Synthesis, luminescence and photocatalyst properties of zirconia nanosheets by modified Pechini method

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Abstract:

Pure tetragonal zirconia nanosheets were successfully prepared by modified Pechini method. In this approach, $\text{ZrOCl}_2 \cdot 6\text{H}_2\text{O}$, tri ethanol amine (TEA) and citric acid (CA) were used as the source of Zr^{4+} , the chelating and polymerization agent, respectively. The effects of heat treatment and TEA:CA: Zr^{4+} ratios on the structure, morphology and zirconia particle size were investigated.

The microstructure of the products was characterized by X-ray diffractometry (XRD), thermogravimetric analysis (TGA) scanning electron microscopy (SEM) and Fourier transform infrared (FT-IR) analysis. The zirconia nanosheets exhibit photoluminescence at room temperature with a broad emission in the blue region of the visible spectrum. Finally, the effect of calcination temperature on the photocatalyst properties of nanosheets was investigated.

Keywords: ZrO_2 , Sol-gel method, Tetragonal zirconia, nanosheet.

1. Introduction

Industrial dyestuffs are one of the organic pollution sources of wastewater pollution and represent an increasing environmental hazard [1]. It is a kind of chemically stable, non-biodegradable, and difficultly decomposed dye pollutant in wastewater that are continuously emitted into the environment from various dyestuff and textile industries[2].Consequently, different strategies have been devised for treatment of wastes containing persistent organic materials.

The biological, physical and chemical treatment methods are ineffective, very slow and not environmentally compatible and lead to the generation of secondary pollutants [3-10]. Advanced oxidation processes (AOPs) such as photocatalysis one promising approach and most effective treatment for selective photodegradation and selective elimination of organic contaminants of waste water [11].

Nanomaterials showed excellent photocatalytic properties on the degradation of organic dyes, due the fact that their unique physical and chemical properties in comparison with those of their bulk counterparts, and their properties based on quantum size effects and high surface area.In recent years, many studies performed on the heterogeneous photocatalysis, where oxide semiconductors such as TiO_2 , ZnO , Fe_2O_3 , ZrO_2 , CuO are applied [12-22],

Nanocrystalline ZrO_2 as a typical semiconductor or insulator showed the excellent characteristics such as high surface area, porosity, surface defects, relatively wide band gap value ($E_g \sim 5.0$ eV depending on synthetic approaches),the high negative value of the conduction band potential (with a conduction band potential of -1.0 V vs. NHE)[23],thermally stable (m.p. 2680°C), chemically inert, excellent physical and chemical properties, non-toxicity, low thermal conductivity, high thermal expansion coefficient, high thermal shock resistance, polymorphic nature, low cost and easy availability[24].

Zirconium dioxide at atmospheric pressure has three structural isomers: monoclinic structure [space group $\text{P}21/\text{c}$] (m-phase), the monoclinic phase is stable below 1172°C , tetragonal structure [space group $\text{P}42/\text{nmc}$] (t-phase) is stable at the temperature range of 1172 - 2347°C , and is transformed to a cubic phase [space group $\text{Fm}3\text{m}$] (c-phase) above 2347°C .

The applications of nanocrystalline zirconia strongly depends on calcination temperature, crystal structure and phase transformations. Tetragonal phase is a good candidate for photocatalysts application [23, 24].

Various methods for synthesis of nanocrystalline zirconia (ZrO_2) have been developed and investigated, including, precipitation technique, combustion synthesis, inert gas condensation, polymeric sol-gel process, hydrothermal process, solvothermal, reverse micelles, spray pyrolysis[25-30]. Among these methods, the non-alkoxide polymeric sol-gel process is the simplest, high purity and cost effective method for synthesizing metal oxide nanoparticles. Furthermore, this type of sol-gel process provides possibility parameter control on the structure, shape, size, and chemical, physical and optical properties [2, 31-35]. Among polymeric sol-gel methods, using citric acid (CA) and ethylene glycol (EG) pair is famous as Pechini method to prepare metal oxide nanoparticles. Loghman-Estarki and coworkers[35] were reported *monoclinic* ZrO_2 nanosheets using Pechini method at calcination temperature of 490°C . Also, SEM and TEM images showed that the thickness of nanosheets were between 15 and 20 nm. Suciua [36] were studies synthesis of ZrO_2 nanoparticles using sucrose as an organic precursor by the sol-gel method at calcination temperature of 900°C . The particle size of 53nm was obtained by this group. Huang *et al.* has reported synthesized ZrO_2 nanosheets using glacial acetic acid and N,N-dimethylformamide with the crystallite size of 13.94 nm and calcination temperature of 600°C [37].

However, the disadvantage of polymeric sol-gel method (especially Pechini method) is that as-obtained nanoparticles are highly agglomerated. In this study, CA-TEA solvents were replaced with CA-EG to obtain gel medium for coordination of Zr^{4+} ions. To the best of our knowledge, there is no report of synthesis of zirconia nanoparticles with CA-TEA as a gel and chelating agent to prepare t-phase of zirconia nanosheets.

Furthermore, in this work, we report for the first time, low temperature synthesis of t- ZrO_2 nanosheets (Table 1) with a new pair of TEA and CA agent to modify Pechini method. Finally, photoluminescence and the catalytic of these nanosheets on the photodegradation of methyl orange were studied.

2. Experimental

2.1. Materials:

ZrOCl₂·8H₂O, citric acid (C₆H₈O₇, CA), tri ethanol amine (C₆H₁₅O₃N, TEA), ethylene glycol (C₂H₆O₂, EG)) were purchased from Merck Company.

2.2. Synthesis of zirconia nanosheets

Zirconium oxychloride octahydrate (ZrOCl₂·8H₂O) was first dissolved in the water and then, according to Table 2, the different moles of citric acid, TEA and EG solution were added to previous solution under vigorous stirring. The sol was obtained by heating mixed solution at 80 °C for 1h. Then, this solution was heated at 120 °C for 1h to remove excess water and obtain viscous solution (gel formation). In continue, the solution was heated at 250 °C for 1 h to obtain brown powder. Finally, the powder was calcined at 380 °C-550 °C for 2h.

2.3. Characterization of zirconia nanosheets

XRD patterns of the samples are registered on a Philips X-pert Pro MPD model X-ray diffractometer (Philips, Eindhoven, the Netherlands) using copper K α radiation ($\lambda = 0.154056$) in the 2θ range of 20-90°. Field emission scanning electron microscopy (FE-SEM) images were obtained by Hitachi (Japan) with operating condition voltage of 15 kV. Before taking FESEM image, the samples were coated with gold by Desk Sputter Coater (Nanostructured coatings Co., DST3 model) made in Iran. From FESEM images, the particle size distributions of as-synthesized samples at temperature of 380°C were calculated from 70 nanoparticles. Thermal analyses were obtained by thermogravimetric analysis (TG) and differential scanning calorimetric analysis (DSC) (model STA-6000, Perkin Elmer) under air atmosphere. FT-IR spectra of the synthesized sample were taken on a Nicolet Magna IR 550 spectrometer (Toronto Area, ON, Canada) in the spectra range 400-4000 cm⁻¹ with using the KBr pellet technique. For comparison of optical properties of nanoparticle with micro-sized (bulk), one sample prepared with Pulse Electrical Explosion (model of PEE50K, Nano Engineering and Manufacturing Co., PNF Co. made in Iran). The UV-Vis absorbance spectra was obtained by applying a Spectro UV-Vis double beam PC scanning spectrophotometer model UVD-2950 (Labomed, Los Angeles, CA) equipped with glass of 1cm path length and the spectra were registered at room temperature in air within the range 200-800 nm.

2.4. Photocatalytic test

The photocatalytic degradation of methyl orange under UV light irradiation (400W Osram UV lamp; Osram Co., Berlin, Germany) was used to investigate photocatalytic activity of as-synthesized ZrO₂ nanoparticles. 25 mg of ZrO₂nanopowders was suspended in 50 mL(C₀=10 ppm) methyl orange dye solution. The solutions were stirred by using a magnetic stirrer in the dark for 1 h to reach adsorption /desorption equilibrium. Thus, photocatalytic degradation was started by irradiating the UV light to the suspension solution. The lamp was inserted at a distance of 50 cm from the suspension solution. The dye suspension solutions were irradiated at 20 min. Then, the suspension solution was centrifuged to ensure that zirconia nanoparticles were removed completely from samples. The concentration of the dyes in the solution was investigated using an UV-vis spectrophotometer. The decolorization rate percentage was found by the following equation:

$$\text{Degradation (\%)} = \frac{C_0 - C}{C_0} \times 100 = \frac{A_0 - A}{A_0} \times 100$$

where C₀ and C denote the dye concentrations before illumination and after a certain irradiation time, respectively, A₀ is the initial absorbance of dye solution, and A is the dye solution absorbance after irradiation at a certain reaction time. Also, the pH effect and calcination temperature on photocatalytic performance of zirconia was investigated. The structure of dyes and λ_{max} are shown in Table 3.

3. Results and discussion

3.1. FESEM study

The morphology of nanostructures was characterized by Field emission scanning electron microscopy (FE-SEM) images. The FE-SEM images of ZrO₂samples (Zr1-Zr6 in Table3) and particle size distributions were shown in Fig.1and Fig. 2, respectively. According to Fig. 1a,by the gel medium was formed with the TEA: CA:Zr mole ratio of 4:4:1, plates like particles with a thickness of 20-30 nm and 500 nm in length was formed. Moreover, the magnified SEM image of this sample (Fig. 1b) shows that some semi-spherical nanoparticles were existed on the surface of some nanosheets. With decreasing amount of CA molecules (TEA:CA:Zr mole ratio =4:1:1, Fig. 1c, 1d) plate-like morphology with relatively higher thickness and length than Fig. 1

was also obtained. Upon adding EG solvent to sample 1 (Zr6 sample), morphology was changed from highly packed nanosheets to separated nanosheets. Each nanosheets is composed of spherical nanoparticles with average size of 38 nm (Fig. 1e, 1f). With using TEA as chelating agent (without CA and EG molecule, TEA:Zr⁴⁺=4:1, Fig. 1g), highly packed particles with the diameter of 45.79 nm and spherical morphology were obtained. In the case of using only CA molecule as chelating agent (CA:Zr⁴⁺ =4:1, Fig. 1h), low agglomerated particle with diameter of 58.52 nm with spherical morphology was observed. By using conventional Pechini method (CA:EG:Zr mole ratio =4:4:1, Fig. 1i) agglomerated particles with average size of ~60 nm was formed. Consequently, FESEM image exhibit with changing different mole ratio of chelating agent various morphologies can be obtained. Furthermore, with using TEA in Pechini method, in all cases only nanosheets consisted of spherical nanoparticle were obtained.

When tri ethanol amine was applied, this molecule can coordinate on the high density of zirconia planes. Thus, the steric hindrance of tri ethanol amine molecules cause the crystal grow limit in one direction. And so, during the crystal growth, the planes grow along the special crystal axes of zirconia. In other hand, citric acid in the nucleation stage can grow initial nuclei in all direction and thus, semi-spherical zirconia nanoparticles were obtained in this case. Schem. 2 show the formation mechanism of ZrO₂ nanostructures with various morphologies.

3.2. Thermal analysis (TG) and differential thermal analysis (DTA)

Fig. 3 shows the TG–DTA curve of Zr₁ precursor before calcination process. A weight loss nearly 10% with endothermic peak can be observed in the temperature range from 50-130 °C correspond to the removal of the adsorbed water. A considerable weight loss of 40% in the temperature range from 250-620 °C accompanied with two exothermic peaks (380 °C and 550 °C), could be related with the combustion of organic molecules (poly ester) and formation of crystalline phases [38]. Another exothermic peak at above 620 °C could be attributed to the phase transformation of zirconia [39]. According to TG/DTA analysis, three calcination temperatures (380 °C, 490 °C, and 550 °C) was selected for calcining step.

3.2. X-ray diffraction and phase structure study

Fig. 4 shows the XRD patterns of Zr_1 sample calcined at different temperatures (380 °C, 490 °C, and 550 °C). The sample calcined at 380 °C (Fig. 4a) were in well agreement with the standard JCPDS card No.01-080-2155. The peaks appeared at around $2\theta = 30.02^\circ$, 34.96° , 50.20° , 59.67° , 62.77° , 73.78° and 81.61° are assigned to the (101), (002), (200)(112), (211), (202), (004), (213) reflections of zirconia, respectively. These planes are associated with the d-spacing values of 2.95, 2.56, 1.80, 1.53, 1.47, 1.28 and 1.17 Å, respectively, and indicates formation of pure tetragonal phase without any impurities (especially, monoclinic phase) for the sample calcined at 380 °C. The lattice parameter of pure tetragonal zirconia was calculated to be $a = b = 3.62$ Å and $c = 5.20$ Å. Furthermore, the diffraction peaks of Zr_1 samples calcined at 380 °C showed significant broadening attributed to the small crystallite size of this sample. The calcination temperature for the formation of t-zirconia in current work was clearly lower as compared with other so-gel method [35, 36, Table 1]. It should be mentioned that all samples prepared with different mole ratios have similar t-phases at 380 °C. Thus, Fig. 4a are typical XRD of these samples. The average crystallite size of the samples calcined at different temperature was estimated with Scherer's formula [42, 43]:

$$D = \frac{0.89\lambda}{\beta \cos \theta}$$

where D is average crystallite size, β is the full width at half maximum (FWHM) of the diffraction peak, λ is the wavelength of X-ray ($\lambda = 0.1540$ nm), and θ is the Bragg angle. The crystallite size of Zr_1 sample calculated from (101) plane was 5.6 nm.

With increasing calcination temperature from 380 °C to 490 °C and 550 °C, mixtures of tetragonal and monoclinic phases were observed (Fig. 4b-c). The crystallite size value of all samples, prepared at various calcination temperatures, was summarized in Table 4. This table shows an obvious increasing the crystallite size by increasing calcination temperature from 380 °C to 490 °C and 550 °C. This result shows pure tetragonal phase was only formed in a small crystallite size ranges (lower than 10 nm [35, 36]).

The volume fractions of monoclinic and tetragonal phases at different calcination temperatures were calculated using the peak intensity ratio formula [44]:

$$V_m = \frac{1.311 x_m}{1 + 0.311 x_m}$$

and X_m is given by:

$$X_m = \frac{I_m(1\bar{1}1) + I_m(111)}{I_m(1\bar{1}1) + I_m(111) + I_t(101)}$$

where V_m is the volume fraction of the monoclinic phase, and I_m represents the diffraction intensity of the lattice planes. The percentage of m-phase for samples calcined at different temperatures are compared and summarized in Table 4. According to this table, with increasing calcination temperature from 380 °C to 550 °C, The % m was increased from zero to 78.66%.

3-3. FT-IR spectroscopy studies

Fig. 5 shows the FT-IR spectra of precursor before calcination process (gel) (a-f) and after calcination process (g-i). The formation of polyester gel was confirmed by the existence of -OH (3416 cm^{-1}), -CH₂ (Asymmetric stretching vibration at 2970 cm^{-1} and symmetric vibration at 2970 cm^{-1}), -COOH (Asym. vibration at 1710 cm^{-1} and sym. vibration at 1628 cm^{-1} of polyester) and -C-H wagging vibrations (1380 cm^{-1}) in the Fig. 5a [45].

Before calcination, the FTIR spectrum of the Zr-TEA complex (Fig. 5c) exhibits several characteristic bands of TEA ligand, e.g. the broad peak with round tip centered at $\sim 3400\text{ cm}^{-1}$ (OH stretching vibration) and other bands around $2930\text{--}2880\text{ cm}^{-1}$ (C-H stretching of -CH₂-group), 1667 cm^{-1} (O-H overtone), 1393 cm^{-1} and 1278 cm^{-1} (C-H bending). The peaks at 1077 and 924 cm^{-1} were attributed to C-N and C-O stretching, respectively while the band at 794 cm^{-1} was ascribed to -CH₂ rocking [34]. The small absorption peaks at 525 and 413 cm^{-1} might be due to M-O or M-N stretching of metal coordinated with TEA ligand.

After calcination process, spectra of all samples (Fig 5.h-j) showed new abroad band at $490\text{--}745\text{ cm}^{-1}$ that are assigned to Zr-O-Zr bond [47]. Moreover, the bands at 3416 cm^{-1} (-OH), 3249 cm^{-1} (-NH), 2916 cm^{-1} (-CH₂) 1628 cm^{-1} (-COOH) confirmed a small amount of organic molecules (polyester) was existed in sample that prevented nanoparticles to be agglomerated [46]. The Zr₁ samples calcined at 380 °C (Fig. 5g) show an abroad band at around 458 cm^{-1} and 626 cm^{-1} , which is attributed to absorption bands of t-ZrO₂. Fig 4.i,h illustrates the formation mixture of tetragonal and monoclinic phases, due to the existence of bands at 422 , 575 and 732 cm^{-1} are attributed monoclinic ZrO₂ phase, and the bands at 489 , 444 cm^{-1} are associated with tetragonal ZrO₂ phase [47-49]. These mixtures of phase were obtained at calcination temperature of $490\text{--}550^\circ\text{C}$.

3.5. Photoluminescence studies

Fig. 6 shows the photoluminescence spectra of the Zr_1 at different calcination temperatures (380-550°C). The PL spectra registered in excitation wavelength of 300 nm. The Zr_1 nanopowders show two prominent peaks in the UV and blue region of the electromagnetic spectrum with emission wavelength centered around 328 nm and 440 nm corresponding to excitation at 300 nm as shown in Figure 6. The intense zirconia emission peak at 328 nm in the samples calcined at 380 °C can be due to the ionized oxygen vacancies (F^+ and F^- centers) from the conduction band [50]. Here UV emission can arise as a result of the radiative recombination of a photogenerated hole with an electron occupying the oxygen vacancy.

In zirconia nanopowders prepared by modified Pechini method, the groups coordinated on the surfaces of the zirconia such as $Zr(OH)$ could form electronic states in a mid-gap of zirconia insulator (dielectric material). They may form dangling Zr bond during the condensation and dehydration process. Because of these surface states, dangling bonds and other factors (such as the influence of O_2 in the atmosphere), there are many Zr^{4+} defect sites. The existence of such defect Zr^{4+} sites (more likely at irregular near-face sites) may photogenerate Zr^{3+} centers by electron capture. The excitation band corresponds to the spectral range of the extrinsic absorption of ZrO_2 caused by pre- existing defects.

It is reported that there is formation of surface traps in the material leading to electron transitions, even with a small amount of excitation energy [51]. The PL emission band observed at 440 nm might be due to the transitions from the surface trap states in the conduction band to lower energy levels close to the valance band. This is in agreement with the results reported in the literature [50-56]. The broadband may be due to the inhomogeneous broadening from a distribution of surface or defect states because of the narrow particle size distribution [50].

In the curve c (Fig. 6) the defects formed by the interfacing sites between the phases monoclinic and tetragonal, configure a wide band gap of the ZrO_2 that contain new energy levels and electron tramps that can producing a wide asymmetric blue emissions at 450 nm.

The variation in the PL intensity and evidence of new peak at 358 nm (Fig. 6b, c) with calcination temperature is effected by the crystallinity of the nanopowders and the quenching mechanism by OH groups. This clearly indicates the reduction of OH groups and increase in Zr–O–Zr, by increasing the treatment temperature, as is evident in the FT-IR spectrum (Fig. 6).

3.6. Photocatalytic activity

The photocatalytic activity of the sample Zr₁ was determined by photodegradation of methyl orange (MO) dyes under UV lamp. It should be mentioned that Zr₁ sample has high efficiency in degradation of MO dye as compared to other samples. Due to this issue, here, the photocatalyst property of this sample was only reported. The photocatalytic degradation of anionic dye such as methyl orange was carried out by t-ZrO₂ nanopowders at optimized conditions (C_0 of dyes = 10 ppm and 25 mg nanopowders) and different pH (Fig. 7). Literatures show that the isoelectric point (pH_{ie}) of zirconia was 4.1 for t-ZrO₂ sample [56-60]. At pH lower than pH_{ie} , the surface of zirconia is positive and at pH higher than pH_{pzc} , the surface of nanostructures is negative. When the solution pH equals 3, the photocatalytic degradation quickly completed (Fig. 7), due to the surface of zirconia nanostructures are positively charged, and this is favorable for the adsorption of MO dye by surface hydroxyl groups over the ZrO₂ particles. Furthermore, the proportion of azo structure of MO dye transformed into quinoid structure at strong acidic environment, and this structure is more likely to be degraded. With increasing the pH value, degradation rate decreases, due to the fact that the acid sites tend to adsorb a large amount of hydroxyls and the activity sites of the catalyst were destroyed, leading to the decrease of the photocatalytic activity [57]. Fig. 8a shows the photodegradation of MO dye by only UV and UV with Zr₁-380 sample. The degradation of 100% was observed after 100 min exposure of UV irradiation at pH=3.

The effect of calcination temperature on the photocatalytic performance was also studied. The degradation performance of Zr₁ sample calcined at 490 °C, 550 °C, was found to be 45%, 62%, after 100 min, respectively (Fig. 8b, c). It is clearly seen that the rate of photocatalytic degradation of pure tetragonal ZrO₂ is higher than mixture of both, tetragonal and monoclinic phases (Fig. 7 and Fig. 8), due to high photocatalytic nature of tetragonal phase of zirconia and lower amount of electron-hole trap as compared with the sample calcined at 490-550 °C (Fig. 6). Moreover, photocatalyst efficiency strongly depends on the light harvesting capability, the prolonged life of photo-induced electron-hole pairs, surface defect state, the presence of oxygen-deficient, facilitate the reactant accessibility to surface active sites, the small Z size distribution, surface area, special morphology and reduction of band gap. As shown in Fig. 9, these absorption peaks in the UV-vis spectra decrease and gradually disappear with irradiation time, due to

degradation ability of the homo- and hetero-poly aromatic rings present in the MO dye molecules (Table 2).

It was reported that the small nanoparticle size facilitated the movement or transfer of electrons, and holes generated inside the crystals to the surface [58]. Moreover, the increasing of structural defects had great influence on the trapping electrons or holes, efficient separation of photogenerated electrons and holes. The mechanism of photocatalytic degradation process can be explained as follows:

The first step at photocatalytic degradation of dyes involves the absorption of dye molecules by surface hydroxyl groups on ZrO_2 . When nanocrystalline zirconia is excited by UV light, the radiation has an energy equal or greater than the band-gap energy of ZrO_2 , thus, the radiation is absorbed, and electrons are transported from the valence band (VB) to the conduction band (CB), corresponding to the formation of a pair of a hole center in the valence band and trapped electron center in the conduction band. The as-formed electron-hole (e^- - h^+) pairs immigrate to the surface of photocatalyst, and react with the oxygen molecules adsorb on ZrO_2 . Thus, superoxide anion radicals ($*\text{O}_2^-$) and hydroxyl radicals ($*\text{OH}$) was produced according to equation 1-5. These radicals react with dye molecules and lead to degradation of MO dyes. The degradation mechanism of photocatalytic over the ZrO_2 nanostructure is shown in Schem.1.

The pseudo first-order kinetics for MO dye was determined by plotting $\ln(C/C_0)$ as a function of time.

$$\ln\left(\frac{C}{C_0}\right) = -k_1 t$$

Where, C is the concentration of dye at reaction time, t is the irradiation time, k is the pseudo-first-order rate constant, C_0 is the initial concentration of dye. Fig.10 shows the plot of C/C_0 versus time. The slopes of all curves show the photodegradation reaction was first order rate constant. Table 5 appeared that the rate of photodegradation of sample calcined at 380 °C is higher than that of samples calcined at 490°C and 550 °C.

4. Conclusions

1. The nanocrystalline zirconia was synthesized using the modified Pechini method.
2. Pure tetragonal zirconia nanosheets were synthesized by reducing calcinations temperatures from 550 °C to 380 °C with CA: TEA: Zr^{4+} mole ratio of 4:4:1 .
3. FESEM images showed that the thickness of as-prepared nanosheets with CA: TEA: Zr^{4+} =4:4:1, 380 °C/2 h was between 15-20 nm.
4. SEM image showed that by changing CA: TEA: Zr^{4+} mole ratio from 4:5:1 to 4:0:1, the shape of sample was varied from nanosheets to semispherical nanoparticles
5. Zirconia nanosheets exhibit a blue emission centered due to the existence of the zirconium-oxygen ion complex. The broad fluorescence band of nanosheets seems to be mostly caused by inhomogeneous broadening from a distribution of surface or defect states.
6. The photocatalytic performance of different phases of zirconia was investigated for degradation of methyl orange dyes. The ZrO_2 calcined at 380 °C sample comparatively appeared higher photocatalytic performance than other samples (ZrO_2 -490 °C and ZrO_2 -550 °C), where can be explained due to the small size and higher amount of t-phase of ZrO_2 -380 °C sample.

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Figure captions

Fig.1. FESEM images of ZrO_2 samples (a, b) Zr_1 (c, d) Zr_2 (e, f) Zr_6 (g) Zr_3 (h) Zr_4 (i) Zr_5

Fig.2.The histograms ZrO_2 samples (a) Zr_3 (b) Zr_4 (c) Zr_5 (d) Zr_6

Fig.3. TG–DTA curve of precursor (gel).

Fig.4. XRD patterns of Zr_1 samples calcined at (a) 380 °C (b) 490 °C (c) 550 °C.

Fig.5. FT-IR spectra of samples before calcination process (a) Zr_1 (b) Zr_2 (c) Zr_3 (d) Zr_4 (e) Zr_5 (f) Zr_6 (g) 380 °C(h)490 °C (i)550 °C.

Fig.6. PL emission spectra samples at different calcination temperatures a: 380 °C c:490 b: 550 °C.

Fig.7. effect of pH on Photocatalytic degradation at the optimized conditions (MO (C_0 = 10 ppm), photocatalyst = 25mg).

Fig.8. Photocatalytic degradation of methyl orange dye over (a) the only UV and UV with t- ZrO_2 nanoparticle calcined at (a) 380 °C (b, c) 490 °C and 550 °C

Fig.9. UV-visible absorption changes of methyl orange solution in the presence of the t- ZrO_2 sample.

Fig.10. The plots of $\ln C/C_0$ versus reaction time

Schem.1.The schematic mechanism of photocatalytic degradation of MO dyes in the presence of ZrO_2 nanopowders.

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Schem. 2 Formation mechanisms of ZrO_2 nanostructures.

Table 1: Comparison of the method synthesized of t- ZrO_2 at different calcination temperature

Table 2: Dyes structure

Table3: The summary of parameter conditions

Table 4: Crystal phase of as synthesized samples obtained from XRD result.

Table 5: Effect of calcination temperature on the rate constant of the Photocatalytic degradation of MO dye using ZrO_2 nanopowders.

Table 1: Comparison of the method synthesized of t-ZrO₂ at different calcination temperature

Method preparation	Temperature calcination (°C)	References
sol-gel method	490	[35]
sol-gel method	900	[36]
Spray pyrolysis	600	[37]
Silica bath/co-precipitation	900	[38]
Single emulsion-assisted direct precipitation	800	[39]

Table 2: Dyes structure

Dye	Molecular structure	$\lambda_{\max}$ (nm)
Methyl orange (Azo structure)	$(\text{CH}_3)_2\text{N}-\text{C}_6\text{H}_4-\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{SO}_3^-$	511
Methyl orange (Quinoid structure)	$(\text{CH}_3)_2\text{N}^+-\text{C}_6\text{H}_4-\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{SO}_3^-$ H	

Table 3: The summary of parameter conditions

Sample code	ZrOCl ₂ .8H ₂ O	CA	TEA	EG	morphology
Zr ₁	1	4	4	-	nanosheets
Zr ₂	1	1	4	-	nanosheets
Zr ₃	1	0	4	-	Agglomerated nanoparticles
Zr ₄	1	4	-	-	Spherical nanoparticles
Zr ₅	1	4	-	4	Semi-spherical nanoparticles
Zr ₆	1	4	2	2	nanosheets

Table 4: Crystal phase of as synthesized samples obtained from XRD result.

Sample	Crystallite size(nm)	Phase	Percentage of Monoclinic phase	Percentage of tetragonal phase
Zr ₁ -380	5.6	t		100
Zr ₁ -490	20.9	t+m	21.34	78.66
Zr ₁ -550	24.0	t+m	54.46	45.53

Table 5: Effect of calcination temperature on the rate constant of the Photocatalytic degradation of MO dye using ZrO₂ nanopowders.

Catalyst	K (10 ² min ⁻¹)	R ²
Zr ₁ -380 °C	1.96	0.9297
Zr ₁ -490 °C	0.63	0.9839
Zr ₁ -550 °C	1.01	0.9625

Fig.1. FESEM images of ZrO_2 samples (a, b) Zr_1 (c, d) Zr_2

Fig.1. FESEM images of ZrO_2 samples (e, f) Zr_6 (g) Zr_3 (h) Zr_4 (i) Zr_5

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Fig.5 (a-f). FT-IR spectra of samples before calcination process (a) Zr₁ (b) Zr₂ (c) Zr₃ (d) Zr₄ (e) Zr₅ (f) Zr₆

Fig.5 (g-i). FT-IR spectra of Zr₁ sample calcined at (g) 380 °C (h) 490 °C (i) 550 °C.

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