



Evaluating the Efficiency of a Trace Amount of Zr Dopant on Photocatalytic Activity of TiO₂ in Decolorization of Azo Dye

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Abstract

Zr-doped TiO₂ nano photocatalyst obtained with a various trace amount of Zr, by using the sol-gel method. Several spectroscopic techniques applied to characterize the structures and properties of nano-photocatalyst. It founded that the effect of doping Zr ions to the TiO₂ lattice led it to improve the surface properties and decreasing the particle size of nano-photocatalyst. Therefore, it causes increasing specific surface area and photocatalytic activity as compared with pure TiO₂. The results revealed that there was an inverse relationship between the growth of the crystallite size of the nano photocatalyst and the decline of the molar ratios of Zr. The photocatalytic activity of the nano photocatalyst employed for the decolorization of Congo red as an Azo dye in the aqueous solution under UV irradiation in a batch reactor. The results exhibited that the TiO₂/Zr_{0.0004} brings the best photocatalytic activity.

Keywords:

TiO₂/Zr Nanocomposite;
Decolorization;
Sol-Gel;
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1- Introduction

One of the most important sources of environmental contamination is dye pollution. Heterogeneous photocatalysis is an interesting method employed for the thorough removal of pollution under solar or artificial light irradiation [1-2]. TiO₂ based photocatalysis enjoys such advantages as low cost, non- toxicity and chemical stability, making it as a good choice for the efficient oxidization and degradation of dye pollutants [3]. It has been shown that photon absorption of anatase TiO₂ is only limited to the UV range due to its large band gap (3.2ev) [2]. A good way to improve photocatalytic activity is through the incorporation of dopant into TiO₂ lattices, introducing additional energy levels and defects into the microstructure of the TiO₂[4]. There are different modification techniques to reduce band gap; these include doping with noble metals like Au, Ag and Pt [5-9], non- precious metals such as Fe, Cu, Cr, Mn, W, Ru, Ni, Sb [10-14], oxides such as ZnO,ZrO₂,SiO₂ [15-16] and non-metallic elements like N, C, S, F and P [17-19]. Zirconium ions, which act as a kind of dopant in TiO₂, have been found to modify the photocatalytic activity and stabilization of anatase phase at high temperatures [20-22]. Many different methods have been proposed for the preparation of Zr-doped TiO₂ nanocomposites; these are such as mechanochemical doping, co-precipitation, chemical vapor deposition and sol-gel methods. However, it must be noted that most of the above-mentioned techniques are time consuming and require expensive equipment. The sol-gel method has the unique advantage that it can synthesize at low temperature, under high purity and easily controlled reaction condition [23-24], its simplicity and possibility of the synthesis of nano photocatalyst at low temperature with high purity [25]. Recently, according to properties of Zr, TiO₂ was used with specific molar ratios of Zr for different applications [26].

In this research, instead of employing the specific molar ratio of zirconium, investigated the effect of trace amounts of zirconium as a dopant in TiO₂ to find the better photocatalytic activity and compare it with pure Titanium dioxide. TiO₂/Zr nanocomposites were prepared using different trace molar ratios of Zr. The nanocomposites were prepared using the sol-gel method and the TiO₂/Zr nano photocatalyst is characterized by several spectroscopic techniques. Such as Fourier Transform infra-red spectroscopy (FT-IR), X-Ray diffraction (XRD), Scanning Electron Microscopy (SEM),

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Brunauer-Emmet-Teller (BET) analysis and High Resolution Transmission Electron Microscope (HR-TEM). Then the photocatalytic activity of the synthesized nano photocatalyst was investigated for the decolorization of Congo red in the aqueous solution and under UV irradiation in a batch reactor.

2- Experimental

2-1-Materials and mMethods

Chemicals reagents used in this work were Titanium Tetra Isopropoxide (TTIP, 97%) (Panreac Co, Spain), Zirconium Tetrachloride ($ZrCl_4$, 98%) (Merck), Hydroxy Propyl Cellulose (HPC) (Merck), Congo red (Merck), Cetyl Trimethyl Ammonium Bromide (CTAB) (Merck), Nitric Acid (65%) (Merck) and Absolute Ethanol (99%)(Bidestan Co; Iran).

2-2- Preparation of Nanocomposites

TiO_2 sample was synthesized by employing the Sol-Gel method. The TiO_2 sol was obtained at room temperature and TTIP was utilized to serve as a precursor in some stages. Initially, TTIP was dissolved in absolute ethanol, with molar ratio of TTIP to ethanol being (1:75) and then stirred for 15 min in order to get a precursor solution; following that, 0.1 g HPC was added as a stabilizer, and the mixture was continuously stirred for 15 min to obtain a yellow transparent Sol (Sol 1). To get To Zr doped- TiO_2 , Zr sol was developed in the following way: First, zirconium tetrachloride was allowed to be dissolved in absolute ethanol (alcoholic solution of $ZrCl_4$), with the molar ratios of Zr to ethanol being (0.0002:1.52, and 0.0004:1.52). It stirred for 5 min and respectively added to the mixture of absolute ethanol, Nitric acid and 0.1 g CTAB (Sol 2). They were added slowly in a dropwise manner during 30 min into the precursor (Sol 1) and then stirred continuously for 15 min to get a transparent Sol. This Sol was aged at room temperature for 48 h in order to develop a Gel. Then, the developed Sol was allowed to be dried in the air and heat-treated for 10 min at 100 °C to remove the water and organic solvents; after that, it was calcinated in an electric furnace at the temperature of 525°C for 4 h. Following the heat treatment method, the samples were naturally cooled. Synthesized samples were coded; the codes specified have been brought in the following Table 1.

Table 1. Sample code.

Photo nano catalyst	Sample code
TiO_2	T
$TiO_2/Zr_{0.0002}$	TZ2
$TiO_2/Zr_{0.0004}$	TZ4

2-3- Characterization of Nanocomposites

FT-IR spectra were got as KBr pellets, with the wave number range of 400–4000 cm^{-1} (Thermo Nicolet Nexus 870FT-IR spectroscopy). Phase identification of the nanocomposites was carried out using XRD from SCIFERT-3003 PTS with CuK α radiation, in the range of 0 to 100 (2θ), at room temperature. SEM (HITACHI S-4160) investigated the morphology and microanalysis of the nanocomposites. Varian UV–Vis spectrophotometer (Cary UV-Vis 100) was employed for the determination of the degradation concentration. The BET measurement was got by utilizing (Quantachrome Nova 2200). The nanostructure of the samples was observed by drawing on TEM (Philips EM 208 electron microscopy).

2-4- Photocatalytic Activity Measurement

Photocatalytic degradation experiments were conducted in a cubic wooden reactor. Six (4 W) UV_C Lamp (Osram) was used to serve as a light source; they were installed inside the reactor (Figure 1). At first, 0.01 g of the catalyst was added to a 25ml aqueous solution of Congo red, which had an initial concentration of 5 ppm.

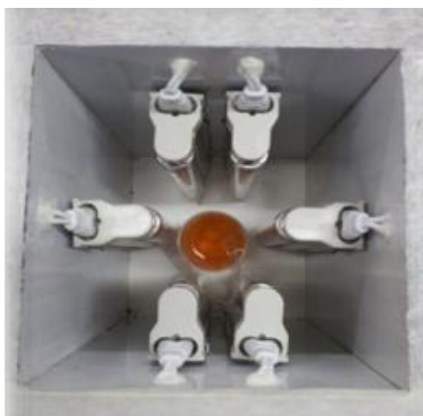
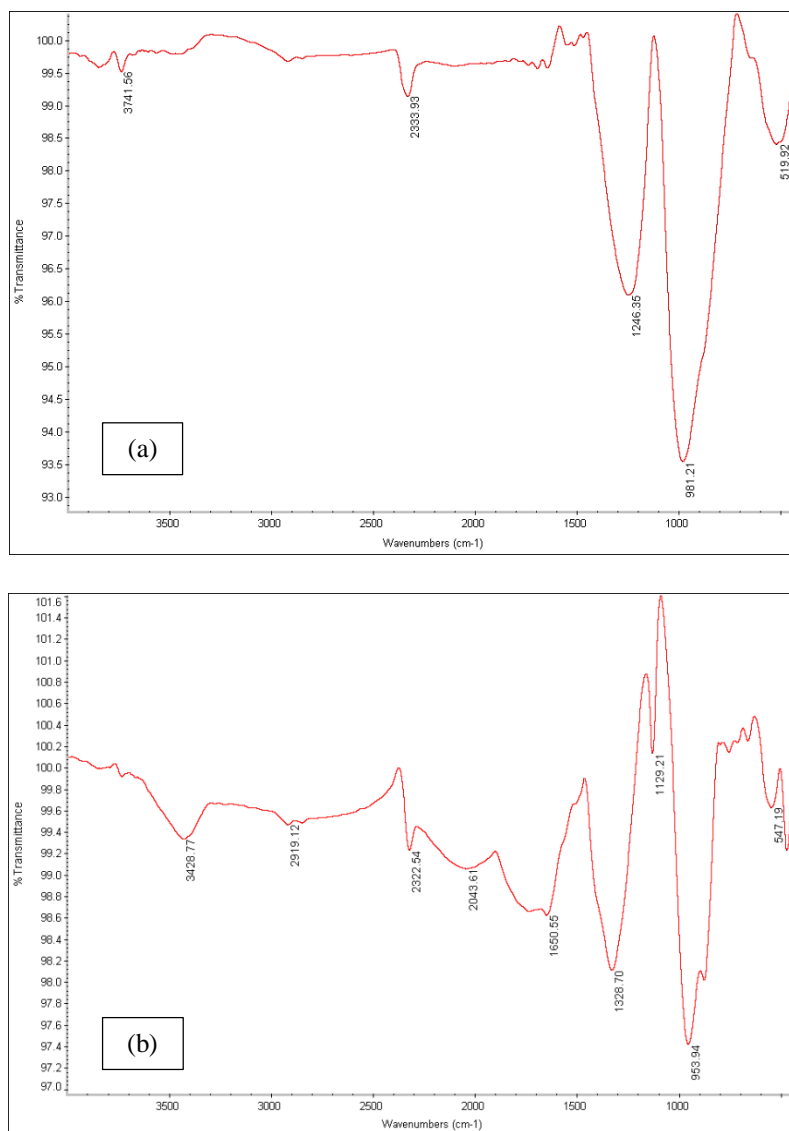


Figure 1. Scheme of the photoreactor system. UV-C Lamp (6 (4 W) UV-C Lamp (Osram)).

3- Results and Discussion

3-1- FT-IR Spectroscopy

FT-IR spectra of the TiO_2 and TiO_2/Zr nanophotocatalyst with various molar ratios of Zr were obtained and the results are shown in (Figure 2) in the wave number range from 4000 to 400 cm^{-1} .



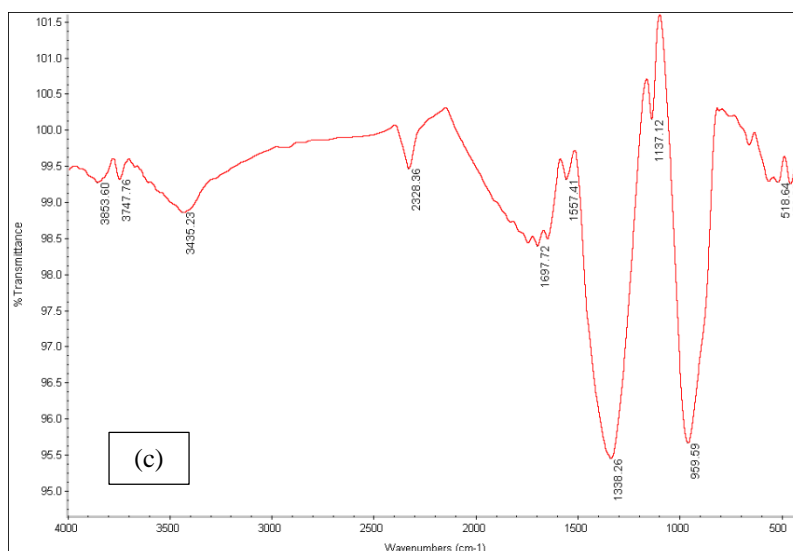


Figure 2. FT-IR spectra of powder samples of nanocatalyst (a) T, (b) TZ2(c)TZ4.

Table 2. FT-IR spectroscopy results Of TiO_2 and Zr doped- TiO_2

Bending stretching vibration (BSV)	O-Ti-O, Ti-O-Ti, Zr-O-Ti, O-Zr-O Zr-O-Zr	$\sim 530\text{-}675\text{ cm}^{-1}$
	H-O-H	$\sim 1615\text{ cm}^{-1}$
stretching vibration (SV)	Ti-O, Zr-O, Zr-OH Ti-OH	$\sim 890\text{-}1260\text{ cm}^{-1}$

3-2- SEM

Surface morphology of the synthesized nano photocatalyst was characterized; their SEM were carried out and the results were shown in seen in (Figure 3). SEM pictures show the effect of metal doping on particle size and morphology. The average particle size of each samples in the X-axis [(a) {35.16 nm}(b){27.34}(c) { 23.44 nm}] was reported. SEM revealed that the particle morphology of TZ4 was the best.

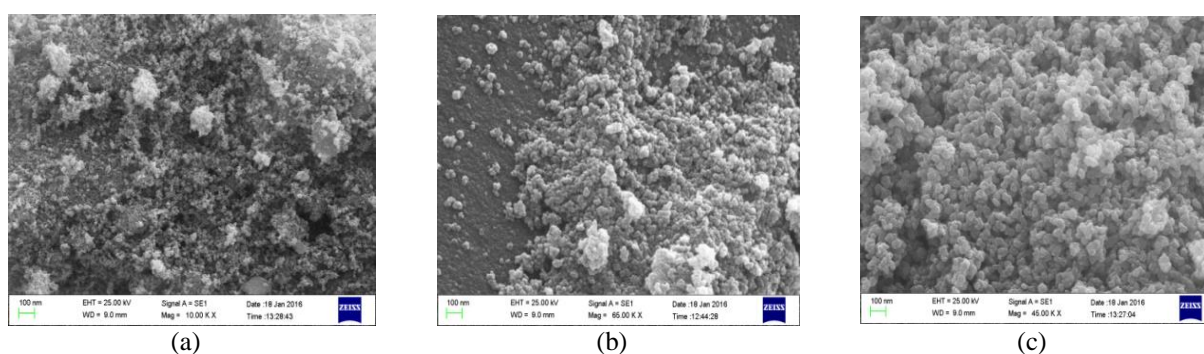


Figure 3. SEM images analysis of catalyst samples of nanocatalyst (a) T, (b) TZ2, (c) TZ4

3-3- XRD

X-Ray diffraction was used to investigate the phase analysis of the samples prepared by the sol-gel process. The XRD patterns of catalysts calcinated at $525\text{ }^{\circ}\text{C}$ can be observed in (Fig.4). Five significant lattices were found to be related to anatase (25.2,37.8,48and 55), rutile (27.5,39,45.2and 51.1), zirconium titanium oxide (30.3,36.5,53.7,62.8and

77.9), titanium oxide (16,31.2,36.3,38,45 and 78) and zirconium oxide phases (36.2,50.2 and 69). Anatase phase, as the main phase, was found in all samples. The crystallite size of samples a–c was found to be and $T=61.4$, $TZ2=59.1$ nm, $TZ4=58.5$ nm, respectively, using the Scherrer equation.

$$d = K\lambda / \beta \cos \theta \quad (1)$$

In this equation, β is the full-width at half maximum (FWHM) of the peak, k is 0.89, λ is 0.154060 nm for $\text{CuK}\alpha$, and d is the average particle size.

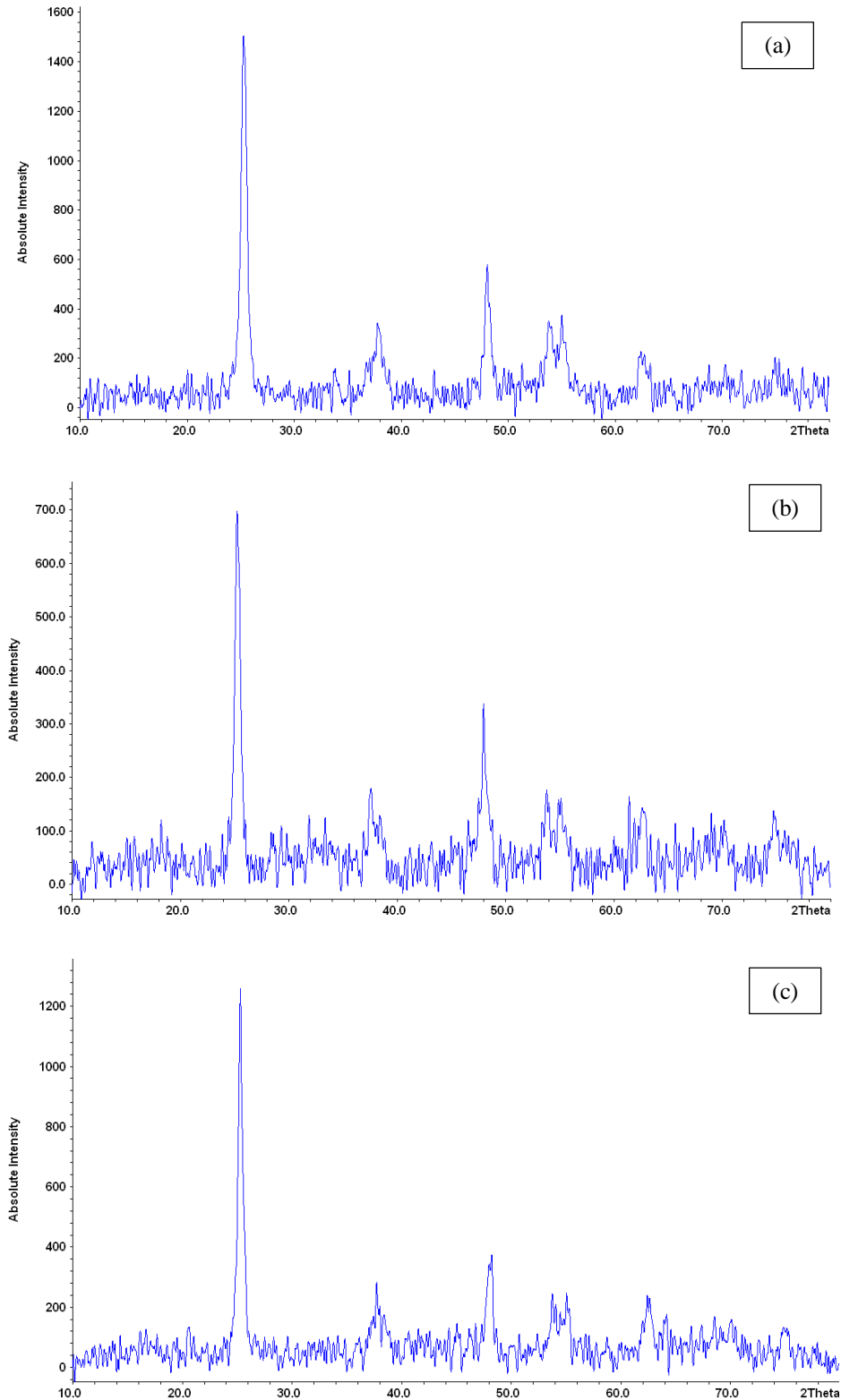


Figure 4. XRD patterns of powder samples (a) T, (b) TZ2, (c) TZ4.

3-4- Photocatalytic Activity

The effect of different amounts of dopant on decolorization of Congo red (5 ppm) was observed in the aqueous solution under UV irradiation, results shown in (Fig.5). As can be seen, with the photocatalytic activity in samples 1–3, the absorbance of Congo red would be reached to 0 after different times, with (T{145 min}, TZ2{90 min}, and TZ4 {75 min} of irradiation. TZ4 could be an effective photocatalyst.

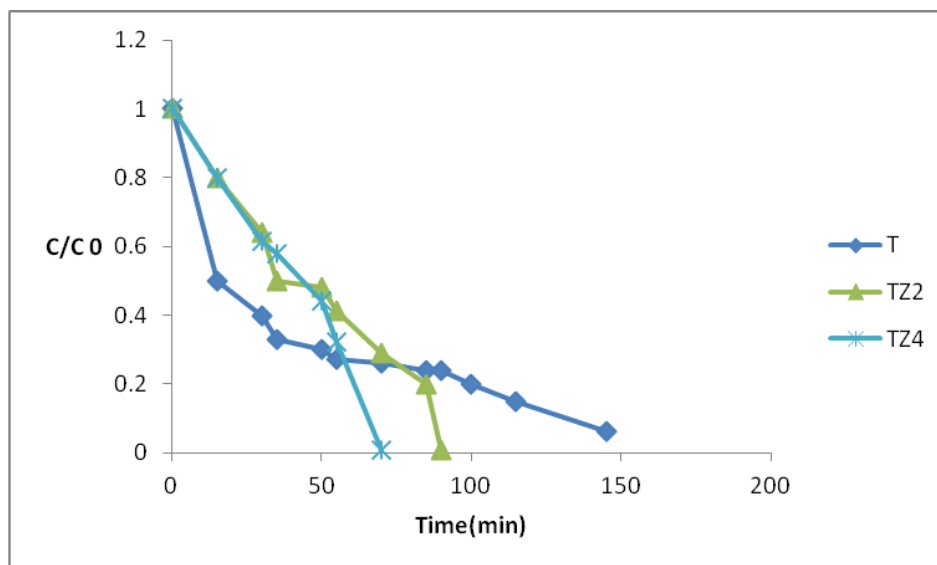


Figure 5. The Photocatalytic activity of powder samples T, TZ2, TZ4.

3-5- BET- Surface Area Analysis

The data related to the BET-surface of all samples can be seen in table 3. The data revealed that by enhancing the molar ratio of Zr, the surface area was increased.

Table 3. BET - Surface Area Analysis

Samples	T	TZ2	TZ4
Surface area (m ² /g)	128	140	182

3-6- TEM

The nanostructure of the samples was observed by TEM (Philips EM 208 electron microscopy); the results are shown in (Figure 6). As can be seen, when the molar ratio of Zr was increased the structures were not aggregated.

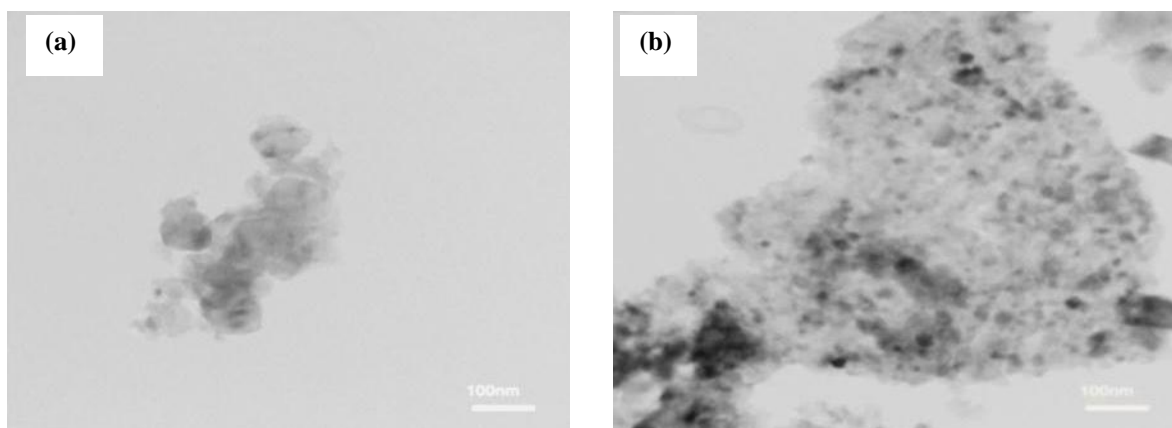


Figure 6. TEM images analysis of catalyst samples. (a) T, (b) TZ4.

4- Conclusion

The Zr-doped TiO₂ nano photocatalyst was organized with a trace amount of Zr applying the Sol-Gel process. The calcination temperature at 525 ± 5 °C was used. According to results, the TZ4 catalyst was obtained the best results in

photodegradation and 0.004 mol ratio of Zr is the best value of dopant. The SEM images showed that the sample TZ4 was well-ordered, with the good size distribution of particles; therefore, it could be applied for photocatalytic dye decolorization. Furthermore, it was observed that this sample had no aggregation, as compared with other samples and with pure TiO₂. It should be noted that for photocatalytic activity, the particle size of the photocatalyst should be homogeneous and important. The results of XRD revealed that in all Zr-Doped samples, the particle size was decreased. The photocatalytic activity of the synthesized nanocomposite was studied for the decolorization of Congo red as an Azo dye, thereby confirming that photocatalytic activity of TZ4 nanocatalyst was the best. The data obtained by BET showed that by increasing the molar ratio of Zr, the surface area was increased. Results of TEM revealed that the TZ4 had good particle size and dispersion without any aggregation. Therefore, a sample of TZ4 could be regarded to have the best photocatalytic activity in comparison to other samples; also, the absorbance of Congo red solution reached to 0 after 75 min of irradiation.

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