Synergistic effect of zinc oxide nanorods on the photocatalytic performance and the biological activity of graphene nano sheets

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ABSTRACT

In this work, decoration of the graphene surface with 5 wt. % ZnO nanorods (ZnO NRs), to ensure the potential photocatalytic performance of the formed nanocomposites, is demonstrated. Graphene oxide (GO) was synthesized with Hummer method followed by reduction to give reduced graphene oxide (RGO). The adjustable nanocompositing exhibited long-sought workability not only in in-situ incorporation of nanorods while reduction of graphene oxide (IZG) but also in ex-situ mixing of RGO or GO with the nanorods, (EZG) and (ZGO) respectively. The demineralization of synthetic wastewater has been evaluated by chemical oxygen demand and the obtained nanocomposites possess enhanced photocatalytic activities with 30 % and 35% over pure RGO and GO, respectively. This higher efficiency could be attributed to the synergistic effect between ZnO and the planner structure of graphene sheets which developed unprecedented polycrystalline structure. Also, the results proved that even the RGO or GO have played a dual function in photocatalysis, adsorption, and degradation. Also, the bactericidal effect of the prepared samples was studied against deleterious microorganisms. The findings of this work pave the way for the new generation of highly efficient photocatalysts based graphene with economic attraction and environmental impact.

1. Introduction

Graphene (G), the keyword of the current technology, is among renowned carbon nanomaterials [1]. It has a wide range of applications thanks to its exceptional properties [1, 2]. Graphene is a two-dimensional platelet comprised of carbon atoms that tightly packed in the honeycomb-like structure [3]. It has a planner structure, in which the carbon atoms are sp2 hybridized in a hexagonal lattice with a bond length of 0.142 nm. This structure gives graphene superior characteristics over traditional materials [3]. Graphene can conduct electricity better than metals in room temperature as the electron mobility is more than 150,000 cm2.V−1.s−1 [4]. Moreover, it is the thinnest material known so far at one atom thick as well as the strongest substance discovered, about 300 times stronger than steel [5, 6]. Also, graphene can absorb light in the range of visible and near-infrared regions [7]. All the aforementioned properties drew attention to utilize graphene in electronics and photo-based applications [8, 9].

In the field of water treatment, photocatalysis is a process in which the organic pollutants are decomposed in the presence of a photocatalyst under the light irradiation [10, 11]. Currently, the photocatalytic activity of the most frequently used catalysts has been improved using graphene to mitigate their limitations in terms of large bandgap energy and fast rate of recombination of photogenerated species along with sustainable performance in the harsh conditions and durability [12, 13, 14]. In these modified photocatalysts, graphene plays essential roles while irradiation. Besides the high adsorption capacity due to the large surface area, it acts as a photo-charge separator at the interface and provides a continuous pathway for the electron transfer process [15]. Martins et.al have used graphene and graphene oxide in compositing with titanium dioxide nanoparticles to remove methylene-blue from industrial wastewater [16]. Both composites were more effective than pure TiO2 under UV irradiation and the degradation rates were increased with the increase of graphene content. Another study was performed to investigate the synergistic effect of the reduced graphene oxide on zinc selenide (ZnSe) and the photocatalytic performance of the prepared composites against 4-nitrophenol degradation.
under solar illumination [17]. The results confirmed 85% degradation efficiency after 30 min compared with controlled ZnSe which recorded only 35% under the same reaction conditions. Ghang and his coworkers have found a 90% conversion of phenol while using copper ferrites/-Graphene oxide composites which indicates high photocatalytic strength of this catalyst under simulated sunlight irradiation [18]. Also, frequent cycles emphasized the high stability and durability of this composite. A novel hybrid material based zinc tetra tert-butyl phthalocyanine (ZnTTBPe) and reduced graphene oxide were prepared via the in-situ reduction method [19]. The resulting composite showed about four times higher degradation rate of 4-nitrophenol under solar irradiation than controlled ZnTTBPe.

Indeed, immense efforts have been done in order to develop new compounds of zinc for environmental applications particularly in photocatalytic degradation of organic pollutants. Zinc oxide (ZnO) is one of the well-known structures of zinc element that is widely used as a photocatalyst [20]. As an alternative to titanium dioxide (TiO2) photocatalyst, ZnO has several advantages such as low cost, high surface reactivity, wide bandgap (3.37 eV), the ability to generate hydroxyl ions more efficiently than (TiO2), and the formed photogenerated holes have a strong oxidizing power to decompose organic compounds under UV irradiation [20, 21, 22, 23]. TiO2 has been used as an effective absorbent for a strong oxidizing power to decompose organic compounds under UV irradiation [20]. Recently, ZnO still has a limited performance in photocatalysis since it is not sustained at higher pH, dramatically decays in the second run and the high rate of electron-hole recombination along with the photo-corrosion [25, 26, 27, 28, 29]. Therefore, enormous work is carried out to enhance its catalytic reactivity while irradiation.

Mostly, the research trend focuses not only on developing new structures by design [29] but also on the modification of ZnO with other materials, either organic or inorganic [30, 31, 32]. ZnO has been tailored into different architectures e.g. nanoparticles [33], nanowires [34, 35], nanotubes [36, 37] and nanorods [38]. The photocatalytic activity of these versatile morphologies has been intensively discussed in the literature. It was found that ZnO nanorods and nanowires have better adsorption of the organic dyes and photodegradation efficiency than the nanoparticles because the one-dimensional nanostructures usually possess a larger surface-to-volume ratio [39]. Moreover, compounding of ZnO with other inorganic photoactive nanomaterials, such as silver [40], TiO2 [41] and gold nanoparticles [42], has recorded a reasonable photodegradation activity for the organic pollutants corresponding to the pure ZnO. In the same context, interesting work has been published recently that refers to surface modification of the nano-sized ZnO with an organic polymer. In which, surface decoration of ZnO nanorods with hyperbranched polyester has been described. This modification step led to an adjustment of bandgap of the ZnO and improvement of its photocatalytic performance [43]. While using ZnO nanocomposites, the results confirmed the successful decontamination of synthetic wastewater with a high rate of degradation compared with the pristine Nanorods.

Without a doubt, graphene paved the way for the next generation of ZnO photocatalyst since in the presence of graphene sheets ZnO displays a high performance in photocatalytic degradation of organic dyes either under UV or visible light irradiation [44]. Lately, a new nanocomposite, based on mesoporous ZnO flowers and reduced graphene oxide sheets, has been reported [45]. The degradation rate of methylene blue dye by photocatalysis of this composite under standard solar light irradiation was found to be six times higher than the pristine components. This strong activity was attributed to the synergetic effect of graphene, porous structure of ZnO nanostructure, and the effective charge separation in the presence of nano-sheets. To this point, graphene has recognized as a privileged additive to most of the semiconductors owing to its intriguing properties.

To the best of our knowledge, investigation of the photocatalytic activity of the neat graphene sheets along with the enhancement of its performance is seldom reported. Thus, this article presents facial approaches for decoration of reduced graphene oxide nano-sheets (RGO or GO) with ZnO nanorods. According to our knowledge, studying the behavior of pure graphene in the photodegradation of organic pollutants was not previously mentioned. Even the treatment of graphene’s surface with few amounts of nano-sized ZnO to enhance the catalytic activity in the photodegradation process has not been investigated earlier. It is known that graphene can absorb light in the UV region [45, 46] and its surface contains many structural defects [47] that are crucial in the degradation of organic pollutants either by adsorption or photocatalysis [46, 47, 48, 49]. In the present work, the hybridization of RGO/GO with a small amount of ZnO significantly increased the photodegradation activities. Ex-situ technique through mixing of GO with ZnO NRs and in-situ technique by reducing of GO in the presence of ZnO NRs have been used. The materials were well characterized by physical techniques and the photodegradation of the organic pollutants has been conducted under UV source relying on the analysis of chemical oxygen demand (COD). Antimicrobial property of the prepared materials has been also discussed against different microorganisms as a support for the mechanism suggested confirming the photocatalytic activity of the graphene and its nanocomposites. It is worth to mention that 5 wt. % of ZnO has been selected to check the potential effect of the lowest amount on the activity of graphene.

2. Experimental

2.1. Materials

Sulfuric Acid (99.9%) and zinc acetate (99.99%) were acquired from Sigma Aldrich, USA. Graphite powder (99.9%) was received from Fisher Scientific, UK. Potassium Permanganate, KMnO4, (>99%) and hydrogen peroxide, H2O2, (30%) were provided from Bio Basic Canada Inc. and Carl Roth GmbH, respectively. Sodium Nitrate, NaN03, (99.99%) and hydradine hydrate, NH2NH2, (99%) were bought from Sd Fine-CHEM limited, India. Phenol, N-(1-naphthyl ethylene diamine) dichloride, and Sulfanilamide as common organic pollutants were purchased from BDH Company. All chemicals were used as received without further treatment.

2.2. Techniques

Investigation of samples’ chemical structures was performed using Perkin Elmer FTIR instrument. Bruker diffractometer, Bruker D 8 advance target, was operated to determine the X-ray diffraction pattern for the solids obtained. The radiation source of the diffractometer was CuKα with secondly monochromator of a wavelength equals to 1.5405Å. Specific surface area and pore size distribution of the obtained materials were investigated using BET (Brunauer–Emmett–Teller) equation [50]. The method involved physical adsorption of nitrogen gas by the prepared samples in Quantochrome Nova-Touch 4LX automated gas-sorption apparatus, USA, at 77K, before each measurement, samples were degassed at 200 °C for two hours. Calculation of the pore size distribution was performed using BJH (Barrett, Joyner and Halenda) method. The atomic percentages were obtained using Energy-dispersive X-ray spectroscopy, EDX, hyphenated with Quanta FEG 250 scanning electron microscopy. The spectra were displayed on TEAM® software at the acceleration voltage equals 20 kV. Transmission electron microscopy (TEM) images were taken on JEOL TEM-1230 at acceleration voltage of 80 kV. The bactericidal performance was checked using the inhibition growth method [41] against Bacillus cereus, Escherichia coli NRRN 3008, and candida Albicans EMCC105 as deleterious Gram-positive bacteria, Gram-negative bacteria, and fungus, respectively. The inhibition zones given by the samples were measured compared with the Cephradine as a commercially available reference antibiotic in the Egyptian markets [51].
2.3. Synthesis of zinc oxide nanorods (ZnO NRs)

Zinc oxide NRs were prepared by thermal treatment of Zinc acetate. (5g) of the precursor was weighed in a ceramic crucible and inserted in a muffle after partially covering. The temperature was increased by 10 ºC/min up to 450 ºC for 4h. Then, the furnace was switched off and left to cool gradually (Figure 1). The formed fine powder was carefully washed several times with distilled water to get rid of the unconverted zinc acetate. The obtained ZnO Nanorods were dried at 60 ºC overnight.

2.4. Synthesis of graphene oxide (GO) and reduced graphene oxide (RGO)

Hummer chemical method has been used to prepare GO and RGO as described before [28]. Briefly, 10g of graphite powder was stirred in a cooled solution of concentrated sulfuric acid and sodium nitrate. Then, 30 g of KMnO₄ was slowly added and the mixture was kept at 33 ºC under the vigorous stirring for 3 h. Distilled water was carefully added to the reaction container and the temperature was elevated up to 98 ºC. Subsequently, 100 mL of H₂O₂ was wisely added to the hot mixture. Finally, the graphite oxide suspension was taken into the sonicator for 30 min, filtered out, and thoroughly washed until neutralization. The obtained GO was dried overnight under vacuum at 60 ºC. To reduce the dried GO into the reduced graphene sheets, 50 μL of hydrazine hydrate was mixed in a solution of GO for one hour and heated in the domestic microwave (1000W for 3 min) to initiate the reduction of GO mixture. Eventually, ZnO NRs modified RGO was filtrated out and washed several times with hot distilled water. The sample was collected and dried at 60 ºC under vacuum overnight, Figure 1C.

2.5. Synthesis of ZnO NRs modified graphene oxide (ZGO)

Modification of GO sheets with ZnO Nanorods could be prepared as follow: 0.5 g of GO was dispersed in 150 mL distilled water. Then, 5 wt. % of ZnO NRs were added and the whole mixture was sonicated for one hour to achieve better dispersion of ZnO NRs in the GO solution. After that, the reaction mixture was exposed to vigorous stirring for 72 h. Finally, the solid content was separated by centrifugation at 3500 rpm for 30 min and dried overnight at 60 ºC under vacuum, (c.f. Figure 1B).

2.6. Synthesis of ZnO NRs modified reduced graphene oxide

The decoration of the RGO surface was performed using in-situ method, in which the nanorods have been added during the synthesis of RGO, and ex-situ method; after the preparation of RGO. The detailed steps could be described as follows:-

2.6.1. Synthesis of In-situ G/ZnO composite (IZG)

A mixture of 0.5 g of GO and 5 wt. % of ZnO NRs were sonicated for 1 h in 150 mL distilled water. The mixture was left under stirring for 72 h. Then, 50 μL of hydrazine hydrate was added to the reaction vessel. After a strong stirring for 1 h, the solution was heated in the domestic microwave (1000W for 3 min) to initiate the reduction of GO mixture. Eventually, ZnO NRs modified RGO was filtrated out and washed several times with hot distilled water. The sample was collected and dried at 60 ºC under vacuum overnight, Figure 1C.

2.6.2. Synthesis of Ex-situ G/ZnO composite (EZG)

A mixture of 0.5 g of RGO and 5 wt. % of ZnO NRs were suspended with sonication for 60 min. Then, the mixture was left under the vigorous stirring for 3 days. Finally, the dispersed solution was filtered out using a centrifuge (4000 rpm) and dried under vacuum at 60 ºC overnight, Figure 1A.

2.7. Photocatalysis experiment

In this experiment, synthetic wastewater was prepared by dissolving 200 mg of catechol, 200 mg Sulfanilamide, and 200 mg N-(1-naphthyl ethylene diamine) dichloride in one liter distilled water. After complete dissolution, 500 mL of the wastewater prepared was loaded into the jar of the photo-reactor. Then, constant weight (typically 0.2 g) of the prepared catalysts, RGO, GO, ZGO, IZG, and EZG was mixed with the pollutants-solution. An aerator was used in order to flash the oxygen into the solution and achieve good mixing of catalyst in the solution. The UV lamp has a range of wavelengths up to 368 nm is used in order to irradiate the catalyst. Analysis of wastewater before and after the photocatalysis process at different time intervals has been performed using chemical oxygen demand (COD) according to water and wastewater examination standard methods (APHA, AWWA, 1995) [43, 51, 52, 53, 54].

3. Results and discussion

3.1. X-ray diffraction (XRD)

XRD spectroscopy has been used to characterize the pristine materials; ZnO NRs, GO and RGO. The spectra in Figure 2A revealed the
disappearance of the anhydrous Zn(AcO)₂ and sharp scattering peaks towards the perfection of the ZnO Nanorods. This confirms the feasibility to use the thermal method as an environmentally friendly technique to prepare the nanomaterials. Moreover, GO has a pronounced peak at 2θ ~13° with greater d-spacing due to enclosure of oxide groups (in the form of carbonyl, epoxide and hydroxide groups) between the carbon layers of graphite and at the edges of the sheets during the chemical oxidation process [55]. Finally, after the reduction step, the characteristic peak of GO was broadened and shifted to a higher angle confirming the de-oxygenation of GO sheets and the distortion of the sp² carbon sites into an amorphous structure. However, the spectrum of graphene nanocomposites, Figure 2B, doesn't provide enough evidence about the type of interaction within the as-prepared nanocomposites since the diffraction peaks of ZnO NRs are embedded under the broad bands of RGO and GO. Also, probably, the low ratio of graphene: ZnO makes graphene peaks more dominant. Nevertheless, one can observe differences in the diffraction patterns after the modification process for all composites. A clear sharpness in the peaks along with a small shift to a lower degree in the characteristic band of GO in ZGO is shown. This can be explained by the strong interaction of the ZnO NRs not only over the surface of GO but also within the interlayer spacing.

In Figure 2A, RGO has broadband at 2θ = 23.7° indicating the distance between graphene layers and 2θ = 43° indicating a short-range order in stacked graphene layers [56]. After the in-situ modification, IZG, the aforementioned peaks (2θ = 23.7°) have been changed in terms of sharpness and intensities i.e. a wide band with a lower intensity. This emphasizes the better incorporation of ZnO NRs between the graphene oxide layers. It is assumed that ZnO assists the exfoliation of graphene oxide layers during the reduction process. In the case of EZG nanocomposite, the probability of re-aggregation of graphene layers can be observed as the main peaks are slightly sharper than that of RGO. Generally, there is no shift in the main peaks of RGO. Figure 2. X-ray diffraction patterns of A: zinc oxide nanorods (ZnO NRs), Graphene (RGO), Graphene Oxide (GO) and B: Graphene nanocomposites (ZGO, IZG, and EZG).

Figure 2. X-ray diffraction patterns of A: zinc oxide nanorods (ZnO NRs), Graphene (RGO), Graphene Oxide (GO) and B: Graphene nanocomposites (ZGO, IZG, and EZG).

Figure 3. TEM images of zinc oxide nanorods (ZnO NRs), Graphene (RGO), Graphene Oxide (GO) and Graphene nanocomposites (ZGO, IZG, and EZG).
while treatment with ZnO NRs either with in-situ or with ex-situ method which confirms a physical interaction on the surface of RGO might be established.

### 3.2. Transmission electron microscope (TEM)

Figure 3 TEM images of the GO and RGO showed partially bent and wrinkled multilayer nanosheets. However, more transparent and folded sheets were obtained while the reduction of GO. Also, the image depicts the successful preparation of ZnO nanorods of an average diameter of ~35 nm. Mostly, the formed NRs have curved edges due to incomplete growth of some particles (c.f. inset ZnO NRs). Generally, TEM micrographs of G/ZnO nanocomposites confirmed the effective modification of the graphene surfaces with ZnO NRs. As mentioned before, some stacked layers of GO incorporated with ZnO NRs are clearly visible in the ZGO composite. Moreover, only nanorods of quite small lateral dimensions have been inserted between GO layers.

However, in the case of the in-situ modification of the RGO surface, IZG, TEM images revealed that ZnO NRs facilitate the exfoliation of G during the reduction process as a few mono-layers of RGO was obtained and the nanorods were homogeneously dispersed over the nanosheets. Moreover, the length and diameter of the nanorods were altered to some extent. This can be attributed to the effect of microwave frequency on the crystallinity and crystallite size of the NRs. It has been reported that the microwave synthesis of ZnO resulted in smaller rods compared to the conventional heating method [57]. Unlike ZGO and IZG without any agglomeration observed, EZG exhibited odd behavior. The image referred quite surface coverage of ZnO with the high probability for aggregation of graphene layers around the nanorods forming bundles like-structure.

### 3.3. Fourier transform infrared (FTIR)

FTIR spectra of G and its nanocomposites compared with ZnO NRs are represented in Figure 4. As shown, the GO spectrum shows significant stretching vibrational bands at 1730 cm\(^{-1}\) (C=O), 1610 cm\(^{-1}\) (C=C), 1340 cm\(^{-1}\) (C-OH), 1040 cm\(^{-1}\) (C-O), and 1230 cm\(^{-1}\) (epoxide groups) [58]. Some peaks were not found in the spectrum of the RGO because of the reduction with the hydrazine hydrate. Other bands such as C=O have lower intensities which confirm their presence in small amounts. ZnO NRs have a significant absorption band at ~ 500 cm\(^{-1}\) corresponds to the stretching vibration of Zn-O bond in zinc oxide [59].

On the other hand, the characteristic absorption bands of ZnO NRs are pronounced in the graphene composites. However, in the case of ZGO, the stretching peak of C=C was shifted to a lower wavenumber by ~ 40 cm\(^{-1}\). Moreover, the Zn-O stretching band showed a chemical shift to a higher wavenumber at ~ 580 cm\(^{-1}\), which refers to bond shortening. This emphasizes a strong interaction of ZnO over GO surface i.e. sharing of π-electrons of phenolic rings present in the GO backbone with 4S orbital on Zn\(^{2+}\) forming a coordination bond.

In the case of treatment of the G surface with ZnO either by the in-situ or the ex-situ, some bands’ positions were changed. The peak positioned at 1560 cm\(^{-1}\) in RGO exhibits a significant shift to a higher wavenumber up to 1640 cm\(^{-1}\) which emphasizes an interaction has been established, in IZG. Most of the characteristic peaks were maintained in EZG which suggests a physical interaction within the composite prepared.

### 3.4. Electron diffraction (ED)

The electron diffraction images (SAED) showed an obvious contrast between all samples, Figure 5. It can be claimed that the crystal structure of ZnO nanorods is kept while incorporation in the graphene mat. However, graphene assists the re-arrangement of the nanorods random crystals indicating the polycrystalline nature of obtained nanocomposites i.e. IZG has the perfect aligned ZnO crystal lattice. Each distinct diffraction ring pattern is ascribed to a fixed plane of nano ZnO. In all SAED images of the nanocomposites, the most predominant planes of ZnO are (100), (102) and (110) for ZGO. Meanwhile, other planes, (101), (004), (110), and (202) were detected in IZG and EZG. It should be noticed that the added amount ZnO is lower than the detecting response of the device so that the results couldn’t be confirmed by XRD. Moreover, the broad-band of graphene contributes to the masking of ZnO diffraction peaks. Thus, SAED was used as a powerful technique that can track the crystalline dopants lower than 5% in the samples. The results of ED confirm TEM findings as the particle size of ZnO NRs was changed while in-situ or ex-situ treatment of the graphene surface. The patterns depicted smaller and fine particles compared with the pristine NRs. As many reports have noticed the structure-properties relationship and confirmed that the highly ordered structure of ZnO exhibited higher photocatalytic performance than the randomly oriented [60].

### 3.5. Energy-dispersive X-ray spectroscopy (EDS)

EDS was performed to determine the ratio of both C and zinc species on the surface of the decorated graphene sheets by taking an average of 4 spots. From Figure 6, it can be noticed that (i) a small amount of carbon in ZnO samples might be attributed to incomplete conversion of acetate. (ii) ZGO has the lowest abundance of Zn species on its surface. This result is quite reasonable as most of ZnO NRs were intercalated between the GO layers forming the nanocomposite. (iii) The percent of ZnO in IZG is the highest, which emphasizes better exfoliation of G in the presence of ZnO NRs forming mono and bi-layers decorated with the nanorods over the surface as shown in section 3.2. This could enrich ZnO abundance on the surface of the obtained nanocomposite. (IV) Heterogeneous distribution of the nanorods on the surface of G in EZG as the nanorods were covered with layers of RGO which led to the reduction of its abundance on the surface. Thus, the C:Zn ratio in EZG is smaller than that of IZG. So, one can notice that EDS results manifest those obtained by TEM images and XRD.

### 3.6. Surface area (BET)

From Table 1, it can be concluded that the surface area was decreased while treatment GO and RGO with zinc oxide nanorods. However, the
Figure 5. Electron Diffraction micrographs of ZnO NRs and nanocomposites (ZGO, IZG, and EZG).

Figure 6. (I) EDS of the prepared zinc oxide nanorods. (II), (III), and (IV) EDS of the obtained graphene nanocomposites.
decrease is more pronounced in the composites of the reduced graphene oxide, which might be attributed to pore blocking by zinc oxide.

### 3.7. Photocatalytic activity of graphene and its ZnO nanocomposites

Photocatalytic activity of RGO and GO was found to be 30% and 45%, respectively, which indicates limited adsorption ability of the pristine graphene (Figure 7A). However, GO exhibits better performance than the reduced form. This might be attributed to a large number of surface functional groups in forms of hydroxyl (–OH), carboxylic (–COOH), carbonyl groups (C=O) and epoxide groups on GO. The amount of adsorbed oxygen on the surface is the main factor affecting the rate of photodegradation as adsorbed oxygen consumed in the photo-reaction [61]. Besides, the quantity of oxygen adsorbed on the surface is largely directly proportional to the number of hydroxyl groups found on the surface. Thus, the rate at the beginning of the reaction was fast due to the enormous amount of surface hydroxyl groups in GO assist in more adsorption of oxygen molecules. Also, the photocatalytic proficiency of pollutant degradation has been increased due to the enhancement of mass transfer. On the other hand, since the photocatalytic activity of ZnO is well known, modification of G or RGO with ZnO nanorods exhibited enhanced photocatalytic activity which might be owing to the synergetic effect of the nanorods on graphene. As can be observed, % COD removal increases in the case of ZGO by the reaction time and the rate at the beginning of the reaction was very high compared with GO sample. This proposes that the activation has occurred prior to ZnO nanorods. The highest COD removal was recorded after only two hours up to ~65%. By comparing the results of IZG and EZG, one can observe the following: (i) no change in the rate at the beginning of the reaction at 20 min, unlike ZGO. (ii) IZG showed better removal than EZG by the end of the reaction. The COD removal was reached 55% and 45% for IZG and EZG, respectively. This can be attributed to the homogenous distribution of ZnO NRs over graphene sheets of IZG, noticing that, both nanocomposites have almost the same surface area. This makes ZnO NRs more abundant on the surface as confirmed by EDS. The obtained results emphasize that the surface area is not the predominant factor affecting the photocatalytic activity.

The durability of various materials was examined through the utilization of the same materials in a second run and investigative their photocatalytic activity with time. Figure 7B gives the following: (i) In the second run, all the samples displayed a decrease in the photocatalytic activity. The decrease was noticeable up to 15 % in the case of using ZGO. The consumption of the most surface OH groups in the first run might be the reason of decreasing of photocatalytic activity by using ZGO in the second run. (ii) The decrease in photocatalytic activity for IZG or EZG was 18% and 22%, respectively. Thus, it can be claimed that the prepared nanocomposites have good photocatalytic performance after repeated periods.

Examination of nanocomposites’ structure after 1st and 2nd run (Figure 7: C1–C3) using XRD, revealed that there is no significant change in peak position which emphasizes that the structure of the prepared composite does not effectively change. Further, it confirms the feasibility of using such materials in photocatalytic reactions more than one time. The researchers have assured the role of graphene in the photocatalytic

![Figure 7](image-url)
degradation of the organic pollutants while included as an additive to most frequently used photocatalysts such as TiO₂ and ZnO. Briefly, they assume that graphene can adsorb the organic compounds on its surface due to the large surface area [20]. While irradiation, the electrons, generated from excitation of the semiconductor, are moved to the graphene sheet, at the interface, leaving holes in the valance band of the attached semiconductor [62, 63]. This prevents the electron-hole recombination and enhances the degradation process. Then, the transferred electrons interact with the dissolved oxygen forming oxygen radicals (O₂⁻) which ultimately produce hydroxyl radicals (OH⁻) and subsequently attack the adsorbed molecules in order to proceed with the decomposition process [63, 64]. Hitherto, this mechanism is common and agreed with the state of the art and these approaches cannot be denied. However, we see that graphene can also behave in another way which resembles the semiconductor.

As far as we know, no reports have provided an understandable mechanism for the photocatalysis of pristine graphene and/or graphene oxide under UV irradiation. Herein, a mechanism is suggested for the behavior of graphene under UV illumination supporting our claim with experimental evidence. In the beginning, it is essential to mention that the debate stresses on graphene oxide sheets and its reduced form prepared with Hummer method followed by hydrazine reduction, respectively. That is because our proposed mechanism might depend a little bit on the way of synthesis. It has been widely reported that graphene and/or graphene oxide can absorb UV due to π-π* and n-π* energy levels. Recently, Unan and his coworkers have intensively studied the absorbance of UV by different exfoliated graphite forms [46]. The results showed significant peaks at 223, 273, 312 and 361 nm corresponding to graphene oxide and graphene dispersions. As mentioned in their article, the latter uncommon peaks might be attributed to the conjugated polyenes that can affect π-π* plasmon peak. Based on this study, it could be claimed that the excitation generated while UV irradiation could be contributed in the photodegradation process through a possible interaction with the dissolved oxygen at the higher transition so that the superoxides are formed. Then, the reactive species produced and holes created could decompose the adsorbed organic substance. Another fact might assist in understanding the degradation of the organic pollutant over the graphene surface during UV exposure. The defects formed on graphene sheets through the oxidation-reduction preparation process are considered as highly reactive sites [65] that can directly degrade the organic compounds adsorbed on the surface. Moreover, it is known that graphene has a zero bandgap and hence it is a superconductor [66]. Nevertheless, the presence of atomic defects together with structural defects along the graphene sheet could create new energy levels, valence and conduction bands, near to the Fermi level which tunes the conductivity of graphene [66]. It is possible for the electrons at the valence band to absorb the quantized energy from UV spectra and excited to the conduction band where the reactive species responsible for the degradation process start to be released. Accordingly, the general proposed pathway for the photocatalytic activity of graphene and/or graphene oxide could be attributed to the photo electron–hole pairs formation due to the developing of new energy levels in the graphene sheets as aforementioned. While UV excitation of the electrons, the dissolved molecular oxygen (O₂) could be reduced at the interface in order to form the superoxide radicals (O₂⁻) which further interact with the water molecules to produce peroxide (•OOH) and hydroxide (•OH) radicals that can attack the anchored pollutants. The holes at the valence band make graphene highly reactive towards oxidation of the organic pollutants and lastly mineralized them. In the same context, the organic pollutant used in this work is phenolic compounds that can be effectively adsorbed at the surface of graphene due to π-π interaction and the potential hydrogen bonding formation on the surface of graphene oxide. Under UV irradiation, some electrons in the adsorbed phenols could be excited due to π-π* transition and then transferred to the conduction band of graphene and/or graphene oxide. This facilitates the oxidation and the final dissociation of the absorbed organic pollutants by the photo-induced reactive species; e.g. O₂•, •OOH, and •OH.

From the previous discussion, it could be recognized that the reported mechanism in considerable research articles lacks important information that should be included if the researchers have shaded the light to the possibilities indicating the photocatalytic activity of the neat graphene. No doubt, our proposed claim might be opposed by some people who are convinced that the adsorption mechanism by graphene prevails in the photocatalysis. Therefore, we provide experimental evidence as proof of our concept. At the same photodegradation experimental conditions but in the dark, by switching off UV lamp, graphene and graphene oxide have been examined against the same organic pollutants. The results confirmed that the COD removal percentages, attributed to adsorption, were so lower than of those irradiated under UV, Figure 8. Also, graphene oxide has recorded higher COD removal than graphene which makes sense due to the high density of the surface functional groups which increases the adsorption capacity. These results are harmonious with the COD removal using the same amounts and the same materials under UV and strongly emphasize that graphene and/or graphene oxide could contribute to photo-degradation by both mechanisms; adsorption and photocatalysis. The proposed reaction mechanism behind the photocatalytic activity of the graphene and its nanocomposite is schematically presented in details in Figure 9.

3.8. Biological activity

As shown in Figure 10 and Table 2, the antimicrobial activities of RGO, GO and their nanocomposites were assessed against two Gram-positive and two Gram-negative bacteria along with yeast as serious human pathogenic multidrug-resistant microorganisms. The inhibition zones recorded rely not only on the isolates but also on the type of bacteria. Indeed, cell wall construction plays a crucial role in the inactivation process of bacteria. The cell wall of Gram-negative bacteria composed of two layers, a thin peptidoglycan layer followed by an outer Lipopolysaccharide membrane unlike the cell membrane of Gram-positive bacteria that is composed of only a thick peptidoglycan layer [67]. The obtained findings showed that GO has a bactericidal effect against Gram-positive bacteria more than Gram-negative bacteria and yeast. Several studies have been reported to illustrate the mode of action of graphene nanostructures against multiple bacterial targets. Some researchers suggested that the bactericidal effect of graphene stems from the electron transfer from the microbial cell toward the graphene surface [68,69]. In more detail, respiration of the bacteria depends on the

Figure 8. COD removal percentage during adsorption in the dark with graphene and graphene oxide.
electrons transport between the proteins present on the surface of microbial membranes, and the external-cellular environment which in turn generates the energy required to support the cell activity [70]. These types of proteins have been determined as n-type semiconductors of a bandgap \( \sim 2.6–3.1 \text{ eV} \) [68]. When the microbial membrane contacts graphene nanosheets, the electrons are forced to move from the cell membrane towards the graphene surface by Fermi level alignment [68]. Thus, the steady electrons’ loss would change the bacterial surface charge an inability to maintain it over time. However, RGO showed less activity against Gram-positive bacteria and zero inhibition zone against Gram-negative bacteria. This might be attributed to the difference in the surface charge of the bacterial species tested. Gram-negative bacteria have a quite less negative charge surface (isoelectric point \( \text{pI} = 4–5 \)) compared to the Gram-positive bacteria (isoelectric point \( \text{pI} = 2–3 \)) [48] i.e. the electron transfer is more from the latter type which implies a faster inactivation than the former type.

Other standpoints of view that might explain the antibacterial activity of graphene and its oxidized form are owing to their physical and

Figure 9. Schematic representation for the suggested mechanism under UV irradiation. (A) First possible mechanism for degradation of the organic pollutants by only graphene. (B) Second possible mechanism through graphene by photosensitization of the organic pollutants. (C) Third common mechanism for degradation of the organic pollutants by ZnO nanorods decorated graphene. It is proposed that all possible mechanisms could be contributed to the photodegradation of the organic pollutants at once.
The antimicrobial performance of ZnO nanostructures is well-documented [77, 79]. Briefly, ZnO NRs dissolve in the dark into Zn$^{2+}$ ions which tightly connected to the negatively charged cell membrane by Coulomb attraction forces [63]. The proteins present in the cell membrane solidify and the synthetase enzyme is destroyed and preventing the proliferating of bacteria. Given the characteristics of the different composites prepared, we discuss a reasonable explanation for the antibacterial mechanism in accordance with the state of the art. Generally, in the prepared nanocomposites, the physical interaction between the sharp edges of graphene nanosheets disrupts the cell membrane which in turn facilitates the transport of Zinc ions across the cell membrane and consequently damages the cell’s components [80, 81, 82].

4. Conclusion

Thermally prepared ZnO nanorods were used to decorate the surface of graphene with the in-situ or ex-situ technique. The chemical structure of the obtained nanocomposites was thoroughly investigated with different analytical and spectroscopic techniques. The demineralization of the synthetic wastewater using the aforementioned materials revealed the low photocatalytic performance of graphene oxide and its reduced form while the photocatalytic activity of modified GO was increased by 30 % compared to its original value. Moreover, ZGO has the highest photocatalytic activity followed by IZG and EZG. The durability examination of the prepared nanocomposites displayed decrease in the photocatalytic activity in the second run by 15, 18 and 22% for ZGO, IZG and EZG respectively. Furthermore, proved mechanistic steps demonstrated and confirmed the unreported photocatalytic activity of pristine graphene. Antibacterial investigations revealed that modified graphene nanosheets have higher nanotoxicity toward yeast, Gram-positive and Gram-negative bacteria. The obtained results manifest the belief that graphene and/or graphene oxide could be used as a promising photocatalyst plays a dual function in photocatalysis, adsorption, and degradation processes beside disinfecting ability.

**Declarations**

**Author contribution statement**

Ahmed F. Ghanem, Abdelrahman A. Badawy, Maysa E. Mohram & Mona H. Abdel Rehim: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.


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The authors declare no conflict of interest.

**Additional information**

No additional information is available for this paper.

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