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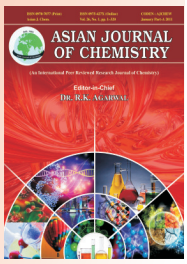

Synthesis and Photocatalytic Activity of BiOCl/Graphene†

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Graphene nanosheets supporting BiOCl catalysts were prepared by hydrothermal method. The structure of BiOCl/graphene was characterized by XRD, SEM, EDS. It's photocatalytic activity was investigated by the photocatalytic degradation of methyl orange under visible light irradiation. The results shows that the presence of graphene nanosheets could improve the photocatalytic activity of BiOCl under visible light irradiation. The degradation rate of methyl orange reaches 90.91 % when molar ratio of graphene and $Bi(NO_3)_3 \cdot 5H_2O$ is 15 %.

Keywords: Graphene, Bismuth oxychloride, Photocatalytic activity.

INTRODUCTION

With the development of industries, increasingly serious environmental pollution has threatened human survival and development. Photocatalytic degradation of pollutant using semiconductor material is an efficient and environmental friendly method. Recently BiOX have been reported as a kind of new visible light driven photocatalysts[1,2]. BiOCl with layer structure belongs to indirect band gap photocatalytic semiconductor, which can promote the separation of electrons and holes effectively to obtain good photocatalytic activity. It was reported that BiOCl could decompose rhodamine-B under visible light irradiation[3]. But it's photocatalysts efficiency for visible light is not high.

Graphene, a monolayer graphite, having attracted an increasing attention in recent years since its discovery in 2004[4]. Graphene sheets possess two-dimensional plate like structure and has many extraordinary properties such as high electronic conductivity, large specific surface area and excellent mechanical strength. Recent studies have revealed that the graphene-involved photocatalysts have excellent attributes: the increasing adsorptivity for pollutants, extended light absorption range and efficient charge transportation and separation[5,6]. So combining BiOCl with graphene is expected to produce a new kind of material which have high photocatalytic activity under visible light irradiation.

In this paper, using graphene as temperate, BiOCl/graphene composite was prepared by hydrothermal method. Photo degradation of the methyl orange in aqueous solution under visible light was investigated by using BiOCl/graphene composite as photocatalyst.

EXPERIMENTAL

Graphite oxide was prepared from graphite powder by Hummers' liquid oxidation method and then the graphene was prepared by using hydrazine hydrate to reduce graphite oxide in the aqueous colloidal suspension.

BiOCl/graphene photocatalyst was prepared by hydrothermal method. $Bi(NO_3)_3 \cdot 5H_2O$ powder was first completely dissolved in HCl solution with certain concentration. Subsequently, graphene (molar ratio of graphene and $Bi(NO_3)_3 \cdot 5H_2O$ being 0, 5, 10, 15 and 20 %, respectively) was added into the solution. After stirring for 0.5 h at room temperature and then transferred into 50 mL Teflon-lined autoclave.The autoclave was then heated at 160 ºC for 4 h, then cooled down to room temperature. The final product was separated by centrifugation, washed with distilled water and absolute ethanol several times and dried under vacuum at 80 ºC for 12 h. A series of BiOCl/graphene named sample $0^{\#}$-$4^{\#}$ (molar ratio of graphene and $Bi(NO_3)_3 \cdot 5H_2O$ being 0, 5, 10, 15 and 20 % accordingly) had been formed.

The phase of product was determined by D5005 X-ray diffractometer, with CuK_α radiation. The size and morphology of product was determined by scanning electron microscopy. The kind of element was determined by XFORD INCA25

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energy dispersive spectrometer. The UV-visible absorption spectroscopy was studied by UV-2100 spectrophotometer.

Degradation for methyl orange: Added BiOCl/graphene to 30 mL aqueous solution of methyl oriange. After stirred 10 min, the mixture solution was placed outside the room and irradiated 0.5 h by sunlight. Separating the solid by centrifugalization, the absorbance of the resulting solution was determined by UV-2100 spectrophotometer. The degradation rate of methyl orange was calculated according to the formula:

$$X(\%) = \frac{(A_0 - A)}{A_0} \times 100\,\%$$

A_0 and A, respectively referred to the absorbance of methyl orange before and after irradiated.

RESULTS AND DISCUSSION

The XRD patterns of products are shown in Fig. 1. Curve 1 shows the characteristic peaks of pure BiOCl. Curves 2-3 shows the similar peaks to that of curve 1 except the intensity of peak. Because the content of graphene in composite is low, the peak of graphene has not been displayed in curve 2-3.

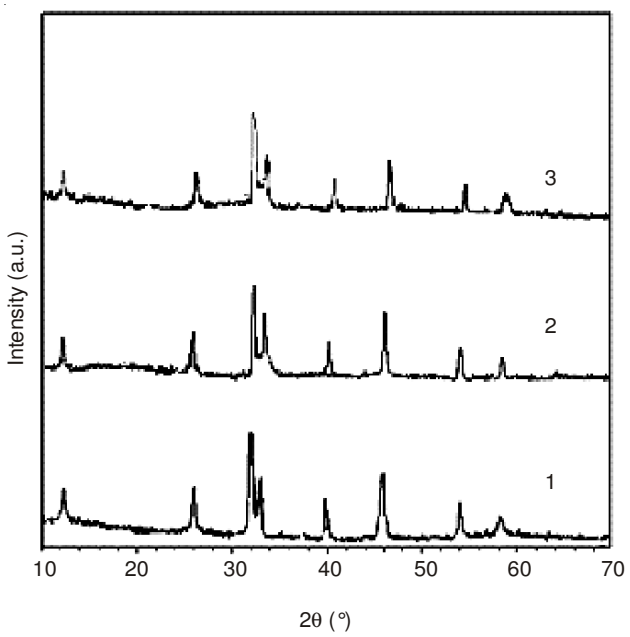
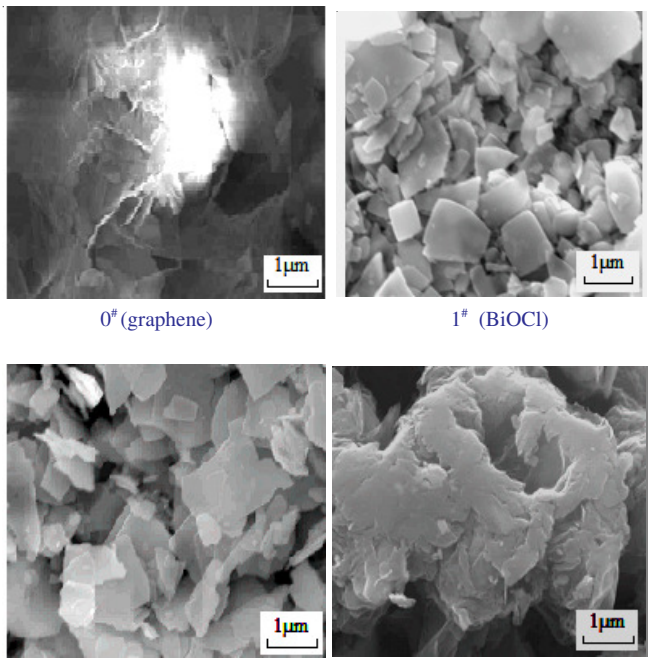


Fig. 1. XRD pattern of samples. 1-sample 0# 2- sample 1# 3- sample 3#

SEM images of graphene, sample 0#, sample 1# and sample 3# are, respectively shown in Fig. 2. Graphene sheets with crumpled surface textures can be clearly seen from Fig. 2. The morphology of BiOCl is flake-like. When the amount of graphene is low, the morphology of BiOCl/graphene is similar to that of BiOCl. When the amount of graphene increasing, more BiOCl particles disposed on the graphene sheet, forming bigger flakes.

Fig. 3 is EDS spectrum of sample 3# scanned along the diameter. It shows that the sample is composed of C, Bi, O, Cl.

The room temperature UV-visible absorbance spectra of the samples, which were ultrasonically dispersed in absolute ethanol, are given in Fig. 4. Fig. 4 shows that these samples



0# (graphene) 1# (BiOCl)

3# (5 % graphene) 5# (15 % graphene)

Fig. 2. SEM images of the samples

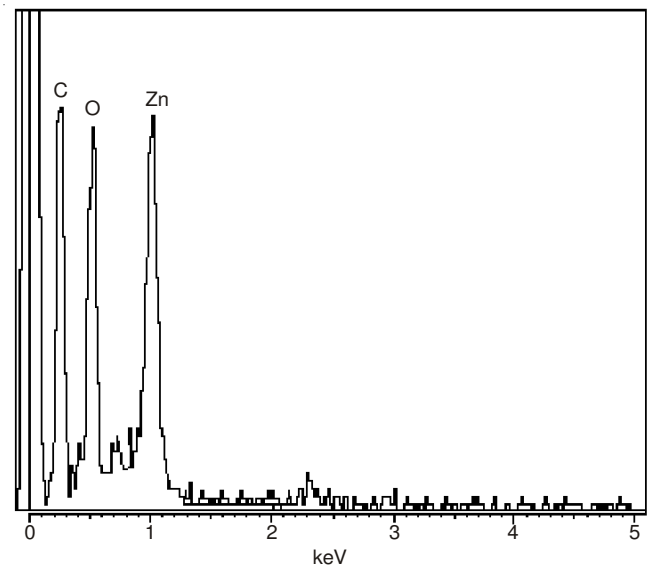


Fig. 3. EDS spectrum of the sample 3#

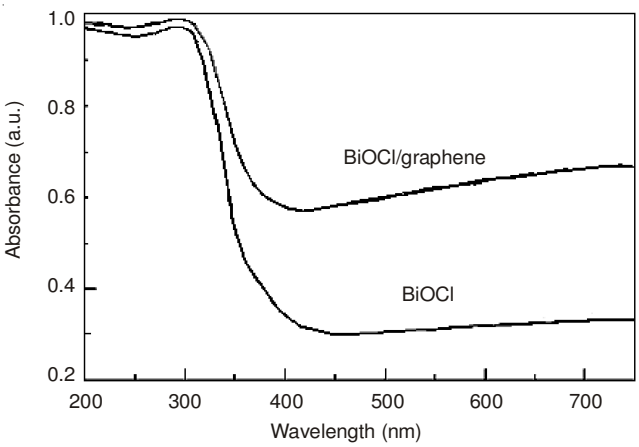


Fig. 4. UV-visible absorption spectrum of samples

have absorption almost in the whole violet light and visible light region. With graphene content increasing, its absorption intensity in visible light region increase.

Fig. 5 is degradation rate curve of methyl orange using sample $0^{\#}$-$4^{\#}$ as photocatalyst, concentration of methyl orange being 20 mg/L, dosage of catalyst being 10 mg. Fig. 5 shows that the degradation rate of methyl orange is the highest (90.91 %) when molar ratio of graphene and $Bi(NO_3)_3 \cdot 5H_2O$ is 15 %.

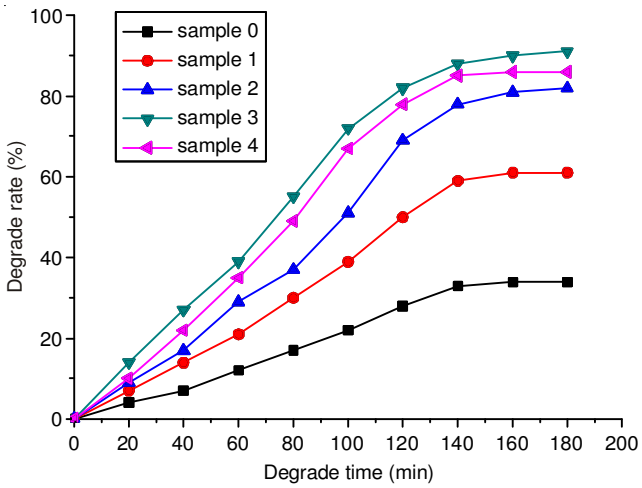


Fig. 5. Photodegradation curves for methyl orange under visible light irradiation

Conclusion

BiOCl/graphene composite was prepared by hydrothermal method. It's photocatalytic activity was investigated by the photocatalytic degradation of methyl orange under visible light irradiation. The results shows that the presence of graphene nano sheets could effectively improve the photocatalytic activity of BiOCl under visible light irradiation. The degradation rate of methyl orange reaches 90.91 % when molar ratio of graphene and $Bi(NO_3)_3 \cdot 5H_2O$ is 15 %.

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