Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supplementary Information

Nitro-oxidized Carboxylated Cellulose Nanofibers based Nanopaper and their PEM Fuel Cell Performance

Conductometric Titration Method

The carboxyl content in carboxycellulose nanofibers (the ionic form) having carboxylate (COO^-Na^+) groups was determined by using the conductivity titration method. In this method, 0.3 g of dried nanofiber sample was dispersed in 55 mL of distilled water. Subsequently, 5 mL NaCl (0.01 M) was added to the above suspension and stirred for 15 min. The suspension was then set to a pH value in the range of 2.5−3 by adding 0.1 M HCl. A 0.04 M NaOH was added to the suspension at a rate of 0.1 mL/min until pH reached 11 (monitored by a pH meter). The carboxylate content of nanofibers was calculated from the conductivity and pH curves.

Fourier Transform Infra-Red Spectrometry (FTIR)

A PerkinElmer Spectrum One instrument was used to record the FTIR curves in the transmission mode, between 450 and 4000 cm^{-1}. A total of 6 scans were taken per sample with a resolution of 4 cm^{-1}. The solid samples were recorded in the attenuated total reflectance (ATR) mode.

Zeta Potential Measurement

A Zetaprobe Analyzer(Colloid Dynamics) equipped with built-in titration set up, pH electrode and ESA sensor probe was used to measure the zeta potential of NOCNF sample. Before analyzing the sample, the pH electrode was calibrated using 3 different pH buffer standards (pH = 4.01, 7.01, and 10.01), followed by a standard titration solution. The ESA sensor was calibrated using the standard zeta probe polar solution (KSiW solution). Upon the completion of calibration test, the NOCNF suspension (0.2 wt %, 250 mL) was filled in the sample holder, where the ESA sensor was then introduced into the sample under magnetic stirring to analyze the zeta potential.

X-ray Photoelectron Spectroscopy (XPS) Measurement

XPS was performed on a custom-built instrument. The x-ray source was from PHI Electronics, spectrometer from V.G. Scientific CLAM 100, and used a VGX900I controller data collection system. The X-ray source used was Al Kα 1,2. An ultrahigh vacuum of torr was used during analysis. Data was collected at a 90º take off angle relative to the sample film. Sample charging was corrected for by correcting the C1s peak to adventitious carbon at 284.8 mV.

Transmission Electron Microscopy (TEM)

TEM studies of CNF-H and CNF-Na obtained from jute fibers fibers were carried out by a FEI Tecnai G2 Spirit BioTWIN instrument, operated at an accelerating voltage of 120 kV and equipped with a digital camera. The instrument also possessed photographic film capability with goniometer and tilt stage accessories, as well as electron diffraction capability. In typical sample preparation, a 10 μL aliquot sample of 1 mg of sample in 10 mL distilled water was deposited on freshly glow discharged carbon coated Cu grids (300 mesh, Ted Pella Inc.), followed by staining with 2 wt % aqueous uranyl acetate solution.

Contact Angle Measurement

Contact angles with water was measured with an OCA 15EC instrument using the sessile drop technique. Samples were mounted onto glass slides using double-sided adhesive tape, a glass syringe with an inner diameter of 0.50 mm was used to obtain 4 μl droplets. The contact angle testing was conducted at four different positions at the membrane surface.

Scanning Electron Microscopy (SEM)

A Zeiss LEO 1550 SFEGSEM instrument was used to record SEM images of nanofibers nanopores. The instrument was composed of an in-lens secondary electron detector in addition to the standard E-T detector, and a Rutherford backscatter electron detector. It was also equipped with an EDS (energy dispersive X-ray spectroscopy) system, provides elemental compositions and X-ray maps of the various phases of the materials examined. Images of surface as well cross section of nanopaper sample were taken to observe the surface morphology of the nanopaper samples.

Wide-Angle X-ray Diffraction (WAXD)

X-ray diffraction measurements were carried out using a Benchtop Rigaku MiniFlex 600 instrument. The samples were prepared by coating nanofibers on sample holders made of glass. The Cu Kα radiation was generated at 40 kV and 40 mA ($\lambda = 0.154$ nm) using a Ni filter. Data collection was carried out using a flat holder in Bragg-Brentano geometry (5-50°; 10°min^{-1}).

$$Cl = \frac{(I_{200} - I_{am})}{I_{200}} \quad \text{Eq. S1}$$

where I_{200} is the intensity of the dominant (200) diffraction peak, I_{am} is the intensity of the amorphous peak evaluated as the minimum peak arise between the dominant (200) peak and the secondary (110) peak.

Cross Polarization/Magic Angle Spinning Nuclear Magnetic Resonance (^{13} C CPMAS NMR)

Solid state ^{13}C CPMAS NMR of CNF-H and CNF-Na were carried out by a Bruker Utrashield 500WB plus (500MHz) NMR instrument, equipped with a 2.5 mm triple resonance magic angle spinning (MAS) NMR probe, capable of spinning samples up to 35 KHz**.** The resonance frequency for ^{13}C was 10,000 Hz and the samples were spun at the magic angle with a speed of 10 KHz.

Atomic Force Microscopy (AFM)

AFM measurements of CNF-H and CNF-Na obtained from jute fibers were performed using a Bruker Dimension ICON scanning probe microscope (Bruker Corporation, U.S.A.) equipped with a Bruker OTESPA tip (tip radius (max.) = 10 nm). A 10 µL of 0.005 wt % nanofibers suspension was deposited on the surface of a silica plate, where the air-dried sample was measured in tapping mode.

Surface Area Measurement using Brunauer−Emmett−Teller (BET) Analysis

The specific surface area of membrane samples was obtained based on the Brunauer-Emmett-Teller (BET) method through N_2 physisorption at 77 K using a NOVALX^2 instrument (Quantachrome Instruments, USA). Firstly, membrane samples were cut into very small pieces and then degassed at 100 °C for 12 h prior to the analysis by N_2 adsorption at -196 °C. The N_2 sorption data was further used to derive the pore size of the Nanopapers based on the Barrett-Joyner-Halenda (BJH) approach at a relative vapor pressure of 0.1−0.9.

Figure S1. Dynamic contact angle measurements of the Nanopaper I and II.

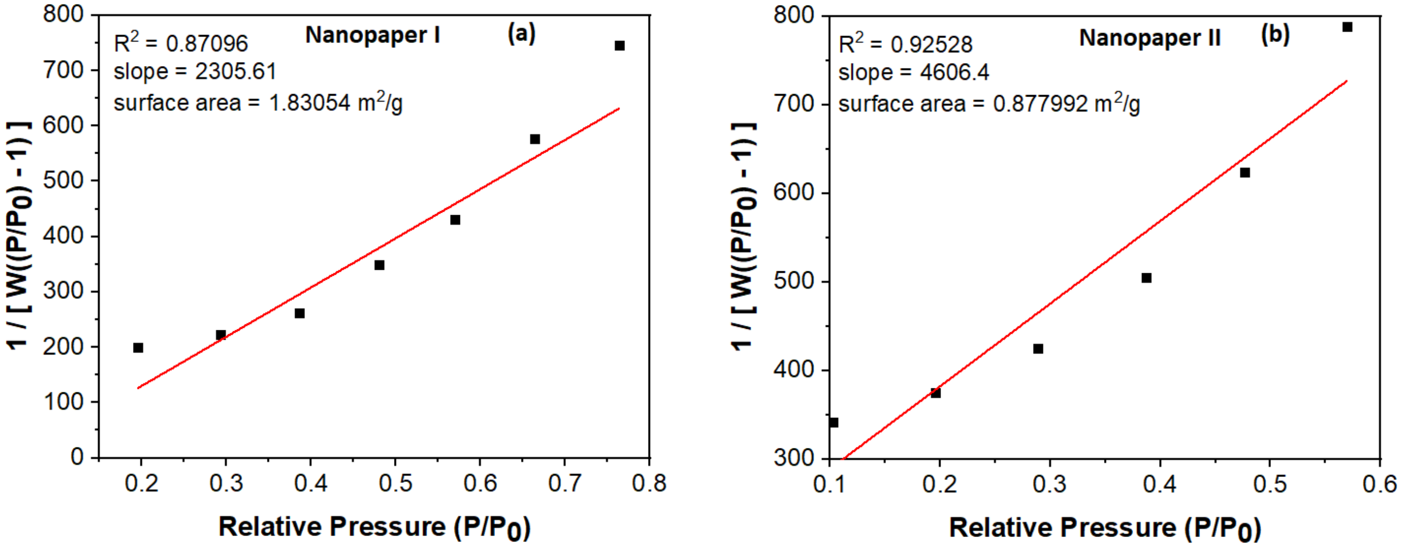

Figure S2. BET surface area plot for Nanopaper I and II.

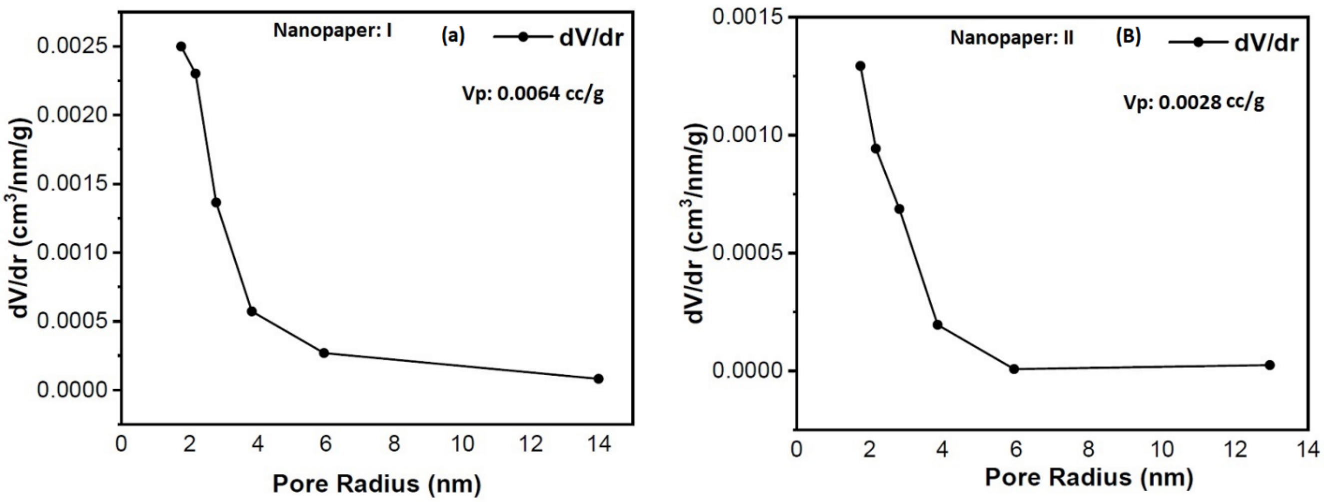

Figure S3. Pore size distribution based on BJH analysis in Nanopaper I and II.

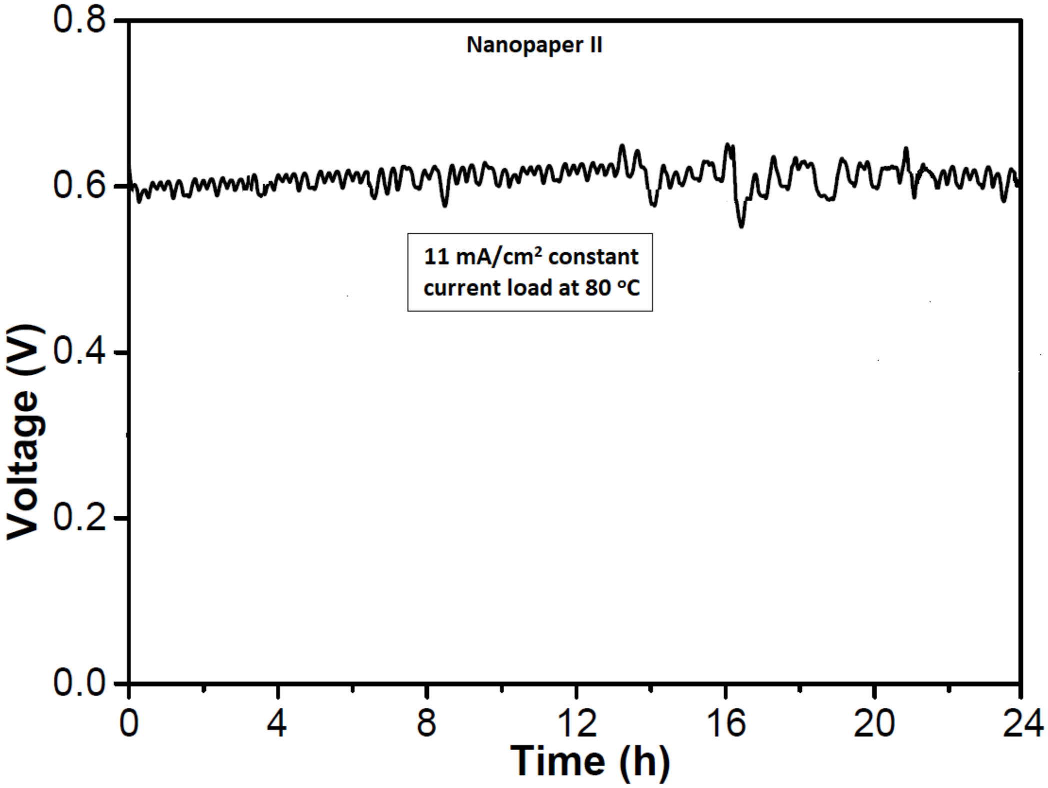

Figure S4. Durability measurement of Nanopaper II based fuel cell at 80 °C with a 11 mA constant load current.