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Fabrication and Characterization of Activated Carbon/ZnO Nanocomposite Films for Use as a Photocatalyst in Degradation of Organic Compounds

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Article

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ABSTRACT

The activated carbon/ZnO nanocomposite films were successfully prepared by a simple doctor blade method. The obtained films were characterised by X-ray diffraction, scanning electron microscopy, Brunauer-Emmett-Teller, X-ray photoelectron spectroscopy, UV-vis diffuse reflectance spectroscopy and Photoluminescence techniques. The photocatalytic properties of all films were carried out by degrading rhodamine B (RhB) dye under solar light irradiation. From the study, it was found that an increment of the efficacy of photocatalytic activities showed in activated carbon/ZnO nanocomposite films as compared to the pure activated carbon and pure ZnO. Moreover, the effect of concentration of activated carbon on the photocatalytic activity of as-prepared nanocomposite films was studied. Results were found that the optimal concentration of 5 wt% activated carbon on the surface of ZnO exhibited the highest efficiency.

KEYWORDS

activated carbon, ZnO, photocatalytic activity, degradation

INTRODUCTION

Numerous increments of wastes discharged from various industries such as textiles, food, painting, plastics and papers have caused environmental pollution [1,2]. These wastes are the main causes that result in wastewater problems. When they are discharged into water resources without proper prior treatment, it leads to negative effects on human health and the ecosystem. Recently, researchers have been searching for suitable treatment methods to eliminate pollutants and impurities from wastewater. To date, the heterogeneous photocatalysis process has received great popularity by using semiconductor oxide as a photocatalyst to degrade organic compounds in wastewater. Various semiconductor oxides such as TiO₂, SnO₂, BiVO₄, BiFeO₃, Bi₂WO₆, WO₃ and ZnO as a photocatalyst are used to remove organic contaminants [3-9]. Among these semiconductor oxides, ZnO is one of the most significant semiconductor oxides, attracting the attention of many researchers for its use as a photocatalyst and for oxidizing organic compounds into water [10,11]. At present, ZnO is used to

replace TiO_2 due to its higher photocatalytic activity, lower cost, good biocompatibility, high physical and chemical stabilities, and band gap energy which is also near to that of TiO_2 [12,13]. However, the recombination of photogenerated charge carriers of bare ZnO is easy. To overcome this issue, the doping or composite of ZnO with other materials such as Fe-ZnO, Au-ZnO, TiO_2/ZnO , SnO_2/ZnO , WO_3/ZnO and BiVO_4/ZnO are also indispensable for improving the charge carrier recombination and the efficacy of photocatalytic capacity [14-19]. Activated carbon (AC) is a green material, which can be a good candidate material for ZnO. It has been regarded as an excellent absorbent and photocatalyst which is broadly used for degrading organic compound water splitting because it has large pore volumes and extensive surface area [20,21]. From these advantages, we have chosen the activated carbon to make a composite with ZnO. Several methods for synthesizing activated carbon/ZnO nanocomposite have been reported such as solvothermal, hydrothermal method, sol-gel method, homogeneous precipitation method, and so on [22-25].

However, the disadvantages of the use of photocatalyst powders in the photocatalysis process are also recognized including the difficulty in agglomeration of particles in suspension, the separation of particles from solution when the complete reaction is difficult, and the difficulty in reuse to continue [26,27]. Therefore, the way to solve these problems is to develop photocatalyst powders in film form. Numerous methods have been used to prepare activated carbon/ZnO nanocomposite films such as spin coating, sputtering, doctor blade, electrochemical deposition, dip-coating and screen printing [28-32].

In this research, the activated carbon/ZnO nanocomposite films were fabricated via a simple doctor blade method. Then the as-prepared film samples were studied for their physicochemical properties by using X-ray diffraction, Scanning Electron Microscopy, Brunauer-Emmett-Teller, X-ray photoelectron spectroscopy, UV-vis diffuse reflectance spectroscopy and Photoluminescence techniques. Rhodamine B (RhB) dye was used as a model organic contaminant to evaluate the photodegradation ability of film samples under solar light irradiation.

EXPERIMENTAL

Materials and Methods

Synthesis of activated carbon/ZnO nanocomposite

For the first step, activated carbon derived from *cocos nucifera* (coconut shell) was synthesized via chemical activation. A coconut shell was washed with deionized water and dried in an electric oven at 80 °C for 2 hours. After that, the coconut shell was turned to charcoal at a temperature of 200 °C, and then the as-prepared charcoal was ground with a mortar and pestle. 6 M of nitric acid (HNO_3) solution was prepared and used to activate large pore volumes in the charcoal. The as-prepared activated

carbon particles were collected and washed with a centrifuge at 5000 rpm for 10 min, and dried at a temperature of 80 °C for 24 hours. Finally, the activated carbon particles were calcined to eliminate other impurities in activated carbon at 600 °C for 1 hour.

The homogeneous precipitation method was used to synthesize ZnO nanoparticles by using zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) and potassium hydroxide (KOH) as precursors. 0.1 M of zinc acetate dihydrate and 0.2 M of potassium hydroxide were dissolved in 50 ml of water. The zinc acetate dihydrate solution was then added to the potassium hydroxide solution together with a vigorous stirrer until it became a homogeneous solution. The nitric acid (HNO_3) solution of 6 M was used to adjust the neutral pH with a magnetic stirrer, and then the as-prepared solution was filtered and washed with deionized water until pH 7. The precipitates were dried by using an electric oven at 80 °C for 24 hours. Finally, the ZnO particles were calcined at 500 °C within 1 hour to eliminate impurities, and then the pure ZnO particles were obtained.

The composite of ZnO nanoparticles with activated carbon was fabricated through an impregnation method. Firstly, the amounts of activated carbon at 1% and 5% (by weight) were homogeneously mixed into 1 g of ZnO nanoparticles in a crucible, and then 1 ml of deionized water was dissolved. The obtained suspension was heated at 500 °C for 1 hour in the furnace. Finally, the activated carbon/ZnO nanocomposite was obtained.

Film preparation

A simple doctor blade method was employed to prepare activated carbon/ZnO nanocomposite films using Triton x-100 as a binder. In a typical process, 0.5 g of nanoparticle powders, 0.5 ml of Triton-x 100 and 1 ml of acetic acid were mixed and ground in a mortar and pestle until they became a homogeneous suspension. The absolute ethanol of 5 ml was slowly added dropwise into the suspension with vigorous grinding. The as-prepared suspension was coated on glass substrates, with scotch tape to control thickness. The obtained films were then annealed to eliminate Triton-x 100 at 500 °C for 1 hour.

Characterization

X-ray diffraction was employed to investigate the crystalline phase of film samples by Philips X'Pert MPD using $\text{CuK}\alpha$ radiation. Scanning electron microscopy was used to study the morphology and cross-section of film samples by using JEOL JSM-6335F. The specific surface area of film samples was observed by Brunauer-Emmett-Teller using Quantachrome. X-ray photoelectron spectroscopy was used to analyze the elemental components of film samples through AXIS ULTRA^{DLD}. The optical absorption property of film samples was analyzed by UV-vis diffuse reflectance spectroscopy using UV-

vis 3600, Shimadzu. Photoluminescence (PL) was applied to record the immigration and separation of charge carriers by using LLS-345 at an excitation wavelength of 345 nm, with an LED lamp.

Photocatalytic activity test

Rhodamine B (RhB) was used as a model dye for the investigation of the photocatalytic activity of activated carbon/ZnO nanocomposite films under solar light irradiation. The concentration of 2.0×10^{-4} M RhB dye was dissolved with deionized water at 100 ml, and then film samples were soaked in dye solution. Before the irradiation, the film samples were kept overnight to ensure the adsorption-desorption equilibrium of film and dye. When the film sample was irradiated using a 100 W halogen lamp, the as-prepared suspension of 3 ml was kept every 15 min to detect the maximum wavelength of RhB dye by UV-vis spectrometer using UV-1700. The percentage of photodegradation efficiency of RhB dye was evaluated through the equation as follows [33]:

$$\text{degradation efficiency}\% = \left(\frac{C_0 - C_t}{C_0} \right) \times 100 \quad (1)$$

Where C_0 and C_t are the initial concentrations of RhB dye at 0 and time t , respectively.

RESULTS AND DISCUSSION

XRD and BET analysis

The XRD patterns of activated carbon film, ZnO film and activated carbon/ZnO nanocomposite film with different weight (activated carbon) concentrations were shown in Figure 1, displaying the diffraction peak of activated carbon with the board peaks located in the range of about 23.88° and 43.12° corresponded to (002) and (100) planes of amorphous carbon phase [34,35]. Meanwhile the ZnO film, the seven main diffraction patterns located at 2θ values of 31.70° , 34.42° , 36.16° , 47.76° , 56.52° , 62.85° and 67.94° , corresponding to the (100), (002), (101), (102), (110), (103) and (112) planes, respectively, which indexed as a hexagonal wurtzite structure of ZnO (JCPDS No. file 36-1451) [36,37]. In the part of the activated carbon/ZnO nanocomposite film, the XRD peaks were similar to the ZnO film. Moreover, it can be seen that the absence of other impurity peaks was detected, showing that the diffraction patterns of whole film samples had a high-purity structure. In addition, the activated carbon amounts deposited on the ZnO particles did not influence the transformation of the ZnO phase and did not emerge the activated carbon peaks owing to a very low amount of deposited activated carbon on ZnO. The surface area amounts of all film samples were measured by using the nitrogen absorption BET technique. From the BET measurement results, it was found that BET specific surface area of activated carbon film, ZnO film and activated carbon/ZnO nanocomposite film with different

weight (activated carbon) concentrations of 1% and 5% was 331.27 m²/g, 38.54 m²/g, 40.90 m²/g and 42.16 m²/g, respectively. Besides, it can be seen that the surface area and active sites of ZnO deposited with activated carbon were increased with the amounts of activated carbon, leading to the augmentation of photocatalytic activity.

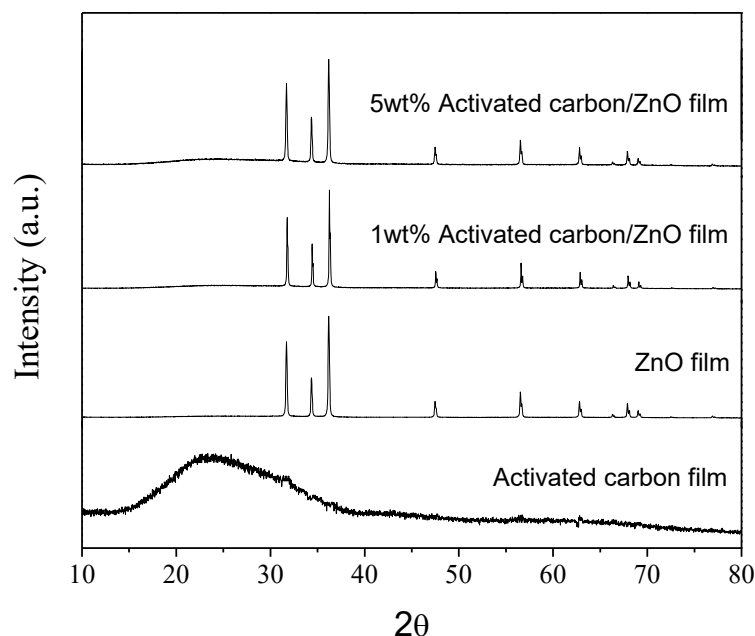


Figure 1. XRD diffraction patterns of activated carbon film, ZnO film and activated carbon/ZnO nanocomposite film with different weight (activated carbon) concentrations

SEM analysis

The morphology and thickness cross-sectional analysis of activated carbon film, ZnO film and 5 wt% activated carbon/ZnO nanocomposite film were investigated using an SEM micrograph, as displayed in Figure 2. The SEM image of activated carbon film was a sheet-like structure, with an average particle size of 50-100 nm, as shown in Figure 2a. In the part of ZnO film, the morphology was a tiny rod-like shape, with 20-50 nm in diameter, as demonstrated in Figure 2b. Meanwhile, the SEM micrograph of activated carbon/ZnO nanocomposite film consisted of a sheet-like shape of activated carbon and a rod-like shape of ZnO, with an average size of around 20-100 nm, as represented in Figure 2c. Thickness cross-sectional SEM micrographs of activated carbon film, ZnO film and 5 wt% activated carbon/ZnO nanocomposite film were shown in Figure 2d-2f. It was found that the agglomerated particles on film were quite uniform, with a similar thickness of about 2.5 µm.

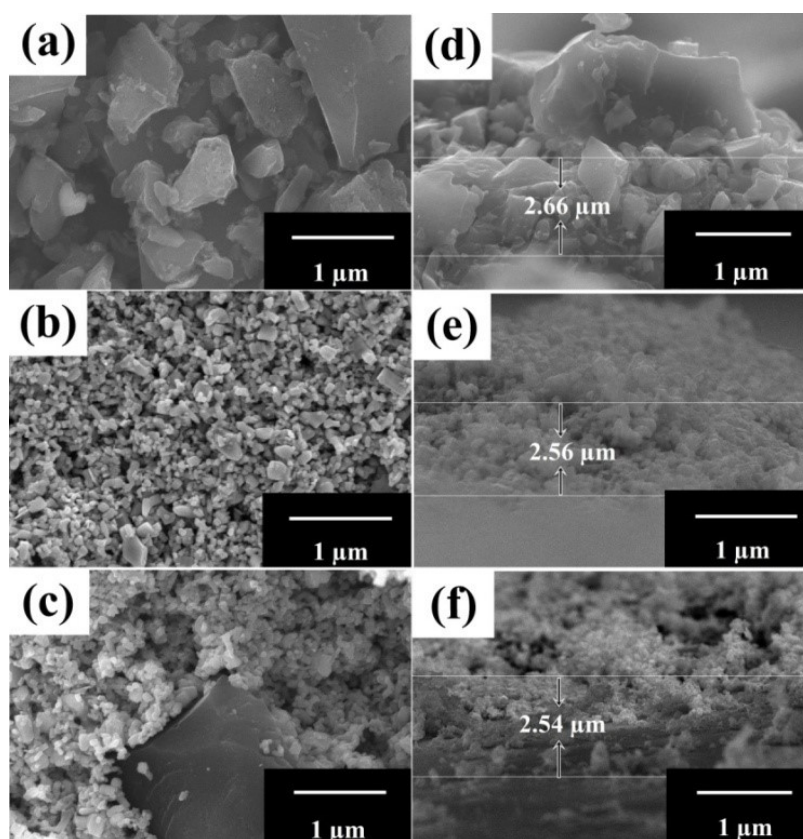


Figure 2. SEM images and cross-section of (a,d) activated carbon film, (b,e) ZnO film and (c,f) 5 wt% activated carbon/ZnO nanocomposite film

XPS analysis

In Figure 3, the XPS technique was used to study the surface elemental components and chemical states in 5 wt% activated carbon/ZnO nanocomposite film. XPS spectra of 5 wt% activated carbon/ZnO nanocomposite film were composed of Zn 2p, O 1s and C 1s ions, respectively. Figure 3a showed XPS peaks of Zn 2p orbital, the binding energies located at about 1022.19 eV and 1045.28 eV corresponding to the Zn 2p_{3/2} and Zn 2p_{1/2}, respectively, which can be indexed as Zn²⁺ ions in the ZnO [38]. For the O 1s orbital, XPS peaks showed four fitting peaks appearing at the binding energies of about 531.06 eV, 532.17, 533.24 eV and 534.57 eV, as represented in Figure 3b. The binding energies located at about 531.06 eV, 532.17, 533.24 eV and 534.57 eV were assigned to chemisorbed oxygen and hydroxyl groups in Zn-O bonding of wurtzite hexagonal ZnO structure [39,40]. In the part of C 1s orbital in activated carbon, the peaks included five peaks, as illustrated in Figure 3c. The peaks took place at the binding energies of 284.44 eV, matching the C-C bonding in activated carbon, while the other peaks at the different binding energies of about 285.39 eV, 286.43 eV, 287.55 eV and 289.40 eV attributing to the C-O, C=O, C-N and O-C=O bonding [41,42], respectively.

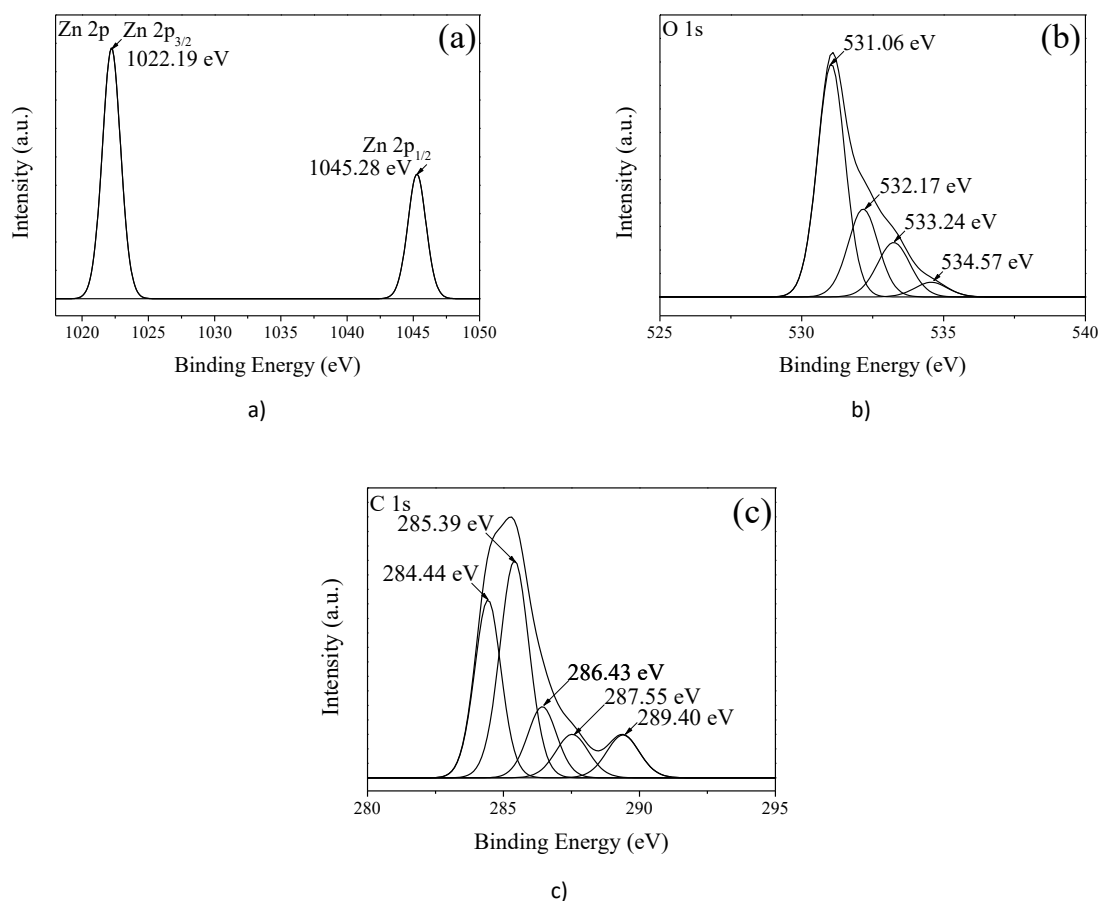


Figure 3. XPS spectra of (a) Zn 2p, (b) O 1s and (c) C 1s of 5 wt% activated carbon/ZnO nanocomposite film

UV-vis DRS analysis

The optical absorption properties of activated carbon film, ZnO film and 5 wt% activated carbon/ZnO film were studied through the UV-vis DRS technique, as displayed in Figure 4. The reflectance and transmission values of all film samples were calculated to obtain the absorbance using the equation: $\%A = 100 - \%R - \%T$. From the investigation results, it was found that the absorption edges of activated carbon film, ZnO film and 5 wt% activated carbon/ZnO film were in the wavelength range of approximately 344 nm, 394 nm and 397 nm, respectively, as depicted in Figure 4a-4c. Moreover, it can be seen that the deposition of activated carbon on the surface of ZnO resulted in the shift to a longer wavelength of UV light. This phenomenon might be due to the tightly chemical bonding between ZnO and activated carbon [43]. In addition, the decoration of activated carbon onto ZnO led to the shift of absorption edge to a longer UV range, which helped to improve the absorption area of ZnO in the photodegradation of organic compounds under solar light irradiation. The band gap energies of activated carbon film, ZnO film and 5 wt% activated carbon/ZnO film were estimated according to

Tauc's equation: $(\alpha h\nu)^{\frac{1}{n}} = A(h\nu - E_g)$, where α , $h\nu$, A and E_g are the absorption coefficient, the photon energy, the constant and the band gap energy, respectively.

Among them, the value of n is derived from characteristics of the photo transition in a semiconductor, and n for activated carbon and ZnO is $1/2$ [44,45]. Therefore, the band gap energy values can be evaluated by the plot of $(\alpha h\nu)^2$ versus E_g , the obtained band gap energies of activated carbon film, ZnO film and 5 wt% activated carbon/ZnO film were 3.68 eV, 3.18 eV and 3.08 eV, respectively, as shown in Figure 4d-4f.

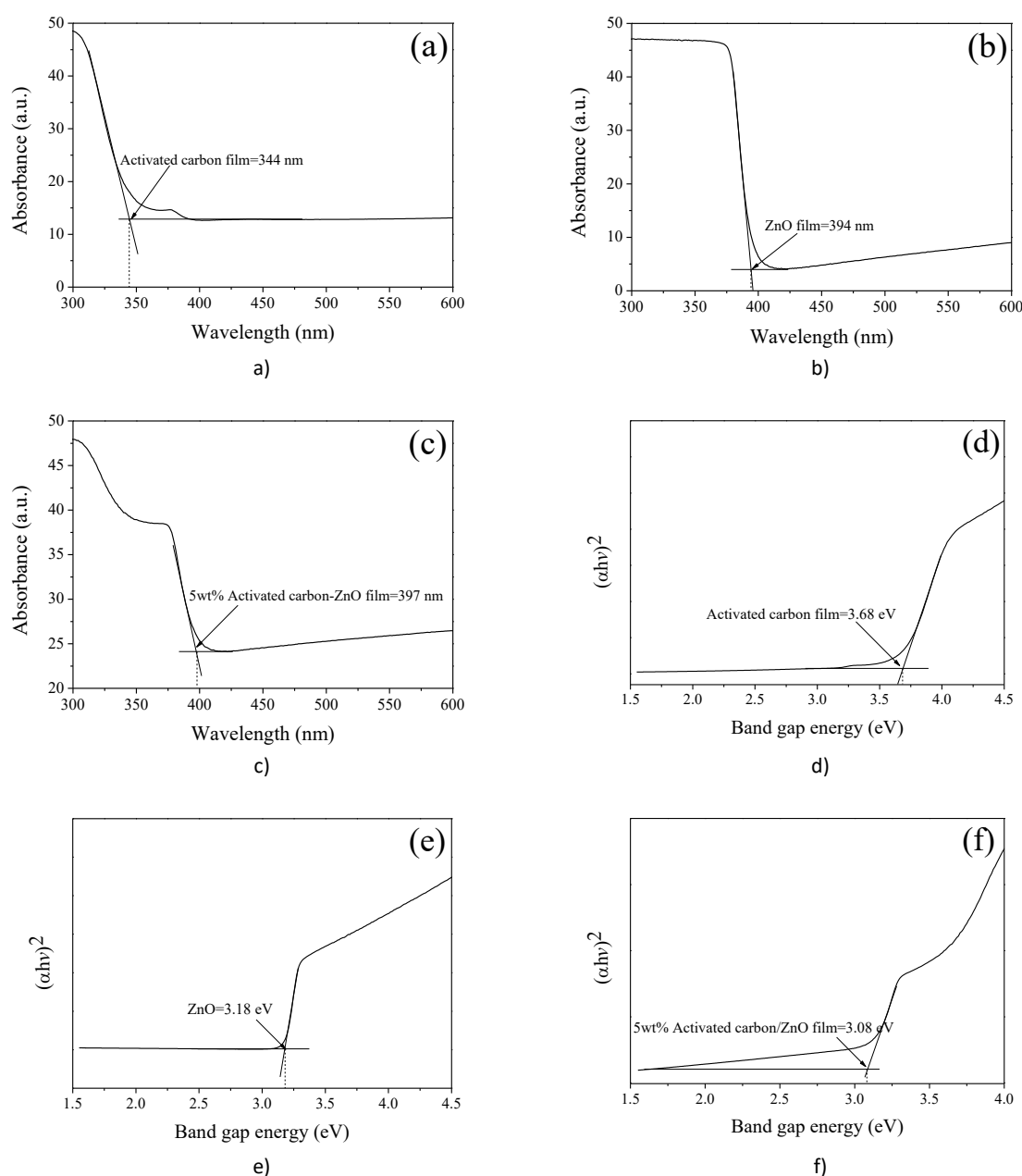


Figure 4. The optical absorption edges and band gap energies of (a,d) activated carbon film, (b,e) ZnO film and (c,f) 5 wt% activated carbon/ZnO nanocomposite film

Photocatalytic activity

In this photodegradation, RhB dye was used as a model dye in the photocatalytic process of activated carbon film, ZnO film and activated carbon/ZnO nanocomposite film with different weight (activated carbon) concentrations of 1% and 5%, as shown in Figure 5a. From the test results, RhB photolysis without film photocatalysts was found to be 3%. Meanwhile, the results of RhB photodegradation in the presence of activated carbon film, ZnO film and activated carbon/ZnO nanocomposite film with different weight (activated carbon) concentrations of 1% and 5% for 180 min under solar light irradiation were estimated to be 16%, 24%, 39% and 60%, respectively. It can be seen that the increment of photocatalytic efficiency exhibited in nanocomposite films compared to pure activated carbon film and pure ZnO film. Moreover, it was found that the concentration of activated carbon had an effect on the photocatalytic performance of nanocomposite films, and 5% (by weight) of activated carbon in ZnO showed a suitable concentration in the degradation of RhB dye under solar light irradiation. The highest photocatalytic activity of 5 wt% activated carbon/ZnO nanocomposite film might be due to the activated carbon deposited into ZnO would help to capture an electron and reduce the charge carrier recombination, resulting in the increment of photoactivity for degradation of RhB dye under solar light irradiation. Interestingly, the surface of ZnO deposited with activated carbon led to its higher surface area and lower band gap energy, which was a crucial factor for better photoactivity in the degradation of RhB dye under solar light irradiation.

The pseudo-first-order kinetic rate of RhB dye photodegradation can be estimated through the equation as follows: $\ln(C_0/C_t) = k_{app} t$, where C_0 , C_t and k_{app} are the starting concentration of dye at 0, the concentration of dye at time t and the pseudo-first-order kinetic rate constant, respectively [45,46]. The kinetic rate constants of photocatalytic performance in the degradation of RhB dye under solar light irradiation were linearly plotted between $\ln(C_0 / C_t)$ versus irradiation time, the concentration of 5 wt% activated carbon in ZnO showed the best k_{app} for the degradation of RhB dye compared with other film samples. The k_{app} of 5 wt% activated carbon/ZnO nanocomposite film was $4.90 \times 10^{-3} \text{ min}^{-1}$, as represented in Figure 5b and Table 1. Moreover, higher and lower concentrations of activated carbon would lead to a decrement in RhB dye photodegradation efficiency, concluding that 5 wt% activated carbon/ZnO nanocomposite film was the optimal concentration for the degradation of RhB dye under solar light irradiation.

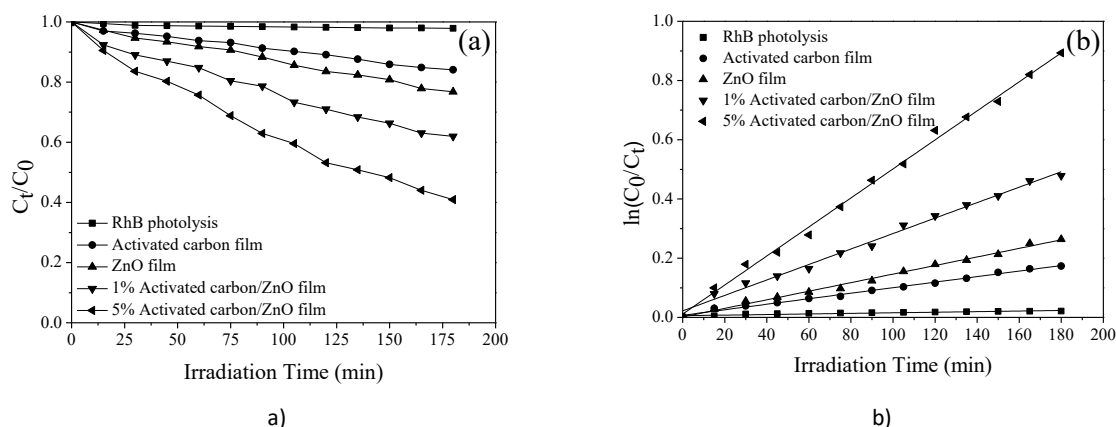


Figure 5. (a) photocatalytic activity and (b) kinetic rate constants of the photodegradation of RhB dye under solar light irradiation

Table 1. Kinetic rate constants (k_{app}) and correlation coefficient (R^2) values of activated carbon film, ZnO film and activated carbon/ZnO nanocomposite film with different weight (activated carbon) ratios of 1% and 5% for degradation of RhB dye under solar light irradiation

Samples	R^2	k_{app}
RhB photolysis	0.846	9.77×10^{-5}
Activated carbon film	0.992	9.32×10^{-4}
ZnO film	0.993	1.45×10^{-3}
1wt% Activated carbon/ZnO film	0.991	2.61×10^{-3}
5 wt% Activated carbon/ZnO film	0.996	4.90×10^{-3}

The 5 wt% activated carbon/ZnO nanocomposite film was expected to have high stability in the reuse of multiple runs for the degradation of RhB dye under solar light irradiation, as illustrated in Figure 6. Therefore, the estimation of the efficacy of 5 wt% activated carbon/ZnO nanocomposite film was a key factor. The reusability test was carried out to define the durability of 5 wt% activated carbon/ZnO nanocomposite film, which was investigated in many runs of the experiment with maximum photodegradation performance. This test is repeated ten runs and after every cycle of the experimental process, the percentage of photodegradation performance was calculated by using equation (1). From the test results, it can be seen that the efficacy of photocatalytic activity for degrading RhB dye showed a petty decrease, demonstrating that the 5 wt% activated carbon/ZnO nanocomposite film had an excellent recyclability during the photodegradation process of RhB dye under solar light irradiation.

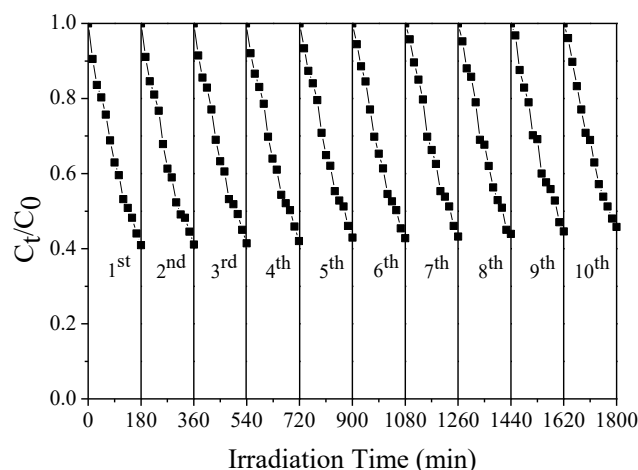


Figure 6. Recycling runs of 5 wt% activated carbon/ZnO nanocomposite film for degradation of RhB dye under solar light irradiation

Photocatalytic mechanism

To explain the photodegradation mechanism of 5 wt% activated carbon/ZnO nanocomposite film, the trapping experiment was used to identify main active species such as superoxide radical anions (O_2^-), hydroxyl radicals (OH) and holes (h^+), resulting in its high stability and photodegradation of RhB dye under solar light irradiation. Therefore, three scavenger species such as benzoquinone (BQ), potassium iodide (KI) and isopropanol (IPA) were used to capture the superoxide radical anions (O_2^-), holes (h^+) and hydroxyl radicals (OH), respectively. For the trapping experiments, 0.002M of BQ (O_2^- scavenger), KI (h^+ scavenger) and IPA (OH scavenger) were added into the photodegradation process of RhB dye over 5 wt% activated carbon/ZnO nanocomposite film. The obtained results revealed that no quencher without scavenger species showed excellent performance under solar light irradiation. In the part of the introduction of BQ, KI and IPA scavengers into the photocatalytic degradation of RhB dye, the results showed that the photodegradation process of RhB dye in the presence of BQ and IPA scavengers exhibited speedily reduced compared with KI scavenger, as depicted in Figure 7. Therefore, it was concluded that O_2^- and OH were strong oxidizing agents which played a key role in the RhB degradation under solar light irradiation.

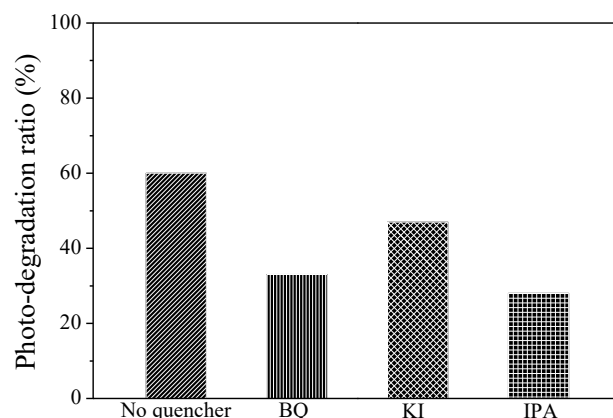


Figure 7. Trapping experiments of 5 wt% activated carbon/ZnO nanocomposite film for degrading RhB dye under solar light irradiation

In Figure 8, the photocatalytic mechanism between activated carbon and ZnO in the degradation of RhB dye under solar light irradiation was studied. When solar light was irradiated on the surface of activated carbon/ZnO nanocomposite film, the photogenerated electrons on the valence band (VB) of ZnO were excited to the conduction band (CB) and then transferred to the ZnO surface. Therefore, the photoinduced electrons on the CB of ZnO would move to the activated carbon surface to act as an electron trap for protecting charge carrier recombination [47]. The occurred electrons on the activated carbon surface would capture with oxygen molecules to theoretically generate O_2^- . Simultaneously, the holes on the VB of the ZnO surface could still help to theoretically generate OH in the ZnO photocatalyst by trapping with OH^- and H_2O molecules. The obtained O_2 and OH were strong active species for the oxidizing and striking of the RhB dye molecules in wastewater, and H_2O and CO_2 were obtained after the complete degradation process [48,49]. Furthermore, the concentration of activated carbon added to the ZnO results in increased surface area and active sites [50,51]. This phenomenon leads to more radical generation and adsorption area for the degradation of RhB dye under solar light irradiation.

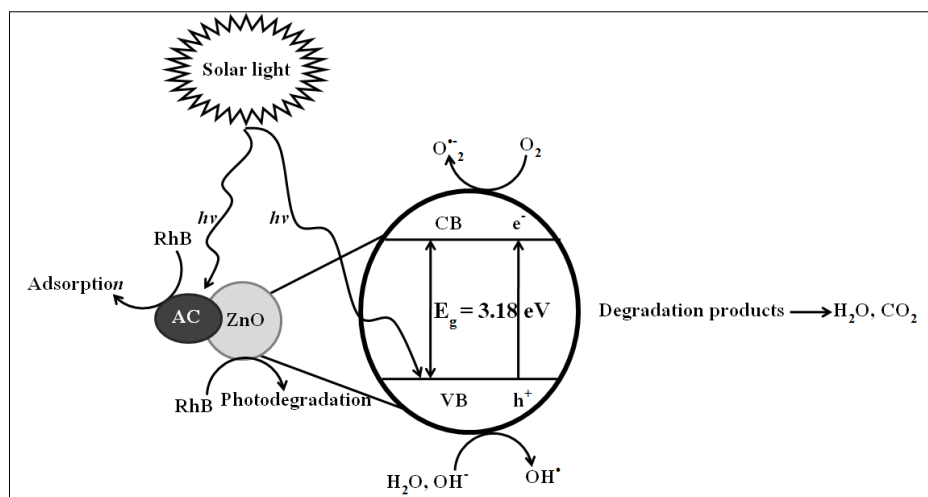


Figure 8. Photocatalytic mechanism of activated carbon/ZnO nanocomposite film in the degradation of RhB dye under solar light irradiation

Photoluminescence analysis

To further highlight the immigration, transfer and separation of charge carriers during the photocatalytic process over ZnO film and 5 wt% activated carbon/ZnO nanocomposite film, the photoluminescence (PL) technique was used, as shown in Figure 9. From the test results, PL spectra of ZnO film showed a higher peak than that of 5 wt% activated carbon/ZnO nanocomposite film, indicating that the separation of electron and hole pairs in ZnO exhibited slower than that of 5 wt% activated carbon/ZnO nanocomposite film. Therefore, it can be concluded that the decoration of activated carbon into ZnO would help to facilitate the separation of charge carriers and reduce the charge carrier's reunion, resulting in the increment of the efficacy of photocatalytic activity in the degradation of RhB dye.

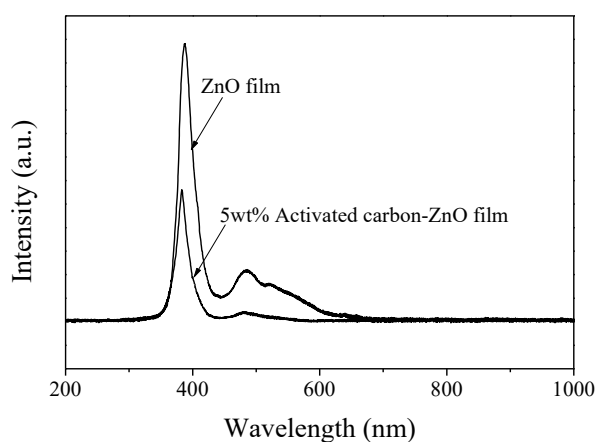


Figure 9. PL of ZnO film and 5 wt% activated carbon/ZnO nanocomposite film

CONCLUSION

In this research, the preparation of activated carbon/ZnO nanocomposite films with the doctor blade method was achieved. The efficacy of photocatalytic activity of activated carbon/ZnO nanocomposite films was higher than that of pure activated carbon film and pure ZnO film, and the suitable concentration of activated carbon introduced into ZnO was 5 wt%. Moreover, the activated carbon decorated into ZnO helped increase active sites and impeded the quick recombination of electron and hole pairs, leading to the increment of the efficacy of photodegradation activity. The results of the recycling test of 5 wt% activated carbon/ZnO nanocomposite film exhibited excellent recyclability after ten runs, demonstrating that a suitable photocatalyst for degrading RhB dye under solar light irradiation was 5 wt% activated carbon/ZnO nanocomposite film. In the part of scavenger species from trapping experiments, both O_2^- and OH were strong oxidizing agents to played a key role in the degradation of RhB dye in wastewater.

Author Contributions

Conceptualization, Chaiwichian S; methodology, Chaiwichian S; formal analysis, Chaiwichian S; investigation, Samran B; writing—original draft preparation, Chaiwichian S; writing—review and editing, Chaiwichian S, Samran B; supervision, Chaiwichian S. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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