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ORIGINAL PAPER

Preparation and dedoping-resistant effect of self-doped polyaniline/cellulose fibers (SPANI/CF) hybrid

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Abstract Self-doped polyaniline/cellulose fibers (SPANI/CF) hybrid was in situ prepared by copolymerization of aniline and metanilic acid in presence of cellulose fibers to improve its dedoping-resistant ability. The results indicated that the SPANI/CF hybrid was remarkably more resistant to dedoping by alkaline aqueous solution than the polyaniline/cellulose fibers (PANI/CF) hybrid. Self-doping did not increase the electrical conductivity of the hybrid, but increased its flame retardancy. Both the electrical conductivity and oxygen index of the SPANI/CF hybrid decreased after ammonia soaking treatment, and the color changed gradually from green to bluish violet with increase of the ammonia concentration. The original (non-dedoped) and dedoped SPANI/CF and PANI/CF hybrids were characterized by attenuated total reflection (ATR) Fourier-transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM) analyses, revealing the occurrence of deprotonation during ammonia soaking treatment. Compared with the PANI/CF hybrid, additional ring substitution with sulfo groups was probably responsible for the significantly better dedoping-resistant ability of the SPANI/CF hybrid.

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Introduction

In the last decade, some studies have shown that conducting polymers such as polyaniline (PANI), polypyrrole (PPy), and poly(3,4-ethylenedioxythiophene) (PEDOT) can be deposited onto cellulose fibers to prepare conductive paper composites via in situ chemical oxidation polymerization (Johnston et al. 2005; Huang et al. 2005a, b; Mihranyan et al. 2008; Ding et al. 2010a, b; Li et al. 2010a, b; Chen et al. 2011; Sasso et al. 2011; Goto 2011; Goto and Kawashima 2012; Youssef et al. 2012; Wang et al. 2013). Furthermore, PPy and PANI also can be in situ deposited onto clay to prepare conductive clay, which can then be coated onto the paper surface to obtain conductive paper (Kang and Ni 2008; Saravanan et al. 2014).

Research has also been carried out on the flame-retardation effect of PANI coating deposited on cellulose paper. A study showed that cellulose fibers with deposited PANI yielded hollow carbonaceous microtubes after burning (Stejskal et al. 2005). In our recent studies, the flame retardancy of a paper composite with deposited PANI doped with three inorganic acids, i.e., sulfuric acid, hydrochloric acid, and phosphoric acid (Wu et al. 2013), two organic acids, i.e., *p*-toluenesulfonic acid (PTSA) and sulfosalicylic acid (SSA; Mao et al. 2014), and phytic acid (Zhou et al. 2015) was investigated. The results showed that PANI-deposited cellulose fibers can be used to manufacture dual-function paper with both electrical conductivity and flame retardancy.

One of the drawbacks of PANI-deposited cellulose fibers is their low dedoping-resistant ability, i.e., high electrical conductivity loss when soaked in alkaline aqueous solution. This drawback limits the application of PANI-deposited cellulose fibers to some extent, because sheet-forming and immersion operations are necessary during production and application of paper; For instance, the paper industry is converting many mills from acidic to alkaline papermaking processes. As another example, decreasing the sensitivity of PANI/cellulose paper composite to alkaline substances would further expand its application fields to, e.g., sensors, actuators, electrodes, etc. So, improvement of the dedoping-resistant ability of PANI-deposited cellulose fibers is a significant issue. In our previous studies, secondary doping with sulfuric acid (Qian et al. 2010) and organic sulfo-acid doping (Mao et al. 2014) were applied to partly solve this problem. However, there is room for further improvement in the dedoping-resistant ability of PANI-deposited cellulose fibers.

Self-doped polyanilines (SPANIs) are PANI derivatives that bear negatively charged functional groups, and they have many properties different from those of the parent PANI (Malinauskas 2004). Since 1990, many papers about SPANIs have been published (Yue and Epstein 1990; Bergeron et al. 1990; Lukachova et al. 2003), dealing with their synthesis and properties. Involvement of aminobenzenesulfonic acid monomers in the polymer chain provides an extension of SPANI electroactivity in neutral and alkaline solutions up to pH 12.

In the present study, self-doped polyaniline/cellulose fibers (SPANI/CF) hybrid was in situ prepared in presence of cellulose fibers in aqueous medium consisting of self-doping monomer (metanilic acid, MAA) and aniline (AN), and its alkaline soaking resistance was investigated. Attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM) analyses were used to reveal the dedoping-resistant mechanism.

Experimental

Materials

Bleached softwood kraft pulp imported from Canada was obtained from Mudanjiang Hengfeng Co., Ltd., and was beaten by Valley beater to beating degree of 30° SR. Aniline (AN) monomer of chemical grade was purchased from Tianjin Tianli Chemical Reagents Co., Ltd., and was distilled under reduced pressure before use. Ammonium persulfate (APS) of chemical grade used as oxidant was purchased from Tianjin Yongda Chemical Reagents Development Center. Metanilic acid (MAA) of analytical grade was purchased from Tokyo Chemical Industry Co., Ltd. Hydrochloric acid (37 %) was purchased from Beijing Yili Fine Chemicals Co., Ltd. Sulfosalicylic acid (SSA) of analytical grade was purchased from Beijing Huateng Chemical Co., Ltd. Ammonia (25 %) was obtained from Tianjin Kermel Chemical Reagent Co., Ltd. All solutions were prepared from distilled water.

Preparation of SPANI/CF hybrid

The preparation procedure of SPANI/CF hybrid was as follows: 4 g (oven-dry weight) pulp fibers was placed in a three-necked flask in an ice bath with a certain amount of monomer (total molar mass of AN and MAA was 0.07 mol), and then hydrochloric acid was poured into the flask at a certain concentration to achieve pulp consistency of 1 %. After stirring for 20 min, APS solution was added dropwise into the reaction system slowly to start the oxidation polymerization reaction. The molar ratio of monomer to APS was 2:1. The reaction was conducted with continuous stirring for 105 min. For comparison, polyaniline/cellulose fibers (PANI/CF) hybrids doped with hydrochloric acid and sulfosalicylic acid (SSA) were also prepared according to almost the same procedure (Wu et al. 2013; Mao et al. 2014).

Dedoping operation

The hybrid prepared according to the above described procedure was fully washed to neutral with tap water, and soaked with a certain concentration of ammonia solution at room temperature for 1 h, then fully washed to neutral with tap water again.

Handsheet preparation

A handsheet with grammage of over 120 g/m^2 was made on a ZCX-200 handsheet former with diameter of 200 mm. The handsheet was pressed at 800 kPa for 5 min and dried at 105 °C for 10 min (5 min each side). The handsheet was conditioned at 23 °C and 50 % relative humidity for 24 h before testing.

Measurement of electrical conductivity (*k*)

Both the square resistance and bulk resistivity of the handsheets were measured by a four-point probe resistance tester and expressed as R (kΩ) and ρ (kΩ cm), respectively. Since the bulk resistivity (ρ) is related to the handsheet dimensions, the thickness (T) and basis weight (W) were measured beforehand. The conductivity k was expressed as the inverse of the bulk resistivity (ρ) in SI units of Siemens per meter (S/m), calculated using the equation $k = 1/10\rho$.

Measurement of oxygen index (OI)

Paper flame retardancy was determined in terms of the oxygen index (OI), which was measured on a JF-3 oxygen index meter made in China. The paper sample was cut into strips (120 mm × 15 mm), and then the strip was placed in the combustor, where a mixture of oxygen and nitrogen flows upwards. The volume content of oxygen was adjusted to keep the lowest oxygen concentration which just supported sustained burning. The oxygen index was expressed in volume percentage. Generally, an oxygen index of more than 25 % is considered to be satisfactory for flame retardancy of paper products (Wu et al. 2013; Mao et al. 2014).

FTIR analysis

Attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectra in the range of 600–4,000 cm^{-1} were recorded on an FTIR spectrometer equipped with an InspectIR microscope (Magna-IR 560 ESP, Nicolet Corp.). The crystal used in the ATR cell was Si. The resolution was 4 cm^{-1}, and 40 scans were averaged.

XPS characterization

XPS spectra were obtained using a *K*-Alpha X-ray photoelectron spectrometer (XPS) system, which was purchased from the Thermo Fisher Scientific Company. The paper samples were cut into small pieces (10 mm × 10 mm) and then fixed on the sample platform. An Al K$_\alpha$ X-ray source (1486.6 eV) was used. The vacuum in the analyzing chamber was 1.0×10^{-8} mbar during analysis. The analyzer was operated at 50 eV pass energy for survey spectra. Elemental atomic concentrations were calculated from the XPS peak areas. The C 1*s* peak at 285 eV was used as an internal standard to correct the peak positions. Data fitting was carried out by a least-squares routine supplied by the instrument manufacturer, using mixed Gaussian–Lorentzian peaks.

SEM observation

The hybrids were observed and images obtained using an FEI Quanta-200 environmental SEM. The samples were coated with gold before observation.

Results and discussion

Electrical conductivity and flame retardancy of SPANI/CF hybrid

Table 1 presents the electrical conductivity and OI values of the paper samples made from SPANI/CF and PANI/CF hybrids. It was found that the optimum molar ratio of MAA/AN for SPANI/CF hybrid preparation was 2:1. In the preparation system, part of the MAA would participate in the copolymerization reaction with AN, while the remaining MAA would be incorporated into the copolymer by doping. The optimum proportion of MAA as reactant monomer and dopant would be obtained when the molar ratio of MAA/AN is 2:1. This may explain why the MAA/AN molar ratio of 2:1 gave the highest electrical conductivity and OI values amongst the three different molar ratios of MAA/AN of 1.5:1, 2:1, and 2.5:1. The electrical conductivity of the paper sample made from SPANI/CF hybrid was lower than that of the paper sample made from SSA-PANI/CF hybrid, but very close to that of the paper sample made from HCl-PANI/CF hybrid. The OI value of the paper sample made from SPANI/CF hybrid was higher than those of the paper samples made from both HCl-PANI/CF and SSA-PANI/CF hybrids.

The paper samples made from SPANI/CF and HCl-PANI/CF hybrids were stored in natural environment,

Table 1 Electrical conductivity (*k*) and OI values of paper samples made from SPANI/CF and PANI/CF hybrids

Sample	*k* (S/m)	OI (%)
Handsheet from MAA1.5-SPANI/CF hybrid (molar ratio of MAA/AN = 1.5:1)	2.29 ± 0.26	30.51 ± 0.16
Handsheet from MAA2.0-SPANI/CF hybrid (molar ratio of MAA/AN = 2:1)	3.16 ± 0.25	34.21 ± 0.10
Handsheet from MAA2.5-SPANI/CF hybrid (molar ratio of MAA/AN = 2.5:1)	0.014 ± 0.49	26.30 ± 0.19
Handsheet from HCl-PANI/CF hybrid	4.63 ± 0.22	25.25 ± 0.11
Handsheet from SSA-PANI/CF hybrid	19.5 ± 0.18	29.19 ± 0.05

and the electrical conductivity values were measured every week to investigate the environmental stability of the paper samples. As shown in Fig. 1, the electrical conductivity values of the paper samples made from both SPANI/CF and HCl-PANI/CF hybrids decreased gradually during the first 4 weeks of storage time, but remained basically unchanged thereafter. The results in Fig. 1 indicate that the paper samples made from both SPANI/CF and HCl-PANI/CF hybrids had very similar environmental conductivity stability. This shows that the decay of electrical conductivity resulted from oxidation rather than deprotonation (dedoping), in accordance with our previous research results (Zhou et al. 2015).

Dedoping-resistant effect of SPANI/CF hybrid

The SPANI/CF and PANI/CF hybrids were dedoped with different concentrations of ammonia solution to investigate their dedoping-resistant effect, and the results are shown in Table 2 and Figs. 2 and 3. The results in Table 2 show that the electrical conductivity of the paper sample made from the SPANI/CF hybrid gradually decreased with increasing concentration of the ammonia solution, but it still could be detected even when the concentration of the ammonia solution reached 0.6 mol/L (pH value close to 11.5). However, the electrical conductivity of the paper samples made from HCl-PANI/CF and SSA-PANI/CF hybrids could not be detected when the concentration of the ammonia solution reached 0.1 and 0.4 mol/L, respectively. In addition, it is observed from Fig. 2 that the colors of the SPANI/CF and PANI/CF hybrids after ammonia soaking treatment changed gradually from green to bluish violet with increasing concentration of the ammonia solution. This provides further evidence that the hybrids were dedoped by ammonia solution. The electrical conductivity of the paper samples showed good correspondence with its color, i.e., the lighter the color, the lower the conductivity.

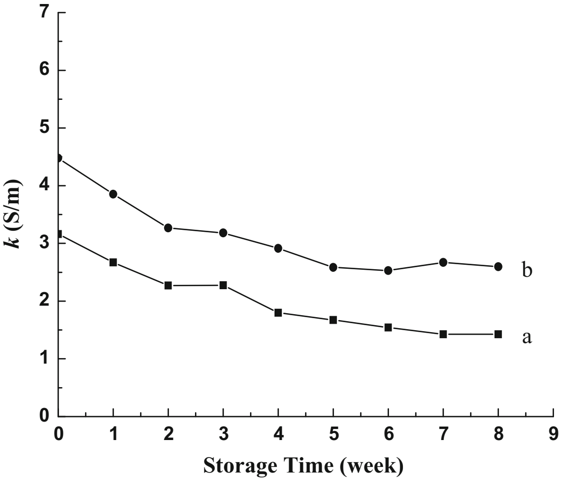

Fig. 1 Change of electrical conductivity (*k*) of paper samples made from SPANI/CF (*a*) and HCl-PANI/CF (*b*) hybrids with storage time

Table 2 Electrical conductivity (*k*) change of paper samples made from SPANI/CF and PANI/CF hybrids treated with different concentrations of ammonia solution

Ammonia concentration (mol/L)	*k* (S/m)		
	SPANI/CF	HCl-PANI/CF	SSA-PANI/CF
Control	3.16	4.63	19.5
0.1	3.06×10^{-1}	OR	3.11×10^{-1}
0.2	2.03×10^{-1}	OR	2.26×10^{-1}
0.3	3.81×10^{-2}	OR	2.48×10^{-3}
0.4	8.93×10^{-3}	OR	OR
0.5	5.53×10^{-3}	OR	OR
0.6	1.44×10^{-4}	OR	OR

OR indicates that the electrical conductivity (*k*) was too low to be obtained because the electrical resistance value was above the maximum range of the meter

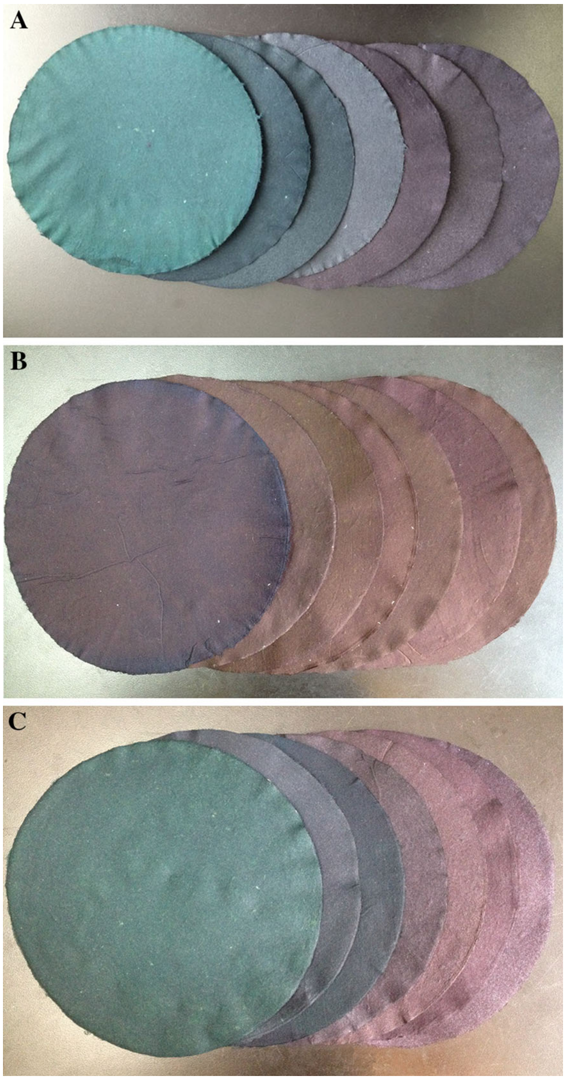

Fig. 2 Color change of paper samples made from SPANI/CF and PANI/CF hybrids treated with different concentrations of ammonia solution: **a** SPANI/CF, **b** HCl-PANI/CF, and **c** SSA-PANI/CF. Samples from *left* to *right*: control (untreated), treated with 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 mol/L ammonia solution. (Color figure online)

The results in Fig. 3 show that the OI value of the paper sample made from the SPANI/CF hybrid gradually decreased with increasing concentration of the ammonia solution, but could still reach flame-retardant grade (more than 26 %) even when the concentration of the ammonia solution reached 0.5 mol/L. However, the OI values of the paper samples made from HCl-PANI/CF and SSA-PANI/CF hybrids were close to 20 % (i.e., the OI value of the paper sample made from pure cellulose fibers) when the concentration of the ammonia solution reached 0.1 and 0.3 mol/L, respectively.

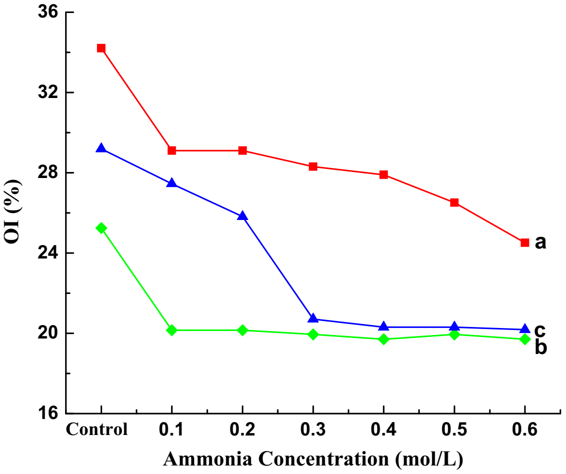

Fig. 3 OI change of paper samples made from SPANI/CF and PANI/CF hybrids treated with different concentrations of ammonia solution: *a* SPANI/CF, *b* HCl-PANI/CF, and *c* SSA-PANI/CF

These results for both the electrical conductivity and flame retardancy show that the SPANI/CF hybrid had excellent dedoping-resistant ability. Compared with the PANI on the HCl-PANI/CF and SSA-PANI/CF hybrids, the PANI on the SPANI/CF hybrid contained ionizable, negatively charged functional groups (i.e., sulfonic groups) in the structural backbone, which acted as inner doping anions bound to the PANI backbone (Malinauskas 2004). Thus, less anion exchange between the PANI and surroundings would take place during ammonia soaking treatment.

ATR-FTIR analysis

ATR-FTIR spectra of paper samples made from non-dedoped and dedoped (using ammonia solution concentration of 0.6 mol/L) SPANI/CF and PANI/CF hybrids are shown in Fig. 4. The band centered at around 1560 cm^{-1} was attributed to the fundamental vibration of aniline ring, while the band near 1490 cm^{-1} was assigned to the C–C aromatic ring-stretching vibration. The absorption band at about 1300 cm^{-1} corresponded to *p*-electron delocalization induced by protonation in PANI. The band characteristic of the conducting protonated form observed at 1243 cm^{-1} was interpreted as a $C–N^{+\cdot}$ stretching vibration in the polaron structure. The 1,2,4-

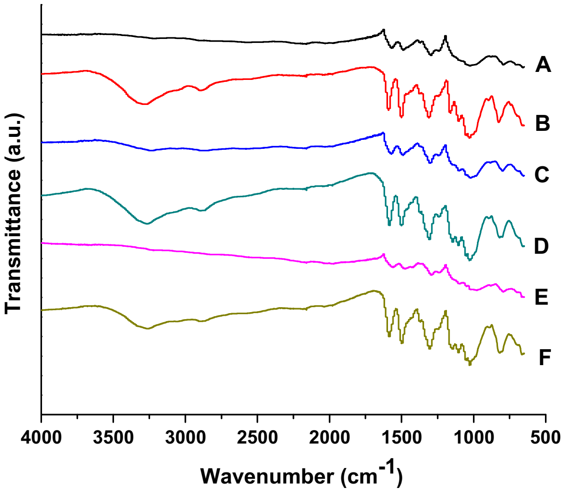

Fig. 4 ATR-FTIR spectra of paper samples made from SPANI/CF and PANI/CF hybrids: *A* non-dedoped HCl-PANI/CF, *B* dedoped HCl-PANI/CF, *C* non-dedoped SPANI/CF, *D* dedoped SPANI/CF, *E* non-dedoped SSA-PANI/CF, *F* dedoped SSA-PANI/CF

substitution pattern was revealed by the bands at 850 and 800 cm^{-1}. After dedoping with 0.6 mol/L ammonia solution, three prominent peaks in the region of 1010–1170 cm^{-1} attributed to the aromatic C–H in-plane bending modes were observed. For the SPANI/CF and SSA-PANI/CF hybrids, the presence of sulfonic groups attached to the aromatic rings was manifested by the peaks of S=O stretching vibration at 1100 cm^{-1}. After dedoping treatment, however, the peak of S=O stretching vibration was masked by the peak of the aromatic C–H in-plane bending modes.

It is interesting to note in Fig. 4 that the characteristic broad band around 3300 cm^{-1} attributed to the stretching of O–H groups in cellulose fibers and the band around 2880 cm^{-1} corresponding to the stretching of C–H groups in cellulose fibers disappeared for the SPANI/CF and PANI/CF hybrids, but reappeared after dedoping with ammonia solution. This indicates that a part of the PANI-coated cellulose fibers were exposed after dedoping treatment.

XPS analysis

The XPS results for the elemental atomic percentages and S/N and Cl/N ratios of the paper samples made from the non-dedoped and dedoped (with ammonia solution concentration of 0.6 mol/L) SPANI/CF and

Table 3 XPS results for elemental atomic percentages and S/N and Cl/N ratios of paper samples made from SPANI/CF and PANI/CF hybrids

Sample	C 1*s* (%)	Cl 2*p* (%)	O 1*s* (%)	N 1*s* (%)	S 2*p* (%)	S/N	Cl/N
A	74.59	1.55	13.39	10.47	–	–	0.148
B	80.13	0.15	9.96	9.75	–	–	0.015
C	69.87	0.6	15.91	10.91	2.71	0.248	0.055
D	71.28	0.39	15.81	10.47	2.05	0.196	0.026
E	60.01	–	28.72	8.66	2.61	0.301	–
F	67.98	–	25.56	9.06	0.58	0.064	–

A non-dedoped HCl-PANI/CF, *B* dedoped HCl-PANI/CF, *C* non-dedoped SPANI/CF, *D* dedoped SPANI/CF, *E* non-dedoped SSA-PANI/CF, *F* dedoped SSA-PANI/CF

Table 4 N 1*s* XPS deconvolution results of paper samples made from SPANI/CF and PANI/CF hybrids

Sample	–N= (%)	–NH (%)	–N$^+$= (%)	–N$^+$– (%)	N$^+$/N
A	8.07	66.36	15.91	9.66	0.256
B	6.52	84.03	2.59	6.86	0.094
C	3.94	71.81	13.92	10.32	0.242
D	14.64	68.36	9.55	7.44	0.170
E	–	57.12	29.86	13.02	0.429
F	–	73.94	14.38	11.68	0.261

A non-dedoped HCl-PANI/CF, *B* dedoped HCl-PANI/CF, *C* non-dedoped SPANI/CF, *D* dedoped SPANI/CF, *E* non-dedoped SSA-PANI/CF, *F* dedoped SSA-PANI/CF

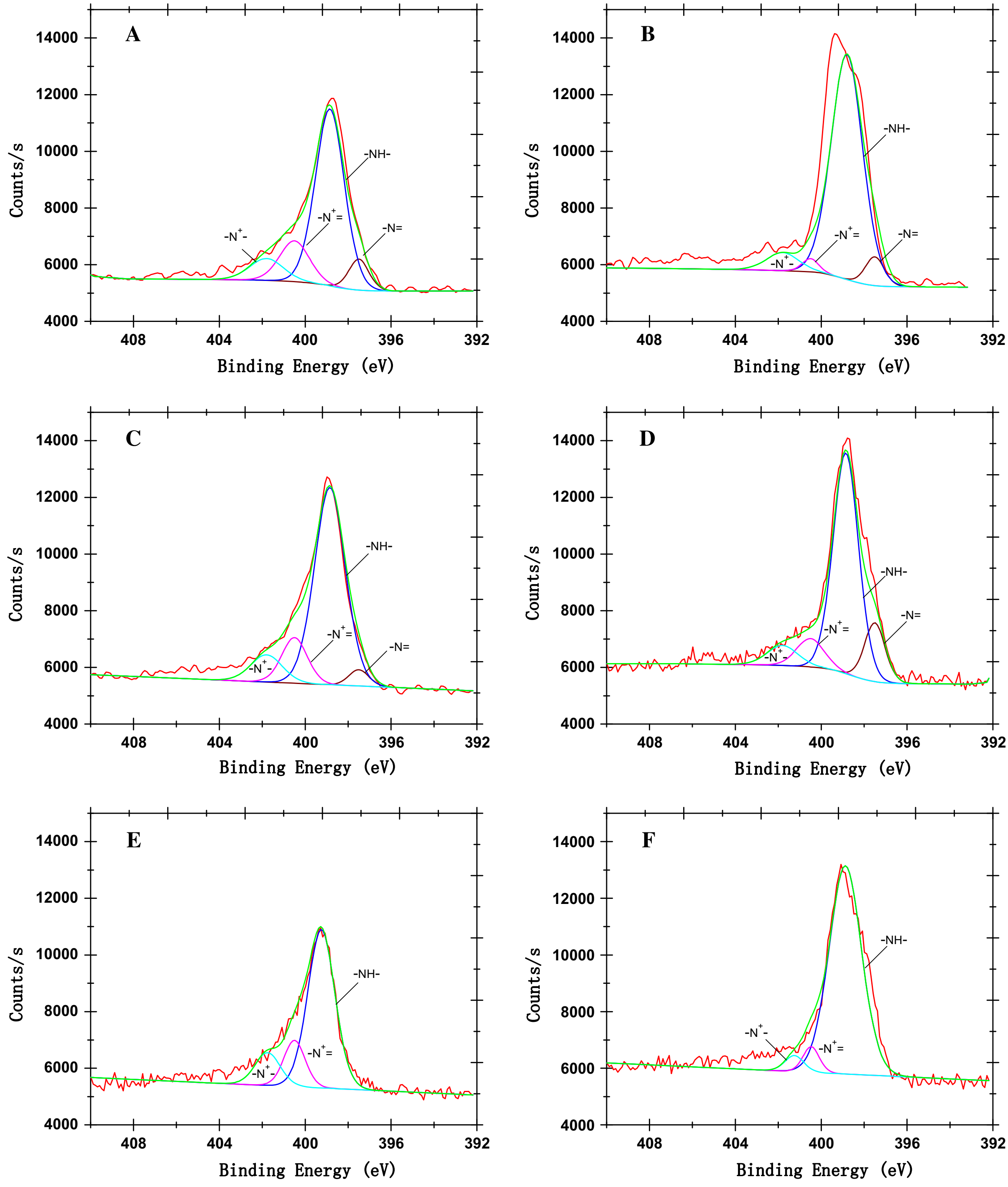

Fig. 5 XPS N 1*s* spectra of paper samples made from SPANI/CF and PANI/CF hybrids: **A** non-dedoped HCl-PANI/CF, **B** dedoped HCl-PANI/CF, **C** non-dedoped SPANI/CF, **D** dedoped SPANI/CF, **E** non-dedoped SSA-PANI/CF, **F** dedoped SSA-PANI/CF

PANI/CF hybrids are presented in Table 3. It was observed that the atomic ratios of sulfur to nitrogen (S/N) and/or chlorine to nitrogen (Cl/N) of both the SPANI/CF and PANI/CF hybrids decreased after ammonia soaking treatment, indicating that the samples were dedoped to varying degrees. However, the

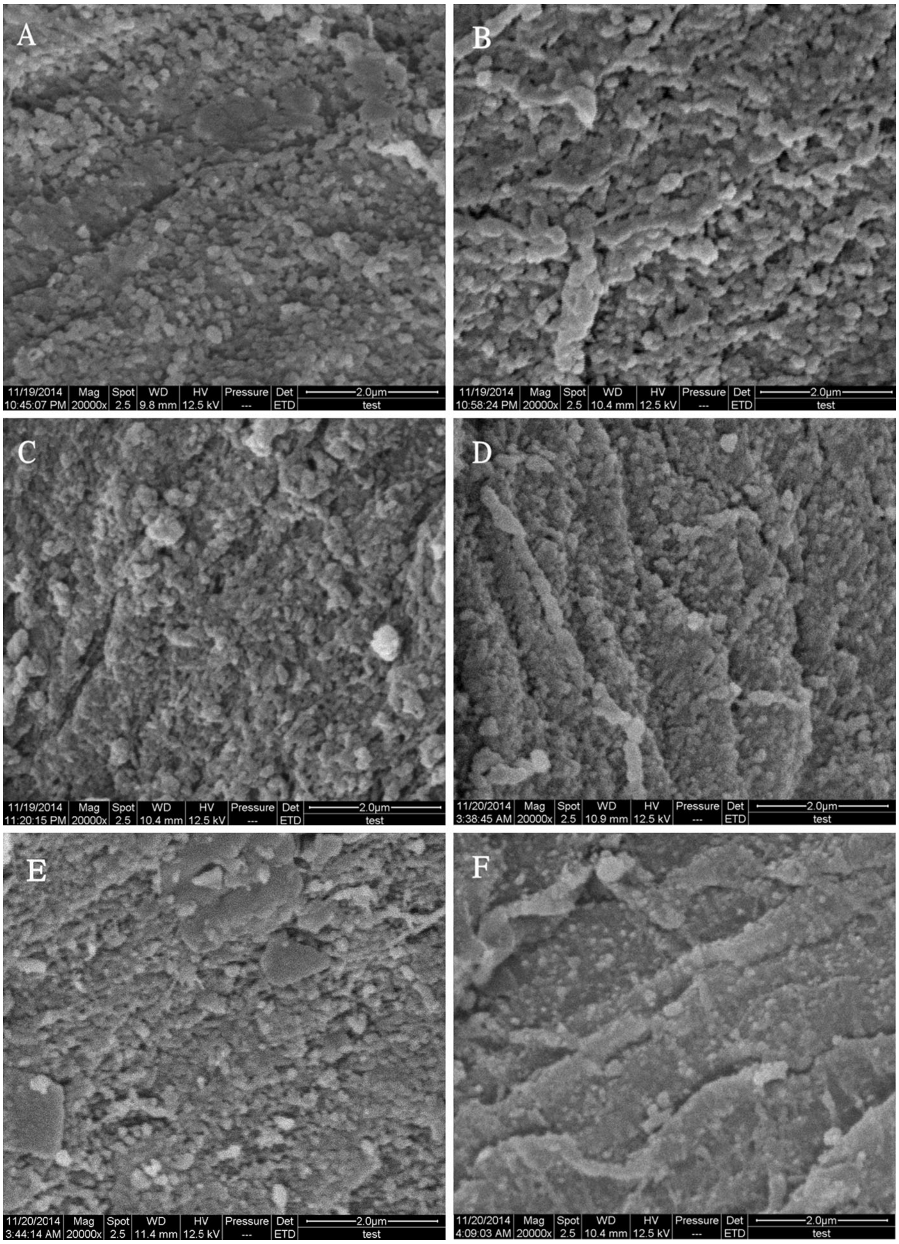

Fig. 6 SEM images of SPANI/CF and PANI/CF hybrids: **A** non-dedoped HCl-PANI/CF, **B** dedoped HCl-PANI/CF, **C** non-dedoped SPANI/CF, **D** dedoped SPANI/CF, **E** non-dedoped SSA-PANI/CF, **F** dedoped SSA-PANI/CF

S/N ratio of the SPANI/CF hybrid decreased much less than that of the SSA-PANI/CF hybrid. This shows that the SPANI/CF hybrid was more dedoping resistant than the SSA-PANI/CF hybrid, which fits well with the electrical conductivity and flame retardancy results.

The N 1*s* XPS deconvolution results of the paper samples made from non-dedoped and dedoped SPANI/CF and PANI/CF hybrids are presented in Table 4 and Fig. 5. The XPS N 1*s* spectra could be deconvoluted into four distinct curves, which were related to the benzenoid amine (–NH) at 398.85 eV, the quinoid imine (–N=) at around 397.5 eV, and two positively charged nitrogen atoms: the protonated imine ($–N^{+}=$) and the protonated amine ($–N^{+}–$) at 400.5 and 401.8 eV, respectively. These two N^{+}

species were related to the existence of different protonation environments, which led to formation of a polaron (at lower eV) and a bipolaron (at higher eV) (Li et al. 2010b; Wu et al. 2013; Mao et al. 2014). The ratio of protonated nitrogen (N^+, i.e., the sum of $–N^+=$ and $–N^+–$) to total nitrogen (N^+/N) represents the doping level. It was noted that the N^+/N ratio of both the SPANI/CF and PANI/CF hybrids decreased after dedoping treatment, indicating that the doping levels of all samples decreased to varying degrees. However, the N^+/N ratio of the SPANI/CF hybrid decreased much less than that of the HCl-PANI/CF hybrid. This fact indicates that the SPANI/CF hybrid was more dedoping resistant than the HCl-PANI/CF hybrid, which fits well with the electrical conductivity and flame retardancy results.

SEM analysis

SEM images of the non-dedoped and dedoped (with ammonia solution concentration of 0.6 mol/L) SPANI/CF and PANI/CF hybrids are shown in Fig. 6. It is observed from images A to D that cellulose fibers were fully coated with PANI particles, and the surfaces of the doped MAA-SPANI/CF and HCl-PANI/CF hybrids were looser and more porous than those of non-dedoped ones, indicating that the hybrids were apparently etched by ammonia during the dedoping treatment. However, it seems that the SPANI/CF hybrid was only slightly affected compared with the HCl-PANI/CF hybrid. Compared with image E, image F shows less pores, which is due to the difficult removal of organic sulfonic acids (SSA) from the SSA-PANI/CF hybrid. These SEM observations are in good agreement with the ATR-FTIR and XPS analyses above.

Conclusions

SPANI/CF hybrid obtained by in situ copolymerization of AN and MAA in presence of cellulose fibers was remarkably more resistant to dedoping by alkaline aqueous solution than PANI/CF hybrids. Self-doping did not increase the electrical conductivity of the hybrid, but increased its flame retardancy. Both the electrical conductivity and oxygen index (OI) of the SPANI/CF hybrid were decreased after ammonia soaking treatment, and the color changed gradually from green to bluish violet with increase of the ammonia concentration. Occurrence of deprotonation during ammonia soaking treatment was confirmed by ATR-FTIR, XPS, and SEM analyses. Compared with the PANI/CF hybrids, additional ring substitution with sulfo groups was probably responsible for the significantly better dedoping-resistant ability of the SPANI/CF hybrid.

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