Preparation of Conductive Polyaniline/Nanosilica Particle Composites through Ultrasonic Irradiation

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ABSTRACT: Polyaniline/nano-SiO_2 particle composites were prepared through ultrasonic irradiation. Polymerization of aniline was conducted under ultrasonic irradiation in the presence of two types of nano-SiO_2: porous nanosilica and spherical nanosilica. The stability of the colloid dispersion, UV–vis spectra, composition, interaction, conductivity, and other characteristics of the composites were examined. It was found that the aggregation of nano-SiO_2 could be reduced under ultrasonic irradiation and that nanoparticles were redispersed in the aqueous solution. The formed polyaniline deposited on the surface of the nanoparticle, which led to a core–shell structure. Two particle morphologies, threadlike aggregates with a few spherical nanoparticles for porous nanosilica and spherical particles with a few sandwichlike particles for spherical nanosilica, were observed. X-ray photoelectron spectroscopy showed that for two types of composites the ratio of Si atoms to N atoms (Si:N) on the surface was much higher than that in the bulk. The UV–vis spectra of the diluted colloid dispersion of polyaniline/nano-SiO_2 composite particles were similar to those of the polyaniline system. Fourier transform infrared spectroscopy suggested strong interaction between polyaniline and nano-SiO_2. The conductivity of the polyaniline/porous nanosilica (23.1 wt % polyaniline) and polyaniline/spherical nanosilica (20.6 wt % polyaniline) composites was 2.9 and 0.2 S/cm, respectively. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 87: 1811–1817, 2003

Key words: polyaniline; ultrasonic irradiation; nanocomposites; conductive; nanosilica

INTRODUCTION

Conducting polymer/inorganic nanoparticle composites with different combinations of two components have attracted more and more attention because they combine the merits of conducting polymers with those of inorganic nanoparticles.[1–6] These types of nanocomposites not only have interesting physical properties but also have potential applications in diverse areas such as chemistry, physics, electronic, optics, material science, and biomedical science. However, conducting polymers are infusible in nature and generally insoluble in the usual solvents, and inorganic nanoparticles are easily aggregated because of their high surface energy. Therefore, the big challenge in making conducting polymer/inorganic nanoparticle composites is that nanoparticles are dispersed at the nanoscale in the composites, which generally demands some encapsulating or entrapping. Clearly, it is difficult to obtain such a true nanocomposite by simple blending or mixing in solution or in the melting state. Making

these nanocomposites demands new methods and new technologies. Armes et al. recently developed a excellent sol technique to prepare conducting polymer/inorganic nanoparticle composites, as follows.[7–10] The colloidal dispersions of conducting polymers/inorganic nanoparticles were prepared in the presence of silica sol with a particle size of about 20 nm. The results of transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) suggested that the precipitating conducting polymer could be adsorbed onto the surface of the sol particles as a thin layer and that it glued the particles together, and therefore a stable colloid of polypyrrole–silica, polyaniline–silica "raspberry" particles could be obtained. The average particle diameter was submicrometer in size. Such composite particles have the potential to be used as marker particles for immunodiagnostic assays. Stejskal et al. investigated the effect of the synthesis parameter on the morphology and size of polyaniline/nanosilica composite particles.[11] A large amount of sol was used in this method. The primary objective of nanocomposite synthesis was to keep the conducting polymer in a good dispersion.

In this study a novel and simple sonochemical method was used to prepare polyaniline/nanosilica particle composites. Ultrasonic irradiation, as a new technology, has been widely used in chemical synthe-
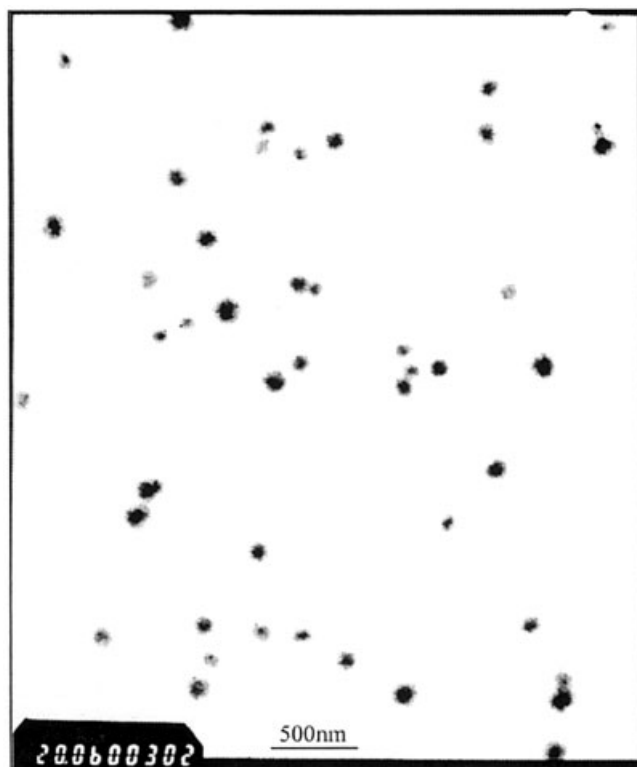
Figure 1 TEM photo of polyaniline particles prepared through ultrasonic irradiation; MNIP: porous nanosilica (~10 nm).

EXPERIMENTAL

Materials

Aniline (ANI; AR, Beijing Chemical Reagent Company, China) was distilled twice under reduced pressure and stored below 4°C in a nitrogen atmosphere. Also used were 10 nm of porous nano-SiO$_2$ (MNIP) and 15 nm of porous spherical nano-SiO$_2$ (MNIS; Zhoushan Mingri Nanomaterials Company Ltd., Zhejiang, China) and sodium lauryl sulfate (SLS; CP, Shanghai Xiangde Chemical Factory, China).

Apparatus

The reaction apparatus used in this study was described in a previous article.[8] The VC-1500 ultrasonic irradiation instrument (Sonic & Material Co.) employed for this investigation had the following characteristics: standard titanium horn 22 mm in diameter, adjustable power, replaceable flat stainless-steel tip, digital thermometer to determine temperature, and gas flowing meter to measure gas flow rate. The glass reactor was self-designed and made in house.

sis. When ultrasonic waves pass through a liquid medium, a large number of microbubbles form, grow, and collapse in a very short time, about a few microseconds, which is called ultrasonic cavitation. Sonochemical theory calculation and the results of corresponding experiments have suggested that ultrasonic cavitation can generate a local temperature as high as 5000 K and local pressure as high as 500 atm, a heating and cooling rate greater than 10^9 K/s, which is a very rigorous environment.[12] Therefore, ultrasound has been extensively applied in the dispersing, emulsifying, crushing, and activating of particles. In previous articles we have reported that the aggregates of nanosilica can be broken apart and that nanosilica can be redispersed in a aqueous medium, thus making possible the preparation of long-term stable poly(n-butyl acrylate)/nanosilica composite latex through ultrasonic irradiation.[13,14] In the present study ultrasonic irradiation techniques were employed to prepare polyaniline/nano-SiO$_2$ shell–core composite particles. By taking advantage of the multiple effects of ultrasound, the aggregates of nano-SiO$_2$ particles can be broken down and the nanoparticles redispersed while polymerization of aniline proceeds. Synthesized polyaniline was deposited on the nano-SiO$_2$ particles, forming polyaniline-coated nanosilica composite particles.
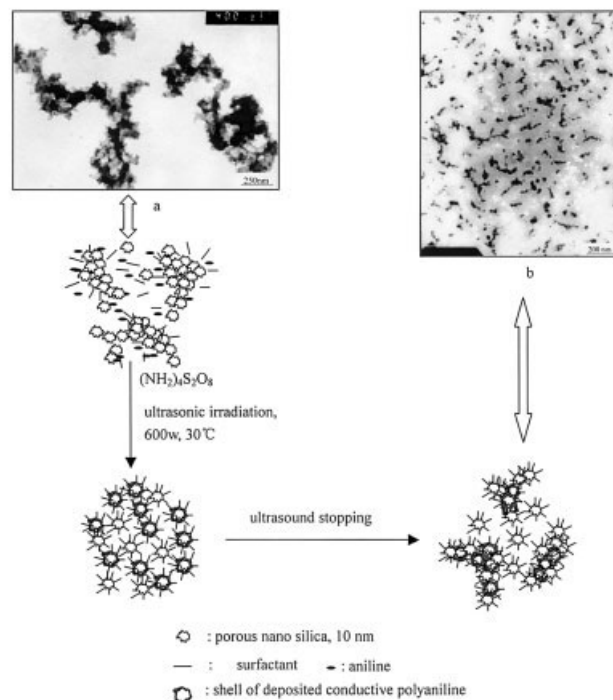

Figure 2 Formation of polyaniline/porous nanosilica composite particles: (a) TEM photographs of aggregates of porous nanosilica in aqueous solution, and (b) TEM photographs of polyaniline/porous nanosilica composite particles obtained through ultrasonic irradiation.
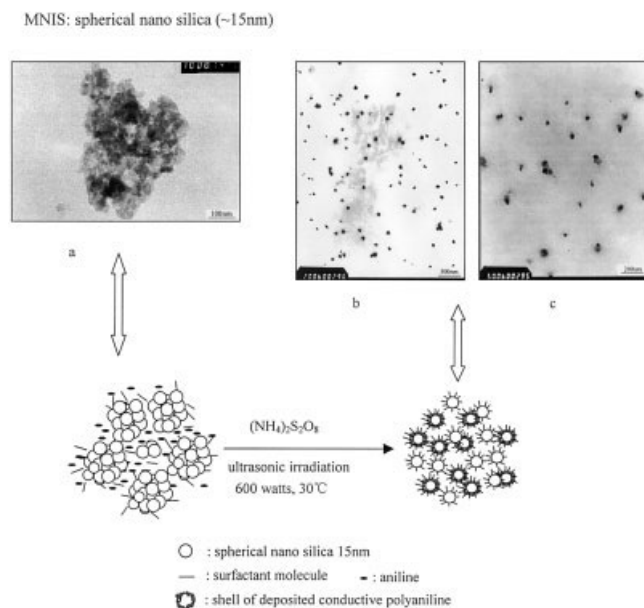
MNIS: spherical nano silica (~15nm)

Figure 3 Formation of polyaniline/spherical nanosilica composite particlesa: (a) TEM micrographs of aggregates of spherical nanosilica in aqueous solution, (b) TEM micrographs of polyaniline/spherical nanosilica composite particles obtained through ultrasonic irradiation (20 k), and (c) TEM micrographs of polyaniline/spherical nanosilica composite particles obtained through ultrasonic irradiation (50 k).

Preparation of polyaniline/nano-SiO$_2$ particle composites through ultrasonic irradiation

The polyaniline/nano-SiO$_2$ particle composites were prepared as follows. Typically, 2 g of SiO$_2$ particles, 1 mL of aniline, 2.5 g of (NH$_4$)$_2$S$_2$O$_8$, 100 mL of 2.4M concentrated HCl aqueous solution, 4 g of SLS, and 90 of mL deionized, distilled water were introduced into the reaction vessel. Deoxygenation was done by bubbling with oxygen-free nitrogen for 2 min in the reaction vessel, and then cooling water was circulated. The APS:ANI molar ratio was 1:1 in all experiments in this study. Ultrasonic irradiation was carried out with the probe of the ultrasonic horn immersed directly in the mixture emulsion system. A thermistor probe was immersed in the solution to measure the temperature variation during polymerization. When the reaction started, the reaction temperature increased from 14°C to 28°C in 3 min. After 1 h of irradiation the reaction was stopped. The polymerized colloid dispersion were precipitated using 100 mL of ethanol and left standing for 48 h without stirring. Then the precipitated mixture was filtrated. The obtained black composite of polyaniline/nano-SiO$_2$ composite particles was washed with a large amount of deionized water, 50 mL of ethanol, and 30 mL of ether and then dried for 48 h under a vacuum at 30°C. The drying temperature was stringently controlled.

Characterization

Stability was evaluated by placing 30 mL of the colloid dispersion in a cylindrical tube with a volume scale and then observing the sediment volume with the time. The particle morphology of all the samples was observed by TEM on a Hitachi H-600 instrument. The sample for observation was prepared as follows. The colloid dispersion (15 mL) was centrifuged with a Bechman J2-HS centrifuge (Bechman Instruments Inc., USA) at 16,000 rpm for 1 h. The supernatant liquid was removed, and the green sediment was redispersed in 50 mL of water. This centrifugation–redispersion cycle was repeated three times. The final sediment was redispersed in 30 mL of water through ultrasonic irradiation, and then the dispersion was dropped on a copper grid to observe the morphology of the polyaniline/nano-SiO$_2$ composite particles. The samples for UV–vis absorption spectra analysis were prepared by diluting the prepared polyaniline colloid dispersion 250 times with water, which then was used to determine the UV–vis electronic absorption spectra on a Shimadzu UV-240 spectrophotometer. Analysis of the samples by Fourier transform infrared (FTIR) spectroscopy was performed on a Nicolet 560 FTIR spectrometer. X-ray photoelectron spectroscopy (XPS) was done on an XSAM 800 X-ray photoelectron spectrometer with an Mg Kα X-ray source. In the data analysis, the binding energy (BE) of the core-level C1s was set at 284.8 to compensate for surface-charging effects. The surface elemental stoichiometries were determined from the ratios of peak areas corrected with the empirical sensitivity factors. The electrical conductivity measurements were made by the conventional four-point method on pressed pellets of composite particles prepared at ambient temperature (15°C).

RESULTS AND DISCUSSION

Polymerization and colloid stability

The polymerization of aniline was conducted in the presence of nano-SiO$_2$. The color of the system changed from light blue to deep blue to dark green. The stability of the colloid dispersion with anionic surfactant SLS was good, and no sedimentation was observed after 1 week. With an increase in the concentration of the surfactant, the stability increased.

Formation of polyaniline/nano-SiO inf2 composite particles

In the absence of nano-SiO$_2$, the size of polyaniline prepared through ultrasonic irradiation was 60–120 nm, as shown in Figure 1. When nanosilica was added, composite particles of a different size and morphology were formed. The formation of composite particles for porous nanosilica and spherical nanosilica is illus-
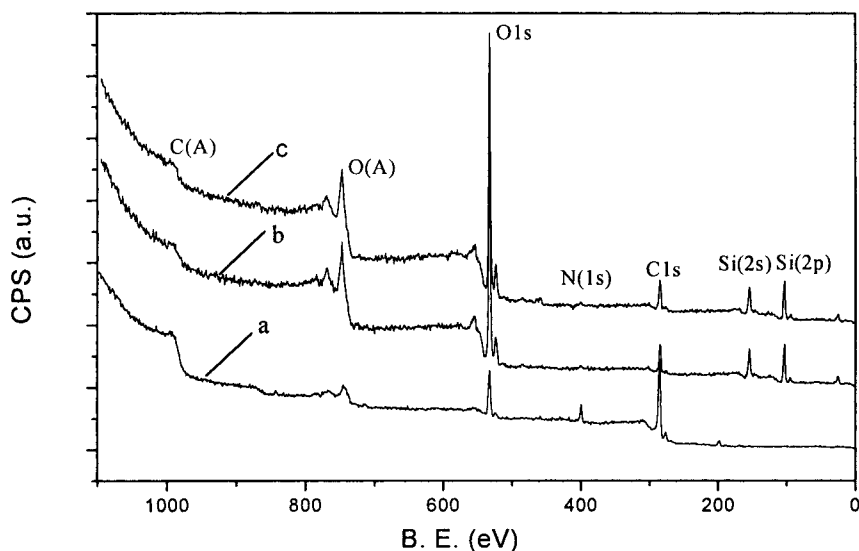
Figure 4 Survey X-ray photoelectron spectra of (a) polyaniline, (b) polyaniline/porous nanosilica composite (23.1 wt % polyaniline), and (c) polyaniline/spherical nanosilica composite (20.6 wt % polyaniline).

trated in Figures 2 and 3, respectively. It can be seen in Figure 2(a) and Figure 3(a) that the original commercially available porous nano-SiO_2 and spherical nano-SiO_2 particles were aggregated in aqueous solution with a irregular shape and that the size was in the submicrometer range. This should be attributed to the high surface energy of the nanoparticles. The prepared polyaniline/porous nano-SiO_2 composite particles in the colloid dispersion with 2 g of SiO_2 particles initially charged are shown in Figure 2(b). Threadlike aggregates with a few spherical nanoparticles (10–40 nm) were observed. A different appearance was observed for the polyaniline/spherical nano-SiO_2 composite particles, which were spherical in shape (15–40 nm) with a few sandwichlike particles, as shown in Figure 3(b,c), of 20 and 50 k, respectively. In the absence of nano-SiO_2, the size of a polyaniline particle prepared through ultrasonic irradiation at the same synthesized condition was relatively larger (60–120 nm; Fig. 1). When nanocrystalline TiO_2 particles were added, the size of composite particles was decreased. So it reasonably can be concluded that polyaniline was mainly absorbed on the surface of nano-SiO_2 because of the small size and large surface area of nanosilica. We believe that whether for porous or spherical nanosilica, there are two types of precursor particles in the colloid dispersion: unencapsulated original nanosilica and polyaniline-encapsulated nanosilica composite particles. Those nanosized particles had the tendency to aggregate when ultrasound was stopped. The difference in the structures of the aggregates for the two kinds of nanosilica, that is, thread- and sandwichlike, were observed. This difference can be explained as follows: porous nanosilica is smaller in size and larger in surface area and has a much stronger ability for

absorption, which can produce a thinner polyaniline shell on the surface of porous nanosilica. Compared with the spherical nanosilica, the unencapsulated porous nanosilica and the formed polyaniline-encapsulated porous nanosilica composite particles have a higher surface energy and a stronger tendency toward aggregation.

As illustrated in Figures 2 and 3, under ultrasonic irradiation the aggregates of nano-SiO_2 were broken down, and nanoparticles were redispersed in the aqueous solution at the nanoscale; at the same time, aniline monomer was polymerized in the presence of $(NH_4)_2S_2O_8$, and the synthesized polyaniline was deposited and absorbed on the surface of nano-SiO_2 particles, which formed the shell of the conductive polyaniline. The surfactants absorbed on the surface of the composite particles had a stabilizing effect.

TABLE I
Binding Energy and Composition of Every Element in the Surface of Polyaniline, Polyaniline/Porous Nanosilica, and Polyaniline/Spherical Nanosilica Particle Composites Obtained through Ultrasonic Irradiation

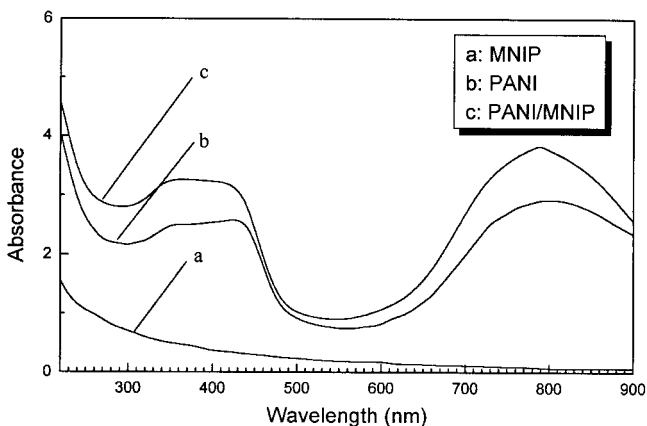| Element	Polyaniline		Polyaniline/ spherical nanosilica particle composite		Polyaniline/ porous nanosilica particle composite	
	BE	At (%)	BE	At (%)	BE	At (%)
C1s	284.8	74.4	284.8	21.6	284.8	18.4
O1s	532.7	14.9	533.2	55.0	533.2	59.5
Si2p	—	—	103.7	21.8	103.7	20.8
N1s	399.4	8.9	399.7	1.6	399.8	1.3
Cl2p	197.4	1.7				

Figure 5 UV–vis absorption spectra of diluted colloid dispersions obtained through ultrasonic irradiation of (a) porous nano-SiO_2, (b) polyaniline, and (c) polyaniline/porous nano-SiO_2 composite particles.

XPS

Figure 4 shows the survey X-ray photoelectron spectra of the samples obtained through ultrasonic irradiation with varying polyaniline content. Table I shows the binding energy and composition of every element in the surface. The peak of the binding energy of every element was slightly shifted because of the change in environment. The ratio of the number of SI atoms to the number of N atoms (Si:N) on the surface of the polyaniline/nano-SiO_2 particle composites was determined by the ratios of the peak areas corrected by empirical sensitivity factors. The SI:N ratio for polyaniline/porous nano-SiO_2 particle composites with ~23.1 wt % polyaniline content (sample a) was ~16, which was much higher than that in the bulk (~5.2). The ratio of the number of SI atoms to the number of N atoms, Si:N, for the polyaniline/spherical nano-SiO_2 particle composites with a ~20.6 wt % polyaniline content (sample c) was ~13.6, much higher than

that in the bulk (~6.1). These results indicate that the presence of unencapsulated nanosilica or polyaniline/nano-SiO_2 composite particles with a much thinner polyaniline shell, which is consistent with the TEM analysis.

UV–vis absorption

The UV–vis absorption spectra of the diluted polyaniline/porous nano-SiO_2 and polyaniline/spherical nano-SiO_2 colloid dispersions obtained by ultrasonic irradiation are shown in Figures 5 and 6, respectively. The absorption spectra are similar to those of the pure polyaniline system. The characteristic peak of polyaniline appears at 325–360 nm, 400–430 nm, and 780–826 nm, which can be attributed to π–π^*, polaron–π^*, and π–polaron transition, respectively,[15,16] suggesting that the prepared polyaniline is in the doped state. Not much difference between the two kinds of conducting polyaniline/nanosilica composites was found.

FTIR

Figure 7 shows the FTIR spectra of the samples obtained through ultrasonic irradiation at different polyaniline concentrations. The characteristic peaks of SiO_2 at ~1639 cm^{-1}, ~1089 cm^{-1}, and ~803 cm^{-1} and of polyaniline at ~1560 cm^{-1}, ~1467 cm^{-1}, ~1293 cm^{-1}, ~1103 cm^{-1}, and ~876 cm^{-1} appeared in the polyaniline/nano-SiO_2 particle composites. As shown in Table II, the incorporation of nano-SiO_2 leads to the shift of some FTIR bands of the polyaniline. The absorption peaks of C=C of the benzoid ring at 1457 cm^{-1} and the quinoid ring at 1103 cm^{-1} for the two kinds of composite particles were both shifted to higher wave numbers. The results suggest that a strong interaction between polyaniline and nano-SiO_2.
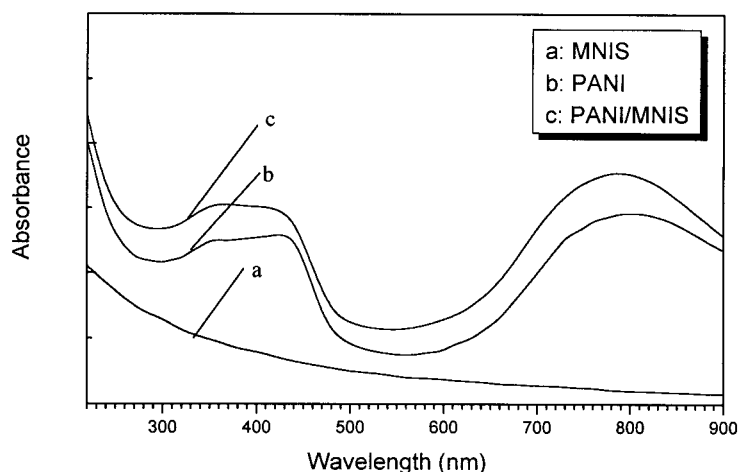

Figure 6 UV–vis absorption spectra of diluted colloid dispersions obtained through ultrasonic irradiation of (a) spherical nano-SiO_2, (b) polyaniline, and (c) polyaniline/spherical nano-SiO_2 composite particles.
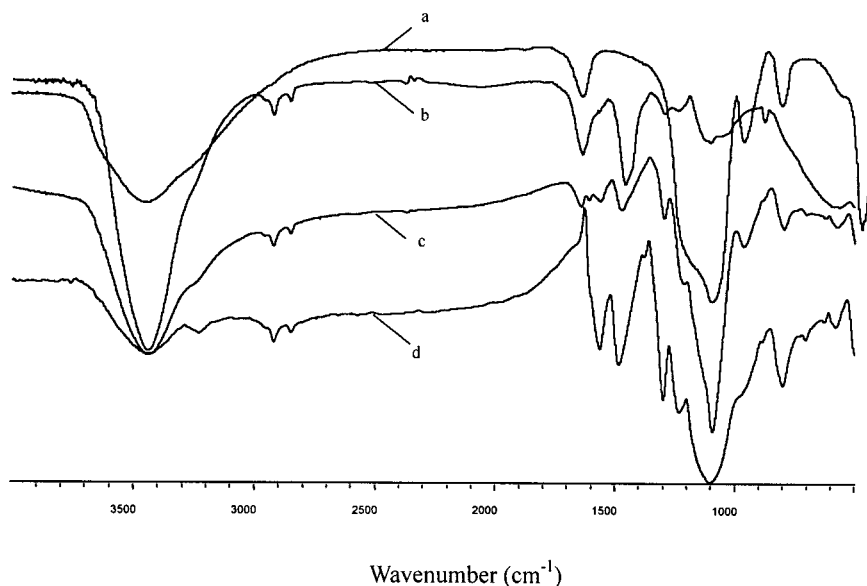
Figure 7 FTIR spectra obtained through ultrasonic irradiation of (a) porous nano-SiO_2, (b) polyaniline, (c) polyaniline/porous nano-SiO_2 particles composite obtained through ultrasonic irradiation, and (d) polyaniline/spherical nano-SiO_2 particles composite.

Conductivity

The conductivity values of the polyaniline/porous nano-SiO_2 composite (23.1 wt % polyaniline) and the polyaniline/spherical nano-SiO_2 composite (20.6 wt % polyaniline) were 2.9 S/cm and 0.2 S/cm, respectively. Conductivity was higher for porous nano-SiO_2, indicating more conductive channels can be formed because of the porous structure. Nanosilica is a kind of insulator, so that when nano-SiO_2 and polyaniline were combined, it hampered the formation of conductive channels. We believe ultrasonic irradiation improves the dispersion of nano-SiO_2 in the composites and the degree of doping of the polyaniline, allowing conducting polymer/inorganic particle composites with low percolation thresholds to be prepared.

CONCLUSIONS

Polyaniline/nano-SiO_2 particle composites were prepared through ultrasonic irradiation. Polymerization of aniline was conducted under ultrasonic irradiation in the presence of nano-SiO_2. Two kinds of nanosilica were used: spherical nanosilica and porous nanosilica. In our study the aggregation of nano-SiO_2 was able to be reduced under ultrasonic irradiation and the nanoparticles redispersed in the aqueous solution. The formed polyaniline deposited on the surface of the nanoparticle, which led to a core–shell structure. Two particle morphologies—threadlike aggregates with a few spherical nanoparticles for porous nanosilica and spherical particles with a few sandwichlike particles for spherical nanosilica—were observed. XPS showed that the ratio of the number of Si atoms to the number of N atoms (Si:N) in the surface was much higher than that in the bulk for two kinds of composites, indicating the presence of unencapsulated nanosilica or polyaniline/nano-SiO_2 composite particles with a much thinner polyaniline shell, which is consistent with the TEM analysis. The UV–vis spectra of the diluted colloid dispersion of the polyaniline/nano-SiO_2 composite particles were similar to those of the polyaniline system. The results of FTIR suggest a strong interaction between polyaniline and nano-SiO_2. The conductivity of the polyaniline/porous nanosilica (23.1 wt % polyaniline) and polyaniline/spherical nanosilica (20.6 wt

TABLE II
Shift of FTIR Bands of Polyaniline, Polyaniline/porous Nano-SiO_2, and Polyaniline/Spherical Nano-SiO_2 Particle Composites Obtained through Ultrasonic Irradiation

	C=C Benzoid ring (cm^{-1})	C=C Quinoid ring (cm^{-1})	C—H (cm^{-1})
Polyaniline	1457.8	1103.6	876.2
Polyaniline/porous nano-SiO_2	1474.4	1092.7	795.6
Polyaniline/spherical nano-SiO_2	1484.9	1102.9	798.1

% polyaniline) composites was 2.9 and 0.2 S/cm, respectively.

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