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Spectral Studies of a Polyaniline/ Diatomite Composite

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ABSTRACT

Polyaniline/diatomite composite was prepared by the oxidation of aniline in the presence of diatomite, and this composite was characterized by Fourier transform infrared spectra, Fourier transform Raman spectra, UV-VIS absorption spectra and wide-angle X-ray diffraction, as well as conductivity. The results of spectral analysis illustrate that polyaniline is not simply blended with diatomite. An interaction exists at the interface of diatomite and polyaniline, which may be associated with hydrogen bonds formed between the surface of diatomite with electronegativity and N–H bonds in the polyaniline macromolecule. The result of wide-

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angle X-ray diffraction shows that polyaniline has no effect on the crystallizability of diatomite, but conductivity of the composite containing 8% polyaniline has reached $2.8 \times 10^{-2} \text{ S}\cdot\text{cm}^{-1}$ at 20°C.

INTRODUCTION

Diatomite is almost pure silicon dioxide. It is a dust varying in color depending on composition, from white-grey to yellow to red, and is extremely stable and does not produce toxic chemical residues in the air. Normal diatomite is an insulator and is insoluble in water. Therefore diatomite is widely used for purification of water, the clarification of liquors and juices, filtration of commercial fluids, and separation of various oils and chemicals. It is also utilized as fillers in paints, paper and rubber.^[1] Polyaniline is generally recognized as the one of the foremost air-stable organic conducting polymers, and has potential for commercial application because of its promising properties.^[2-4] Recently, work on composites of polyaniline and inorganic materials have been reported.^[5-10] Among which, Xia and Wang^[8] succeeded in obtaining conductive polyaniline/nanocrystalline titanium oxide composite by ultrasonic irradiation. The results reveal that the polyaniline deposited on the surface of nanoparticles leads to a core-shell structure and the presence of nanocrystalline titanium oxide strengthens the UV absorption of the polyaniline. Moreover, J. M. Yeh et al.^[6] prepared a series of nanocomposite materials, which consisted of an emeraldine base of polyaniline and layered montmorillonite (MMT) clay, via in-situ polymerization. Many results have shown that these composites have better mechanical, physical and chemical properties.

In this letter, we report the first spectral characterization of the polyaniline/diatomite composite. The results suggest that polyaniline is not simply blended with diatomite, but an interaction exists at the interface of diatomite and polyaniline. Although this composite only contains 8% conducting polyaniline by mass, its conductivity has reached $2.8 \times 10^{-2} \text{ S}\cdot\text{cm}^{-1}$ at 20°C. It has potential commercial applications for fillers to improve antistatic properties of paints, paper and rubber.

EXPERIMENTAL

Aniline (Shanghai Chemical Works, China) was used after double distillation. Diatomite (Shanghai Chemical Works, China) was used without further purification. Other chemicals used were of analytical reagent grade. Water used in this investigation was de-ionized water.

Polyaniline/diatomite composite was prepared as follows: 1 *ml* aniline was injected into 80 *ml* of 2 *M* HCl containing 1 *g* diatomite. After the aniline was uniformly dispersed on the surface of diatomite over about 10 hours, 2~3 drops FeSO₄ (5%) aqueous solution were first added as a catalyst, and 1 *g* (NH₄)₂S₂O₈ (dissolved in 20 *ml* de-ionized water) was then added to the solution with constant stirring. The polymerization was allowed to proceed for 5 hours at room temperature. The product was filtered under gravity, and washed with 100 *ml* of de-ionized water to remove residual aniline hydrochloride and ammonium sulfate. Finally it was dried at 60°C for 24 hours under vacuum to obtain a fine green powder.

Polyaniline was prepared as follows: 1 *ml* aniline was injected to 80 *ml* of 2*M* HCl. After 2~3 drops FeSO₄ (5%) aqueous solution were added, 1 *g* (NH₄)₂S₂O₈ (dissolved in 20 *ml* de-ionized water) was dropped into the solution with constant stirring. The polymerization was allowed to proceed for 5 hours at room temperature. The product was filtered, washed and dried to obtain a fine dark green powder.

Fourier-transform infrared spectra of the powder samples in the range of 400~4000 cm⁻¹ were made with a fully computerized Bruker VECTOR22 spectrometer. Measurements were performed in the transmission mode for which samples were palletized with KBr powder. Fourier-transform Raman spectra of powder samples were recorded on an RFS100 FT-Raman spectrometer. Light from Nd-YAG laser, wavelength 1060 nm, and maximum output power 350 mW, was focused onto the surface of the sample through an optical microscope. In order to avoid decomposition of the sample by heat, we took low output power for all samples (25 mW). UV-VIS absorption spectra of powder samples were taken on a Shimadzu UV-2401PC spectrophotometer. Using an integrating sphere and BaSO₄ as a white standard, diffuse reflectance spectra were recorded as R_{stand}/R_{sample} vs. the wavelength, which R was the absolute reflection intensity. Measurements of wide-angle X-ray diffraction were carried out on a Shimadzu XD-3A instrument using CuK_α radiation (λ = 0.154 nm). Conductivity measurements were taken on compressed pellets of the powder using a conventional four-point probe technique at ambient temperature (20°C).

RESULTS AND DISCUSSION

Figure 1 shows Fourier-transform infrared spectra of doped polyaniline, diatomite and polyaniline/diatomite composite, respectively. Several characteristic peaks associated with doped polyaniline (curve—a) are assigned as follows: the peak at 3445 cm⁻¹ is attributable to N—H



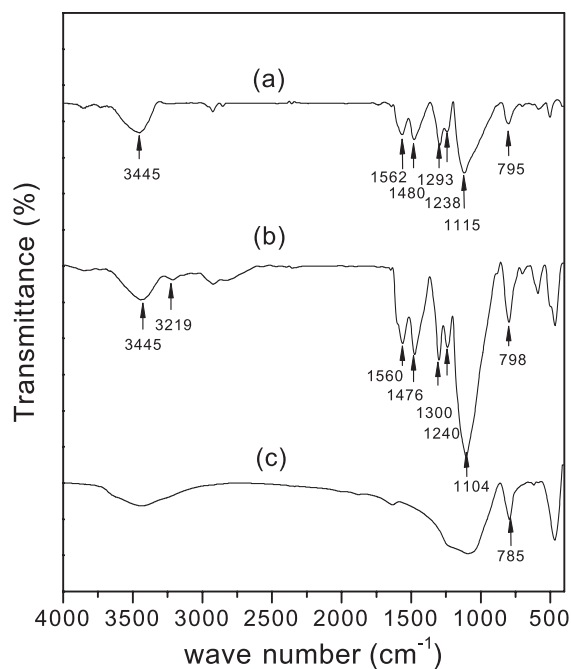


Figure 1. Fourier-transform infrared spectra of doped polyaniline (a), polyaniline/diatomite composite (b) and diatomite (c).

stretching mode. C=N and C=C stretching modes for the quinoid and benzenoid rings occur at 1562 cm^{-1} and 1480 cm^{-1} , the peaks at about 1293 cm^{-1} and 1238 cm^{-1} have been attributed to C-N stretching modes for the benzenoid ring, while the peak at 1115 cm^{-1} is assigned to an in plane bending vibration of C-H (mode of $\text{N}=\text{Q}=\text{N}$, $\text{Q}=\text{N}^+\text{H}-\text{B}$ and $\text{B}-\text{N}^+\text{H}-\text{B}$), which is formed during protonation, and the peak at 795 cm^{-1} is due to C-C and C-H out-of-plane bending vibration of the benzenoid ring.^[11] Figure 1b indicates that the main characteristic peaks of doped polyaniline appear in the polyaniline/diatomite composite, which are 3445 cm^{-1} , 1560 cm^{-1} , 1476 cm^{-1} , 1300 cm^{-1} , 1240 cm^{-1} , 1104 cm^{-1} and 798 cm^{-1} , respectively. Comparing Figure 1a with Figure 1b, it can be found that the peak at 1115 cm^{-1} , which is formed during protonation, obviously shifts to lower wave numbers (from 1115 to 1104 cm^{-1}), and its relative intensities also change. In addition, a new peak (3219 cm^{-1}) appears in the polyaniline/diatomite composite. It can be attributed to

hydrogen bonded N–H stretching mode.^[11] These results indicate that hydrogen bond is formed between the surface of diatomite with electronegativity and N–H bond in polyaniline macromolecule.

The Raman spectrum is a powerful means of researching the interaction between substrate surface and absorbed materials. Figure 2 reveals FT-Raman spectra of doped polyaniline, diatomite and polyaniline/diatomite composite, respectively. From Figure 2b, it can be clearly seen that the characteristic peaks of doped polyaniline appear in the polyaniline/diatomite composite. Among which, the peaks at 1594 cm^{-1} and 1171 cm^{-1} are associated with the benzenoid rings, and the peaks at 1502 cm^{-1} and 1371 cm^{-1} have been attributed to C=C and C=N stretching modes of quinoid rings.^[11,12] Figure 2b also shows that the intensity of peaks at 1171 cm^{-1} and 1502 cm^{-1} strengthens for the polyaniline/diatomite composite, and a shoulder peak (1328 cm^{-1}) appears beside peak at 1371 cm^{-1} . These results demonstrate that the polyaniline is not simply deposited on the surface of diatomite, and there is an interaction at the interface of polyaniline and diatomite. This interaction perhaps associates with hydrogen

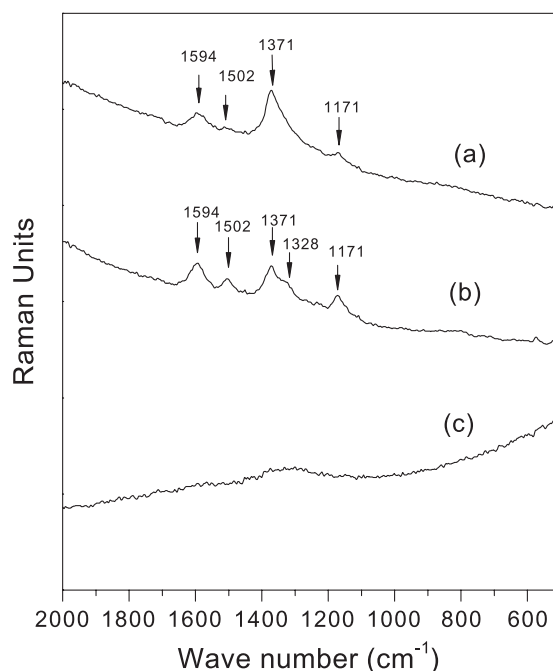


Figure 2. Raman spectra of doped polyaniline (a), polyaniline/diatomite composite (b) and diatomite (c).



bonding formed between the surface of diatomite with electronegativity and the N–H bond in polyaniline macromolecule.

UV-VIS absorption spectra of doped polyaniline, diatomite and polyaniline/diatomite composite are given in Figure 3. Figure 3a shows that three distinctive peaks of doped polyaniline appear at about 300 nm, 450 nm and 850 nm, which are attributed to the $\pi-\pi^*$, polaron- π^* and π -polaron transition,^[3,8] respectively. Figure 3b indicates that two peaks at 300 nm and 450 nm have combined into a flat peak for the polyaniline/diatomite composite, and the peak at 850 nm due to the π -polaron transition is obviously shifted from 850 nm to 760 nm. This result indicates there is an interaction at the interface of polyaniline and diatomite. Figure 3b also suggests that the polyaniline/diatomite composite not only can strongly absorb the UV light but also can absorb the visible and near-IR light.

Figure 4 is the comparison of wide-angle X-ray diffraction patterns for doped polyaniline, diatomite and polyaniline/diatomite composite at room

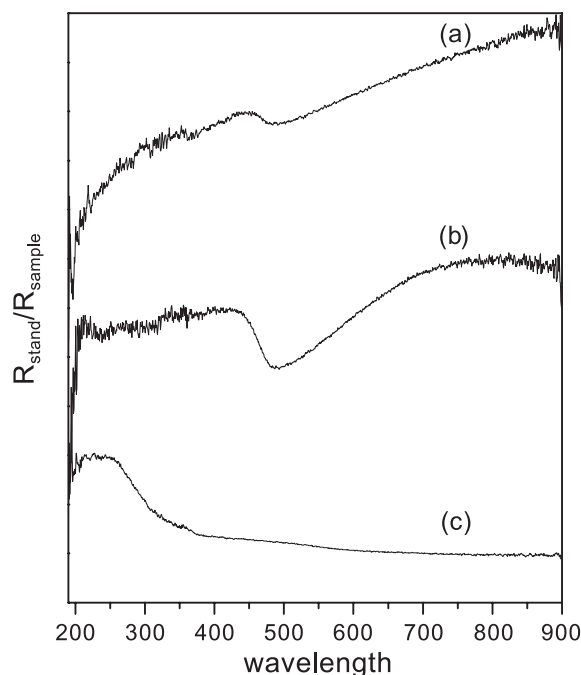


Figure 3. UV-VIS absorption spectra of doped polyaniline (a), polyaniline/diatomite composite (b) and diatomite (c).

temperature from $2\theta = 5^\circ$ to 55° . Figure 4c reveals that the doped polyaniline has also some degree of crystallinity. Four broad peaks appear in the region of $2\theta = 5$ to 30° , while a maximum is around 25° for doped polyaniline. These peaks may be assigned to the scattering from polyaniline chains at interplanar spacing.^[5] From Figure 4b, it can be found that the characteristic peaks of doped polyaniline do not emerge in the polyaniline/diatomite composite. This observation suggests that an interaction exists at the interface of polyaniline and diatomite, which restricts aggregation of polyaniline to form bulk polymer. Therefore the four weak peaks disappear gradually in the polyaniline macromolecule. Figure 4b also shows that polyaniline deposited on the surface of diatomite has no effect on the crystallizability of diatomite, and the polyaniline/diatomite composite is more ordered than pure polyaniline.

Conductivity of the polyaniline/diatomite composite was $2.8 \times 10^{-2} \text{ S}\cdot\text{cm}^{-1}$ at 20°C . This means that conductivity of the polyaniline/diatomite

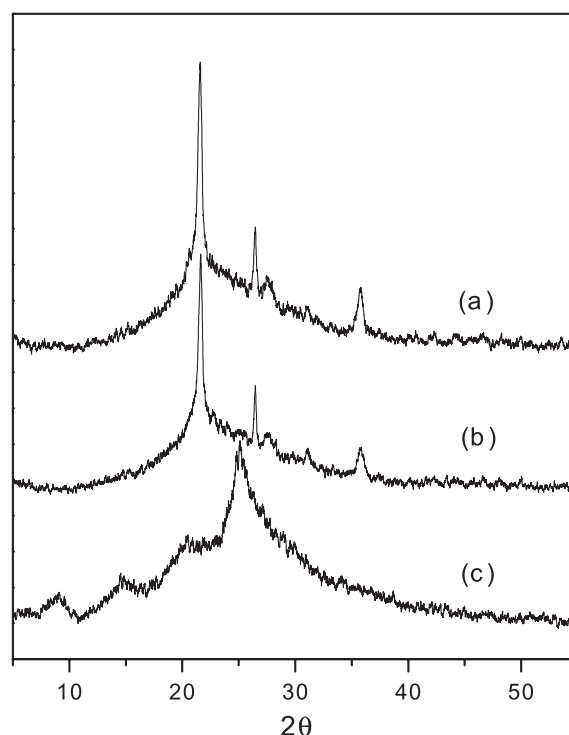


Figure 4. Wide-angle X-ray diffraction patterns of diatomite (a), polyaniline/diatomite composite (b) and doped polyaniline (c).



composite has reached the semiconductor level. Although its conductivity is lower than pure polyaniline prepared at the same condition ($1.3 \text{ S}\cdot\text{cm}^{-1}$), it is still useful to enlarge the applied fields of insulator diatomite.

CONCLUSION

The polyaniline/diatomite composite was obtained by the oxidation of aniline in the presence of diatomite, and this composite was characterized in different ways. The results of spectral analysis demonstrate that polyaniline is not simply blended with diatomite. An interaction exists at the interface of diatomite and polyaniline, which is associated with hydrogen bonding formed between the surface of diatomite with electronegativity and N–H bond in the polyaniline macromolecule. The result of wide-angle X-ray diffraction confirms that polyaniline deposited on the diatomite has no effect on the crystallizability of the diatomite. The conductivity of this composite containing 8% polyaniline reached $2.8 \times 10^{-2} \text{ S}\cdot\text{cm}^{-1}$ at 20°C . It has potential commercial applications for fillers to improve antistatic properties of paints, paper and rubber.

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