Stable Aqueous Dispersion of Conducting Polyaniline with High Electrical Conductivity

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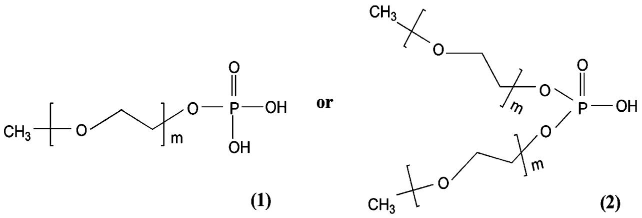
Introduction. Polyaniline is one of the most extensively investigated conducting polymers because of its good stability, low cost, and valuable electronic properties.[1] Though processing is always a hard work for polyaniline, great progress has been achieved especially in solution processing in the past 2 decades, greatly pushing forward its practical application in many fields.[2−4] However, most of these processes are carried out in organic solvents, and the increasing environmental concerns about organic solvents require nontoxic aqueous solution or dispersion processing.[5] Water-soluble self-doped polyaniline has been prepared by incorporating sulfonic groups on the aromatic ring or nitrogen atom in PANI, via post-sulfonation on as-polymerized parent polyaniline.[6−8] Self-doped PANI derivatives can also be obtained by the polymerization of sulfonated monomers, for example, a fully sulfonated self-doped poly(2-methoxyaniline-5-sulfonic acid) with good solubility and conductivity of 0.04 S/cm was prepared from a sulfonated monomer containing an electron donative group by Shimizu.[9] However, the presence of substituents on the aromatic rings or nitrogen atoms usually reduces the electrical conductivity. In another respect, in situ synthesis of aqueous polyaniline dispersion in the presence of a water-soluble polymeric stabilizer or polymeric acid dopant was carried out, but the yield of stable dispersion was generally low. Then there is the tedious separation of the polyaniline dispersion from a mixture of unreacted monomer, oligomer, residue acid, salt, etc.; moreover, the electrical conductivity of the obtained dispersions was still quite low (10^{-9} to 10^{-2} S/cm).[10−13] Our earlier work succeeded in preparing water-soluble conducting polyaniline employing phosphate acid with long hydrophilic segment as dopant for emeraldine base, the structure of the phosphate acid used is shown in Scheme 1.[14]

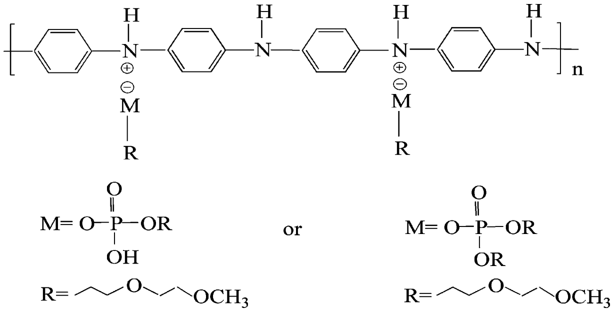
When *m* was set as 7, water-soluble cPANI could be made, though pseudo-gelation generally took place upon 1 month storage, and the electrical conductivity of the water-soluble polyaniline was still below 10^{-1} S/cm.[14]

Considering that the relatively lower electrical conductivity was probably due to the low polyaniline content (below 20 wt % in the above cPANI), we proposed a dispersion idea in this communication, where a new phosphate acid dopant with reduced length of hydrophilic segment was used. As shown in Scheme 2, a dispersion of cPANI employing phosphate acid containing short hydrophilic ethylene glycol segment (PAEG) as dopant was prepared. The electrical and electrochemical properties of the dispersion will be discussed. It should be noted that no modification of the parent polyaniline structure was necessary in the whole procedure.

Scheme 1. Structure of Phosphate Acid: (1) Monoester Phosphate; (2) Diester Phosphate



Scheme 2. Polyaniline Doped with Phosphate Acid Having a Hydrophilic Segment



Experimental Section. Materials. Diethylene glycol monomethyl ether (DEGME) was provided from Aldrich. $POCl_3$ was of analytical grade. Polyaniline emeraldine base was the product of Benan Co. licensed under this laboratory.

Preparation of Phosphate Acid Dopant. The typical procedure was shown as follows.[15] First, 100 mL of DEGME was dropped into 15 mL of $POCl_3$, and then the mixture was heated to 65 °C. After the mixture was stirred for 24 h, 12 mL of distilled water was added, and the mixture was kept stirring for 0.5 h. The mixture was decolored by activated carbon, the phosphate acid PAEG (a mixture of $[CH_3(OCH_2CH_2)_2OH]P(O)(OH)_2$ and $[CH_3(OCH_2CH_2)_2OH]_2P(O)(OH)$ in which the molar ratio of monoester to diester was 1.38) was collected as a colorless transparent liquid.

Preparation of cPANI Water Dispersion. The cPANI dispersion was prepared by adding 0.6 g of PANI and 1.8 g of PAEG (molar ratio is 0.5:1) into 10 mL of distilled water, with stirring at 50 °C for 8 h.

Characterization. The hydrodynamic diameter of cPANI particle was determined by hydrodynamic light scattering (DLS) at 25 °C with a vertically polarized He−Ne laser (DAWN EOS, Wyatt Technology, laser wavelength of 690 nm). Samples for electrical conductivity study were dried at room temperature and pressed into pellets, standard four-probe method was used to measure the conductivity. XPS measurement was made on a VG ESCALAB MkII spectrometer with a Mg Ka X-ray source (1253.6 eV photos). The X-ray source was operated at 14 kV and 20 mA. The sample was mounted onto standard VG sample stud with double-sided adhesive tape. The pressure in the XPS analysis chamber was maintained at 10^{-9} mbar or lower during data collection. The sample position and tilt angle were fine-tuned for optimal data acquisition. The C 1s neutral carbon peak at 284.6 eV was used as the reference for all binding energies (BEs). The core-level spectrum was deconvoluted into Gaussian component peaks. UV−vis spectra were recorded on a UV-3000 spectrometer. Cyclic voltammetry of aqueous cPANI dispersion was carried out in buffer solution of different pH value using a Solartron 1287 electrochemical interface analyzer, with Ag/AgCl electrode as reference electrode, a platinum wire as auxiliary electrode, and a glassy carbon as working electrode.

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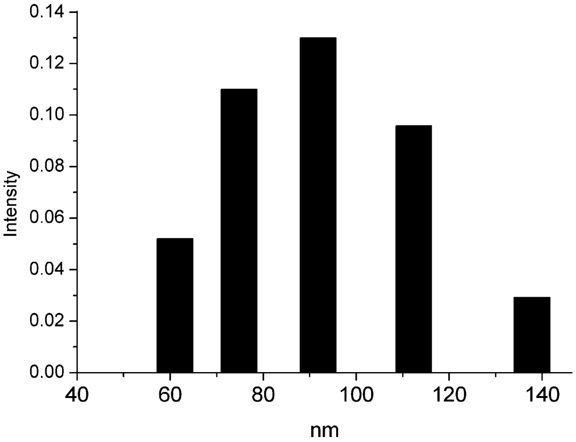

Figure 1. Hydrodynamic light scattering (DLS) spectra of the dispersion.

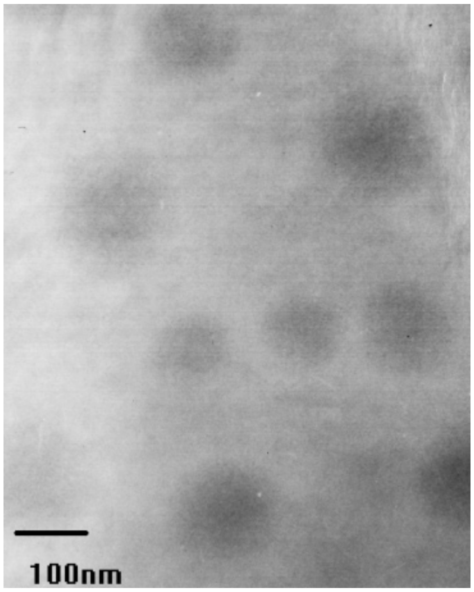

Figure 2. TEM image of PANI/PAEG dispersion particles.

Results and Discussions. The particle size of the dispersion was determined by DLS technique and shown in Figure 1. The mean hydrodynamic diameter of the PAEG doped PANI spherical particle was around 100 nm, with most of the particle size located between 60 and 140 nm. The TEM studies of PANI/PAEG (Figure 2) indicated that PAEG doping of PANI produced spherical particles with size range 80−120 nm, which was in agreement with the DLS results. The resultant PANI/PAEG dispersion was green in color, it was very stable in that no precipitation was observed after 3 months, and the particle size distribution was almost unchanged. Moreover, the dispersion could be freely diluted, indicating the effective stabilization of emeraldine salt in aqueous environment by the phosphate acid.

The electrical conductivity of the PANI/PAEG was 4.5 S/cm, much higher than those of earlier reported waterborne cPANIs (10^{-9} to 10^{-2} S/cm).[6−13] One possible explanation came from the increased PANI content in cPANI, moreover, the smaller size of PAEG may enhance its mobility compared with the polymeric acid, which would facilitate complete doping.

XPS provided a useful tool for the quantitative analysis of the redox state and doping level of PANI. As shown in Figure 3a, the N 1s spectrum of polyaniline base can be deconvoluted into two component peaks centered at 398.2, 399.7 eV, which can be assigned to the quinonoid imine (═N−) and benzenoid amine (−NH−), respectively. The nearly equal area fractions of the two peaks indicated equal amounts of quinonediimine and benzenediamine in polyaniline emeraldine. When PANI was doped with PAEG, a dramatic change was observed in the N 1s line shape as shown in Figure 3b, where the imine peak at 398.2 eV disappeared completely and shoulders appeared at 401.1 eV and 402.2 eV (nearly 50% of total area) which should be attributed to positively charged nitrogen atom (═NH$^+$−).[16] These results lead to conclusion that all the imine nitrogen atoms have been converted to the positively charged species, and the doping level was 50% in PANI doped by PAEG, reaching its maximum, which provided good support for its high electrical conductivity.

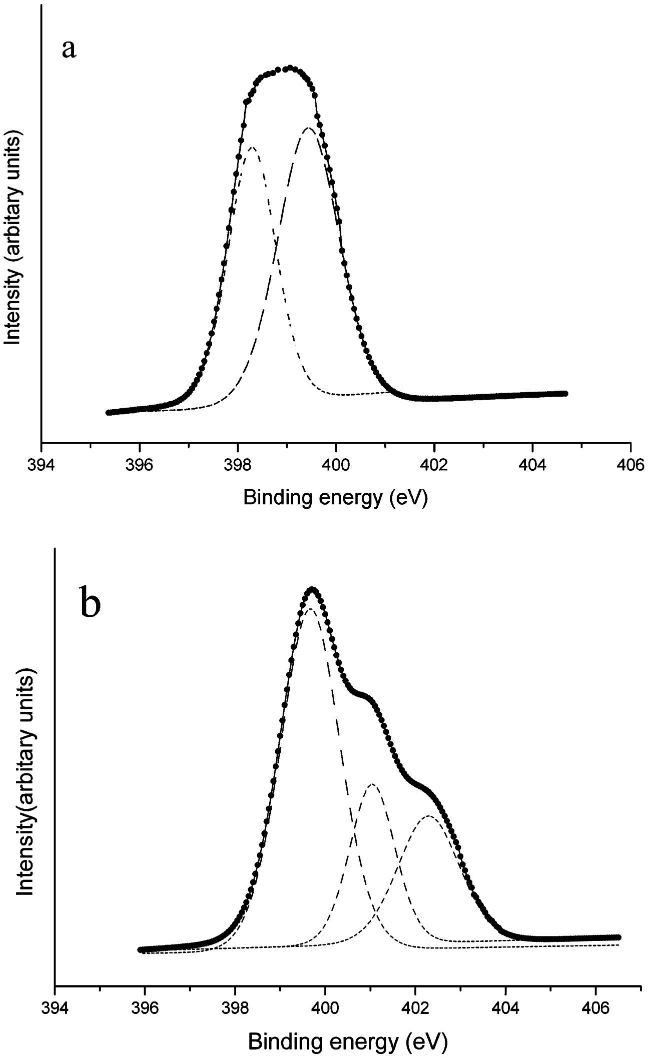

Figure 3. N(1s) XPS core-level spectra of (a) polyaniline base powder and (b) PANI doped with PAEG.

The as-prepared PANI/PAEG dispersion showed a pH of 3, as shown in Figure 4, a broad, strong, and plateau polaron band starting from 850 nm was observed in addition to the band at 440 nm characteristic of the protonated PANI, indicating the formation of the conductive cPANI.[2] The presence of near-infrared absorption suggested a more extended conformation of cPANI chain, which was consistent with its high conductivity.

To understand the dedoping behavior, the cPANI dispersion was titrated with 1 M NaOH, and their UV−vis spectra were recorded in Figure 4. When pH value was raised from 3 to 6, the broad band at 850 nm underwent a red-shift accompanied by a color change from green to turquoise. When the pH value further increased from 6 to alkaline value, a broad shoulder at 570 nm appeared, meanwhile the peak at 440 nm disappeared,

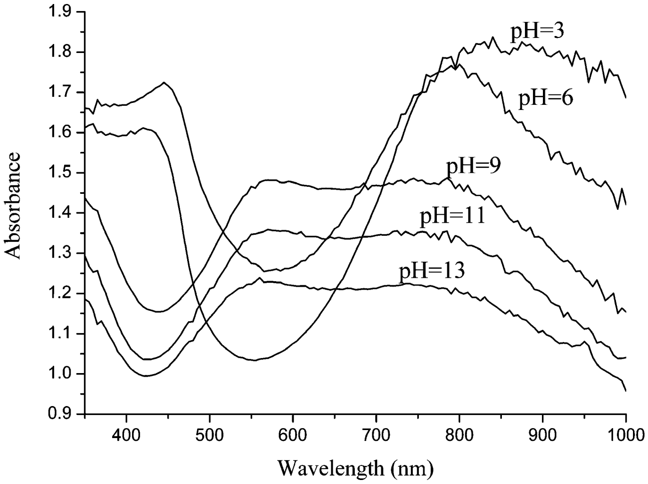

Figure 4. Progressive UV−vis spectra change of PANI/PAEG dispersion titrated with 1.0 M NaOH.

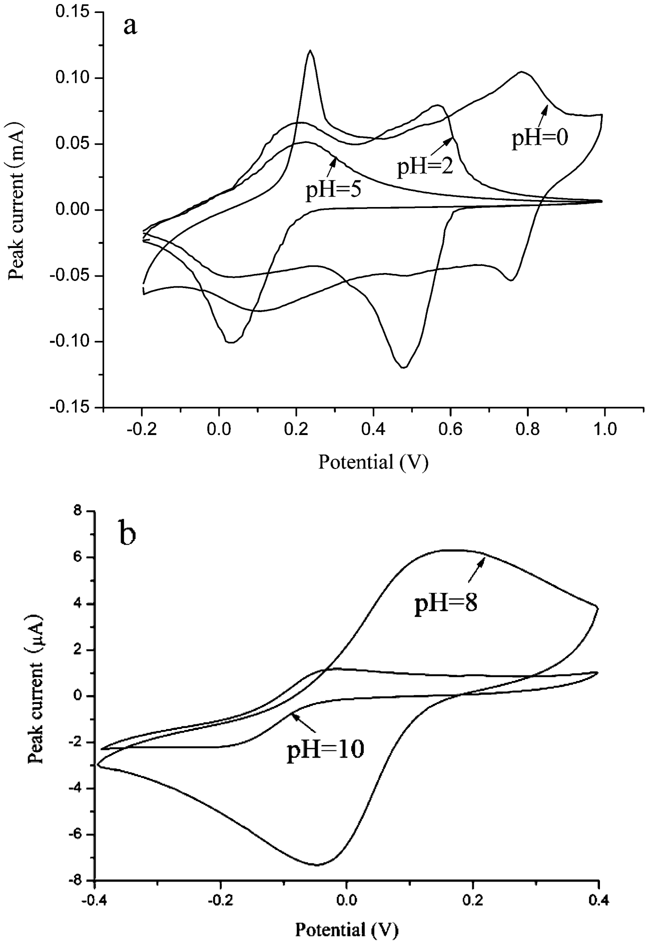

Figure 5. Cyclic voltammograms of aqueous dispersion of PANI/PAEG in different pH buffer solution.

and the color of the mixture changed to blue and violet, suggesting that cPANI was dedoped according to the common sense in conducting polyaniline research. However, the band at 750−800 nm remained even at pH of 14, and the relative intensity of the 570 nm to 750−800 nm bands maintained 100%, almost constant in the whole process, indicating incomplete dedoping of the original emeraldine salts. In comparison, PANI cannot be doped when the equilibrium pH value of hydrochloric acid doped solution was over 4, and it was rapidly and fully dedoped to EB at pH > 8.[17] Similar phenomenon was observed in PANI/calixSO_3H aqueous dispersion by Wallace.[18] They attributed this exceptional inertness to alkaline dedoping to Donnan effects arising from a high electrostatic field in the region close to the calix−SO_3H acid. In our case, a series of sodium salts of the polymer formed by progressive neutralization of the phosphate acid with sodium hydroxide[8] may be responsible for this phenomenon. This phenomenon will be discussed in context.

The cyclic voltammograms of PANI/PAEG in different pH buffer solutions were recorded and shown in Figure 5. In pH = 0 solution, two redox peaks were observed at $E_{1/2} = 0.18$ and 0.76 V, respectively, which was quite similar to that of PANI doped with common protonic acid,[1] indicating that electrochemical behavior of PANI−PAEG was typical of PANI. As the pH value of the media increased, the two sets of peaks shifted closer and overlapped at pH = 5. Similar behavior was observed in doping PANI with camphosulfonic acid by Lukacliova.[19] When the pH increased further to alkaline value, as shown in Figure 5b, a couple of redox peaks could still be observed in both pH = 8 and 10 buffer solutions, implying that PANI/PAEG salts were electroactive even in alkaline solution. This result provided support for the above phenomenon that the PANI/PAEG was not dedoped completely in alkaline media, since PANI base was not redox active in this condition. Further evidence was provided by the conductivity obtained after exposure of sample pellets to water soaking. The PANI/PAEG pellet still has electrical conductivity of 0.15 S/cm after 1 day immersion in pH = 8 aqueous solution, in contrast to the almost complete loss of conductivity of the HCl doped polyaniline. The conductivity decreased gradually with prolonging soaking time, and after 8 days soaking in pH = 8 solution, neither electrical conductivity nor electroactivity of PANI/PAEG could be measured.

Conclusion. In summary, aqueous cPANI dispersion was prepared employing phosphate acid having hydrophilic segment as dopant of PANI. The method has the following advantages:

(1) The direct doping on EB in water could avoid a tedious purification procedure, and the resulting aqueous dispersion could be directly used at a late stage.

(2) The electrical conductivity of cPANI from this dispersion could reach as high as 4−5 S/cm, which was comparable with that of HCl doped polyaniline.

(3) In addition to protonic acid doping, the hydrophilic phosphate acid provided a good water dispersible effect, leading to aqueous dispersion of cPANI which can be freely diluted and stored for a long period without precipitation.

(4) This cPANI dispersion showed great improvement in stability against alkaline dedoping and retained redox activity up to a pH between 8 and 10.

Therefore, bearing the advantages of simple synthetic procedure, good stability and high electrical conductivity, this aqueous cPANI dispersion would be useful to waterborne coatings and inorganic−organic nanocomposites for multiple purposes.

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