

Synthesis and Characterization of Polyaniline/Partially Phosphorylated Poly(vinyl alcohol) Nanoparticles

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Abstract The polyaniline/partially phosphorylated poly(vinyl alcohol)(PANI/P-PVA) nanoparticles were prepared by the chemical oxidative dispersion polymerization of aniline monomer in 0.5 mol/L HCl aqueous media with the partially phosphorylated poly(vinyl alcohol) (P-PVA) as the stabilizer and co-dopant. The PANI/P-PVA nanoparticles were characterized by transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA), X-ray diffraction (XRD), electrical conductivity measurements and re-dispersion stability testing. All the results were compared with the properties of the conventional polyaniline in the emeraldine salt form (PANI ES). It was found that the feeding ratio of P-PVA obviously affected the morphology, re-dispersion stability and electrical conductivity of the PANI/P-PVA nanoparticles. When the feeding ratio of P-PVA ranged from 40 wt% to 50 wt%, the PANI/P-PVA nanoparticles showed spherical shape with good uniformity, significant re-dispersion stability in aqueous media and good electrical conductivity.

Keywords: Conducting polyaniline; Phosphorylated poly(vinyl alcohol); Colloidal dispersion.

INTRODUCTION

Polyaniline (PANI) has received extensive attention in the past two decades due to its ease of synthesis, high electrical conductivity, excellent chemical or electrochemical redox reversibility and good environmental stability^[1]. It also has potential applications in organic storage batteries^[2], electromagnetic shielding devices^[3], adsorbent materials^[4], anticorrosion coatings^[5, 6] and so on. However, some potential applications have not been exploited because of its insolubility and poor processability. In order to overcome these shortcomings, various approaches, such as introducing side groups to PANI chains^[7, 8], doping PANI base with a functionalized protonic acid^[9, 10] and preparing colloidal PANI dispersion with a polymeric stabilizer^[11, 12], have been developed. And preparation of the colloidal PANI dispersion with the polymeric stabilizers is a widely accepted one^[13–16]. But PANI particles prepared with polymeric stabilizers usually have poor re-dispersion stability in common solvents, which affects the compatibility of the PANI particles with other materials/matrix. So it is significant to develop the colloidal PANI particles possessing both excellent re-dispersion stability and good electrical conductivity.

The partially phosphorylated poly(vinyl alcohol) (P-PVA) is a phosphoric ester prepared by the phosphorylation of PVA with phosphoric acid^[17]. The P-PVA has attracted considerable interest because it can

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be used as metal complexes, cation exchange resins, anionic polyelectrolyte hydrogels and polymeric stabilizer^[18–20]. While report about the conducting polymer nanoparticles stabilized with the P-PVA has not been found. In present work, colloidal PANI nanoparticles with excellent electrical conductivity and high re-dispersion stability were prepared by employing the P-PVA as a stabilizer and co-dopant *via* chemical oxidative polymerization of aniline.

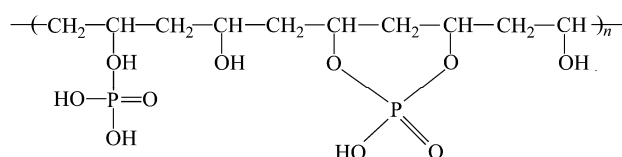
EXPERIMENTAL

Materials

Poly(vinyl alcohol) (PVA) with a degree of polymerization of 1700 was supplied by Tianjin Chemicals Company, China. Aniline (99.9%) was supplied by Tianjin Chemicals Company, China, and was distilled under reduced pressure. Ammonium peroxydisulfate (APS, 99.9%) was supplied by Tianjin Chemicals Company, China. Hydrochloric acid (HCl, 36%–38%) was supplied by Baiyin Chemicals Company, China.

Preparation of the Colloidal PANI/P-PVA Dispersion

Partially phosphorylated poly(vinyl alcohol) (P-PVA) was prepared by the phosphorylation of PVA with phosphoric acid in an aqueous medium according to the method of the related reference^[21], and the specific structure of P-PVA is shown in Scheme 1. The degree of substitution (DS) of the P-PVA was determined by pH titration and molybdenum blue method^[19].



Scheme 1 Specific structure of P-PVA (The DS of the P-PVA is 12.9 mol.)

The colloidal polyaniline/partially phosphorylated poly(vinyl alcohol) (PANI/P-PVA) dispersion was synthesized as follows: a certain amount of the P-PVA was introduced into a 250 mL round-bottom flask containing 100 mL 0.5 mol/L HCl aqueous solution, and the temperature of the system was raised to 80 °C to dissolve the P-PVA stabilizer. The mixture was then lowered to 0 °C by putting the flask in an ice bath, and the flask was charged with 1 g aniline in one shot. The solution mixture was stirred for another 1 h in the ice bath. And then, 50 mL 0.5 mol/L HCl aqueous solution containing 1.25 g APS was added drop by drop into the system in 1 h under stirring. Polymerization was carried out at 0 °C for 24 h. Finally, a dark-green colloidal dispersion (with the volume of 150 mL) was obtained.

The resulting dark-green PANI/P-PVA dispersion was separated by being centrifuged at 12000 r/min for 12 min, and washed repeatedly with distilled water to ensure the complete removal of the inorganic salts and the eventually unattached polymeric stabilizer. After being washed with ethanol, the PANI/P-PVA nanoparticles were dried at 60 °C under vacuum for 24 h for the further analysis.

According to the above approach, numerous samples of the colloidal PANI/P-PVA dispersions (and the colloidal PANI/P-PVA nanoparticles) with different feeding ratios of P-PVA were obtained (Feeding ratio of P-PVA = $W'/W \times 100$ wt%; W is the weight of aniline and W' is the weight of P-PVA, respectively.). For comparison, the PANI/PVA aqueous dispersions with different feeding ratios of PVA were prepared according to the similar method as the colloidal PANI/P-PVA dispersions. And the conventional polyaniline in the emeraldine salt form (PANI ES) was also prepared without any stabilizers.

Characterization of PANI/P-PVA Nanoparticles

Transmission electron microscope (TEM) images of the samples were obtained with a JEOL JEM-1200EX/S transmission electron microscope. Samples for TEM observations were prepared by drop casting of diluted aqueous dispersion on carbon-coated copper grids. The Fourier transform infrared (FTIR) spectra of the samples were recorded using an FTIR spectrometer (Impact 400, Nicolet, Waltham, MA). Thermal gravimetric analysis

(TGA) of the samples was carried out with TGA 2050 thermogravimetric analyzer at the range of room temperature to 800 °C with a heating rate of 10 K/min under nitrogen. X-ray diffraction (XRD) analysis of the samples was performed using a 3 kW Rigaku D/MAX 2000 diffractometer equipped with the Cu K α radiation in the reflection mode.

The PANI/P-PVA powder was compressed into a disk pellet of 10 mm in diameter with a hydraulic pressure at 30 MPa, the electrical conductivity of the PANI/P-PVA nanoparticles was measured using an SDY-4 four-probe meter at room temperature. The PANI ES, PANI/P-PVA, and PANI/PVA nanoparticles were coated over the Pt electrode with a thickness of *ca.* 10 μ m, respectively. The electrochemical behavior of the (PANI ES)/Pt, (PANI/P-PVA)/Pt, and (PANI/PVA)/Pt electrodes in 0.5 mol/L HCl aqueous solution were investigated by cyclic voltammetry (CV) studies. A Pt counter electrode and an Ag/Ag/Cl reference electrode were used throughout the studies.

The Re-dispersion Stability Testing

The re-dispersion stability testing was conducted to evaluate the re-dispersion stability of the PANI/P-PVA nanoparticles in an aqueous system and implemented as follows: the dark-green PANI/P-PVA sediment (PANI/P-PVA nanoparticles), separated from 10 mL of the colloidal PANI/P-PVA dispersion and washed repeatedly with distilled water, was re-dispersed in a cylindrical glass cell containing 10 mL distilled water in ultrasonic bath for 1 h. The appearance of the PANI/P-PVA re-dispersion in cell was observed at regular intervals.

RESULTS AND DISCUSSION

Morphology of PANI/P-PVA

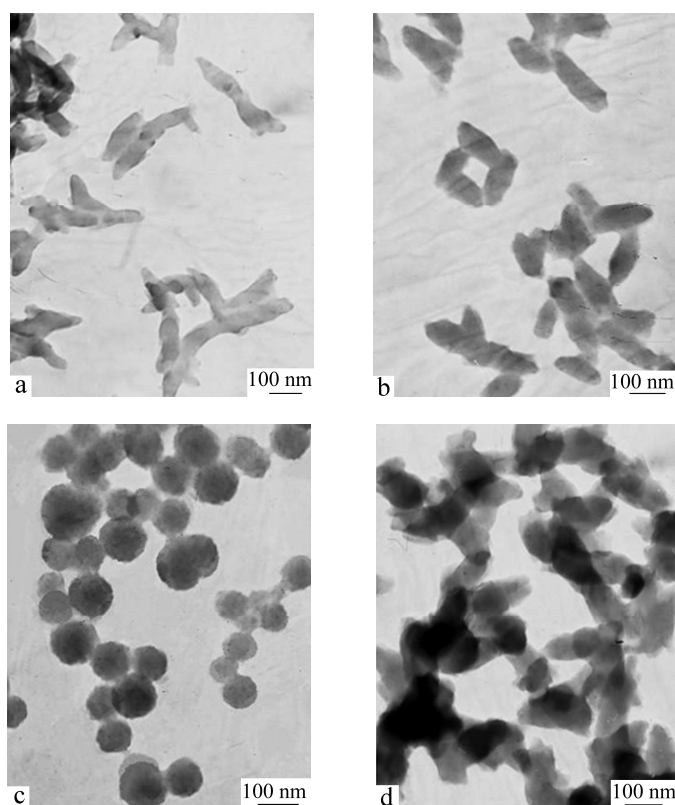
The effect of the feeding ratio of P-PVA on the performances of the colloidal PANI/P-PVA nanoparticles is shown in Table 1. TEM images of the PANI/P-PVA and PANI/PVA nanoparticles are shown in Fig. 1. It is observed clearly that the coral-like particles were formed when the feeding ratio of P-PVA was 20 wt% (Fig. 1a); the rice-like particles were produced when the feeding ratio of P-PVA was 30 wt% (Fig. 1b); and the homogenous spherical particles were obtained when the feeding ratio of P-PVA was 40 wt% (Fig. 1c), respectively. But the PANI/PVA dispersion yielded the rice-grain particles with aggregation to some extent even the feeding ratio of PVA increased to 40 wt% (Fig. 1d).

PANI particles' shape is affected drastically by two factors: one is the primary PANI particles formation rate; another is the efficiency of the stabilizer attachment^[22]. If the formation rate of the primary PANI particles is low, the primary PANI particles can efficiently attach to the stabilizer and the locally reduced concentration of the free stabilizer could be easily compensated by the diffusion of the stabilizer from other regions. A stabilizer with effective attachment will lead to the formation of the spherical dispersion particles. On the other hand, the local depletion of the free stabilizer could not be compensated when the formation rate of the primary PANI particles is much higher than the diffusion rate of the stabilizer. And the PANI particles covered partially by the stabilizer could attach each other, resulting in non-spherical shapes. In this work, when the feeding ratio of P-PVA was lower than 40 wt%, the particles were non-spherical, and the spherical particles could be formed when the feeding ratio of P-PVA ranged from 40 wt% to 60 wt%. But the higher feeding ratio of P-PVA (> 60 wt%) would result in the aggregation of the particles due to the bigger PANI particles formed in the high-viscosity solution. Comparatively, at both the low PVA concentration (feeding ratio of PVA, 20 wt%) and the high PVA concentration (feeding ratio of PVA, 60 wt%), the spherical particles were obtained hardly in the PANI/PVA aqueous dispersion.

The results suggest that the P-PVA is a more effective polymeric stabilizer for the PANI aqueous dispersion because of its high polarity and high adsorption rate. An appropriate dose of the P-PVA stabilizer could lead to the formation of homogenous spherical PANI/P-PVA nanoparticles.

Table 1. Performance of PANI/P-PVA nanoparticles

Aniline (g/150 mL)	Feeding ratio of P-PVA (wt%)	Particle size (nm)	Morphology	Re-dispersion stability (time)
1.0	10	300–600	coral-like	10 min
1.0	20	200–350	coral-like	1 h
1.0	30	100–150	rice-like	1 day
1.0	40	60–110	spherical	>14 days
1.0	50	60–110	spherical	>14 days
1.0	60	60–110	spherical	>14 days
1.0	70	–	aggregation	–
1.0	80	–	aggregation	–

**Fig. 1** TEM images of PANI/P-PVA particles with feeding ratios of 20 wt% (a), 30 wt% (b) and 40 wt% (c); and TEM image of PANI/PVA particles with feeding ratio of 40 wt% (d)**FTIR Spectral Analyses**

The FTIR spectra of P-PVA, PANI ES and PANI/P-PVA are presented in Fig. 2. The FTIR spectrum of the P-PVA shows an absorption peak at 1026 cm^{-1} due to the stretching frequency of the $-\text{P}-\text{O}-\text{C}-$ groups and a strong absorption peak at 1690 cm^{-1} attributed to the stretching vibration of the $-\text{P}=\text{O}-$ [23]. For PANI ES, the peaks at 1502 and 1630 cm^{-1} are assigned to the non-symmetric benzene ring stretching vibration. The peaks around 1280 cm^{-1} are attributed to the stretching vibration of the $\text{C}-\text{N}$ ($-\text{N}-\text{benzenoid}-\text{N}-$) [24]. The peak at 1130 cm^{-1} is assigned to the in-plane-bending vibration of the $\text{C}-\text{H}$, indicating the protonation of PANI [25]. For PANI/P-PVA, the strong absorption peak at 1060 cm^{-1} is due to the overlap of the absorbance frequency of the $-\text{P}-\text{O}-\text{C}-$ groups (P-PVA) and the in-plane-bending vibration of the $\text{C}-\text{H}$ (PANI). The absorption peak at 1690 cm^{-1} is assigned to the $-\text{P}=\text{O}-$ groups of the P-PVA. The results suggest the P-PVA molecules had been adsorbed and/or doped in the PANI particles.

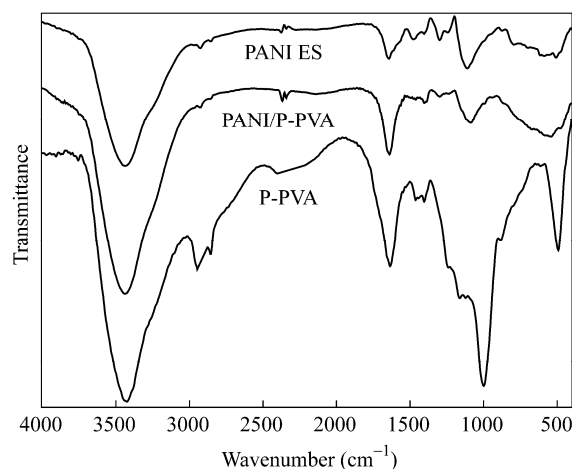


Fig. 2 FTIR spectra of P-PVA, PANI ES and PANI/P-PVA

TGA Analyses

The TGA curves of P-PVA, PANI ES and PANI/P-PVA are shown in Fig. 3. For P-PVA, the mass loss takes place up to 160 °C due to the H-bonded water, whereas the large decrease after 280 °C is attributed to the breakage of the main chain^[26]. For the PANI ES, the weight loss before 250 °C is responded to the residual water and the dedoping of the HCl doped. And the mass loss after 250 °C should be due to the thermal degradation of PANI. For PANI/P-PVA nanoparticles, the weight loss occurred between 200 °C and 300 °C due to the release of the H-bonded water of the P-PVA and the dedoping of doped HCl. The weight loss occurred between 450 °C and 600 °C is mainly due to the breakage of the main chains of PANI/P-PVA. Compared with the PANI ES doped with HCl, the doping structure with the P-PVA as co-dopant in the present work is more stable. So, the PANI/P-PVA nanoparticles could not be de-doped at 200 °C.

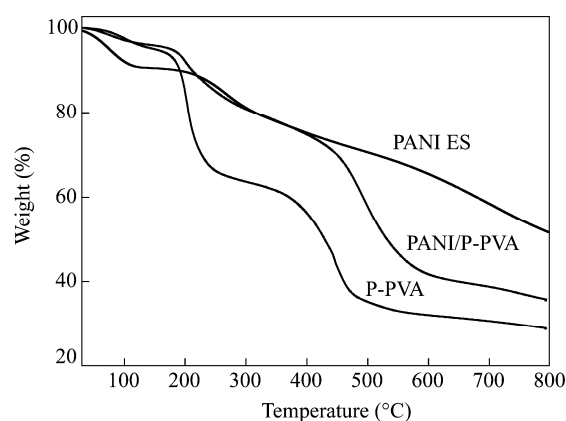


Fig. 3 TGA curves of P-PVA, PANI ES and PANI/P-PVA

XRD Patterns

XRD patterns of P-PVA, PANI ES and PANI/P-PVA are shown in Fig. 4. For the pure P-PVA, broaden peaks at about $2\theta = 20^\circ$ indicated the crystalline structure of the P-PVA^[18]. Meanwhile, the crystalline peaks of PANI ES appeared at $2\theta = 20.5^\circ$, 26.4° and 29.4° are attributed to the periodicity perpendicular to the polyaniline chain in its emeraldine salt form^[27], indicating that PANI ES was partly crystalline (crystalline and amorphous). For the PANI/P-PVA, the numerous peaks at around $2\theta = 20^\circ$ were due to the P-PVA crystallites, and the diffraction peaks at about $2\theta = 25.4^\circ$ were related to the partly crystalline PANI ES, indicating that the crystallization of the PANI/P-PVA was achieved by the polymerization of aniline in the present of phosphorylate ester groups^[27].

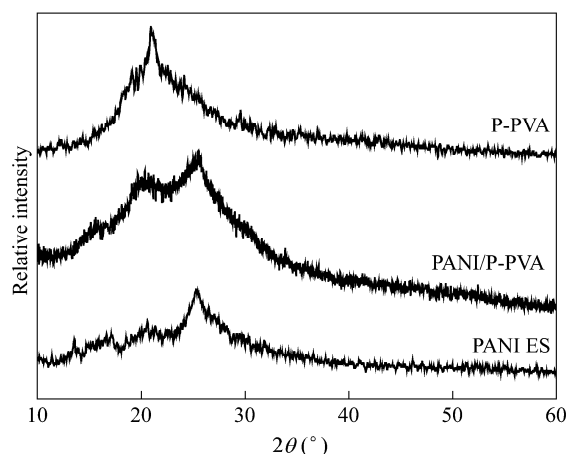


Fig. 4 XRD patterns of P-PVA, PANI ES and PANI/P-PVA

Electrical Conductivity

The effect of the feeding ratio of P-PVA on the electrical conductivity of the PANI/P-PVA nanoparticles is illustrated in Fig. 5. It is observed clearly that the electrical conductivity of the PANI ES (only doped by HCl) was 5.02 S/cm. With increasing the feeding ratio of P-PVA, the electrical conductivity was enhanced in the earlier stage and weakened later. PANI/P-PVA nanoparticles with the feeding ratio of P-PVA between 30 wt% and 50 wt% showed higher electrical conductivity. When the feeding ratio of P-PVA was 40 wt%, the PANI/P-PVA nanoparticles possessed the maximum electrical conductivity of 6.94 S/cm. By comparison, the electrical conductivity of the PANI/PVA nanoparticles decreased linearly with increasing the feeding ratio of PVA. It could be concluded that the P-PVA plays the role of the co-dopant in this system to improve the dope level. The decrease of the electrical conductivity could be considered as the result of the insulating nature of the P-PVA.

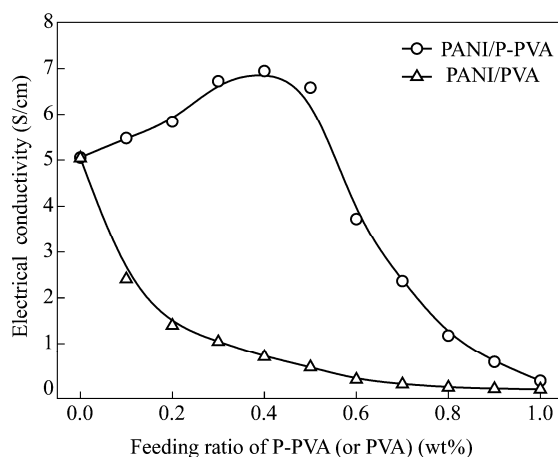


Fig. 5 The effect of feeding ratio of P-PVA (or PVA) on conductivity values of PANI nanoparticles

Electroactivity

The PANI ES, PANI/P-PVA (feeding ratio of P-PVA, 40 wt%) and PANI/PVA (feeding ratio of PVA, 40 wt%) coated Pt electrodes were subjected to cyclic voltammetry (CV) in the present of 0.5 mol/L HCl aqueous solution, and the results are shown in Fig. 6. Two couples of redox peaks were observed from the CV curve of the PANI ES sample, corresponding to the leucoemeraldine/emeraldine and emeraldine/pernigraniline redox transitions^[28]. For the PANI/P-PVA sample, redox peaks become more characteristic, indicating a higher electroactivity. And the peaks corresponding to the ES/LS transition are shifted to lower potential values. This may be accounted for by the co-dopant of P-PVA. For the PANI/PVA sample, there was an obvious decrease in

peak current due to non-conductive PVA. It could be concluded that appropriate dose of P-PVA can improve the electroactivity of PANI.

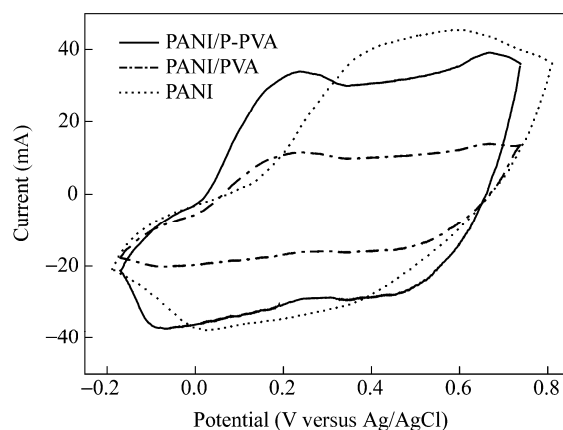


Fig. 6 Cyclic voltammograms of PANI ES, PANI/P-PVA and PANI/PVA coated Pt electrodes in 0.5 mol/L HCl aqueous solution

Re-dispersion Stability

It can be seen from Table 1 that the feeding ratio of P-PVA has distinctly affected the re-dispersion stability of the colloidal PANI/P-PVA nanoparticles. Figure 7 shows the photographs of re-dispersions of PANI ES, PANI/P-PVA and PANI/PVA after being stated for 14 days. The re-dispersions of the colloidal PANI/P-PVA nanoparticles, prepared from the colloidal PANI/P-PVA dispersions with the feeding ratio of the P-PVA range of 40 wt%–60 wt%, remained well-dispersed in distilled water. By contrast, the stable re-dispersion of the PANI/PVA particles could not be found even with a high feeding ratio of PVA (60 wt%). The results also indicate that the P-PVA is a more effective polymeric stabilizer for the PANI dispersion.

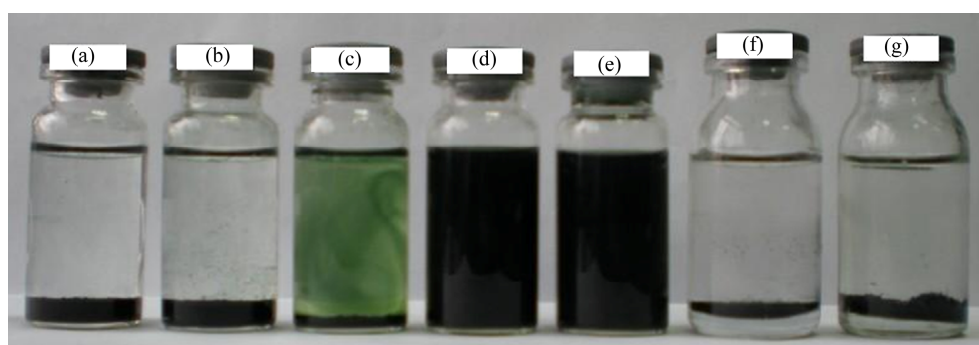


Fig. 7 Photographs of the PANI re-dispersions: PANI ES (a); PANI/P-PVA with feeding ratios, 20 wt% (b), 30 wt% (c), 40 wt% (d) and 60 wt% (e); PANI/PVA with feeding ratios of 40 wt% (f) and 60 wt% (g)

CONCLUSIONS

The colloidal PANI dispersion was synthesized in 0.5 mol/L HCl aqueous solution using the P-PVA as a stabilizer and co-dopant. The feeding ratio of P-PVA distinctly affected the morphology and re-dispersion stability of the colloidal PANI nanoparticles, and the electrical conductivity was enhanced in the earlier stage and weakened later with increasing the feeding ratio of P-PVA. When the feeding ratio of P-PVA ranged from 40 wt% to 50 wt%, the colloidal PANI/P-PVA nanoparticles showed spherical shape, significant re-dispersion stability in aqueous media and good electrical conductivity. This kind of conducting colloidal PANI/P-PVA nanoparticles could be used as the conducting additives in nontoxic aqueous systems.

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