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Preparation and Characteristics of Expanded Graphite loaded with ZnO

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Abstract: The composites of expanded graphite loaded with ZnO (ZnO/EG) was prepared using flake graphite with a particle diameter of 0.3 mm as raw material, $KMnO_4$ as oxidant, sulfuric acid (H_2SO_4) as inserting agent and $Zn(OAc)_2$ as auxiliary intercalating agent. The influence of the amount of $KMnO_4$、H_2SO_4、$Zn(OAc)_2$, reaction time and temperature on expanded volume (EV) were studied. The feasible conditions were detected as follows: mass ratio of $m(C) : m(KMnO_4) : m(H_2SO_4) : m(Zn(OAc)_2)$ was 1:0.28:5.0:0.4, the reaction lasted 40 min at 40°C, and ZnO/EG with a EV of 617 mL/g obtained at 800°C. Meanwhile, the flake graphite and the prepared specimens were characterized by means of Fourier transform infrared, X-ray diffraction and scanning electron microscope. The results testified that $Zn(OAc)_2$ inserted into layers of flake graphite, and after expansion at 800°C, $Zn(OAc)_2$ in the graphite intercalation compound turned into ZnO particles with the structure of hexagonal crystal system, and they widely distributed in the cavities and the network pores of EG. After 100 min under UV-irradiation, the decoloration rate of 0.2 g ZnO/EG for 100 mL methylene blue with an initial concentration of 100 mg/L reached 94.4%.

Key words: $Zn(OAc)_2$, Expanded graphite, Characteristics, Methylene blue, Decoloration.

Introduction

Expanded graphite (EG) is a kind of bulky soft and highly porous worm-like material, and it is prepared by intercalating reaction of flake graphite under oxidation and intercalation of oxidants and intercalators, respectively. When graphite is oxidized, its layers will open gradually, and then the molecules or ions of non-carbonaceous substance enter into the interspace of graphite layers forming various graphite intercalation compounds (GICs). When heated, the intercalators will decompose or react with graphite, the released volatile gas make GICs expand along Z axis, and then get EG[1,2]. EG has many excellent features, such as heat-resistant, corrosion-resistant, lower density and poriferous structure; so it has been used as adsorbent for adsorbing treatment of oils and dyes[3-5].

Semiconductor photocatalytic oxidation technology has the excellent features of low energy consumption, easy operation and no secondary pollution; thus it has been widely used in the treatment of the organic pollutants [6, 7]. ZnO is a new type semiconductor material which has the excellent features of non-toxic, high catalytic activity, strong oxidation ability and good stability[8,9]. It was reported that ZnO was more efficient for degradation of various organic compounds and dyes. With thermal evaporation method, Wan synthesized the tetrapod-branched ZnO with nano structures and detected its photodegradation for Rhodamine B. Compared with P25(TiO_2), the prepared ZnO shown an enhanced photocatalytic activity[10]. Li synthesized ZnO nano particles through roasting the composites of $Zn(NO_3)_2$ and poly(vinyl pyrrolidone), and its photo degradation efficiency for methyl orange reached 97.84% [11].

However, for its higher surface energy, the agglomeration of ZnO power is easily occured in application as photodegradation catalyst, and it is hard to recycle at the same time. All this limit ZnO widely application in the field of wastewater treatment. This shortage can be solved by appling a carrier material to support the photocatalyst. ZnO and graphene composites (ZnO/GRs) was synthesized by a hydro-thermal reaction[12], and ZnO particles were coated by the graphene sheets. The decoloring efficiency of 0.05 g ZnO/GRs and ZnO for 100 mL methylene blue (MB) with an initial concentration of 10 mg/L reached 72.1%，70%, when exposed to the UV irradiation produced by a 20 W UV light, respectively. Kong prepared ZnO/alginate fibers by thermal decomposition of zinc alginate fiber [13], and photocatalytic degradation of MB dye from aqueous solution shown that ZnO nanostructures possessed good photo catalytic reactivity, decoloring efficiency for MB with a contration of 200 mg/L reached 50%.

It is known that EG possesses porous structure and higher specific surface area, it can be used as carrier of ZnO. The composites not only combine the adsorption capacity of EG and the photo-decomposition capacity of ZnO, but can also solve the shortage of aggregation and recycle of the power of ZnO in the solution. Three kinds of ZnO/EG composites[14], marked as ZnO/EG-1, ZnO/EG-2 and ZnO/EG-3, were prepared by heating a mixture of zinc acetate and water-washed expandable graphite, zinc acetate and dried expandable graphite, zinc acetate and EG, respectively. Results shown the dipping method markedly influenced the distribution of ZnO particles on EG, and ZnO/EG-3 had the highest remove capacity for methyl orange.

In this experiment, graphite intercalating compound (GIC) with high dilatability was prepared firstly through the oxidizing and intercalating reaction of graphite with flake graphite as raw material, $KMnO_4$ as oxidant, H_2SO_4 as intercalating agent, precursor $Zn(OAc)_2$ of ZnO as auxiliary agent, and then ZnO/EG obtained by roasting the GIC under high temperature. The dosages of $KMnO_4$, H_2SO_4, and $Zn(OAc)_2$, H_2SO_4 weight concentration (wt), reaction temperature and time were optimized through single-factor experiment, and GIC expansion property was characterized by expandable volume (EV). The obtained samples were characterized by means of Fourier transform infrared (FTIR), X-ray diffraction (XRD) and scanning electron microscope (SEM). The discoloring capacity of the prepared ZnO/EG for methylene blue water solution was detected.

Experimental Procedure

Instrument, materials and agents

SX3-4-13 Muffle furnace (Tientsin, China. precision of temperature ±0.1%-0.4% °C), Y-2000 X-ray diffractometer (Dandong, China), FTS-40 FTIR spectrograph (America Biorad), Electron microscope TM3000 (Japan) and T6 New Century UV spectrophotometer (Puxi Tongyong Instrument Limited Company of Beijing) were used in this experiment.

Natural flake graphite with a carbon content of 90% was provided by Action Carbon CO. LTD, Baoding, China; and an average flake size was 0.18 mm. $Zn(OAc)_2$, H_2SO_4 (98%) and $KMnO_4$ were all analytical agents.

Preparation of ZnO/EG

In a 250 mL beaker, certain volumes of sulfuric acid with 98 wt % was diluted to a specified concentration with de-ionized water, and then added the weighed $Zn(OAc)_2$ under stirring until it dissolved. Then the quantified reactants were added and stirred in the order of C and $KMnO_4$ under various reaction temperatures. After reaction, the solid phase was washed with deionized water and dipped in water for 2.0 h until pH of the waste water reached to 6.0-7.0, then GIC obtained after filtration and drying at 60-70°C for about 5.0 h. GIC roasted in muffle oven at a high temperature, and ZnO/EG gained.

Characterization of the specimens

In order to prove the occurrence of graphite intercalating reaction and ZnO in ZnO/EG, a series of measurements of EV, FTIR, XRD and SEM were employed to characterize these composites.

EV was an important factor to judge dilatability of EG, it was measured as follows: a 0.300g of GIC roasted for 10S in Muffle furnace at a high temperature, and then the obtained volume was detected and converted into mL/g.

The FTIR spectra of the prepared GIC and ZnO/EG were recorded between 4000-400 cm^{-1} using a FTIR spectrometer with a resolution of 2 cm^{-1}.

XRD pattern was obtained on a Y-2000 X-ray diffractometer operating at 40 kV, 30 mA, employing Ni-filtered Cu K_α radiation with 2θ ranging from 10° to 70°.

SEM was employed to observe the porous structure and the existence of ZnO particles in or on ZnO/EG.

Results and discussion

Optimization of influence factor in the preparation of ZnO/EG

The adsorption capacity of expanded graphite (EG) has a close relationship with its EV. Generally, there is a positive correlation[15]. ZnO is a good photocatalyst, the adsorption capacity and the photo-decomposition capacity of ZnO/EG will be improved if ZnO enters into the interspace of graphite layers successfully. The effects of various factors on dilatability of the ZnO/EG were optimized through single-factor experiment including the dosages of $KMnO_4$, H_2SO_4, $Zn(OAc)_2$, and H_2SO_4 concentration, reaction time, reaction and roasting temperature.

Influence of H_2SO_4 concentration on ZnO/EG dilatability

Changes of H_2SO_4 wt % affected oxidation ability of $KMnO_4$. Under mass ratio C:$KMnO_4$:H_2SO_4 (98%):$Zn(OAc)_2$ of 1.0:0.28:5.0:0.4, the reaction maintained 40 min at 40°C, and roasting temperature set as 800°C, the influence of H_2SO_4 wt % in the range of 65~85 on EG dilatability was detected and shown in Fig. 1. It is found that when at low H_2SO_4 concentration (65~80 wt %), EV increases with the increasing of H_2SO_4 wt %, and when it reaches 80, the ZnO/EG with a maximum EV of 600 mL/g is obtained. But when the wt % further increases, an excessive oxygenation of graphite occurs, which lead to a decrease in EV. Overall, the feasible H_2SO_4 wt % is 80.

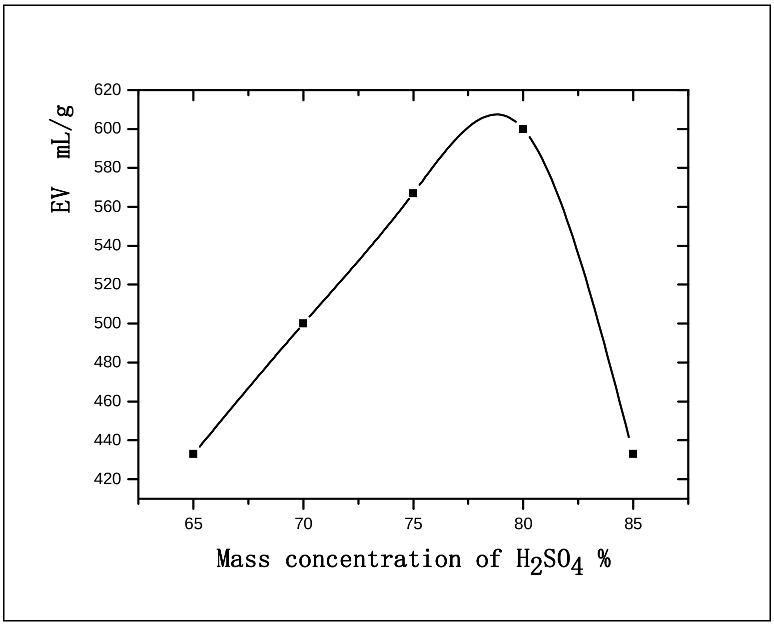


Fig.1 The influence of the H_2SO_4 wt % on EV

Influence of H_2SO_4 dosage on ZnO/EG dilatability

As an important intercalating agent, H_2SO_4 dosage in reaction has obvious effect on EG dilatability. To find its influence and feasible dosage, H_2SO_4 dosage was changed in the range of 3.5~5.5 g/g. Experiments were carried out under the constant mass ratio C:$KMnO_4$:$Zn(OAc)_2$ of 1.0:0.28:0.4; H_2SO_4 was diluted to 80 wt %, and the reaction lasted 40 h at 40°C. Fig. 2 shows that the best mass ratio of H_2SO_4 to C is 5.0 g/g. Under this ratio, EV of ZnO/EG reaches 600 mL/g. Insufficiency H_2SO_4 dosage causes an incomplete intercalation and leading to the decrease of dilatability. On the other hand, superfluous H_2SO_4 leads to the relative scarcity of $KMnO_4$ and incomplete oxygenation for graphite.

Influence of $KMnO_4$ dosage on ZnO/EG dilatability

Under acidic conditions, $KMnO_4$ has a strong oxidation, so the graphite layers can open gradually and completely, and inserting agents enter into the interspace of graphite layers forming GICs. Experiments were carried out under the constant mass ratio C: H_2SO_4 (98%): $Zn(OAc)_2$ of 1.0:5.0:0.4. Before reaction, H_2SO_4 was diluted to 80 wt %, $KMnO_4$ dosage was changed in the range of 0.15~0.3 g/g, and other conditions were controlled as mentioned above. The results show in Fig.3 reveal that ZnO/EG EV increases along with the increase of the $KMnO_4$ dosage before $KMnO_4$ dosage reaching 0.28 g/g, and then it decreases with the increasing $KMnO_4$. When the mass ratio of $KMnO_4$ to graphite is controlled as 0.28 g/g, the prepared ZnO/EG possesses a maximum EV of 600 mL/g.

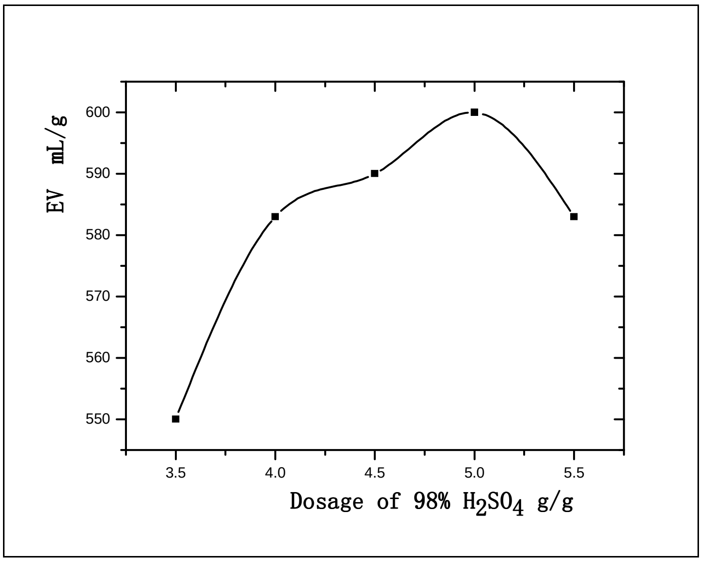


Fig.2 The influence of H_2SO_4 dosage on EV

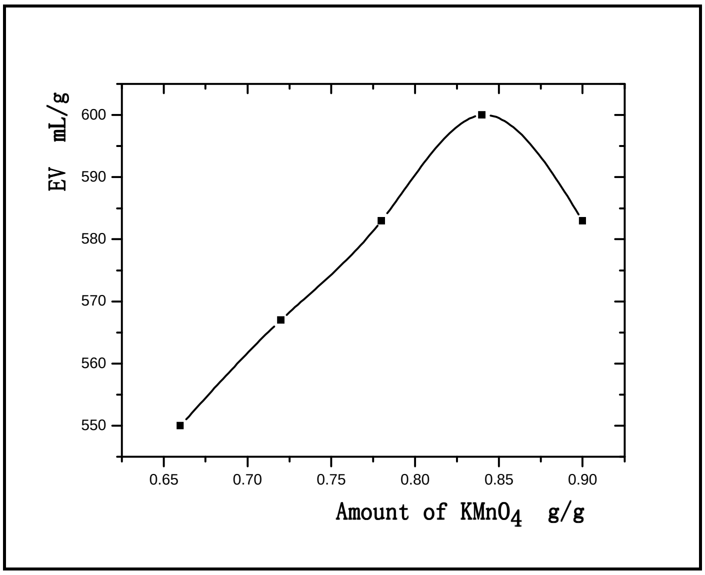


Fig.3 Influence of $KMnO_4$ dosage on EV

Influence of $Zn(OAc)_2$ dosage on ZnO/EG dilatability

Under the mass ratio C:$KMnO_4$:H_2SO_4(98%) of 1.0:0.28:5.0, H_2SO_4 was diluted to 80 wt %, and other conditions were controlled as mentioned above, the influence of $Zn(OAc)_2$ dosage was detected in the range of 0.2~0.6 g/g. As an assistant intercalating agent, increase of $Zn(OAc)_2$ dosage improves EG dilatability as shown in Fig. 4. When the mass ratio of $Zn(OAc)_2$ to C is controlled as 0.4 g/g, ZnO/EG with an maximum EV of 600 mL/g is gained. Superfluous $Zn(OAc)_2$ leads the relative scarcity of $KMnO_4$ and incomplete oxygenation of graphite.

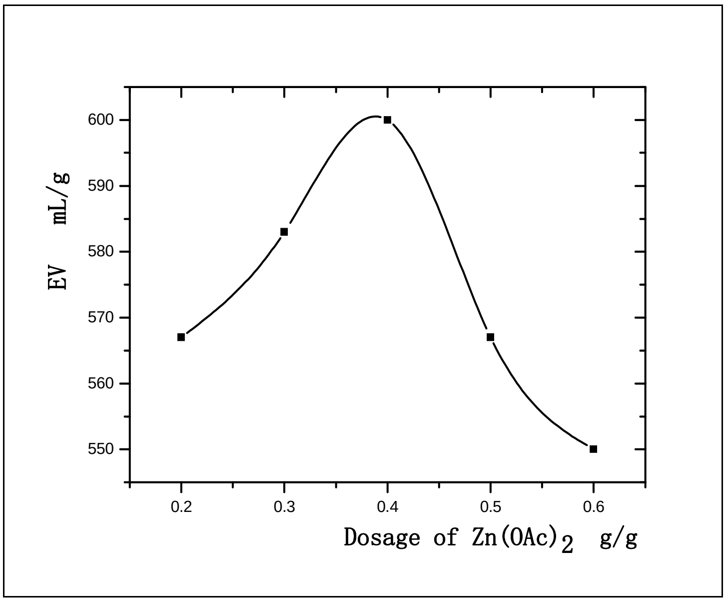


Fig.4 The influence of $Zn(OAc)_2$ dosage on EV

Influence of reaction time on ZnO/EG dilatability

Influence of reaction time on EV was detected under mass ratio $C:KMnO_4:H_2SO_4(98\%):Zn(OAc)_2$ of 1.0:0.28:5.0:0.4, H_2SO_4 diluted to 80 wt % before reaction; reaction temperature and roasting temperature set as 40°C and 800°C, respectively. Experimental results show that the increase of reaction time improves ZnO/EG dilatability in the former 40 min, and then its influence can be ignored. Therefore, the feasible reaction time sets as 40 min.

Influence of reaction temperature on ZnO/EG dilatability

Under mass ratio $C:KMnO_4:H_2SO_4(98\%):Zn(OAc)_2$ of 1.0:0.28:5.0:0.4, reaction lasted 40min and other conditions controlled as mentioned above, the influence of reaction temperature on EV was detected. When it is less than 40°C, the increase of temperature improves EG dilatability. However, too high temperature leads to the exothermic reaction releasing more heat and excessive oxygenation of graphite. So the feasible reaction temperature sets as 40°C.

Influence of roasting temperature on ZnO/EG dilatability

According to the results shown in Fig.5, when the roasting temperature is not high enough, the intercalated agents in GIC can not get enough energy and the EV is lower. When it is higher than 800°C, the EV decreases with the increase of roasting temperature, caused by the over oxidation of graphite. So the feasible roasting temperature sets as 800°C.

Feasible Condition of ZnO/EG Preparation

According to the experiment results, the feasible condition to prepare ZnO/EG is described as follows. Mass of $C:KMnO_4:H_2SO_4(98\%):Zn(OAc)_2$ is 1.0:0.28:5.0:0.4; H_2SO_4 is diluted to 80 wt % before reaction, intercalating reaction lasts 40 min at 40°C. The intercalating product written as GIC is roasted at 800°C. ZnO/EG, with an EV of 617 mL/g is obtained.

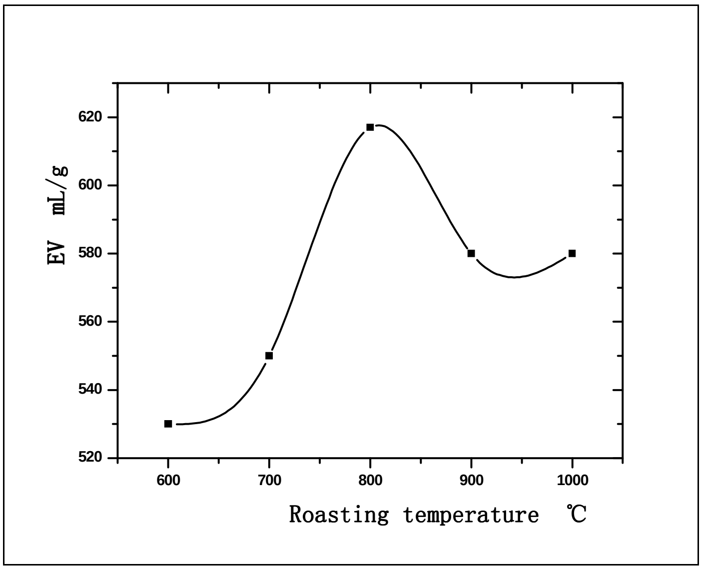


Fig.5 The influence of roasting temperature on EV

Preparation of EG_1 with no $Zn(OAc)_2$ intercalation

Compared with ZnO/EG, EG_1 is prepared under mass ratio C:$KMnO_4$:H_2SO_4(98%) of 1.0:0.28:5.0, other conditions are controlled as mentioned above. The intercalating product is written as GIC_1, and the EV of its expansion product EG_1 is 267 mL/g (at 800°C). So, the auxiliary intercalation of $Zn(OAc)_2$ increases dilatability of GIC.

FTIR analysis of samples

Fig.6 presents FTIR of blank GIC_1 and GIC. As shown in Fig.6 (a) and (b), 3429cm^{-1}and 3423cm^{-1} exhibit the characteristic peaks of O-H respectively. It's caused by the intercalation of H_2SO_4/HSO_4^- into graphite layers. The peaks observed at 1630cm^{-1}and 1380cm^{-1} are the characteristic peaks of C-O in both samples. While compared with the blank GIC_1, the characteristic peaks of C-O in the GIC are stronger. The reason is that the symmetric and the asymmetric stretching vibration absorption peaks of COO- in $Zn(OAc)_2$ also appear in these two positions [16]. Compared with the blank GIC_1, there are new characteristic peaks of 2978.69cm^{-1} and 471.23cm^{-1} in GIC, which correspond to the characteristic absorption of CH_3- and Zn-O, respectively[17]. The results reveal that Zn $(OAc)_2$ has intercalated into graphite layers successfully. **Fig.7** presents the FTIR of EG_1 and ZnO/EG. Compared with EG_1, 497.42cm^{-1} exhibits the characteristic peaks of Zn-O in ZnO/EG [18]. The above results suggest that $Zn(OAc)_2$ converts to ZnO when GIC is roasted under high temperature.

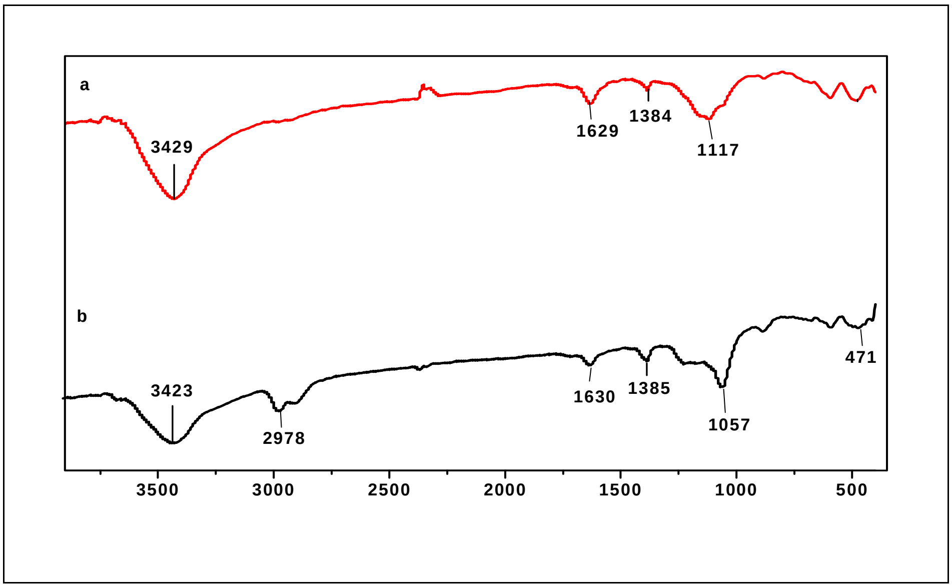


Fig.6 FTIR spectra of GIC_1 and GIC

(a) GIC_1 (b) GIC

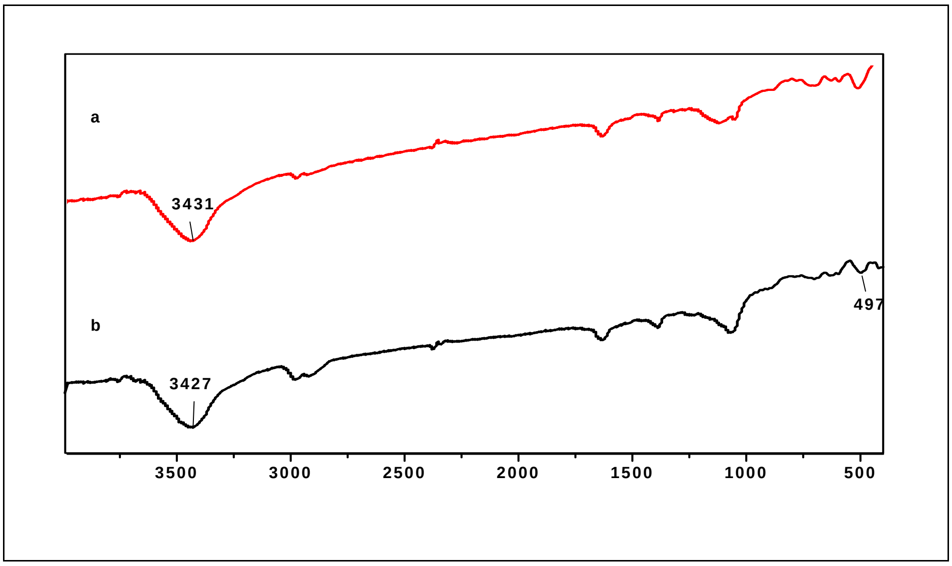


Fig.7 FTIR spectra of samples a and b
(a) EG_1 (b) ZnO/EG

XRD analysis of the prepared samples

In order to confirm the layer structure of graphite and its intercalation product, XRD spectrum of natural graphite, GIC and ZnO/EG are recorded. As shown in Fig. 8 (a), the two peaks with the interplanar crystal spacing of 3.34 Å and 1.67 Å corresponding to diffraction angle of 26.6°, 54.8° are the characteristic spectrums of natural graphite[14]. After intercalation, as shown in Fig. 8 (b), the characteristic peak of GIC transfer to a small angle of 26.1°, and it corresponds to a big interplanar crystal spacing of 3.41 Å. The results show that there are new compounds intercalating into graphite layer and changing the structure of the crystal. At the same time, two new reflection peak caused by the intercalation of $Zn(OAc)_2$ can be observed at 12.5° and 16.5° with crystal spacing of 7.03Å and 5.36 Å, respectively.

When GIC is heated, sulfuric acid will react with graphite and then the formed CO_2 and H_2O gases escape from EG layer structures [19]. At the same time, the intercalated $Zn(OAc)_2$ will completely decompose when the temperature above 370°C and release CO_2. As a result, in ZnO/EG XRD pattern of Fig. 8 (c), a “worm like” expanded graphite generates and the diffraction peak appears again at 26.50° with a clearly reduced intensity due to the structure of expanded graphite becoming disordered. At the same time, there are several characteristic diffraction peaks of ZnO crystal, corresponding to 31.7°, 34.4°, 36.2°, 47.9°, 56.5° and 62.8°, respectively. According to PDF standard cards, they are corresponding to the (100), (002), (101), (102), (110) and (103) crystal faces of ZnO crystal in the hexagonal crystal system, respectively. This indicates $Zn(OAc)_2$ has converted to ZnO after a high-temperature roasting, and the loaded ZnO has a typical hexagonal crystal structure.

SEM analysis of samples

Fig. 9 presents morphological characteristics of EG_1 and ZnO/EG, they all show a microporous network structure as described for the “worm-like” expanded graphite [2]. Compared with EG_1, some white powders of ZnO are observed, they disperse in the cavities and the network pores of EG. The results indicate the intercalation of $Zn(OAc)_2$ into graphite and roasting under high temperature making ZnO load on the EG.

Detection of decoloring capacity of ZnO/EG

To test the decoloring capacity of the prepared ZnO/EG, dye of methylene blue was selected as reference compound, and spectrophotometer was used to record the changes of absorbance values at the 664 nm. Decoloring experiment was carried out at 20°C in a 250 mL beaker with the mass of ZnO/EG to solution volume fixed at $M/V=0.200$ g/ 0.1L=2.000 $g \cdot L^{-1}$. When exposed to the UV irradiation produced by a 20 W UV light, the decoloration rate of ZnO/EG for 100 mL methylene blue with an initial concentration of 100 mg/L reaches 94.4% after 100 min irradiation.

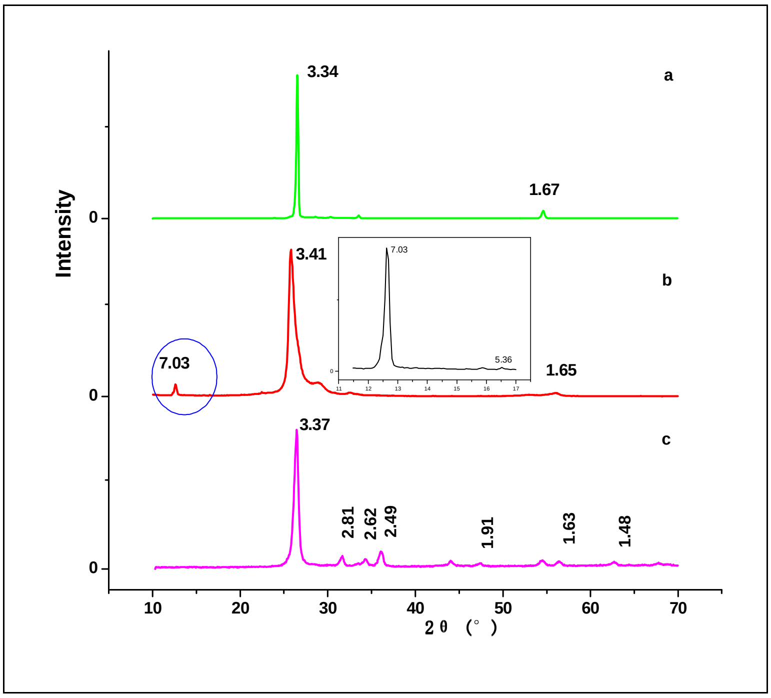
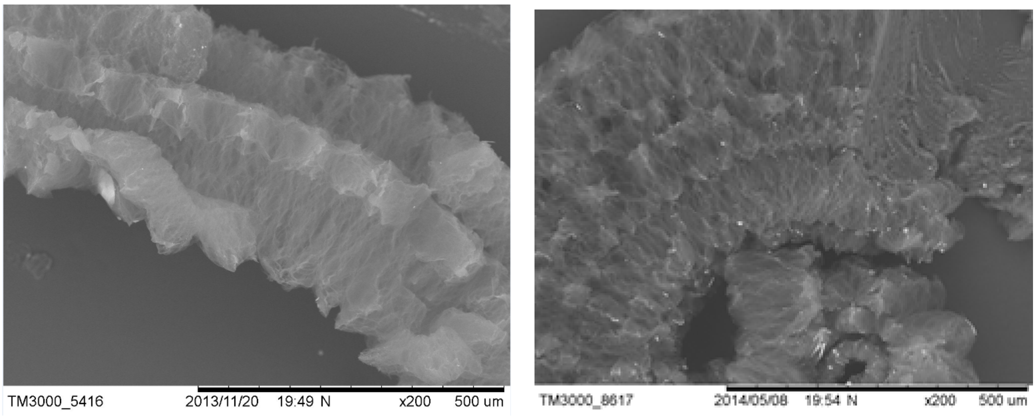


Fig. 8 X-ray diffraction spectrum of graphite (a), GIC (b) and ZnO/EG (c)



(a) EG1

(b) ZnO/EG

Fig. 9 SEM images of EG_1 and ZnO/EG

Conclusions

This study has provided an insight into the preparation and characteristics of ZnO/EG. From the results, we can get the following conclusions:

(1) ZnO/EG can be prepared according to the mass ratio C:$KMnO_4$:H_2SO_4(98%): $Zn(OAc)_2$ of 1:0.28:5.0:0.4, H_2SO_4 is diluted to 80 wt %, and intercalating reaction lasts 40 min at 40°C. The intercalating product GIC is roasted at 800°C, and then ZnO/EG with an EV of 617 mL/g is obtained.

(2) FTIR, XRD and SEM results show that $Zn(OAc)_2$ has intercalated into graphite layers, and it can be converted to ZnO when roasted at a higher temperature.

(3) The prepared ZnO/EG possesses a higher decoloration capability for methylene blue under UV irradiation.

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