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Study nanostructures of semiconductor zinc oxide (ZnO) as a photocatalyst for the degradation of organic pollutants

ABSTRACT

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In the present study, comparison of photocatalytic activity of nanostructures semiconductor zinc oxide (ZnO) was prepared using the different methods on the degradation of organic dye such as methylene blue that was investigated. Previous studies have proved that such semiconductors can degrade most kinds of persistent organic pollutants, such as detergents, dyes, pesticides and volatile organic compounds, under UV-irradiation. in some observed reports the photocatalytic activity of the coupled photocatalysts, evaluated by using organic dyes photodegradation as a probe reaction which shows increase the photocatalytic activity in different coupled photocatalysts. In this survey, the activities of ZnO nanostructures and ZnO nanocrystalline, for degradation of methylene Blue are different. Also the rate of operation photocatalysts ZnO nano composites on the organic dye is different too. Measurements of catalyst characteristics were obtained by BET, XRD, TEM, AFM, Raman and FTR-IR spectroscopy.

INTRODUCTION

Nanometer-sized zinc oxide as an important inorganic function material is widely used in rubber, coat, catalyst, electronic engineering fields [1]. Nanoparticles of semiconductors such as titanium dioxide (TiO_2), zinc oxide (ZnO), iron oxide (Fe_2O_3), and cadmium sulfide (CdS) have become popular as a photocatalyst for the degradation of organic pollutants in water and air[2,3]. In the past two decades, zinc oxide has attracted much attention with respect to the degradation of various pollutants due to its high photosensitivity, stability and wide band gap. Zinc oxide is thought to be as a low cost alternative photocatalyst to TiO_2 for degradation of organics in aqueous solutions.

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The dispersion and surface area of zinc oxide, which depend on the synthesis method, are important factors for determining its photocatalytic activity. Zinc oxide nanoparticles can be prepared by various methods, such as, alkali precipitation, thermal decomposition, hydrothermal synthesis, organo-zinc hydrolysis, spray pyrolysis and microwave irradiation, plasma heat-decomposing, etc. Composites of zinc oxide and silica nanoparticle could be formed through co-precipitation route; in this case, the zinc oxide could be coated on the silica nanoparticle surface[1].Photocatalyst is also called photochemical catalyst and the function is similar to the chlorophyll in the photosynthesis. In a photocatalytic system, photo-induced molecular transformation or reaction takes place at the surface of catalyst. A basic mechanism of photocatalytic reaction on the generation of electron–hole pair and its destination is as follows: when a photocatalyst is illuminated by the light stronger than its band gap energy, electron–hole pairs diffuses out to the surface of photocatalyst and participates in the chemical reaction with electron donor and acceptor. Those free electrons and holes transform the surrounding oxygen or water molecules into OH free radicals with super strong oxidization. It can oxygenolyse various kinds of organic compounds and some parts of minerals. It may also deoxidize harmful substances like benzene, formaldehyde, and ammonia into CO_2 and water free of poison, harm, and odor. Therefore, photocatalyst may kill germs, viruses, epiphytes, pollen, and the like and may decompose formaldehyde, benzenes, ammonia, and other harmful gases, and it will not bring secondary environmental pollution [7]. The degradation of the pollutants catalyzed by ZnO has been studied widely. ZnO is known to be one kind of the important photocatalysts because of its unique advantages, such as its low price, high photocatalytic activity, and nontoxicity. However, the disadvantage of this catalyst is that its catalytic activity is still not high enough for the commercial applications [4-9].

EXPERIMENTAL

Recently, quality drinking water has become a major concern worldwide due to the ever-increasing population and decreasing energy resources. Due to this reason, the efficient treatment of wastewaters have become immediate importance among scientific communities around the globe as there is a growing need to come out with the state-of-the-art technologies that are capable to solve the problems. Ideally, an effective wastewater treatment is to mineralize completely all the toxic contaminants in wastewater without leaving any hazardous residues. In addition, the wastewater treatment process should be cost-effective and feasible for large-scale applications [10].

RESULTS AND DISCUSSION

ZnO nanoparticles

Figure 1a shows the SEM pictures of ZnO nano-crystalline particles produced by the spray pyrolysis, Single-phase primary particles, nearly in spherical shape, were observed. The average diameter obtained from the SEM pictures was about 20nm. Figure 1b shows the TEM pictures of ZnO nanoparticles produced by the flame spray pyrolysis, Agglomerates of single-phase primary particles, nearly in spherical shape, were observed. The average diameter obtained from the TEM pictures was about 20 nm. From the analysis of X-ray diffraction pattern, as shown in Figure 2 the clear crystallinity of the ZnO nanoparticles was observed.
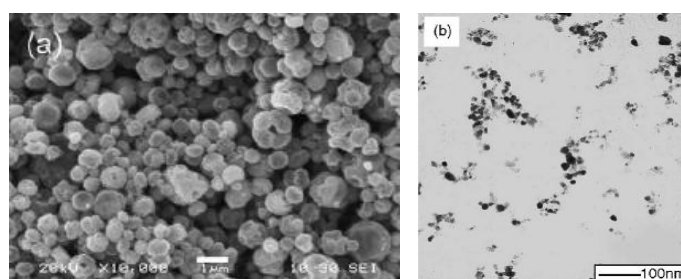

Fig.1.(a) SEM pictures of ZnO nano-crystalline particles produced by the spray pyrolysis
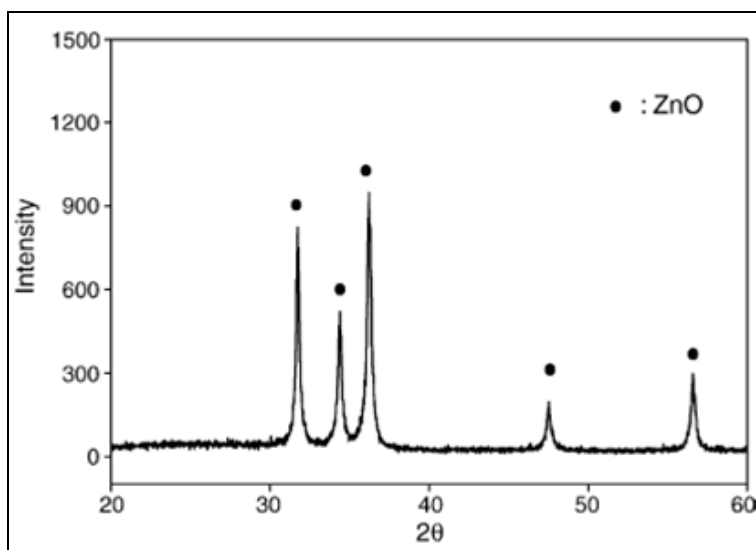(b)TEM pictures of ZnO nanoparticles produced by flame spray pyrolysis

Fig.2. X-ray diffraction pattern of the particles produced by the flame spray pyrolysis

Photocatalytic activity of two kinds of ZnO photocatalyst was investigated by measuring the photocatalytic degradation of methylene blue in water under the illumination of UV light. The ZnO nanoparticles of 20 nm in average particle diameter and the ZnO nano-crystalline particles of 20 nm in mean grain size were chosen for the evaluation of photocatalytic activity.

As shown in Figure 3, it was found that the ZnO nanoparticles were more effective on the degradation of the methylene blue than the nano-crystalline particles. Higher photocatalytic activity of the ZnO nanoparticles is considered due to the higher surface area of the ZnO nanoparticles (58 m2/g) than that of the ZnO nano-crystalline particles (15 m2/g). At higher surface area, larger contact area between photocatalyst and target material can be obtained. It also meant that higher degree of UV light absorption could occur at the smaller particle size in the test solution. The degradation of residual of methylene blue was gradually increased up to 90% after 2 hours regardless of the loading nano-crystalline particles (Figure 3). [2].
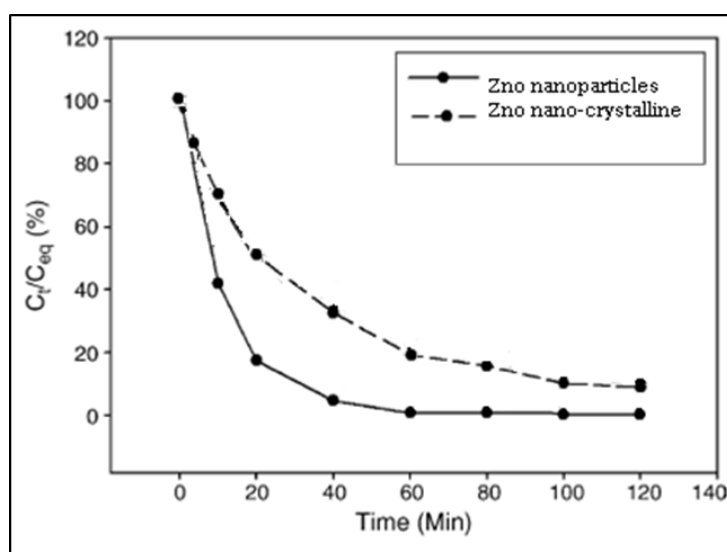

Fig.3. Effect of catalyst loading on the photodegradation of methylene blue using ZnO particles and ZnO nano-crystalline

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Co-doped ZnO powder

The Co-doped ZnO powder was prepared under hydrothermal conditions as follows: zinc acetate dihydrate ($Zn(C_2H_4O_2)_2 \cdot 2H_2O$) and cobalt acetate tetrahydrate ($Co(CH_3COO)_2 \cdot 4H_2O$) were co-precipitated by KOH in aqueous solution, using concentrations of 0.5 and 0.77 mol/L of acetate and KOH, respectively. The mixture was sealed and hydrothermally reacted at 240℃ for 16 h. XRD patterns of the prepared $Zn_{1-x}Co_xO$ samples were shown in Figure 4. The diffraction peaks of each sample were quite similar to those of bulk ZnO, which could be indexed as the hexagonal wurtzite structure ZnO.

The photocatalytic decolorization of methylene blue on $Zn_{0.97}Co_{0.03}O$ photocatalysts at pH 10.5 under visible light irradiation was shown in Figure5. It was found that pure ZnO had little ability to mineralize methylene blue under visible light irradiation. All the Co-doped ZnO photocatalysts exhibited higher photocatalytic activity than that of pure ZnO under visible light irradiation. The $Zn_{0.97}Co_{0.03}O$ photocatalyst exhibited the highest photocatalytic decolorization efficiency; with the MB concentration reduced as much as 100% in 300 min. [11].
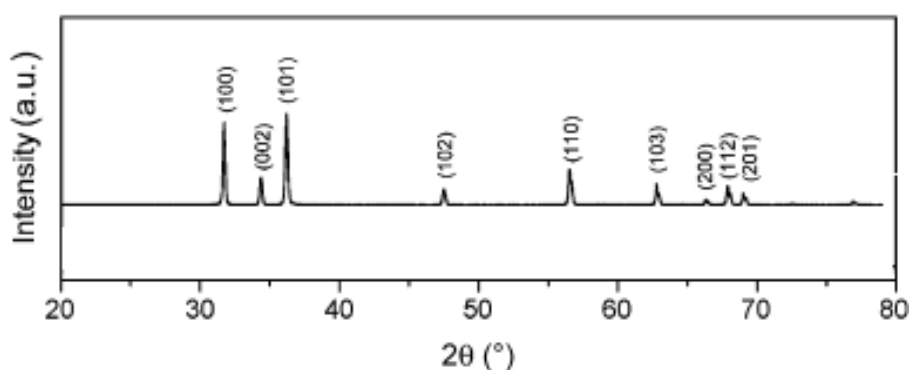

Fig.4. XRD patterns of Zn0.97Co0.03O photocatalysts

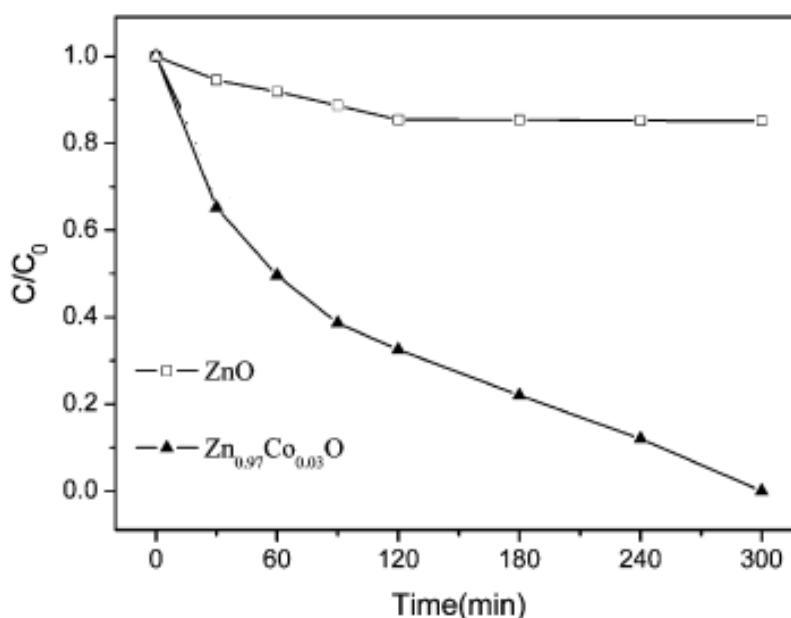**Fig.5.**Photocatalyticdecolorization kinetics of MB using Zn0.97Co0.03O photocatalysts

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ZnO–C and ZnO–Si nanoparticle

The zinc oxide particles were prepared by precipitation and starch gel dispersion methods. The special surface area of ZnO–C and ZnO–Si were 17.7 and 47.3m2/g, respectively, The XRD patterns of ZnO–C and ZnO–Si were shown in Figure 6. The particle size of ZnO–C and ZnO–Si that were estimated by Scherrer's equation were 46 and 32 nm, respectively.
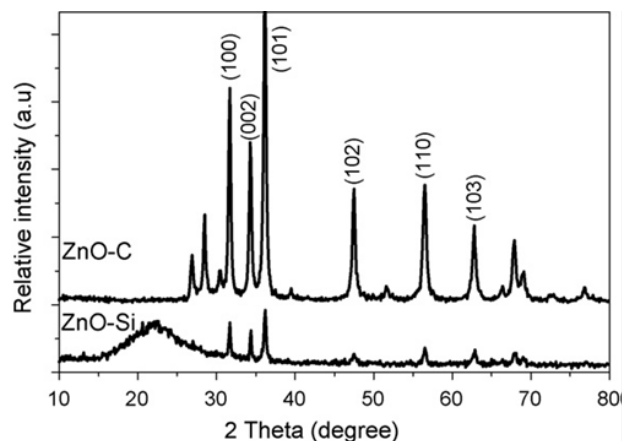

Fig.6. The X-ray diffraction patterns of ZnO–C and ZnO–Si

Figure 7 illustrates the TEM micrographs of the ZnO–C and ZnO–Si nanoparticles. TEM images showed that the particles are agglomerated up to some extent. The average nanoparticle diameter of ZnO–C was around 60 nm and aggregated to chain; some pores appeared between these particles. The ZnO–Si nanoparticles existed about 20–50 nm.

Figure 8 shows the degradation of methylene blue as a function of time using ZnO–C and ZnO–Si. It is clear that the decomposing ratio increased with the degradation time. The decomposition ratio of ZnO–C was much slower and only 20% methylene blue was degraded after 60 min. While the ZnO–Si displayed higher degradation activity, more than 70% and more than 90% methylene blue were decomposed in 20 and 60 min, respectively. The ZnO–Si had less particle size and well-dispersed because it was deposited on the silica nanoparticle surface, and showed higher photocatalytic activity than that of ZnO–C. Moreover, it is easier to separate from solution due to its higher density (2.1 g/cm3). This provided simply a route to synthesize zinc oxide with

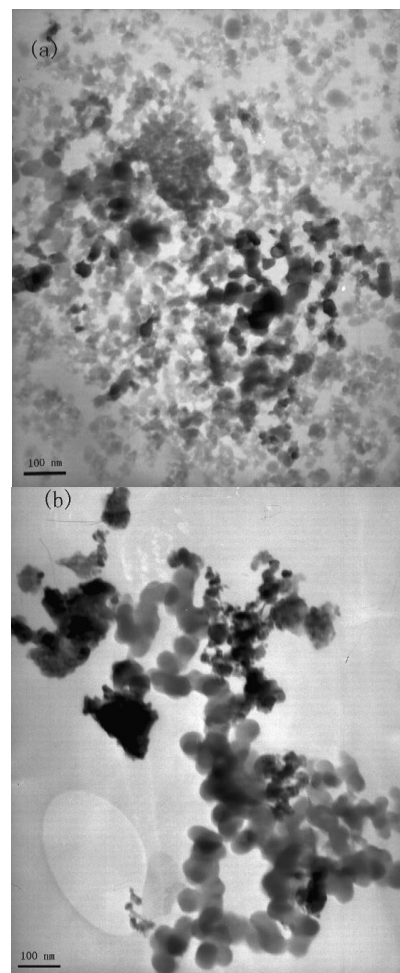excellent photodegradation property for methylene blue [1].

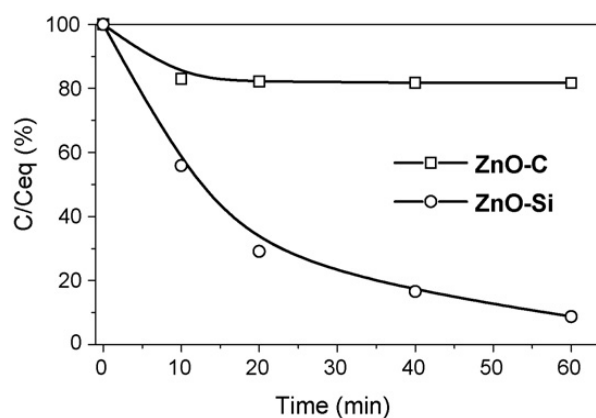
Fig.7. The TEM images of ZnO–Si (a) and ZnO–C (b).

Fig.8. Photodegradation of methylene blue using ZnO–C (a) and ZnOSi (b) (initial concentration of methylene blue: 100 mg/l).

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Two-dimensional (2D) zinc oxide (ZnO) nanopellets

The as-synthesized 2D ZnO nanopellets as reported [12] were refluxed for 8.0 h (at 60℃ under continuous purge of Ar gas with robust stirring) in pyridine to remove excessive oleic acid that capped on the surface of ZnO nanopellets. It was observed that some of the large-sized 2D ZnO nanopellets tend to form precipitate at the bottom of the flask after refluxing due to the successful removal of oleic acid from its surface. The sample was centrifuged to obtain the precipitation of 2D ZnO nanopellets in greyish form. The precipitation was subjected to disperse in anhydrous hexane and was precipitated by anhydrous ethanol with the assistance of centrifugation up to three times to remove the oleic acid that initially capped on the surface of 2D ZnO nanopellets. Finally, the precipitate was dried overnight in the oven. However, most of these ZnO nanostructures were 1D ZnO. As a result, the intensive efforts made in the studies of 1D nanostructures [13,14] have neglected the development of 2D ZnO nanostructures. Until now, there are limited reports on the application of 2D ZnO nanostructures especially as photocatalyst materials. Figure 9 shows the TEM micrograph of the as-synthesized 2D ZnO nanopellets before and after refluxing process. The average edge length of the sample before reflux falls within the range of 40–125nm and it has shown "shape distribution" both in triangular and hexagonal thin pellet form (Figure 9a). On the other hand, the average edge length of the sample that has been refluxed for 8.0 h in pyridine does not show significant changes (Figure 9b).
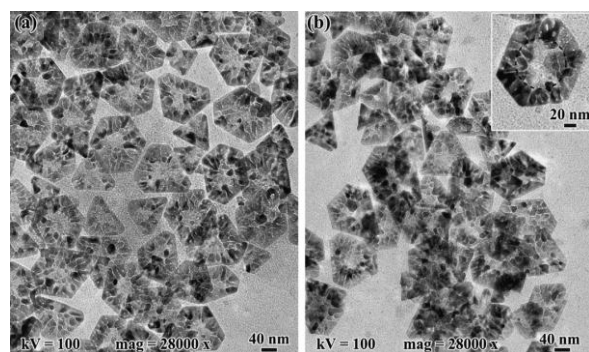
Figure 10 shows the efficiency comparison of 2D ZnO nanopellets as a function of irradiation times. Therefore, these 2D ZnO nanopellets are less compact and could provide more active reaction sites for the absorption of MB after the removal of oleic acid. Refluxed nanopellets has successfully decomposed 97.16% of MB.
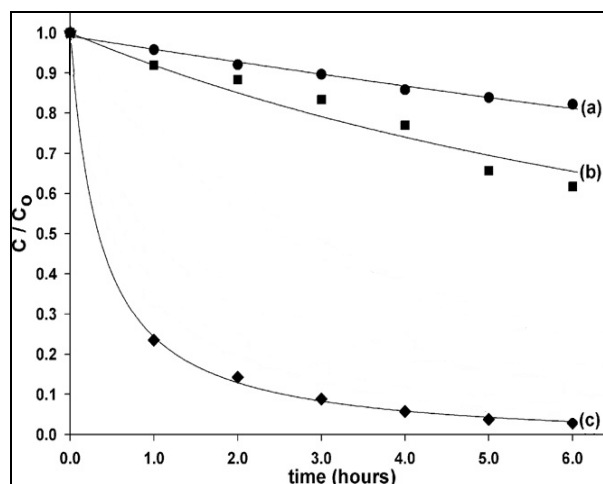

Fig.10. Efficiency comparison of photocatalytic rate for: (a) MB without catalyst, (b) nanopellets before refluxed in pyridine, (f) nanopellets after reflux in pyridine.

In order to elucidate the stability of the photoactivity for refluxed 2D ZnO nanopellets, cyclic experiments were carried out under the same experiment conditions. After the first run, the same nanopellets were reused for the subsequent cycle up to three cycles. According to the results (Figure 11), only slight deactivation was observed after three cycles of photocatalytic tests. As a comparison between the repeatability test in first run and third cycle at sixth hour (Figure 11), the amount of MB left in third cycle is slightly more than first run (0.43%). Hence, this implies that the as-synthesized2D ZnO nanopellets are exhibiting excellent stability and recyclability.

Fig.9. TEM micrograph (magnification 28000×) of ZnO nanopellets annealed at 317 ◦C for 120 min (a) before refluxed (b) after refluxed in pyridine (inset: high-magnification (45000×) of selected 2D ZnO nanopellet with a hole at the center forming a ring structure).

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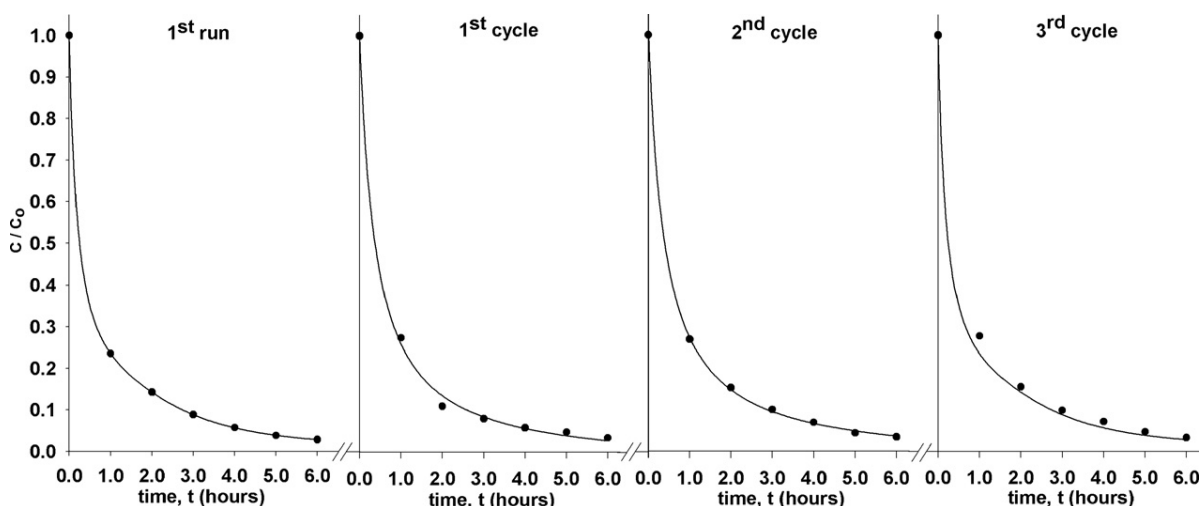
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Fig.11. Repeatability tests on photodecomposition of MB for three cycles by refluxed 2D ZnO nanopellets

Figure 12 shows the XRD pattern of the refluxed 2D ZnO nanopellets before (Fig. 12(a)) and after (Fig. 12(b)) three cycles of photocatalytic test on the photodecomposition of MB. As shown in the XRD spectrums, there are not any significant changes even though after three cycles of photocatalytic test. All the peaks of both spectrums can be indexed to that of the standard ZnO with hexagonal wurtzite crystal structures [15-17].This implies that the as-synthesized 2D ZnO nanopellets are highly stable and suitable for photocatalytic applications, and it does not undergo any chemical changes if compared to other II–VI semiconductors [10].
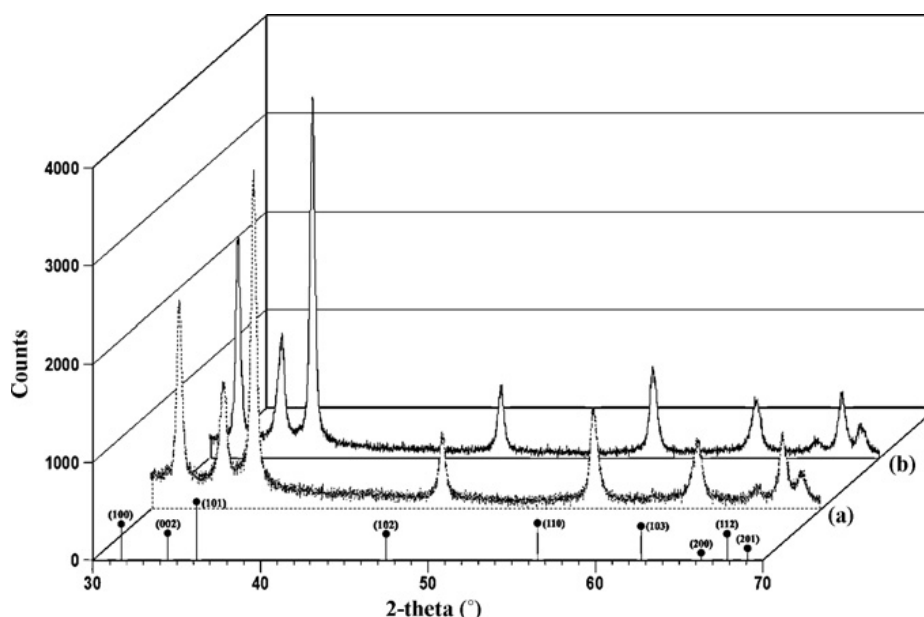

Fig.12. XRD pattern of the refluxed 2D ZnO nanopellets (a) before photocatalytic test and (b) after three cycles of photocatalytic test on the photodecomposition of MB (● is the standard diffraction pattern).

Table 1. Photocatalytic degradation rate of methylene blue using photocatalyst at different prepared method

Photocatalyst system	Synthesis method	Deg. Time(min)
ZnO nanoparticles	the flame spray pyrolysis	100% after 60 min
ZnO nano-crystalline	the spray pyrolysis	90% after 120 min
Co-doped ZnO powder	prepared under hydrothermal conditions	100% in 300 min
ZnO–C nanoparticles	precipitation and starch gel dispersion methods	20% in 60 min
ZnO–Si nanoparticles	precipitation and starch gel dispersion methods	90% in 60 min
2D ZnO nanopellets	organo-zinc hydrolysis	97.16% in 360 min
pure ZnO		10% in 300 min

The results are shown in Table 1 comparison ZnO Photocatalyst system and rate of operator nanostructured zinc oxide (ZnO) were prepared using the different methods on the degradation of organic dyes. It shows at 300 minutes of pure zinc oxide 10% degradation occurs and the time to destroy dyes by nanostructures semiconductor zinc oxide according to the method of preparation is variable. But higher rate of operator Photocatalytic ZnO nanoparticles synthesis by method the flame spray pyrolysis which shows 100% degradation at 60 min [18-20].

CONCLUSION

The present work investigated the nanostructueres of semiconductor zinc oxide as a photocatalytic degradation of the model molecule reactive organic dyes by modified ZnO samples. This photocatalysts prepared by different methods and its photoactivity was studied by investigating the photodegradation efficiency of active organic dyes under artificial solar and UV irradiation. Resulted survey performanced of ZnO nanostructures, shows that activity of ZnO nanoparticles are higher than ZnO nanocrystalline for degradation of methylene blue and rate of oprator photocatalysts ZnO nano composites of degradation on the organic dyes are faster than commercialized ZnO nanoparticles. This study has shown that the as-synthesized 2D ZnO nanopellets which have undergone refluxing process are exhibiting better photocatalytic ability in the

photodecomposition of methylene blue than that of without refluxed. On the other hand, method of preparation of photocatalyst systems based on metal oxides is very important for the degradation of organic dyes.

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