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Sonosynthesis and Characterization of TiO_2/ZrO_2 Nanocomposite and Photocatalytic degradation of Congo red Dye under UV Light

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Abstract

NanoTiO_2, nanoZrO_2 and TiO_2/ZrO_2 nanocomposite were prepared via sol gel method by using ultrasonic irradiation. The precursor sol of zirconium was prepared from an aqueous solution of $ZrCl_4$ and titanium tetra 2-propoxide was diluted by 2-propanol and deionized water The TiO_2/ZrO_2 nanocomposite was synthesized from directly mixing Titanium dried gel into Zirconium gel. The reaction mixture was placed under ultrasonic irradiation probe for 2 hours. The filtrated composite gel was washed and calcinated at 500 °C for 3h in furnace. The FT-IR spectroscopy and the XRD study were exhibited that the crystal structure and purity of the TiO_2/ZrO_2 nano composite FESEM images were indicated the morphology and the average size of the NPs. The mean crystallite size of the NanoTiO_2, nanoZrO_2 and TiO_2/ZrO_2 nanocomposite were determined 57, 19 and 23 nm respectively. The photo-catalytic performance was highly increased when nano-composite of TiO_2/ZrO_2 was used to degradation of Congo red (CR) solution. The TiO_2/ZrO_2 nano composite was shown higher photo-degradation efficiency than the pure nanoTiO_2 and nanoZrO_2.

Keywords: *Nanocomposite, Photocatalyst, Ultrasonic, Zirconia, Titania .*

Introduction

Photo-catalytic material is coming more attractive due to its great potential to solve environmental problem. Combining some semiconductors with different band gaps to form hetero-junctions in photo-catalytic systems has become a primary focus of researchers in recent year because of their

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somewhat unique properties not existed in the individual nano-material arising from the interfacial interaction at the nano-scale. For example, it can efficiently reduce the recombination rate of the photo-generated charge carriers in the use of environmental purification and remediation. It also can significantly enhance the optical adsorption of photocatalyst [1–4]. TiO_2 has proved to be one of the most promising materials for various applications such as solar energy conversion, fuel cells, paints and photo-catalysts, especially in environmental remediation processes, due to its high chemical stability, availability and low cost [5].

Titanium dioxide (TiO_2) has been a well-known photo-catalyst for the degradation of wastewater due to its high photo-catalytic activity absence of toxicity, relatively low cost, and excellent chemical stability under various conditions [6]. When TiO_2 is irradiated by ultraviolet light, electron-hole pairs are generated and then produce a powerful reactive oxygen species, which can decompose most organic compounds. However, TiO_2 can only absorb a small portion of solar spectrum in the ultraviolet region and has high recombination probability of photo-induced electron-hole pairs. The efficient use of solar light becomes an appealing challenge for developing photo-catalysis. One approach for achieving this objective is compositing other materials [7]. ZrO_2 has unique characteristics, such as weak acidity, basicity, red-ox and high thermal stability Since the beneficial physical–chemical properties strongly depend on the particle size, the controlled and reliable preparation of nano-ranged materials represents a particular challenge being reflected by numerous approaches, for instance flame synthesis [8], chemical vapor deposition [9], sol–gel processes [10], hydrothermal synthesis [11] and combustion synthesis [12]. Due to its unique properties ZrO_2 is widely used for gas sensors, ceramics, sorbents and catalysts; concerning the latter, ZrO_2 is particularly employed as catalyst carrier in the selective catalytic reduction of NO by NH_3 [13].

In most cases, the precursors are soluble zirconium salts like $ZrO(NO_3)_2$ xH_2O, $Zr(NO_3)_4$, $ZrOCl_2$ xH_2O and $ZrCl_4$ [14-16] whereas organic zirconium compounds have been used as well [17-19]. Moreover, the sol–gel method allows for the homogeneous mixing of transition-metal ions at a molecular level, which enhances the formation of polycrystalline particles with special properties [20]. The crystalline phase of ZrO_2 strongly influences its catalytic activity, selectivity and photo-degradation [21-23]., The composition of two semiconductors provides a novel approach to achieve more efficient charge separation, an increased lifetime of the charge carriers, and an enhanced interfacial charge transfer to adsorbed substrates [24]. TiO_2 /ZrO_2 binary oxides catalysts have been investigated for their catalytic properties with organic compounds, especially for degradation reactions in environmental remediation {25–33]. Recently, the ultrasonic irradiation has been used extensively to generate nano materials with unusual properties, since it can form particles of much smaller size, higher surface area and more narrow size distribution than those prepared by other methods [34-40].

Experimental

Materials and Preparations

The reagents and solvents were commercially available from Merck Co. and were used without further purification. The IR spectra were performed as KBr disks from 4000 to 400 cm-1 on a Bruker Tensor 27 FT-IR spectrometer. X-ray powder diffraction (XRD) measurements were performed using an X'pert diffractometer (Philips Company) with monochromatized Cu-Kα radiation (λ = 1.54056 Å). The samples were characterized with a Field Emission Scanning Electron Microscope (Hitachi S4160 (Cold Field Emission) with gold coating.

Synthesis of Nano TiO_2

25 ml H_2O_2 solution (%30 v/v) was added slowly to 100 ml mixed solution of 2-propanol and deionized water containing Titanium tetra 2-propoxide (20ml). The pH of the solution was adjusted 1.5 by adding nitric acid solution. After aging time (2 days) the precipitant was filtrated and washed and it was dried at room temperature. The product was calcinated at 500 °C for 3 h in furnace.

$$Ti\ (OC_3H_7)_4 + 4\ H_2O \xrightarrow{H^+} Ti(OH)_4 + C_3H_7OH$$

$$Ti(OH)_4 \xrightarrow{\Delta} TiO_2 + 2H_2O$$

Synthesis of Nano ZrO_2

Firstly $ZrCl_4$ (0. 1 mol, 2.4g) was dissolved in 2-propanol (50ml) to get a precursor solution. 5 ml H_2O_2 solution (%30 v/v) was then dropped into the precursor solution under stirring. The pH of mixture was adjusted 9 by adding ammonium solution (2M) until Zirconium gel {$Zr(OH)_4$} was prepared. After aging and stirring for 2days the ZrO_2 gel was placed under probe of ultrasonic irradiation for 30 min. After filtrating, the Zirconium gel was calcinated at 500 °C for 3 h. The white powder of nano zirconia was produced.

$$ZrCl_4 + 2H_2O_2 \longrightarrow Zr(OH)_4 + 2\ Cl_2$$

$$Zr(OH)_4 \xrightarrow{\triangle} ZrO_2 + 2H_2O$$

Synthesis of TiO_2/ ZrO_2 Nanocomposite

The Titanium precipitant gel was added into Zirconium gel and they were mixed together then the mixtures were irradiated by the probe of ultrasonic instrument for 2h. The mixture was stirred for 48h, then it was filtrated and washed several time. After drying at room temperature, the white precipitated was calcinated at 500 º C for 3h in furnace.

Photo-degradation process

In order to test the photo-catalytic activity of the as-prepared nanoTiO_2, nanoZrO_2 and TiO_2/ ZrO_2 nano-composite catalysts, we were chose Congo red (Formula: $C_{32}H_{22}N_6Na_2O_6S_2$) as a model of water pollution to evaluate the catalytic behavior of the samples. Photo-degradation of 10 parts per million (ppm) Congo red (CR) solution was used to evaluate the performance of, nanoZrO_2, nano TiO_2 and nano TiO_2/ ZrO_2 photo-catalyst. For each condition, 0.075 g of photo-catalyst was dispersed into 150 ml of 10 ppm CR aqueous solution. The 200 ml beaker containing the photo-catalyst and CR solution was placed on a magnetic stirrer plate and a stirrer bar placed in the solution ensured full suspension of the particles throughout the experiment. The photo-catalytic reaction was conducted at room temperature under UV light from a single 15W UV tube at 254 nm positioned horizontally above the liquid surface. The distance between the lamp and the base of the beaker was 10 cm. Each experiment was conducted for 2 h with 5ml sample aliquots extracted every 15 min (Figure 1) .The decomposition of CR was monitored by measuring the absorbance of the aliquot solution at 502 nm (λ max of CR) using the UV–Vis spectrophotometer (HITACHI ,U-3010). The photo-catalytic degradation (PD) was calculated by the following formula:

$$\%PD = \left[\frac{Ao - A}{Ao}\right] \times 100 = \left[\frac{Co - C}{Co}\right] \times 100$$

Where Ao is the initial absorption of CR solution which reached absorbency balance and At is the absorption of the dye solution at the irradiation time (t).

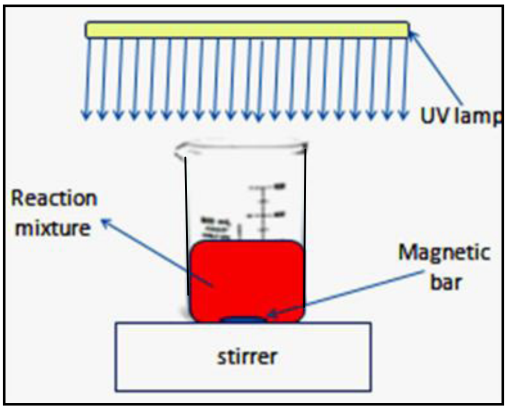

Figure1. Schematic process of photo-degradation.

Results and discussion

FT-IR Analysis

The most significant features of FT-IR spectra of the nanoTiO_2, nano ZrO_2 and TiO_2/ ZrO_2 nano-composite catalysts are shown in Fig. 2 at the wave number range from 4000 to 400 cm^{-1}. In comparing Figure 2 a, b and c, can be assigned the stretching and bending the modes of vibration of TiO_2/ ZrO_2 nanocomposite. Vibrational modes of nano TiO_2 and nano ZrO_2 are summarized in Table 1.

Table1. Identification of Infrared vibrational modes of nano TiO_2 and nano ZrO_2.

Nano TiO_2		Nano ZrO_2	
Wave number (cm^{-1})	Characterization of Vibration	Wave number (cm^{-1})	Characterization of Vibration
3214	O-H symmetry and asymmetry stretching	3447	O-H symmetry and asymmetry stretching
1627	O-H bending	1630	O-H bending
647	Ti –O-Ti vibration	595	Zr–O-Zr vibration

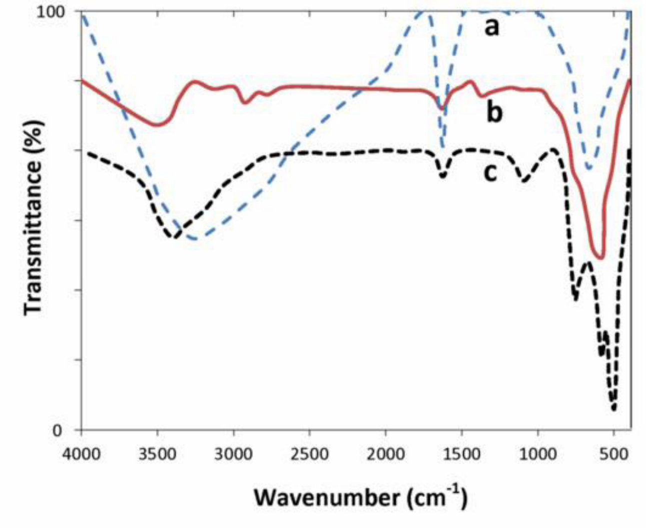

Figure 2. FT-IR spectra of (a) nano $TiO_2$and (b) nano ZrO_2 and (c) TiO_2/ ZrO_2 nanocomposite.

In Figure 2c, the wide peak at 3420 cm^{-1} has been assigned to the OH symmetry and asymmetry stretching vibration of water molecules. The peak at 1627 cm^{-1} resulted from bending vibration of the adsorbed H_2O molecules, which were not removed completely after sol–gel synthesis. The peaks at 756, 683 and 507 cm-1 can be attributed to vibration of the Ti-O-Ti, Zr-O-Ti and Zr-O-Zr bonds respectively. The mass of Zr atom is more than the mass of Ti atom. The vibration frequency of the Zr-O bonds is less than vibration frequency of the Ti-O bonds. According the following formula:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}\ c^{-1}$$

Where: ν is the “wave number”, k is the“force constant” and μ is the “reduced mass” ($\mu = \frac{m1+m2}{m1m2}$ the m_1 and m_2 are the mass of the atoms of bond).

X-ray Diffraction (XRD) analysis

In Figure 3a the peaks indicate the respective Joint Committee on Powder Diffraction Standards (JCPDS) Card No. 21-1272 for TiO_2 and the vertical lines in Figure 3b according to the JCPDS Card No. 37-1484, for ZrO_2. The XRD patterns of the TiO_2/ ZrO_2 nano-composite is shown in Figure 3c the distinct peaks corresponding to TiO_2 and ZrO_2 are observed. It is concluded that both the materials exist in perfect crystalline phases and retain their physical structure and hence confirmed to form a TiO_2/ZrO_2 nano-composite. The TiO_2/ZrO_2 nanoparticles are seen pure. The average size of crystals Dv was also roughly calculated based upon the XRD spectra for quantitative purpose using the Debye - Scherer equation [41].

According to XRD Patterns, the crystallite size of nanoTiO_2, nano ZrO_2 and TiO_2/ ZrO_2 nano-composite are estimated to be 57, 19 and 23 nm respectively.

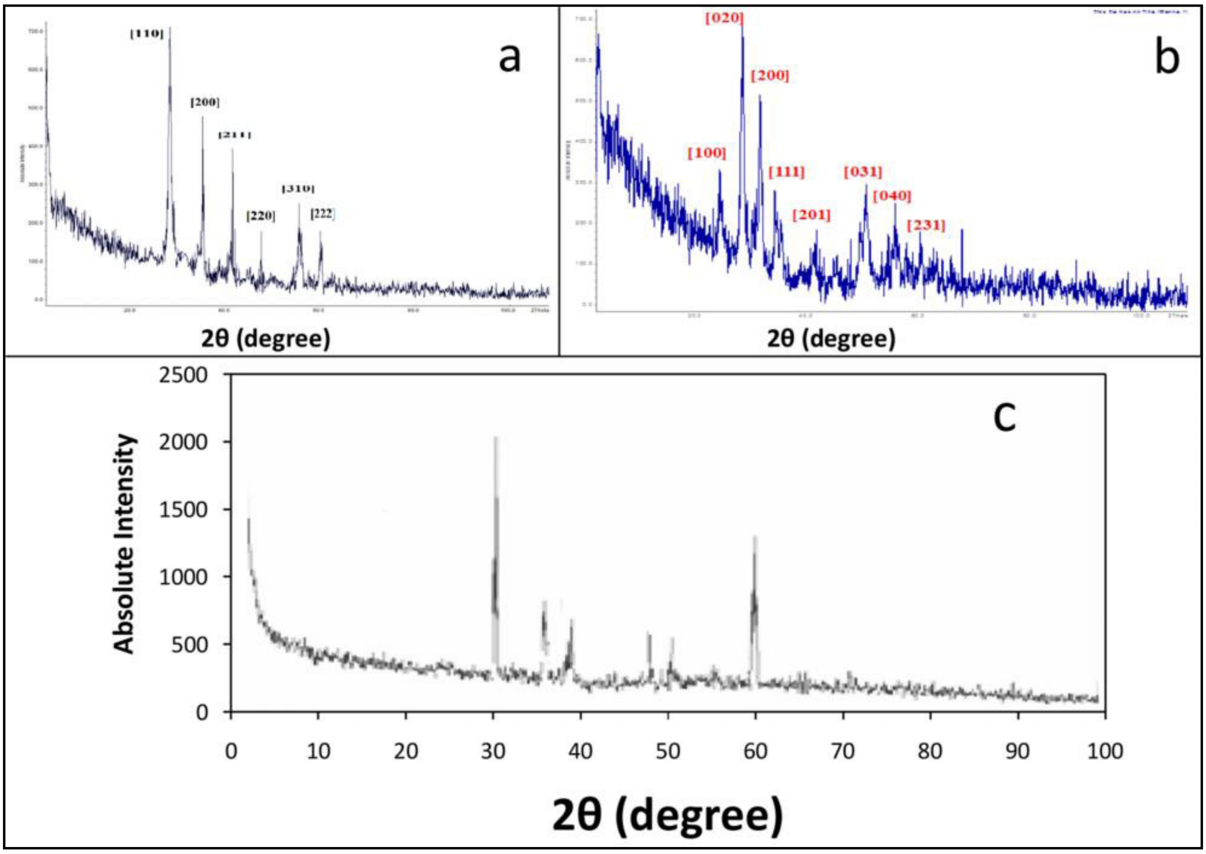

Figure 3. XRD patterns of (a) nano TiO_2, (b) nano ZrO_2 and (c) TiO_2/ ZrO_2 nanocomposite.

FESEM Analysis

The morphology of nanoTiO_2, nano ZrO_2 and TiO_2/ ZrO_2 nano-composite are shown in Figures 4a, b and c respectively. The nano-materials are almost unique. According to Figure 4a the nano TiO_2 samples possess nearby spherical shape and the particles size can be observed between 60-80 nm. In Figure 4b the nano ZrO_2 is shown porous particles and their size are between 28-38 nm. The morphology of TiO_2/ ZrO_2 nano-composite is illustrated in Figure 4c. The particles size is between 35-40 nm.

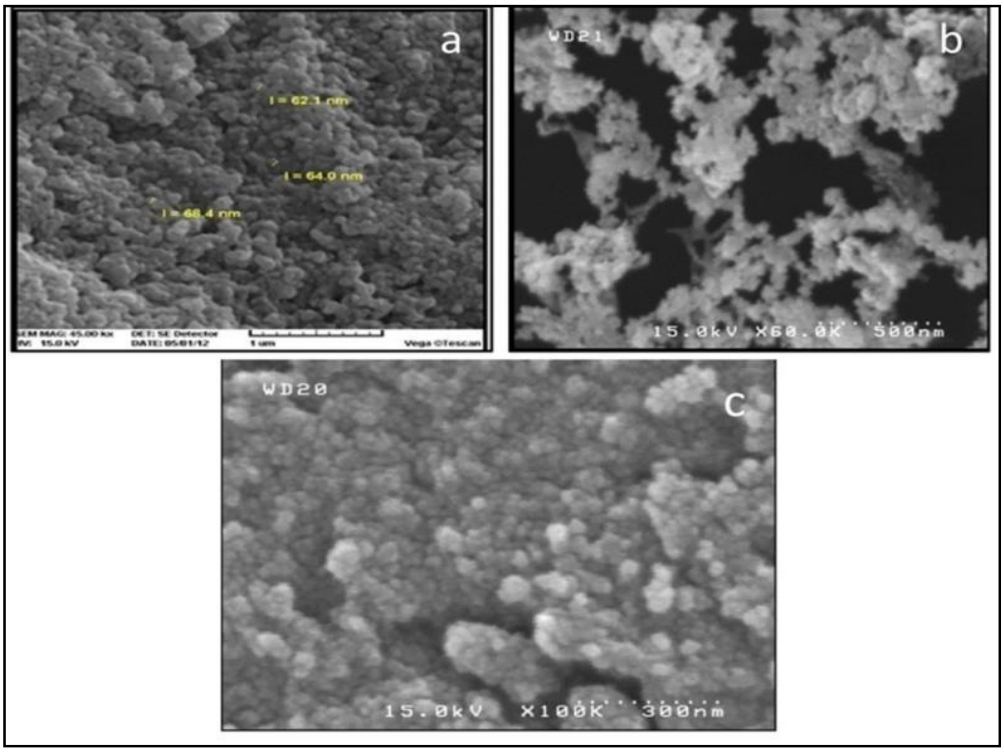

Figure 4. FESEM photographs of a) nanoTiO_2, b) nano ZrO_2 and c) TiO_2/ ZrO_2 nanocomposite.

nano-composite under UV light irradiation is shown in Figure 5. The blank experiment without any catalyst was rarely decomposited with about 10% of degradation of CR within 2

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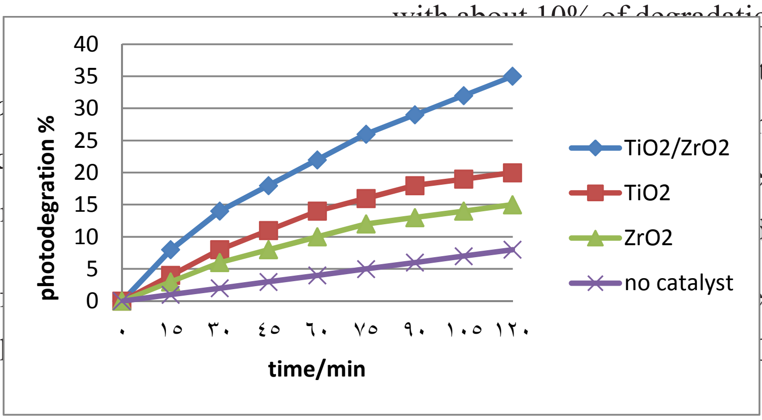

Figure 5. Plot of photo degradation of CR versus reaction time by nanoTiO_2, nano ZrO_2 and TiO_2/ ZrO_2 nanocomposite.

Photo-degradation mechanisms

As shown in Fig6, the TiO_2/ZrO_2 nano-composite can be excited by photons with energy lower than the band gap energy (*Eg*), a great number of electrons are promoted from valence band (VB) to the conduction band (CB) of TiO_2 and ZrO_2, leading to the generation of electron/hole (e^-/h^+) pairs. The electrons transfer from the CB of TiO2 to the CB of ZrO_2, and conversely, the holes transfer from the VB of ZrO_2 to the VB of TiO_2 give rise to decrease the pairs' recombination rate. Obviously, the energy level for electron injection is decreased after composing nano ZrO_2 and nano TiO_2, which increases the driving force for electron injection and hence reduce recombination between electrons and holes. On the other hand, TiO_2 can increase concentration of free electrons in the CB of ZrO_2, this result is reduced the charge recombination in the process of electron transport .All above of results increase the availability of the pairs on the surface of the photo-catalyst and consequently an improvement of the occurrence of red-ox processes can be expected. Therefore, it has concluded the TiO_2/ZrO_2 nano-composite can largely enhance the photo-catalytic efficiency of degradation the organic compounds, and thus, the determination time is shortened and the sensitivity is increased. As shown the below reaction, the products of photo-degradation of CR are safety for environment.

$$C_{32}H_{22}N_6Na_2O_6S_2 + (45+1/2)O_2 \xrightarrow[hv]{TiO_2/ZrO_2} 2\,H_2SO_4 + 6HNO_3 + 32CO_2 + 5H_2O$$

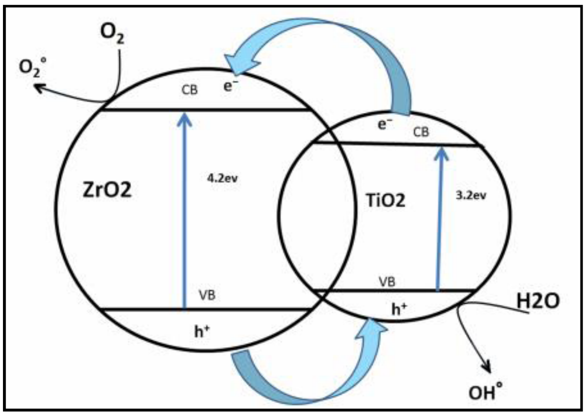

Figure 6. Schematic band gap and electron–hole pair separation of TiO_2/ZrO_2 nano-composite

Particles size and band gap are the effective factors on photo-catalytic activity of nano-catalyst. The photo-catalytic activities of the nano particles are increased when the particle diameter is decreased, where the band gap is more important, because the crystal and particle size of nano TiO_2 are greater than nano ZrO_2 and the nano ZrO_2 has porous structure, but the photo-catalyst property of nanoTiO_2 is more than the nano ZrO_2. The band gap of nano TiO_2 is smaller than ZrO_2 (3.2 and 5.6 eV respectively). The composition of nano-semiconductors is one of the ways to improve the photo-catalytic property. As it is well accepted that the photocatalytic degradation of CR solution accords with a pseudo first- order kinetic [42, 43] the relationship between $-Ln(C/C_0)$ and reaction time were plotted and shown in Figure 7. The rate constant of TiO_2/ZrO_2 nano-composite is three times more than nano TiO_2 and nano ZrO_2

+2NaOH

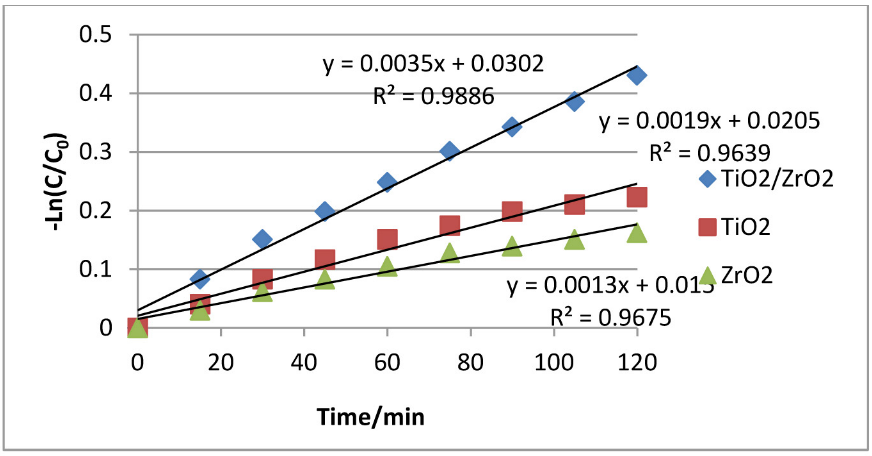

Figure 7. Relationship between -Ln(C/C_0) and reaction time for photodegradation of CR by nanoTiO_2, nano ZrO_2 and TiO_2/ ZrO_2 nanocomposite.

Conclusion

In this work nanoTiO_2, nano ZrO_2 and TiO_2/ZrO_2 nano-composite have been synthesized by a facile sol–gel method using ultrasonic irradiation. Comparison of the FT-IR spectra of TiO_2/ZrO_2 nano-composite with the pure TiO_2 and pure ZrO_2 NPs has been showed formation of ZrO_2/ TiO_2 nanocomposite. Crystal phase and particle size of NPs can be detected by XRD and FESEM. The highest photo-catalytic activity was illustrated by TiO_2/ZrO_2 nano-composite. The plot of photo-degradation versus reaction time was revealed apparently improvement of the degradation value for the nano-composite. The photo-catalytic property of TiO_2/ZrO_2 nano-composite was enhanced, because the decreasing of diameter of nano particles and band gap energy of nanocomposite.

Acknowledgments

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