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RESEARCH PAPER

CeO_2/ZnO Ceramic Nanocomposites, Synthesized via Microwave Method and Used for Decolorization of Dye

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ABSTRACT

CeO_2/ZnO nanocomposites were synthesized by microwave method that is the fast process. One of an eco-friendly solvent, ethylene glycol were used the effect of time and power of irradiation were investigated on morphology and size of nanoparticle. Prepared CeO_2/ZnO nanocomposites are characterized with X-ray diffraction (XRD) analysis, Transmission Electron Microscopy (TEM), Fourier Transform Infrared (FT-IR) spectroscopy, Scanning Electron Microscopy (SEM) and UV–Visible absorption spectroscopy. For this nanocomposites photocatalyst test were applied against four colors, Methyl violet, Methylene blue, Rhodamin b and Erythrosine. the percent of decolorization for each color under UV light after 120 min were 92% and 60% were obtained respectively.

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INTRDUCTION

Water pollution is defined as the presence of toxic chemicals and biological agents that exceed what is naturally found in the water and may pose a threat to human health and the environment [1, 2]. In recent years, implementation of water reclamation and reuse is gaining attention rapidly worldwide due to the water scarcity occurred as a result of climate change and poor water resource management [3, 4]. Access to clean water is becoming an ever-increasing problem in an expanding global economy and population countries. Water pollution becomes a critical issue around the world, and carbon-based chemical substances contribute to major pollution in water. The management of water pollution has been mainly focused on several strategies involving adsorption, membrane separation and coagulation [4-7].

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For wastewater treatment, there are four different methods that categorized as advanced oxidation processes (AOPs): photocatalysis, direct decomposition of water, electrochemical processes and ozone treatment[8]. For its interesting inherent properties, photocatalysis is more attractive. The photocatalytic process can be applied for removal of various organic pollutants at the ambient temperature and pressure [9, 10]. In this process, semiconductor photocatalyst absorbs enough energy from the light and generates the highly reactive oxygen species, i.e. superoxide anions ($^{\bullet}O^{2-}$) and hydroxyl radicals ($^{\bullet}OH$). Then generated reactive species attacks to the organic pollutants and decompose them [8, 11]. Till now, various semiconductors have been applied for photocatalytic process [12-15]. ZnO nanostructures are one of the most promising

and low-cost photocatalyst. Zinc oxide has some electronic and stability based disadvantages that restrict its photoelectrochemical applications. Adding another nanostructure to the ZnO and formation of nanocomposite can improve its photoactivity and thermal stability during catalyst preparation [16, 17]. Huo et al have synthesized temperature sensitive PNIPAM@ ZnO/C composite as a controllable photocatalytic activity for the photocatalytic degradation of tetracycline under different temperatures. PNIPAM@ZnO/C was prepared by cross-linking polymerization technology with N-isopropyl acrylamide as a functional monomer, N,N'-methylene bis(acrylamide) as a cross-linking agent, ammonium persulfate as an initiator, and 3-(trimethoxysilyl) propyl methacrylate as a surface modification reagent[18].

Nano-sized copper doped TiO_2/ZnO was synthesized via sol-gel method by Shafeeyan et al. they investigated photoactivity of prepared nanocomposite by measuring decolorization efficiency of methyl orange (MO) and methylene blue (MB). Results showed that the designed photocatalyst can degrade 85.45% and 73.20% of MO and MB under optimal conditions respectively[19].

Song et al have prepared three-dimensional (3D) Ag/ZnO assemblies with porous nanosheets. The as-prepared 3D Ag/ZnO architectures were studied as a photocatalyst for decolorization of organic pollutants from aqueous solution. Results showed that nearly 100% of 10 ppm 4-nitrophenol was degraded just for 25 min[20].

In this study, CeO_2/ZnO nanocomposite is synthesized via hydrothermal method at the different condition. The prepared nanocomposite is characterized with XRD, TEM, SEM, EDS, and VSM. Finally, CeO_2/ZnO nanocomposite is applied as a photocatalyst to decolorization of Methyl violet (MV), Methylene blue (MB), Rhodamin b (RB) and Erythrosine as organic pollutants in aqueous solution under UV light.

MATERIAL AND METHOD

$Ce(NO_3)_3.6H_2O$ and $Zn(CO_2CH_3)_2.2H_2O$ ethylene glycol was purchased from Merck and all the chemicals were used as received without further purifications. XRD patterns were recorded by a Philips, X-ray diffractometer using Ni-filtered CuKα radiation. Fourier transform infrared (FT-IR) spectra were detected by means of Nicolet Magna-550 spectrometer in KBr pellets. The UV–Vis diffuse reflectance analysis of the as-prepared CeO2/ZnO nanocomposite was done by applying a UV–vis spectrophotometer (Shimadzu, UV-2550, Japan). SEM images were obtained using a TESCAN instrument model Mira3 to taking images, the samples were coated by a very thin layer of Pt to make the sample surface conductor and prevent charge accumulation, and obtaining a better contrast. GC-2550TG (Teif Gostar Faraz Company, Iran) were used for all chemical analyses. Transmission electron microscopy (TEM) image was achieved via a Philips EM208 transmission electron microscope with an accelerating voltage of 200 kV.

Synthesis CeO_2/ZnO nanocomposites

0.23 mmol $Ce(NO_3)_3.6H_2O$, 0.23 mmol $Zn(CH_3COO)_2.2H_2O$ and 10 ml ethylene glycol were mixed together on the magnetic stirrer with 2 rpm. at room temperature After dissolving precursor and acquired the clear solution, transported that on a microwave oven. Different conditions were applied that listed in Table 1. Obtained sediment was washed with distilled water for twice and dry at 60 °C for 24 h. For achieving CeO2/ZnO nanocomposites, sediment was calcined at 700 °C for 3 h. To illustrate the path of synthesis CeO_2/ZnO nanocomposites, the schematic was drawn that showed in Fig. 1.

Preparation photocatalytic test

Photocatalytic activity of CeO_2/ZnO nanocomposite was performed by monitoring the decolorization of methylene blue and rhodamine B in aqueous solution, under irradiation with UV light. Decolorization process was performed in

Table 1. Different reaction condition.

Sample No.	Ce (mmol)	Zn (mmol)	ethylene glycol (ml)	Time of irradiation (min)	Power of irradiation (watt)
1	0.23	0.23	10	5	900
2	0.23	0.23	10	10	900
3	0.23	0.23	10	15	900
4	0.23	0.23	10	10	750
5	0.23	0.23	10	10	900 cyclic
6	0.23	0.23	10 PG*	10	900

PG*: Propylene glycol

a quartz photocatalytic reactor. Photocatalytic decolorization was carried out with 10 ppm solution of dyes and 0.05 g of nanocomposites. Then the mixture was placed in photoreactor under UV light and stirred for 20 min at dark to ensure proper adsorption desorption equilibrium of the dye molecules on the surface of the nanostructures required to act as an efficient photocatalyst. To maintain the solution oxygen saturated throughout the reaction, the air was blown into the vessel via a pump. Then CeO_2/ZnO was separated from the 5 ml samples, taken from the degraded solution at various time intervals, using 5 min centrifuging at 12,000 rpm. The dye concentration was determined with aid of a UV–vis spectrophotometer.

RESULT AND DISCUSSION

Fig. 2 showed the XRD pattern of CeO_2/ZnO nanocomposites. As well as shown, verifying attendance of both cubic phases of CeO2 (JCPDS No. 34-0394, space group: Fm-3m) and Hexagonal phase of ZnO (JCPDS No. 80-0075, space group: P63mc). XRD pattern also showed that there are no impurities. Crystalline sizes are calculated from Scherrer equation, Dc= Kλ/βCosθ, where β is the width of the observed diffraction peak at its half maximum intensity (FWHM), K is the shape factor, which takes a value of about 0.9, and λ is the X-ray wavelength (CuKα radiation, equals to 0.154 nm) were about 24 nm for CeO_2/ZnO nanocomposite [21,22]. The FT-IR spectrum of as-prepared CeO_2/

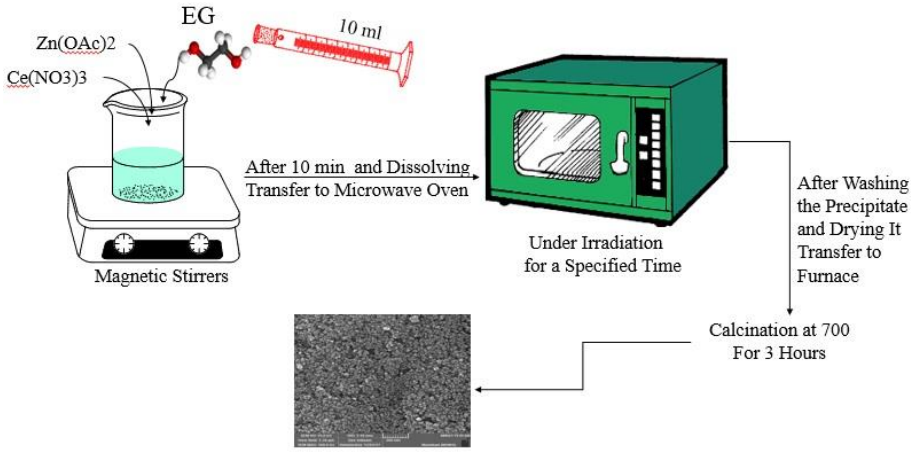

Fig. 1. Schematic diagram of the formation CeO_2/ZnO nanocomposites.

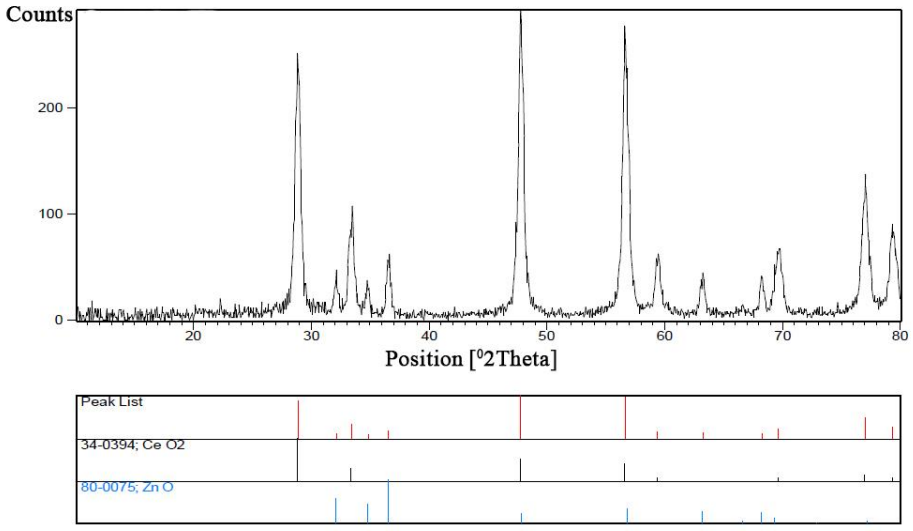

Fig. 2. XRD pattern of CeO_2/ZnO nanocomposite synthesized at 10 minute and 900W

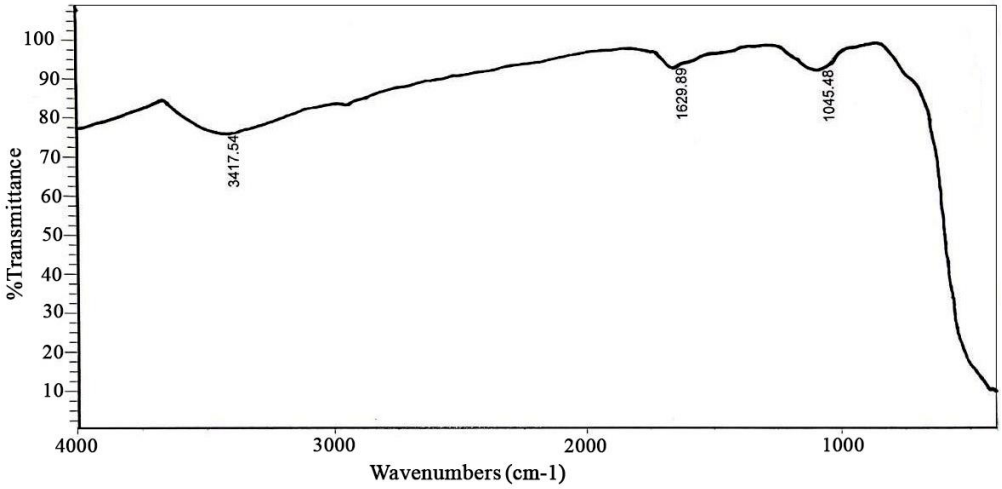

Fig. 3. FT-IR spectra of CeO_2/ZnO nanocomposite prepared at 10 minute and 900W

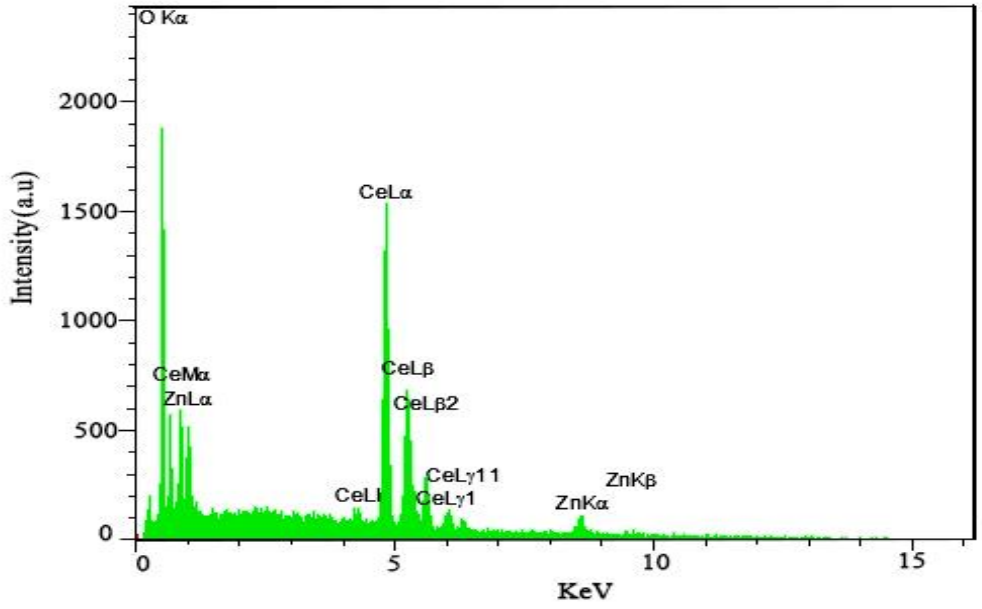

Fig. 4. EDS spectra of CeO_2/ZnO nanocomposite.

ZnO nanocomposite showed in Fig. 3. The peak at 3448 and 1633 cm^{-1} both related to O–H of water attraction to the surface of nanocomposite. A wide peak at about 500 refers to stretching vibration M-O, Ce-O and Zn-O respectively. To confirm the presence of the desired elements in the product EDS analysis was recruited. The result as shown in Fig. 4 confirms the presence of Zinc, Cerium and oxygen elements which indicates the high purity of the product.

For investigation the effect of different conditions such as a power of irradiation, solvent, cyclic irradiation and time of irradiation on the morphology of nanocomposites, SEM analyzed were employed. Fig. 5 illustrated SEM images prepared at 5 (a, b), 10 (c, d) and 15 (e, f) min under irradiation of microwave by 900-watt power. As can be seen from 5 to 15 the size of the nanoparticle increase due to the agglomeration of nanoparticle created by increases in the temperature and the high activity of nanoparticle. For study effect of power on the morphology of nanoparticle two powers (900 and 750 watt) were applied.

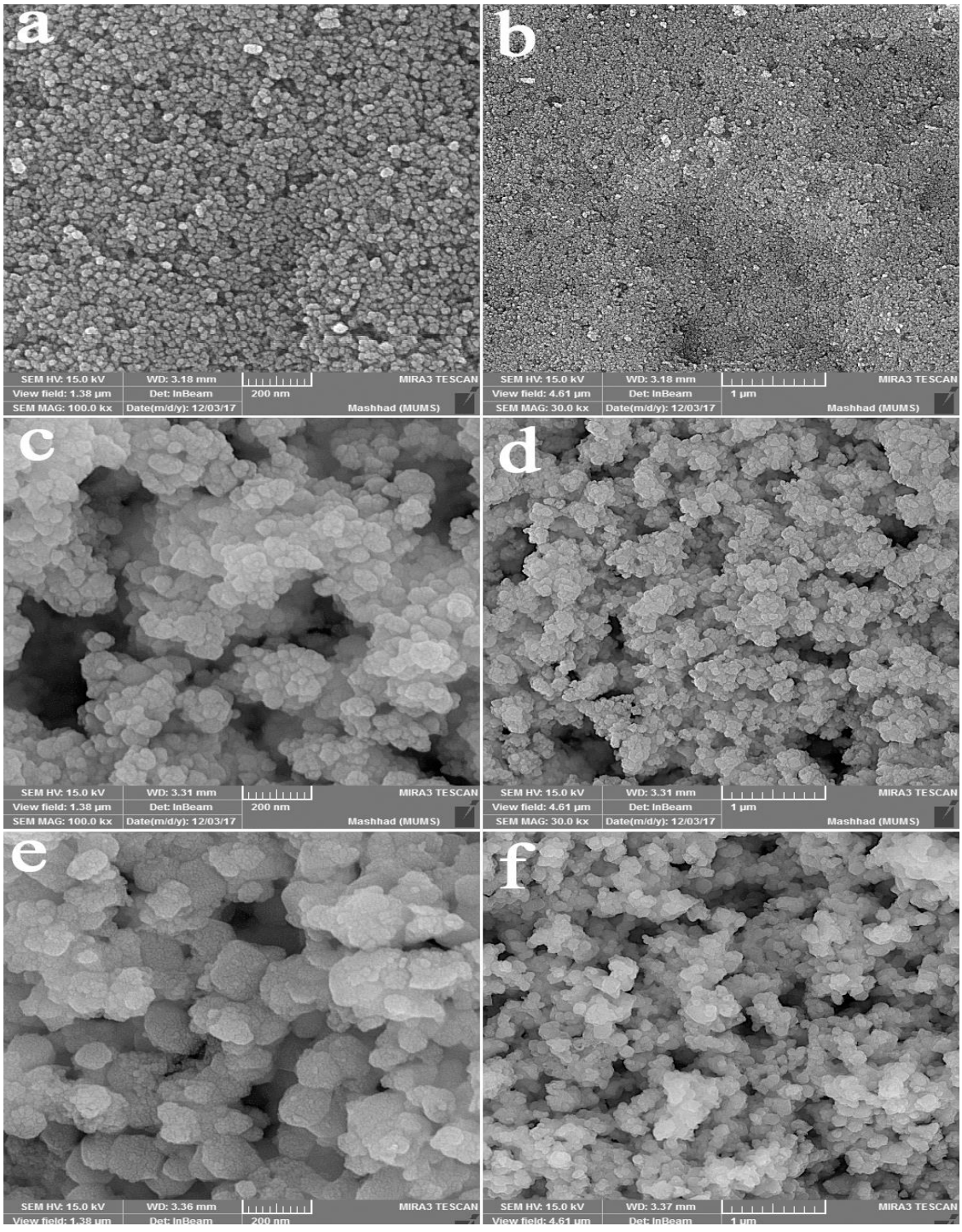

Fig. 5. SEM images prepared at 5 (a, b), 10 (c, d) and 15 (e, f) min under 900 watt.

In Fig. 6 (a-c), typical histograms of the particle diameters for samples no 1-3 are displayed. For nanoparticle synthesized at 5, 10 and 15 min the particle size about 22, 35 and 85 nm respectively.

Fig. 7 showed SEM images of nano composites prepared under 750 watt irradiation for 10 min. As shown, the size of nanoparticles prepared under 750-watt not much different in comparison

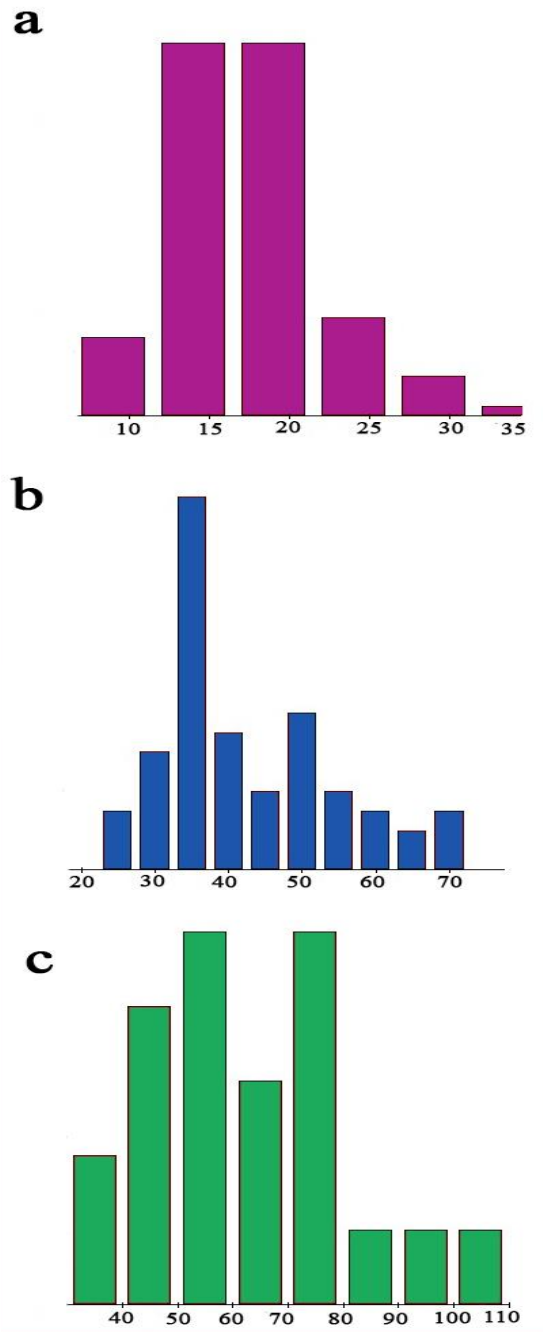

Fig. 6. Particle size distribution of samples number1-3, a) 5 min, b) 10 min and c) 15 min

to nanoparticles prepared under 900 watt; but nanoparticles synthesized under 750 watt were more monodispersed that can be attributed to low of the temperature. One of parameter investigated in microwave method is cyclic irradiation. Fig. 8 (a, b) illustrated nanocomposite prepared by cyclic irradiation for 10 min as ½ power (30 min off, 30 min on); due to the increases of time and time for growth, the nanoparticles agglomerated and the size increased. The SEM images of different solvent were showed in Fig. 8 (c, d); when used propylene glycol as a solvent, the size of nanoparticle were increase due to the high activity of synthesized nanoparticle and in continues agglomeration. By examining the size and morphology of the nanoparticles, the sample was prepared at 900 watts for 5 min were selected as the optimum sample. To describe the exact morphology and particle size of the as-synthesized nanocomposite product, TEM images of an optimum sample were taken. The TEM images show that nanoparticles have a spherical shape, and are adhered together. Furthermore, Fig. 9 demonstrates that the average particle size about 25nm. Diffuse reflectance spectra (DRS) of CeO_2/ZnO nanocomposite in Fig. 10 illustrates optical absorption capability in the region from 200-600nm. The optical energy band gap of the nanocomposite was determined using the relation [23]:

$$(\alpha h\vartheta) = C(h\vartheta\text{-}Eg)^{1/2} \quad (1)$$

For this nanocomposite, two band gap estimated: 3.28 eV for CeO_2 and 3.5 eV for ZnO. Calculated band gap reveals that prepared nanocomposite can be used as a good catalyst in photocatalytic process. Table 2 listed some various band gap was reported for each CeO_2 and ZnO. To investigation photocatalytic activity of synthesized nanocomposite, the decolorization of MV, MB, RB and Erythrosine in aqueous solution under UV irradiation were done. Fig. 11 reveals that prepared nanocomposites catalyze process effectively. When pollutants expose to prepared CeO_2/ZnO nanocomposites and UV light, decreasing of pollutants concentration begins. The photocatalytic efficiency calculates via [24]:

$$\text{Color removal } (\%) = (C_0 - C_t/C_0) \times 100 \quad (2)$$

Where C_0 (mg L^{-1}) is the initial concentration of MV, MB, RB and Erythrosine in solution, and C_t (mg L^{-1}) is the concentration of MV, MB, RB and Erythrosine at any irradiation time (min). The photocatalyst process was performed for a period of 120 min. Photocatalytic activity was measured in neutral pH, which was about 98%, 95%, 92% and 60% decolorization for MV, Erythrosine, MB and RB respectively.

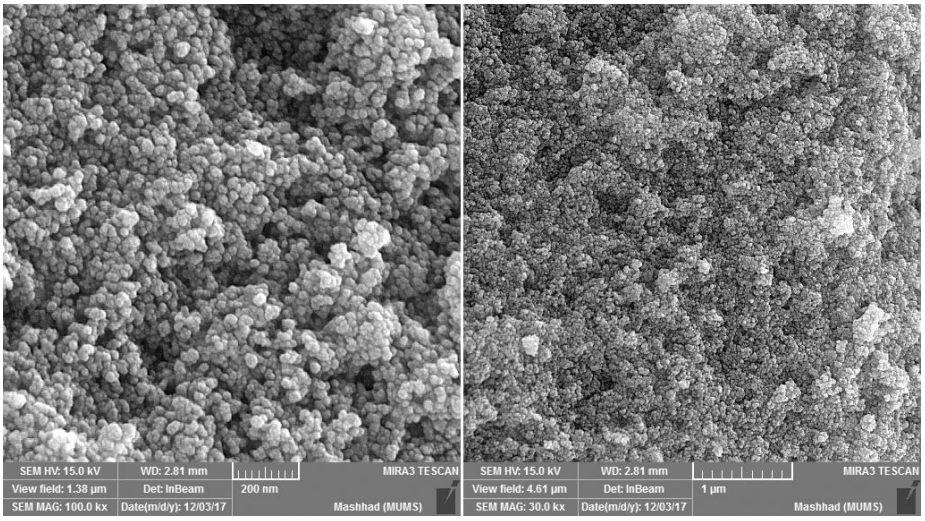

Fig. 7. SEM images of nano composites prepared under 750 watt irradiation for 10 min in two magnification

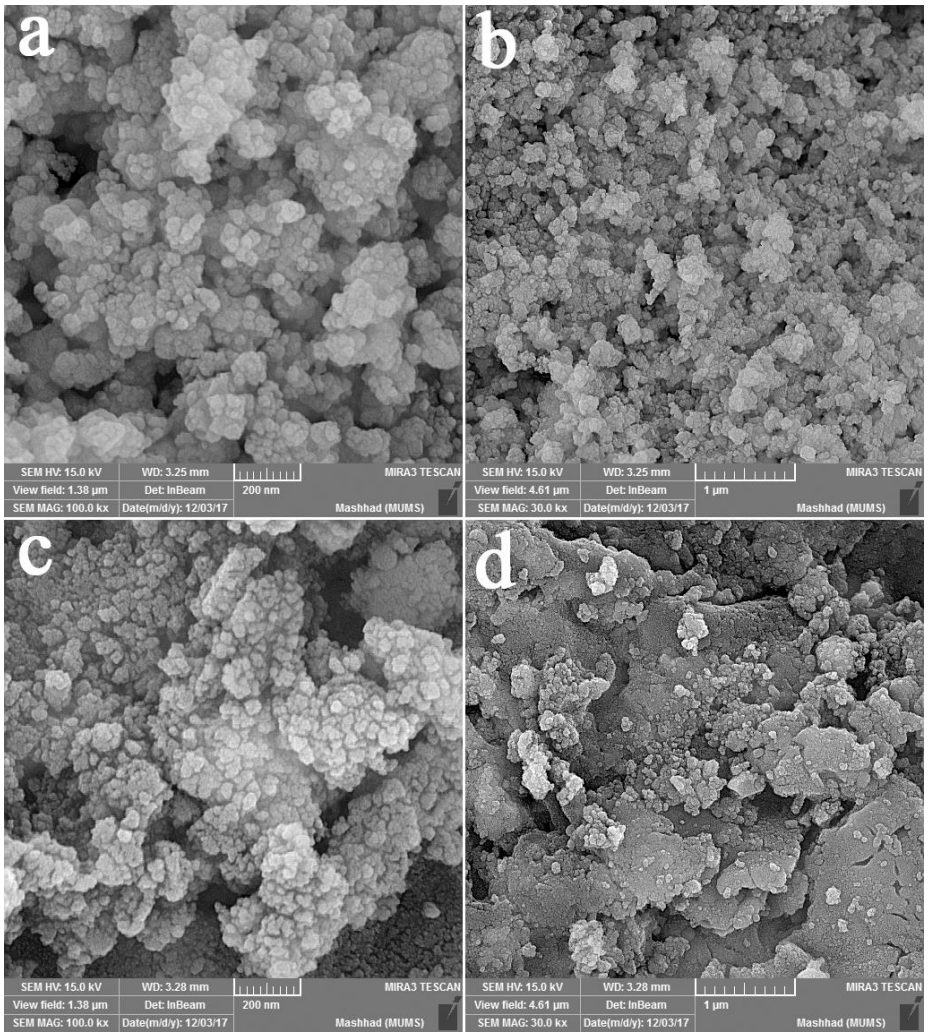

Fig. 8. SEM images of CeO_2/ZnO nanocomposite prepared under 900 watt irradiation for 10 min (a,b) cyclic irradiation and (c,d) propylene glycol used as solvent

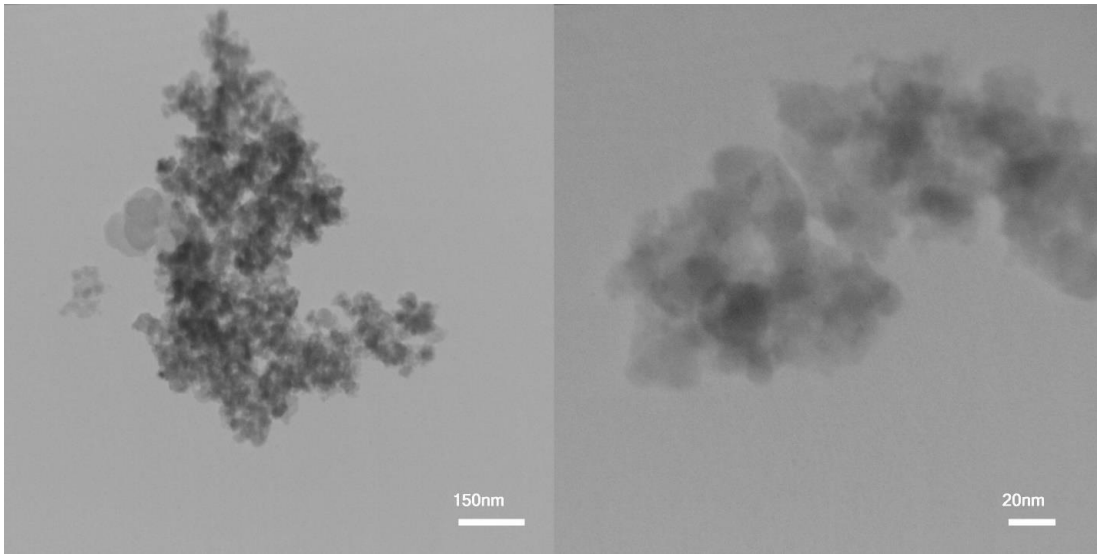

Fig. 9. TEM image of CeO_2/ZnO nanocomposite

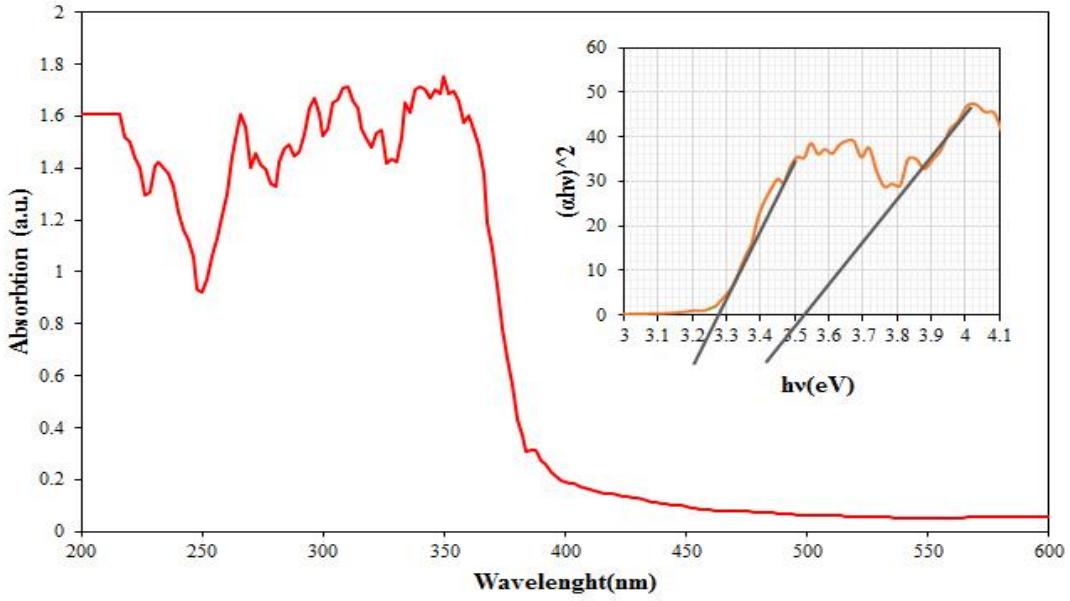

Fig. 10. Diffuse reflectance spectra (DRS) of CeO_2/ZnO nanocomposite prepared at 10 min 900W

Table 2. Band gap (eV) reported for CeO_2 and ZnO.

Nanoparticle	Band gap (eV)	Reference
CeO_2	3.57	[21]
	3.35	[22]
	3.07	[23]
ZnO	3.13 to 4	[24]
	3.3	[25]
	3.6	[26]

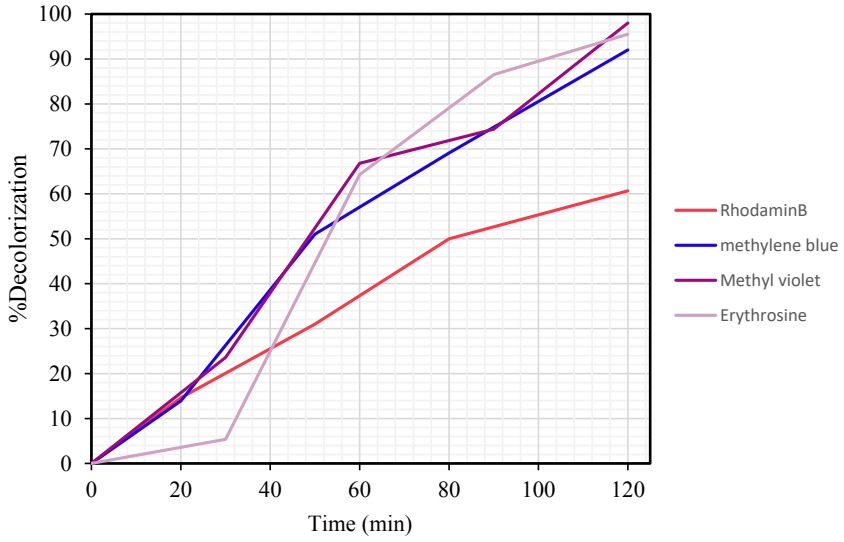

Fig. 11. Photocatalytic activity of CeO_2/ZnO nanocomposite on decolorization of colors

CONCLUSION

In this work, CeO_2/ZnO nanocomposites synthesized with microwave method. Different conditions were applied. Effects of type of solvent, time and power of irradiation were investigated. Eventually, the sample prepared at 900 watt irradiation for 5 min were chosen as an optimum sample and used as a photocatalyst. Photocatalyst proses were done to dyes and 98, 95, 92 and 60% decolorization were obtained for Methyl violet, Erythrosine, Methylene blue and Rhodamin b respectively.

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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