

Thu hồi vật liệu từ pin sơ cấp thải để tổng hợp chất xúc tác quang composite trên cơ sở ZnO: vai trò của graphene

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TÓM TẮT

Pin sơ cấp đặc biệt là pin alkaline và Zn-C được sử dụng phổ biến trong các thiết bị điện tử gia dụng nhưng có vòng đời ngắn, chỉ dùng một lần và đang trở thành nguồn rác thải điện tử nguy hại nếu không được xử lý đúng cách. Trong nghiên cứu này, ba composite ZnO/X với chất nền X = graphene, graphitic carbon (g-C₃N₄), và graphene-graphitic carbon (graphene/g-C₃N₄) đã được tổng hợp bằng phương pháp thủy nhiệt với nguồn nguyên liệu ban đầu Zn, và C được thu hồi từ pin sơ cấp thải. Kết quả của phương pháp kính hiển vi điện tử quét (SEM), nhiễu xạ tia X (XRD), hồng ngoại biến đổi Fourier (FT-IR), quang phổ điện tử tia X (XPS), phổ tán xạ năng lượng tia X (EDS) và phổ phản xạ khuếch tán UV-Vis DRS đã làm rõ vai trò của graphene ảnh hưởng lớn đến: (i) khả năng hình thành tinh thể ZnO trên các vật liệu nền, (ii) cấu trúc bề mặt vật liệu đã làm giảm khả năng kết tụ các hạt ZnO, (iii) cải thiện khả năng hấp thụ ánh sáng khả kiến của vật liệu. Ảnh hưởng của graphene đến vật liệu composite được khẳng định thông qua phản ứng phân hủy kháng sinh rifampicin trong vùng ánh sáng khả kiến. Kết quả cho thấy ZnO/graphene có khả năng phân hủy rifampicin gấp 1,5 và 1,7 lần ZnO/graphene/g-C₃N₄ và ZnO/g-C₃N₄ trong cùng điều kiện khảo sát.

Từ khóa: Thu hồi pin sơ cấp thải, composite ZnO, ảnh hưởng graphene.

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Recycling of spent primary batteries for the synthesis of ZnO-based photocatalysts: the role of graphene

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ABSTRACT

Primary batteries, particularly alkaline and zinc–carbon (Zn-C) types, have a relatively short service life and are frequently discarded in landfills, leading to potential environmental risks and health concerns. To address this issue, we synthesized ZnO-based photocatalysts coupled with graphene, graphitic carbon ($g\text{-C}_3\text{N}_4$), and a graphene/ $g\text{-C}_3\text{N}_4$ hybrid via a hydrothermal method, using ZnO, and graphene recovered from spent primary batteries. Techniques such as scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier Transform infrared (FT-IR), X-ray photoelectron spectroscopy (XPS), and diffuse reflectance ultraviolet-visible spectroscopy (UV-vis DRS) have been employed to elucidate the strong influence of graphene on the crystal structure, surface morphology, optical characteristics, and photocatalytic performance of the synthesized composites. The results demonstrate that the ZnO/graphene catalyst exhibits 1.5- and 1.7-fold higher rifampicin degradation efficiency than ZnO/graphene/ $g\text{-C}_3\text{N}_4$ and ZnO/ $g\text{-C}_3\text{N}_4$ under the same conditions.

Keywords: Recovery spent primary batteries, composite ZnO-based, influence of graphene.

1. INTRODUCTION

The increasing amount of spent batteries, including non-rechargeable and lithium-ion batteries, is a key factor contributing to environmental pollution and health issues. Recently, considerable attention has been given to the recycling of spent primary batteries to recover valuable secondary resources such as Zn, Mn, and graphite, which serves as an effective approach to minimizing risks and mitigating environmental impacts at the end of life.¹⁻³

As a metal oxide semiconductor, ZnO possesses properties such as excellent chemical stability, strong oxidizing capability, and cost-effective production, offering broad

application prospects. However, ZnO absorbs only ultraviolet light due to its large band gap, while its photoexcited electrons and holes undergo rapid recombination, an intrinsic limitation that reduces photocatalytic efficiency.⁴ Consequently, considerable efforts have been made to enhance its optical absorption and photocatalytic activity under illumination with visible light, for example by combining ZnO with graphene or $g\text{-C}_3\text{N}_4$.⁵⁻⁷ Nevertheless, the effect of substrate on the structural and optical properties of ZnO-based composites remains unclear. Additionally, comparing the degradation efficiency of rifampicin antibiotic (Rif) under LED light is a practical approach to exploring the role of graphene in boosting the photocatalytic

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efficiency of ZnO/graphene, ZnO/g-C₃N₄, and ZnO/graphene/g-C₃N₄.

This work aims to develop a sustainable approach for synthesizing ZnO-based materials from alkaline battery waste, with subsequent applications in photocatalytic reactions. Notably, in this work, graphene was also synthesized from the graphite foil recovered from the spent batteries, further enhancing the sustainability of the process. In particular, the influence of graphene is clarified through various characterization techniques, which reveal its effects on the crystallinity of ZnO on the supporting substrate, the surface morphology, and the visible-light absorption properties.

2. EXPERIMENT

2.1. Material synthesis process

Chemicals

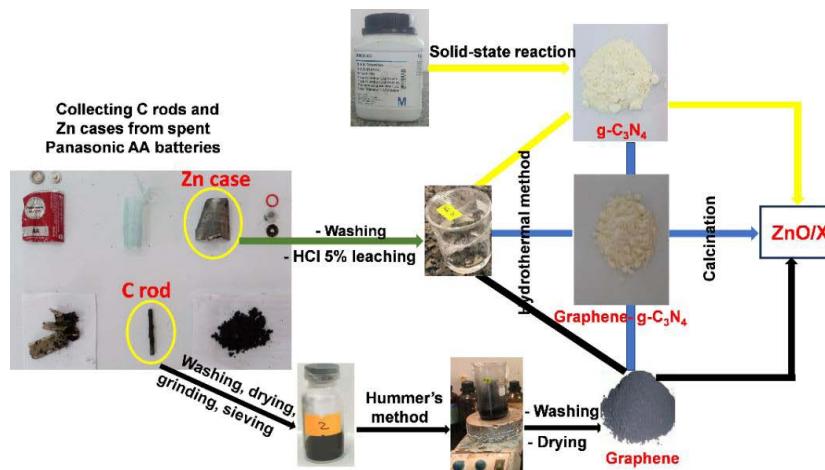
Spent primary Zn-C batteries (Panasonic AA 1.5 V). Sulfuric acid (H₂SO₄, 98%), sodium nitrate (NaNO₃), hydrochloric acid (HCl, 36.5%), hydrogen peroxide (H₂O₂, 30%), potassium permanganate (KMnO₄, 99%) were received from Xilong, China. Melamine (C₃H₆N₆, 99%), and rifampicin (95%) were Sigma-Aldrich, German.

Synthesis of composites ZnO/X (X = graphene; g-C₃N₄; graphene-g-C₃N₄)

- The substrate X: graphene was synthesized from the graphite foil of the spent batteries through a modified Hummer's method. In brief, the cell case was carefully dismantled, and the

carbon rod was collected and subsequently washed with distilled water to eliminate residual electrolytes. The graphite foils were initially washed with distilled water, dried, ground, and sieved to obtain graphite powder, which served as the precursor for graphene synthesis. Graphene powder was then produced using the modified Hummer's method, while g-C₃N₄ was prepared through the solid-state reaction of melamine.⁸ Finally, g-C₃N₄/graphene composite was fabricated via a hydrothermal process, following the procedure reported in our earlier works.⁹

- The composite ZnO/X (X = graphene; g-C₃N₄; graphene-g-C₃N₄) were hydrothermally synthesized in ethanol from a dispersed mixture of as-synthesized substrate X and ZnCl₂ solution, which was leached from the Zn case of spent primary batteries with HCl 5% acid (Scheme 1). Specifically, 0.5 g of substrate X powder was dispersed to 100 mL of ethanol and stirred for 1 h with a magnetic stirrer to form a homogeneous suspension. Subsequently, 2 mL of ZnCl₂ solution was slowly introduced and stirred for an additional 2 h. The mixture was then transferred into a Teflon-lined autoclave and heated at 180 °C for 8 h. The resulting product was centrifuged, thoroughly washed with distilled water and ethanol until neutral pH was reached, dried in air at 80 °C for 12 h, and finally calcined at 300 °C for 2 h. The obtained samples were denoted as ZG, ZN, and ZGN, respectively.



Scheme 1. Illustration of the synthesis reaction for ZnO/X preparation.

2.2. Materials characterization

The crystalline structure was determined by powder X-ray diffraction (Bruker D2 Advance) with Cu-K α radiation ($\lambda = 0.154$ nm), and diffraction data were collected within a 2θ range of 10 – 70°. Elemental compositions and chemical states were examined by X-ray photoelectron spectroscopy (XPS), with binding energy values referenced to the adventitious carbon C 1s peak at 284.8 eV. Fourier-transform infrared (FT-IR) spectra were recorded on a Shimadzu FTIR-Ifrranity-1S spectrometer (S/N ratio 30000:1) using KBr pellets containing 1 wt% of sample. The morphology and elemental compositions of the obtained materials were analyzed using scanning electron microscopy combined with EDS (SEM, HITACHI S-4800). Optical properties were investigated by UV-Vis diffuse reflectance spectra (DRS) were measured with a Scinco S-4100 spectrophotometer, and absorption spectra were obtained using a Shimadzu UV-1800 instrument.

2.3. Photocatalytic study

The photocatalytic activity of the synthesized materials was evaluated by the degradation of Rifampicin antibiotic. Rif was prepared in a fixed concentration (20 mg/L), and the prepared solution was allowed to settle in the dark for 10 hours. To evaluate the photocatalytic activity, 20 mg of catalyst was dispersed in 80 mL of Rif solution contained in a 250 mL flask and kept in the dark box. The suspension was magnetically stirred for 1 hour to establish adsorption–

desorption equilibrium. Afterwards, the solution was exposed to visible light irradiation from an LED lamp (30 W). At every 10-minute interval, 5 mL of the suspension was collected and centrifuged to separate the catalyst. The remaining Rif concentration in the supernatant was analyzed by a photometric colorimetric method using a Shimadzu 1800 spectrometer.

3. RESULTS AND DISCUSSION

As shown in Figure 1a, the diffraction peaks of the ZG composite appearing at $2\theta = 31.7$, 34.4, 36.2, 47.5, 56.6, 62.9, and 66.3° are indexed to the (100), (200), (101), (102), (110), (103), and (113) lattice planes of ZnO, which are consistent with the standard JCPDS card No. 36-1451. Moreover, the XRD pattern of the ZG sample shows an additional broadened diffraction peak at $2\theta = 25.9$ ° besides the peaks assigned to ZnO, which is the characteristic peak of the (002) plane of graphene.¹⁰ However, comparing the XRD curves of the ZN and ZGN composites with those of ZG, it can be observed that the major peaks are identical to those of g-C₃N₄ at 12.7 and 27.1°. And the weak ZnO-related peaks could be clarified due to the low content of this component. The XRD pattern analysis indicates that the graphene substrate can provide a substrate that facilitates or promotes the growth of well-crystallized ZnO, while g-C₃N₄ likely interacts more strongly with Zn²⁺, suppressing crystallization, resulting in poorly crystalline ZnO nanoparticles that are similar to our observed previous findings on TiO₂-based composites.^{8,11}

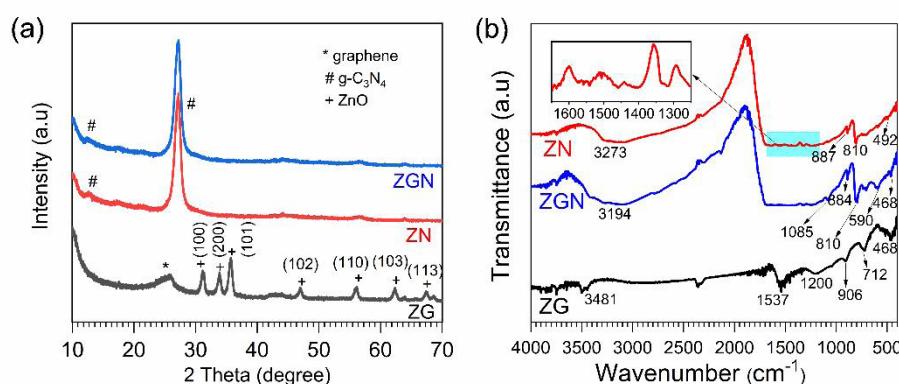


Figure 1. XRD patterns (a) and FTIR spectra (b) of the as-prepared ZG, ZN, and ZGN samples.

FTIR analysis was performed to identify the vibrational bands and displayed in Figure 1b. For ZG, the characteristic bands at 468 cm^{-1} are attributed to Zn–O vibrations, while the broad band around 3481 cm^{-1} is associated with O–H stretching of surface hydroxyl groups. The absorption peaks located at 1537 cm^{-1} and $1200\text{--}906\text{ cm}^{-1}$ can be assigned to C=C and C–O stretching of graphene, respectively. In the cases of ZN and ZGN, the broad band in the region of $3194\text{--}3273\text{ cm}^{-1}$ originates from N–H vibrations and O–H of adsorbed H_2O molecules. The intense peak at 810 cm^{-1} corresponds to the out-of-plane bending of the s-triazine ring in g- C_3N_4 . Moreover, the characteristic bands of CN heterocycles and C–N–C groups between 1250 and 1630 cm^{-1} overlap into a broad band, which becomes more pronounced upon ZnO crystallization, as also observed by Anshu Sharma et al.¹² Additionally, the Zn–O stretching

vibrations appear weak at 468 cm^{-1} (ZGN) and 492 cm^{-1} (ZN), suggesting that ZnO is either poorly crystallized or present in a low amount. This observation is in good agreement with the XRD results.

The UV–vis diffuse reflectance spectra were recorded to investigate the optical characteristics of the composite and their corresponding Tauc plots¹³ were used, and the obtained results are shown in Figure 2. As expected, the ZG sample (Figure 2a) exhibits absorption in the visible region, which can be attributed to the incorporation of graphene into ZnO. For ZN, a bandgap of 2.77 eV is obtained, which is shown in Figure 2b, while the bandgap is 2.62 eV for ZGN (Figure 2c). These results indicate that graphene enhances visible-light absorption and promotes electron–hole separation, thereby improving photocatalytic activity.

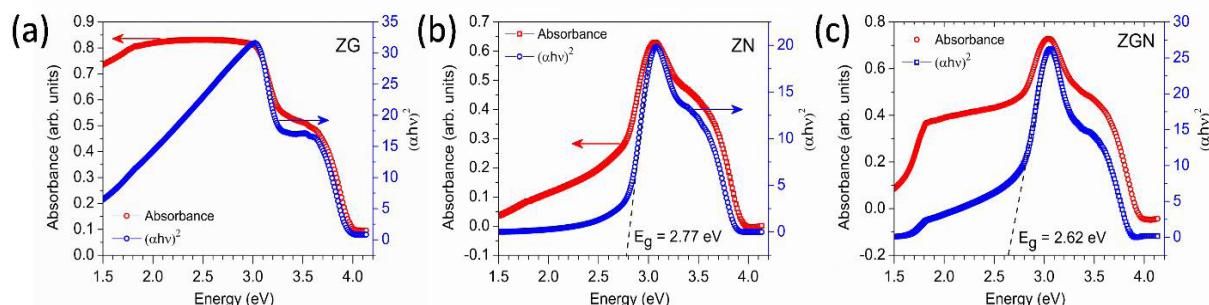


Figure 2. UV-Vis DRS and the associated Tauc plots of ZN (a), ZN (b) and ZGN (c).

The SEM-EDS analysis investigated the morphology and surface elements of the as-synthesized composites, as shown in Figure 3. Distinct morphologies of the ZG, ZN, and ZGN composites were observed, highlighting the influence of graphene incorporation on particle dispersion and surface structure. Figure 3a shows ZnO/graphene with a wrinkled appearance with multiple folds. These highly crumpled structures offer a large surface area and facilitate the uniform anchoring of ZnO nanoparticles. The intimate contact between ZnO and graphene

may promote effective interfacial charge transfer and suppress particle agglomeration, which are essential for enhancing photocatalytic activity. Additionally, the EDS analysis of the ZG sample (Figure 3b) reveals that the major elements are C, O, and Zn, while minor and trace elements such as Ca, Cl, Si, Na, Al, and S are also detected. The presence of these elements is attributed to the use of precursors derived from spent Panasonic AA primary batteries.

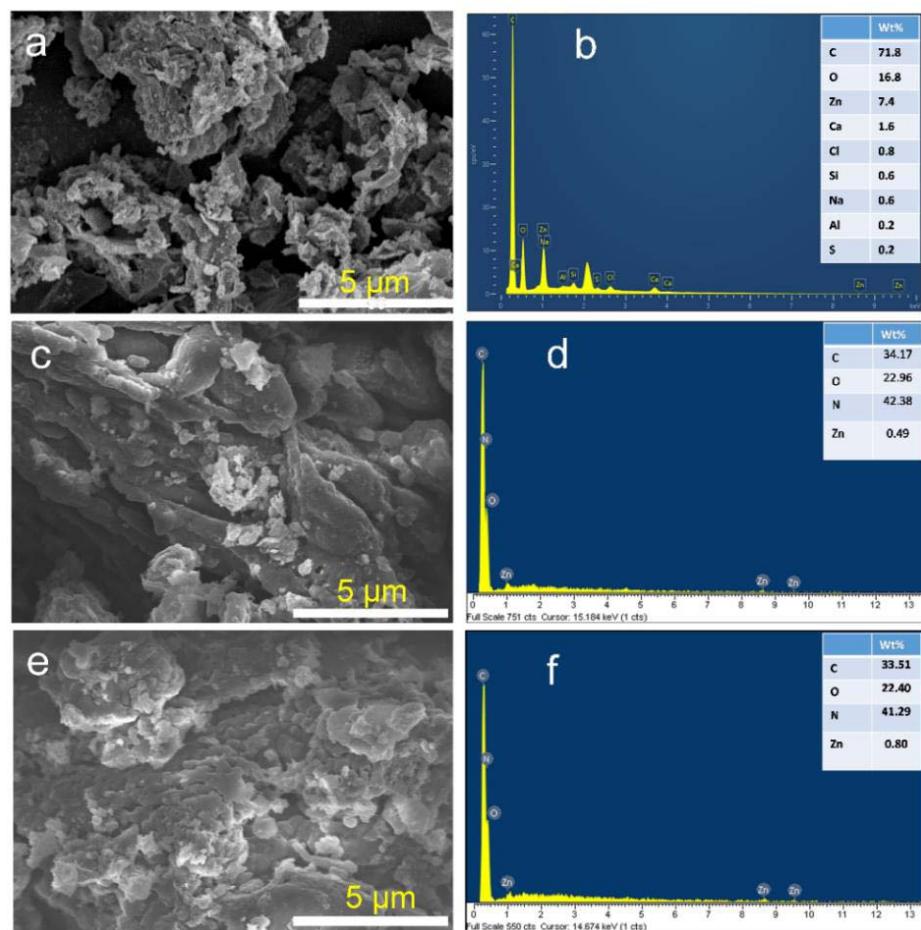


Figure 3. SEM image and EDS of ZG(a, b); ZN (c, d), and ZGN (e, f).

In contrast, the ZN sample (Figure 3c) exhibits a densely aggregated morphology, with irregularly shaped ZnO particles forming compact clusters, resulting in significant particle agglomeration and reduced dispersion. Although a two-dimensional lamella structure with wrinkles and irregular folding structure for ZGN (Figure 3e) is still observed, which suggests partial retention of the graphene structure, the ZnO particles are less uniformly distributed in comparison with ZG. This indicates that the observed morphology suggests less effective suppression of aggregation compared to the ZG sample. Nevertheless, the morphology is improved relative to the ZN composite, implying a moderate enhancement in interfacial interactions. Notably, the Zn content in ZN (0.49 wt%) (Figure 3d) and ZGN (0.80 wt%)

(Figure 3f) is significantly lower than that in ZG (7.4 wt%) (Figure 3b), suggesting that the incorporation of graphene components facilitates higher Zn loading in the ZG composite.

The surface chemical state of ZGN was investigated using the XPS technique. As shown in Figure 4a, the XPS survey spectra include signals of Zn 2p, F 1s, O1s, N1s, and C1s corresponding to the composition of ZnO, graphene, and g-C₃N₄. The presence of fluorine in the composite, as indicated in the XPS survey spectrum, can be attributed to residual fluoride compounds derived from spent primary Panasonic AA batteries. According to Figure 4b, the Zn 2p core-level of the ZnO spectrum has two peaks located at approximately 1044.1 and 1021.1 eV, corresponding to the binding energies

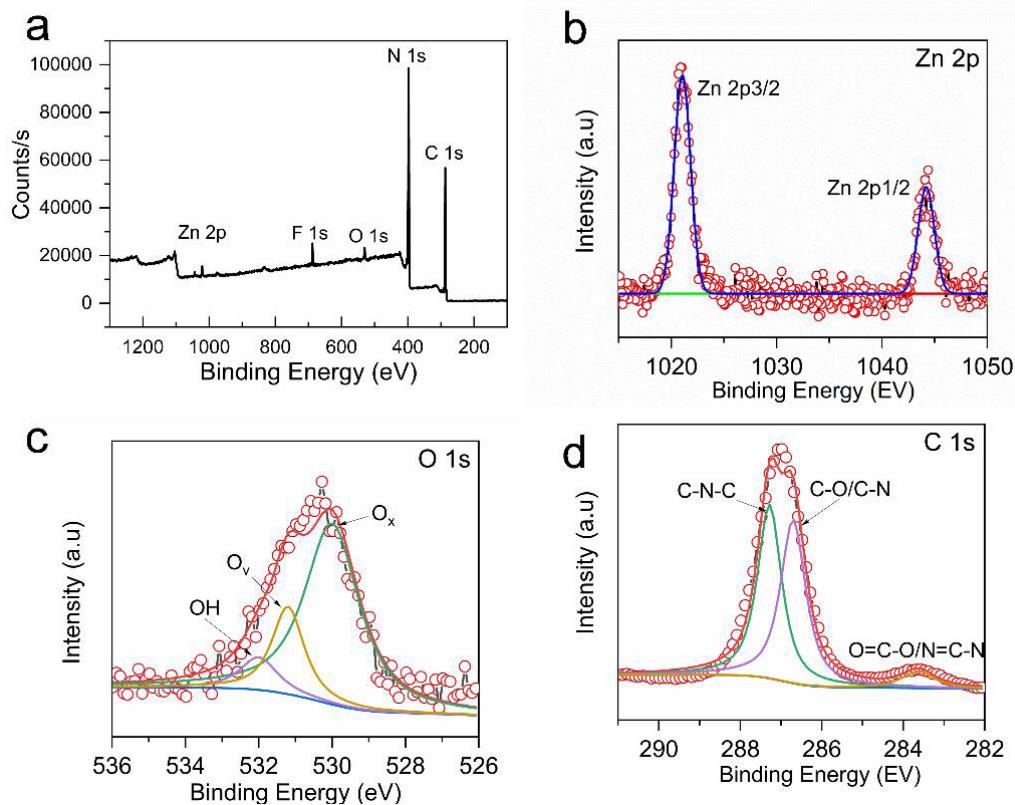


Figure 4. (a) XPS survey of ZGN composite (b) Zn 2p, (c) O 1s, and (d) C 1s spectral regions.

of Zn 2p3/2 and Zn 2p1/2, indicating that the chemical valence of Zn at the surface of ZnO is a +2 oxidation state. In the O 1s spectrum (Figure 4c), three peaks are observed at 529.9, 531.2 and 532.0 eV, which can be assigned to oxygen in ZnO lattice (O_x), oxygen vacancies in the ZnO lattice (O_v), and surface hydroxyl groups attached to Zn²⁺ ions (O–OH), respectively. The C 1s spectrum of ZGN (Figure 4d.) indicates C–N–C at 287.3 eV, C=N/C=O at 286.7 eV, and N–C=N/O–C=O at 283.6 eV, respectively.

Figure 5a shows the decrease of Rif concentration as a function of irradiation time by the photocatalysts, including ZN, ZGN, and ZG. In comparison, the concentration of Rif as a function of exposure time in the absence of a catalyst shows virtually no self-degradation. The results demonstrate that, after

60 minutes of light irradiation generated by the LED lamp, the ZN, ZGN, and ZG cause Rif degradation of approximately 25.5%, 27.5%, and 41%, respectively. Additionally, the rate degradation of Rif (Figure 5c) by the highest photocatalytic activity is linked to its enhanced kinetic characteristics for ZG (Figure 5b), which exhibits 1.5 - 1.7 times higher activity than ZGN and ZN individually. Figure 5d shows the absorption spectra for the degradation process of Rif solution of the best with extended time under visible light irradiation. The enhanced photocatalytic performance of the ZG can be attributed to improved kinetic properties resulting from the ZnO content control, the well-distributed and wrinkled graphene-based morphology, and enhanced visible light absorption achieved through the contribution of graphene.

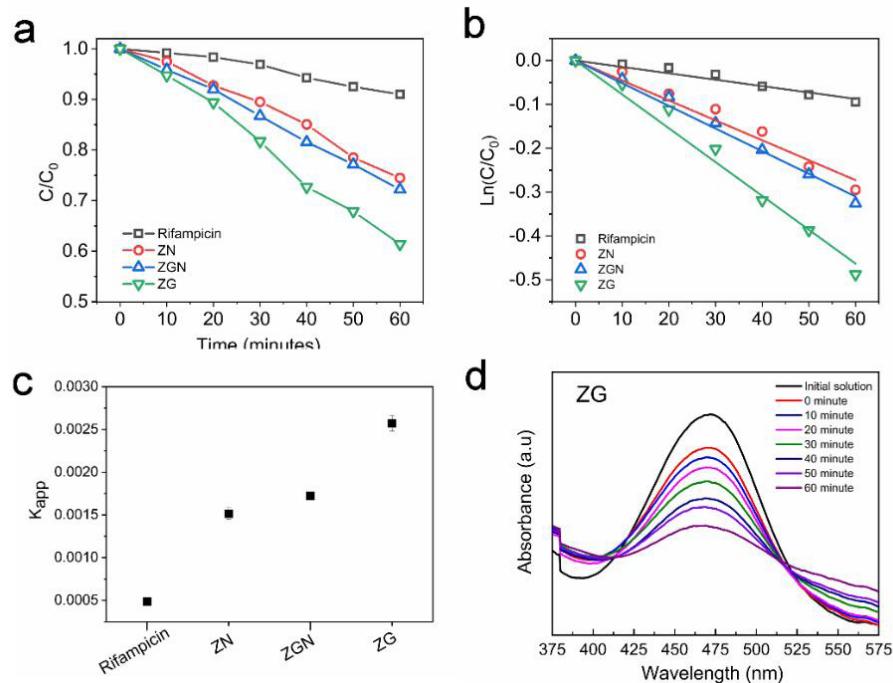


Figure 5. Photocatalytic degradation of Rif in the presence of ZG, ZN, and ZGN photocatalysts (a); the degradation kinetic plots (b); the degradation rate (k_{app}) of Rif obtained for materials (c); and UV-vis absorption spectra of ZG for different irradiation times (d).

4. CONCLUSION

In summary, three ZnO/X (X=graphene, g-C₃N₄, and graphene-g-C₃N₄) photocatalysts were prepared via a hydrothermal method using Zn, C recovered from spent primary batteries, and g-C₃N₄ from melamine. A comparative study has been conducted to demonstrate the role of graphene enhanced visible-light response and charge separation in the synthesis of ZnO-based photocatalysts. It is revealed that graphene provided a more favorable substrate for ZnO crystallization, improved particle dispersion, and enhanced visible light absorption, as confirmed by XRD, IR, SEM-EDS, and UV-Vis DRS. The photocatalytic efficiency of the synthesized materials under visible light exposure, evaluated by the degradation of the antibiotic rifampicin, was highest for the ZG composite, confirming the beneficial effect of graphene in the composite.

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