Synergic Influence of a Surfactant and Ultrasonication on the Preparation of Soluble, Conducting Polydiphenylamine/Silica-Nanoparticle Composites

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ABSTRACT: Conducting polydiphenylamine was used to encapsulate silica nanoparticles through the oxidative polymerization of diphenylamine in the presence of ultrasonic irradiation. The polymerization was performed in the presence of sodium lauryl sulfate as a surfactant. Experiments performed in the absence of ultrasound clearly demonstrated that the application of ultrasonication played multiple roles in the preparation of a composite of polydiphenylamine with silica nanoparticles. Ultrasonication dispersed the silica nanoparticles, converted sodium lauryl sulfate to lauryl alcohol, and augmented the dispersion of the silica-nanoparticle/polydiphenylamine composite in an organic medium. Silica-nanoparticle/polydiphenylamine composites were also prepared in the absence of ultrasound and/or sodium lauryl sulfate. The silica-nanoparticle/polydiphenylamine composites were characterized with Fourier transform infrared spectroscopy, ultraviolet–visible/near-infrared spectroscopy, and thermogravimetric analysis. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 3912–3918, 2006

Key words: nanocomposites; nanoparticles; silicas; surfactants

INTRODUCTION

Nanocomposites consisting of a conducting polymer and inorganic nanoparticles can have the combined characteristics of the conducting polymer and inorganic nanoparticles,[1–5] and their preparation and characterization have received increasing attention. The physical mixing of inorganic nanoparticles and a conducting polymer in a solution or in the solid state does not result in a true nanocomposite. The insoluble nature of the conducting polymer and tendency of agglomeration of inorganic nanoparticles (due to the higher surface area) are the major problems in making a true composite with nanoparticles. New experimental approaches or strategies need to be developed for the preparation of genuine nanocomposites of inorganic nanoparticles and conducting polymers.

In this study, we employed a conducting polyaniline (PANI) derivative, polydiphenylamine (PDPA), to form nanocomposites with silica nanoparticles. Ultrasonic irradiation was used to disperse the nanoparticles and also to improve the solubility of the resulting composites.

The modification of silicon and silica nanoparticles can result in new and useful materials for device applications. Silicon nanoparticles have a few preferred advantages in the fabrication of nanoscale optoelectronic devices.[6] Silicon nanoparticles find applications as sensors,[7,8] tunable lasers,[9] and photodetectors.[10] Good biocompatibility[11] high photoluminescence efficiency,[12] and stability against photobleaching[13] make silica nanoparticles ideal materials for biological assays. The surface modification of silica particles by polymer deposition[14–17] improves the performance characteristics in sensor, electroluminescent, and hybrid devices, and so studies related to those aspects are receiving greater interest. Newer synthetic approaches need to be developed for the preparation of silica nanoparticles with conducting polymers.

In the group of conducting polymers, PANI shows high electrical conductivity, electrochemical redox switchability, and environmental stability.[18] However, the restricted solubility of PANI in common organic solvents limits its use in practical applications. PDPA, a polymer of N-substituted aniline, exhibits different electrochemistry, conductivity, and luminescence and possesses better solubility than PANI.[19–26] Reports on

the preparation of composites of PDPA with inorganic nanoparticles are, however, scarce.

Ultrasonic irradiation has been widely used by chemists for different purposes.[27,28] Cavitation arising from the passage of ultrasonic radiation through the medium of the reaction causes chemical reactions.[27] The sudden formation of bubbles and implosive collapse of the bubbles in the medium result in a huge rise in the temperature (750 K) and pressure (>20 MPa) with a very high cooling rate (10^{10} K/S). These conditions favor many physical and chemical changes in the medium subjected to ultrasonic irradiation. Chemical effects have been effectively used for the preparation of CdS and ZnS nanoparticles.[29,30]

In this study, nanocomposites of PDPA with silica nanoparticles were prepared in the presence of ultrasonic irradiation. We used multiple effects of ultrasound to make processable nanocomposites. First, ultrasound dispersed the silica nanoparticles, breaking the aggregates. Additionally, the use of sodium lauryl sulfate (SLS) as a surfactant stabilized the dispersed silica nanoparticles under ultrasonic irradiation. As a result of dispersion and stabilization, PDPA could be coated onto silica nanoparticles, and this resulted in silica-nanoparticle/PDPA composites. Interestingly, we anticipated that SLS could also undergo decomposition to result in lauryl alcohol (LA), which would provide a better environment for the solubility of the formed nanocomposites. The morphology and structural aspects of the nanocomposites prepared in the presence and absence of SLS and in the presence and absence of ultrasonic irradiation are critically compared.

EXPERIMENTAL

Materials

Diphenylamine (DPA), received from Sigma–Aldrich (United States), was used. Ammonium persulfate (APS; Merck), tetraethoxysilane (Aldrich), sulfuric acid (DC Chemical Co., Ltd., Korea), aqueous ammonia (25%; DC Chemical), ethanol (DSP, Korea), and SLS (DC Chemicals) were used as received. Silica nanoparticles with a mean diameter of 110 nm (±30 nm) were prepared as follows.

Briefly, tetraethoxysilane was subjected to hydrolysis and condensation for 12 h at the ambient temperature in an ethanol/aqueous ammonia (25%)/water mixture (50 : 1 : 2 v/v/v) to obtain amorphous silica nanoparticles.

Preparation of the silica-nanoparticle/PDPA composites in the presence of a surfactant under ultrasonic irradiation

A typical procedure for the preparation of the silica-nanoparticle/PDPA composites under ultrasonication and in the presence of SLS is outlined. To a solution of 90 mL of 0.03M DPA in 4M H_2SO_4 having 4 g of SLS, 0.2 g of silica nanoparticles was added. Pure nitrogen was purged for 5 min to remove the dissolved oxygen from the solution. Ten milliliters of 0.3M APS was added to the solution, which was subjected to ultrasonic irradiation by the immersion of an ultrasonic probe into the solution. Irradiation was continued for 1 h. The reaction mixture separated into two layers. The top layer was green, and the bottom one was colorless. The top layer was removed and treated with water and ethanol. The precipitate was filtered, washed with water, and dried in a vacuum oven.

Preparation of the silica-nanoparticle/PDPA composites in the absence of a surfactant under ultrasonic irradiation

A typical procedure is outlined here. Silica nanoparticles (0.2 g) were added to a solution of 90 mL of 0.03M DPA in 4M H_2SO_4. The experiment was also carried out in the absence of SLS in the medium with a procedure similar to that described in the previous section. After irradiation (1 h), the green precipitate was filtered, washed, and dried in a vacuum oven.

Silica-nanoparticle/PDPA composites were also prepared similarly in the absence of ultrasound but with conventional stirring. In these cases, the nanocomposites were also obtained as green powders.

Characterization

Fourier transform infrared (FTIR) spectra were recorded with a Bruker IFS 66v FTIR spectrophotometer in the region of 500–4000 cm^{-1} with KBr pellets. Ultraviolet–visible (UV–vis) spectra were recorded in dimethylformamide (the solution concentration was 0.05 mg/mL) with a Shimadzu UV–vis spectrophotometer. Thermogravimetric analysis was carried out with a TA Instrument 951 at a rate of 10°C/min in an atmosphere of N_2. The morphology of the samples was examined with transmission electron microscopy (TEM; H-7100, Hitachi).

RESULTS AND DISCUSSION

Silica-nanoparticle/PDPA composites were prepared by the chemical oxidative polymerization of DPA with silica nanoparticles in the medium of the polymerization. The polymerization was performed under ultrasonication in the presence or absence of the surfactant, SLS. To determine the influence of ultrasonication, the polymerization was also carried out in the absence of ultrasonication but with conventional stirring.

Role of the surfactant in the ultrasonic-irradiation-initiated formation of the PDPA/silica nanocomposites

Figure 1 presents photographs of the reaction system taken after the preparation of the silica-nanoparticle/PDPA composites with SLS in the polymerization medium under ultrasonication. The polymerization medium was separated into two layers [Fig. 1(a)]: a green top layer and a transparent bottom layer. On the contrary, no such separation into two layers was noticed [Fig. 1(b)] when the silica-nanoparticle/PDPA composites were prepared with SLS in the medium in the absence of ultrasonication or with conventional stirring. In the absence of ultrasonication, the polymerization medium was stirred during the formation of the silica-nanoparticle/PDPA composites.

We presume that under ultrasonication SLS plays a role in the formation and stabilization of silica-nanoparticle/PDPA composites and that in that process the medium can be separated into two layers. This presumption was confirmed by the preparation of the silica-nanoparticle/PDPA composites without SLS in the medium. Silica-nanoparticle/PDPA composites were also prepared with ultrasonication and conventional stirring independently. The polymerization medium did not show any separation into two layers [Fig. 1(b)]. The reason for the separation into two layers [Fig. 1(a)] in the presence of SLS and ultrasonication can be explained. Under ultrasonication, SLS changes into LA and subsequently separates into two layers. Now, the interesting aspect is the presence of the green silica-nanoparticle/PDPA composite in the LA layer [Fig. 1(a)].

Silica-nanoparticle/PDPA composites were present in the aqueous medium or precipitated when the nanocomposites were prepared without SLS in the polymerization either under ultrasonication or with conventional stirring. Even in the case of silica-nanoparticle/PDPA composite formation with SLS
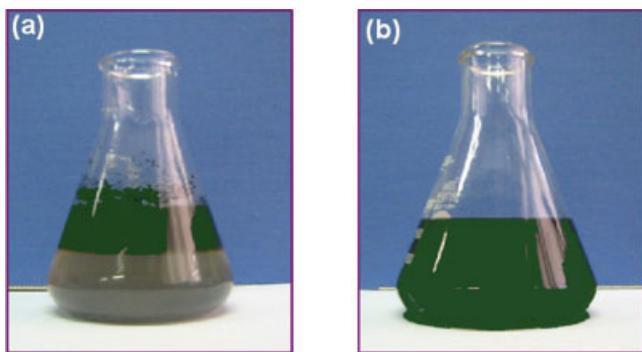
Figure 1 Photographs taken after the formation of Si/PDPA nanocomposites in the presence of SLS with (a) ultrasonic radiation and (b) conventional stirring. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
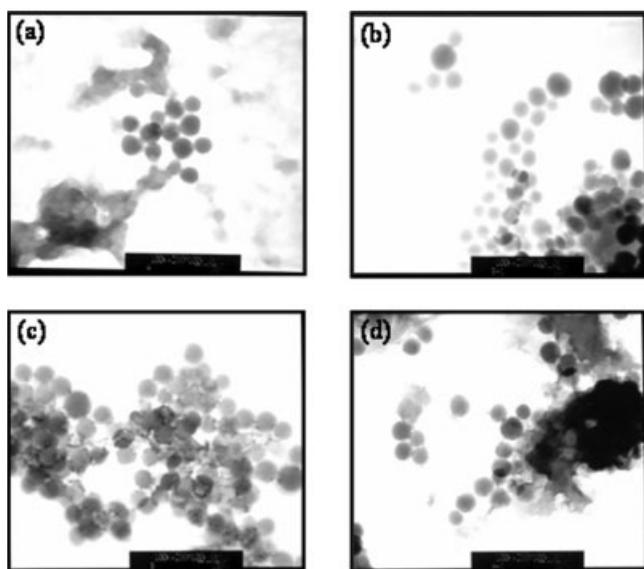
in the medium, conventional stirring resulted in aqueous dispersions of the silica-nanoparticle/PDPA composites. Otherwise, the silica-nanoparticle/PDPA composites were distributed into the LA layer only when the composites were prepared under ultrasonication.

Simultaneously, under ultrasonication, a portion of SLS changed into LA and subsequently separated into two layers. It is known that a cavitation effect induced by ultrasonication can cause a huge rise in the temperature.[27] The condition is ideally suited for a chemical reaction to occur. Hence, under ultrasonication, a relatively weak O—S link in SLS can be broken. Hydrogen radicals are also generated from the hydrolysis of water. The reaction of radicals generated from the cleavage of the O—S link in SLS with hydrogen radicals could form LA. For ascertaining the formation of LA under ultrasonication from SLS, an aqueous solution with a similar concentration of SLS was subjected to ultrasonication.

FTIR spectra of an aqueous solution of SLS after ultrasonication [Fig. 2(a)] and an aqueous solution of SLS that was not subjected to ultrasonication [Fig. 2(b)] are presented. For the simple aqueous solution of SLS, a band corresponding to antisymmetric SO_3 stretching appears around 1210 and 1180 cm^{-1} [Fig. 2(a)]. Also, a less intense symmetric SO_3 stretching band appears around 1065 cm^{-1} [Fig. 2(a)]. Strikingly, a peak corresponding to a primary alcohol such as LA can be observed around 1098 cm^{-1} for the aqueous solution of SLS that was subjected to ultrasonication. This peak is virtually absent in Figure 2(a). The clear presence of a peak around 1098 cm^{-1} in Figure 2(b) signifies the formation of LA upon the ultrasonication of SLS. Peaks representing the symmetric and asymmetric vibrations of —CH_2— groups are present around 2920 and 2850 cm^{-1} in Figure 2(a,b). The broad band around 3450 cm^{-1} signifies the presence of hydrogen-bonded —OH groups [Fig. 2(b)]. The appearance of a band around 3450 cm^{-1} in Figure 2(b) might be due to the presence of moisture in the sample. The band features that appear around 500–800 cm^{-1} in Figure 2(a,b) correspond to —CH_2— groups. These observations show that SLS upon ultrasonication was transformed into LA and that the silica-nanoparticle/PDPA composite was soluble in LA and existed in the organic layer. Now, it is important to analyze the properties of the silica-nanoparticle/PDPA nanocomposite that was soluble in LA [Fig. 1(a)].

Generally, PANI and its derivatives are insoluble in aqueous media or in organic solvents and hence precipitate. In this case, the silica-nanoparticle/PDPA composite was present in the organic phase [LA; Fig. 1(a)] when the composite was formed with SLS under ultrasonication. The synergic influence of ultrasonication on the formation of the composite was the reason for this interesting observation. Ultrasonication broke

Figure 2 FTIR spectra of (a) SLS and (b) LA.

the aggregation of the silica nanoparticles and kept the particles separated. The dispersed silica particles were transformed into a uniform core–shell-type composite, with silica nanoparticles as the core and PDPA as the shell. During the initial periods of ultrasonication, some SLS may have protected the dispersed silica nanoparticles. At the end of the polymerization, a silica-nanoparticle/PDPA composite existed in the LA layer (Scheme 1). The formation of silica-nanoparticle/PDPA composites with conventional stirring is described in Scheme 2. Silica nanoparticles are present as aggregates in the absence of ultrasonication. Layers of PDPA can be formed over the aggregates of silica nanoparticles. On the contrary, under ultrasonication,

the core–shell-type silica-nanoparticle/PDPA composite was stabilized by LA and preferred to be present in the organic phase [Fig. 1(a)].

For confirming the formation of core–shell-type nanocomposites and the difference in the morphology for the composites prepared under different conditions, TEM micrographs of composites prepared under different conditions were recorded (Fig. 3). The nanocomposites prepared with ultrasonication and conventional stirring in the presence or absence of SLS showed different morphologies. A TEM photograph of the silica-nanoparticle/PDPA composite prepared in the presence of SLS under ultrasonication [Fig. 3(a)] shows that spherical silica nanoparticles were dispersed uniformly and coated with PDPA to a thickness of 10–40 nm. In the TEM images (Fig. 3), the black, spherical units represent the PDPA-coated silica nanoparticles, and the gray ones are uncoated silica nanoparticles. Interestingly, most of the silica nanoparticles were coated with PDPA under ultraso-

Scheme 1 PDPA/silica nanocomposite formation with SLS in the medium under ultrasonication: (A) change from SLS to LA and (B) uniform core–shell-type PDPA/silica nanocomposite formation in the presence of ultrasound. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Scheme 2 (a) PDPA/silica nanocomposite formation with SLS in the medium with conventional stirring. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
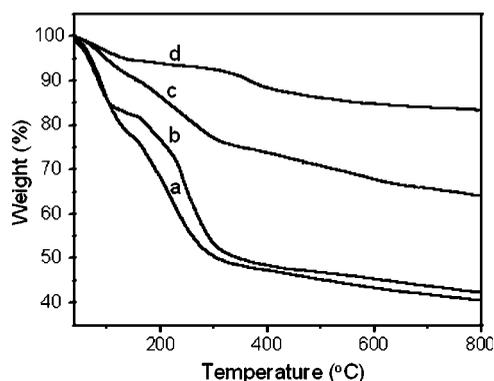
Figure 3 TEM photographs of PDPA/silica nanocomposites prepared with SLS in the medium with (a) ultrasonic radiation and (b) conventional stirring and without SLS in the medium with (c) ultrasonic radiation and (d) conventional stirring.

Figure 4 Thermograms of PDPA/silica nanocomposites prepared with SLS with (a) ultrasonic radiation and (b) conventional stirring and without SLS with (c) ultrasonic radiation and (d) conventional stirring.

Characterization of the PDPA/silica nanocomposites

The silica-nanoparticle/PDPA composites prepared under ultrasonication and conventional stirring are designated as silica/PDPA(U) and silica/PDPA(CS), respectively. Thermograms of silica/PDPA(U) and silica/PDPA(CS) prepared with and without SLS are presented in Figure 4. In general, thermograms of silica/PDPA(U) and silica/PDPA(CS) have the thermal transitions corresponding to neutral PDPA.[26] However, silica/PDPA(U) showed different thermal characteristics [Fig. 4(a,c)] than silica/PDPA(CS) [Fig. 5(b,d)]. Silica/PDPA(U) prepared with SLS in the medium had two stages of weight loss. The first weight loss, extending in the range of 120–200°C, was attributed to the loss of moisture and adsorbed LA in silica/PDPA(U). In this temperature range, the silica/PDPA(CS) nanocomposites did not show any weight loss similar to that of silica/PDPA(U). The weight losses beyond 250°C for silica/PDPA(U) and silica/PDPA(CS) were attributed to the decomposition of the backbone units of PDPA. Comparatively, the weight proportion of PDPA in the nanocomposites was greater for silica/PDPA(U) [Fig. 4(a,c)] than

nication in the presence of SLS [Scheme 1(B)]. On the other hand, for the nanocomposite prepared with conventional stirring, few of the silica nanoparticles remained uncoated, and the thickness of the PDPA coat on the silica nanoparticles was less [10–20 nm; Fig. 3(b)]. Few of the uncoated silica nanoparticles were also found in the silica-nanoparticle/PDPA composite prepared with conventional stirring. This observation indicated that silica nanoparticles were not uniformly dispersed. Hence, silica nanoparticles present in the interior of the aggregation were not coated [Fig. 3(c,d)]. Furthermore, nearly an aggregated mass could be seen for the nanocomposite prepared with conventional stirring in the absence of SLS [Fig. 3(d)]. TEM analysis of the nanocomposites also reveled that the amount of PDPA coated onto the silica nanoparticles was more for the nanocomposites prepared in the presence of SLS than those prepared in the absence of SLS. This was due to the fact that silica nanoparticles in the dispersed state could have more surface area and therefore be coated with PDPA to a larger extent. This was also confirmed by the thermogravimetric analysis of the nanocomposites.
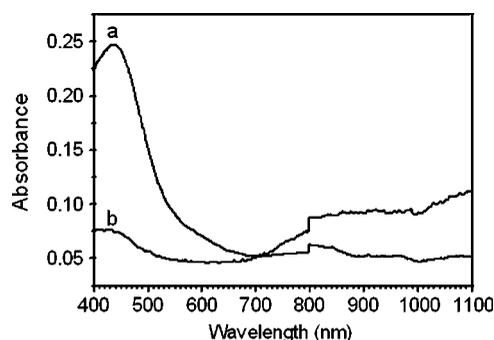
Thermogravimetry, X-ray diffraction, and UV–vis spectroscopy analysis of the silica-nanoparticle/PDPA composites confirmed that the silica-nanoparticle/PDPA composites that formed under ultrasonication had different thermal behavior, morphology, structural characteristics, and electronic properties than the composites prepared with conventional stirring.

Figure 5 UV–vis/near-infrared spectra of PDPA/silica nanocomposites prepared with (a) ultrasonic radiation and (b) conventional stirring.
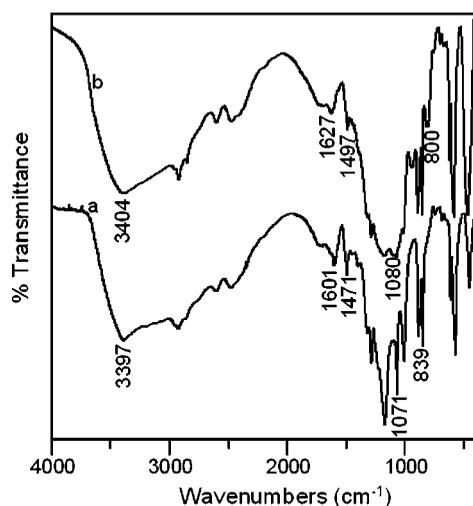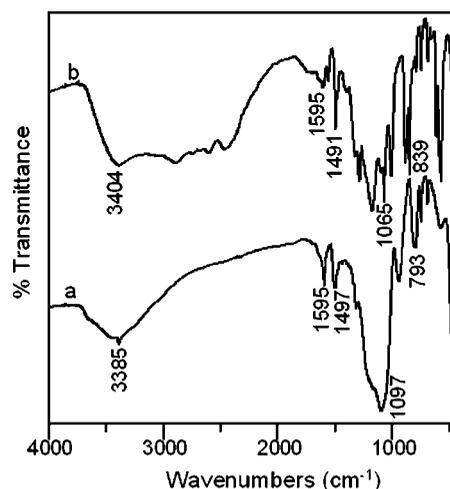
Figure 6 FTIR spectra of PDPA/silica nanocomposites prepared with SLS in the polymerization medium (a) in the presence and (b) in the absence of ultrasonic radiation.

silica/PDPA(CS) [Fig. 4(b,d)]. For comparison, the weight loss at 400°C was considered. Silica/PDPA(U) that formed in the presence of SLS showed a weight loss of 52% versus a 15% weight loss in the absence of SLS. Obviously, silica/PDPA(U) that formed in the presence of SLS had much higher weight proportions of PDPA. This was in accordance with the TEM analysis. Similarly, silica/PDPA(CS) that formed in the presence of SLS showed a weight loss of 48% versus an 8% weight loss in the absence of SLS. These facts show that ultrasonication results in the dispersion of silica nanoparticles and provides more surface area for silica particles. This is in accordance with Schemes 1 and 2. A comparison of the thermograms of the silica/PDPA nanocomposites prepared with and without SLS revealed that the proportion of PDPA coated on the silica surface was greater in the presence of SLS.

Figure 5 shows the UV–vis absorption spectra of colloidal dispersions of silica/PDPA(U) and silica/PDPA(CS). There is was difference in the position of the polaron band of PDPA between silica/PDPA(U) and silica/PDPA(CS). The polaron band appeared around 440 and 430 nm for silica/PDPA(CS) and silica/PDPA(U), respectively. This indicated that there could be differences in the binding between silica nanoparticles and PDPA that influenced the band position of the polaron band. The presence of an absorption band beyond 650 nm gave further support for this supposition. The absorption spectra of silica/PDPA(U) and silica/PDPA(CS) crossed over at 710 nm. Furthermore, silica/PDPA(U) showed a broad band around 780 nm. This information also suggests that the difference in the binding of PDPA with silica nanoparticles may be the cause for the difference in the absorption characteristics. In the presence of SLS

and under ultrasonication, the interaction between PDPA and silica nanoparticles arises from a core–shell-type silica-nanoparticle/PDPA composite. On the other hand, PDPA is wrapped over the aggregates of silica nanoparticle, as presented in Scheme 2. The core–shell-type structure of silica/PDPA(U) influenced the band position of PDPA as it provided intimate proximity of amine groups in PDPA for interaction with OH groups in silica nanoparticles. As a result, some of the amine units in the PDPA backbone structure could be converted into imine units. Otherwise, the nanocomposites prepared with ultrasonication may have had higher extents of doping (imine units in PDPA). This observation was further supported by FTIR analysis.

FTIR spectra of silica/PDPA(U) and silica/PDPA(CS) prepared in the presence and absence of SLS are presented in Figures 6 and 7. The spectra of the nanocomposites display the main characteristic bands of silica nanoparticles ($\sim$ 1080 and 830 cm^{-1}) and PDPA ($\sim$ 1490, 1600, and 1170 cm^{-1}). There are differences in the positions of the bands of the PDPA units in the nanocomposites in comparison with pristine PDPA. Specifically, the peak around 1170 cm^{-1}, corresponding to the diphenodiquinone diimine structure of PDPA, is stronger in silica/PDPA(U) than in silica/PDPA(CS). The band around 1600 cm^{-1}, which is characteristic of C=N stretching of the quinone imine type, is more intense for silica/PDPA(U) than silica/PDPA(CS). These observations indicate that PDPA was more oxidized or doped in silica/PDPA(U). This observation is consistent with UV–vis analysis, in which a change in the optical characteristics was noted for silica/PDPA(U). The increased doping is evident from the presence of a broad band in the UV–vis spectrum beyond 720 nm for silica/PDPA(U) (Fig. 7).

Figure 7 FTIR spectra of PDPA prepared without SLS in the polymerization medium (a) in the presence and (b) in the absence of ultrasonic radiation.

CONCLUSIONS

Processable and core–shell-type nanocomposites of PDPA with silica nanoparticles were prepared by a one-pot synthesis involving the polymerization of DPA in the presence of silica nanoparticles and SLS under ultrasonication. Ultrasonication was shown to have multifarious roles. It dispersed silica nanoparticles and augmented the formation of core–shell-type nanocomposites. Also, it converted SLS to LA and stabilized the nanocomposites in the organic phase. The silica/PDPA nanocomposites prepared under ultrasonication showed different thermal characteristics and electronic behavior in comparison with silica/PDPA nanocomposites prepared with conventional stirring. This investigation, therefore, demonstrates that the combined usage of a surfactant and ultrasonication for the preparation of a PANI-based conducting polymer nanocomposite could result in a processable nanocomposite. This methodology can be extended to making conducting, processable nanocomposites with other types of conducting polymers.

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