PARTICLE TECHNOLOGY AND FLUIDIZATION

Preparation of Polyaniline/Phosphorylated Poly(vinyl alcohol) Nanoparticles and Their Aqueous Redispersion Stability

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A novel approach for the preparation of the colloidal conducting polyaniline (PANI) nanoparticles was developed. The polyaniline/partially phosphorylated poly(vinyl alcohol)(PANI/P-PVA) nanoparticles were prepared by the chemical oxidative dispersion polymerization of aniline monomer in 1.0 M HCl aqueous media with the partially phosphorylated poly(vinyl alcohol) (P-PVA) as the stabilizer and codopant. The PANI/P-PVA nanoparticles were characterized by transmission electron microscopy (TEM), Fourier transform infrared (FTIR), thermal gravimetric analysis (TGA), electrical conductivity measurement, and redispersion 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 P-PVA/aniline feeding ratio obviously affected the morphology, redispersion stability and electrical conductivity of the PANI/P-PVA nanoparticles. When the P-PVA/aniline feeding ratio ranged from 50 to 60 wt %, the PANI/P-PVA nanoparticles showed spherical shape with good uniformity, significant redispersion stability in aqueous media, and good electrical conductivity up to 7 S/cm.
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Keywords: conducting polyaniline, partially phosphorylated poly(vinyl alcohol), colloidal dispersion, redispersion stability

Introduction

The organic polymers that process the inherent conductivity in nature due to the presence of a conjugated electron system in their structure, are termed as intrinsically conducting polymers (ICPs).[1] A high-electrical conductivity (near metallic) can be achieved in ICPs through oxidation-reduction, as well as doping with a suitable dopant.[2] In the family of the available ICPs, polyaniline (PANI) is found to be the most promising one because of its ease of synthesis, excellent electrical conductivity, good environmental stability and low cost.[3,4] PANI has potential applications in organic storage batteries,[5] electrochromic displays,[6] electromagnetic shielding devices,[7] adsorbent materials,[8] anticorrosion coatings,[9,10] and so on. However, some potential applications have not yet to be exploited because of its insolubility and poor processability. In order to overcome these shortcomings, various approaches, such as introducing side groups to PANI chains,[11,12] doping PANI base with a functionalized protonic acid[13,14] and preparing colloidal PANI dispersion with a polymeric stabilizer,[15–18] have been developed.

Among the aforementioned approaches, preparation of the colloidal PANI dispersion with the polymeric stabilizers is a widely accepted one. Poly(N-vinyl pyrrolidone),[19,20] poly (methyl vinyl ether),[21,22] poly(vinyl alcohol) (PVA),[23,24] poly[(N-vinylpyrrolidone)-co-(vinylalcohol)],[19] and poly(ethylene oxide) (PEO)[25] have been most frequently used as polymeric stabilizers for the colloidal PANI dispersions. Table 1

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Table 1. Performances of the Conducting PANI Particles Prepared in 1.0 M HCl Aqueous Media with Different Polymeric Stabilizers

Stabilizer	Particle size (nm)	Conductivity (S/cm)	References
Poly(*N*-vinyl pyrrolidone)	10-295	5.1	[19]
Poly(methyl vinyl ether)	~250	4.96	[21]
Poly(methyl vinyl ether-alt-maleic acid)	~180	0.9	[22]
Poly(vinyl alcohol)	40-100	2.5	[23]
Poly[(N-vinylpyrrolidone)-co-(vinylalcohol)]	100-200	0.5	[19]

shows the performances of some conducting colloidal PANI particles prepared in the presence of polymeric stabilizers and have good dispersion stability.

The colloidal dispersion of the conductive PANI has been discussed frequently in connection with the anticorrosion coatings. It has been reported that the PANI-based coatings, prepared by adding the chemically synthesized PANI as additives in the dispersion coatings, can prevent corrosion even in scratched areas where the steel surface is exposed to the aggressive environment.[10] Due to the strong aggregation tendency, PANI particles usually have poor redispersion stability (which affects the compatibility of the anticorrosion coatings) in common solvents. To exploit the application of PANI as the anticorrosion additives in the anticorrosion systems, such as in the nontoxic aqueous anticorrosive coatings, it becomes important to develop the colloidal PANI particles with well redispersion stability.[26] However, few researches about the redispersion stability of the conducting PANI particles have been done. For example, almost all the studies in Table 1 had not investigated the redispersion stability of the colloidal PANI particles in aqueous media. So it is significant to synthesize the colloidal PANI particles possessing both excellent redispersion stability and good electrical conductivity.

To overcome such a problem, we proposed an novel idea in the preparation of the colloidal PANI dispersion employing the partially phosphorylated poly(vinyl alcohol) (P-PVA) as both the stabilizer and codopant for the first time. The P-PVA is a phosphoric ester prepared by the phosphorylation of PVA with phosphoric acid.[27,28] The P-PVA has attracted considerable interest because it can be used as metal complexes, cation exchange resins, and anionic polyelectrolyte hydrogels.[29,30] Suzuki et al. demonstrated the preparation of the ionic conducting polymer materials based on PVA and the effects of the P-PVA on the ionic conductivity. With increasing the degree of substitution (DS) of the P-PVA, the ionic conductivity and carrier mobility decreased but the carrier density increased for the P-PVA/poly(ethylene glycol) systems.[30] Li et al. prepared the P-PVA in the esterification reactor, and the experiment results showed that the effect of the DS of P-PVA on the separation properties of the P-PVA composite membrane is remarkable.[31] By far, report about the conducting polymer nanoparticles stabilized with the P-PVA has not been found.

In this work, the P-PVA was used as the stabilizer and codopant for the colloidal PANI dispersion. The colloidal PANI dispersion was prepared by the chemical oxidative polymerization of aniline in 1.0 M HCl aqueous solution with APS as oxidant. The effects of the P-PVA on the PANI particles morphology, electrical conductivity and redispersion stability were investigated, respectively.

Experimental

Materials

Poly(vinyl alcohol) (PVA) with a degree of polymerization of 1,700 in the form of 88% hydrolyzed was supplied by Tianjin Chemicals Co., China. Phosphoric acid (H_3PO_4, 85%) and urea ($((NH_2)_2CO$, 99.9%) were supplied by Guangzhou Chemicals Co., China. Aniline (99.9%) was supplied by Tianjin Chemicals Co., China, and was distilled under reduced pressure. Ammonium peroxydisulfate (APS, 99.9%) was supplied by Tianjin Chemicals Co., China. Hydrochloric acid (HCl, 36–38%) was supplied by Baiyin Chemicals Co., China.

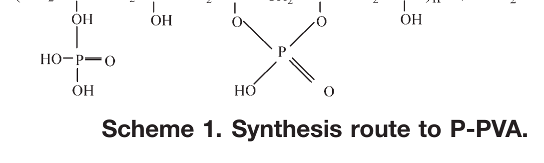
Phosphorylation of PVA

Partially phosphorylated poly(vinyl alcohol) (P-PVA) was prepared by the phosphorylation of PVA with phosphoric acid in an aqueous media according to the method of the related references,[27,28] and the general synthesis pathway is shown in Scheme 1. First, 50 g phosphoric acid, 20 g PVA and 0.4 g urea were added to 50 mL distilled water in a flask and stirred for 24 h at room-temperature. The mixture was heated to 90°C and stirred thoroughly for about 3 h until the pH value of the mixture was 5-6. The reaction product was precipitated with ethanol to remove residue phosphoric acid. Then, the precipitate was dried *in vacuo* at 60°C to obtain the P-PVA powder.[28,32] In this work, phosphorus content was used to represent the degree of substitution (DS) of the P-PVA, and the phosphorus content of the P-PVA was 5.42 wt %, determined by the titration method.

Preparation of the colloidal PANI/P-PVA dispersion

The colloidal PANI/P-PVA dispersion was synthesized as follows: the certain amount of the P-PVA was introduced into a 250 mL round-bottom flask containing 150 mL 1.0 M HCl aqueous solution, and the temperature of the system was raised to 60°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 (10.98 mmol) in one shot. The solution mixture was stirred for another 1 h in the ice bath. Then, 50 mL 1.0 M HCl aqueous solution containing 5.49 mmol 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 200 mL) was obtained.

The resulting dark-green PANI/P-PVA dispersion was separated by being centrifuged at 12,000 rpm for 12 min, and washed repeatedly with distilled water to ensure the complete removal of the inorganic salts and the eventual unattached polymeric stabilizer. After being washed with



Scheme 1. Synthesis route to P-PVA.

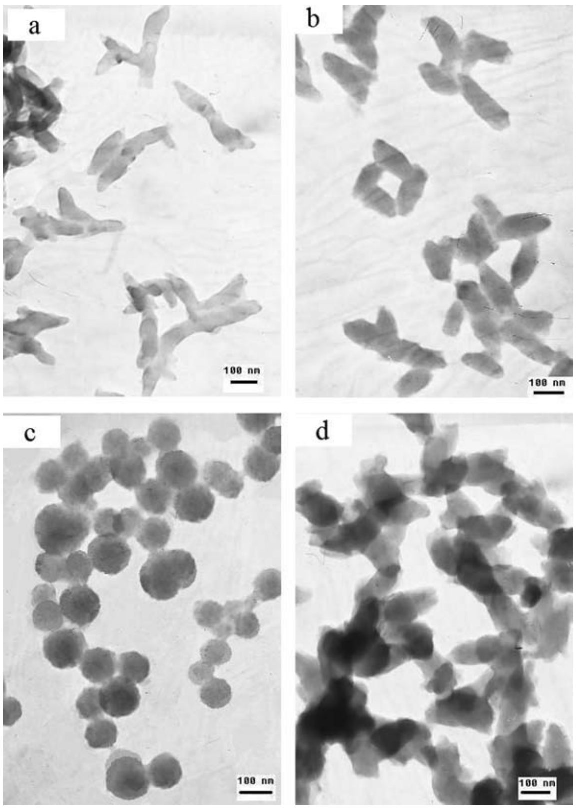


Figure 1. TEM images of PANI particles prepared with different P-PVA/Aniline feeding ratios (a) 20 wt %, (b) 40 wt %, (c), 60 wt %, and (d), PVA/Aniline feeding ratio of 60 wt %.

ethanol, the PANI/P-PVA nanoparticles were dried at 60°C *in vacuo* for 24 h for the further analysis.

According to the aforementioned approach, numerous samples of the colloidal PANI/P-PVA dispersions (and the colloidal PANI/P-PVA nanoparticles) with different P-PVA/aniline feeding ratios were obtained. There were three parallel samples for each P-PVA/aniline feeding ratio. For comparison, the PANI/PVA aqueous dispersions with different PVA/aniline feeding ratios were prepared according to the similar method as the colloidal PANI/P-PVA dispersions. The feeding ratios of P-PVA/aniline and PVA/aniline are defined as follows

$$\text{P-PVA/Aniline feeding ratio} = \frac{W_{\text{P-PVA}}}{W_{\text{Aniline}}} \times 100\,\text{wt.\%} \quad (1)$$

$$\text{PVA/Aniline feeding ratio} = \frac{W_{\text{PVA}}}{W_{\text{Aniline}}} \times 100\,\text{wt.\%} \quad (2)$$

where $W_{\text{P-PVA}}$, W_{PVA}, and W_{Aniline} are the weights of P-PVA (between 0.05 g and 1.0 g), PVA and aniline (1.0 g), respectively.

Characterizations

The Fourier transform infrared (FTIR) spectra of the samples were recorded using the FITR spectrometer (Impact 400, Nicolet, Waltham, MA).

Thermal gravimetric analysis (TGA) of samples was carried out with TGA 2050 thermogravimetric analyzer at the range of room-temperature to 800°C at the heating rate of 10°C/min, performed under nitrogen.

Transmission electron microscope (TEM) images of samples were obtained with a JEOL JEM-1200EX/S transmission electron microscope. Samples for TEM were prepared by drop casting of diluted aqueous dispersion on carbon-coated copper grids.

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 SDY-4 four-probe meter at room-temperature.

The redispersion stability testing

The redispersion stability testing was conducted to evaluate the redispersion 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 redispersed in a cylindrical glass cell containing 10 mL distilled water in ultrasonic bath for 1 h. The appearance of the PANI/P-PVA redispersion in cell was observed at regular intervals. The redispersion stability can be indicated by the time that the PANI/P-PVA nanoparticles could keep redispersed well.

Results and Discussion

Morphological analysis

Effects of the P-PVA/aniline feeding ratio on the morphology and the redispersion stability of the PANI/P-PVA nanoparticles were studied particularly in this article. TEM images (Figure 1) are used to view the morphology and size of the PANI/P-PVA nanoparticles. It is observed clearly that the coral-like particles (average length 200–350 nm) were formed when the P-PVA/aniline feeding ratio was 20 wt % (Figure 1 a); the rice-like particles with size range 80–150 nm were produced when the P-PVA/aniline feeding ratio was 40 wt % (Figure 1b); and the homogeneous spherical particles of approximately 60–100 nm dia. were obtained when the P-PVA/aniline feeding ratio was 60 wt % (Figure 1c), respectively. For comparison, the TEM image of PANI/PVA aqueous dispersion with the PVA/aniline feeding ratio of 60 wt % is shown in Figure 1d, it can be seen that the PANI/PVA dispersion yielded the rice-grain particles with aggregation to some extent.

The diversity of particles shape is a common phenomenon in the synthesis of PANI, and two factors have drastically affected on the morphology of PANI particles: one is the primary PANI particles formation rate which mostly depends on the experimental conditions including the nature of the oxidant, the polymerization temperature. and the nature of the dispersant medium; another is the efficiency of the stabilizer attachment.[33,34] When the formation rate of the primary PANI particles is low during the polymerization, the primary PANI particles can efficiently attach to the stabilizer. The locally reduced concentration of the free stabilizer is compensated by the diffusion of the stabilizer from other regions. An adequate amount of stabilizer with effective attachment will led to the formation of the spherical dispersion particles.

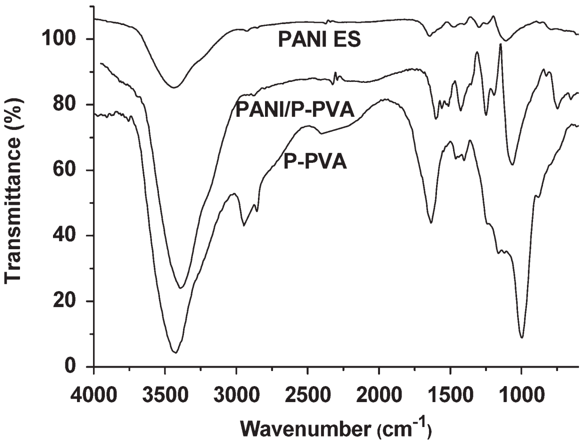


Figure 2. FTIR spectra of P-PVA, PANI ES and PANI/P-PVA.

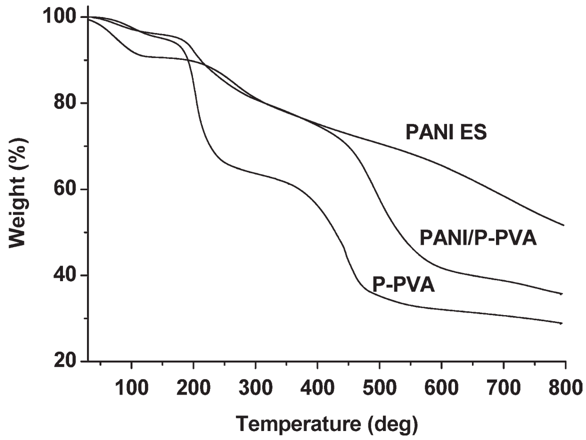


Figure 3. TGA curves of P-PVA, PANI ES, and PANI/P-PVA.

When the formation rate of the primary PANI particles is much higher than the diffusion rate of the stabilizer, the local depletion of the free stabilizer could not be compensated because the mobility of the stabilizer is slow or the adsorption rate of the stabilizer is lower than the polymerization rate. Therefore, the PANI particles which are covered partially by the stabilizer could attach each other. As a result, the nonspherical shapes were formed. In a word, the shape of particles such as needle, rice or sphere is determined by the balance between the adsorption rate of stabilizers and the formation rate of the primary PANI particles.

In this work, when the P-PVA/aniline feeding ratio was lower than 40 wt %, the particles were nonspherical because the dose of the P-PVA stabilizer was too low; and the spherical particles could be formed when the P-PVA/aniline feeding ratio ranged from 50 to 60 wt %. However, the higher P-PVA/aniline feeding ratio (>60 wt %) resulted in the aggregation of the particles. It might be due to the bigger PANI particles formed in the high-viscosity solution. Comparatively, at both the low PVA concentration (PVA/aniline feeding ratio, 40 wt %) and the high PVA concentration (PVA/aniline feeding ratio, 60 wt %), the spherical particles were obtained hardly in the PANI/PVA aqueous dispersion, with other experimental conditions remaining constant.

The results suggest that the P-PVA is a more effective polymeric stabilizer for the PANI aqueous dispersion probably because of its high polarity and high-adsorption rate due to the P-PVA radical anion. When the P-PVA is used as the stabilizer for the PANI dispersion, the locally reduced concentration of the P-PVA stabilizer is balanced easily by the diffusion of the P-PVA from the other regions, and the P-PVA more effectively deposits on the surface of the PANI particles. Therefore, the appropriate dose of the P-PVA stabilizer can lead to the formation of the homogeneous spherical PANI/P-PVA nanoparticles.

FITR Spectral analyses

The FITR spectrums of the P-PVA, the PANI ES and the PANI/P-PVA nanoparticles are presented in Figure 2. The FITR spectrum of the P-PVA shows an absorption peak at 1026 cm^{-1} due to the stretching frequency of the -P-O-C- groups and a strong absorption peak at 1,690 cm^{-1} attributed to the stretching vibration of the –P═O-.[26] All the aforementioned indicate that PVA had been successfully phosphorylated with phosphoric acid. The characteristic peaks of the PANI ES at 1,502 and 1,630 cm^{-1} are assigned to the nonsymmetric benzene ring stretching vibration. The peaks around 1,280 cm^{-1} are attributed to the stretching vibration of the C-N (mode of -N-benzenoid-N-).[35] The peak at 1,130 cm^{-1} is assigned to the in-plane-bending vibration of the C-H (mode of -N═quinoid═N- and quinoid═N^{+}H-benzenoid), which should occur during the protonation.[36] The peak at 3525 cm^{-1} is assigned to the N-H stretching. The FITR spectrum of the PANI/P-PVA shows a strong absorption peak at 1,060 cm^{-1} due to the overlap of the absorbance frequency of the -P-O-C- groups of the P-PVA and the in-plane-bending vibration of the C-H of PANI. The absorption peak at 1,441 cm^{-1} is assigned to the C-O bonds, and the absorption peak at 1690 cm^{-1} is assigned to the -P═O- groups of the P-PVA. The obvious step up of the absorption peak around 3390 cm$-^{1}$ is attributed to the -OH stretching. The result suggests the P-PVA molecules had been adsorbed and/or doped in the PANI particles.

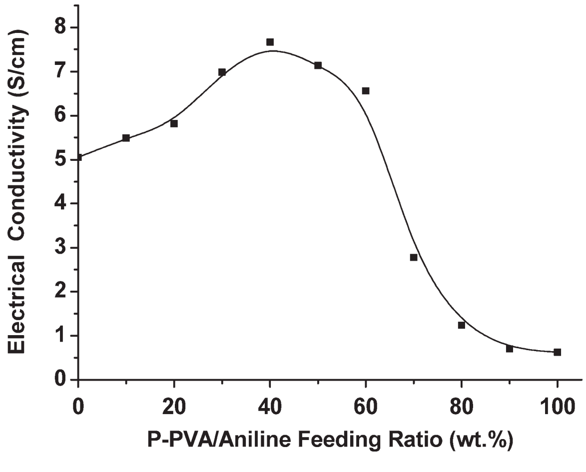


Figure 4. The effect of the P-PVA/Aniline feeding ratio on conductivity values of PANI/P-PVA nanoparticles.

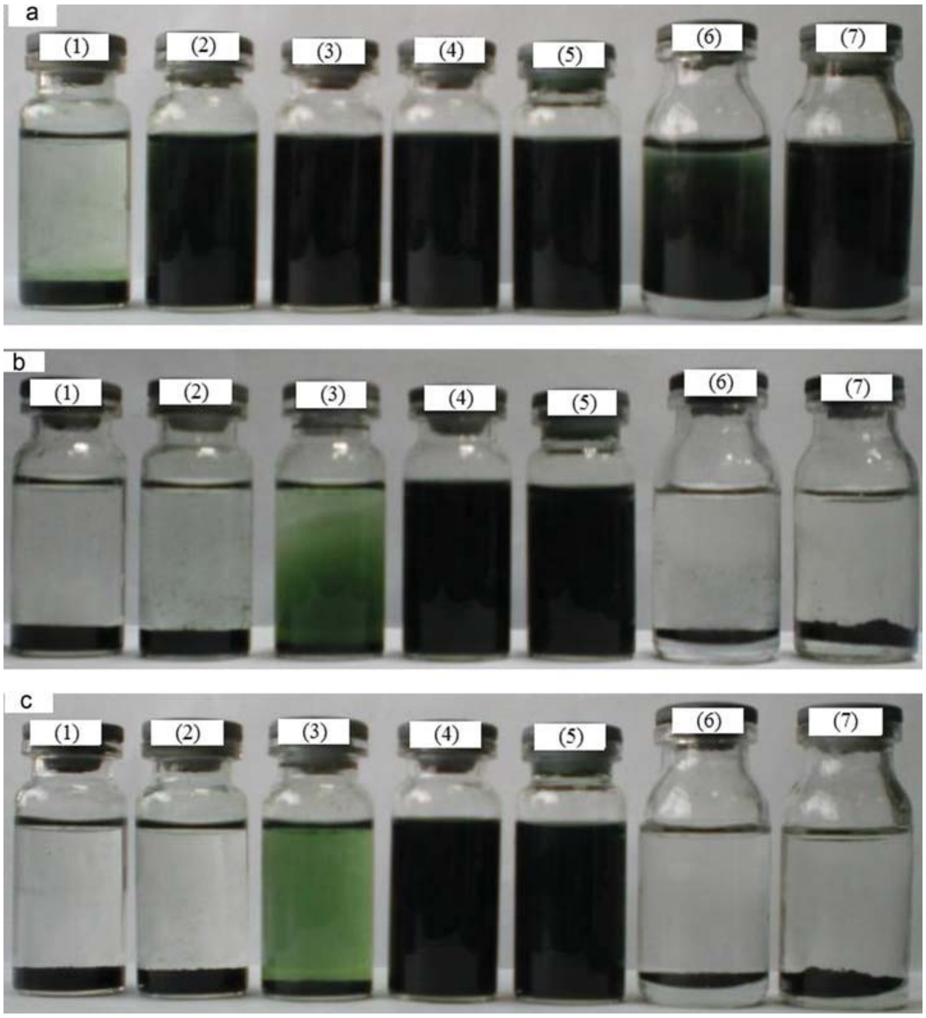


Figure 5. Photographs of the colloidal PANI redispersions after being redispersed for (a) 1 h, (b) 3 days, and (c) 14 days; (1): PANI (HCl 1.0 M); (2–5): P-PVA/Aniline feeding ratios of 20 wt %, 40 wt %, 50 and 60 wt %; (6–7): PVA/Aniline feeding ratios of 60 and 100 wt %.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TGA analyses

The TGA curves of the P-PVA, the PANI ES (doped with HCl), and the PANI/P-PVA nanoparticles are shown in Figure 3. The curve of the P-PVA shows three main degradation steps: the slight weight decrease of the P-PVA below 100°C is due to the moisture-lossing, the mass loss take place up to 280°C is regarded as the H-boned water, whereas the large decrease after 280°C is attributed to the breakage of the main chain.[37] In the case of the PANI ES, the initial weight loss of about 8.0% up to 100°C is due to the residual water and undoped HCl. The weight loss about 5% in the temperature range of 100–300°C is responded to the dedoping of the HCl doped. The mass loss after 250°C should be due to the thermal degradation of PANI.[38] For the PANI/P-PVA nanoparticles, two main weight losing stages are found. One occurred in the temperature range of 200–300°C, which is superposition of the release of the H-boned water of the P-PVA and the dedoping of doped HCl. The other occurred in the temperature range of 450–600°C is mainly due to the breakage of the main chains of both polymers (P-PVA and PANI). It can be found that the thermal stability of the P-PVA had been improved obviously in the presence of PANI. Compared with the PANI doped with the small dopants such as HCl, the dopaing structure with the P-PVA as codopant in this work is more stable. The PANI/P-PVA nanoparticles could not be dedoped at 200°C. So, it is expected that the electrical conductivity of the PANI/P-PVA nanoparticles can be maintained up to 200°C.

Electrical conductivity

In this work, the electrical conductivity with each P-PVA/aniline feeding ratio was the average of the three parallel samples', and the relative error of each measurement data was less than 1%. The effect of the P-PVA/aniline feeding ratio on the electrical conductivity of the PANI/P-PVA nanoparticles is illustrated in Figure 4. With increasing the P-PVA/aniline feeding ratio, the electrical conductivity was enhanced in the earlier stage and weakened later; there was the maximum electrical conductivity of 7.66 S/cm at a P-

Table 2. The Effect of the P-PVA/Aniline Feeding Ratio on the Performances of the Colloidal PANI/P-PVA Nanoparticles

Aniline (g/200 ml)	P-PVA/aniline ratio (wt %)	Particle size (nm)	Morphology stability	Re-dispersion
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	1day
1.0	40	80-150	rice-like	2 days
1.0	50	60-100	spherical	>14 days
1.0	60	60-100	spherical	>14 days
1.0	70	—	aggregation	—

PVA/aniline feeding ratio of 40 wt %. It is observed clearly that the electrical conductivity of the PANI/P-PVA nanoparticles was clearly improved at certain contents of P-PVA compared to the PANI ES doped by HCl singly (5.05 S/cm).

Thus, it could be concluded that the P-PVA plays the role of the codopant in this system to improve the dope level and the anion groups in the P-PVA are linked partially with the polymer backbone.[35] The decrease of conductivity could be considered as the result of the nature of the P-PVA. The P-PVA is an insulating material and easy to form membranes, the excessive P-PVA perceptibly decreases the electrical conductivity of the PANI/P-PVA nanoparticles. Therefore, in order to get the PANI/P-PVA nanoparticles with good electrical conductivity, the P-PVA/aniline feeding ratio should be in the range from 30 to 60 wt %.

Redispersion stability

The colloidal PANI/P-PVA nanoparticles were redispersed in the cylindrical glass cell containing distilled water in ultrasonic bath for 1 h. Then, the redispersion samples were observed at regular interval. Figure 5 presents the photographs of the colloidal PANI/P-PVA redispersions after being stated for 1 h, 3 days, and 14 days. For comparison, the redispersions of the PANI ES and the PANI/PVA particles are also shown in Figure 5. Note that Figure 5 (6) and Figure 5 (7) show the photographs of the colloidal PANI/PVA redispersions with PVA/aniline feeding ratios of 60 and 100 wt %, respectively. The morphologies and the redispersion stabilities of some PANI/P-PVA samples are summarized in Table 2.

It can be seen from Figure 5 that the P-PVA/aniline feeding ratio has distinctly affected the redispersion stability of the colloidal PANI/P-PVA nanoparticles. The redispersions of the colloidal PANI/P-PVA nanoparticles, prepared from the colloidal PANI/P-PVA dispersions with the P-PVA/aniline feeding ratio range of 50–60 wt %, remained well-dispersed in distilled water for at least 14 days; and no sedimentation of the PANI/P-PVA was observed in the redispersions. By contrast, the stable redispersion of the PANI/PVA particles could not be found with higher PVA/aniline ratios. Through experiments, we also found that the redispersion stability of the PANI/PVA particles which prepared in low PVA/aniline ratios was poor, too. The results also indicate that P-PVA is a more effective polymeric stabilizer for the PANI dispersion. The redispersion stability of the colloidal PANI/P-PVA nanoparticles can be improved observably by adding a small amount of the P-PVA stabilizer.

Certainly, the storage stability of the colloidal PANI/P-PVA dispersion was found to be good during storage, too. The particle size of the colloidal PANI/P-PVA dispersions stabilized with the P-PVA (P-PVA/aniline feeding ratio, 50–60 wt %) was not significantly changed during the storage of dispersions for 5 months, and sedimentations were hardly observed in the colloidal PANI/P-PVA dispersions during the storage.

According to all the aforementioned results, it can be concluded that the PANI/P-PVA nanoparticles showed optimal comprehensive performance, such as spherical shape with good uniformity, significant redispersion stability in aqueous media and good electrical conductivity, when the P-PVA/aniline feeding ratio ranged from 50 to 60 wt %.

Conclusions

It was aimed to develop the colloidal conducting PANI/P-PVA nanoparticles with significant redispersion stability in aqueous media and good electrical conductivity. So the colloidal PANI dispersion was synthesized in 1.0 M HCl aqueous solution using the P-PVA as a stabilizer and codopant. The effects of the P-PVA stabilizer on the PANI particles morphology, redispersion stability and electrical conductivity are particularly investigated. Investigations revealed that the P-PVA/aniline feeding ratio had distinctly affected the morphology and redispersion stability of the colloidal PANI nanoparticles, and the electrical conductivity was enhanced in the earlier stage and weakened later with increasing the P-PVA/aniline feeding ratio.

When the P-PVA/aniline feeding ratio ranged from 50 to 60 wt %, the colloidal PANI/P-PVA nanoparticles showed spherical shape with good uniformity, significant redispersion stability in aqueous media, and the PANI/P-PVA nanoparticles were possessed of conductivity up to 7 S/cm. The conducting colloidal PANI/P-PVA nanoparticles can be used as the anticorrosion additives in the nontoxic aqueous anticorrosive coatings.

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