**ZnO/CdO/ reduced graphene oxide and its high catalytic performance towards degradation of the organic pollutants**

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*Abstract*: ZnO/CdO nanoparticles on the reduced graphene oxide (ZnO/CdO/reduced graphene oxide) were prepared by a hydrothermal process. The Structure and morphology were investigated by FTIR, UV-Vis, XRD, EDX, DRS, SEM and TEM. The sonocatalytic properties of ZnO/CdO/reduced graphene oxide were evaluated in degradation of mefenamic acid (MEF), methyl orange (MO), rhodamin (RhB) and 4-nitroaniline (4-NA) with ultrasonic irradiation. Based on the results, effective and high degradation efficiency of azo dyes (MO: 84%, RhB: 80%), MEF: 93% and 4-NA: 95% were observed in 120 min after beginning of the reactions. The effects of factors such as ZnO/CdO/reduced graphene oxide dosage, initial concentration of organic pollutant, ultrasonic power and the presence of ROS (reactive oxygen species) scavengers on the degradation efficiency were reviewed. It was found that the presence of scavengers suppressed the sonocatalytic degradation efficiency. This research indicates the as-prepared nanocomposites exhibit much higher catalytic activity than ZnO/CdO nanoparticles and reduced graphene oxide (rGO).

*Key words*: Sonocatalysis, 4-nitroaniline, Degradation, mefenamic acid, Azo dyes, Ultrasonic waves, scavengers

**INTRODUCTION**

In recent years NSIDS (non-steroidal anti-inflammatory drugs) have been wildly used. MEF, a common NSIDS, is one of diphenylamine derivative pollutant. Diphenylamine derivative pollutants release their toxins in waters. These compounds cannot be removed from waste waters by conventional methods 1–4. Beside them, Azo dyes and nitro aromatic compounds are among the most important groups of industrial chemicals5. Due to growing use of these compounds, the resulted pollution of waste waters is becoming an important problem. These pollutants have unfavorable effects on environment or human. Thus removal of these pollutants from waste waters is essential6–8. In recent years semiconductor nanoparticles have received much attention due to their unique catalytic properties. These properties make them suitable material for potential applications in various fields .These fields include waste water treatment, electrochemical sensors, drug delivery and antibacterial effects9–11. However these semiconductor nanoparticles have some limitations, their small size and large surface area can lead to particle-particle aggregation, making physical handling of nanoparticles difficult in liquid and dry forms12,13,14. Graphene as a two-dimension carbon nanomaterial has properties like fast electron transportation, high aspect ratio, high mobility of charge carries and so on15. With these properties, graphene oxide is a promising support. Combining semiconductor nanoparticles with graphene is considered a more preferable technique. Nanocomposites with semiconductor nanomaterial are used for various applications such waste water treatment, bio nanoelectronic devices and capacitors16–18. The conjugated structure and functional groups at the edge of graphene like carboxyl and carbonyl can increase its interaction with semiconductors. With strong interaction, electrons in the conduction band of semiconductors transfer to graphene, thus leading to electron hole separation and enhanced efficiency of the nanocomposites19. There are several studies that investigated the synthesis and properties of graphene- semiconductor nanoparticles20–22. Lv et al prepared ZnO/rGO composite, which had enhanced photocatalytic properties to degrade methylene blue23. Han et al synthesized CdS/ZnO/graphene composite and they found high efficiency photo electrochemical activity of the nanocomposite under solar irradiation24. Ahmad et al investigated sonocatalytic and sonophotocatalytic degradation of RhB using ZnO/CNT composites25. Zhu et al fabricated PbSe-TiO2-graphene sonocatalyst and applied it as sonocatalyst for decolorization of industrial dyes 26.

As one of the most promising semiconductor, ZnO has gotten an extensive attention due to its high oxidative capacity, low cost and easy of availability27–29. Technological applications of ZnO is limited by its band gap(3.0-3.8ev) 30, and the requirement for UV light to create hole-electron pairs. Further CdO is an important semiconductor with band gap of 2.2 ev 31. CdO has the advantage of a low resistivity, high transmittance in the visible region. These properties make it useful for variety of applications such as photodiodes, photovoltaic cells, liquid crystal displays, catalyst, etc32,33. Coupling of ZnO and CdO can reduce the band gap, extending the absorption range to visible light region, leading to electron-hole separation and consequently achieving higher activity, so it was a valuable research to combine ZnO, CdO and graphene for improvement of semiconductor catalyst. In the present study, ZnO/CdO nanoparticles have been synthesized and immobilized on the surface of reduced graphene oxide via hydrothermal method. The sonocatalytic activity of as-prepared nanocomposites was studied toward degradation of MEF, azo dyes and 4-NA. A series of parameters such as combination ratio of ZnO/CdO nanoparticles and reduced graphene oxide, ultrasonic power, dosage of catalyst and initial concentration of MEF were optimized. Based on the results remarkable high activity of as-prepared nanocatalyst in degradation of MEF, MO, RhB and 4-NA under ultrasonic irradiation were observed.

**EXPRIMENTAL**

*Instruments and Reagents*

All materials were commercial reagent grade. FT Infrared (FT–IR) spectra were obtained as potassium bromide pellets in the range of 400–4000 cm-1 with a Bruker tensor 27DTGS. UV-Vis spectra were recorded on Lambda 35 spectrophotometer. XRD pattern was recorded by Jeol JDX-8030 with Cu kα radiation (λ=1.54 Å) in the range of 2θ = 10-80°. The morphology, particle size, elements distribution and energy dispersive spectroscopy (EDS) of samples were observed by a scanning electron microscopy (SEM, KYKY-EM3200) and atransmission electron microscope (Zeiss-EM10C-(100 KV) German). Ultrasonic experiments were done on ultrasonic processor, Chrom Tech Korea, ultrasonic frequency 20 kHz and output power of (500W-1200W) through manual adjusting. Diffuse reflectance spectroscopy (DRS) was carried out on Avantes (Ava Lamp-DH-S Ava spec2048- Tec).

*Synthesis of Graphene oxide (GO)*

GO was synthesized from purified natural graphite powder via a modified Hummers method according to the literature34.

*Synthesis of ZnO/CdO nanoparticles*

ZnO/CdO nanoparticles were synthesized via template assisted route, according to the literature 28. Briefly 4 mL of 0.5 M solution of Zn(CH3COOH)2.2H2O and 4 mL of 0.5 M solution of Cd(CH3COO)2.2H2O were added to a conical flask containing mixed solution of 50 mL distilled water, 2.8 g NaOH, 10 mL of PEG (Mw= 400), blended well by stirring for 15 min at 70 °C. Subsequently, the mixed solution was left for 4 days at room temperature. White crystalline products were collected, centrifuged, washed with distilled water and ethanol several times and dried at 60 °C in an oven, then calcinated at 400 °C for 1 h.

Synthesis of ZnO/CdO/reduced graphene oxide (the nanocomposites )

A serios of ZnO/CdO/reduced graphene oxide nanocomposites from 0 to 15% were prepared by changing the amount of added ZnO/CdO in the process and labled as ZnO/CdO/reduced graphene oxide (0/100), ZnO/CdO/reduced graphene oxide (5/100), ZnO/CdO/reduced graphene(10/100) and ZnO/CdO/reduced graphene oxide (15/100). The typical route of ZnO/CdO/reduced graphene oxide composites synthesis, for example, when the mass ratio of ZnO/CdO/reduced graphene oxide is 10/100, is as follows: 0.21 g of graphene oxide was dispersed in 30 mL of deionized water by sonication for 1 h. Then 20 mL of deionized water containing 0.02 g of as-synthesized ZnO/CdO nanoparticles was slowly added into the GO suspension. The mixture was sonicated for another 1 h, then 20 mL of N2H4.H2O was added into the above system and the solution was then sealed in a 100 mL teflon lined stainless steel autoclave for hydrothermal reaction at 180 °C for 8 h. After the autoclave was cooled down to room temperature, the ZnO/CdO/reduced graphene oxide product was collected, washed with water several times and dried at 60 °C for 10 h. The pure reduced graphene oxide was synthesized in the absence of ZnO/CdO nanoparticles.

*Adsorption and sonocatalytic studies*

1.2 g/Las prepared ZnO/CdO/reduced graphene oxide was added in to 25 mL MEF, RhB, MO and 4-NA aqueous solution with concentration of 10 mg/L. After dispersed completely, the suspension was stirred in dark to reach the adsorption/desorption equilibrium. The temperature was fixed to be 25 °C with water bath. By the observations of UV-Vis spectrum, it was clear that the absorption spectrum of organic pollutants reached almost a constant value after 30 min.Then, the ultrasonic waves were applied for degradation. At different time intervals, 1mL of solution was withdrawn from the reaction mixture and the concentration of the solutions was measured using UV-Vis spectrometer. UV–Vis spectral changes of substrates in the presence of ZnO/CdO/reduced graphene oxide nanocomposites as a function of time under ultrasonic irradiation were studied.

To investigate the effect of the ZnO/CdO/reduced graphene oxide, some experiments were performed to make sure that degradation of the organic pollutants occurred as a result of the catalytic activity of the ZnO/CdO/reduced graphene oxide and not because of the ultrasound or adsorption only. The degradation of the organic pollutants was studied (1) with only ultrasound, (2) with ZnO/CdO nanoparticles, (3) with rGO and (4) with ZnO/CdO/reduced graphene oxide nanocomposites.

*Evaluation of reactive oxygen specious (ROS)*

Firstly, three 5 mL 1,5 diphenylcarbazide (DPCI) solution (10-2 M) were added to three volumetric flasks marked with 1-3, respectively. And then two 1.2g/L ZnO/CdO/reduced graphene oxide were added to 1 and 3, respectively. All of the three solutions were diluted to 25 mL with distilled water. The solutions 1 and 2were put into an ultrasonic apparatus away from light directly under ultrasonic irradiation and the solution 3 was placed away from light without ultrasonic irradiation, just under stirring. After 45 min, from each samples 10 mL solution was taken and extracted with benzene-tetrachloride carbon (volume ratio =1:1), then their UV-Vis spectra of all solutions were determined.

*Determination the kind of ROS*

Three 5 mL DPCI solution (10-2 M) were added in to three volumetric flasks marked as a-c respectively. And then 1.2 g/L of ZnO/CdO/reduced graphene oxide was added to each one. 2.5 mL of {( L-His, Thiourea and Vitamin C (VC)) 5×10-3M} added into (a-c) flasks, respectively. All solutions were diluted to 25 mL with double distilled water. Any of the solution was transferred in to two conical flasks. Then one of the conical flasks placed under ultrasonic irradiation and the other one was stored under stirring. After 45 min, from each samples 10 mL solution was taken and extracted with benzene-tetrachloride carbon (volume ratio =1:1), then the UV-Vis spectra of all solutions were obtained.

**RESULT AND DISCOSSION**

*Structure and properties characterization*

Fig. 1 shows the XRD spectra of Graphene oxide, rGO and the as-synthesized nanocomposites. In Fig. 1(a) the diffraction peak at 2θ= 10.1° can be indexed to (002) crystallographic plane of graphene oxide35. In the XRD pattern of rGO nanosheets, the disappearance of the peak at 2 θ = 10.1°, confirms that the graphite oxide has been flaked to rGO24 . Also rGO exhibited broad peak at 24.6 which correspond to (002) plane. As can be seen in Fig. 1c the main dominant peaks for ZnO were identified at 2θ =31.8°, 35.0°, 36.2°, 48.4°, 56.2°, 63.4°, 66.1°, 67° and 68.0° which can be indexed as (100), (002), (101), (102), (110), (103), (200), (112) and (201) associated to the diffraction of hexagonal wurtzite phase (JCPDS 79-0208). The peaks at 2θ= 33°, 38.6°, 55.7°, 66.5° and 69° can be indexed to(111), (200), (202), (311) and (222) crystallographic planes of cubic structure of CdO (JCPDS 65-2908).

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Fig. 1.XRD pattern of (a) Graphene oxide (b) rGO and (c) ZnO/CdO/reduced graphene oxide.

Fig. 2(a) shows ZnO/CdO nanoparticles with the size around (15-80 nm). As shown in Fig. 2(b, c) the ZnO/CdO nanoparticles attached to the surface of the graphene nanosheet. The slight agglomeration of the nanoparticles is observed. The elemental composition was analyzed by an energy dispersive spectrometer (EDS) spectrum equipped with SEM. The EDS (Fig. 2(d)) analysis shows the presence of zinc (26.2%) along with Cadmium (12.1%), carbon (42.9%) and oxygen (18.8%), which are the main elements for catalytic ctivity of as-prepared nanocomposites.

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Fig. 2.SEM images of ZnO/CdO nanoparticles on reduced graphene oxide with different magnifications (a-c), (d) EDX spectrum of ZnO/CdO/reduced graphene oxide

The TEM images of ZnO/CdO/reduced graphene oxide (10/100) are shown in Fig. 3(a-c). As can be seen, the ZnO/CdO nanoparticles distributed on the surface of GO. Some of the nanoparticles have hexagonal morphology.

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Fig. 3.TEM images of ZnO/CdO nanoparticles on reduced graphene oxide with different magnification (a-c)

The FTIR spectra of GO exhibits the characteristic peaks as follows: the strong and broad absorption band at 3400 cm-1 originates from stretching vibration of O-H. The peaks at 1720, 1635,1170, 1060 cm-1 are attributed to the stretching vibrations of C=O, C=C, C-O-C and C-O. The FTIR spectrum of the rGO shows absorption band at 1635 cm−1 due to the C=C stretching vibration. In the FTIR spectrum of the as-synthesized nanocomposites, The absorption at 1720, 1170 cm-1 has decreased, the absorption at 1060 cm-1 has vanished and the characteristic peak at 1635 cm-1 is not changed. The absorption band around 464 cm-1 is assigned to Cd-O28 .The absorption band at 577 cm-1 can be assigned to Zn-O vibration36. The decreasing oxygen containing groups (C=O and C-O-C) and vanishing (C-O) in the FTIR spectra of as-prepared nanocomposites indicated of anchore ZnO/CdO nanoparticles on the surface of rGO. This phenomenon could provide enough adhesion strength to inhibit the aggregation and loss of ZnO/CdO nanoparticles during sonocatalytic process and excellent stability (Fig. S1 in supplementary materials).

Fig. S2 in supplementary materials shows the absorption spectra of GO, ZnO/CdO nanoparticles and ZnO/CdO/reduced graphene oxide. In the absorption spectra of GO, the absorption peak at 270 nm is assign to π-π\* transition of aromatic C-C band, which has red shift in the ZnO/CdO/reduced graphene oxide. Also in Fig. S2 (c), it can be seen the disappearance of a shoulder peak at 300 nm (n-π\* transition of C=O band). Moreover the absorption intensity are significantly increased in the whole visible region.

*Adsorption properties of the as-prepared nanocomposites*

From Fig. S3 , it can be noticed that after 30 min 30% of MEF, 23% of RhB, 25% of MO and 33% of 4-NA were adsorbed. By the observations it was clear that after 30 min, the absorption spectrum of the organic pollutants reached almost a constant value. The percentage of the organic pollutant degradation (Deg %) was calculated as follows

(1)

where and Cf are the initial and final organic pollutants concentrations, respectively.

*Sonocatalytic properties of the as-synthesized nanocomposite*

Fig. 4 shows the sonocatalytic degradation of the organic pollutants under different conditions.1- with only ultrasound irradiation, Fig. 4 indicates that little changes observed on the degradation efficiency of the organic pollutants after only ultrasonic irradiation. It was found that the substrates are stable and cannot be simply degraded by ultrasonic irradiation. 2- with ZnO/CdO nanoparticles, it is obvious that ZnO/CdO nanoparticles show enhanced sonocatalytic efficiency (Fig. 4 ). The synergetic effects of CdO and ZnO enhanced the degradation efficiency, however due to agglomeration of small nanoparticles, the degradation efficiency cannot proceed to high level. 3- with rGO, as can be seen in Fig. 4, with extraordinary properties of graphene, degradation efficiency to a certain level occurs, however single layer of graphene has strong tendency of agglomeration in to multilayer graphite through strong π-π stacking and vanderwaals interaction. 4- with as-prepared nanocomposite, Fig. 4 indicates the highest degradation efficiency of substrates were observed in presence the as-prepared nanocomposite and ultrasonic irradiation together. The degradation efficiency increased almost linearly with increasing ultrasound irradiation time. Thus it gives us an insight into the sonocatalysis of organic pollutants by ZnO/CdO/reduced graphene oxide is powerful and efficient in dark state.

Fig. S4 (a-d) in supplementary materials shows that the max absorption peak of MEF (217 nm), RhB (511nm) and MO (465 nm) and 4-NA (379) decreased gradually as the reactions proceeds in 30, 60, 90, 120 min after the beginning of the reactions under ultrasonic irradiation. It was not observed any other peak that show by-product is produced.

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Fig. 4.Comparing degrdation efficiency in different conditions: in presence a) Only ultrasound,, b) ZnO/CdO nanoparticles c) rGO d) ZnO/CdO/reduced graphene oxide

Reaction condition for all of experiments: initial concentration of MEF, 4-NA and azo dyes 10 mg/L, volume of solution: 25 mL, reaction time: 120 min, catalyst amount (ZnO/CdO nanoparticles, rGO, the as-prepared nanocomposites: 1.2 g/L) and pH=7.5.

Effect of the reactive oxygen specious

According to the method of oxidation extraction photometry (OEP) 26 ROS could be detected by UV-Vis absorption spectrum. The ROS with great oxidizing ability can oxidize DPCI in to 1, 5 diphenylcarbazone (DPCO). DPCO show strong absorption at 563 nm. Fig. 5 shows absorption of DPCO, in different conditions.

From the intensity of absorbance of DPCO (Fig. 5), it can be found the quantity of generated ROS in presence of ZnO/CdO/reduced graphene oxide is more than other conditions.

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Fig. 5.UV–vis spectra of DPCO in different condition. Experimental condition: ([DPCI] = 1.0 × 10-2 mol/L, [ZnO/CdO/reduced graphene oxide] = 1.2g/L and ultrasonic time: 45 min.

*Effects of different parameters on sonocatalytic reaction*

To investigate different parameters on sonocatalytic reaction, degradation of MEF was chosen as a model reaction.

*Optimizing Combination ratio of ZnO/CdO/ reduced graphene oxide*

A serios of ZnO/CdO/reduced graphene oxide nanocomposites were prepared. The prepared composites were applied in degradation of MEF as a model reaction and the degradation ratio was calculated with Ce/C0 where C0 is the initial concentration and Ce is the concentration of MEF at different times. Fig. 6 shows the time profile of Ce/C0 using the main absorption peak of MEF( 217 nm in supplementary under irradiation) . As evident in the figure, ZnO/CdO/reduced graphene oxide (5/100),ZnO/CdO/reduced graphene oxide (10/100) and ZnO/CdO/reduced graphene oxide (15/100) samples exhibited improved sonocatalytic activity when compared to that of pure ZnO, CdO and rGO. Also Fig.6 indicates an obvious advantage of ZnO/CdO/reduced graphene oxide (10/100).

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Fig. 6. The sonocatalytic degradation of MEF under ultrasonic irradiation

Experimental condition: initial concentration of MEF: 10 mg/L, ultrasounic power: 1200W/L, catalyst: 1.2g/L, pH=7.5.

*Effect of ZnO/CdO/reduced graphene oxide dosage*

The dosage of the catalyst plays an important role in sonocatalytic degradation. Four different amounts of catalyst (0.3, 0.6, 0.9 and 1.2 g/L) were considered. With increasing dosage of as-synthesized nanocomposite, the active sites of catalyst were increased. Thus more radicals were produced and the degradation efficiency was increased. Fig. 7 presents the results of the experiments, the 1.2 g/L catalyst has shown maximum removal efficiency (93%).

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Fig. 7. Effect of dosage of catalyst on sonocatalytic reaction

Experimental condition: initial concentration of MEF: 10 mg/L, ultrasounic power: 1200W/L, catalyst: ZnO/CdO/reduced graphene oxide (10/100), pH=7.5.

*Effect of initial concentration of organic pollutant*

To study the effects of initial concentration of organic pollutant on sonocatalytic reaction, four different amount of initial concentration of MEF (5, 10, 15 and 20 mg/L) were considered. Fig. 8 shows that with increasing the initial concentration of MEF, the number of the MEF is increased whereas the number of hydroxyl radicals is constant. More hydroxyl radicals are required for degradation of all of the molecules, therefore the degradation efficiency is decreased. The results show initial concentration of MEF (10 mg/L) is suitable.

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Fig. 8. Effect of initial concentration of MEF on sonocatalytic reaction

Experimental condition: ZnO/CdO/reduced graphene oxide (10/100): 1.2 g/L, ultrasounic power: 1200W/L pH=7.5.

*Effect of ultrasonic power*

Fig. 9 shows that with changing the ultrasonic power from 200W/L to 1200W/L, acoustic cavitation is increased, so more hydroxyl radicals are produced and the degradation efficiency is increased. Hence the ultrasonic power is chosen 1200W/L.

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Fig. 9. Effect of ultrasonic output power to degradation MEF.

Experimental condition: ZnO/CdO/reduced graphene oxide (10/100): 1.2 g/L, initial concentration of MEF: 10 mg/L pH=7.5.

Fig. 10 shows the removal efficiency of the nanocomposite in optimized condition. With increasing reaction time, the removal efficiency increased linearly for all substrates. After the end of 120 min, under ultrasonic irradiation, MEF (93.0%), MO (84.0%), RhB (80.0%) and 4-NA (95.0%) were removed by as-synthesized nanocomposite.

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Fig. 10.Removel efficiency of the as-synthesized nanocomposites with MEF, azo dyes and 4-NA.

Reaction condition: ZnO/CdO/reduced graphene oxide (10/100): 1.2 g/L, initial concentration of MEF, azo dyes, 4-NA: 10 mg/L, ultrasonic power 1200W/L pH=7.5.

*The kinetic study of the sonocatalytic reaction*

For sonocatalytic reaction of MEF, 4-NA and azo dyes, an approximately linear correlation of lnC0/C vs time is observed (Fig. 11). So sonocatalytic reaction is pseudo first order. The kapp values of rate of sonocatalytic degradation are listed in TABLE I. The results show the kapp value of MEF sonocatalytic degradation is higher than the other substrates.

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Fig. 11. The pseudo first order kinetics of sonocataltic reactions of MEF, azo dyes under ultrasounic irridation.

TABLE I. Rate coefficient of sonocatalytic reactions

|  |  |
| --- | --- |
| Substrate | kapp (min)-1 |
| 4-NA | 7.1× 10-3 |
| MEF | 8.0 ×10-3 |
| MO | 4.0× 10-3 |
| RhB | 3.8× 10-3 |

*Sonocatalytic mechanism of as-prepared nanocomposite*

Fig. 12 illustrates the electron transfer mechanism in the sonocatalytic degradation of the organic pollutants. The enhanced degradation achieved in the presence of ZnO/CdO/reduced graphene oxide. It can be attributed to the fact that presence of ZnO/CdO/reduced graphene oxide in the liquid medium enhances the formation of the reactive radicals such as •H and•OH (Eq. (3)) through the pyrolysis of water. Also when the ZnO/CdO/reduced graphene is irridated by ultrasonication, both CdO and ZnO semiconductors are excited and the electrons are excited from the valence band to conduction band, forming electron-holes pairs37–41. The energy band gap of the as-synthesized nanocomposite is 1.5 ev calculated with DRS spectra of ZnO/CdO/reduced graphene oxide using Tauc relation:

(2)

where is the absorption coefficient and h is the frequency of photons. A is a proportionality constant and m=4. Since the conduction band of CdO and ZnO are very close together, electrons are injected from conduction band of CdO in to conduction band of ZnO. This process can lead to high concentration of electrons in the conduction band of ZnO and charge separation. Afterwards the electrons can easily transfer to rGO due to the good conductivity of rGO, which can effectively improve the separation of sonogenerated e- -h+ pairs enhancing the efficiency of the sonocatalytic degradation. The electrons can combine with O2 in solution to form the strong oxidative species, on the other hand some of the excited holes at the valence band of ZnO would transfer to the valence band of the CdO via graphene. h+ can react with surface adsorbed H2O to produce •OH radical or directly oxidize organic pollutants to CO2, H2O and some other small molecules (Eqs. (4)-(11)).

To investigate what is the dominant controlling mechanism of the sonocatalytic degradation (pyrolysis or free radical attack), the effects of the scavengers on the sonocatalytic degradation was considered. For this purpose MEF degradation was chosen as a model reaction. The experiments were carried out using carbonate, iodide as inorganic scavengers and tert-Butyl alcohol (T-Butanol), as organic scavengers. As it is shown in Fig. S5 after adding CO32-, I- and T-Butanol as radical scavengers, degradation efficiency of MEF was decreased from 93% to 80%, 76% and 58% at the reaction time of 120 min, respectively. Among the scavengers, T-Butanol, has led to the greatest reduction in degradation efficiency. The results suggests, the degradation of MEF was mainly done by and. Thus it can be concluded that free radical attack is the dominant controlling mechanism of the sonocatalytic degradation of MEF.

In order to further understand the sonocatalytic mechanism of, trapping experiments using L-His, thiore and VC as the quenching agents were carried out to determine the main reactive oxidant species. Fig. S6 clearly displays the addition of effectively reducers. In general L-Histidine can quench the singlet molecular oxygen (1O2) and •OH, Thiourea quenches the hydroxyl radical (•OH) and Vitamin C can quench most kinds of radicals42,43.

As can be seen in Fig. S6, with ZnO/CdO/reduced graphene oxide and ultrasonication, the absorbance of DPCO at 563 nm decreased by 66%, 74% and 81% in presence of L-His, Thiourea and Vitamin C (VC), respectively. Utilization of these scavengers inhabits to produce 1O2 and •OH radicals. Thus absorbance of DPCO is decreased. It is found that •OH and 1O2 are major kinds of ROS with ultrasonic irradiation. Based on the above results, the mechanisms of ultrasonic wave’s absorption, charge transfer, and the reaction pathways as follows):

(3)

(4)

(5)

(6)

(7)

(8)

(9)

(10)

(11)

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Fig. 12. Sonocatalytic degradation mechanism for the organic pollutants over ZnO/CdO/reduced graphene oxide composite under ultrasonic irradiation.

*Reusability test*

For practical applications, the reusability test on ZnO/CdO/reduced graphene oxide catalyst was carried out. Fig. 13 shows that in optimized condition for MEF, azo dyes and 4-NA solution, the stability of the catalyst was excellent. The sonocatalytic degradation ratios of MEF, azo dyes and 4-NA showed very slight decrease during 4 recycle times.

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Fig. 13. The catalytic performance of as-syntesized nanocomposite for 4 successive cycles. Reaction condition: the cleaned ZnO/CdO/reduced graphene oxide nanocomposites were immersed in ethanol for 6h and rinsed with dionized water and then dried at 70°C. ZnO/CdO/reduced graphene oxide (10/100): 1.2 g/L, initial concentration of MEF, azo dyes, 4-NA: 10 mg/L, ultrasonic power 1200W/L. pH=7.5

**CONCLUSIONS**

ZnO/CdO/reduced graphene oxide nanocomposites was prepared by hydrothermal method characterized, by FTIR, XRD, EDX, DRS, SEM, TEM and UV-Vis techniques. The sonocatalytic properties of as-prepared nanocomposites were evaluated in degradation of MEF, 4-NA and azo dyes under ultrasonic irradiation. The improved ability of the ZnO/CdO/reduced graphene oxide composites to degrade pollutants compared with that of ZnO/CdO nanoparticles can be ascribed to formation of π-π stacking between pollutant molecules and aromatic regions of graphene, which is noncovalent. the acceleration of interfacial electron transfer from ZnO/CdO nanoparticles to rGO significantly hindered the recombination of charge carriers and this process improved sonocatalytic activity. The parameters which affect the sonocatalytic degradation like (dosage of catalyst, initial concentration of organic pollutant and ultrasonic power) were optimized using MEF degradation as a model reaction. Based on the results in sonocatalytic degradation, the degradation efficiency after 120 min for MEF, 4-NA, RhB and MO are (93.0%), (95.0%), (80.0%) and (84.0%), respectively. Moreover, the kinetics of the sonocatalytic degradation follows the pseudo first order kinetics. This study demonstrated that ZnO/CdO/reduced graphene oxide has excellent removal efficiency in sonocatalytic reactions. The results of experiments verified that free radical attack is the dominant controlling mechanism of the sonocatalytic degradation of the organic pollutants.

The prepared nanocomposites can be reused for several times with very slight decrease in degradation efficiency. This article may be beneficial for the treatment of wastewaters in the future.

Acknowledgments

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References

1. C. G. Daughton, T. A. Ternes, *Environ. Health Perspect.* **107** (1999) 907–938.

2. T. A. Ternes, M. Meisenheimer, D. McDowell, F. Sacher, H.-J. Brauch, B. Haist-Gulde, G. Preuss, U. Wilme, N. Zulei-Seibert, *Environ. Sci. Technol.* **36** (2002) 3855–63.

3. O. Drzyzga, *Chemosphere* **53** (2003) 809–818.

4. B. Soulet, A. Tauxe, J. Tarradellas, *Int. J. Environ. Anal. Chem.* **82** (2002) 659–667.

5. L. J. Nadeau, J. C. Spain, *Appl. Environ. Microbiol.* **61** (1995) 840–3.

6. M. M. Nassar, M. S. El-Geundi, *J. Chem. Technol. Biotechnol.* **50** (2007) 257–264.

7. K. R. Ramakrishna, T. Viraraghavan, *Water Sci. Technol.* **36** (1997) 189–196.

8. C. O’Neill, F. R. Hawkes, D. L. Hawkes, N. D. Lourenço, H. M. Pinheiro, W. Delée, *J. Chem. Technol. Biotechnol.* **74** (1999) 1009–1018.

9. T. Harifi, M. Montazer, *J. Mater. Chem. B* **2** (2014) 272–282.

10. S. A. Vanalakar, V. L. Patil, N. S. Harale, S. A. Vhanalakar, M. G. Gang, J. Y. Kim, P. S. Patil, J. H. Kim, *Sensors Actuators B Chem.* **221** (2015) 1195–1201.

11. J. Yi, D. Lu, X. Li, S. Hu, W. Li, J. Lei, Y. Wang, *J. Solid State Electrochem.* **16** (2012) 443–448.

12. B. Lim, M. Jiang, P. H. C. Camargo, E. C. Cho, J. Tao, X. Lu, Y. Zhu, Y. Xia, *Science* **324** (2009) 1302–1304.

13. A. Halder, S. Patra, B. Viswanath, N. Munichandraiah, N. Ravishankar, *Nanoscale* **3** (2011) 725–730.

14. T. Yu, J. Zeng, B. Lim, Y. Xia, *Adv. Mater.* **22** (2010) 5188–5192.

15. K. S. Novoselov, *Science*  **306** (2004) 666–669.

16. X. Yang, A. Wolcott, G. Wang, A. Sobo, R. C. Fitzmorris, F. Qian, J. Z. Zhang, Y. Li, *Nano Lett.* **9** (2009) 2331–2336.

17. C. Hariharan, *Appl. Catal. A Gen.* **304** (2006) 55–61.

18. B. H. San, J. A. Kim, A. Kulkarni, S. H. Moh, S. R. Dugasani, V. K. Subramani, N. D. Thorat, H. H. Lee, S. H. Park, T. Kim, K. K. Kim, *ACS Nano* **8** (2014) 12120–12129.

19. Q. Xiang, J. Yu, M. Jaroniec, *Nanoscale* **3** (2011) 3670.

20. X. Chen, Y. He, Q. Zhang, L. Li, D. Hu, T. Yin, *J. Mater. Sci.* **45** (2010) 953–960.

21. Y. Yang, L. Ren, C. Zhang, S. Huang, T. Liu, *ACS Appl. Mater. Interfaces* **3** (2011) 2779–2785.

22. Q.-P. Luo, X.-Y. Yu, B.-X. Lei, H.-Y. Chen, D.-B. Kuang, C.-Y. Su, *J. Phys. Chem. C* **116** (2012) 8111–8117.

23. T. Lv, L. Pan, X. Liu, T. Lu, G. Zhu, Z. Sun, *J. Alloys Compd.* **509** (2011) 10086–10091.

24. W. Han, L. Ren, X. Qi, Y. Liu, X. Wei, Z. Huang, J. Zhong, *Appl. Surf. Sci.* **299** (2014) 12–18.

25. M. Ahmad, E. Ahmed, Z. L. Hong, W. Ahmed, A. Elhissi, N. R. Khalid, *Ultrason. Sonochem.* **21** (2014) 761–773.

26. L. Zhu, J. Chung, W.-C. Oh, *Ultrason. Sonochem.* **27** (2015) 252–61.

27. X. Zhu, Y. Zhu, S. Murali, M. D. Stoller, R. S. Ruoff, *ACS Nano* **5** (2011) 3333–3338.

28. M. Lashanizadegan, H. Mirzazadeh, *J. Ceram. Process. Res.* **13** (2012) 389–391.

29. P. K. Sahoo, B. Panigrahy, D. Bahadur, *RSC Adv.* **4** (2014) 48563–48571.

30. A. A. Ashkarran, B. Mohammadi, *Appl. Surf. Sci.* **342** (2015) 112–119.

31. M. Ristić, S. Popović, S. Musić, *Mater. Lett.* **58** (2004) 2494–2499.

32. J. Chang, V. V. Todkar, R. S. Mane, D. Ham, T. Ganesh, S. H. Han, *Phys. E Low-Dimensional Syst. Nanostructures* **41** (2009) 1741–1745.

33. S. Kumar, A. K. Ojha, B. Walkenfort, *JPB* **159** (2016) 111–119.

34. H. N. Tien, V. H. Luan, T. V. Cuong, B.-S. Kong, J. S. Chung, E. J. Kim, S. H. Hur, *J. Nanosci. Nanotechnol.* **12** (2012) 5658–5662.

35. A. F. De Faria, D. S. T. Martinez, S. M. M. Meira, A. C. M. de Moraes, A. Brandelli, A. G. S. Filho, O. L. Alves, *Colloids Surfaces B Biointerfaces* **113** (2014) 115–124.

36. Z. Wang, H. Zhang, L. Zhang, J. Yuan, S. Yan, C. Wang, *Nanotechnology* **11** (2002) 11–15.

37. M. Salavati-Niasari, F. Davar, M. Farhadi, *J. Sol-Gel Sci. Technol.* **51** (2009) 48–52.

38. R. W. Matthews, *J. Phys. Chem.* **91** (1987) 3328–3333.

39. C. Petrier, A. Jeunet, J.-L. Luche, G. Reverdy, *J. Am. Chem. Soc.* **114** (1992) 3148–3150.

40. T. J. I. Edison, M. G. Sethuraman, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **104** (2013) 262–264.

41. T. Ghosh, K. Ullah, V. Nikam, C. Y. Park, Z. Da Meng, W. C. Oh, *Ultrason. Sonochem.* **20** (2013) 768–776.

42. C. Xiao-jun, X. U. Han-hong, W. Yu-jian, H. U. Shan, Z. Zhi-xiang, Z. Yao-mou, *Agric. Sci. China* **6** (2007) 458–465.

43. S. ichiro Umemura, N. Yumita, K. Umemura, R. Nishigaki, *Cancer Chemother. Pharmacol.* **43** (1999) 389–393.