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# A Facile Construction of Supramolecular Complex from Polyaniline and Cellulose in Aqueous System

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S *Supporting Information*

Recently, polyaniline (PANI) has attracted much attention due to its simple and facile synthesis, good environment stability, and controllability,[1,2] and PANI materials offer enticing prospects on the basis of new findings such as conductive thin films, nanorods, chiral materials, nanofibers, helical nanofibers, hollow fibers, hollow nanotubes, metallic polymers, and organic/inorganic hybrids.[3,4] Conducting polymers offer the promise of achieving a new generation of materials which exhibit the good electrical and optical properties and which retain the attractive mechanical properties and processing advantages.[5] To improve the processability and mechanical properties of PANI, numerous attempts in blending with conventional polymers, depositing PANI on microporous cellulose acetate membranes using in situ chemical polymerization techniques, and conducting PANI graft copolymer have been reported.[6] It is worth noting that Jean-Marie Lehn has introduced the term "supramolecular chemistry", which bearing on the organized entities of higher complexity that result from the association of two or more chemical species held together by intermolecular forces.[7] The supramolecular complex constructed through the noncovalent interaction has attracted increasing interest because of their fascinating properties, and new routes to fabricate supramolecular copolymer pairs by hydrogen bonding, dual-responsive supramolecular polymer gel and noncovalently connected micelles have been opened up.[8] Cellulose is a prime candidate for replacing oil-based feedstocks, but only through the use of specific solvents which disrupt hydrogen bonds cellulose can be dissolved.[9] In our laboratory, 7 wt % NaOH and 12 wt % urea aqueous solution with cooling have been used to rapidly dissolve cellulose. The good dissolution of cellulose in the aqueous system at low temperatures arises as a result of a self-assembly process among solvent (NaOH, urea, and water) and the cellulose macromolecules, leading to the formation of an inclusion complex (IC) surrounded by urea through hydrogen bonds.[10] Furthermore, from the cellulose dope, various regenerated cellulose fibers, films, microspheres, and hydrogels have been fabricated successfully by using a simple and "green" process.[11] It is noted that noncovalent interactions in aqueous media are important for obtaining a better understanding and control of supramolecular chemistry.[12] Moreover, PANI doped by phosphate ester having short hydrophilic segment exhibits the certain dispersion in water.[13] A worthwhile endeavor would be to utilize hydrogen-bonding interactions between PANI and cellulose to induce dissolution of PANI and then to construct advanced materials associated with the two components. In the present work, supramolecular complex from hydrophilic cellulose and hydrophobic PANI in the NaOH/urea aqueous solution at low temperature through rearrangement of hydrogen bonds were constructed for the first time.

The cellulose solution was prepared by dissolving cellulose in 7 wt % NaOH/12 wt % urea aqueous solutions precooled to −12 °C, and then PANI doped with acidic phosphate ester was immediately dispersed to the cellulose solution to obtain a blue PANI/cellulose complexes solution within 5 min (Figure S1). Interestingly, PANI could not be dissolved in NaOH/urea aqueous solution without cellulose, suggesting that supramolecular complex formed from cellulose and PANI during the dissolution. In our findings, cellulose played an important role on the dissolution of PANI. The PANI/cellulose solution in the NaOH/urea aqueous system was stable for 1 month, whereas the original PANI solution turned into a suspension to delaminate within 1 day (Figure S1b). $^{13}$C NMR spectra of the cellulose solution and PANI/cellulose solution in 7 wt % NaOH/12 wt % urea/$D_2O$ are shown in Figure 1. The chemical shifts at 171.1 and 131.2 ppm of the PANI/cellulose solution were assigned to a quaternary carbon adjacent to the nitrogen atom and the aromatic ring tertiary carbons of the PANI backbone, respectively. These characterized peaks are similar to the $^{13}$C CP/MAS NMR spectra reported for PANI and the substituted PANI.[14] These results confirmed that PANI was dissolved well in the cellulose solution in the aqueous system. Most peaks for the cellulose in the PANI/cellulose solution were similar to those in the pure cellulose solution, confirming the existence of the cellulose IC in this system.[10] The chemical shifts of C1 (106.1 ppm), C4 (81.6 ppm), C2(76.3 ppm), and C6 (62.9 ppm) for cellulose in the solution indicated that the native cellulose was completely dissolved in the present solvent. As a result of the possible hydrogen-bond interactions between the −NH group of PANI and the −OH group in cellulose, the chemical shifts of C2 and C6 for cellulose in the PANI/cellulose complex system shifted to higher field than those in the cellulose solution by about 2.4 ppm. It was confirmed that the hydrogen-bonding sites between the cellulose and PANI chains were located on the hydroxyl groups of C2 and C6; these hydrogen bonds were slightly weaker than those between cellulose themselves, resulting in the chemical shifts moving upfield. The

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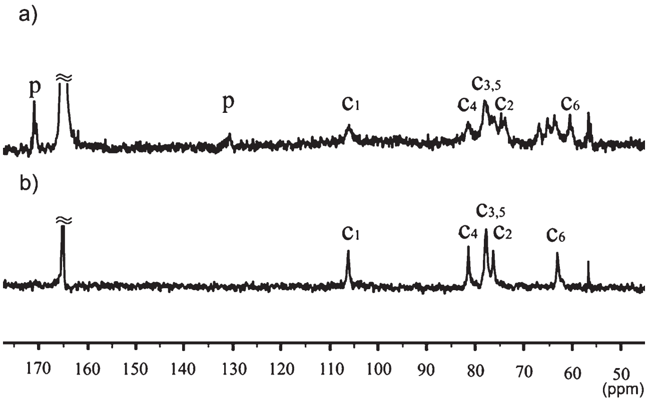

**Figure 1.** $^{13}$C NMR spectra of PANI/cellulose solution (a) and cellulose solution (b) in NaOH/urea aqueous system.

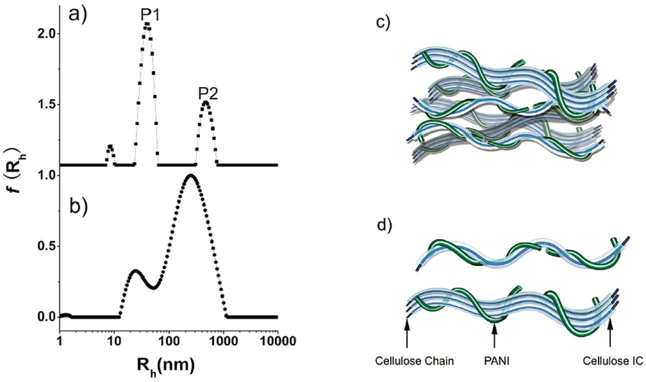

**Figure 2.** Left: DLS profiles of PANI/cellulose solution (a) and cellulose solution (b) in NaOH/urea aqueous system. Right: a schematic model to describe the dissolution of PANI in the cellulose solution; PANI/cellulose complex aggregate (c), PANI/cellulose complex (d).

peaks at 63.9−66.9 ppm were relative to the aliphatic carbon of the acidic phosphate ester. No covalent derivatives were formed in the PANI/cellulose solution, confirming that the PANI dissolution in the cellulose aqueous solution was a physical process through the noncovalent interaction.

Figure 2 shows the distribution of hydrodynamic radius ($R_h$) for PANI/cellulose and cellulose dilute solutions in NaOH/urea aqueous system by dynamic light scattering (DLS). The $R_h$ for cellulose in the aqueous solution was 25 and 250 nm, corresponding to its single chains and aggregates, respectively. It is difficult to truly disperse cellulose molecules in solvents at the molecular level, and the aggregation of cellulose molecules also exists in viscose and *N*-methylmorpholine-*N*-oxide (NMMO)-based solution.[10] Interestingly, there were two peaks with larger $R_h$ values than that in the cellulose solution, and the original peaks (Figure 2b) in the cellulose solution disappeared in the PANI/cellulose system (Figure 2a). The results revealed firmly that PANI and cellulose formed a new complex, and the individual complex and its aggregates coexisted in the aqueous system. The new peak, namely $R_h$ of 40 nm, which was slightly more than that of both cellulose and PANI having number-average molecular weight ($M_w$) of $3.0 \times 10^4$, was assigned to the complex associated with PANI molecule and cellulose IC, and that with $R_h$ of 468 nm represented their aggregates. The partial destruction of the urea shell by adding PANI led to the aggregation of the PANI/cellulose complex in the solution, resulting in the increased $R_h$ values. The particle size of the original PANI aqueous suspensions was in the range from 1 to 40 $\mu$m (Figure S2). Obviously, the size of the PANI/cellulose aggregate was much smaller than the particle size of the original PANI, confirming that large PANI particles were cleaved through the formation of new hydrogen bonds between cellulose and PANI to construct their supramolecular complex in the solution. From the results of $^{13}$C NMR and DLS, the dissolution of PANI in the cellulose aqueous system indicated actually that the noncovalent interaction existed between cellulose and PANI. We proposed a schematic model to describe the dissolution of PANI in the cellulose solution, as shown in Figure 2c,d. PANI doped with acidic phosphate ester was dispersed in the cellulose aqueous system, and the ester could be immediately broken by alkali to expose −NH groups. Simultaneously, the cellulose IC, which has wormlike conformation surrounded with urea, could be destroyed partly by the addition of PANI with violent stirring, leading to the exposure of certain −OH groups of IC. Thus, PANI and the cellulose IC were bound together to form a new supramolecular complex through the hydrogen-bonding interaction, bringing PANI into the aqueous solution, leading to the slightly larger $R_h$ value than that of the cellulose IC, supported by peak 1 in Figure 2a. As a result of the strong self-association force of cellulose molecules, a PANI molecule could hold one to multiple cellulose chains, as shown in Figure 2d. Moreover, the PANI/cellulose complex could further aggregate (Figure 2c), leading to the relatively high $R_h$ value, supported by peak 2 in Figure 2a. In our findings, the water-soluble cellulose IC could act as a cosolvent between PANI and the aqueous solution, resulting in the PANI dissolution. Moreover, the PANI/cellulose solution was more stable than the cellulose solution, since the entangled PANI greatly reduced the self-association of the cellulose IC.

A series of PANI/cellulose films with different PANI content were constructed from the composite solution by coagulating with 5 wt % HCl and coded as P04, P08, P15, and P25, corresponding to 4, 8, 15, and 25 wt % PANI content in the PANI/cellulose films. The dried films were dark green and transparent (Figure 3, left), suggestive of the homogeneity of the supramolecular structure. Furthermore, the scanning electron microscopy (SEM) images of surface and cross section for the cellulose films and P15 film at the wet state are shown in Figure S3 and Figure 3, right. The PANI/cellulose films had a homogeneous network structure, showing pore diameter of 490 nm with wall thickness of about 50 nm. AFM topography images (Figure S4) showed a continuity consistent with the two components. These results demonstrated the PANI/cellulose films were miscible. It was not hard to imagine that the cellulose chains were to bind tightly with PANI, leading to a good compatibility between PANI and cellulose in the composite films.

The data of the FI-IR spectra (Figure S5) indicated that the intensity of the −OH peak of cellulose at 3400 cm$^{-1}$ in the PANI/cellulose composite films decreased dramatically, and all major peaks for PANI shifted to higher wavenumber, suggesting an existence of hydrogen bonding force between PANI and cellulose. The XRD patterns of regenerated cellulose (RC) and PANI/cellulose films (Figure S6) revealed that the $\chi_c$ values of the composite films were lower than that of cellulose and decreased with an increase of PANI content. This could be as a result of the association between PANI and cellulose to reduce the apparent crystalline size of PANI/cellulose films.

Figure 4 shows DSC thermograms and stress−strain ($\sigma$−$\varepsilon$) curves for these films. PANI and cellulose do not exhibit the

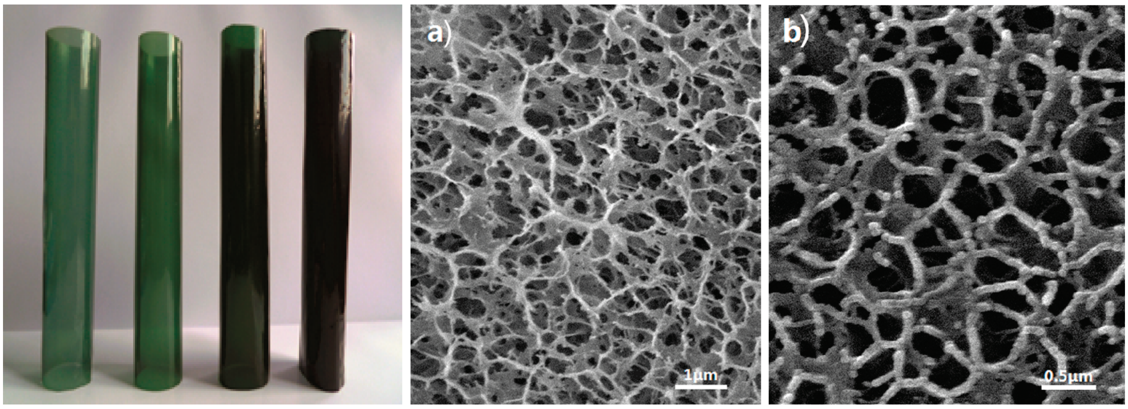

**Figure 3.** Photographs of PANI/cellulose films of P04, P08, P15, and P25 from left to right (left) and SEM images of surface (a) and cross section (b) for the P15 film by the freeze-dried method (right).

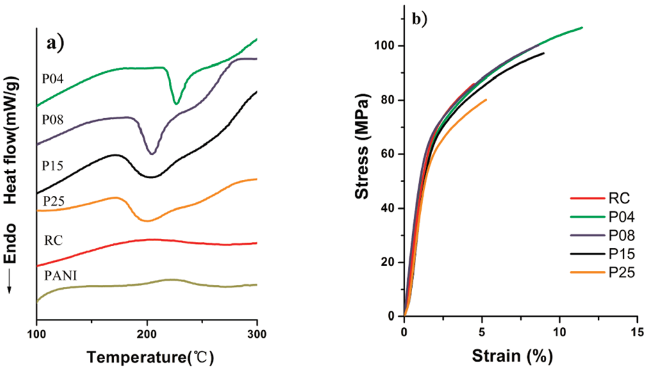

**Figure 4.** DSC thermograms and stress−strain ($\sigma-\varepsilon$) curves for the cellulose film (RC) and PANI/cellulose films of P04, P08, P15, and P25.

glass-transition temperature ($T_g$) and melting point because they have a rigid chain and close packing through hydrogen bonds and degrade before the melting temperature. Interestingly, the PANI/cellulose composites films displayed a new endothermic peak, as shown in Figure 4a. The endothermic transition was not believed to be $T_g$ based mainly on its irreversible nature upon heating and cooling (Figure S7). This could be attributed to cleavage of the hydrogen bonds between PANI and cellulose, which was irreversible in this case. As mentioned above, the formation of the hydrogen bonds between PANI and cellulose only occurred in NaOH/urea aqueous solution at low temperature. This proved that the hydrophilic cellulose and hydrophobic PANI in the aqueous solution could construct complex only through hydrogen bonding under special condition rather than simple aggregation. The mechanical properties of materials are important factors for their applications. As shown in Figure 4b, the addition of PANI improved the mechanical properties of the cellulose films on the whole. The enhancement of the tensile strength ($\sigma_b$) and elongation at break ($\varepsilon_b$) of the composite films was in the order of P04 > P08 > P15 > P25. The P04 film exhibited the maximum values of $\sigma_b$ and $\varepsilon_b$, indicating the best miscibility of the P04 composite film. Therefore, the new PANI/cellulose supramolecular complex materials were created successfully via a simple method in the aqueous system, leading to the improved significantly processability and mechanical properties.

The electrical conductivity of the PANI/cellulose films (Figure S8) increased monotonically with the PANI content, correlated with their homogeneous structure. Interestingly, the conductivity of the PANI/cellulose/carbon black composite films doped by acidic phosphate ester, HCl, and carbon black was improved significantly. This could be explained that there were many meshes in the cellulose matrix, which provided a cavity and attractive force for the embedding and adsorbing of the carbon black. We hope to open up a completely new avenue to fabricate conductive materials by using association of polyaniline and the porous cellulose matrix in aqueous media.

In summary, we developed a new route to construct supramolecular complex of PANI/cellulose through the noncovalent interaction. PANI doped with acidic phosphate ester could be dissolved rapidly the cellulose aqueous solution in NaOH/urea aqueous system with cooling through formation of new complex, in which the water-soluble cellulose inclusion complex surrounded by urea could be entangled by PANI through hydrogen bonds, leading to the dissolution of PANI. Moreover, from the complex solution the PANI/cellulose films were constructed, indicating a good processability of PANI. The composite films displayed highly homogeneous structure and improved mechanical properties as a result of good miscibility between PANI and cellulose. The electrical conductivity of the composite films could be enhanced significantly via doping of acid and the carbon black. This work has opened up a new avenue to fabricate the supramolecular complex from the hydrophilic cellulose and hydrophobic PANI via a facile and environmentally friendly process.

## ■ ASSOCIATED CONTENT

**Ⓢ Supporting Information.** Preparation of materials, characterization, and experimental results. This material is available free of charge via the Internet at http://pubs.acs.org.

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