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聚苯胺/碳纳米管复合材料的制备及其光催化性能

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摘　要：以碳纳米管(CNT)为模板，采用原位聚合法合成了聚苯胺/碳纳米管复合材料，采用 X 射线衍射、透射电子显微镜、红外光谱和能谱分析对产物进行了表征。通过光催化降解甲基橙实验，对所制备的 PANI/CNT 复合材料的光催化活性进行了考察。结果表明，产物是由聚苯胺均匀包裹在碳纳米管上构成的一种纳米复合材料，管径约 60~80 nm。聚苯胺/碳纳米管作为光催化剂表现出较高的可见光催化活性。当碳纳米管和聚苯胺的摩尔比为 30%时，在可见光照射下，甲基橙的降解率最高。

关键词：聚苯胺；碳纳米管；原位聚合；光催化活性
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Preparation and Photocatalytic Property of Polyaniline/Carbon Nanotubes Composite

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Abstract: Polyaniline/carbon tubes (CNT) nanocomposite was synthesized *via* in-situ polymerization. The samples were characterized by X-ray diffraction, transmission electron microscopy, Fourier transform infrared spectroscopy and energy dispersive spectroscopy, respectively. The photocatalytic activity was investigated *via* the photocatalytic degradation of methyl orange. The results show that the nanocomposite is composed of carbon nanotubes coated evenly by polyaniline, with the diameters of 60-80nm. Polyaniline/CNT nanocomposite as a photocatalytic agent has a better photocatalytic activity under visible light irradiation. The 30%CNT-added (*in* molar ratio of CNT and aniline) nanocomposite has the maximum degradation rate for methyl orange under sunlight irradiation.

Keywords: polyaniline; carbon nanotubes; *in-situ* polymerization; photocatalytic property

1　Introduction

Due to their unique physical and chemical properties, carbon nanotubes (CNT) have broad applications in nanoelectronics[1–2], catalysis[3–4], sensors[5], and so on. Recently, CNT based nanocomposite has aroused researchers' great interest because of its potential application in many areas.

Conjugated polymers (CPs), such as polyaniline, polythiophene and their derivatives, have shown great promises due to their high absorption coefficients in the visible part of the spectrum, high mobility of charge carriers and good stability[6–7]. Furthermore, many CPs in their excited state are electron donor upon visible light irradiation. Recently, combining CPs with wide band gap inorganic semiconductors is an emerging area of researches [8–9].

CNT has good conductivity, large surface area and hollow structure. So combining polyaniline nanoparticles with CNT is expected to produce a new kind of material which have high photocatalytic activity under visible light irradiation.

In this paper, using CNT as temperate, polyaniline/CNT nanocomposite was prepared by in-situ polymerization. Its photocatalytic activity was investigated by the photocatalytic degradation of methyl orange.

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2 Experimental

2.1 Preparation of CNT

CNT was synthesized by the catalytic decomposition of acetylene using Co-Mo mixtures supported on zeolite as catalysts[10].

CNT was purified by 6 h refluxing of mixed acid (H_2SO_4:HNO_3 = 3:1), followed by filtration and thoroughly washing with deionized water until pH = 7.

2.2 Preparation of polyaniline/CNT

Polyaniline/CNT nanocomposite was prepared by in-situ polymerization method. All the chemicals used were analytical grade reagents.

Firstly, CNT was dispersed in ethyl alcohol under ultrasonic assistance. Secondly, 10 mL aniline, 20 mL diluted hydrochloric acid and 200 mL distilled water were added to a three-neck flask under vigorous stirring. Then, a suitable amount of CNT and 0.2 g dodecylbenzene sulfonic acid (DBS) were added. After stirring 30 min, ammonium persulfate was added dropwisely. The resulting mixture reacted for 3 h in ice water. The slurry was filtered and the cake was washed with hydrochloric acid, deionized water, and ethyl alcohol, respectively, until pH = 7. Finally, the cake was dried at 70 ℃ in vacuum. A series of polyaniline/CNT nano-composite samples were obtained, and named as S0, S10, S20, S30, S40, and S50 according to CNT content (x = 0, 10%, 20%, 30%, 40%, and 50%), respectively.

2.3 Characterization method

The crystal phase was determined by X-ray diffractometer (Simens, Model D5005), with Cu K_α radiation. The size and morphology was determined by a transmission electron microscope (Hitachi, Model H-7500). The chemical composition was determined by an energy dispersive spectrometer (OXFORD, Model INCA25). The infrared absorption behavior was measured by Fourier transforming infrared spectrometer (Model NE XWS470) using KBr tabletting.

To measure the degradation for methyl orange(MO), the catalyst was dispersed in 70 mL methanol-water mixture under vigorous stirring. A tungsten lamp (350 W) was used as the source of the visible light. After the suspension had been mixed 0.5 h under ultrasonication, irradiation switches on, and the total irradiation time for each samples was 3 h. After separating the solids by centrifugation, the absorbance of the resulting solution was determined by a spectrophotometer (Shimadzu, Model UV-2100). The MO degradation rate X was calculated according to formula (1):

$$X = [(A_0 - A)/ A_0]\times 100\% \qquad (1)$$

where, A_0 and A referred to the absorbance of MO before and after irradiated, respectively.

3 Results and discussion

3.1 XRD analysis

The XRD patterns of products are shown in Fig. 1. The pattern of sample S0 shows the characteristic peaks of pure polyaniline. Patterns of samples S10, S30, and S50 show the peaks of polyaniline and CNT. These peaks are similar except the peak intensity of CNT.

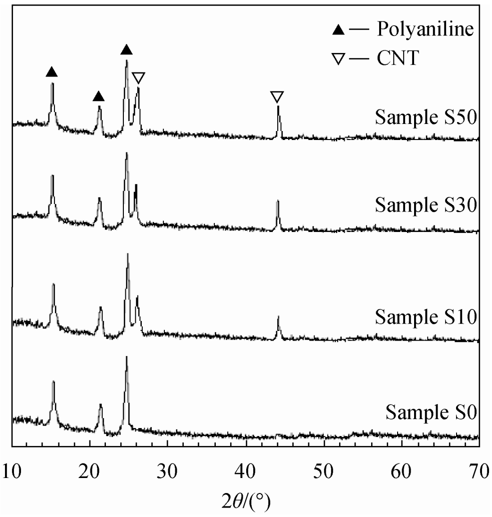


Fig. 1 XRD patterns of samples

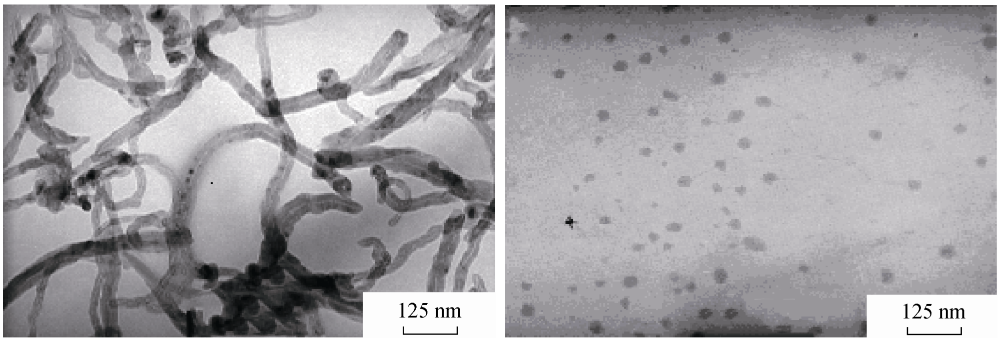
3.2 TEM analysis

Figure 2 shows the TEM images of CNT, samples S0, S30 and S50, respectively. The diameter of CNT is about 20–30 nm, and the wall is smooth (Fig. 2(a)). Sample S0 is pure polyaniline, showing the particle size of 20–30 nm (Fig. 2(b)). When CNT was added, polyaniline adsorbed on the wall of CNT, so the wall of CNT became coarser and wider, with diameter about 60–80 nm (Fig. 2c, Fig. 2d).

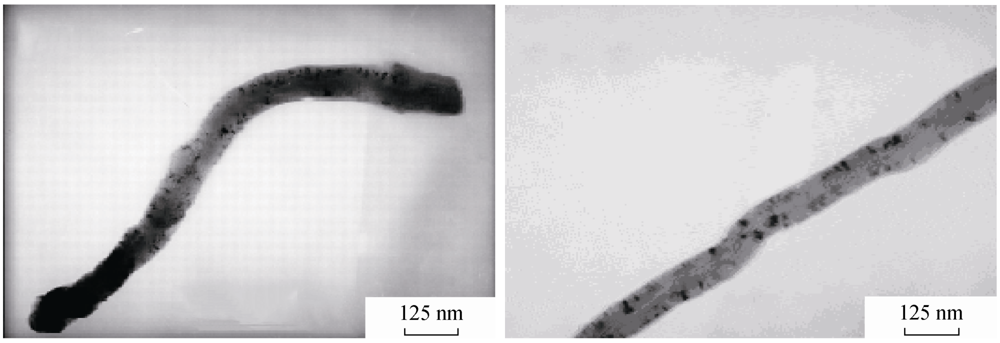
Figure 3 is energy dispersion spectra (EDS) of sample S30 scanned along the diameter. It shows that the sample is composed of C, N and O, which indicates that polyaniline has disposed on the wall of CNT.

3.3 IR analysis

The FT-IR spectra of samples S0 and S30 are shown in Fig. 4. In spectrum of sample S0, there is only absorption peak of polyaniline. The peaks at 1 589.54 cm^{-1} and 1 496.87 cm^{-1} are assigned to the adsorption of benzene ring. The peak at 1 589.54 cm^{-1} is assigned to the adsorption of N=Q=N, and peak at 1 496.87 cm^{-1} is assigned to the adsorption of N–B–N. The peaks at 1 372.45 cm^{-1} and 1 303.23 cm^{-1} are assigned to the adsorption of Ar-N. The peaks at 1 158.96 cm^{-1} and 814.31 cm^{-1} are assigned to the adsorption of in-plane bending vibration and out-plane bending vibration of benzene ring. In spectrum of sample S30, besides of absorption peak of polyaniline, there are absorption peaks at 3 446.94 cm^{-1} and 1 736.23 cm^{-1}. The peak at 3 446.94 cm^{-1} is assigned to the adsorption of OH^- in CNT, while the peak at 1 736.23 cm^{-1} is caused by —COOH and >C=O in CNT. OH^-, —COOH and >C=O were produced during the synthesis and purification of CNT.



(a) CNT　(b) Sample S0



(c) Sample S30　(d) Sample S50

Fig. 2　TEM images of the samples

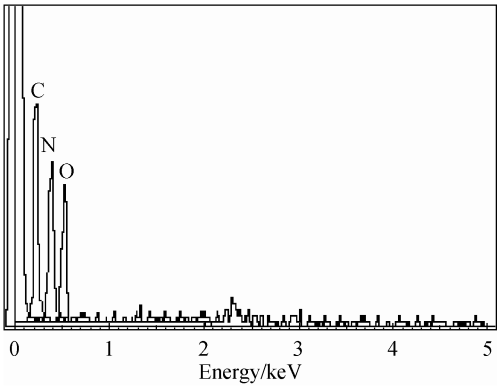


Fig. 3　EDS profile of the sample S30

3.4　Photo degradation of MO

Figure 5 shows the MO degradation rate of S0–S50. It is shows that the highest MO degradation rate is acquired for sample S30.

Polyaniline is a p-type semiconductor with low band gap (2.8 eV) that its absorption can extend into the range of visible light and exhibit good environmental stability. Furthermore, polyaniline is electron donor upon visible light irradiation. Under visible light irradiation, polyaniline produce electron-hole pairs. When polyaniline attaches onto the surface of CNT, due to the strong interfacial connection between polyaniline and CNT, the excited e^- of the conduction band of polyaniline can migrate to CNT, which is relatively good electron acceptors. So the recombination of the electron-hole pairs is retarded. Meanwhile, CNT has larger surface area, so O_2 can easily be adsorbed on the surface of CNT and accepts e^- to form more OH, which is very reactive to eliminate organic molecules. So polyaniline/CNT nanocomposite has better photocatalytic activity for visible light than pure polyaniline does. When the content of CNT is less than 30%, the degradation rate of MO increases with the CNT content increasing. When the content CNT is larger than 30%, the content of polyaniline accordingly decrease. Meanwhile. CNT twists each other more easily, which enhances the chance that electron-hole pairs recombining, so the degradation rate of methyl orange decreases. The degradation mechanism can be expressed as follows:

$$\text{polyaniline} + h\upsilon \rightarrow \text{polyaniline}\ (e^- + h^+)$$

$$h^+ + H_2O \rightarrow H^+ + OH\bullet$$

$$h^+ + OH^- \rightarrow OH\bullet$$

$$e^- + O_2 \rightarrow O_2\bullet^-$$

$$\text{MO} + \text{O}_2\bullet^{-}(\text{或 OH}\bullet)\rightarrow \text{degradation products } (\text{CO}_2 + \text{H}_2\text{O})$$

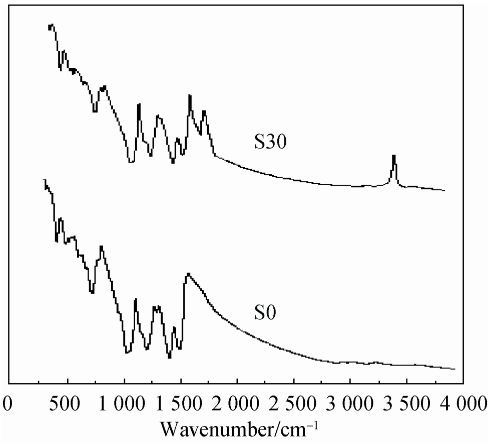


Fig. 4 FTIR spectrum of samples S0 and S30

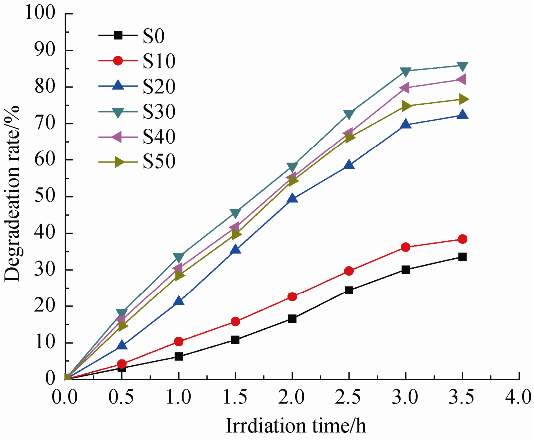


Fig. 5 Photo degradation curves for the methyl orange under visible light irradiation

4 Conclusions

Using CNT as template, polyaniline/CNT nanocomposite was synthesized by in-situ polymerization method.It's photocatalytic activity was investigated by the photocatalytic degradation of methyl orange. The results showed that nanocomposite was composed of carbon nanotubes coated evenly by polyaniline, with a diameter of 60–80 nm. As photocatalytic agent, polyaniline/CNT nanocomposite has better photocatalytic activity for visible light. Nanocomposite with 30% CNT addition had the highest degradation rate for methyl orange under the visible light irradiation.

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