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Orthogonal test design for preparation of TiO_2/Graphene composites and study on its photocatalytic activity

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Abstract

An one-step hydrothermol method was developed to synthesize TiO_2/Graphene composites (TiO_2/GR) by employing graphene oxide and tetra-n-butyl titanate. The factors affecting the photocatalytic activity of TiO_2/GR were studied by using orthogonal design, and the optimum conditions are: reaction temperature 180 °C, reaction time 16 h and pH value 3.0. TiO_2/GR was characterized on crystal structure, particle size, morphology and specific surface area by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and BET analysis. The results show that the TiO_2 in composites is anatase and the average diameter is about 18 nm. The BET specific surface area of the TiO_2/GR is 170 m^2/g and the average pore diameter is 12.45 nm. Under visible light ($\lambda > 420$ nm), the photodegradation of RhB by TiO_2/GR indicates that the best photocatalytic activities is observed with TiO_2/GR, compared to P25 and bare TiO_2 obtained by the same conditions.

Keywords: graphene; hydrothermol method; orthogonal design; TiO_2/Graphene; photocatalytic activities

1. Introduction

TiO_2 has potential for a wide use in photocatalyst, solar cell and biomaterial [1-3]. Particularly, nano TiO_2, due to photocatalytic decontamination, has attracted increasing attention. However, nano TiO_2 has several outstanding problems in actual application, such as difficult recycle, low visible utilization and so on [4-5]. So synthesis of TiO_2 which has excellent properties including good photocatalytic character and easy-recycled is important.

Recent years, to modify photocatalytic properties, the composites of TiO_2 and carbon nanotubes are created and good results have been achieved [6-8]. Faria *et al*. [9-10] prepared MWNT/TiO_2 composite catalysts by a modified sol-gel method and found that the synergetic effect of CNT could improve activity of the composite catalysts, because MWNT on the composite catalysts may act as adsorbent and photosensitizer.

Graphene has a 2D planar structure and several excellent properties superior to CNT, such as the large specific surface area [11] and the high transparency [12]. Thus, the combination of TiO_2 and graphene could lead to an approach to better results. Xiao yan Zhang *et al*. [13] have synthesized TiO_2/Graphene sheets composite using tetrabutyl titanate and graphene as the starting materials by a sol-gel method and an obvious absorption in the visible light region has been observed. Hao Zhang *et al*. [14] have obtained a chemically bonded P25-graphene nanocomposite photocatalyst and found that the composite covers three excellent attributes: the increasing adsorptivity of pollutants, extended light absorption range and facile charge transportation and separation. The TiO_2/Graphene composite generally uses graphene as the starting materials, which often need reduce graphene oxide (GO) before experiment [13,15-16]. In this paper, a facile one-step hydrothermal method has been developed to synthesize TiO_2/Graphene composite. During the hydrothermal reaction, both of the reduction of graphene oxide and loading of TiO_2 were achieved [14,17]. Under visible light ($\lambda > 420$ nm), the as-prepared TiO_2/Graphene photocatalyst exhibits a highest photocatalytic activity compared to the P25 and bare TiO_2 obtained by the same conditions. This high performance photocatalyst is anticipated to open new possibilities in environment remediation.

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2. Experimental

2.1. Sample Preparation

First, graphene oxide (GO) was synthesized by the modified Hummers' method [18-19]. In detail, 13 g of nature graphite powders were purified by 20 ml 30 wt.% NaOH and 16 ml concentrated HCl [20]. 10 g of purified graphite powders were first oxidized by reacting them with 621 g of concentrated H_2SO_4 and 7.5 g of $NaNO_3$. The reaction vessel was immersed in an ice bath, and 45 g of $KMnO_4$ was added slowly. The reaction was allowed to go on for 120 h to fully oxidize graphite into graphite oxide. Then the mixture was diluted with 1000 cm^3 of 5 wt.% H_2SO_4 and 30 g 30 wt.% H_2O_2, and the product was filtered until pH 7. After the exfoliation in a mixture of ethanol and water by ultrasonication for 1 h, the concentration of GO solution was about 1 mg/ml. The GO was reduced to graphene nanoplatelets by refluxing the GO solution with Hydrazine Hydrate for 20 h [21].

The TiO_2/Graphene composite (TiO_2/GR) was obtained via a hydrothermal method. Briefly, 1 ml 1 mg/ml GO solution and 1 ml tetrabutyl titanate were dissolved in 40 ml absolute ethanol and fully stirred to get a homogeneous suspension. The suspension was then placed in a 50 ml Teflon-sealed autoclave and maintained at certain temperature and time to simultaneously achieve the reduction of GO. Finally, the resulting composite was recovered by filtration, rinsed by deionized water and absolute ethanol several times, and dried at 60 °C. The product was then dried at 60 °C overnight and subsequently calcined in static air at 400 °C for 1 h. The heating rate was set to 0.2 °C/min from 180 °C to 220 °C, which could avoid the decomposition of graphene at rapid heating [22].

2.2. Characterization

Identification of phases was characterized by powder X-ray diffraction (XRD) using a Bruker AXS D8 diffractometer with a step of 0.02 in the 2θ range of 20° - 80°. The morphological feature and structural characteristics of the as-prepared sample were observed by scan electron microscopy (SEM) (FE-SEM, Philips XL30) and transmission electron microscope (TEM)(JEOL, JEM-2010). The optical properties of sample were investigated by a U-3010 UV-vis spectrophotometer. The chemical structure of sample was studied by Fourier transform infrared spectrometer (FTIR) (NEXUS 670 , Thermo Electron Company).

2.3. Photocatalytic experiments

The photocatalytic activities of the samples were evaluated by degrading RhB under visible light ($\lambda > 420$ nm). 30 mg of TiO_2/GR was added into 50 ml 1.0×10^{-5} mol/L RhB solution and the pH of the dispersion was kept at certain pH. Under fully stirring, the mixed solution was placed in a dark environment for 30 min to ensure the establish the balance of catalyst, RhB and water. The photocatalytic activities in dark environment and visible light without catalyst were also presented as comparisons.

3. Results and discussion

Concerning about the influence of reaction temperature, reaction time and pH value of RhB solution, $L_9(3^4)$ orthogonal test is applied with reaction rate constant K as the indexes. The detailed orthogonal experiment and related results is listed in Tables 1 and 2 respectively.

By variance analysis, the order of influence for photocatalytic ability is reaction temperature, reaction time and pH value. The optimum experiment conditions is: reaction temperature 180℃, reaction time 16h and pH value 3.0.

Fig. 1 shows SEM images and XRD patternof graphene. It can be seen that the size of graphene is up to 500 nm. The

Table 1. Three levels of every factor in orthogonal experiment

Factors levels	Temperature (ºC)	Reaction time (h)	pH
1	100	12	7.0
2	140	16	3.0
3	180	20	9.0

Table 2. Results of orthogonal experiment

Factors experiment	*A* (*T* / ºC)	*B* (*t* / h)	*C* pH	Raction rate constant (K)
1	1	1	1	0.00110
2	1	2	2	0.00345
3	1	3	3	0.00212
4	2	1	2	0.00369
5	2	2	3	0.00334
6	2	3	1	0.00386
7	3	1	3	0.00304
8	3	2	1	0.00438
9	3	3	2	0.00429
I (total index of 1 level)	0.00667	0.00783	0.00934	
ii (total index of 2 level)	0.01089	0.01117	0.01143	
iii (total index of 3 level)	0.01171	0.01027	0.00850	
I=i/3	0.00222	0.00261	0.00311	Optmum levels: $A_3B_2C_2$
II=ii/3	0.00363	0.00372	0.00381	
III=iii/3	0.00390	0.00342	0.00283	
R	0.00168	0.00111	0.00098	The order of influence: *A*>*B*>*C*

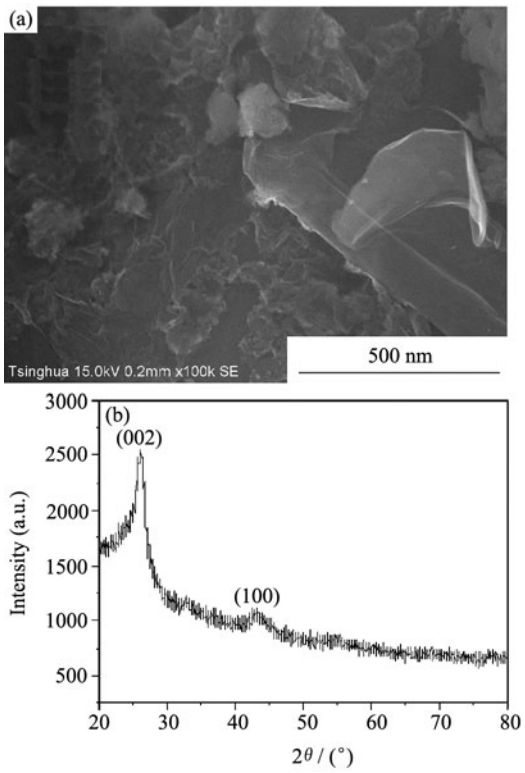

Fig. 1. SEM image (a) and XRD pattern (b) of graphene.

(002) diffraction peaks at 26° can be indexed as graphite structure, which indicates that during reduction process, the GO has removed the functional groups on it and graphitization appears[23].

Fig. 2 shows the TEM image and XRD pattern of TiO_2/GR. From the Fig. 2 (a), it can be seen that the TiO_2/GR is a nanometer titania sphere-shaped agglomeration, in which graphene is unvisible because of the high transparency due to its one-atom thickness. The excited electrons of TiO_2 could well transfer from the conduction band to graphene via a percolation mechanism [24] and the charge recombination will be effectively suppressed [13-14]. Contrast to PDF standard card (JCPDS, CARD No. 73-1764), as-prepared bare TiO_2 and TiO_2 on the TiO_2/GR all are anatase phase and the related (101) diffraction peaks is observed at 25.367° (Fig. 2 (b)). The (002) characteristic diffraction peaks for graphene aren't observed in the composite, which might overlap the (101) characteristic diffraction peaks for TiO_2 [15]. According to the (200) diffraction peaks of TiO_2/GR and Scherer formula, the average sizes of TiO_2 on the TiO_2/GR is 18 nm.

The dark and none in Fig. 3 (a) are the degradation curve of TiO_2/GR-RhB system and vis-RhB system respectively, and no abvious degradation of RhB is observed. Compared with P25 and bare TiO_2 obtained by the same conditions, the photocatalytic activities of TiO_2/GR are best, and the decol-

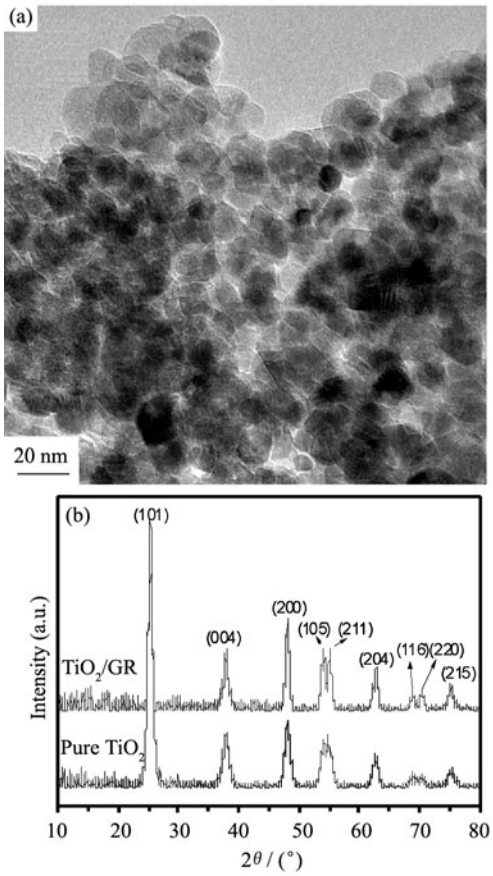

Fig. 2. TEM image (a) and XRD pattern (b) of TiO_2/GR.

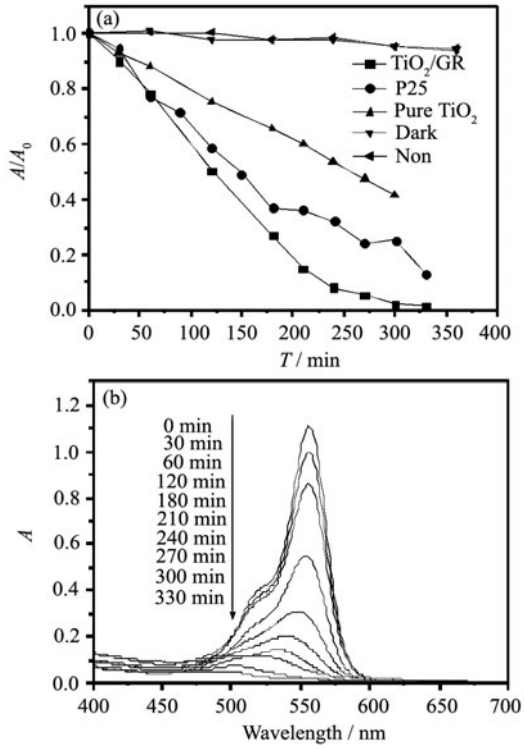

Fig. 3. Photocatalytic results of TiO_2/GR, P25 and bare TiO_2 (a); UV-vis absorption spectra of RhB in the presence of TiO_2/GR (b).

oration rate can reach up to 90% with 240 min reaction time. The decomposition reaction of RhB in the presence of TiO_2/GR is a second order reaction and its kinetic equation is c = -0.00452t + 1.10974, and the linear correlation coefficient is -0.9993. As degradation of RhB goes on, the absorbance value of the maximum absorption wavelength 554nm decreases gradually and the absorption peak shows a slight blue shift (554 nm → 500 nm) (Fig. 3 (b)), which indicates that under visible light, the degradation reactions and some deethylation reaction are carried on simultaneously [25].

Fig. 4 (a) shows the UV-vis absorption spectra of TiO_2/GR, and it can be seen that though there is an obvious red shift of 20 ~ 30 nm in the absorption edge of P25, compared to TiO_2/GR, TiO_2/GR have a higher absorbance for UV rays (200 ~ 350 nm) and visible rays (400 ~ 500 nm), which might be attributed to the synergetic effect of graphene on the TiO_2/GR [9,26]. Inserted curve in Fig. 4 (a) shows the absorption band gap E_g value of the TiO_2/GR is 3.26 eV, which is in agreement with E_g value of anatase(3.20 eV). Fig. 4 (b) shows the nitrogen adsorption-desorption isothermal curves and Barret-Joyner-Halenda (BJH) aperture distributing curve (illustration) of TiO_2/GR. According to the IUPAC classification, the isothermal type of TiO_2/GR is type IV, and hysteresis loops resembles the H4-type. These suggestes that TiO_2/GR is a representative mesoporous material and homogeneously dispersed sphere-shaped agglomeration. The BJH distributing curve reveals that the diameter of apertures is 9.26 nm. The total pore volume, average pore diameter and BET surface area are 0.5293 cm^3/g, 12.45 nm and 170 m^2/g (> P25, 135 m^2/g), respectively.

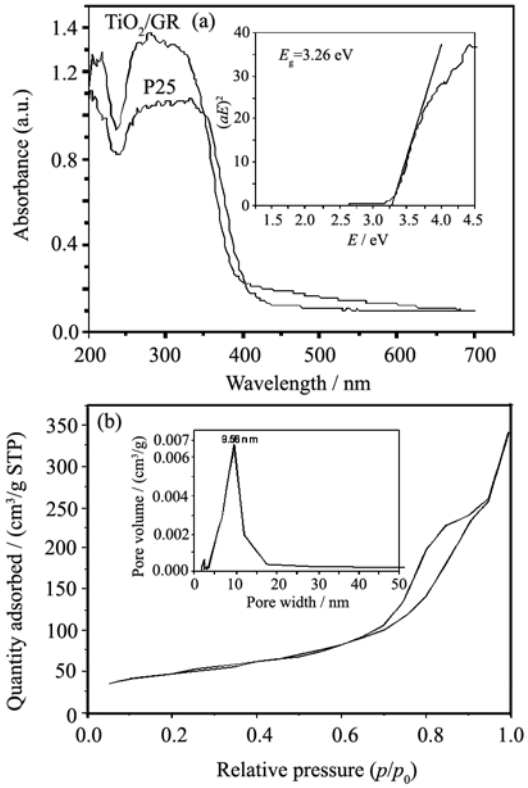

Fig. 4. UV-vis absorption spectra (a) and BET curve of TiO_2/GR (b)

4. Conclusion

The TiO_2/GR are successfully synthesized by an one-step hydrothermol method. The orthogonal design shows that the optimum conditions are reaction temperature 180 °C, reaction time 16 h and pH value 3.0. The total pore volume, average pore diameter and BET surface area of TiO_2/GR are 0.5293 cm^3/g, 12.45 nm and 170 m^2/g (> P25, 135 m^2/g), respectively. The photodegradation of RhB indicates that the graphene introduced could enhance the photocatalytic activities of TiO_2/GR, and Under visible light (> 420 nm), TiO_2/GR exhibits highest efficiency than P25 and bare TiO_2 obtained by the same conditions.

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