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## Sono-Synthesis and characterization of ZrO<sub>2</sub>/ZnO nanocomposite, composition effect on enhancing of photocatalytic properties

### ABSTRACT

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Nanocomposite of ZrO<sub>2</sub>/ZnO was prepared under ultrasonic irradiation by sol gel process from directly mixing Zirconium and Zinc gels. The mixture was placed under ultrasonic irradiation for 2 hours. After the aging time and filtration of the reaction mixture, the filtrated composite gel was calcinated at 500 °C for 3h in furnace. The precursor gels of zirconium and zinc were prepared from dissolving of ZrCl<sub>4</sub> and Zn(CH<sub>3</sub>COO)<sub>2</sub>.2H<sub>2</sub>O into deionized water(DI). Nano ZnO, Nano ZrO<sub>2</sub> and ZrO<sub>2</sub>/ZnO nanocomposite were characterized. The FT-IR analysis and the XRD study were exhibited that the crystal structure and purity of the ZrO<sub>2</sub>/ZnO nanocomposite FESEM images were indicated the morphology and the average size of the NPs. The average size of the Nano ZnO, Nano ZrO<sub>2</sub> and ZrO<sub>2</sub>/ZnO nanocomposite were determined 54, 23and 37 nm respectively. The photocatalytic performance was increased when nanocomposite of ZrO<sub>2</sub>/ZnO was used to degradation of Congo red (CR) solution. The ZrO<sub>2</sub>/ZnO nanocomposite was shown higher photo-degradation efficiency of Congo red than of pure nano ZrO<sub>2</sub> and nano ZnO.

**Keywords:** *Sol-gel; Ultrasonic; Irradiation; Nanocomposite; Photocatalyst; Congo red.*

### INTRODUCTION

In recent years, there has been increasing interest in the application of nano size Zirconia and Zinc oxide for catalysts and supports, ceramics, inorganic membranes, gas sensing, water purification and solar energy conversion [1, 2]. ZrO<sub>2</sub> has unique characteristics, such as weak acidity, basicity, red-ox and high thermal stability.

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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 [3], chemical vapor deposition [4], sol–gel processes [5], hydrothermal synthesis [6] and combustion synthesis [7]. 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  $NH_3$  [8]. In most cases, the precursors are soluble zirconium salts like  $ZrO(NO_3)_2 \cdot xH_2O$ ,  $Zr(NO_3)_4$ ,  $ZrOCl_2 \cdot xH_2O$  and  $ZrCl_4$  [9-11] whereas organic zirconium compounds have been used as well [12, 13]. 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 [14]. The crystalline phase of  $ZrO_2$  strongly influences its catalytic activity, selectivity and photo-degradation [15-17].

More attention has been paid to ZnO nanostructures because ZnO is an important low cost basic II–VI wide band gap semiconductor material which is used considerably for its catalytic, electrical, photoelectrical and photo-degradation properties [18, 19].

In this research the nano  $ZrO_2$ , nano ZnO and  $ZrO_2/ZnO$  nanocomposite were synthesized then composition effect of the synthesized heterogeneous catalysts was also investigated on the performance of photo-degradation of Congo red (as an azo dye).

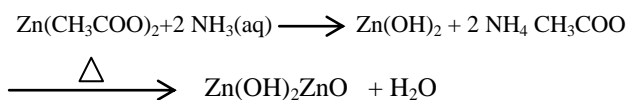
## EXPERIMENTAL

The chemical reagents used in this experiment were analytical grade and without further purification. De-ionized (DI) water was used in all experiments.

### Preparation of Nano ZnO

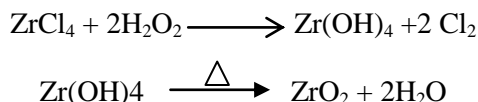
4.4 g (0.2mol) Zn  $(CH_3COO)_2 \cdot 2H_2O$  was firstly dissolved in DI water (100 ml) and stirred to get a precursor solution. 15 ml (2M)  $NH_3(aq)$  solution was then dropped into the precursor solution until pH of mixture was adjusted 9 and the

white suspension of  $Zn(OH)_2$  was appeared.. After that, the mixture was continuously stirred for 2days then the tip of ultrasonic probe was introduced into the mixture and it was irradiation under ultrasonic irradiation for 30 min to achieve a ZnO homogenous gel. The nano ZnO was prepared when the filtrated Zinc gel was heated in furnace at  $500^\circ C$  for 3 h.



### Preparation of Nano $ZrO_2$

Firstly  $ZrCl_4$  (4.7g, 0.2 ml) was dissolved in 2-propanol (100ml) to get a precursor solution A solution of  $H_2O_2$  (6 ml, 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 and calcinations at  $500^\circ C$  for 3 h, the white powder of nano zirconia was produced



### Preparation of $ZrO_2/ZnO$ Nanocomposite

For production of the  $ZrO_2/ZnO$  nanocomposite, the prepared ZnO gel was directly incorporated into the  $ZrO_2$  gel to get the  $ZrO_2/ZnO$  composite gel. The mixture was continuously stirred for 6h then the tip of ultrasonic probe was introduced into the mixture and it was irradiated under ultrasonic irradiation for 30 min to achieve a  $ZrO_2/ZnO$  homogenous gel. After filtering the product was calcinated in furnace at  $500^\circ C$  for 2h. The white powder of nanocomposite of  $ZrO_2/ZnO$  was prepared (Figure 1).

### Photo-degradation process on NPs

In order to test the photo-catalytic activity of the as-prepared nano  $ZrO_2$ , nano ZnO and  $ZrO_2/ZnO$  nanocomposite catalysts, we were chose Congo Red (Figure 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) solutions was used to evaluate the performance of, nano  $ZrO_2$ , nano ZnO and nano  $ZrO_2/ZnO$  photocatalyst. 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.

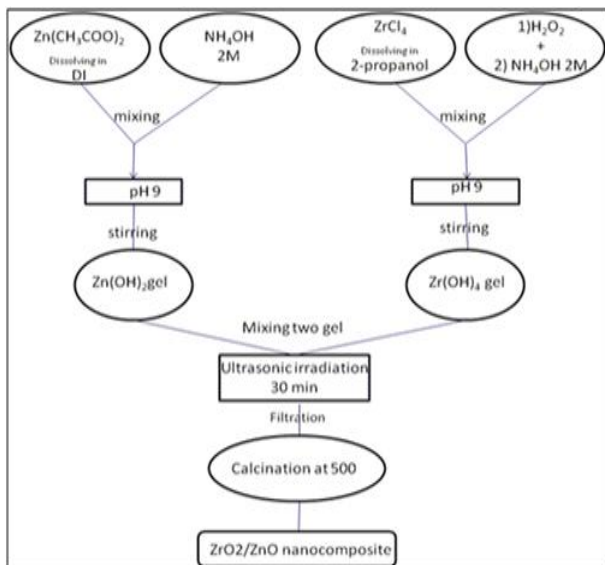


Fig. 1. Flow chart of the synthesis of  $ZrO_2/ZnO$  Nanocomposite.

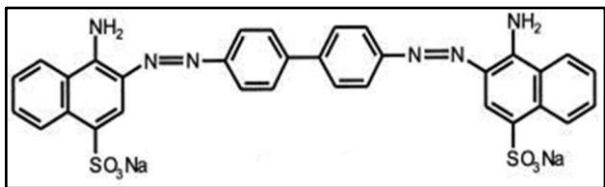


Fig. 2. Structural formula of Congo red,  $C_{32}H_{22}N_6Na_2O_6S_2$ .

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. The decomposition of CR was monitored by measuring the absorbance of the aliquot solution at 502 nm ( $\lambda_{max}$  of CR) using

the UV-Vis spectrophotometer (U-3010, HITACHI).

The photocatalytic degradation (PD) was calculated by the following formula:

$$PD = \left[ \frac{C_0 - C_t}{C_0} \right] \times 100\%$$

Where  $C_0$  is the initial concentration of CR solution which reached absorbency balance and  $C_t$  is the concentration of the dye solution at the irradiation time (t).

## RESULTS AND DISCUSSION

### X-ray Diffraction (XRD) analysis

In Figure 3a the peaks indicate the respective Joint Committee on Powder Diffraction Standards (JCPDS) card no. 37-1484 for  $ZrO_2$  and the vertical lines in Figure 3b according to the JCPDS Card NO.36-1451, for ZnO. The XRD patterns of the  $ZrO_2/ZnO$  nanocomposite is shown in Figure 3c the distinct peaks corresponding to ZnO 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  $ZrO_2/ZnO$  nanocomposite. The  $ZrO_2/ZnO$  nanoparticles are seen pure. The average size of crystals  $D_v$  was also roughly calculated based upon the XRD spectra for quantitative purpose using the Scherer equation:

$$D_v = \frac{K\lambda}{\beta \cos \theta}$$

Where:  $D_v$  is the “volume weighted” crystallite size =  $\frac{3}{4} d$  (crystallite diameter)  $K$  is the “Scherer constant” (around 0.9),  $\lambda$  is the wavelength of the X-rays here is  $\lambda$ ,  $CuK\alpha = 1.541 \text{ \AA}$ ,  $\theta$  is the Bragg angle for the peak at  $2\theta$ ,  $\beta$  is the “integral breadth” of the peak at  $2\theta$ . The  $\beta = (\pi/2)$  FWHM (full width at half maximum) for a Gaussian shaped peak. According to XRD Patterns, the crystallite size of nano  $ZrO_2$ , nano ZnO and  $ZrO_2/ZnO$  nanocomposite are estimated to be 23, 54 and 37 nm respectively.

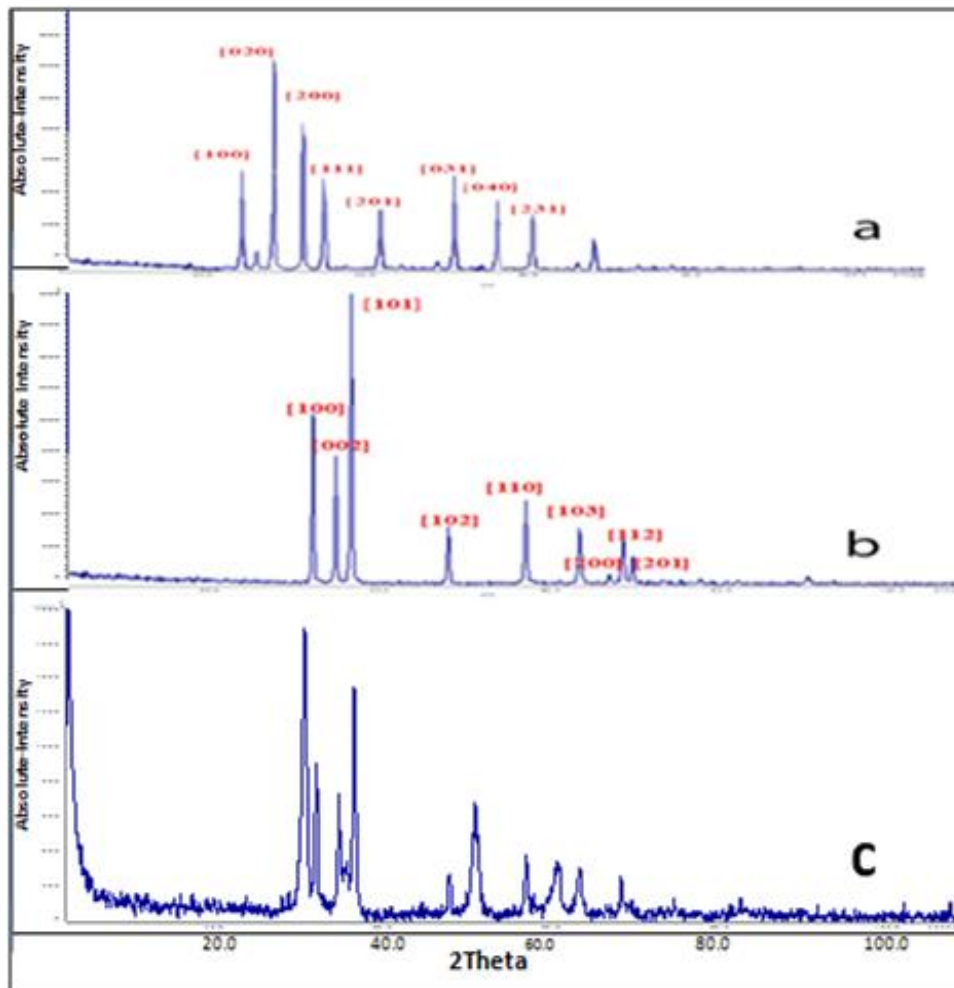


Fig. 3. XRD patterns of (a) nanoZrO<sub>2</sub>, (b) nano ZnO and (c) ZrO<sub>2</sub>/ZnO nanocomposite.

### FT-IR analysis

FT-IR spectra of the NPs are shown in Figure 4, in the wave number range from 4000 to 400 cm<sup>-1</sup>. In comparing Figure 4 (a, b, c), can be assigned the stretching and bending vibrational vibration of ZrO<sub>2</sub>/ZnO nanocomposite. Vibrational modes of nano ZrO<sub>2</sub> and nano ZnO are summarized in Table 1.

The peaks at 420 - 497 cm<sup>-1</sup> can be attributed to stretching vibration of the Zn-O-Zn and O-Zn-O bonds respectively. The peaks at 567, 671 and 762 cm<sup>-1</sup> can be assigned to symmetric and asymmetry stretching vibration of the Zr-O-Zr bond and O-Zr-O flexion. The peaks at 869 cm<sup>-1</sup> were attributed to the vibration mode of Zn-O-Zr. The peak at 1630 cm<sup>-1</sup> resulted from bending vibration of the adsorbed H<sub>2</sub>O molecules, which were not removed completely after sol-gel

synthesis. The peak at 1390 cm<sup>-1</sup> can be caused from M-O-H bending of surface groups. The wide peak at 3448 cm<sup>-1</sup> has been assigned to the OH symmetry and asymmetry stretching vibration of water molecules.

### Morphology of the Nanoparticles

Surface and particle morphology of the synthesized nano ZrO<sub>2</sub>, nano ZnO, and ZrO<sub>2</sub>/ZnO nanocomposites have been studied and their FESEM images are shown in Figure 5a, b and c respectively. It is shown that the surface of the NPs is smooth but the morphology of NPs is different from each other. Figure 5c is shown the ZrO<sub>2</sub>/ZnO nanocomposite is pores on surface, therefore the photo-catalyst activity of ZrO<sub>2</sub>/ZnO were improved.

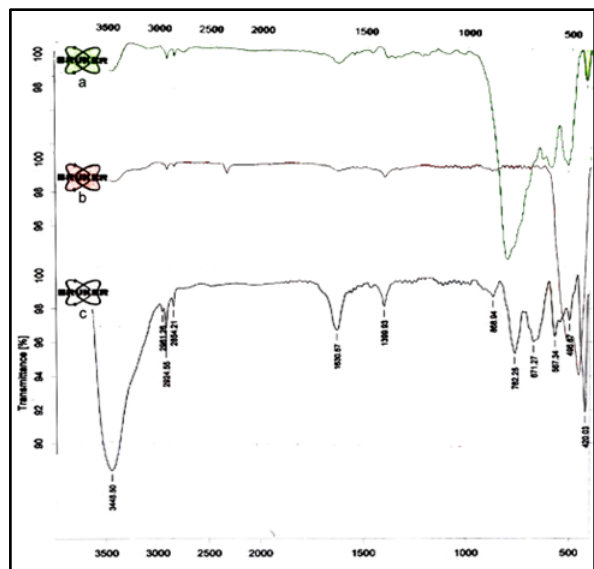


Fig. 4. FT-IR spectra of (a) nano ZrO<sub>2</sub>, (b) nano ZnO and (c) ZrO<sub>2</sub>/ZnO nanocomposite.

Table 1. Identification of Infrared vibrational modes of nano ZrO<sub>2</sub> and nano ZnO.

Nano ZrO <sub>2</sub>	
Frequency (cm <sup>-1</sup> )	Characterization of Vibration
427	Zr -O- Zr bending
507	O- Zr-O bending
879	Zr -O stretching
1630	H-O-H bending
3300 - 3400	H-O-H sym. and asym. stretching
Nano ZnO	
Frequency (cm <sup>-1</sup> )	Characterization of Vibration
441	Zn-O- Zn bending
495	O- Zn-O bending
880	Zn -O stretching
1630	H-O-H bending
3300 - 3400	H-O-H sym. and asym. stretching

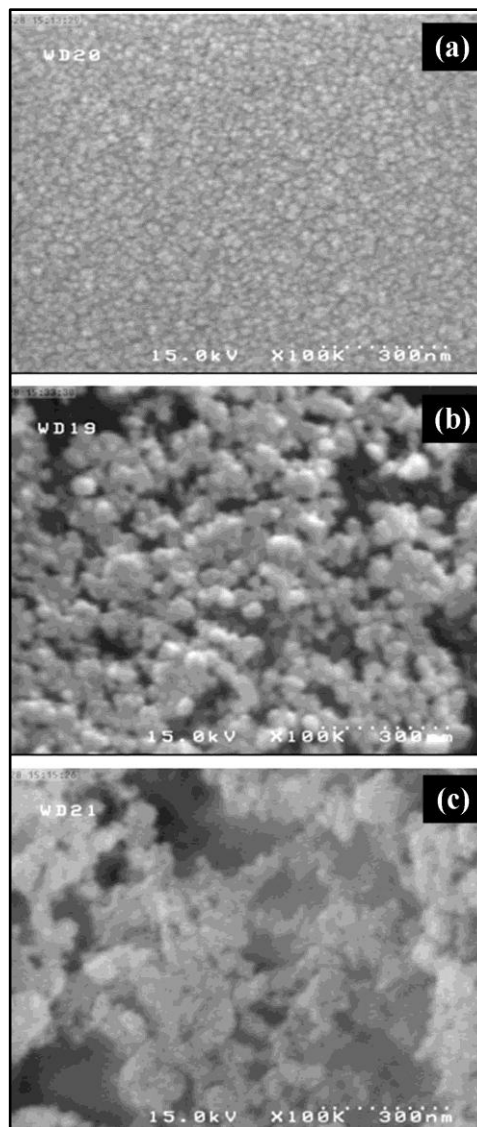


Fig. 5. FESEM images of (a) nano ZrO<sub>2</sub>, (b) nano ZnO and (c) ZrO<sub>2</sub>/ZnO nanocomposite.

**Photo-catalytic activity of NPs**

In Figure 6, is shown the photo-catalytic degradation efficiency of CR using nano ZnO, nano ZrO<sub>2</sub> and ZrO<sub>2</sub>/ZnO nanocomposite under UV light irradiation. The blank experiment without catalyst was rarely decomposed with about 10% of degradation of CR within 2 h of UV irradiation. It could be found that CR is hardly photo-decomposed by using nano ZrO<sub>2</sub> and nano ZnO as photocatalyst. Of course nano ZnO is shown better catalytic property than nano ZrO<sub>2</sub> because the band gap (E<sub>g</sub>) of ZnO is shorter than ZrO<sub>2</sub> (3.2 and 4.2ev respectively). The most efficiency of degradation of

CR could be seen on the nanocomposite of  $ZrO_2/ZnO$  photocatalyst. Approaches to 95% after 2h. The  $ZrO_2/ZnO$  nanocomposite was exhibited very high photo-catalytic performance than the nano  $ZnO$  and nano  $ZrO_2$  photocatalysts. The composite of nano-semiconductors is one of the ways to improve the photo-catalytic property.

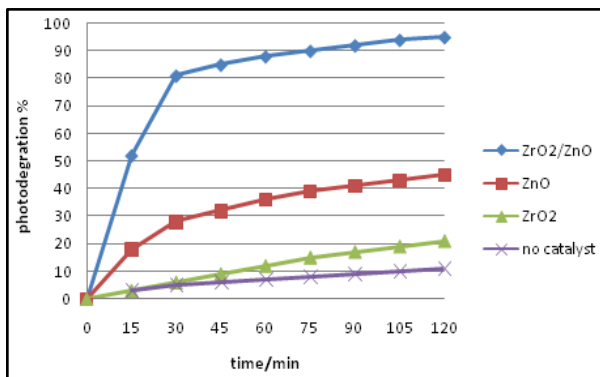


Fig. 6. Plot of photo degradation of CR versus reaction time.

### Photo-degradation mechanisms

In Figure 7, is shown, the  $ZrO_2/ZnO$  nanocomposite excited by photons with energy lower than the band gap ( $E_g$ ), a great number of electrons are promoted from valence band (VB) to the conduction band (CB) of  $ZnO$  and  $ZrO_2$ , leading to the generation of electron/hole ( $e^-/h^+$ ) pairs. The electrons transfer from the CB of  $ZnO$  to the CB of  $ZrO_2$ , conversely the holes transfer from the VB of  $ZrO_2$  to the VB of  $ZnO$  give rise to decrease the pairs' recombination rate. Obviously, the energy level for electron injection is decreased after composing nano  $ZrO_2$  and nano  $ZnO$ , which increases the driving force for electron injection and hence reduce recombination between electrons and holes. On the other hand,  $ZnO$  can increase concentration of free electrons in the CB of  $ZrO_2$ , this result implies that the charge recombination is reduced in the process of electron transport [20].

All above of results increase the availability of the pairs on the surface of the photocatalyst and consequently an improvement of the occurrence of red-ox processes can be expected. Therefore, it can be concluded that the  $ZrO_2/ZnO$  nanocomposite can largely enhance the photocatalytic efficiency of degradation the organic compounds, and thus, the determination time is shortened and the sensitivity is increased.

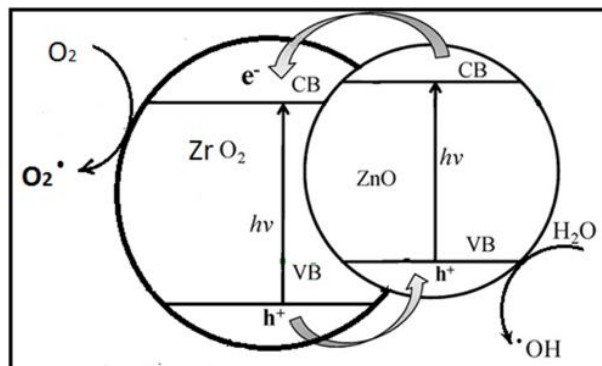
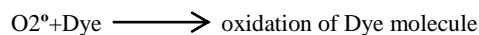
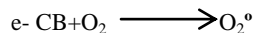
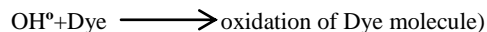
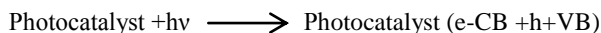


Fig. 7. Schematic band gap and electron-hole pair separation of  $ZrO_2/ZnO$  nanocomposite.

The photocatalytic activities of the nano particles increased, possibly because when the particle diameter decreased, the chance of recombination for photo-induced electron-hole pairs increased because of their slow arrival to reaction sites at the surface.



Here the photocatalysts are nano  $ZrO_2$ , nano  $ZnO$  and  $ZrO_2/ZnO$  nanocomposite.

### CONCLUSIONS

In this work, nano  $ZrO_2$ , nano  $ZnO$  and  $ZrO_2/ZnO$  nanocomposite have been synthesized by a facile sol-gel method using ultrasonic irradiation.  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  and  $\text{ZrCl}_4$  have been used as starting materials. The composite of  $Zr/Zn$  oxides with 1:1 molar ratio was calcinated at  $500^\circ\text{C}$ . Comparison of the FT-IR spectra of  $ZrO_2/ZnO$  nanocomposite with the pure  $ZrO_2$  and  $ZnO$  nanoparticles have been showed formation of  $ZrO_2/ZnO$  nanocomposite. Crystal phase and particle size of NPs can be detected by XRD. According to XRD Patterns, the calculated value as crystallite size of nano  $ZrO_2$ , nano  $ZnO$  and

ZrO<sub>2</sub>/ZnO nanocomposite was obtained 23, 54 and 37 nm respectively. The highest photocatalytic activity was illustrated by ZrO<sub>2</sub>/ZnO nanocomposite the degradation yield of CR was approached 95% after 2h. The plot of photodegradation versus reaction time was revealed apparently improvement of the degradation value for the nano composite. The photocatalytic property of ZrO<sub>2</sub>/ZnO nanocomposite was enhanced, possibly because the decreasing of diameter of nano particles and the more important reason is the generation of electron/hole (e<sup>-</sup>/h<sup>+</sup>) pairs.

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