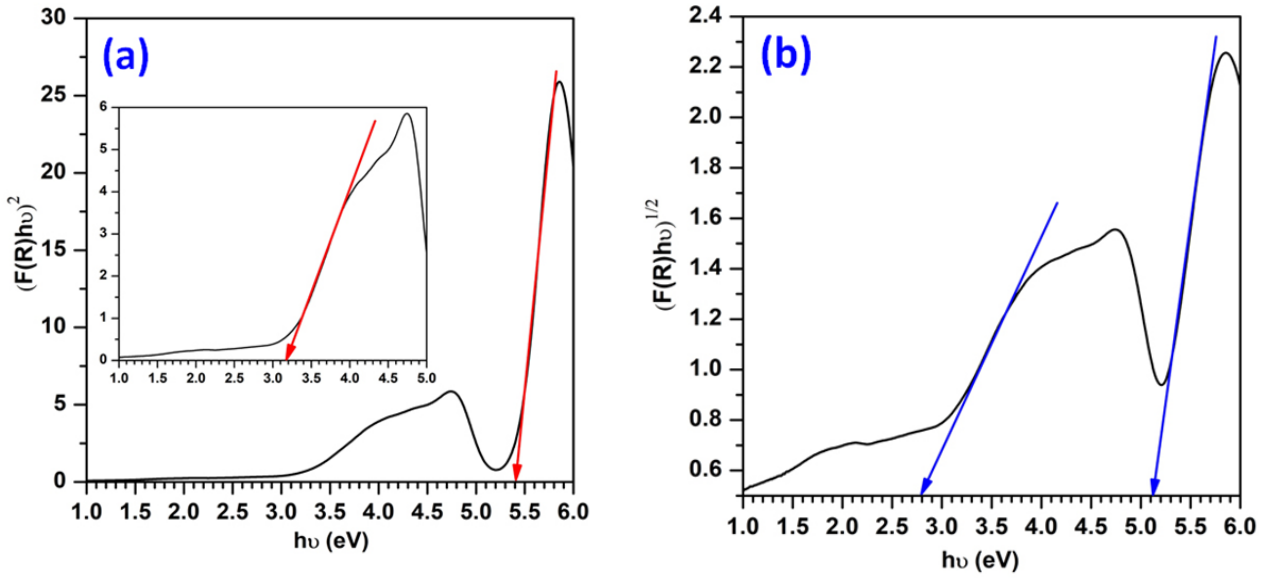

Fig. (6) The direct and indirect band gap between of the synthesized of zirconium oxide nanoparticles (ZC sample).

According to the color analysis methods, color parameters determined according to CIE-Lab and CIE-LCH methods. The values of L/a/b/c/h calculated to be 91.62, 0.85, -1.08, 1.37 and 231.93 for ZC sample. The calculated data reflected the white color of the synthesized zirconium oxide. Light and solar reflectance of the synthesized ZC sample determined by using JISK5602:2008 and JISA5759:2008 methods according to the eq. No. (1) [41]. The value of light and solar reflectance using JISA5759:2008 determine to be 79.77 % and 77.5%. Also, the solar reflectance determined in the UV-VIS, NIR and total solar reflectance using JISK5602:2008 method to be 78.86%, 75.60% and 77.43%, respectively [42, 43].

5.Conclusion

Zirconium oxide nanoparticles were synthesized using a sol-gel auto combustion method and the obtained ashes calcined at 500 °C for one hour. Various analytical methods, including Fourier transform infrared spectroscopy (FT-IR), and X-ray diffraction (XRD) are used for the characterization of the synthesized zirconium oxide. The average crystallite size of the calcined zirconium oxide was determined to be 15.65 nm. UV-VIS-NIR diffuse reflectance spectra of calcined zirconium oxide displayed the reflectance edge between 220-280 nm. The band gap calculated to be 3.2- 5.4 eV and 2.8 -5.1 eV for the direct and indirect band gap, respectively. The values of color parameters (L/a/b/c/h) calculated to be 91.62, 0.85, -1.08, 1.37 and 231.93 for ZC sample. Light and solar reflectance of the synthesized sample determined to be 79.77% and 77.5%. Also, the solar reflectance determined to be 78.86%, 75.60% in UV-VIS, NIR region and the total solar reflectance determined to be 77.43 %.

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Reference

[1]. **S.P. Sagadevan, JibanDas, Isha,** Hydrothermal synthesis of zirconium oxide nanoparticles and its characterization, Materials Science: Materials in Electronics, vol.27,pp. 5622-5627,2016.

[2]. **L.X. Zhou, Jie Li, Xiaoqiang Wang, Feng,** Metal oxide nanoparticles from inorganic sources via a simple and general method, Materials Chemistry and Physics, vol.97,pp.137-142,2006.

[3]. **J.Y. Joo, Taekyung Kim, Young Woon Park, Hyun Min Wu, Fanxin Zhang, Jin ZHyeon,** Taeghwan Multigram scale synthesis and characterization of monodisperse tetragonal zirconia nanocrystals, the American Chemical Society, vol.125 ,pp. 6553-6557,2003.

[4]. **J.F. Tang, Jason Robinson, Richard D Zhu, Yimei Herman, Irving P Steigerwald, Michael LBrus,** Louis E Solid-Solution Nanoparticles: Use of a Nonhydrolytic Sol−Gel Synthesis To Prepare HfO_2 and $Hf_x Zr_{1-x} O_2$ Nanocrystals, Chem. Mater, vol.16 ,pp. 1336-1342,2004.

[5]. **B.L. Xia, I WuledOkuyama,** Kikuo Novel route to nanoparticle synthesis by salt-assisted aerosol decomposition, Adv. Mater, vol.13,pp. 1579-1582,2001.

[6]. **H. Kominami, MasaakiTakada, Yoko Inoue, Masashi Inui, Tomoyuki Kera,** Yoshiya Hydrolysis of titanium alkoxide in organic solvent at high temperatures: a new synthetic

method for nanosized, thermally stable titanium (IV) oxide, ndustrial engineering chemistry research,vol. 38 ,pp. 3925-3931,1999.

[7]. **C. Rao, BC Govindaraj, A Zirconia nanotubes,** Chem. Commun,vol,14,pp. 1581-1582, 1997.

[8]. **P.G.T. McCormick, Takuya Robinson, John SDing, Jun,** Nanopowders synthesized by mechanochemical processing, Adv. Mater, vol.13,pp. 1008-1010,2001.

[9]. **M.P. Niederberger, Nicola Polleux, Julien Antonietti,** Markus A general soft-chemistry route to perovskites and related materials: synthesis of $BaTiO_3$, $BaZrO_3$, and $LiNbO_3$ nanoparticles, Angew. Chem, vol.116,pp. 2320-2323,2004.

[10]. **K.K. Okuyama, Yasuo Tohge ,Noboru Yamamoto, Satoru Wu, Jin Jwang Flagan, RC Seinfeld,** JH Production of ultrafine metal oxide aerosol particles by thermal decomposition of metal alkoxide vapors, AIChE Journal,vol. 32 ,pp. 2010-2019,1986.

[11]. **A.A. Khaleel,** Nanostructured pure γ-Fe_2O_3 via forced precipitation in an organic solvent, Chemistry–A European Journal,vol. 10 925-932,2004.

[12]. **Q.Z. Tang, Qinghong Wang, Ping Wang, Ye Wan, Huilin,** Characterizations of cobalt oxide nanoparticles within faujasite zeolites and the formation of metallic cobalt, Chem. Mater, vol.16 ,pp. 1967-1976,2004.

[13]. **S.V. Park, John M Gorte, Raymond,** Direct oxidation of hydrocarbons in a solid-oxide fuel cell, Nature, vol.404,pp. 265-267,2000.

[14]. **Y.H. Li, Dehua Cheng, Su. Zhenxing, Li.Caili, Zhu.Junrong, Qiming,** Effect of calcium salts on isosynthesis over ZrO_2 catalysts, J. Mol. Catal. A: Chem., 175 (2001) 267-275.

[15]. **P.E. Wright, G.Anthony,** Mechanisms governing the performance of thermal barrier coatings, Current opinion in solid state Materials Science,vol. 4,pp. 255-265,1999.

[16]. **P.D.l.R.-C. Salas, E.Diaz-Torres, L.A.Castano, V.M.Melendrez, R.Barboza-Flores,** Monoclinic ZrO2 as a broad spectral response thermoluminescence UV dosemeter, Radiation Measurements,vol. 37,pp. 187-190,2003. [

[17]. **Q.S. Zhang, Jun.Wang, Jue.Wu, Guangming Chen ,**Lingyan Sol–gel derived ZrO2–SiO2 highly reflective coatings, Int. J. Inorg. Mater,vol. 2,pp. 319-323,2000.

[18]. **E.M. Subbarao, H.S.,** Oxygen sensors and pumps, Advances in Ceramic,vol.24,pp.731-747,1988.

[19]. **C.M. Piconi,** G, Zirconia as a ceramic biomaterial, Biomaterials,,vol.20,pp. 1-25,1999.

[20]. **R.L.M. Ibáñez, Famos-Barrado, JR Leinen,** D, Optimization of spray pyrolysis zirconia coatings on aluminized steel, Surface coatings technology,vol.200,pp. 6368-6372,2006.

[21]. **A.A. Ali, I.S. Ahmed, A.S. Amin, M.M. Gneidy,** Auto-combustion Fabrication and Optical Properties of Zinc Oxide Nanoparticles for Degradation of Reactive Red 195 and Methyl Orange Dyes, J. Inorg. Organomet. Polym Mater,vol.31,pp. 3780-3792,2021.

[22]. **G.-Y.C. Guo, Yu-Li,** A nearly pure monoclinic nanocrystalline zirconia, J. Solid State Chem,vol.178,pp. 1675-1682,2005.

[23]. **J.J. Liang, Liu.Xin, Ge.Deng, Zhaoxiang Zhuang, Li.Jing, Li.Fuli,** Yadong Characterization and synthesis of pure ZrO2 nanopowders via sonochemical method, Materials research bulletin,vol.38,pp. 161-١٦٨,2003.

[24]. **M.D. Salavati-Niasari, Mahnaz Davar, Fatemeh,** Synthesis and characterization of pure cubic zirconium oxide nanocrystals by decomposition of bis-aqua, tris-acetylacetonato zirconium (IV) nitrate as new precursor complex, Inorganica Chimica Acta, vol.3 ٦٢ ,pp.٣٩٦٩ -٣٩٧٤,2009.

[25]. **V.V.W. Srdić,** Markus Comparison of nanosized zirconia synthesized by gas and liquid phase methods, J. Eur. Ceram. Soc,vol.26,pp. 3145-3151,2006.

[26]. **R.S. Purohit, S Tyagi,** AK Combustion synthesis of nanocrystalline ZrO2 powder: XRD ,Raman spectroscopy and TEM studies, Materials Science Engineering: B,vol. 130 ,pp. 57-60 ,2006.

[27]. **I.A.P. Rahman,** Vejayakumaran Synthesis of silica nanoparticles by sol-gel: size-dependent properties, surface modification, and applications in silica-polymer nanocomposites—a review, Journal of Nanomaterials,vol,201,pp.410-587٢٠١٢.

[28]. **G.J.S. Owens, Rajendra KForoutan, Farzad Alqaysi, Mustafa Han,** Cheol-Min Mahapatra, Chinmaya Kim, Hae-Won Knowles, Jonathan C Sol–gel based materials for biomedical applications, Prog. Mater Sci,vol.77,pp. 1-79,2016.

[29]. **K. Kajihara,** Recent advances in sol–gel synthesis of monolithic silica and silica-based glasses, Journal of Asian Ceramic Societies,vol.1,pp. 121-133,2013.

[30]. **L.L.W. Hench,** Jon K The sol-gel process, Chem. Rev,vol.90,pp. 33-72,1990.

[31]. **M.M.W. Collinson, Hanming Makote, Rajendra Khramov,** Alexander The effects of drying time and relative humidity on the stability of sol–gel derived silicate films in solution, Journal of Electroanalytical Chemistry,vol.519,pp. 65-71,2002.

[32]. **A.A. Ali, M.Y. Nassar, S.A. Shama, A.M. El Sharkwy, N.E. El Sayed,** Sol-Gel Auto-Combustion Synthesis and Identification of Silicon Dioxide Nanoparticles forThe Removal of Sunset Dye from Aqueous Solutions, J Benha Journal of Applied Sciences,vol.5,pp. 217-229 ,2020.

[33]. **A.A. Ali, S.A. Shama, S.R. EL-Sayed, Fabrication,** structural and adsorption studies of zirconium oxide nanoparticles, J Benha Journal of Applied Sciences,vol.5,pp. 245-253,2020.

[34]. **A.A. Ali, I.S. Ahmed, A.S. Amin, M.M. Gneidy, Preparation,** characterization and optical properties of copper oxide nanoparticles via auto-combustion method, Journal of Basic and Environmental Sciences,vol.7,pp. 93-98,2020.

[35]. **A.A. Ali, M.Y. Nassar, A.E.M. El Sharkwy, I.S. Ahmed, M. Abd, E.A. Elhalim,** Fabrication and study of Nickel oxide nanoparticles via low combustion synthesis method using different fuels, Journal of Basic and Environmental Sciences,vol.6,pp. 183-186,2019.

[36]. **A.A. Ali, S.A. Shama, A.S. Amin, S.R. El-Sayed,** Synthesis and characterization of ZrO_2/CeO_2 nanocomposites for efficient removal of Acid Green 1 dye from aqueous solution, Mater. Sci. Eng., B,vol.269,pp. 115-167,2021.

[37]. **B.W. Li, Yan.Xiaohui, Li.Minyu,** Longtu Preparation and characterization of nano-TiO_2 powder, Materials Chemistry Physics,vol.78,pp. 184-188,2003.

[38]. **R.R. Vijayalakshmi,** V, Synthesis and characterization of nano-TiO_2 via different methods, Arch. Appl. Sci. Res,vol.4,pp. 1183-1190,2012.

[39]. **A.S. Jaroenworaluck, W Kosachan, N Stevens,** R, Characteristics of silica-coated TiO_2 and its UV absorption for sunscreen cosmetic applications, Surface Interface Analysis: An International Journal devoted to the development application of techniques for the analysis of surfaces, interfaces thin films,vol.38,pp. 473-477,2006.

[40]. **D.T.J. Bokov, Abduladheem Chupradit, Supat Suksatan, Wanich Javed Ansari, Mohammad Shewael, Iman H Valiev, Gabdrakhman H Kianfar, Ehsan**, Nanomaterial by sol-gel method: synthesis and application, Advances in Materials Science Engineering,vol.221 ,pp.78-89,٢٠٢١.

[41]. **H. Abd El-daim, F. Taher, N. Morsy, G. Turky ,A. Ali,** Electrically conductive and UV protective graphene surface-modified polyester blends, Journal of Materials Science: Materials in Electronics,vol.32,pp. 28358-28372,2021.

[42]. **I.S.A. Ayman A.Ali,** Sol-gel auto-combustion fabrication and optical properties of cobalt orthosilicate: Utilization as coloring agent in polymer and ceramic, Mater. Chem. Phys,vol. 238,pp. 121888-121902,2019.

[43]. **A.A. Ali, E. El Fadaly, I.S. Ahmed,** Near-infrared reflecting blue inorganic nano-pigment based on cobalt aluminate spinel via combustion synthesis method, Dyes and Pigments,vol.158,pp. 451-462,2018.