Supporting Information

Genetically Engineered Proteins based Nacre-like Nanocomposites with Superior Mechanical and Electrochemical Performance

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Materials.

The expandable graphite used in this study to fabricate reduced graphene oxide (RGO), was provided by Asbury Carbons (USA) (Product Number: 3772). The Cellulose nanofibrils (CNFs), was obtained by the disintegration of the never-dried bleached birch hardwood Kraft pulp (UPM-Kymmene Oyj, Finland). The 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) based oxidation was carried out by disintegrating the pulp through a high-pressure micro-fluidizer (Microfluidics M700, Microfluidics Int. Co., Newton MA, USA) for six passes, to obtain the CNFs with a final concentration of ~1.8wt. % solids, following a similar approach as reported in our earlier studies. The dimensions of CNFs fabricated were of diameter ~20 \pm 8 nm with surface carboxylic group content of ~0.1 mmol/g.

dCBM-RLP-HFBI fusion protein production and purification steps.

dCBM-RLP-HFBI is a recombinant chimeric protein containing two cellulose-binding modules (CBMs) and hydrophobin (HFBI) connected through a responsive polypeptide linker resilin protein (RLP). The dCBM-RLP-HFBI fusion protein-encoding gene was constructed

from HFBI and CBMs derived *Trichoderma reesei* and with codon-optimized Rec1-resilin synthetic gene from *Drosophila melanogaster*. The *T. reesei* strain M658 was transformed with the gene expression cassette containing the designed gene sequence, following the protocol described in our earlier studies ^{1 2 3}. The resulting *T. reesei* strain M1230 expressing the designed fusion protein was grown in an in 8 L using a Biostat C10 (B. Braun Biotech International) in media containing 6% lactose, 3% spent grain extract, 5 g/L KH₂PO₄, 5 g/L (NH₄)₂SO₄, 2.4 mM MgSO₄, 4.1 mM CaCI₂, 3.7 mg/L CoCI₂·6H₂O, 5 mg/L FeSO₄·7H₂O, 1.4 mg/L ZnSO₄·7H₂O, and 1.6 mg/L MnSO₄·7H₂O and lactose feed., for 5 days and the dCBM-RLP-HFBI secreted into the culture media was collected. The protein analysis and purification have been described earlier ³.

Protein binding to RGO and NFC

To determine the binding isotherm of the fusion protein towards RGO, NFC and RGO/NFC suspensions, dCBM-RLP-HFBI, was prepared at different concentrations. RGO, NFC, and RGO/NFC (at 1:1 concentration of RGO and NFC), at a concentration of ~2 g/L each, was mixed with the protein at different concentrations (equal volumes of ~50 μ l) through pipetting. The suspensions containing protein was incubated at room temperature for 2 hours followed by centrifugation at ~11,000 rpm (maintained at ~10°C) for 15 minutes to separate the suspended particles. The supernatant containing the free protein was carefully removed and analyzed with ultra-high performance liquid chromatography (UHPLC), Thermo Scientific Vanquish. The samples were placed in an auto-sampler maintained at 4°C and measured using a photodiode array detector (PDA fitted with a C4 Acquity BEH300 column, precalibrated with known protein concentration. The one site Langmuir models ⁴ which assumes the formation of a monolayer of adsorbate onto the adsorbent surface was used to determine the interaction parameters and adsorption capacity of fusion proteins,

$$C_B = \frac{[C_{max}] \times [C_F]}{K_d + [C_F]}$$

where C_B represents the concentration of bound protein, C_{max} refers to maximum binding capacity, C_F is the concentration of free protein (in mg/ml) and K_d is equilibrium binding dissociation constant, defining the strength of interaction of NFC and RGO with the fusion protein.

However, the genetically engineered protein, dCBM-RLP-HFBI, used in this study is made up of three protein constructs due to which it poses multiple sites for interaction with NFC and RGO, which was evaluated using the Hill equation ⁵ (based on non-linear curve fitting),

$$C_B = \frac{\left[C_{max}\right] \times \left[C_F\right]^n}{K_a^n + \left[C_F\right]^n}$$

where *n* represents the Hill coefficient which defines the type of cooperative association between the protein and NFC/RGO species. K_a , refers to the association constant and the apparent dissociation constant K_d can be calculated as $K_d = (K_a)^n$ measured under equilibrium conditions.

Exfoliation and modification of reduced graphene oxide (RGO)

The exfoliation of expandable graphite (EG, 99.9%) into reduced graphene oxide (RGO), followed by its partial oxidation was carried out following the protocol mentioned in our earlier reported study ⁶. EG was thermally exfoliated in a muffle furnace with a preset temperature of ~750°C for a time period of ~2 min. The obtained RGO was partially oxidized by dispersing it into methanol in presence of ~2 wt. % hydrogen peroxide using a tip sonicator (at an amplitude of ~30% for approximately ~ 30 mins). The oxidized RGO was homogeneously dispersed in methanol, which was centrifuged and washed (with water) for several times to remove the trace fractions of chemicals present in it. The obtained RGO paste was dried into a powdered form in a hot air oven. In present study the partialally oxidized RGO sheets obtained had a lateral size dimensions of ~3.8±0.8 μ m.^{7 8}

Fabrication of Reduced Graphene Oxide (RGO)/Nanocellulose (NFC) based nanocomposites

To evaluate the reinforcing efficiency and pH-responsive characteristics of the dCBM-RLP-HFBI fusion protein, nanocomposite films at a various ratio of RGO and NFCs, protein concentrations and in the presence of different pH buffers were fabricated. The modified RGO was dispersed at a concentration of ~ 2g/L into a buffer (of pH~7), through sonication with a micro-tip (Vibra-Cell VCX 750, 2 mm stepped microtip, Sonics and Materials Inc., U.S.A.) maintained at ~40% amplitude for 20 min. To prevent overheating and induce better mixing the sonicator was programmed to carry out sonication at an interval of ~2 seconds on/off mode (with RGO suspension placed on ice). Thereafter, the required amount of NFC was added to prepare the RGO/NFC films with a final concentration of 1:1, 1:2, 1:3 and 1:5 (ratio of NFC: RGO). The NFC/RGO suspension was further sonicated for ~10 min at same amplitude to form a uniform suspension. To NFC/RGO suspensions, fusion protein dCBM-RLP-HFBI at a concentration of ~2.2 g/L was added followed by sonication at ~20% amplitude for 10 mins (in an ice bath). The uniformly dispersed slurry of RGO/NFC suspension was poured on petridish and allowed to air-dry for 3-5 days placed inside a fume-hood. The films with different ratio of RGO and NFCs were represented as NFC_RGO_1_1, NFC_RGO_1_2, NFC_RGO_1_3 and NFC_RGO_1_5, respectively.

To understand the effect of the fusion protein, different concentrations of dCBM-RLP-HFBI at ~1.5, 2.2 and 3.3 g/L was added to RGO/NFC suspensions. For all the films prepared, the RGO/NFC concentration was fixed at 1:3 and processed with a buffer of pH ~7 and following the rest of the protocol, as mentioned above. The films with different content of fusion protein (fPROT) was represented as NFC_RGO_1_3_1.5fPROT NFC_RGO_1_3_2.2fPROT and NFC_RGO_1_3_3.3fPROT, respectively.

The RGO/NFC films with buffers of three different pH~ 4.5, 7.0 and 11.0 as dispersing agents were used for fabrication of nanocomposite films, following the similar procedure as mentioned above. The ratio of RGO and NFC was fixed at a concentration of 1:2 and the protein content of 2.2g/L were added to the suspension. The films fabricated with three different pH buffers designated as NFC RGO 1 2 pH4, NFC RGO 1 2 pH7 are and NFC RGO 1 2 pH11 respectively. Furthermore, following the same protocol three films at different pH was also fabricated without the addition of any protein, as a reference. It should be noted that the films after drying through evaporation induced -self-assembly approach (slow process of drying) didn't showed formation of any salt precipitates in all the pH conditions (as seen in Figure 1(b)).

Fabrication of all Solid –State Flexible Supercapacitor

The RGO/NFC films were cut into dimensions of $\sim 1 \text{ cm x 1cm}$ (length x breadth) with a thickness of $\sim 10 \text{ }\mu\text{m}$, were cleaned and immersed into 6M KOH solution used as an electrolyte for $\sim 5 \text{ min}$. The copper foil (with adhesive at one side) which acted as a current collector was carefully affixed to the RGO NFC films to ensure good electrical contact of the electrodes. The symmetrical two electrodes EDLC solid-state supercapacitor device was fabricated by sandwiching a 6M KOH saturated filter paper (Whatman Grade A) as a porous separator between two identical RGO/NFC films as electrodes. The electrodes were assembled and placed in between metal case laminates and pressed to ensure good electrical contacts. To evaluate the performance of the developed flexible supercapacitors in daily commodities (as

shown in Figure 4(f)) the RGO/NFC nanocomposite films were pressed and laminated in between two transparent polyethylene films.

Instrumentation and Characterizations

Mechanical testing of NFC/RGO nanocomposites

The RGO/NFC films for mechanical testing were cut into specimens of dimensions 30 mm x 5 mm (length x width) and conditioned in a humidified room maintained at ~23°C and 50% humidity overnight. The thickness of films was measured with digital thickness gauge caliper (Ueetek 0.5). The tensile tests were carried out with dynamic mechanical analyzer (DMA), TA instruments, DMA Q800 using a tensile mode film-type geometry. The tests were carried out at a nominal strain rate of 0.5 mm/min and with a gauge length maintained at 10 mm.

Morphological Characterizations

For morphological investigations, RGO/NFC films were firstly immersed in liquid nitrogen and subsequently cracked to study the cross-section of the films. The air-dried films were coated with gold using a sputtering unit (Emitech K950X/K350) and placed on a carbon-tape carefully in a perpendicular direction to the electron beam. The samples were imaged using Field emission scanning electron microscopy (FESEM), Zeiss Sigma VP at an accelerating voltage of 3kV with the in-lens mode.

Structural and physicochemical properties of films

The structural properties of RGO/NFC films were investigated with X-Ray Diffractometer (XRD) (Rigaku Model Smart Lab 4800), equipped with copper-based K_{α} X-ray source operating at a voltage of ~40 kV and current of ~40 mA. The RGO/NFC nanocomposite films were placed flat on a film-type sample holder and scanned from 2 θ =1 to 40° at a scanning speed of 0.05°/min and step size of 0.01°. The chemical properties of RGO/NFC films were measured with Raman spectroscopy attached with a microscope (Alpha 300, WITec, Ulm Germany). The samples were scanned with Nd: YAG green laser of the excitation wavelength of~ 532 nm in the range of 500-3500 cm⁻¹ with an exposure time of ~5 seconds for 1024 number of scans at a resolution of 2 cm⁻¹ to obtain the Raman spectra.

Electrical Conductivity Measurements

The electrical resistance of the RGO/NFC nanocomposite films was measured with a four-point linear probe (Jandel Model RM3000 test unit, Jandel Engineering Ltd) which is equipped with Keithley 2400 source meter. The measured sheet resistance (Rs, Ω /sq) was converted to

specific resistance (Ω) taking into consideration the thickness of films, as described earlier ⁹. The electrical conductivity (S/m) of the nanocomposite were subsequently measured calculating the reciprocal of the specific resistance of films.

Electrochemical Characterizations

The electrochemical measurements of all the RGO/NFC based electrodes were performed using a potentiostat -galvanostat Reference 600+ (Gamry Instruments, USA) in a threeelectrode system in 6M KOH (aq) electrolyte. The NFC/RGO films (of dimensions 1cm×1cm) were placed on a copper foil (with adhesive at one side) as current collector and used as working electrode, with the platinum electrode and Ag/AgCl electrode as counter and reference electrode respectively. The cyclic voltammetry (CV) tests were performed over a potential 1.0 V to 0.5 V at different scan rates of 10, 25, 50 and 100 mV/s. The window from galvanostatic charge-discharge (GCD) measurements were measured with potential ranging from 0 to $\pm 1V$ at different current densities of 1, 2, 3 and 5 mA/cm². The electrochemical impedance spectra (EIS) was determined at open circuit potential with an amplitude of ~10 mV over a frequency range of 0.01 to10⁵ Hz. The Nyquist plot obtained from EIS measurements were fitted and processed with software Gamry Echem Analyst to develop the equivalent electrical circuit. For the CV and CD studies of the nascent RGO, was carried out by suspending RGO in water at similar concentration of 2g/L (used for films fabrication), and deposited onto the nickel foam which is used as current collector in presence of the 5% Nafion[®] solution as binder. For all the electrochemical data reported, the tests were repeated on newly fabricated EDLC devices each time with at least three different samples.

Electrochemical Performance Evaluation

The specific areal super-capacitance (F/cm²) values of NFC/RGO films were calculated from the discharge curves using the following equation:

$$C = \frac{I \times t}{A \times \Delta V}$$

where I is the constant discharge current (mA/cm²), t represents time for discharge (in secs), ΔV is the drop in potential (V) during discharging cycles(taking into consideration the IR drop wherever necessary) and A denotes the area of electrode used for assembly of full-cell. The real and imaginary components of areal capacitance, represented as C'(f) and C''(f), (F/cm²) were calculated as per the following equation:

$$C'(f) = \frac{-Z''(f)}{2\pi f |Z(f)|^2}$$
$$C''(f) = \frac{-Z'(f)}{2\pi f |Z(f)|^2}$$

where Z'(f) and Z''(f) are the real and imaginary components of impedance and f represents the frequency. The time constant (τ_o), or the knee frequency (f_o) was calculated from the maxima of the C''(f) vs frequency (f) plots of the NFC/RGO films. The time constant (τ_o), is a measure of time required for the extraction of the half of the charge stored in the capacitors. The τ_o takes into consideration the ionic, electrical and cell resistance arising from the assembled two-electrode system used for the study.



Figure S1: (a) Schematic representation of the hybrid protein dCBM-RLP-HFB, developed from the individual amino acid sequence through *ab initio* modelling (using the Quark online program) and (b) Photographs of the flexible RGO/NFC films processed under different pH conditions pH 4, pH 7 and pH 11, with the presence of mirror-like glossy characteristics suggesting highly ordered lamellar structure of the RGO sheets and NFC at a concentration ratio of 1:3. The appearance of background objects such as house-hold tube light and the photographer is captured onto the surface of the film.

Table S1: The parameters for binding coefficients of NFC, RGO, and NFC: RGO (1:1) with the protein dCBM-RLP-HFB determined using the Langmuir model and Hill equation.

Samples								
NFC	3.4	5.8	0.851	0.17	0.48	2.44	0.981	
RGO	4.9	6.1	0.889	0.38	0.77	3.85	0.990	
NFC:RGO at (1:1)	7.6	13.5	0.752	0.20	0.63	4.21	0.988	



Figure S2: Morphological investigations of films containing different ratio of NFC:RGO processed at pH~7 with addition of dCBM-RLP-HFB at constant concentration of ~2.2g/L (a) cross-sectional view, (b) top view of films with NFC:RGO at 1:2, (c) presence of brick-mortar patterns in NFC_RGO_1_32.5fPROT films, (d) and (e) shows high-resolution micrographs of selected regions represent improved interfacial adhesions of NFC to RGO surface, cross-sectional view of (g) NFC_RGO_1_1 films with bundles of NFC and (h) NFC-RGO_1_5 films showing agglomerated restacked RGO sheets.



Figure S3: Morphological investigations of films with NFC: RGO of ~ 1:3 containing a constant dCBM-RLP-HFB concentration of ~2.2g/L processed at different conditions with buffers of (a) pH~4 with (b) high-resolution image at the selected area and (c) pH~11 respectively (with inset showing high-resolution image of selected region).



Figure S4: Raman spectra of selected region 2500-3000 cm⁻¹ (from Figure 2 (e)) for the NFC/RGO films processed at different pH. The curves show multiple Lorentzian fits (red line), and the green curves show the individual Lorentzian components corresponding to the 2D peak of spectrum. The blue line shows the shift in the 2D peak to lower wavenumber for the NFC/RGO films processed at pH 7 and 11 respectively in comparison to RGO.



Figure S5: (a) Stress-strain curve and (b) Young's Modulus and toughness of the NFC/RGO films fabricated at NFC: RGO concentration of 1:2 processed at different pH conditions without addition of any fusion protein, dCBM-RLP-HFBI.



Figure S6: (a) A summarized plot showing the ultimate tensile strength and toughness of the RGO/NFC films fabricated at different ratio of NFC/RGO, concentration of fusion protein which are processed at three different pH conditions (~4, 7 and 11), and (b) Ashby plots of natural nacre and other graphene-based artificial nacres reported in literature showing the effect of different types of molecular interactions.



Figure S7: Effect of the different ratio of NFC and RGO concentration (with constant protein content of \sim 1.5 g/L at pH 7) on (a) CV curves of the free-standing films measured at a constant scan rate of 100mV/s with a filter paper immersed in 6M KOH acting as separator and (b)

shows comparison of the charge and discharge cycles of the different NFC/RGO films measured at a constant current density of $\sim 2mA/cm^2$, (c) CV and (d) charge discharge (CD) curves for the nascent RGO (at a concentration of 2g/L) measured at a constant current density of $\sim 1mA/cm^2$.



Figure S8: The variation in electrochemical properties of NFC/RGO films with frequency (a) imaginary capacitance versus frequency plots, with the maxima representing knee frequency (f_o) from which the time constant (τ_o) is calculated, (b) real capacitance versus frequency curves, (c) comparison of cyclic stability of the NFC/RGO films based supercapacitors measured at current density of 25mA/cm² over a period of 1000 cycles (d) cyclic performance of NFC_RGO_1_3_pH7 film measured at a lowered current density of ~1mA/cm² for a period

of 1000 cycles, (e) shows the high flexibility and bendability of the fabricated NFC/RGO films and (f) CV measurements of NFC/RGO films measured under the flat and bending stresses over a cylindrical object of diameter ~1 cm.



Figure S9: Schematic illustration of NFC/RGO films micro-structure prevailing at different pH conditions and understanding the mechanism of ion transport dynamics through the interlayers spacings. The KOH electrolyte used in this study has solvated radius of 2.92Å which either adsorbs onto the surface or penetrates in the inter-galleries of RGO. The ion transport mechanism is governed by the processing conditions of films (i.e. pH) and depending upon the filling density of the inter-layers.

Table S2:	The equivalent	circuit parameters	calculated from	the fitted	Nyquist plots.
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Electrodes	Rs	R _{ct}	W _d	Yo	n	Ср
	(Ω)	(Ω)	$(\mathbf{S} \times \mathbf{s}^{1/2})$	$(\mathbf{S} \times \mathbf{s}^n)$		(F)
NFC_RFO_1_3_pH4	1.08	1.54	134.8× 10 ⁻⁶	456.6× 10 ⁻³	0.88	17.8×10^{-3}
NFC_RFO_1_3_pH7	0.78	1.24	9.4 × 10 ⁻⁶	77.3× 10 ⁻³	0.98	24.3× 10 ⁻³
NFC_RFO_1_3_pH11	0.64	1.26	76.3× 10 ⁻⁶	117.5×10^{-3}	0.82	83.2× 10 ⁻³

Table S3: Comparision of the electrochemcial performance and mechanical properties of nanocellulose based hybrid composites reported in the literature.

Electrodes	Areal Capacitance	Volumetric Capacitance	Equivalent series	Tensile Strength	Ref.
	(mF/cm ²)	(F/cm ³)	resistance	(MPa)	
Cobalt	12.25	-	1.12 Ω	63	10
Oxide/Graphene/Bacterial	$(3mA/cm^2)$				
Cellulose					
Graphene/Cellulose paper	46	-	1.1 Ω	8.6	11
	(2mV/s)		-		
Cellulose	0.8	-	$1.48 \ \Omega/cm^2$	765	12
Naocrystal/Graphene films	(0.5 mA/cm)				
Cellulose/RGO/silver	2044	75.7	6 Ω	-	13
/Fe ₂ O ₃ hybrid film	$(2mA/cm^2)$				
Carbon woven fabric/	197	-	1.6 Ω	-	14
polyaniline/ graphene	(1mA/cm^2)				
composite					
Reduced graphene	510	8.5	5.3 Ω	162	15
oxide/polypyrrole/cellulose	(0.51)				
hybrid	mA/cm^2)	40.5	100		1.6
Cellulose fibers/single-	330	40.5	1.8 Ω	-	16
walled carbon	(0.2 mA/cm^2)				
nanotubes/polyaniline					
Delymyrrele costed nener	420		450		17
Polypyrrole-coaled paper	420 (1m A / 2m ²)	-	4.3 12	-	1/
Granhana callulaga tiggua	(IIIIA/CIII ⁻) 75				10
oraphene-centulose tissue	$(0.2 \text{m} \text{ A}/\text{a}\text{m}^2)$	-	-	-	10
Cellulose coupled	(0.2111A/CIII) 363		340	12	10
graphene/polypyrrole	$(0.5 \text{ m}\text{A/cm}^2)$	-	J.4 22	42	19
Graphene/Carbon	495		29.0.0	57	20
Nanotube/Bacterial	(30 mA/cm^2)		29.0 32	57	20
Cellulose					
rGO/cellulose paper flash	24	2.4	80Ω	_	21
reduction process	(0.5 A/g)		0.0 ==		
Reduced graphene oxide	71.2	89.0	0.63 Ω	421	This
/Nanocellulose/genetically	(2 mA/cm^2)				work
engineered proteins hybrid	×				

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