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Thu hồi vật liệu từ pin sơ cấp thải: ảnh hưởng của graphene đến cấu trúc và tính chất quang của composite ZnO

TÓM TẮT

Pin sơ cấp đặc biệt là pin alkaline and Zn-C đang được dùng rộng rãi trong các thiết bị điện tử trong hộ gia đình. Với vòng đời ngắn, chỉ sử dụng một lần, pin sơ cấp thải đang trở thành nguồn rác thải điện tử nguy hiểm. Nếu không được thu gom và xử lý đúng cách, phần lớn pin sơ cấp thải sẽ bị đốt hoặc chôn vào đất, gây ảnh hưởng nghiêm trọng và lâu dài đến môi trường cũng như sức khoẻ con người. Trong nghiên cứu này, chúng tôi đã tổng hợp ba composite của ZnO/X với chất nền X=graphene, g-C_3N_4, và graphene-g-C_3N_4 bằng phương pháp thuỷ nhiệt với nguồn nguyên liệu ban đầu Zn, và C được thu hồi từ pin sơ cấp thải Panasonic AA. Bằng các phương pháp phân tích lý hoá hiện đại như 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), phương pháp 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) quá trình 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) tăng cường khả năng hấp thụ ánh sáng trong vùng khả kiến của vật liệu. Kết quả tính chất quang xúc tác của các vật liệu thông qua phản ứng phân huỷ kháng sinh rifampicin dưới ánh sáng khả kiến đã khẳng định ảnh hưởng của graphene đến vật liệu composite được tổng hợp.

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

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

ABSTRACT

Primary batteries, especially alkaline and zinc-carbon (Zn-C) batteries, often end up in landfills due to their short lifespan, which aggravates health issues and poses environmental threats. To address these issues, herein, we synthesize three photocatalyst composites ZnO/X by coupling ZnO with X = graphene, g-C_3N_4, and graphene-g-C_3N_4 substrates using a hydrothermal method with ZnO, and graphene is recovered from spent primary Panasonic AA batteries as the Zn and C source. 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 properties, and photocatalytic performance of the synthesized composites.

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, numerous efforts have been devoted to the spent primary batteries and recycling or recovery of value-added secondary raw materials such as Zn, Mn metals, and graphite, helping to reduce the risk and negative environmental impact at the end of life.[1-3]

As a metal oxide semiconductor, ZnO exhibits characteristics of strong chemical stability, high oxidation ability, and low production cost, thereby offering excellent application prospects. Unfortunately, ZnO absorbs low amounts of sunlight and performs high recombination of photogenerated electron-hole pairs due to its large bandgap.[4] Consequently, considerable efforts have been made to enhance its optical absorption and photocatalytic performance under visible light irradiation, including the combination of ZnO and graphene, as well as the formation of a heterojunction between g-C_3N_4 to improve its photocatalytic performance.[5-7] However, the influence of graphene on the structural and optical properties of ZnO-based composites remains unclear. Additionally, comparing the degradation efficiency of rifapicin antibiotic (Rif) under LED light is a practical approach to exploring the role of graphene in improving the photocatalytic performance of ZnO/graphene, ZnO/g-C_3N_4, and ZnO/graphene/g-C_3N_4.

This work aims to develop a sustainable approach for synthesizing ZnO-based materials from alkaline battery waste, with subsequent applications in photocatalytic reactions. In particularly, 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 optical absorption in the visible light range. The ZnO/graphene composite exhibits significantly improved photocatalytic performance, with a degradation efficiency of approximately 41% of Rif removed after 60 min of irradiation, which is 1.5 and 1.7 times higher than that of ZGN and ZN, respectively.

2. EXPERIMENT

2.1. Material synthesis process

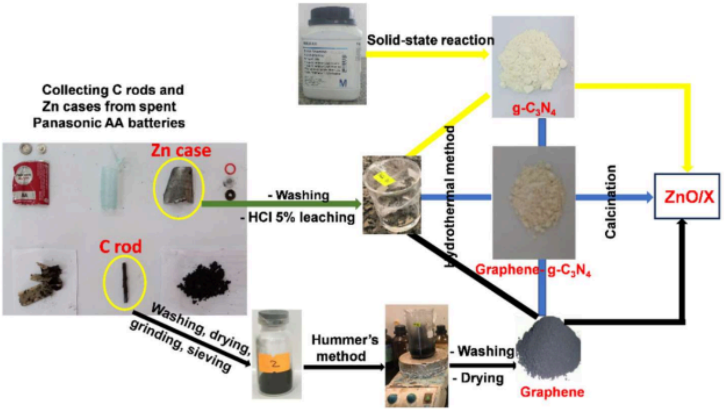
Chemicals

Spent primary Zn-C batteries (Panasonic AA 1.5 V) were collected locally from Gia Lai province. Sulfuric acid (H_2SO_4, 98%), sodium nitrate ($NaNO_3$), hydrochloric acid (HCl, 36.5%), hydrogen peroxide (H_2O_2, 30%), potassium permanganate ($KMnO_4$, 99%) were received from Xilong, China. Melamine ($C_3H_6N_6$, 99%), and rifampicin (95%) were Sigma-Aldrich, Germany. All the chemicals were used as received without further purification.

Synthesis of composites ZnO/X (X = graphene; g-C_3N_4; graphene-g-C_3N_4)

- *The substrate X:* graphene synthesized from graphite foil of spent Panasonic AA 1.5 V batteries through modified Hummer's method. Briefly, the cell case was dismantled carefully, then collecting the carbon rod followed by a wash with distilled water to remove the electrolytes. Firstly, the graphite foils were washed with distilled water, dried, ground, and sieved into graphite powder, which was used as a precursor to synthesize graphene. Subsequently, graphene powder was synthesized by the modified Hummer's method, and g-C_3N_4 was obtained through a solid-state reaction of melamine. Next, the g-C_3N_4/graphene composite was subsequently prepared via a hydrothermal method, as described in our previous studies. [8-9]

- The ZnO/X (**X = graphene; g-C_3N_4; graphene-g-C_3N_4**) composites (Scheme 1) were hydrothermally synthesized in ethanol from a dispersed mixture of as-synthesized *substrate X* and $ZnCl_2$ solution, which was leached from the Zn case of spent primary Panasonic AA 1.5 V batteries with HCl 5% acid. Firstly, 0.5 g of substrate *X* powder was added to 100 mL of ethanol (99%) and stirred for 1 hour using a magnetic stirrer to obtain a homogeneous suspension. Subsequently, 2 mL of $ZnCl_2$ solution was slowly added and stirred continuously for 2 hours. After that, the mixture was transferred into a Teflon container and heated up to 180 °C for *8* hour. Finally, the product was centrifuged to collect the solid, which was further washed in distilled water and ethanol until reaching neutral pH value, then dried in air at 80 °C for 12 hours, followed by a calcination at 300 °C for 2 hours, denoted ZG, ZN, and ZGN, respectively.



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

Materials characterization

The surface morphology of the synthesized materials was characterized by scanning electron microscopy (SEM) using a HITACHI S-4800 microscope. The crystalline structure of the samples was investigated using powder XRD on a Bruker D2 Advance diffractometer, equipped with a Cu-Kα X-ray source (λ = 0.154 nm). The spectra were acquired in the 2θ range of 10 – 80°. The XPS peaks of the elements were calibrated by referencing the C 1s peak of adventitious carbon to 284.8 eV. The Fourier-transform infrared (FT-IR) spectroscopy was carried out on FTTR-iffranity-1S, Shimadzu spectrophotometer, ratio S/N: 30000:1, with a sample concentration of 1% in weight in a KBr pellet. The UV-Vis diffuse reflectance spectra of the catalysts were investigated using Scinco S-4100 UV-Vis spectrophotometer. UV-Vis absorption spectra were measured using a Shimadzu 1800-Vis spectrophotometer.

Photocatalytic study: The photocatalytic activity of the synthesized ZnO/X materials was evaluated by the degradation of Rifapicin 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. Then, 20 mg of the photocatalyst was added to 80 mL of the Rif solution in a 250 mL flask and placed inside a dark box. The mixture was stirred in the dark for 1.0 hours to reach the adsorption–desorption equilibrium. Subsequently, the prepared solution was irradiated with the photocatalytic material under visible light conditions using an LED lamp with a power of 30 W. After a specific irradiation time (10 minutes), 5 mL of the mixed suspension was withdrawn and centrifuged to remove the solid photocatalyst. The Rif concentration of the sample was determined using the photometric colorimetric method with a Shimadzu 1800 spectrometer.

3. RESULTS AND DISCUSSION

According to Figure 1a, the diffractions of the ZG including peaks at 2θ = 31.7, 34.4, 36.2, 47.5, 56.6, 62.9, 66.3, 67.9, 69.2 and 77.0° which correspond to the (100), (200), (101), (102), (110), (103), (200), (112), (201) and (202) crystalline planes of ZnO, respectively ascribing to PDF#JCPDS No. 36-1451. Moreover, the XRD pattern of the ZG sample shows an additional broadened diffraction peak at 2θ = 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-C_3N_4 at 12.7 and 27.1°. And the inconsiderable ZnO-related peaks could be clarified due to the low content of this component.

The XRD pattern analysis indicates that the graphene substrate can produce more formation of well-crystallized ZnO, while C_3N_4 likely interacts more strongly with Zn^{2+}, suppressing crystallization, resulting in poorly crystalline ZnO nanoparticles that are similar to our observed previous findings on TiO_2-based composites.[8,11]

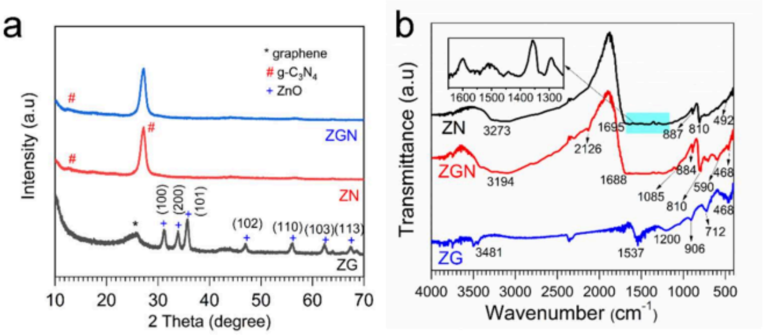


Figure 1. XRD patterns (a) and FT-IR (b) of the as-synthesized ZG, ZN, and ZGN composites

FTIR analysis was performed to identify the bond groups and displayed in Fig. 1b. For ZG, characteristic bands appeared in the range of 468 cm^{-1} corresponding to the Zn-O bond vibration, and another band around 3481 cm^{-1} corresponds to the hydroxyl group stretching vibrations. The absorption peaks at 1537 cm^{-1} and 1200, 906 cm^{-1} are related to the C-H and C-O stretching vibration bands. For ZN and ZGN, a broad band at 3194-3273 cm^{-1} appears due to N-H groups and the hydroxyl group of adsorbed H_2O molecules. The strong band observed at 810 cm^{-1} indicated the out-of-plane bending vibration of the s-triazine unit of g-C_3N_4. However, the characteristic bands in 1250–1630 cm^{-1} of stretching modes of CN heterocycles and C–N–C aromatic rings are getting merged to a broad absorption band as a result of ZnO crystallization, which Anshu Sharma et. al also observes.[12] Additionally, the weak Zn–O stretching vibrations at 468 cm-1 (for ZGN) and 492 cm-1 (for ZN) possibly resulted from the low amount of ZnO, which is in good agreement with XRD data.

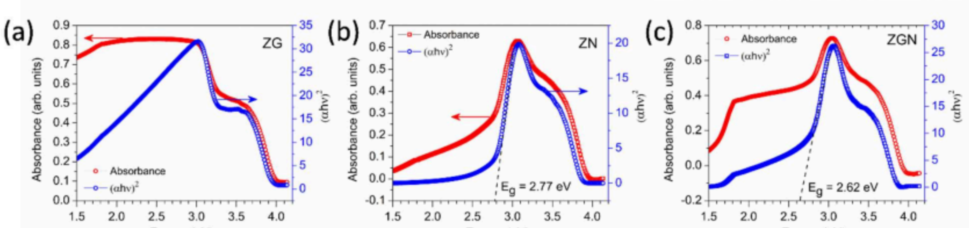


Figure. 2. UV-Vis diffuse reflectance spectra and the corresponding Tauc plots of ZN (a), ZN (b) and ZGN (c)

To study the optical properties of composites, the UV-vis diffuse reflectance spectra and their corresponding Tauc plots[13] were used, and the obtained results are shown in **Fig. 2**. As expected, the ZG sample (Fig. 2a) absorbs in the whole visible region due to the presence of graphene on ZnO. For ZN, a bandgap of 2.77 eV is obtained, which is shown in Fig. 2b, while the bandgap is 2.62 eV for ZGN (Fig. 2c). Therefore, it is noticeable that a narrower bandgap is obtained for ZGN due to the contribution of graphene in the composite. These observations may suggest an increase in the absorption of visible light in the composite due to the introduction of graphene, which could lead to modifications of the fundamental process of electron/hole pair formation during irradiation.

The SEM-EDS analysis investigated the morphology and surface elements of the as-synthesized composites, as shown in Fig. 3. Distinct morphologies of the ZG, ZN, and ZGN composites were observed, highlighting the influence of graphene incorporation on particle dispersion and surface structure. Fig. 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 (Fig. 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. In contrast, the ZN sample (Fig. 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 (Fig. 3e) is still observed, which suggests partial retention of the graphene structure, the ZnO particles are less uniformly distributed compared to ZG. This indicates that the graphene content in ZGN is insufficient to completely suppress particle aggregation. Nevertheless, the morphology is improved relative to the ZN composite, implying a moderate enhancement in interfacia interactions. Notably, the Zn content in ZN (0.49 wt%) and ZGN (0.80 wt%) is significantly lower than that in ZG (7.4 wt%), suggesting that the incorporation of graphene components facilitates higher Zn loading in the ZG composite.

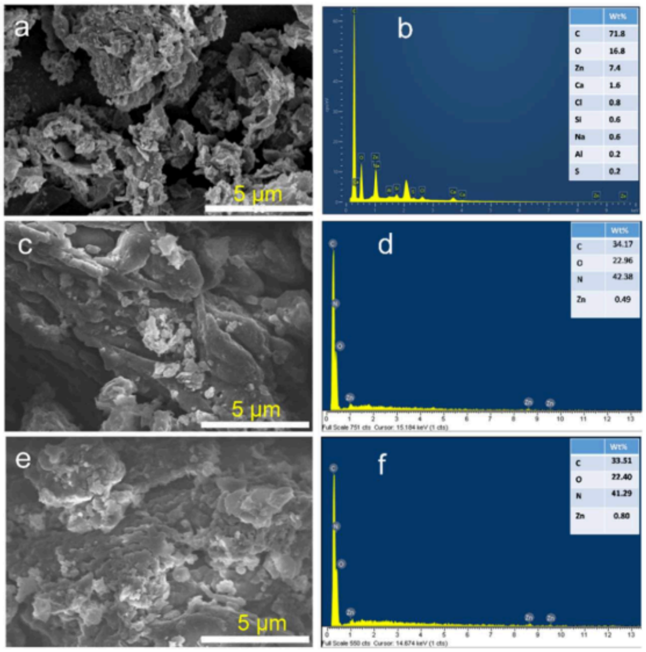


Figure 3. SEM image and EDS of ZG(a, b); ZN (c, d), and ZGN (e, f)

The surface chemical state of ZGN was investigated using the XPS technique. As shown in Fig. 4a, the XPS survey spectra include signals of Zn2p, Cl1s, O1s, N1s, and C1s corresponding to the composition of ZnO, graphene, and g-C_3N_4. 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 Fig. 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 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 in Fig. 4c, three peaks are observed at 529.9. 531.2, and 532.0 eV can correspond to oxygen in the ZnO lattice (O_X), the oxygen vacancy in the ZnO lattice (O_V), and the OH groups attached to Zn^{2+} ions (O_{OH}), respectively. The C1s spectrum of ZGN 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.

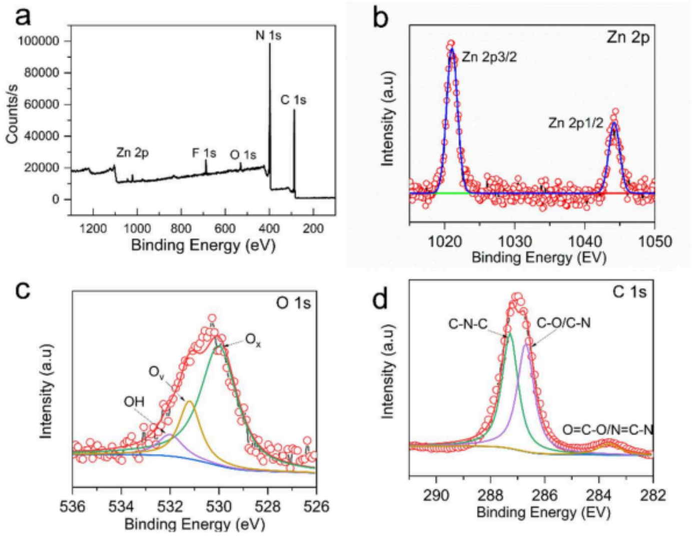


Figure 4. (a) XPS survey of ZGN composite (b) Zn 2p, (c) O1s, and (d) C1s spectral regions.

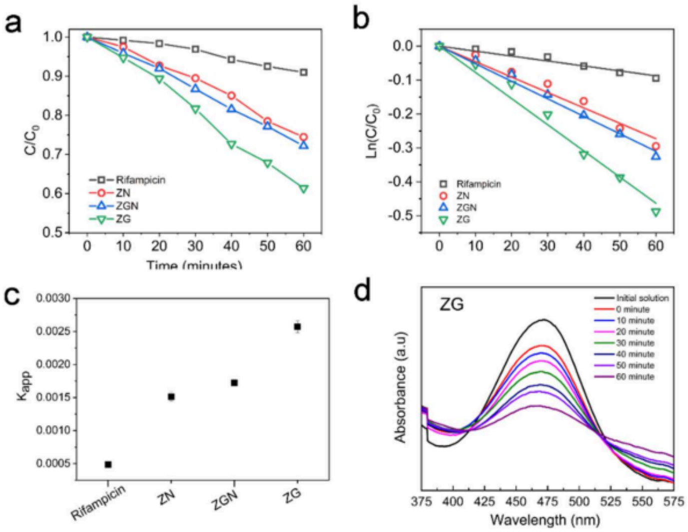


Fig. 5. Photodegradation of Rif as a function of irradiation time, as-synthesized (a); the corresponding kinetic plots (b); the degradation rate (k_{app}) of Rif obtained for materials (c); and the absorption spectra for the degradation process by ZG (d).

The visible-light photocatalytic performances of the materials are presented in Fig. 5. Fig. 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 by the highest photocatalytic activity is linked to its diminished kinetic characteristics for ZG, which exhibits 1.5 - 1.7 times higher activity than ZGN and ZN individually. 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.

4. CONCLUSION

In summary, three ZnO/X (X=graphene, g-C$_3$N$_4$, and graphene-g-C$_3$N$_4$) composites were prepared via a hydrothermal method using Zn, C recovered from spent primary batteries, and g-C$_3$N$_4$ from melamine. A comparative study has been conducted to demonstrate the role of graphene in the synthesis of ZnO-based photocatalysts. Although the amounts of precursors were similar (2 mL of ZnCl$_2$ solution and 0.5 g of substrate X) at the same synthesis conditions, it is revealed that the crystallization of ZnO on the substrate graphene became more favorable, improved particle dispersion, and enhanced visible light absorption, as confirmed by XRD, IR, SEM-EDS, and UV-Vis DRS. The photocatalytic performance of the as-prepared materials under visible light irradiation, 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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