

Review

ECO-FRIENDLY WATER-BORNE CONDUCTING POLYANILINE*

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Abstract Among the intrinsically conductive polymers, polyanilines have been of great interest in the past decades due to their wide applications in many fields, thanks to their reasonably good conductivity, easy preparation, and special redox properties. Ever-increasing environmental considerations make the processing of polyanilines shift from toxic organic solvent-based system to eco-friendly water-based system. The present paper reviews the synthesis of water-borne conducting polyanilines, and possible applications are discussed including supercapacitor electrode material, metal free corrosion protection coating, lithium oxygen battery cathode material and ultraviolet curable resin.

Keywords: Water-borne; Polyaniline; Supercapacitor; Corrosion protection; Lithium oxygen battery; Ultraviolet curable.

INTRODUCTION

Polyanilines consisting of phenyl diamine and quinine diimine repeating units have been considered as very important intrinsically conductive polymers receiving worldwide investigation, owing to their special electrical, optical and electrochemical properties^[1–4]. Many promising applications in various fields are explored in the past decades, such as metal free corrosion protection^[5–9], electromagnetic interference shielding^[10], electrostatic discharge^[11], chemical and biological sensors^[12–15], supercapacitor^[16, 17], actuators^[18] molecular wires^[19], gas separation membranes^[20] and artificial muscles^[21] *etc.* As far as polyaniline processing is concerned, organic solvent-based system dominates in which conducting polyanilines are dispersed or dissolved in toxic solvents like *m*-cresol and chloroform, or volatile organic solvents like xylene or toluene, which causes serious environmental pollution and potential human health damage. Therefore, eco-friendly processings of water-borne conducting polyanilines are badly needed^[22–25]. Currently, water-based polyanilines have been successfully prepared by various techniques with electrical conductivity variable from 10^{-9} to 10^1 S·cm⁻¹, and their applications are explored.

Prof. Fosong Wang initiated academic research on conducting polymers since 1981, he founded a long last research team in Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, for conducting polyaniline since 1983. This research team has been active since then, covering from preparation, structure and properties of polyaniline based materials to industrialization of polyanilines for transparent anti-static coating in electronic industry and metal free anti-corrosion coating for steel or aluminum alloy. Wang was the pioneer for commercialization of conducting polyaniline in China. This review will not go to the details of all the researches

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Invited paper dedicated to Professor Fosong Wang on the occasion of his 80th birthday

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in polyaniline in this team, but will focus on the water-based processing of conducting polyaniline, including synthesis of water soluble polyanilines with different electrical conductivity and their various applications such as active electrode material in supercapacitor, anti-corrosive pigment in metallic corrosion protection, additive in ultraviolet curable coating, and electrode material of lithium battery.

Synthesis of Water-borne Conducting Polyaniline

Various approaches have been reported to prepare water-borne polyanilines, including self-doping, template polymerization and counter-ion induced method. The self-doping approach has been widely used to prepare water-based conducting polyanilines, in which the sulfonic or phosphoric acid group linking onto the aromatic ring or nitrogen atom^[26, 27] served as hydrophilic segment to provide water soluble or dispersible properties. The hydrophilic unit can be connected to two active reaction sites, aromatic ring or amine nitrogen of polymer backbone. Epstein and co-workers have successfully prepared water-based self-doped conducting polyaniline by reaction of polyaniline emeraldine base with fuming sulfuric acid^[28–34], where sulfonic acid groups were functionalized onto the aromatic rings of polymer backbone (Fig. 1a) to give electrical conductivity from $10^{-1} \text{ S}\cdot\text{cm}^{-1}$ to $10^{-3} \text{ S}\cdot\text{cm}^{-1}$. Chen *et al.* claimed that water-borne conductive polyanilines can be synthesized, where the amine nitrogen in the polyaniline backbone was linked by hydrophilic segment, such as propane sulfonic acid group^[35, 36], *p*-(3-bromopropyl)benzenesulfonic acid group^[37] or benzoysulfonic group^[38], by reacting emeraldine base with 1,3-propanesultone (Fig. 1b), *p*-(3-bromopropyl)benzenesulfonic acid (Fig. 1c) or *o*-sulfobenzoic anhydride (Fig. 1d), respectively. Recently, Jo *et al.*^[39] synthesized water soluble self-doped conducting polyaniline graft copolymer, poly(styrenesulfonic acid-*g*-aniline), in which styrenesulfonic acid unit served as water-soluble moiety and self-doping moiety, and its electrical conductivity can reach $10^{-1} \text{ S}\cdot\text{cm}^{-1}$. We prepared self-doped water-borne conducting polyanilines through the co-polymerization of 2-sulfoaniline and aniline using potassium hexacyanoferrate (III) as oxidant, in which the doped state is directly obtained with hexacyanoferrate (II) anion and sulfonate group surrounding imine and amine atoms in polyaniline backbone (see Fig. 2). From the scanning electron microscope (SEM) morphology of the water-based polyaniline shown in Fig. 3, it can be seen hollow spherical polyaniline particles with a diameter of 300–600 nm and a shell thickness of 50–68 nm were readily obtained, whose electrical conductivity can reach *ca.* $1.5 \text{ S}\cdot\text{cm}^{-1}$.

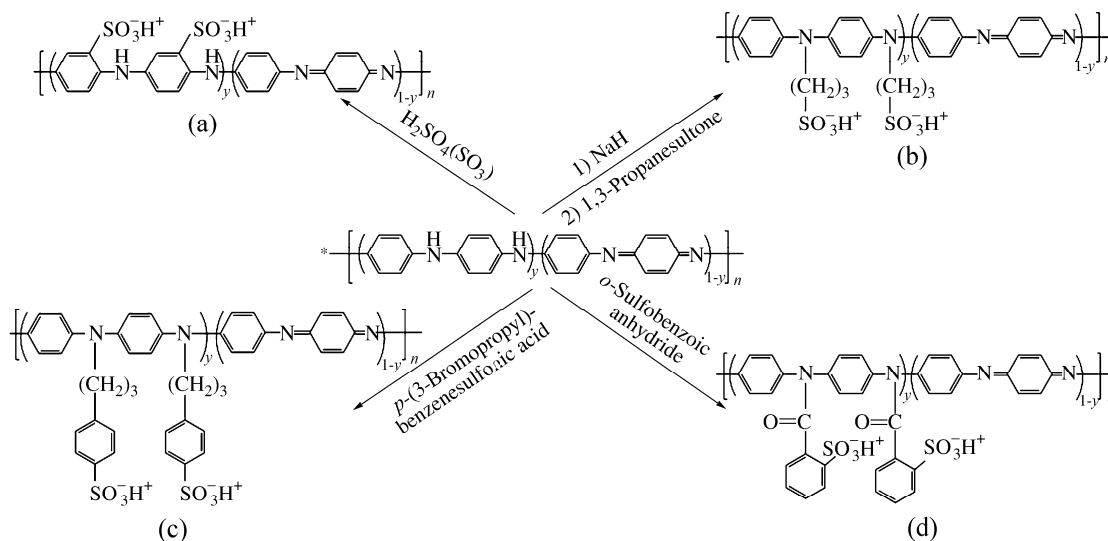


Fig. 1 Self-doped approach to water-borne polyanilines by reaction between emeraldine base and (a) fuming sulfuric acid, (b) 1,3-propanesultone, (c) *p*-(3-bromopropyl)benzenesulfonic acid and (d) *o*-sulfobenzoic anhydride, respectively

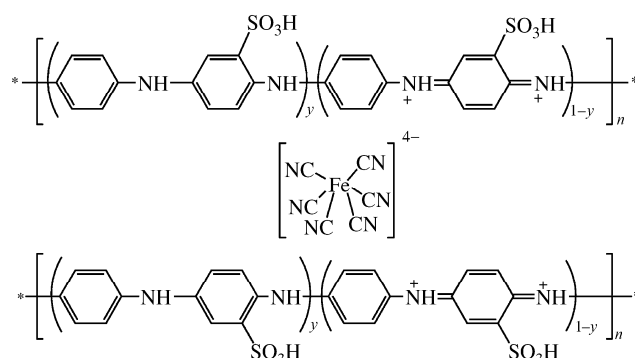


Fig. 2 Chemical structure of self-doped water-borne conducting polyaniline

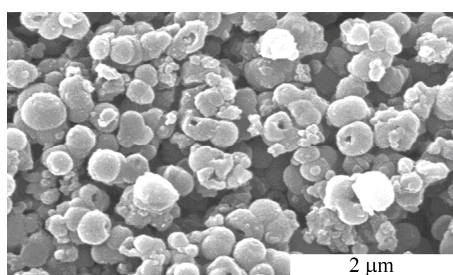


Fig. 3 SEM image of self-doped water-borne conducting polyaniline

Water-borne conducting polyaniline can also be prepared using template polymerization, in which water soluble polyacrylamide^[40–44], poly(2-acrylamido-2-methyl-1-propane-sulfonic acid)^[45, 46], poly(4-styrenesulfonate acid)^[47, 48] or poly(vinylsulfonic acid)^[49] was used as a template as well as hydrophilic segments. A typical water-borne conducting polyaniline from template polymerization method is shown in Fig. 4, where poly(styrenesulfonic acid) was used as a template. First, the aniline monomers were protonated onto positively charged anilinium ions and combined with negative charged sulfonate groups of the poly(4-styrenesulfonate acid) in aqueous solution to form anilinium ion-PSS complex by electrostatic interaction^[50]. Then the polymerization of aniline using ammonium persulfate as an oxidant led to water soluble polyaniline-poly(4-styrenesulfonate acid) (PANi-PSSA), which was assumed to exhibit a double-strand structure and much improved stability. Co-existence of polyaniline and insulated polymer for template polymerization was also not beneficial for high conductivity, a low electrical conductivity ranging from 10^{-8} S·cm⁻¹ to 10^{-2} S·cm⁻¹ was obtained.

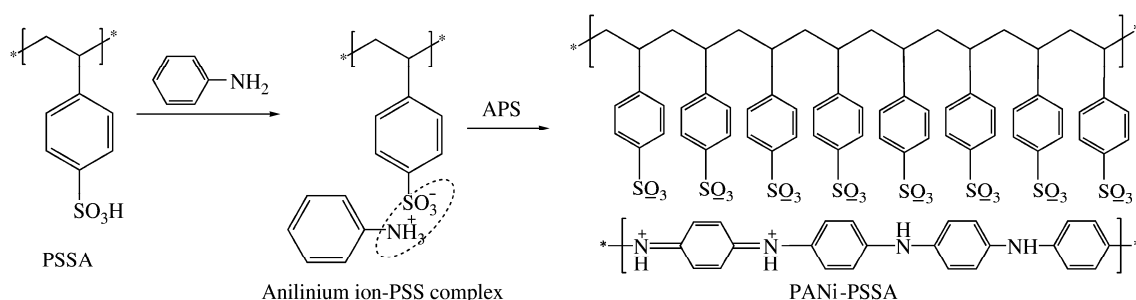


Fig. 4 Schematic illustration of the preparation of water-based polyaniline obtained from template polymerization method, using poly(styrenesulfonic acid) as a template (Reproduced with permission from the Ref. [50])

Counter-ion induced method^[51, 52] was an important approach to water-borne conducting polyaniline through a simple neutralization reaction between alkaline polyaniline emeraldine base and acidic dopant, in which the hydrophilic segment of anion from dopant prompted the polymer to disperse or dissolve in water to give water-borne conducting polyaniline. Phosphate ester dopant with different numbers of ethylene glycol repeating units ($x = 1-16$) composed of monoester and diester was prepared^[53-59], as shown in Fig. 5, and water-borne conducting polyaniline can be obtained when the emeraldine base was doped by the acidic phosphate ester through counter-ion induced method. When the number of repeating ethylene glycol unit x was set as 7, water soluble polyaniline with electrical conductivity of $10^{-1} \text{ S}\cdot\text{cm}^{-1}$ was prepared^[56]. As the x decreased to 2, a stable water-dispersible conducting polyaniline was obtained^[57] with electrical conductivity of $4.5 \text{ S}\cdot\text{cm}^{-1}$. The resultant dispersion with nano-particle diameter of 60–140 nm was very stable, no precipitation was observed

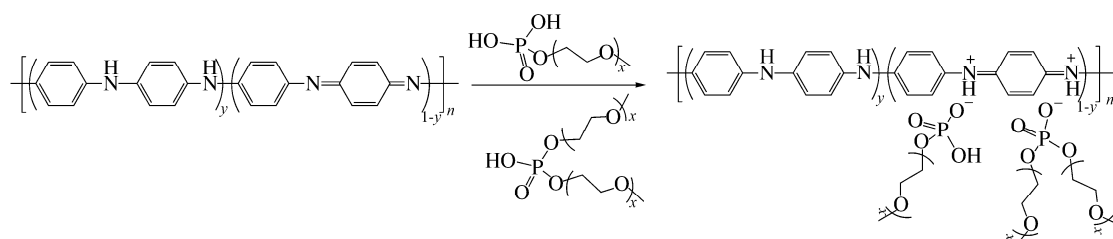


Fig. 5 Structure of water-borne conducting polyaniline obtained from counter-ion induced method (x is an integer, $x = 1-16$.)

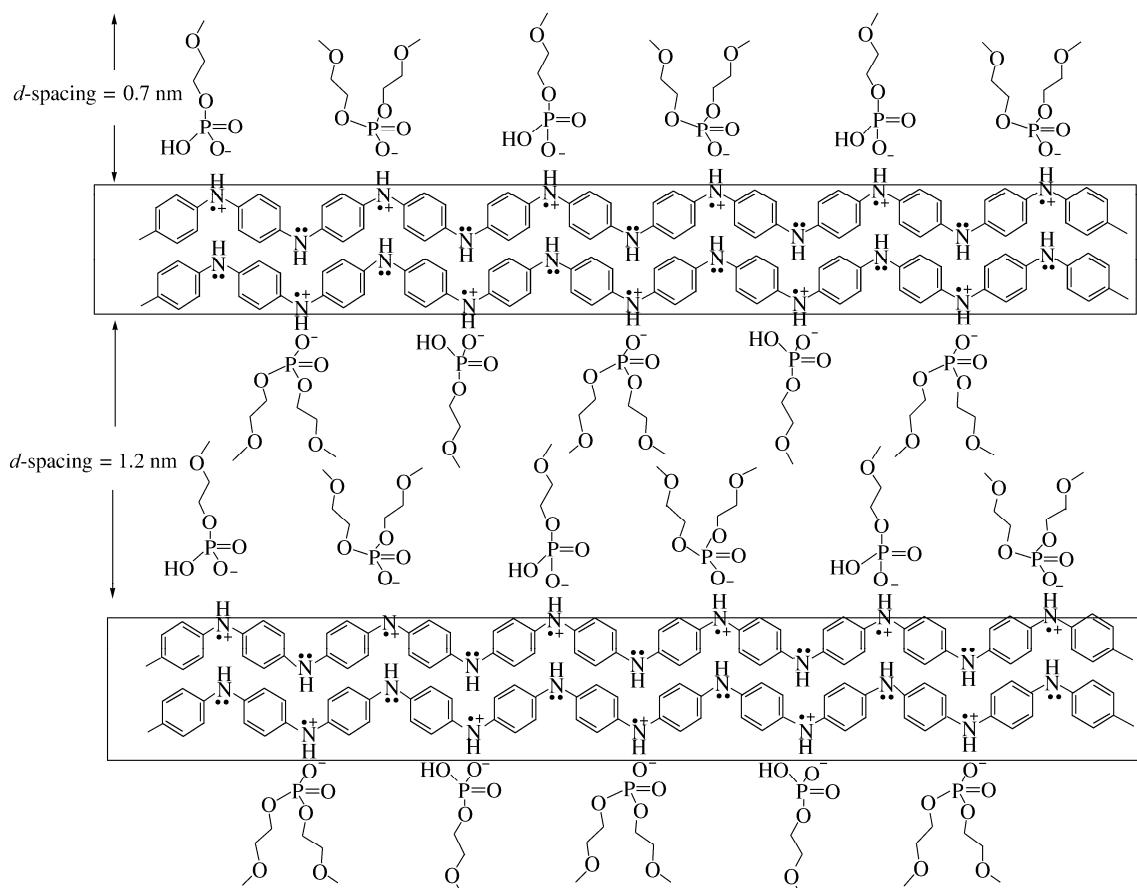


Fig. 6 Schematic illustration of the lamellar structure consisting of alternating polyaniline layers and phosphate ester side chain layers (Reproduced with permission from the Ref. [58])

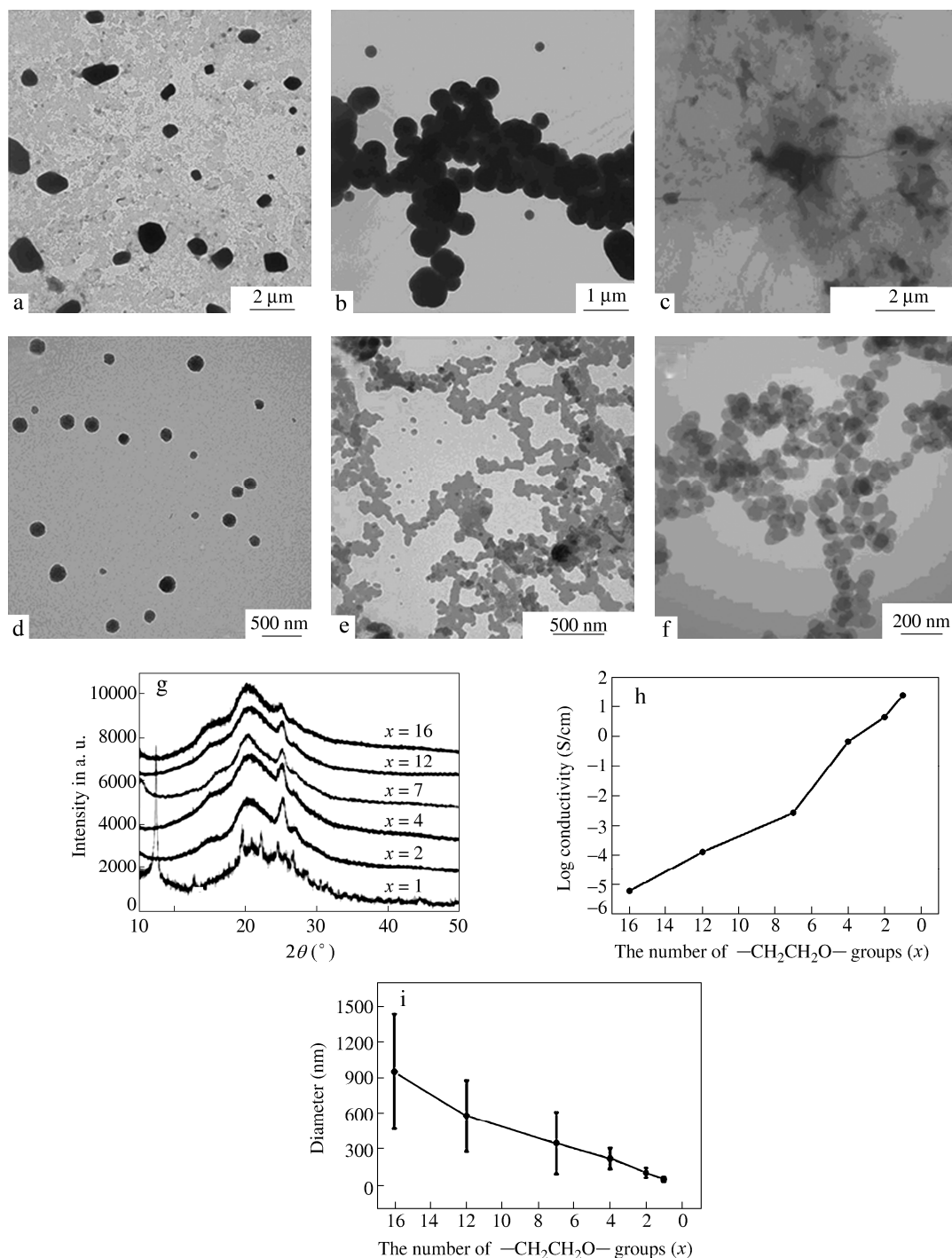


Fig. 7 TEM images of water-borne conducting polyaniline with different numbers of ethylene glycol units (a) $x = 16$, (b) $x = 12$, (c) $x = 7$, (d) $x = 4$, (e) $x = 2$ and (f) $x = 1$; The WAXD patterns of polyaniline films (g); The influence of x value on the average diameter (h) and electrical conductivity (i) (Reproduced with permission from the Ref. [59])

after 3 months, and the particle size distribution was almost unchanged. When the number of ethylene glycol repeating unit x further decreased to 1, water-borne conducting polyaniline^[58, 59] nanoparticles with diameters ranging from 20 nm to 80 nm was synthesized. Its electrical conductivity can reach as high as $25 \text{ S}\cdot\text{cm}^{-1}$, which

was much higher than that of the earlier reported water-based polyanilines^[56, 57]. More importantly, lamellar self-assembly and crystalline structure (shown in Fig. 6) was found with alternating polyaniline and phosphate ester side chain layers. The side chain crystalline structure showed the periodicity of *ca.* 1.2 nm. The high electrical conductivity can be caused by the side chain crystalline forced lamellar structure. Lamellar structure due to side chain crystalline confinement may be a new way to improve the electrical conductivity of conducting polyaniline. This water-borne conductive polyaniline has been found to form supramolecular complex with cellulose in aqueous systems^[60], and furthermore, it can improve the rheological behavior of cellulose^[61]. As described above, properties of water-borne conducting polyanilines strongly depended on the phosphate ester dopant with different numbers of repeating ethylene glycol units. The influence of the side chain length of the dopant on the chain packing of conducting polyanilines was found to be highly dependent on the *x* value in dopant side chains (Fig. 7), when *x* decreased from 16 to 2, the conducting polyaniline film changed slowly from amorphous to partially crystalline^[59], as indicated by the increasing relative intensity of peak at 25.7° (Fig. 7g), in the meantime, its electrical conductivity increased from $5.9 \times 10^{-6} \text{ S}\cdot\text{cm}^{-1}$ to $4.5 \text{ S}\cdot\text{cm}^{-1}$ (Fig. 7h), and the average diameter of polyaniline particles in the dispersion decreased from 950 nm to 100 nm (Fig. 7i). The transition from disorder to order structure may provide a new insight for preparation of highly conducting polyaniline by means of highly crystalline or regular stacking.

In summary, each synthetic method has its advantage and shortcoming. As for self-doped approach, the water-solubility of polyaniline is caused by the hydrophilic sulfonic acid group on the benzene ring or sulfonic acid derivatives on amine nitrogen of polyaniline, however, it's just the hydrophilic moieties that they damage the conjugation structure of polyaniline backbone and thus high electrical conductivity can't be obtained. Simple and easy to operate is the advantage of this method. For template polymerization method, insulated water-soluble polymers used as template prohibit the formation of a higher electrical conductivity. On the other hand, the water-borne polymer templates promote the formation of excellent free standing films. For the counter-ion induced technique, high conductivities over $10^1 \text{ S}\cdot\text{cm}^{-1}$ can be achieved, but the film is found to be too fragile to form an excellent free standing conducting film. An excellent free standing film with a high conductivity from water-borne conducting polyaniline is very important for the application on high end electrical market, therefore, an appropriate dopant needs to be further investigated for this method.

Electrode Material for Supercapacitor

Due to the ever-increasing environmental concerns and the up-coming depletion of fossil fuels, considerable efforts have been devoted to the development of alternative energy storage/conversion devices with high power and energy densities^[62–64]. Supercapacitors are energy storage devices with short charging times combining the high energy-storage capacity of conventional batteries and high power-delivery capacity of conventional capacitors^[65, 66], higher power density, energy density and specific capacitance are required for corresponding electrode materials^[67]. So far, electrode materials mainly focus on carbon based materials^[68–71], intrinsically conducting polymers^[72–75] and transition metal oxide^[76, 77] *etc.* Among the electrical conducting polymers, polyaniline^[78, 79] has been considered as one of the most promising electrode materials for supercapacitors^[80], not only for its high electrical conductivity and superior redox properties, but also for its easy synthesis, good environmental stability and relatively low cost. Li and co-workers^[81] reported that a super-hydrophilic conducting polyaniline can give a specific capacitance of $500 \text{ F}\cdot\text{g}^{-1}$ at a constant current density of $1.5 \text{ A}\cdot\text{g}^{-1}$ in 0.1 mol/L H_2SO_4 aqueous solution, moreover, the capacitance still maintained about $400 \text{ F}\cdot\text{g}^{-1}$ after 5000 consecutive cycles, the super-hydrophilicity of electrode materials was considered for aqueous electrolyte system redox supercapacitors, since good hydrophilic properties were beneficial for the diffusion of aqueous electrolyte during the charge/discharge process. Self-doped water-based polyaniline nanofibers with diameters in range of 60–90 nm obtained from electrochemical polymerization of aniline and *m*-aminobenzoic onto the platinum, reported by Mousavi *et al.*^[82], can provide a specific capacitance ($480 \text{ F}\cdot\text{g}^{-1}$), specific power ($436 \text{ W}\cdot\text{kg}^{-1}$) and specific energy ($9.40 \text{ Wh}\cdot\text{kg}^{-1}$) in a 1 mmol/L HCl and 1 mol/L KCl aqueous electrolyte at a current density of $5 \text{ mA}\cdot\text{cm}^{-2}$. After 900 cycles, the specific capacitance decreased from the initial $480 \text{ F}\cdot\text{g}^{-1}$ to $247 \text{ F}\cdot\text{g}^{-1}$, *i.e.*, a 45% capacitance loss was found.

Most researches are carried out in aqueous electrolyte, as mentioned above, especially for water-based polyaniline system. However, practical supercapacitor is fabricated in organic electrolyte, obstacles such as the poor stability for long-term charging and discharging exist, especially in organic electrolyte, which has much higher resistance than aqueous analogue^[83, 84]. Therefore, investigation of water-borne polyaniline in organic electrolyte is of great importance for this material of practical value for supercapacitor.

Aqueous dispersed polyaniline nanofibers with diameter of 17–26 nm were successfully prepared^[85–87], in which polyaniline nanofibers were prepared using ferric nitrate as oxidant through pseudo-high dilution technique, and then doped by phosphate ester with one ethylene glycol repeating unit^[88]. The electrical conductivity of the film from aqueous dispersed polyaniline nanofibers can reach as high as $32 \text{ S} \cdot \text{cm}^{-1}$, where a highly crystalline structure was found. The aqueous dispersible nanofibrous polyaniline is used as electrode material for supercapacitor in non-protonic solvent system (Fig. 8). For polyaniline nanofibers of 17–26 nm diameter, a specific capacitance as high as $160 \text{ F} \cdot \text{g}^{-1}$ at a discharge rate of $0.4 \text{ A} \cdot \text{g}^{-1}$ from -1 V to 1 V in $1 \text{ mol} \cdot \text{L}^{-1}$ tetraethylammonium tetrafluoroborate/propylene carbonate ($\text{PC}/\text{Et}_4\text{N}^+ \cdot \text{BF}_4^-$) solution was obtained, and the discharge/charge efficiency reached 92%, indicating good electrochemical reversibility. For nanofibrous polyaniline of 100–120 nm in diameter and non-fibrous polyaniline, the specific capacitance (SC) was only $120 \text{ F} \cdot \text{g}^{-1}$ and $90 \text{ F} \cdot \text{g}^{-1}$, respectively. The difference was due to the various specific surface area, it was 70, 21 and $13 \text{ m}^2 \cdot \text{g}^{-1}$ for thin nanofibrous, thick nanofibrous and non-fibrous water-based polyaniline, respectively, higher surface area can lead to higher SC value, as also found in the latest report^[89].

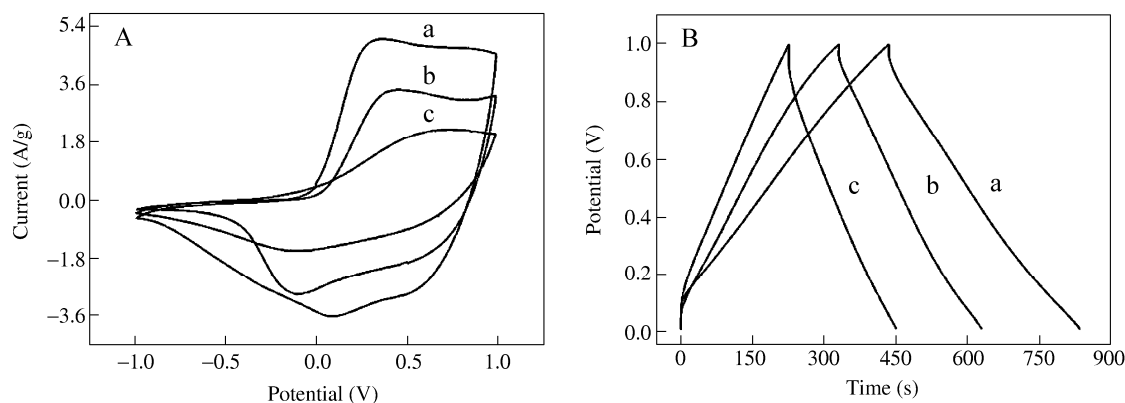


Fig. 8 (A) Cyclic voltammograms and (B) galvanostatic charge/discharge curves for (a) thin water-borne polyaniline nanofiber electrode, (b) thick water-based polyaniline nanofiber electrode and (c) non-fibrous water soluble polyaniline electrode (Reproduced with permission from the Ref. [85])

Scan rate for cyclic voltammograms: $20 \text{ mV} \cdot \text{s}^{-1}$; Current density for galvanostatic charge/discharge: $0.4 \text{ A} \cdot \text{g}^{-1}$

Aqueous dispersed conducting polyaniline can provide excellent SC, however, the cycle stability is unsatisfactory, especially for the long-term charging/discharging processes, which is the main obstacle for its commercial application. The instability of pure polyaniline electrode is mainly owing to the internal stress change derived from the dopant anion intercalation and dissociation during the long-term charging and discharging processes. In general, various strategies have been employed to promote the long-term cycle stability, such as compositing polyaniline with carbon materials^[62] (carbon nanotubes or graphene) to improve the porosity and allow room for the swelling and shrinkage of PANI composites. As a superior carbon-based nanomaterial, graphene is extremely attractive. The single-layered graphene is composed of sp^2 hybrid carbon atom with a honeycomb crystal structure, demonstrating many unprecedented properties, among which the high specific surface area, excellent electrical and electrochemical performance are most interesting for its application in electrochemical capacitors. In fact, it has been demonstrated that the graphene layers can be assembled onto the surface of positive charged colloid spheres^[90], and Yang *et al.* reported that graphene-encapsulated nanoparticles could be fabricated by ionic interactions between negatively charged graphene oxide and positively

charged oxide nanoparticles^[91]. Graphene-wrapped aqueous dispersible polyaniline nanofiber electrode material^[92] was obtained by co-assembly of negatively charged graphene oxide with positively charged aqueous dispersible polyaniline nanofibers with diameter of 120–150 nm in an aqueous dispersion, followed by the reduction of the graphene oxide (Fig. 9a). The transmission electron microscopy (TEM) images of graphene-wrapped polyaniline nanofibers (Fig. 9b) obviously revealed that polyaniline nanofibers were successfully decorated by graphene layers, and in some cases, the neighboring polyaniline nanofibers were linked by the graphene layers. As shown in Fig. 10(a), the maximum SC value of $250 \text{ F} \cdot \text{g}^{-1}$ for Gra100-wrap-PANI-NF was obtained at a current density of $0.5 \text{ A} \cdot \text{g}^{-1}$ in a $1 \text{ mol/L Et}_4\text{N}^+ \cdot \text{BF}_4^-/\text{PC}$ electrolyte, which was much higher than that of the pristine polyaniline nanofibers. From the continuous charging/discharging cycle tests at a current density of $1 \text{ A} \cdot \text{g}^{-1}$ in a $1 \text{ mol/L Et}_4\text{N}^+ \cdot \text{BF}_4^-/\text{PC}$ electrolyte for pristine polyaniline nanofibers and Gra100-wrap-PANI-NF shown in Fig. 10(b), the Gra100-wrap-PANI-NF displayed a higher initial SC of $236 \text{ F} \cdot \text{g}^{-1}$, and retained as $173.3 \text{ F} \cdot \text{g}^{-1}$ after 1000 charging/discharging cycles with a 26.27% capacitance loss, which was a sharp difference compared with that of pristine PANI (56.2% capacitance loss). Due to the superior chemical and electrochemical stability, graphene can act as a good protecting layer of the active materials, retarding the degradation of polyaniline material and the capacity fading during the long-term charging and discharging cycle processes. This provided a route to improve the cyclic stability of water-borne conducting polyaniline based electrode material for supercapacitor.

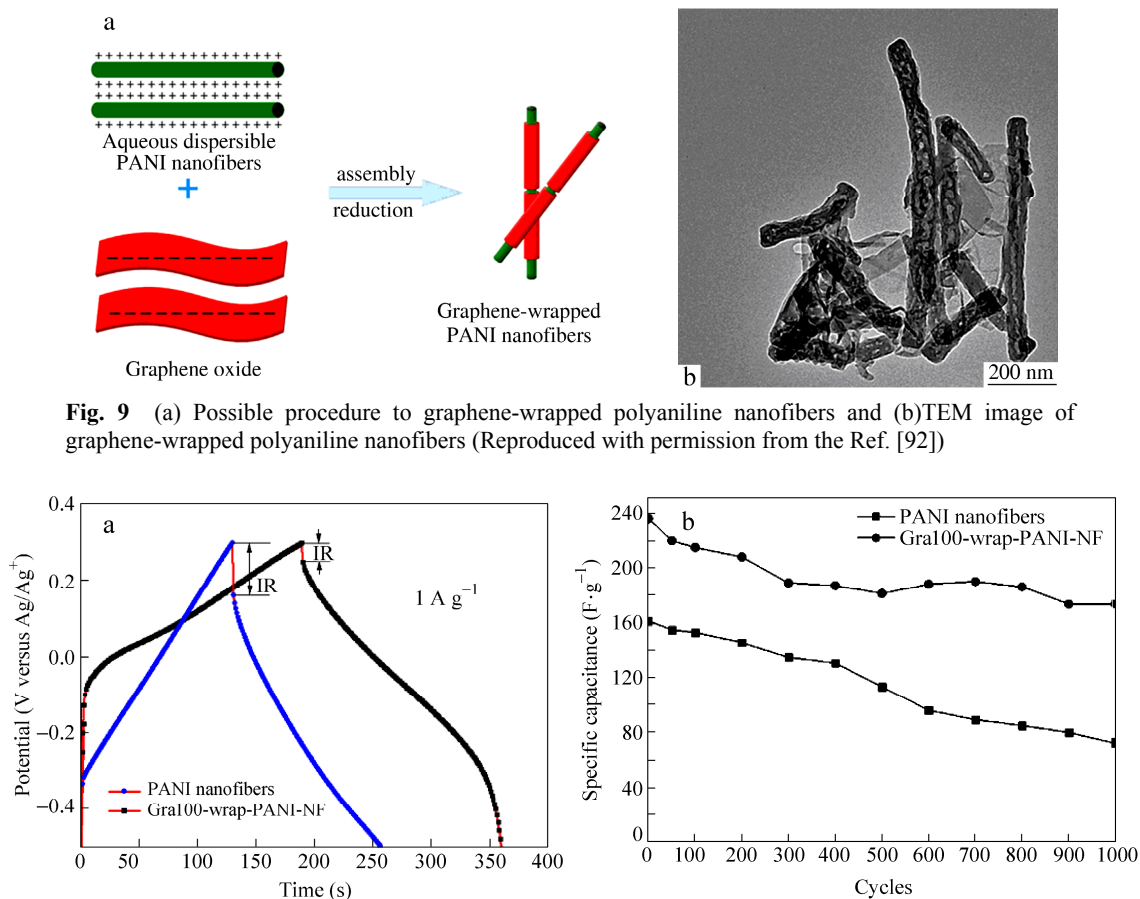


Fig. 10 (a) Galvanostatic charging/discharging curves and (b) cycle stabilities of pristine polyaniline nanofibers and graphene-wrapped polyaniline nanofibers Gra100-wrap-PANI-NF (Reproduced with permission from the Ref. [92]).

Gra100-wrap-PANI-NF represents the mass ratio of polyaniline nanofibers to graphene oxide is 1000:100.

Cathode Material for Lithium Battery

Rechargeable lithium-ion batteries attract more and more attention, due to ever-increasing demands for consumer devices such as mobile phones, personal computers and various electric vehicles^[93–103], therefore, it is of great significance to develop high-energy-density rechargeable batteries. A potential way to improve the performance of electrode materials of lithium-ion batteries is introduction of conducting polymers^[104]. Up to now, many electrode materials have been developed, *e.g.*, $\text{SnO}_2/\text{polypyrrole}$ ^[105], sulphur/polypyrrole^[106], $\text{LiMn}_2\text{O}_4/\text{polypyrrole}$ ^[107], $\text{LiFePO}_4/\text{polypyrrole}$ ^[108, 109], $\text{LiV}_3\text{O}_8/\text{polypyrrole}$ ^[110, 111], $\text{LiV}_3\text{O}_8/\text{polyaniline}$ ^[112], $\text{Li}_2\text{SnO}_3/\text{polyaniline}$ ^[113], polyaniline/ TiO_2 ^[114] and $\text{V}_2\text{O}_5/\text{polyaniline}$ ^[115], which show improved cycling performance in lithium battery.

Cao *et al.*^[116] reported a novel electrode material for lithium battery with long cycle life through self-assembled polyaniline nanotubes for sulfur encapsulation, it could retain a discharge capacity of $837 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ after 100 cycles, indicating an excellent cyclic life. Rye *et al.* prepared polyaniline films doped with Li salt and protonic acid, showing capacity of almost $90 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ at 100th cycle in lithium secondary battery test^[117, 118]. Gu *et al.* prepared polyaniline/ carbon nanotube array composites for lithium-ion battery cathodes, giving a capacity of $48 \text{ mA} \cdot \text{h} \cdot \text{g}$ at 260 C rates^[119].

Huang *et al.*^[120, 121] reported cathode materials for lithium-ion batteries, where a composite was formed from polyaniline and carbon-coated LiFePO_4 (C-LFP) *via* the H-bond interaction between the H atom of the $-\text{NH}^{3+}$ group in polyaniline and the O atom in LiFePO_4 particles. The composite exhibits a *ca.* 15% capacity enhancement at 0.2 C and 40% enhancement at 5 C compared to the parent C-LFP.

We employed the aqueous dispersed polyaniline nanofibers^[86] as cathode of the lithium-oxygen battery, as shown in Fig. 11, at a current density of $0.05 \text{ mA}/\text{cm}^2$, after an initial degradation from $3260 \text{ mA} \cdot \text{h}/\text{g}$ to $2320 \text{ mA} \cdot \text{h}/\text{g}$ polyaniline (PANI) during the first three cycles, the discharge capacity kept relatively stable in the next 27 cycles with only a 4% loss. The initial large degradation may be due to the deactivation of polyaniline nanofibers directly exposed in the gas phase.

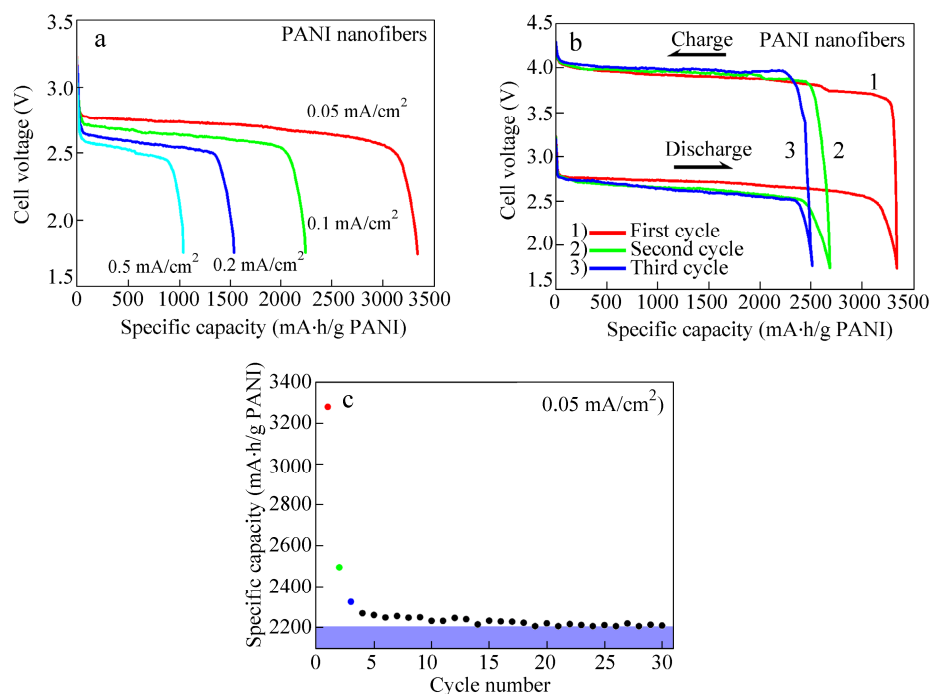


Fig. 11 The discharge curves (a), charge-discharge curves (b) and discharge capacities versus cycle number (c) for the lithium-oxygen battery based on polyaniline nanofibers cathode at current density of $0.05 \text{ mA}/\text{cm}^2$ (Reproduced with permission from the Ref. [86])

The scan rate for cyclic voltammograms is $20 \text{ mV}/\text{s}$.

Application on Corrosion Protection

Intrinsically conducting polymers such as polyaniline^[122, 123], polypyrrole^[124, 125], polythiophene^[126, 127] and polyindole^[128] *etc.*, have been successfully used for anti-corrosion of various metals, not only for their excellent anticorrosion capability, but also for their environment friendly property free of toxic heavy metals, which may open a new route for environmental friendly anti-corrosion materials^[129–137]. Polyaniline is recognized to be one of the best pigments for the anti-corrosion coatings due to their excellent environment stability and unique redox property^[138–141].

Ever since DeBerry^[142] found that stainless steel electrodes coated with thin layers of polyaniline remained passive in acid solutions, polyaniline has been investigated for corrosion protection of various metals, such as mild steel^[143, 144], stainless steel^[145–149], iron^[150–155], copper^[9], zinc^[156, 158], aluminum^[159, 160] and Mg-Li alloy^[161] *etc.* The increasing environmental considerations make the research on anti-corrosion coatings shift from solvent-based systems to water-based systems^[162, 163]. Kalendova *et al.*^[164] claimed that polyaniline dispersions can be utilized to prepare the water-based corrosion protection coating in a form of dispersion, this indicated the water-borne anti-corrosive coatings can be easily obtained through the addition of water-based polyaniline to water-borne resin. Liu *et al.*^[165] reported the water-borne conducting polyaniline anti-corrosion coating, where different contents of polyaniline/partially phosphorylated poly(vinyl alcohol) (PANI/P-PVA) spherical nanoparticles were dispersed in water-based epoxy resin emulsion. They claimed that PANI/P-PVA coating containing 2.5 wt% of PANI was highly protective in comparison with that containing 2.5 wt% PANI emeraldine salt. Bagherzadeh *et al.*^[166] reported in an epoxy resin coating with excellent corrosion protection properties even only 0.02 wt% nanoscale polyaniline was added.

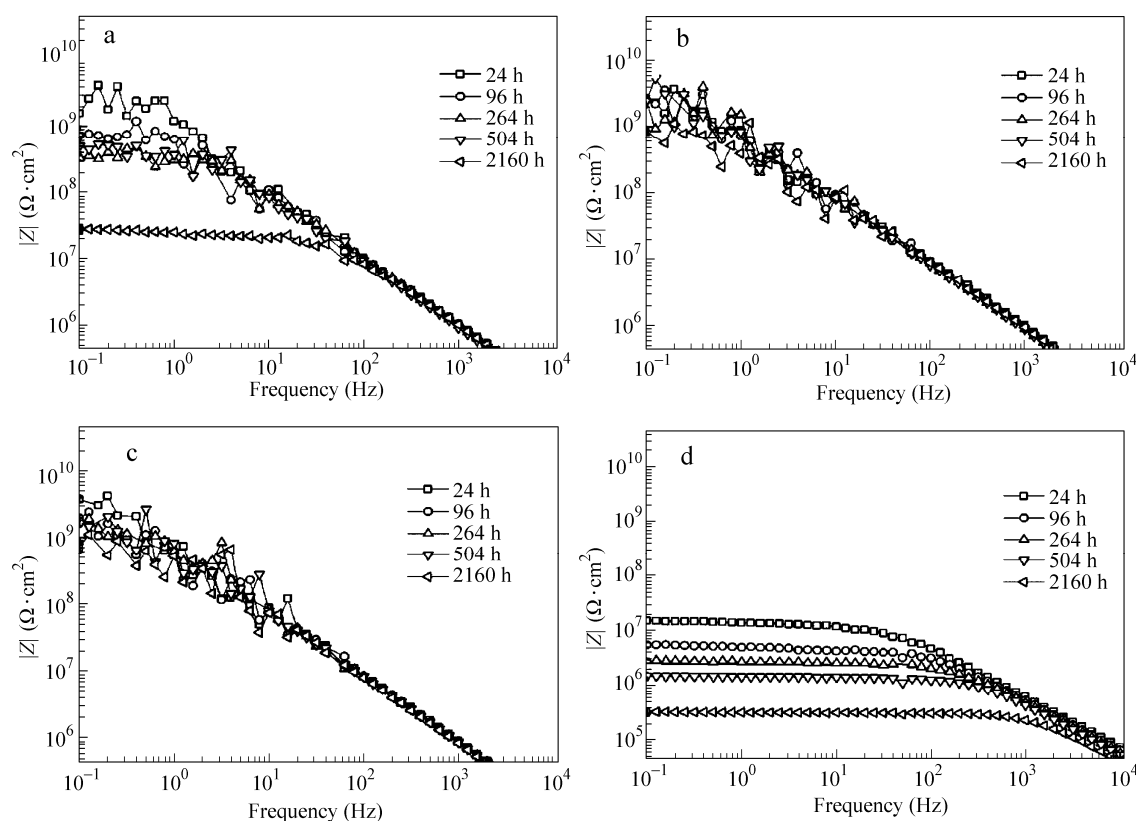


Fig. 12 Impedance plots for steel coated with water-borne anti-corrosion coating with different contents of polyaniline after different immersion time periods, (a) 0 wt%, (b) 0.1 wt%, (c) 1.0 wt% and (d) 3.0 wt% (Reproduced with permission from the Ref. [167])

We prepared a water-borne conducting polyaniline anti-corrosion coating^[167], where polyaniline doped with phosphate containing ethylene units was used as anti-corrosive additive and water-borne epoxy was used as matrix. Figure 12 shows the impedance plots for steel coated with water-borne anti-corrosion coating with different contents of polyaniline after different immersion time periods, it can be seen that the value of $|Z|_{0.1\text{Hz}}$ decreased from initial $1.6 \times 10^9 \Omega \cdot \text{cm}^2$ to $2.8 \times 10^7 \Omega \cdot \text{cm}^2$ for pure water-borne epoxy (0 wt%), however, no obvious change for anti-corrosion water-borne coatings, indicating that water-based polyaniline can improve the anti-corrosion performance.

The coating was immersed in 3.0 wt% NaCl solution for different time periods, as shown in Fig. 13, the peaks at 710.7 eV and 725 eV were found both in the water-borne epoxy resin-coated and the corrosive coating-coated steel specimens, indicating that Fe_2O_3 film was formed, since the peak at 710.7 eV and 725 eV can be ascribed to $\text{Fe } 2\text{p}^{3/2}$ and $\text{Fe } 2\text{p}^{1/2}$ of Fe_2O_3 , respectively^[154]. The strong peaks at 706.8 eV and 720 eV ascribed to iron^[126, 127] can be obtained after 19 min for water-borne epoxy resin, whereas they were found in a shorter time (5 min) for anti-corrosion coatings, suggesting that the polyaniline accelerates the formation of a thinner and compact protective passive layer and prevents further corrosion of steel.

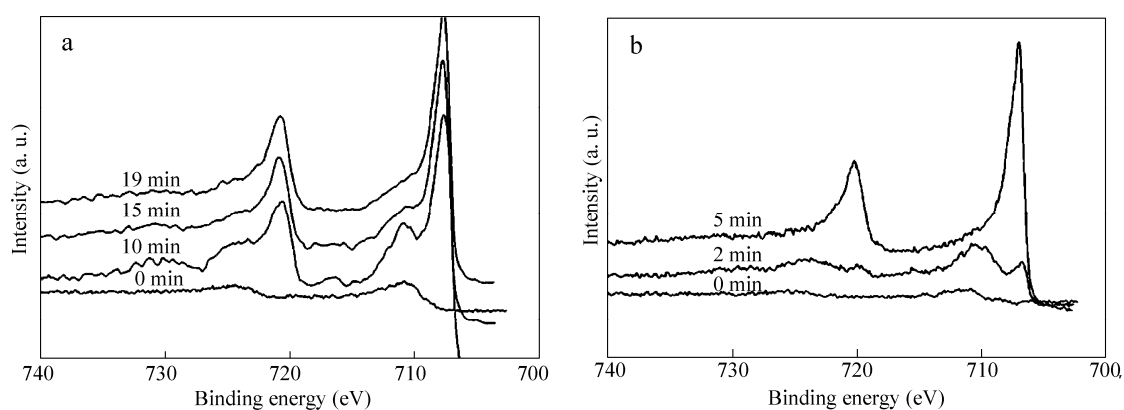


Fig. 13 XPS spectra of Fe 2p depth profiles for water-borne epoxy resin-coated mild steel (a) and anti-corrosion coatings with 1 wt% of polyaniline coated mild steel (b) after different immersion time periods in 3.0 wt% NaCl solution (Reproduced with permission from the Ref. [167])

The element P from phosphate ester dopant anion was found in the anti-corrosion coating-coated mild steel, since the peak at 133.5 eV can be ascribed to $\text{P } 2\text{p}^{3/2}$ (shown in Fig. 14), implying the occurrence of redox process of polyaniline. An insoluble phosphate ester anion-iron salt was formed and it further passivated the mild steel. In fact, the corrosion protection performance of polyaniline with dopants like phosphoric^[168–171], hydrochloric^[172–174], phosphonic^[175] and sulfonic acids^[176–181] has been reported in polyaniline solvent-system corrosion protection coatings.

Water-borne polyaniline anticorrosion coatings were also prepared once the aqueous dispersed polyaniline nanofibers were added to the epoxy resin, where nanofibrous polyaniline was prepared using ferric nitrate as oxidant and phosphate ester containing one ethylene unit as dopant^[182]. Another water-based polyaniline corrosion protection coating^[183] was also obtained by adding water soluble conducting polyaniline to the water-based polyurethane, where the resin was synthesized using polyethyleneglycol adipate or polybutyleneglycol adipate as soft segment and trimethylolpropane was used as internal crosslinking agent to improve the mechanical performance of the film. The strong H-bond between the water-borne polyaniline and polyurethane formed a semi-interpenetrating network and improved largely the anti-corrosive properties.

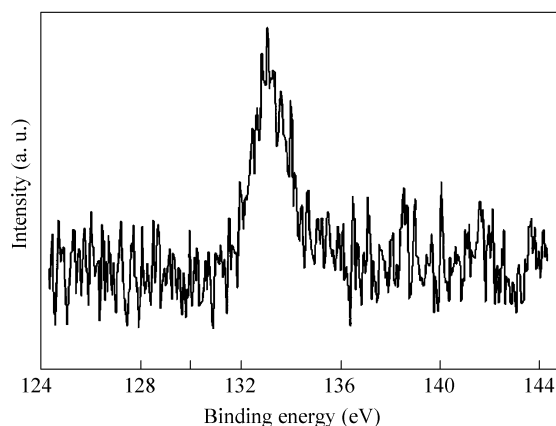


Fig. 14 XPS P2p spectrum of anti-corrosion coating with 1 wt% of polyaniline coated mild steel (Reproduced with permission from the Ref. [167])

Ultraviolet Curable Coatings Containing Polyaniline

Since 1968, Germany's Bayer AG pioneered the use of ultraviolet (UV) curable technique, and developed the first generation of commercial UV curable coatings, in which unsaturated polyester resin was used as main UV group, styrene as active dilution agent and benzoin ether as photoinitiator. The UV coatings have achieved fast growth in coating market, especially in the last 20 years, their application has widened from the first market of furniture to fields including electronics, printing, automotive, medic devices and optical fibers, due to their fast production rates, low temperature cure and volatile organic compound reduction. However, in the traditional UV-curable coating system, the reactive diluents used to reduce the viscosity have strong odor, toxicity and cause skin irritation. In order to reduce the use of volatile organic compounds and reactive diluents, water-borne UV curable coatings have been developed recently.

Based on water-borne conducting polyaniline, an eco-friendly UV curable coating has been developed. The pH value of water-borne conducting polyaniline should be ranged from 5 to 6, since the conducting polyaniline can be de-doped by alkali compounds. Water-borne UV curable unsaturated resins can be divided into anionic, cationic and non-ionic types, based on different hydrophilic groups. Considering the acidic system of water-borne conducting polyaniline, the suitable water-borne UV curable resin must be cationic or non-ionic type, since anionic resin can deteriorate the electrical conductivity and even demulsificate the water-borne polyaniline. Cationic water-borne urethane acrylate^[184] was prepared using diethanolamine or its derivatives as hydrophilic chain extender and acrylate monomer containing one hydroxyl as blocking agent, the product was obtained after neutralization by acid. We prepared water-borne antistatic coatings by adding water-based conducting polyaniline to cationic or non-ionic water-borne urethane acrylate^[185], where an excellent transparent antistatic film with 1.8×10^6 ohm/sq was found after UV curing process (Fig. 15). Compared with traditional solvent-type heat-curable antistatic coatings, this coating owns excellent merits, such as, surface electric resistance can easily be adjusted from 1×10^3 ohm/sq to 1×10^9 ohm/sq, fast and completely curable with a speed of 20–26 M/min, saving energy by 70%, everlasting antistatic properties with rate of rise 1.3%–8% after one year. A water-borne UV-thermal dual-curable anti-corrosion coating^[186, 187] was also reported, in which water-borne polyaniline was added as anti-corrosion pigment to the cationic or non-ionic water-borne urethane acrylate, polyurethane resin and hydrophilically-modified polyisocyanate hardening agent to prepare a novel anti-corrosion coating, the dual networks were formed after 15–30 s UV-curing and then 2–5 min heat-curing. A satisfied anti-corrosion effect with over 570 h salt fog tests was found. Compared with the traditional solvent-type anti-corrosive coatings, this water-borne coating is no doubt eco-friendly and energy saving.

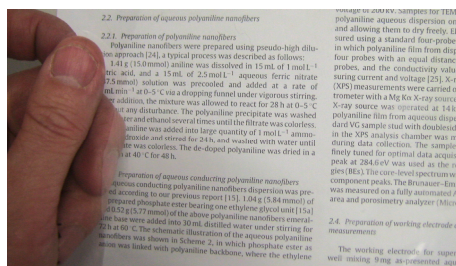


Fig. 15 Photograph of antistatic film based on water-borne conducting polyaniline

CONCLUSIONS AND OUTLOOK

With the increasing environmental concern, eco-friendly water-based polyaniline is showing increasing importance compared with its solvent analogue. Water-based polyanilines with various structure and morphology have been prepared by counter-ion induced strategy, the water-borne polyaniline nanoparticles showed diameters from 20 nm to 80 nm, and the electrical conductivity can reach as high as $25 \text{ S} \cdot \text{cm}^{-1}$ which was comparable with that of solvent-based systems. Water-based polyaniline nanofibers with diameter of 17–26 nm and electrical conductivity of $32 \text{ S} \cdot \text{cm}^{-1}$ were also obtained using the same method. Furthermore, as an active electrode material, it can give a specific capacitance as high as $160 \text{ F} \cdot \text{g}^{-1}$ in organic electrolytes.

Even though much progress has been made, further development of water borne polyaniline is full of challenge, detailed work is necessary to improve the electrical conductivity and electrochemical cyclability for future applications, such as anti-static application, electrode material for lithium battery or supercapacitor, also the long-term anti-corrosion performance for the water-borne polyaniline coatings needs further improvement, since the compact and adhesion of the water-borne coating is still an unsolved problem.

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