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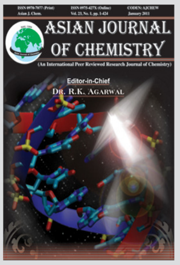

Preparation and Gas Sensitivity Properties of Polyaniline/Carbon Nanotubes Composite

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Polyaniline/carbon nanotubes nanocomposite was synthesized by *in situ* polymerization. The samples were characterized by XRD, TEM, IR and EDS. The gas sensitivity properties of the sensors made from polyaniline/carbon nanotube nanocomposite were studied. The results showed that nanocomposite was composed of carbon nanotubes coated evenly by polyaniline, with a diameter of 60-80 nm. The gas sensitivity of polyaniline/carbon nanotube nanocomposite was higher than that of pure polyaniline. The sensor doped with 30 % mol carbon nanotubes has the highest gas sensitivity and highest selectivity for formaldehyde.

Key Words: Polyaniline, Carbon nanotubes, *In situ* polymerization, Gas sensitivity.

INTRODUCTION

Due to their unique physical and chemical properties, carbon nanotubes (CNT) have broad applications in nanoelectronics[1-4], catalysis[5], sensors[6], *etc*. Recently, carbon nanotubes based nanocomposite has aroused researchers' great interest because of its potential application in many areas.

Polyaniline has sensitivity to some gases at room temperature because of its special conjugated structure, so it is a kind of important chemical sensor[7-10]. But the gas sensitivity properties of polyaniline are poor. Only doped with other material, polyaniline has good gas sensitivity properties.

Carbon nanotubes has good conductivity, large surface area and high capability of absorbing gas. So combining polyaniline nanoparticles with carbon nanotubes is expected to produce a new kind of material with enhanced gas sensitive properties. In this paper, using carbon nanotubes as temperate, polyaniline/carbon nanotube nanocomposite was prepared by *in situ* polymerization. The sensitive performances of the sensors made from polyaniline/carbon nanotube nanocomposite were studied.

EXPERIMENTAL

Preparation of carbon nanotubes: Carbon nanotubes was synthesized by the catalytic decomposition of acetylene using Co-Mo mixtures supported on zeolite as catalysts[11].

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

Preparation of polyaniline/carbon nanotubes: The molar ratios of carbon nanotubes and aniline is 0, 10, 20, 30, 40 and 50 %.

Polyaniline/carbon nanotube nanocomposite was prepared by *in situ* polymerization method. All the chemicals used were analytical grade reagents. Firstly, carbon nanotubes was dispersed in absolute ethyl alcohol with ultrasonic assisted. Second, 10 mL of aniline, 20 mL of diluted hydrochloric acid and 200 mL of distilled water were added to three-neck flask under vigorous stirring. Then to this solution, carbon nanotubes and 0.2 g dodecylbenzene sulfonic acid were added. After stirring 0.5 h, ammonium persulfate was added dropwise to the reaction solution. The resulting mixture left for 3 h in ice water. The slurry was filtered and the cake was washed with hydrochloric acid and deionized water respectively until pH = 7. Finally the cake was washed three times with absolute ethyl alcohol. Dried the cake at 70 ºC under vacuum. A series of polyaniline/carbon nanotube nanocomposites named sample $0^{\#}$-$5^{\#}$ according to carbon nanotubes content had been got.

Fabrication of gas sensors: The final powders were mixed and ground with an adhesive in an agate mortar to form gas-sensing paste. The paste was coated on a ceramic tube on which a pair of Au electrodes was printed, dried under IR light for several minutes in air and then dried at 100 ºC for 24 h under vacuum. At last, a Ni-Cr heating wire was inserted to form a side-heated gas sensor. In order to improve their stability and repeatability, the sensors were left at 300 ºC for 10 days in air.

Characterization method: The phase of product was determined by D5005 X-ray diffractometer, with CuK_α

radiation. The size and morphology of product was determined by HitachiH-7500 transmission electron microscopy. The kind of element was determined by XFORD INCA25 energy dispersive spectrometer. The infrared light absorption behaviour of product was studied by NEXWS 470 Fourier transform infrared spectrometer, KBr tabletting.

The sensitivity of sensor was measured on Wei Sheng test system for gas sensors (Zheng Zhou Wei Sheng Electronics Technology Limited Company). The gas sensitivity was defined as S = Rg/Ra,where Rg and Ra were the resistances of a sensor in a test gas and in air,respectively.

RESULTS AND DISCUSSION

XRD analysis: The XRD patterns of products are shown in Fig. 1. Curve 1 shows the characteristic peaks of pure polyaniline. Curves 2-4 show the peaks of polyaniline and carbon nanotubes. These peaks are similar except the peak intensity of carbon nanotubes.

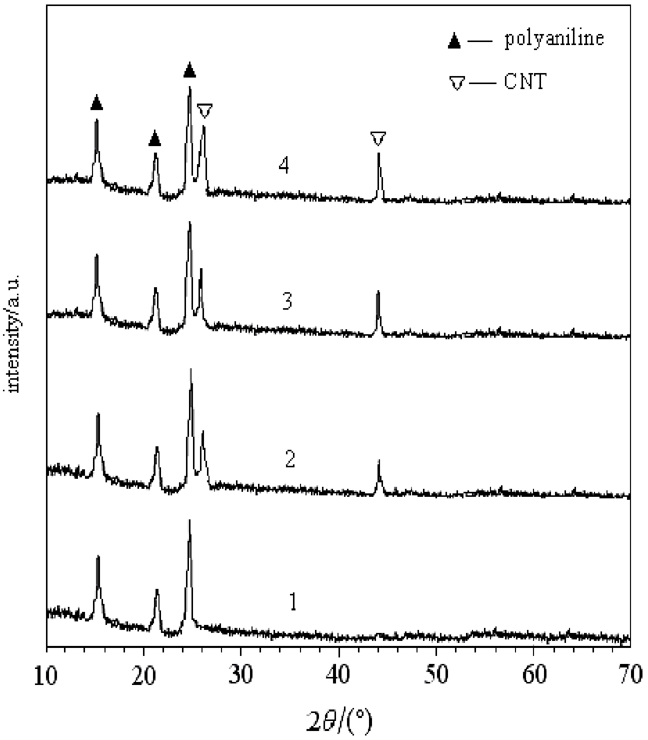

Fig. 1. XRD pattern of samples; (1) Sample $0^{\#}$ (2) Sample $1^{\#}$ (3) Sample $3^{\#}$ (4) Sample $5^{\#}$

TEM analysis: TEM images of carbon nanotube, sample $0^{\#}$, sample $3^{\#}$ and sample $5^{\#}$ are respectively shown in Fig. 2. The diameter of carbon nanotube is *ca.* 20-30 nm and the wall is smooth. Sample $0^{\#}$ was prepared without carbon nanotubes in the synthesis system, being pure polyaniline with the size of 20-30 nm. When carbon nanotubes was added to the synthesis system, polyaniline disposed on the wall of carbon nanotubes, so the wall of carbon nanotubes became coarser and wider, with diameter *ca.* 60-80 nm.

Fig. 3 is EDS spectrum of sample $3^{\#}$ scanned along the diameter. It shows that the sample is composed of C,N,O, which indicates that polyaniline has disposed on the wall of carbon nanotubes.

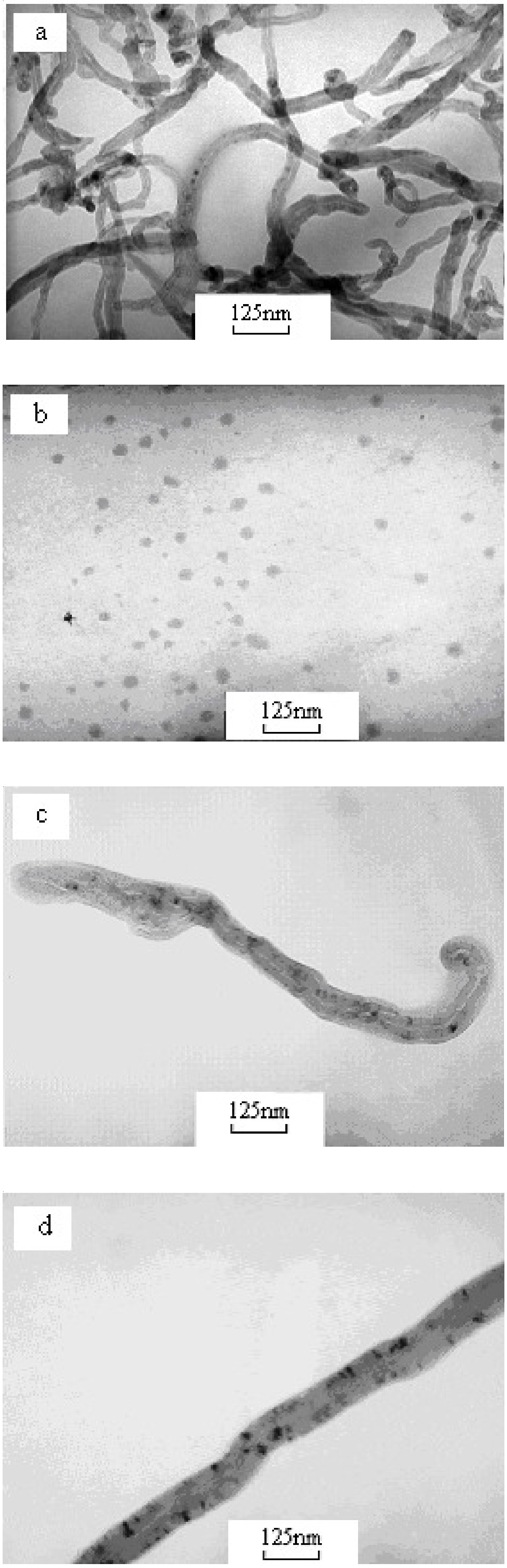

Fig. 2. TEM images of the samples; (a) carbon nanotube, (b) sample $0^{\#}$, (c) sample $3^{\#}$, (d) sample $5^{\#}$

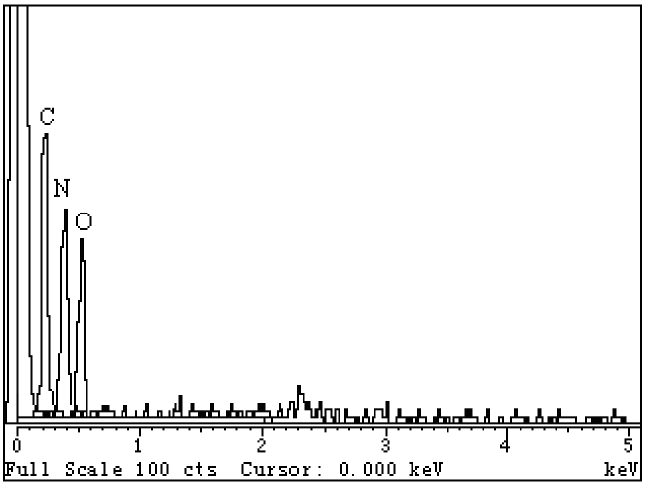

Fig. 3. EDS of the sample 3#

IR analysis: The FTIR spectra of sample 0# and 3# are shown in Fig. 4. In curve 1, there is only absorption peak of polyaniline. The peaks in 1589 and 1496 cm^{-1} region are the peaks of benzene ring. The peak at 1589 cm^{-1} is adsorption peak of N=Q=N and in 1496 cm^{-1} is adsorption peak of N-B-N. The peaks in 1372 and 1303 cm^{-1} are adsorption peaks of Ar-N. The peaks at 1158 and 814 cm^{-1} are respectively adsorption peaks of in-plane bending vibration and out-plane bending vibration of benzene ring. In curve 2, besides absorption peak of polyaniline, there are absorption peaks at 3446 and 1736 cm^{-1}. The peak at 3446 cm^{-1} is absorption peak of OH$^-$ in carbon nanotubes, while the peak at 1736 cm^{-1} is caused by -COOH and >C=O in carbon nanotubes. OH$^-$, -COOH and >C=O were produced during the synthesis and purification of carbon nanotubes[12].

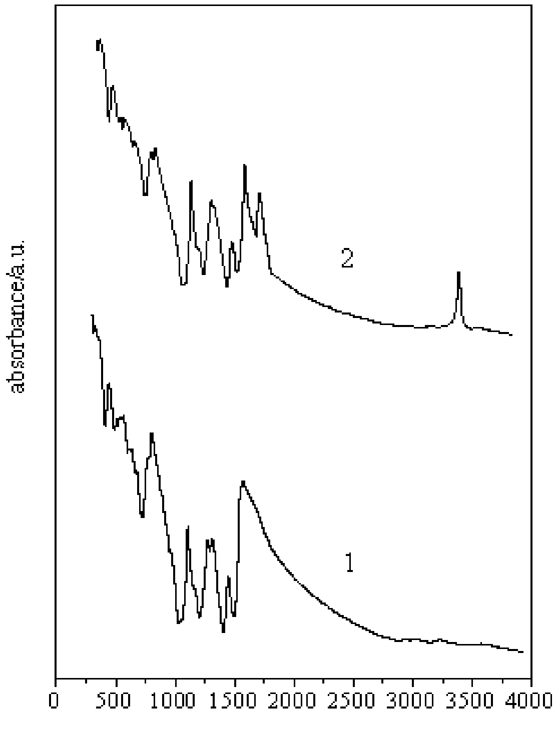

Fig. 4. FTIR spectrum of samples; (1) Sample 0#, (2) Sample 3#

Gas sensing properties of sensors: Fig. 5 is sensitivity curve of sensor containing different content of carbon nanotubes to 80 ppm formaldehyde at room temperature. It shows that adding carbon nanotubes can greatly increase the sensitivity of sensor to formaldehyde and the sensitivity of sensors increases with the content of carbon nanotubes increasing. When the content of carbon nanotubes is 30 %, the sensitivity of sensor is the highest. When the content of carbon nanotubes is larger than 30 %, the sensitivity of sensor almost do not change with the content carbon nanotubes increasing. Because formaldehyde is reductive gas, while polyaniline is P-type semiconductor, its resistance increases when it adsorbs reductive gas. So it has gas sensing property. When polyaniline doped with carbon nanotubes, carbon nanotubes has large surface area,which increase the adsorption of sensors to formaldehyde, so its resistance increases when it adsorbs reductive gas and its sensitivity to formaldehyde increases. When content of carbon nanotubes is larger than 30 %, the adsorption of gas has gotten saturation, so the resistance of sensor do not change appreciably and the sensitivity almost doesn't change with the content of carbon nanotubes increasing.

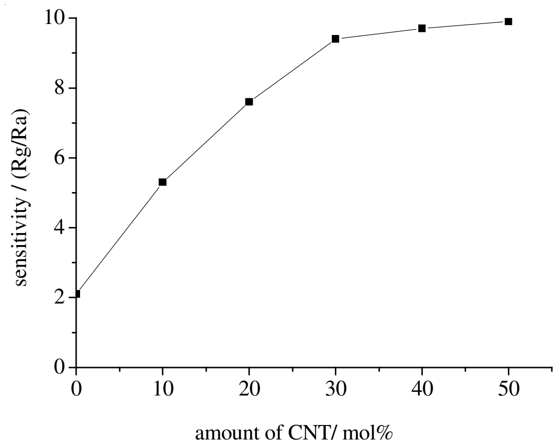

Fig. 5. Sensitivity curve of sensors doped different amount of carbon nanotubes to 80 ppm HCHO

Fig. 6 is sensitivity curve of sensors doped with 30 % carbon nanotubes to formaldehyde with different concentration at room temperatrue. It shows that the sensitivity of sensor

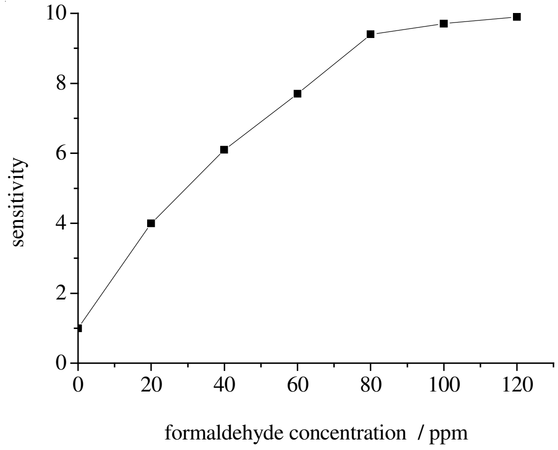

Fig. 6. Variation in sensitivity of the sensor with HCHO concentration

increases with the concentration of formaldehyde increasing. When the concentration of formaldehyde is larger than 100 ppm, the sensitivity of sensor varies little. Gas adsorbed on the surface of sensors has an equilibrium concentration. When the concentration of gas get saturation, there are no sites where gas has not been absorbed. So continuing to increase the concentration of gas, the amount of gas adsorption can not increase and the sensitivity of sensor almost not change.

Fig. 7 is sensitivity curve of sensors doped with 30 % carbon nanotubes to formaldehyde, methanol,alcohol and acetone at room temperature. It shows that the sensor has larger gas sensitivity to formaldehyde than to other gas. So the sensor has better selectivity for formaldehyde.

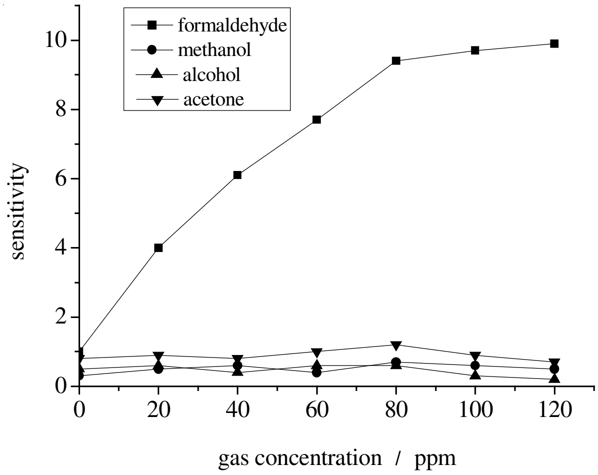

Fig. 7. Sensitivity curves of carbon nanotubes-doped sensor in 80 ppm formaldehyde, methanol, alcohol and acetone at 4 V heating voltage

The response recovery process of sensor is a process of gas adsorption and desorption. At room temperature, the response time of sensor doped with 30 % carbon nanotubes to 80 ppm formaldehyde is *ca.* 17 s and response can recover in 200 s.

Mechanism: Formaldehyde is a kind of reductive gas and electron donor. Polyaniline is P-type semiconductor. When polyaniline contacts with formaldehyde, formaldehyde is adsorbed on the surface of polyaniline and the electron transfer from formaldehyde to polyaniline, so its resistance increase. When polyaniline doped with carbon nanotubes,which has large surface area and can increase the adsorption of sensors to formaldehyde, so its resistance increase, sensitivity to formaldehyde also increases.

Conclusion

Using carbon nanotubes as template, polyaniline/carbon nanotube nanocomposite was synthesized by *in situ* polymerization method.The formaldehyde sensitive performances of the sensors made from polyaniline/carbon nanotube nanocomposite were studied. The results show that the sensitivity of polyaniline/carbon nanotube nanocomposite for formaldehyde gas is higher than that of pure polyaniline and the sensor doped with 30 % carbon nanotubes has the highest sensitivity and highest selectivity to formaldehyde.

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