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Effects of various surfactants on alkali lignin electrospinning ability and spun fibers

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1 **ABSTRACT**

2 Anionic, cationic, and non-ionic surfactants with varying concentrations (0.2 - 1.2 %) were
3 introduced to neutralize beads on lignin nanofibers by decreasing the surface tension of
4 spinning dopes. The surfactants used in this work were sodium dodecyl sulfate (SDS), N,N,N-
5 trimethyl-1-dodecanaminium bromide (DTAB), and Triton™ X-100 (TX-100). The effects of
6 viscosity, rheological properties, surface tension, and conductivity of the solutions on the
7 morphology and physicochemical performances of fibers were investigated. As expected, the
8 presence of certain amounts of surfactants eliminated the beads and resulted in the formation
9 of smooth and bead-free fibers with small diameters. Furthermore, the gravimetric capacitance
10 of carbon mat with 1 % SDS was slightly improved from 66.3 to 80.7 F g⁻¹. The results
11 suggested that the surfactants benefit the electrospinning of lignin and allow for the control
12 over nanofiber morphology without compromising their performance as supercapacitor
13 electrodes.

14

15 **KEYWORDS:** *lignin, electrospinning, surfactant, carbon nanofiber, supercapacitor*

16

1 INTRODUCTION

2 As a variant of electrostatic spraying, electrospinning is a technique for forming continuous
3 nanofibers with a high voltage supplier, a syringe, and a collector plate or drum.¹⁻⁴ The spinneret
4 is connected to a syringe where the polymer solution (or melt) is hosted until being fed into the
5 spinneret. After exposure to a high-voltage electric field, polymer solutions or melts are
6 expelled from the syringe and solid fibers are deposited onto the collector. The high drawing
7 rate or elongation (up to $1,000,000\text{ s}^{-1}$)⁵ and solvent evaporation cause the fiber diameters to
8 dramatically decrease from hundreds of micrometers to as small as tens of nanometers very
9 quickly (within 50 ms). Since the revival of electrospinning in the 1990s,^{6, 7} the technique has
10 been extensively studied and applied in various fields including electric, catalysis, tissue
11 engineering, and others.⁸⁻¹¹

12
13 Lignin is composed of three monomer building blocks: *p*-hydroxyphenyl (H), guaiacyl (G),
14 and syringyl (S).^{12, 13} As the second most abundant biopolymer and the most abundant aromatic-
15 containing polymer in nature, lignin has gained extensive interest for preparing certain valuable
16 materials. The electrospinning of lignin has grown popular over the years since being first
17 reported by Lallave et al.¹⁴ as a convenient technique for producing nanofibers. Lignin-based
18 nanofibers and carbon nanofibers have furthered advancements in response, battery, and
19 supercapacitor applications.¹⁵⁻¹⁷ For most cases, electrospinning of lignin requires the
20 incorporation of other polymers.^{14, 18, 19} For instance, PVA,²⁰⁻²³ PEO,^{24, 25} and PAN^{26, 27} have
21 been used to facilitate polymer entanglement and improve the electrospinning abilities of
22 lignins.

1

2 The formation of lignin-based beaded fibers has been widely reported in the literature;^{24, 26,}
3 ²⁸ and many previous researchers have explored the formation of beaded fibers for other
4 precursors. Fong et al.²⁹ suggested that the viscoelasticity and surface tension of the solution
5 are the key factors influencing the formation of beaded fibers. Lin et al.³⁰ found that insufficient
6 stretching of the polymer jet due to the weak charging forces can lead to the formation of the
7 beaded fibers. For lignin electrospinning, beaded fibers are mainly attributed to the
8 viscoelasticity of the solution.²⁵

9

10 Surfactants are amphiphilic molecules containing hydrophilic and hydrophobic parts.
11 Surfactants have numerous useful applications due to their ability to lower surface free energy
12 and thus surface tension.³¹ When used in the electrospinning, surfactants can 1) lower the
13 surface tension of the solution; 2) enhance the conductivity of the solution **in case of ionic**
14 **surfactants**; 3) modulate the molecular structure and interactions of polymers;³² and 4) alter the
15 rheology and viscoelasticity of the solution. All of these effects can prompt the formation of
16 bead-free and thin fibers while assisting the electrospinning process.

17

18 **There are four main types of surfactants used in the electrospinning technique: Anionic,**
19 **cationic, non-ionic, and amphoteric ones.** Lin et al.³⁰ found that the addition of cationic
20 surfactant eliminates the beads on polystyrene fibers, but that the addition of non-ionic
21 surfactant only reduces the number of beads. Bhattarai et al.³³ introduced non-ionic surfactant
22 to improve both the spinnability of chitosan solution and the resulting fiber structure. The

1 effects of different types and contents of surfactants on the electrospinning of various polymer
2 solutions have also been explored by several researchers.^{32, 34-39}

3

4 This paper presented a simple and effective method to modulate the morphology and
5 diameter of alkali lignin-based nanofibers by utilizing surfactants to tune the rheology and other
6 properties of the spinning solutions. Various types (ionic, cationic, and non-ionic) and contents
7 of surfactants were added into lignin-PVA solutions and the morphology and size of the as-spun
8 fibers were assessed. It was found that the electrochemical properties of carbonized nanofibers
9 as electrodes for supercapacitors were uncompromised by the addition of surfactants.

10

11 **EXPERIMENTAL SECTION**

12 **Materials.** Alkali lignin powder was purchased from Sigma-Aldrich (catalog number
13 471003) with average molecular weight of 10,000 and 4 % sulfur content. Poly (vinyl alcohol)
14 (PVA) powder was also purchased from Sigma-Aldrich with molecular weight ranging from
15 85,000 to 124,000 and hydrolysis degree of 87-89%. Anionic surfactant sodium dodecyl sulfate
16 (SDS) was purchased from Aladdin (catalog number 108347). Cationic surfactant N,N,N-
17 trimethyl-1-dodecanaminium bromide (DTAB) was also purchased from Aladdin (catalog
18 number 105301). Non-ionic surfactant Triton™ X-100 (TX-100) was obtained from Sigma-
19 Aldrich (catalog number 900502). All chemicals were used as-received without further
20 purification.

21

1 **Electrospinning.** First, 0.7 g alkali lignin was dissolved in 9 g deionized water by stirring at
2 room temperature, and 0.3 g PVA powder was then added to the aqueous solution under stirring.
3 The resulting mixture was heated to 75 °C and stirred continuously until the PVA was totally
4 dissolved. Next, the surfactants were added to the cooled solution and stirred for 1 h to prepare
5 spinning dopes with surfactant mass percentages of 0.2, 0.4, 0.6, 0.8, 1.0, and 1.2. The dopes
6 were loaded into a plastic syringe attached to a 22G needle (inner diameter of 0.41 mm) and
7 spun with an electrospinning machine (JFD 04, Nayi Instruments, Changsha, China). The
8 electrospinning conditions included an applied voltage and distance between the needle and
9 collector of 22 kV and 15 cm, respectively. The feeding rate was 1 mL h⁻¹ and the collector
10 drum rotating speed was 300 rpm. The as-spun nanofiber membranes were finally vacuum dried
11 at 60 °C overnight.

12
13 **Stabilization and Carbonization.** Some of the spun membranes (control, 1% SDS, 1%
14 DTAB, 1% TX-100) were stabilized and carbonized to test the effects of surfactant addition on
15 the electrochemical properties of the carbonized mats. The membranes were attached to a
16 copper mesh with adhesive tape (heat-resistant up to 280 °C) and placed in a tube furnace (SK-
17 G08123K, Zhonghuan Furnace, Tianjin, China). The heating procedure was taken from the
18 literature⁴⁰ as follows: 1) The temperature was increased from 25 to 105 °C at 5 °C min⁻¹ then
19 2) held at 105 °C for 1 h, 3) increased from 105 to 180 °C at 1 °C min⁻¹, 4) held for 16 h, 5)
20 increased from 180 to 220 °C at 0.5 °C min⁻¹, 6) held for 6 h, then 7) naturally cooled down
21 to room temperature. A constant air flow was maintained during the whole process.

22

1 The stabilized membranes were placed in a quartz boat and carbonized under nitrogen flow
2 in the same tube furnace. The heating process was as follows: 1) Temperature was increased
3 from 25 to 900 °C at 5 °C min⁻¹, then 2) held for 1 h and 3) naturally cooled down to room
4 temperature. The carbonized nanofiber membranes were washed with deionized water three
5 times to remove any impurities and vacuum dried at 60 °C overnight. The carbonized mats
6 were labeled as CNF-C, CNF-SDS, CNF-DTAB, and CNF-TX for fibers spun from solutions
7 without surfactant, 1.0 % SDS, 1.0 % DTAB, and 1.0 % TX-100, respectively.

8

9 **Characterization.** The apparent viscosity of the solution was measured with a viscometer
10 (DV II+ Pro, Brookfield, USA). The rheological properties were recorded on a rheometer
11 (MCR 301, Anton Paar, Austria), and shear stress σ (Pa) was recorded as a function of shear
12 rate (s⁻¹) ranging from 10⁻³ to 10³ s⁻¹. Solutions were equilibrated to 25 °C prior to all
13 measurements. Measurements were fitted to the power law model:^{32, 41}

$$14 \quad \sigma = K \dot{\gamma}^n \quad (1)$$

15 where K is the consistency coefficient and n is the flow behavior index. If the flow behavior
16 index n equals 1, the solution behaves as a Newtonian liquid. If it is smaller than 1, the solution
17 is a shear thinning liquid; if it is larger than 1, the solution is shear thickening.

18

19 The surface tension and conductivity of each solution was measured with a fully automatic
20 surface tension meter (QBZY, Fangrui Instruments, Shanghai, China) and a portable analytic
21 instrument with a portable analyzer (HQD 40, Hack Instruments, USA), respectively.

22

1 The morphology of the resulting membranes was examined with a scanning electron
2 microscope (SEM, HitachiS-5500). The average diameter and diameter distribution were
3 measured with image analysis software (ImageJ, NIH, USA) from >50 randomly selected fibers
4 for each sample.

5
6 The FT-IR spectra of nanofiber membranes were collected on a Thermo Scientific Nicolet
7 iN 10 FT-IR Microscopy (Thermo Nicolet Corp., Madison, WI) equipped with a liquid nitrogen
8 cooled MCT detector. Thirty-two scans were taken for each sample with a resolution of 4 cm^{-1}
9 in the reflection mode. Each sample was spread on a plate before spectra collection.

10

11 Differential scanning calorimetry (DSC) characterization was carried out with a differential
12 scanning calorimeter (DSC 214 Polyma, NETZSCH-Gerätebau GmbH, Selb, Germany).
13 Samples of approximately 5 mg were loaded into DSC pans and then equilibrated at $25\text{ }^{\circ}\text{C}$ for
14 5 min before heating from 25 to $300\text{ }^{\circ}\text{C}$ at a rate of $5\text{ }^{\circ}\text{C min}^{-1}$. The temperatures of samples
15 and reference pans were measured as a function of oven temperature to determine the heat flow.
16 The results reported here are an average of three measurements.

17

18 A symmetrical two-electrode cell was assembled as prototype supercapacitor using
19 carbonized mats as electrodes (size $\sim 1.0\text{ cm}^2$) without any polymeric binder or conductive
20 additive. Two pieces of platinum sheet were used as current collectors. Electrochemical
21 characterizations including cyclic voltammetry (CV) and galvanostatic charge/discharge of the
22 CNF membranes were conducted with a two-electrode cell in 6M KOH aqueous solution with

1 an electrochemical workstation. CV studies were performed at scanning rates from 5 to 2000
2 mV s⁻¹ within the voltage window from 0 to 1 V.

3

4 **RESULTS AND DISCUSSION**

5 **Apparent Viscosity of the Solution.** The apparent viscosities of solutions with surfactants
6 of varying types and contents were measured under a constant shear rate of 50 s⁻¹ (Fig. 1). The
7 lignin-PVA solution showed an apparent viscosity of 241.1 mPa s. The addition of small
8 amounts of **each** surfactant reduced the viscosity of the solution. After introducing 0.2 % SDS,
9 DTAB, or TX-100, the viscosity of the solution decreased to 216, 174, and 158.8 mPa s,
10 respectively. Viscosity has a marked impact on the size of nanofibers,^{25,42} therefore the diameter
11 of fibers can be adjusted by simply adding surfactants accordingly. However, the viscosity
12 increased as SDS content increased while the parameter continued to decrease as further adding
13 DTAB and TX-100. The viscosity of the solutions with 0.8 - 1.2 % SDS even surpassed the
14 value of the solution without surfactant.

15

16 Different **variation** trends in viscosity may be attributable to the varying strength patterns of
17 the surfactant-polymer interaction depending on the chemical properties of the polymer and
18 surfactant.⁴³⁻⁴⁵ Ionic surfactants could bind cooperatively to non-ionic polymers once the
19 content surpasses its critical micelle concentration (cmc)³⁴ which, in this case, was PVA (Fig.
20 2). This cooperative binding, driven by electrical or hydrophobic interactions, led to the
21 formation of surfactant-polymer complexes. For PVA-only solutions, such complexes formed
22 as the incorporated ionic surfactants strongly interacted with the alkyl groups thus increasing

1 the viscosity.³⁴ In the presence of alkali lignin, the anionic group containing polymers (cationic
2 surfactant, DTAB) interacted with lignin through electrostatic force upon reaching its cmc
3 (approximately 0.5 %). The viscosity continued to decrease as the DTAB content increased.
4 Because there was no such electrostatic force between SDS and lignin, the hydrophobic
5 interactions among the surfactant, lignin, and PVA formed the compounds and hence increased
6 the viscosity. For non-ionic surfactant (TX-100), there was no cooperative binding due to the
7 non-ionizing properties, and the viscosity of its solution decreased as the content increased.

8

9 **Rheology of the Solution.** Next, solutions with all surfactants of several concentrations (0,
10 0.2, 0.6, 1.0 %) were explored for their rheological properties. Flow curves were measured over
11 a shear range of 10^{-3} - 10^3 s⁻¹ and consistency coefficient K and flow behavior index n were
12 calculated by fitting the curves to the power law equation (1) (Table 1). The consistency
13 coefficient K of solutions followed the viscosity trends. For instance, K decreased as adding
14 0.2 % SDS and subsequently increased as the SDS content surpassed its cmc (about 0.25 %).
15 For DTAB and TX-100, K decreased as the surfactant content increased. In the case of DTAB,
16 there was only a small difference between the K values of 0.6 % and 1.0 % solutions while the
17 K values of solutions with TX-100 were similar. This may have been due to the fact that the
18 cmc of DTAB was about 0.5 % and that of TX-100 was about 0.02 %. After reaching the cmc,
19 the further addition of surfactants had little effect on the consistency of the solution. Rheology
20 tests on the solution with 0.01 % TX-100 was conducted to further verify this observation. As
21 shown in Table 1, K of the solution was 0.48 – much larger than that of the solutions with 0.2,
22 0.6, or 1.0 % TX-100.

1

2 The n indices of all solutions were smaller than 1, indicating shear thinning behavior. A
3 reduced n is an indicator of reinforced polymer entanglement, which is essential for
4 electrospinning.^{32, 46-49} As shown in Table 1, the flow behavior indices of solutions with SDS
5 decreased while those of solutions with DTAB and TX-100 increased. An increasing amount
6 of SDS facilitated the entanglement of polymers while that of DTAB or TX-100 hindered the
7 electrospinning process. When the content of each surfactant was below its respective cmc,
8 however, the n value was smaller than that of the solution without surfactant (0.79). These
9 trends differ from those reported by Kriegel et al. in a similar study.³² They found that the
10 addition of SDS reduced n due to electrostatic attraction between SDS and chitosan, a cationic
11 polymer.

12

13 The phenomenon observed can be explained as follows. When the contents were below cmc,
14 the surfactants were in their molecular form and above the cmc, the molecules aggregated
15 together and formed micelles. For DTAB, the cationic surfactant, the micelles interacted with
16 the anionic groups on the lignin (hydroxyl, carboxyl, and sulfonyl) and formed a complex.
17 Since lignin exhibited a highly-branched structure, the complex was likely to be spherical or
18 oval. This destroyed the entanglement between lignin and PVA. The electrostatic repulsion
19 (between SDS and lignin) prevented aggregation similar to the DTAB-lignin complex. On the
20 other hand, the cooperative bonding among SDS, lignin, and PVA reinforced the polymer
21 entanglement and this was why the flow behavior index continued to decrease as the content
22 exceeded cmc.

1

2 **Surface Tension of the Solution.** The surface tension of polymer-surfactant solution as a
3 function of surfactant content is shown in Fig. 3. The PVA-lignin solution exhibited a surface
4 tension of 35.87 mN m⁻¹. The addition of all surfactants significantly reduced the surface
5 tension. In anionic surfactant-containing mixture, the surface tension first decreased to a
6 minimum of 29.79 mN m⁻¹ and then increased as a result of reaching the cmc of SDS (0.25 %).
7 When SDS concentration was 1.2 %, the surface tension of the corresponding solution was
8 31.56 mN m⁻¹. A similar trend was observed for DTAB, lignin, and PVA solutions. The surface
9 tension first decreased to a minimum of 28.39 mN m⁻¹ when DTAB concentration was 0.4 %
10 and then increased upon further addition of the cationic surfactant. The addition of TX-100 also
11 greatly decreased the surface tension but larger amounts of TX-100 had little effect in this
12 regard.

13

14 Surfactants, regardless of types, all decreased the surface tension of lignin-PVA solution as
15 postulated. The decrease of the surface tension was due to the directional alignment of
16 surfactant molecule on the gas-liquid interface as well as the interaction between the polymers
17 and surfactant. For ionic surfactants (SDS and DTAB), when the content was below cmc, the
18 surfactant molecules were directional aligned on the gas-liquid interface and thus reduced the
19 surface free energy and surface tension of the solution. When surfactant concentration exceeded
20 cmc, the redundant molecules formed micelles. For SDS, the micelles interacted with PVA
21 through cooperative binding and the surface tension was slightly increased. For DTAB, the
22 hydrophilic head group interacted with lignin by electrostatic attraction while the other

1 hydrophobic one formed cooperative bonds with PVA. The compact lignin-DTAB complex
2 discussed above increased the surface tension. Similar tendencies have been observed by other
3 researchers as well.^{30, 34, 46} For non-ionic surfactants, there were two main reasons for the even
4 curve of surface tension versus concentration. On the one hand, the addition amounts were all
5 above cmc because non-ionic surfactants inherently have smaller cmc than ionic ones. On the
6 other hand, there was no interaction among TX-100 and polymers.

7

8 Generally, reduction in surface tension benefits the electrospinning of polymer solutions as
9 smaller surface tension allows the polymer to escape the Taylor cone more easily,^{1, 50} and the
10 decreased surface tension lowers the required electric field strength for jet initiation.
11 Furthermore, surface tension has a direct effect on the formation of beads and morphology of
12 fibers.²⁹

13

14 **Conductivity of the Solution.** Fig. 4 shows the solution conductivity dependence per various
15 surfactant types and concentrations. PVA-lignin solution alone exhibited a conductivity of 9.68
16 mS cm⁻¹. The continuous incorporation of ionic surfactants (SDS and DTAB) increased the
17 conductivity of the solution while the addition of the non-ionic surfactant (TX-100) had little
18 effect. This difference was expected, as SDS and DTAB ionized in the aqueous solution and
19 provided extra ions thus increasing the conductivity. The enhanced electroconductibility
20 reinforced the electric field strength and benefitted the electrospinning process while preventing
21 bead formation and ensuring smaller fiber sizes.³⁰

22

1 **Fiber Morphology and Diameter.** Solution properties including apparent viscosity,
2 rheological properties, surface tension, and conductivity were characterized as discussed above.
3 As hypothesized, the different surfactants had different effects on fiber morphology.

4

5 SEM images of nanofibers from the lignin-PVA solution are shown in Fig. 5. In Fig. 5B
6 (2500 ×), some fibers were stuck together forming bundles, and the beaded fibers were also
7 observable in this image. As shown in Fig. 5A (500 ×) and the left bottom side of Fig. 5B,
8 there were many lumps in the electrospun membranes that might have been caused by excess
9 surface tension of the solution. High surface tension made it difficult for the polymers to escape
10 the Taylor cone, and caused the droplet on the tip of the needle to be enlarged as the solution
11 was fed from the syringe. When the solution accumulated to a certain threshold, the droplet
12 ejected from the tip of the needle and electrospayed on the collector formed lumps.

13

14 SEM images of fibers from solutions with surfactants are shown in Fig. 6. All these samples
15 were free of lumps due to the reduced surface tension. The introduction of a small amount of
16 SDS enlarged the beads on the fiber instead of removing them, however the beads disappeared
17 upon further addition of SDS. This was in accordance with the flow behavior index tendency
18 described in Section 3.2. In other words, enhanced polymer entanglement led to the formation
19 of smooth fibers.

20

21 For the DTAB and TX-100 counterparts, the incorporation of surfactants at a concentration
22 of 0.2 % entirely eliminated the beaded fibers. Nevertheless, beaded fibers were spun from

1 solutions with surfactants at higher concentrations. Complexes formed as a result of
2 electrostatic attraction between DTAB and lignin which greatly reduced the polymer
3 entanglement and generated beaded fibers. As shown in Fig. 7, the incorporation of SDS of
4 DTAB reduced the average fiber diameter and its distribution, which could be attributed to the
5 increased surface tension and conductivity. The average diameter of fibers from the lignin-PVA
6 solution was 289.8 ± 69.8 nm while that of fibers from the solution with 0.6 % SDS or DTAB
7 was only 163.5 ± 18.3 and 137.2 ± 27.2 nm, respectively. For TX-100 counterparts, the
8 average fiber diameter and its distribution decreased first and then increased as the content
9 increased. The fiber diameter distribution of fibers with 1.0 % TX-100 was 58.9 nm, which was
10 much larger than those of fibers with SDS and DTAB. This tendency may be attributable to the
11 excess amount of surfactant micelles.³⁴

12
13 **FT-IR of Fibers.** FT-IR analysis was conducted to further confirm whether the surfactant
14 had any notable effect on the electrospun fibers.⁴¹ The FT-IR spectra of fibers from different
15 solutions are shown in Fig. 8. The characteristic absorption bands for fibers from pure lignin-
16 PVA solution were as follows. The –OH related peaks included hydrogen bonded –OH at 3350
17 -3400 cm^{-1} as well as free –OH at ~ 2930 cm^{-1} .⁵¹ The peak at ~ 1135 cm^{-1} is associated with the
18 crystallization of PVA and the primary hydroxyl group in PVA located at ~ 1045 cm^{-1} as well
19 as the C-C bonds in PVA corresponding to the peak at ~ 850 cm^{-1} .⁵² The peak at 1722 cm^{-1} is
20 likely the characteristic absorption of C=O in the lignin side chain or remaining vinyl acetate
21 produced by PVA. Adsorption bands at 1594 and 1505 cm^{-1} are assigned to the aromatic ring
22 skeleton and C-O deformation in primary aliphatic, phenolic, secondary ether while aliphatic –

1 OH was attached to the peak at 1043 cm^{-1} .^{51,53} All of these peaks indicated that lignin and PVA
2 were successfully spun into nanofibers.

3

4 The spectra of fibers prepared from solutions with SDS and DTAB (Fig. 8A) showed a new
5 peak at $\sim 2855\text{ cm}^{-1}$, which is assigned to the alkyl chain on the surfactants. In addition, as shown
6 in Figs. 8B and 8C, the intensity of the peak increased as the surfactant concentration increased.
7 SDS and DTAB were successfully integrated into the fibers, to this effect. The characteristic
8 vibration was not observed in the spectra of the TX-100 counterparts, possibly due to 1) the
9 non-ionized characteristics of TX-100 or 2) the absence of TX-100 in the fibers as the molecules
10 mostly aggregated in the solution.

11

12 **DSC and Electrochemical Characterization.** The electrospun fibers were subjected to
13 DSC measurements to determine the effects of surfactants on the thermostabilities and
14 microstructures of fibers (i.e., crystallinity). The temperatures of the samples and reference pans
15 were measured as a function of oven temperature to determine the heat flow. All samples
16 exhibited glass transition temperatures (T_g), which represented the degree of orientation in the
17 fiber microstructures. The alkali lignin and PVA exhibited T_g values of ~ 86 and $92\text{ }^\circ\text{C}$,
18 respectively. After being electrospun into fibers, the T_g converted to $152.36 \pm 1.17\text{ }^\circ\text{C}$ (Table
19 2), which indicated successful crosslinking between lignin and PVA.^{54,55}

20

21 As listed in Table 2, the addition of surfactants (regardless of types or concentrations)
22 elevated the T_g values of the fibers, which indirectly proved the presence of surfactants inside

1 fibers. In other words, the crystallinity of fibers was improved by the incorporation of
2 surfactants in the electrospinning process. The fiber formed due to enhanced polymer
3 entanglement, reduced surface tension, and increased conductivity (for SDS and DTAB) during
4 electrospinning; these factors altogether improved the orientation of fiber microstructures.
5 Continuously adding SDS and DTAB increased the T_g of the samples while an increased
6 concentration of TX-100 reduced the T_g . When 0.2% SDS or DTAB was added, T_g was 163.75
7 ± 1.22 and 163.10 ± 1.30 °C, respectively. When the concentration of ionic surfactants was
8 increased to 1%, T_g increased to 169.65 ± 0.52 and 166.40 ± 0.35 °C, respectively. For
9 counterparts of TX-100, as the concentration increased from 0.2 to 1.0%, the T_g value decreased
10 from 158.41 ± 2.34 to 154.18 ± 1.53 °C. This trend was fitted to the transitions of rheological
11 properties, surface tension, and conductivity discussed above.

12

13 Electrochemical characterization was performed by using two-electrode symmetrical system
14 in 6M KOH aqueous solution. The CV curves of all samples (Fig. 9A) were quasi-rectangular
15 except for CNF-TX. All CNFs, apart from CNF-TX, showed excellent electrical double-layer
16 capacitive behavior. In Fig. 9A, the CV curve of CNF-SDS has the largest loop area, indicating
17 that it is better suited as a supercapacitor electrode material than the other materials we tested.

18

19 The galvanostatic charge-discharge method was adopted to test the performance of the
20 electrochemical capacitors. The charge-discharge curves of different samples were obtained at
21 a constant current density of 1 A g^{-1} with the potential range of 0-1 V in 6M KOH aqueous
22 electrolyte. The charge-discharge curves of CNFs were approximately isosceles, suggesting

1 favorable capacitive performance. CNF-SDS showed the longest discharging time, i.e., best
2 material capacitance.

3

4 The capacitance of each electrode was calculated based on the following equation:

18
$$C = \frac{2 \times I \times \Delta t}{\Delta V \times m}$$

5 where I is the discharge current (A), ΔV is the voltage window during the discharge in volt
6 (V), Δt is the discharge time in the selected potential difference in seconds (s), m is the mass
7 of an electrode in grams (g), and C is the gravimetric capacitance (F g^{-1}). The gravimetric
8 capacitance of CNF-C, CNF-SDS, CNF-DTAB, and CNF-TX measured at 1 A g^{-1} was 66.3,
9 80.7, 62.6, and 34.0 F g^{-1} , respectively. The capacitance improvement in CNF-SDS as compared
10 to CNF-C was attributable to its reduced size and smoother fiber morphology. The decreased
11 diameter and beads of fibers facilitated the ion transportation inside the membrane and provided
12 more pores for ion storage. By contrast, the capacitance of CNF-TX was well below that of
13 CNF-C in accordance with their CV curves. The larger diameter of CNF-TX lowered the
14 surface area so that the storage space for electrolyte ions was reduced as well as capacitance.
15 Furthermore, the existence of beads in CNF-TX impeded the diffusion of electrolyte.⁵⁶ The
16 above results together indicated that SDS could not only facilitate the electrospinning of lignin
17 but also improve the electrochemical performance of the carbonized membrane.

19

20 CONCLUSIONS

21 In this study, several kinds of surfactants were incorporated in the electrospinning of lignin by
22 simply adding them into the lignin-PVA solution. It was found that the addition of surfactants

1 had marked effects on the morphology, magnitude, and nanostructure of the spun nanofibers.
2 Surfactant addition (regardless of type or concentration) eliminated lumps, reduced the average
3 diameter of nanofibers, and enhanced the orientation of fiber microstructures, and adding
4 certain amounts of surfactants formed bead-free fibers with small-diameter distribution. These
5 phenomena were examined by assessing the solution properties. The elimination of beads and
6 reduction of fiber size were attributed to reduction in surface tension and enhanced polymer
7 entanglement. By testing various concentrations, it was observed that the critical micelle
8 concentration (cmc) of surfactants plays an important role in modulating the polymer solution
9 and nanofibers. FT-IR verified the existence of SDS and DTAB in the spun fibers but the
10 incorporation of TX-100 was not observed, as its side chain differed from those of the other
11 two chemicals. The addition of SDS and DTAB did not compromise the electrochemical
12 performance of carbonized nanofiber membranes as supercapacitor electrodes. The efficient
13 modulation of nanofiber morphology and simple, effective electrospinning process without loss
14 of terminal performance may have remarkable commercial potential, as lignin-based and
15 carbon nanofibers are useful in ion batteries, supercapacitors, sensors, and other applications.

16

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FIGURE CAPTIONS

Figure 1. Apparent viscosity values of solutions with surfactants of varying types and contents.

Figure 2. Schematic illustration of the incorporation of surfactants into the lignin-PVA solution.

Figure 3. Surface tension values of solutions with surfactants of varying types and contents.

Figure 4. Conductivity values of solutions with surfactants of varying types and contents.

Figure 5. SEM images of nanofibers from the solution without surfactants (A: feeding rate of 1 mL h⁻¹, magnification times 500 ×; B: feeding rate of 1 mL h⁻¹, 2500 ×).

Figure 6. SEM images of fibers from solutions with (A1) 0.2 % SDS, (A2) 0.4 % SDS, (A3) 0.6 % SDS, (A4) 0.8 % SDS, (A5) 1.0 % SDS, (A6) 1.2 % SDS, (B1) 0.2 % DTAB, (B2) 0.4 % DTAB, (B3) 0.6 % DTAB, (B4) 0.8 % DTAB, (B5) 1.0 % DTAB, (B6) 1.2 % DTAB, (C1) 0.2 % TX-100, (C2) 0.4 % TX-100, (C3) 0.6 % TX-100, (C4) 0.8 % TX-100, (C5) 1.0 % TX-100, (C6) 1.2 % TX-100.

Figure 7. Average diameters of nanofibers from solutions with surfactants of varying concentrations (0.2%, 0.6%, 1.0%).

Figure 8. Infrared absorbance spectra of electrospun lignin–PVA–surfactant fibers at wave numbers ranging from 4000 to 600 cm^{-1} . (A) Spectra of fibers without surfactant, with 1.0% SDS, 1.0% DTAB and 1.0% TX-100; (B) spectra of fibers without surfactant, with 0.2% SDS, 0.6% SDS, 1.0% SDS; (C) spectra of fibers without surfactant, with 0.2% DTAB, 0.6% DTAB, 1.0% DTAB; (D) spectra of fibers without surfactant, with 0.2% TX-100, 0.6% TX-100, 1.0% TX-100.

Figure 9. Electrochemical characterizations of carbon fiber membranes from solutions with varying surfactants. (A) CV curves at 50 mv s^{-1} ; (B) Galvanostatic charge-discharge curves at 1 A g^{-1} .

TABLES

Table 1. Consistency coefficient K , flow behavior index n of solutions with surfactants of varying types and contents

Surfactant Concentration (%)	K			n		
	SDS	DTAB	TX-100	SDS	DTAB	TX-100
0	0.55	0.55	0.55	0.55	0.55	0.55
0.01	-	-	0.48	-	-	0.76
0.2	0.39	0.23	0.11	0.84	0.74	0.90
0.6	0.57	0.07	0.08	0.72	0.84	0.91
1.0	0.62	0.04	0.05	0.70	0.95	0.96

Table 2. Glass transition temperatures (T_g) of samples measured by DSC at a scanning rate of $5\text{ }^\circ\text{C min}^{-1}$ from room temperature to $300\text{ }^\circ\text{C}$

Surfactant concentration (%)	T_g ($^\circ\text{C}$)		
	SDS	DTAB	TX-100
0	153.36 ± 1.17	153.36 ± 1.17	153.36 ± 1.17
0.2	163.75 ± 1.22	163.10 ± 1.30	158.41 ± 2.34
0.6	165.01 ± 1.22	163.78 ± 0.47	156.44 ± 0.29
1.0	169.65 ± 0.52	166.40 ± 0.35	154.18 ± 1.53

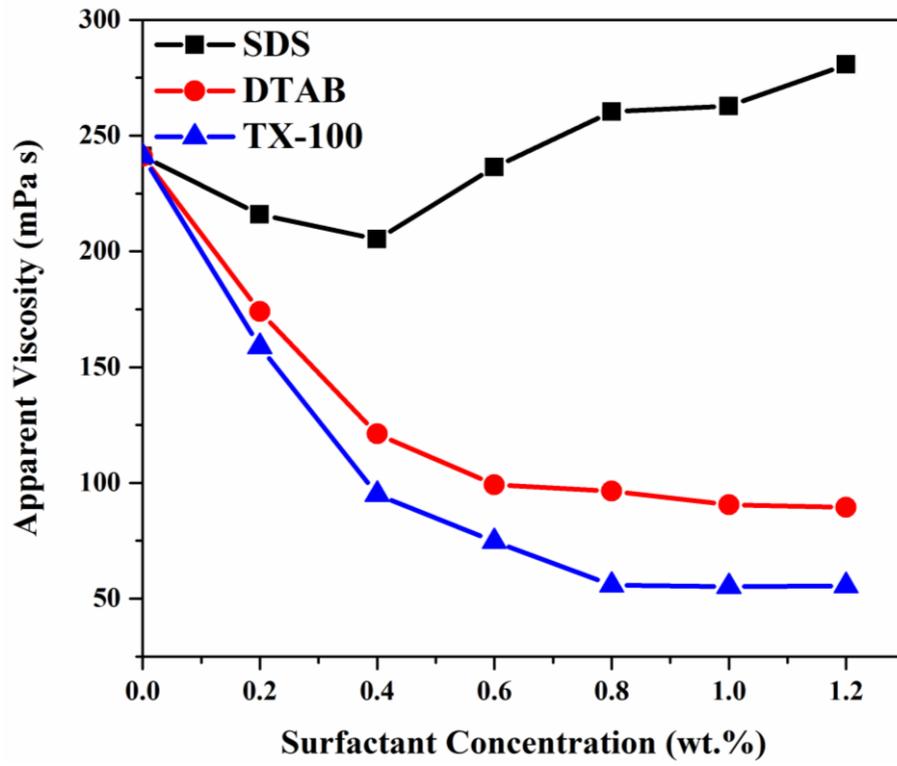


Figure 1.

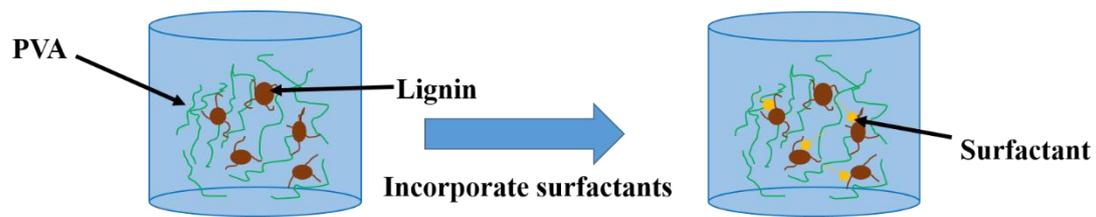


Figure 2.

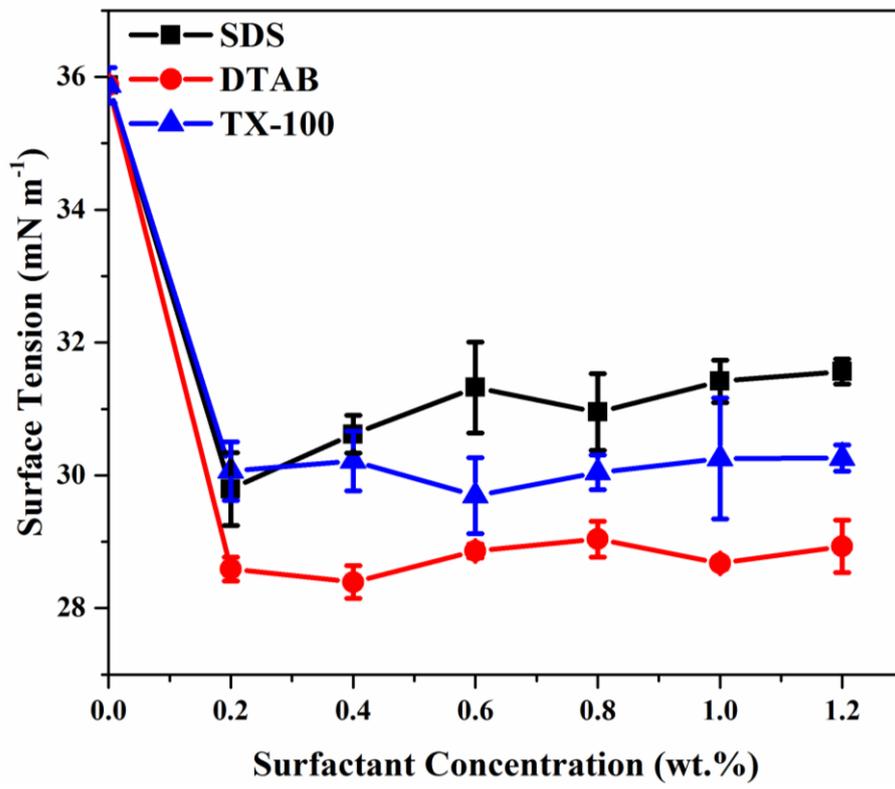


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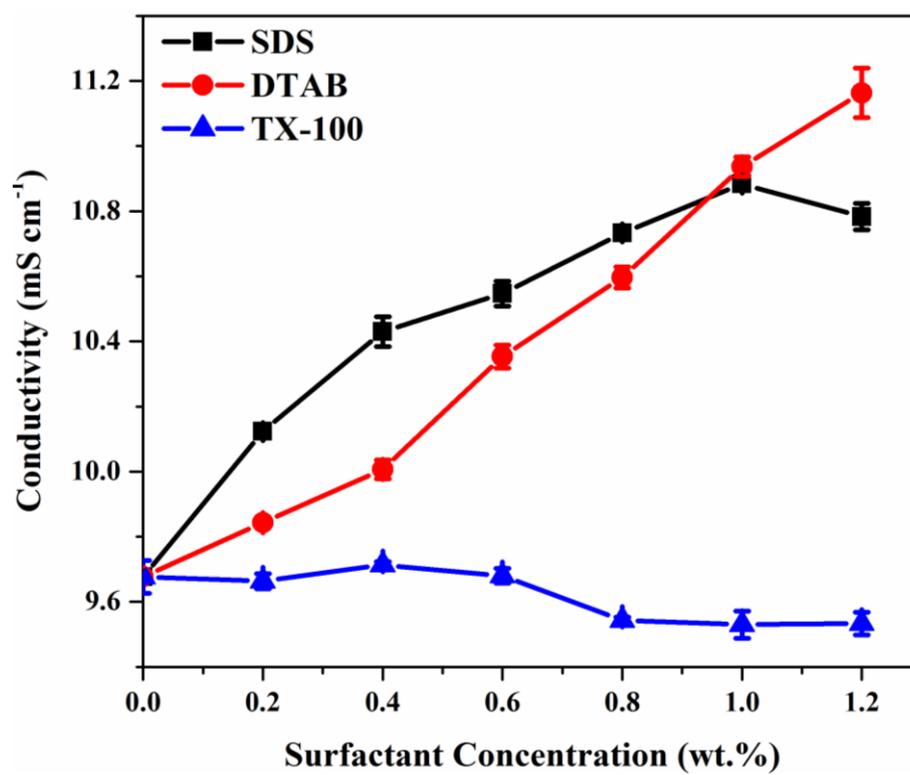


Figure 4.

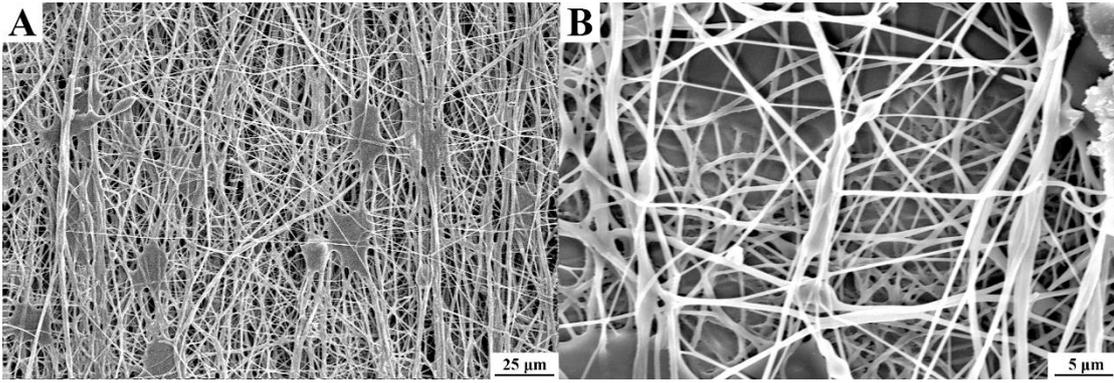


Figure 5.

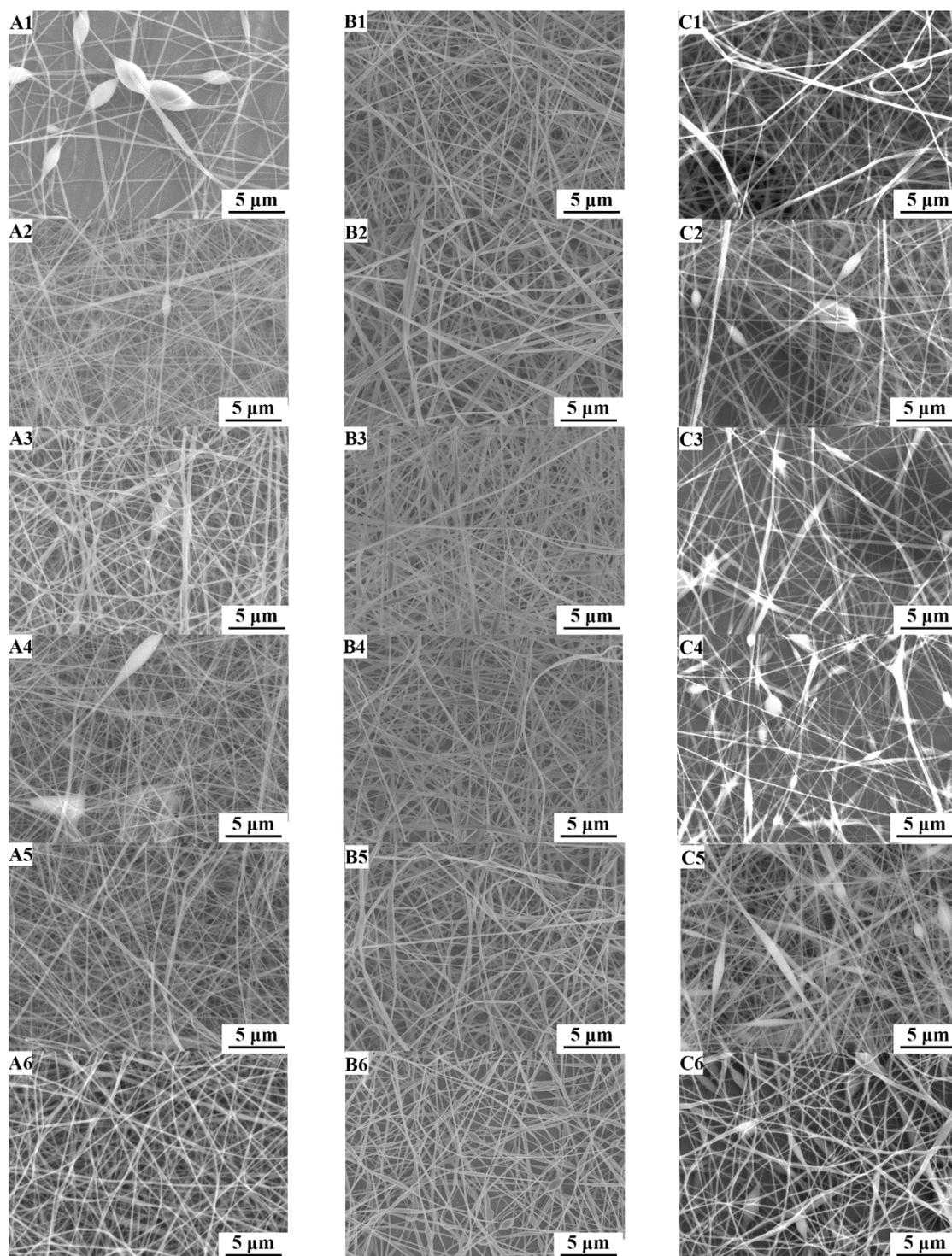


Figure 6.

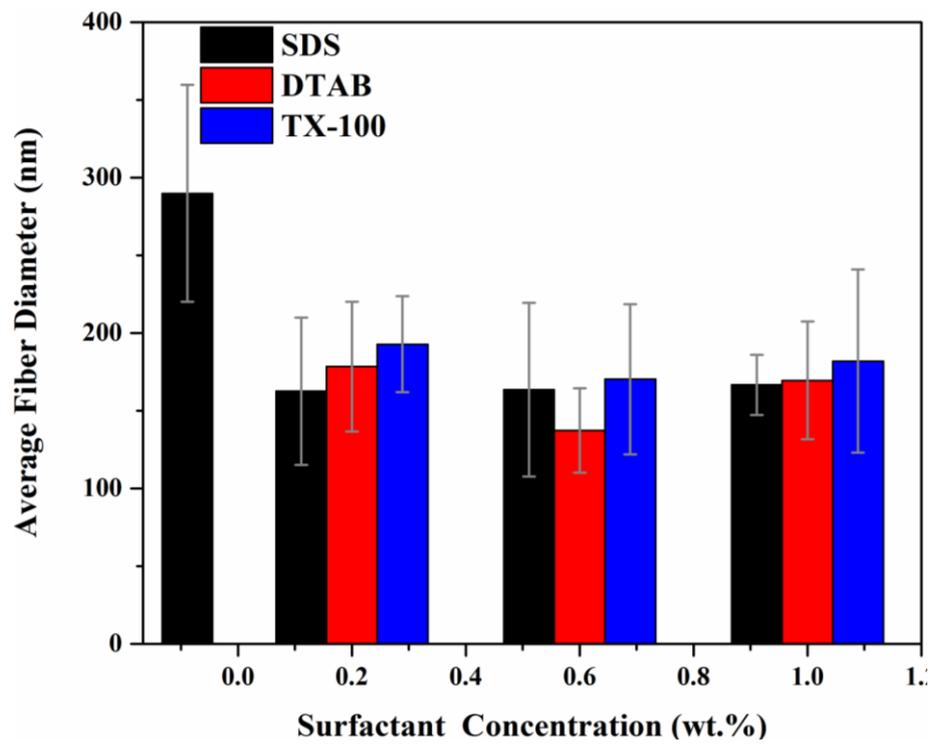


Figure 7.

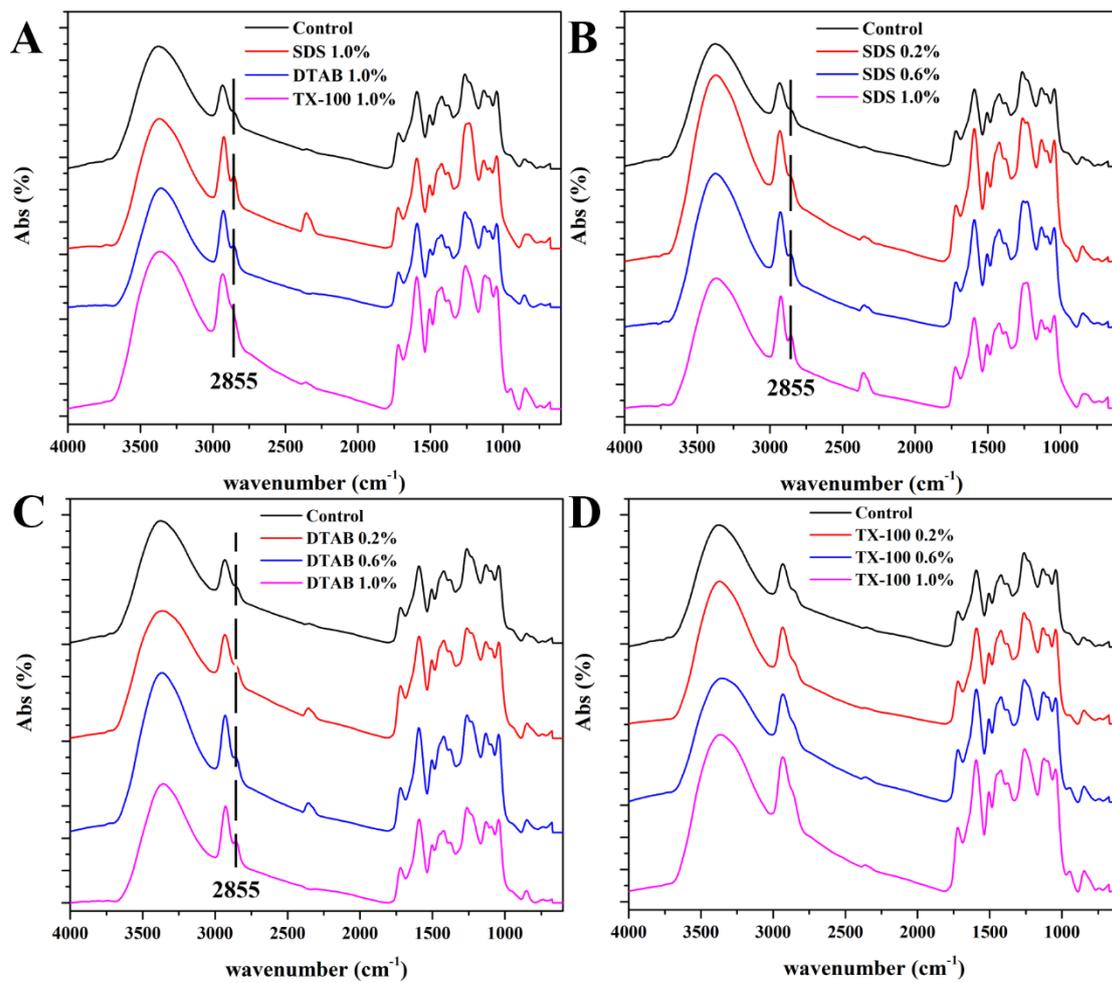


Figure 8.

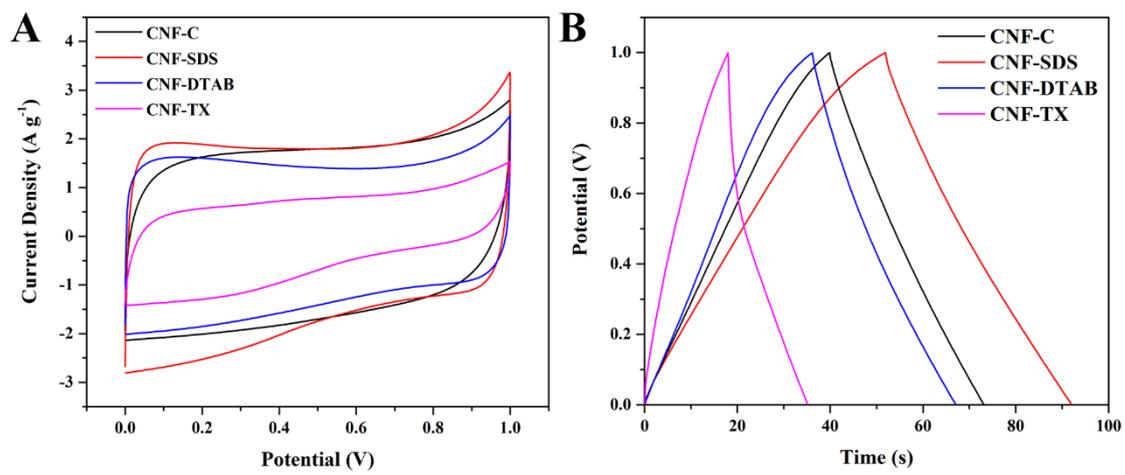


Figure 9.

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