

Synthesis and properties on polyaniline in the presence of nickel chloride

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Abstract. Both Conducting and Ferromagnetic polyaniline containing nickel (abbreviated as PANI-Ni) is synthesized in a solution containing aniline, HCl and NiCl₂, using peroxydisulphate as an oxidant and horseradish peroxidase as a catalyst. The conductivity of PANI-Ni is about 10⁻¹ S cm⁻¹. The result of electron paramagnetic resonance (EPR) spectra indicated that there were unpaired electrons in PANI-Ni, and the spin density of the PANI-Ni was 1.09·10¹⁹ spins g⁻¹. The plot of magnetization (*M*) against the magnetic field (*H*) indicated that the PANI-Ni was soft ferromagnetic at about 300 K, the saturation magnetization (*M_s*) and the coercive force (*H_c*) of which were 4.5 emu g⁻¹ (electromagnetic unit per gram) and about 55 Oe, respectively. UV-Visible (UV-vis) and Fourier Transform Infrared (FTIR) spectra showed that there was strong interaction between Ni²⁺ and PANI chains, but the backbone chains of PANI-Ni were hardly changed compared with PANI. Cyclic voltammogram results indicated that the PANI-Ni film was of excellent electrochemical activity.

Keywords: polymer synthesis, polyaniline, ferromagnetic, hysteresis loop, nickel

1. Introduction

For many years chemists and physicists have striven to synthesize organic materials with both conducting and ferromagnetic properties due to their potential applications in batteries, electrical-magnetic shields, sensors and microwave-absorbants [1–3]. Several approaches such as electrochemical and in-situ chemical polymerizations have been reported to prepare conducting polymer with ferromagnetic property [4–7]. Wan and co-workers reported a method for synthesizing a composite of PANI/Fe₃O₄ with both conducting and ferromagnetic functions [8]. Apesteguy *et al.* reported preparation and characterization of Ni-Gd ferrite polyaniline composite of both conducting and ferromagnetic characterizations [9]. Alam *et al.* reported the effect of ferrofluid concentration on electrical and magnetic properties of the Fe₃O₄/PANI nanocomposites [10]. As far as the compos-

ites were concerned, phase separation was a commonplace due to their poor compatibility between polymer matrix and inorganic particles [11]. Rajca and his colleagues reported a ferromagnetic phase below 10 K in a polymeric form of a high spin state aromatic molecule [12]. Recently Zaidi *et al.* reported the polymer of PANi-TCNQ (tetracyanoquinodimethane) produced from polyaniline and tetracyanoquinodimethane at ambient temperature. It is difficult to tell whether PANi-TCNQ is a polymer with both conducting and ferromagnetic properties because no conductivity data are available in the literature [13]. Ichinohe and co-workers reported that ferromagnetic poly(*m*-phenylenediamine) was synthesized by using H₂O₂ as an oxidant and horseradish peroxidase (HRP) as a catalyst in the mixture of aqueous buffer solution and 1,4-dioxane or in reversed micellar solution, and the obtained polymer was attracted to a permanent

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magnet, but no conductivity data were available in the paper, either [14]. Niu and co-workers reported the oxidation of *m*-phenylenediamine by using H₂O₂ as an oxidant and horseradish peroxidase as a catalyst in 0.02 mol dm⁻³ B-R buffer solution, and 2,7-diaminophenazine was only obtained under the selected reaction condition [15]. We tried to duplicate the former results, however, only 2,7-diaminophenazine was still obtained and no precipitates were observed in the mixture of aqueous buffer solution and 1,4-dioxane.

Gosk and his colleagues reported that high-spin Fe³⁺ complex could be formed with imine and amine nitrogen in polyaniline [16]. Sun and co-workers presently reported that Co²⁺ ion might bind to more than one nitrogen site in a PANI chain or form inter-chain linkage among several adjacent PANI chains by coordination, and both intra-chain and inter-chain connections might lead to a more coil-like conformational change or a more twisted aggregation of PANI chains [17].

This paper will present a new and easy approach that synthesizes both conducting and ferromagnetic polyaniline with trace metal ions at ambient temperature. This is because there are unpaired electrons and vacant orbit in some metal ions [18] and donating ability of the lone-pair electrons on the nitrogen atom in conducting polyaniline chains [19]. When metal ions are added in the synthesized system of conducting polyaniline, the metal ions may interact with the nitrogen atoms in conducting polyaniline chains and form with both conducting and ferromagnetic polymers. The method is different from what Wan and co-workers described [8] and the resulting product is a complex rather than a composite entrapped with Fe₃O₄ as core and polyaniline as shell.

2. Experimental methods

2.1. Materials

The monomer aniline (reagent grade) was distilled into colorless under reduced pressure before use. Ammonium peroxydisulphate (APS), N,N-dimethylformamide (DMF) and other chemicals were reagent grade and used as received without further treatment. All of the aqueous solutions were prepared with double distilled water.

2.2. Polymerization

The PANI were synthesized in 0.1 dm³ of solution containing 0.5 mol dm⁻³ HCl, 0.1 mol dm⁻³ aniline, 4 mg HRP, with and without 0.1 mol dm⁻³ NiCl₂·6H₂O. APS of same molar ratio as aniline was added into the solution. The chemical polymerization of aniline was carried out for 24 hours at 30°C. The solution was stirred in an ultrasonic bath. The products were firstly separated by filtration, then washed with both double distilled water and ethanol, and finally dried at 65°C for 24 hours.

2.3. Analysis

The UV-vis spectra of all samples were obtained on UV-2550 spectrometer (Shimadzu) in the range of 250 ~ 900 nm. DMF was used as a solvent. Fourier Transform Infrared (FTIR) spectra were taken on a Tensor 27 FTIR spectrometer (Bruker) using KBr pellets at a resolution of 4 cm⁻¹. The morphologies of products were observed using a transmission electron microscope (TEM, TENCNAI-12). Conductivity of the resulting products was measured by using standard four-probe method. The standard deviation was less than 2.0% in our experiments using an YJ8312 model current source (Shanghai Huguang Instrument Works, China) and M92A digital multimeter (Mastech). Wide-angle X-ray diffraction patterns for the powder samples were taken on a M03XHF²² diffractometer (Mac Science, Japan) using Cu-K_α radiation ($\lambda = 1.541 \text{ \AA}$), which was used to analyze the crystallinity of polyaniline. The hysteresis loops were obtained on a Vibrating Sample Magnetometer (VSM, USA). The Electron Paramagnetic Resonance (EPR) spectra were carried out by using an A300-10/12 spectrometer (Bruker) operating in X-band (9.856 GHz). The microwave power was set at 0.2 mW and the amplitude was controlled at 2.00 G. X-ray photoelectron spectroscopy (XPS) was performed with a VG EscaLab 220i spectrometer using a standard AlK_α X-ray source (300 W). The cyclic voltammogram (CV) was performed on a CHI 407 electroanalysis apparatus. An electrolytic cell for cyclic voltammetry consisted of a PANI working electrode, a platinum counter electrode and a saturated calomel electrode (SCE).

3. Results and discussion

3.1. Electrical and magnetic properties

Figure 1 shows the plots of magnetization (M) against the magnetic field (H) of PANI (curve a), deprotonated PANI with $\text{NH}_3 \cdot \text{H}_2\text{O}$ (curve b) and PANI-Ni (curve c), respectively. Curves (a) and (b) indicate that PANI and deprotonated PANI with $\text{NH}_3 \cdot \text{H}_2\text{O}$ are not ferromagnetic. Curve (c) clearly exhibits hysteresis loop at about 300 K, which indicates that the PANI-Ni is ferromagnetic. The inset in Figure 1 is $M-H$ plot of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ under the same condition. It can be seen from the inset that the magnetization of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ increases linearly

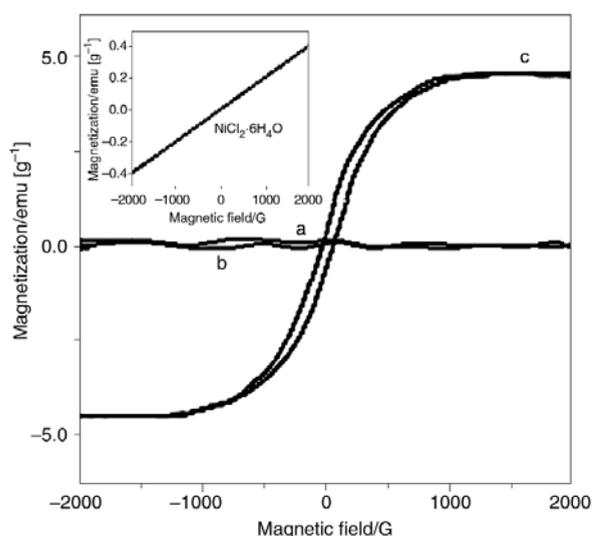


Figure 1. $M-H$ plot of PANI (a), deprotonated PANI (b) and PANI-Ni (c)

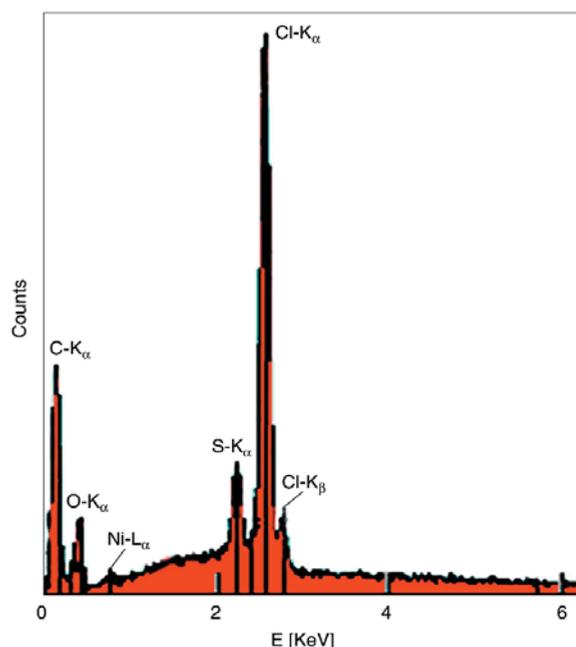


Figure 2. XPS spectrum of PANI-Ni

with increasing applied magnetic field and there is no hysteresis loop at ambient temperature, which imply that $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ is just a paramagnetic salt. According to the result of XPS (Figure 2) of PANI-Ni, there is only trace amount of nickel in the PANI-Ni ($<0.5\%$), so the nickel ions can't give noticeable contribution to the ferromagnetic property of the PANI-Ni. The result of EPR shows that there are unpaired electrons in the PANI-Ni and the spin density of the resulting product is $1.09 \cdot 10^{19}$ spins g^{-1} . It is well known that the ferromagnetic state not only requires (quasilocal) magnetic moments but also requires that the moments remain mutually aligned [20]. The results of VSM and EPR show that PANI-Ni is in keeping with the requirement of ferromagnetic state. The result of TEM in Figure 3 shows that the morphology of PANI-Ni (Figure 3b) is very similar with that of the PANI-Co, both of which are quasi-spherical morphologies. Sun and co-workers thought that Co^{2+} ion might bind to more than one nitrogen site in a PANI chain or form inter-chain linkage among several adjacent PANI chains by coordination, and both intra-chain and inter-chain connections might lead to a more coil-like conformational change or a more twisted aggregation of PANI chains [17]. It is deduced that the interaction between Ni^{2+} and PANI chains may be favorable to form ferromagnetic domain. The forming mechanism of conductive ferromagnetic PANI-Ni is suggested as Figure 4 [21]. However, more researches are needed to understand the behavior better.

It is seen from Figure 1 that the saturation magnetization (M_s) and the coercive force (H_c) of the PANI-Ni are 4.5 emu g^{-1} (electromagnetic unit per gram) and about 55 Oe, respectively. The low coercive value implies that the PANI-Ni is a soft ferromagnetic material [14].

It is difficult to understand that the content of nickel in the resulting PANI is hardly related with the con-

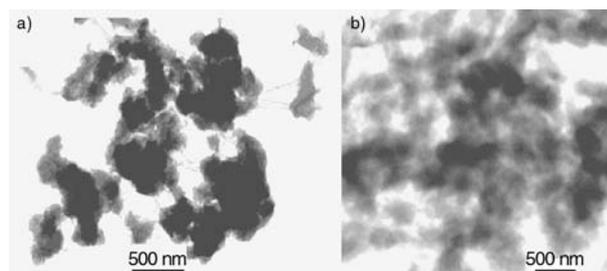


Figure 3. TEM morphology of PANI (a) and PANI-Ni (b)

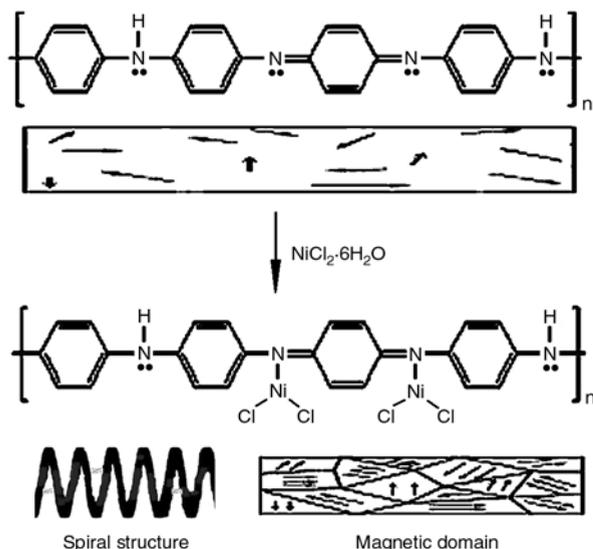


Figure 4. The possible forming mechanism of ferromagnetic PANI-Ni

centration of NiCl_2 in reaction system. We consider that this phenomenon can be easily explained with Pearson's theory of Hard and Soft acids and bases (HSAB), Hard acids prefer to bind to hard bases and soft acids prefer to bind to soft bases [22]. Based on similar system of HSAB's classification reported in the literature, H^+ [22] and PANI [23] are hard acid and hard base respectively, so PANI can be easily doped by H^+ . Ni^{2+} is borderline acids [22], so PANI is just able to be coordinated with trace Ni^{2+} compared with H^+ .

The conductivities of PANI-Ni and PANI are 0.22 and 0.13 S cm^{-1} , respectively. It indicates that Ni^{2+} has little effect on the conductivity of PANI.

As it is mentioned above, PANI-Ni is a conducting and ferromagnetic material at ambient temperature.

3.2. UV-vis spectra and FTIR spectra

Figure 5 is the UV-vis spectra of PANI (curve a), PANI-Ni (curve b) dissolved in DMF, and solid PANI (curve c), respectively. It is seen obviously from Figure 5a and Figure 5b that there are two absorption bands in the two curves: one location is $\sim 350 \text{ nm}$ and the other is $\sim 600 \text{ nm}$. It was reported that PANI showed two strong absorptions at $320\text{--}340$ and $600\text{--}660 \text{ nm}$ respectively [24]. The first band was assigned as $\pi\text{--}\pi^*$ transition and the other were associated with the transition of benzenoid rings into quinoid rings. In fact, the PANI we synthesized is in the protonated form, the

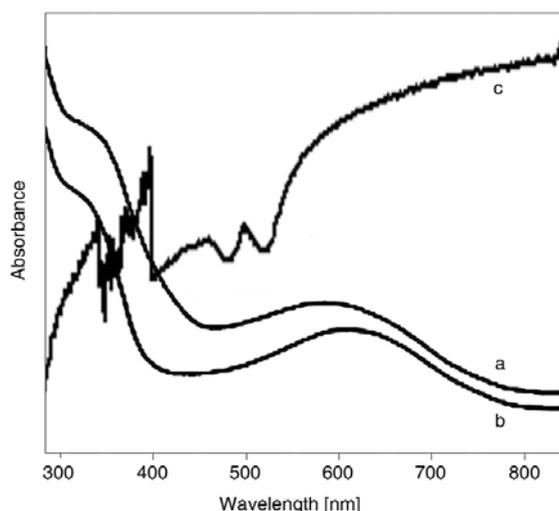


Figure 5. UV-vis spectra of PANI (a), PANI-Ni (b) and solid PANI (c)

absorption band of the transition of benzenoid rings into quinoid rings should be at more than 700 nm . This may be due to the presence of the hydrogen-bonding interaction of the $\text{C}=\text{O}$ group in DMF with the NH group in PANI. Since the $\text{C}=\text{O}$ group can interact or form hydrogen bond with the dopant, which could prevent the PANI from acid-doping [25]. This can be confirmed by a broad absorption band at more than 700 nm in the UV-vis spectrum of solid PANI (curve c).

Compared curve (b) with curve (a) in Figure 5, the peak of quinoid ring transition shifts from 585 to 621 nm when Ni^{2+} is added in the reactive system. The reason may be that 'compact coil' of PANI-Ni chain make the energy gap of quinoid ring transition narrower, thus transition of electrons becomes easier. The peak of $\pi\text{--}\pi^*$ transition in PANI seldom shifts, so it can be inferred that the interaction of both Ni^{2+} and the nitrogen atoms on the quinoid ring is predominant.

Figure 6 shows the FTIR spectra of PANI (curve a) and PANI-Ni (curve b) respectively. IR spectra over 2500 cm^{-1} are omitted in Figure 6 because they are really identical with and without NiCl_2 . 1570 and 1490 cm^{-1} are attributed to the stretching vibrations of $\text{N}=\text{Q}=\text{N}$ ring and $\text{N}\text{--}\text{B}\text{--}\text{N}$ ring respectively. The peak at 1300 cm^{-1} corresponds to $\text{C}\text{--}\text{N}$ stretching vibration. The peaks at 1109 and 800 cm^{-1} can be attributed to bands characteristic of $\text{B}\text{--}\text{NH}\text{--}\text{Q}$ or $\text{B}\text{--}\text{NH}\text{--}\text{B}$ bonds, and out-of-plane bending vibration of $\text{C}\text{--}\text{H}$ of benzene rings (where B refers to the benzenic-type rings and Q refers to

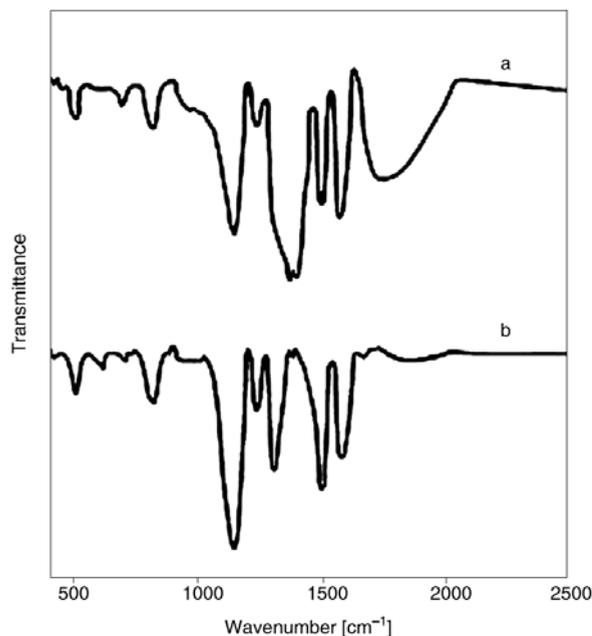


Figure 6. FTIR spectra of PANI-Ni (a) and PANI (b)

the quinonic-type rings) [24, 26, 27]. It is confirmed by our result (as shown in Figure 6) that band at 1400 cm^{-1} assigned to N–H bending mode shifts to 1303 cm^{-1} when Ni^{2+} is added in the reactive system of PANI, which indicates that the Ni^{2+} can interact with nitrogen atoms of the PANI chains.

It can be inferred from the results of UV-vis and FTIR spectra that backbone chain of PANI-Ni hardly changes compared with that of PANI. So the PANI-Ni is a complex polymer under the aforementioned condition.

3.3. Cyclic voltammogram

Figure 7 is the cyclic voltammogram of PANI film (curve b) and PANI-Ni film (curve a) in 0.5 mol dm^{-3} HCl aqueous solution in the range from -0.2 to 0.9 V at $60\text{ mV}\cdot\text{s}^{-1}$. It can be seen obviously from Figure 7 that the PANI-Ni is of electrochemical activity.

There are three pairs of redox peaks in the two curves. Peaks 1 and 3 have been identified as oxidation of PANI to its radical cation (polaron) and further oxidation to quinoid (bipolaron) states, respectively [28]. Peaks 1' and 3' correspond to the inverse process of Peaks 1 and 3 [29, 30]. The 'middle' peaks 2 and 2' have been attributed to the presence of ortho-coupled polymers [31] and the

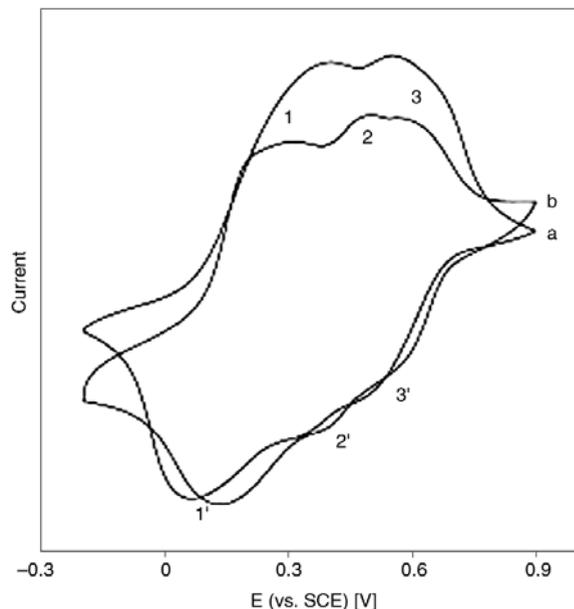


Figure 7. The cyclic voltammograms of PANI (a) and PANI-Ni film (b) 0.5 mol dm^{-3} HCl, 60 mV/s

degradation of PANI (soluble species such as benzoquinone and hydroquinone) [28].

Compared curve (b) with curve (a), the two curves are similar in shape. The oxidation-reduction peaks show slight shifts. For example, the anodic peaks at 0.05 and 0.33 V for PANI film shift to 0.13 and 0.40 V for the PANI-Ni, respectively. These shifts may result from the interaction between Ni^{2+} and PANI chains.

3.4. X-ray diffraction spectra

Figure 8 shows the XRD patterns of $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ (curve c) and PANI (curve b) and PANI-Ni (curve a). The X-ray diffractogram of $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ (curve c) indicates the characteristic diffraction peaks of $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ centered at $2\theta = 16.5, 18.6, 29.2, 32.8, 35.5, 37.5^\circ$. However, these diffraction peaks didn't appear in the XRD patterns of PANI-Ni. This may be because there is only trace amount of nickel in PANI-Ni. The PANI (curve a) and PANI-Ni (curve b) have a broad hump peak at $2\theta = 20^\circ$, which shows that PANI-Ni is an amorphous polymer [32]. This result is in agreement with those reported in literature [33]. Based on the similar diffractogram of curves (a) and (b) in Figure 8, it maybe because there is hardly effect of Ni^{2+} on the crystallinity of PANI-Ni.

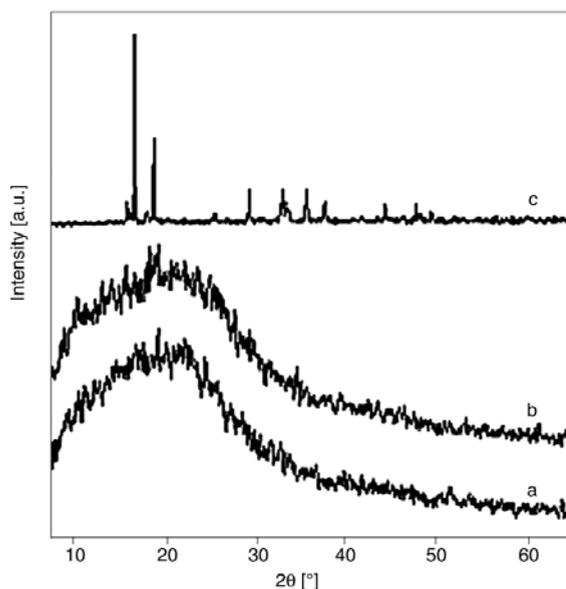


Figure 8. XRD pattern of PANI-Ni (a), PANI (b) and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (c)

4. Conclusions

The conductive and ferromagnetic PANI-Ni is synthesized successfully in the system containing NiCl_2 at ambient temperature. The result of VSM indicates that PANI-Ni is of ferromagnetism at about 300 K. The UV-vis and FTIR spectra show that the structure of backbone chains of PANI-Ni hardly changes compared with PANI. The PANI-Ni is a complex polymer rather than a composite.

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