Electronic Supplementary Material (ESI) for RSC Advances.

Ultra-light nanocomposite aerogels of bacterial cellulose and reduced graphene oxide for specific absorption and separation of organic liquids

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Supplementary movies:

Movie S1. Surface absorption by BC aerogel

Movie S2. Absorption by BC aerogel with delayed addition of cyclohexane

Movie S3. Absorption by BC+GO aerogel (50+50) with delayed addition of cyclohexane

Movie S4. Absorption by BC+rGO aerogel (80+20) with delayed addition of cyclohexane

Movie S5. Separation experiment of water and cyclohexane on BC aerogel

Movie S6. Separation experiment of water and cyclohexane on BC+GO aerogel (50+50)

Movie S7. Separation experiment of water and cyclohexane on BC+rGO aerogel (80+20)

Experimental section

Materials

Gluconacetobacter xylinus of the strain DSM 46605 was obtained from Leibniz Institute DSMZ-German Collection of Microorganisms and Cell Cultures (Braunschweig, Germany). Grapheme flakes of 325 mesh (99.8%) was purchased from Alfa Aesar (Karlsruhe, Germany). Deionized water (DI water) was used in all experiments. The other chemicals are all of analytical grade and used as received.

Biosynthesis of bacterial cellulose

Bacterial cellulose (BC) was biosynthesized using *G. xylinus* culture in Hestrin-Schramm medium.[1] Briefly, 20.0 g glucose, 5.0 g yeast extract, 5.0 g bacterial peptone, 2.7 g sodium phosphate dibasic ($Na_2HPO_4 \cdot 2H_2O$), 1.2 g citric acid and 5.7 g magnesium sulfate ($MgSO_4$) were dissolved in 1 l DI water. Then, the pH value of the solution was adjusted to around 5 using 3 N HCl aqueous solution. Then, the growth medium was divided into 10 equal volumes of 100 ml each in a 250 ml flask. After that, the initial strain solution was added into the growth medium and the solutions were incubated at 30°C for 7 days. Obtained BC pellicles were purified three times in 0.1 N aqueous NaOH solution at 80°C, once in 0.1 N aqueous citric acid at 80°C and then washed with DI water until neutral pH. Finally, BC was freeze-dried at -50°C under a vacuum of 0.1 mbar.

Synthesis of GO

Graphene oxide was prepared as described.[2] Briefly, 3 g graphene flakes and 18 g $KMnO_4$ suspended in 9:1 mixture of 360 ml H_2SO_4 (98%) and 40 ml H_3PO_4 (85%) were treated at 50°C for 18 h. After cooling down, the slightly lilac suspension was poured into 600 ml ice containing 3 ml H_2O_2 (30%). After standing at RT for 12 h, the solid was separated via centrifugation. The precipitate was purified using 140 ml water, 140 ml aqueous HCl solution (36%), and twice with 140 ml ethanol (99%). Finally, obtained graphene oxide (GO) was suspended in 100 ml water and treated with ultrasonication for 1 h before further use.

Nanocomposite aerogels of BC, BC/graphene oxide (BC/GO) and BC/reduced graphene oxide (BC/rGO)

Dry BC was immerged in water at a given concentration and the suspension was stirred for 2 days. The swollen BC was chopped firstly with a blender and then Ultra-Turrax T25 (IKA®-Werke GmbH & Co. KG, Staufen, Germany) at 18000 rpm for 30 minutes, leading to an

aqueous suspension of nanofibrillated BC. Then, the BC suspension was degased via 5 min ultrosonication, frozen at -65°C, and freeze-dried at -50°C under vacuum. For the preparation of BC/GO aerogels, 100 ml of BC suspension (1.7 g/l) was mixed with defined volume of GO suspension at 10 g/l, so that the final weight ratio of both lay at 50:50 and 80:20. Then, the suspensions were mixed at RT for 3 h, degased via 5 min ultrosonication, frozen at at -65°C, and freeze-dried at -50°C under vacuum. In order to prepare BC/rGO aerogels, obtained BC/GO aerogels were reduced in a HORST oven (Horst GmbH, Lorsch, Germany) at 200 °C for 4 h under a hydrogen gas stream of 200 cm^3/min.

Methods

NMR

Solid-state CP/MAS ^{13}C NMR spectroscopy was performed on a Bruker Avance II+ 400 WB spectrometer (Bruker Biospin, Ettlingen, Germany) at room temperature (RT) with a ^{13}C frequency of 400 MHz,10 kHz spinning speed, 5 ms contact time and ^{1}H decoupling of 20 tppm.

Scanning Electron Microscopy (SEM)

For SEM on a Philips XL30 FEG high-resolution scanning electron microscope (HR-SEM) (FEI Deutschland GmbH, Frankfurt/Main, Germany) operating at 2 kV, purified and dried BC samples were coated with thin palladium/platinum film.

Transmission Electron Microscopy (TEM)

TEM was measured on a Philips CM20 transmission electron microscope (FEI) with LaB6-Kathode operating at 200 kV.

Liquid Absorbency and Porosity

The liquid absorbency of the aerogel for organic liquids including DMF and cyclohexane were measured. Aerogels after weighting were put into a 25-mL flask containing 20 mL of organic liquid and allowed to absorb to saturate at room temperature. Then, the saturated aerogels were removed to a filter and their weights were measured until no liquid flowed down.

The absorbency (g/g) was calculated as:

$Absorbency = \frac{(m_e - m_o)}{m_o}$ (1), where m_0 and m_e are the weights of saturated and dry aerogels, respectively. The absorbency was measured twice for each aerogel and the average value of the measurement was shown.

The porosity of each aerogel was calculated as:

$Porosity(\%) = \left(1 - \frac{\rho_a}{[w*\rho_c + (1-w)*\rho_g]}\right) \times 100\%$ (2), where ρ_a is the density of the aerogel, ρ_c is the density of cellulose (taken as 1.6 g/cm^{-3});[3] ρ_g is the density of GO (measured as 0.9127 g/cm^{-3}); w is the proportion of cellulose in the mixture of BC/GO (w/w). The porosity was measured twice for each aerogel and the average value was shown.

Raman Spectroscopy

Raman spectra were recorded on Horiba LabRam HR 800 micro Raman spectrometer (Horiba Jobin Yvon, Bensheim, Germany) equipped with an air-cooled Argon ion laser (emission line l=514.5 nm).

The Raman spectrum of GO showed characteristic signals at 1352 and 1574 cm^{-1} ascribed to D bands (A_{1g} symmetry mode) and G bands (E_{2g} mode of the sp^2 carbon atoms), respectively.[4] After the reduction, the intensity of D/G bands for rGO increased significantly, indicating the increase of sp^2 domain and thus successful reduction of GO.

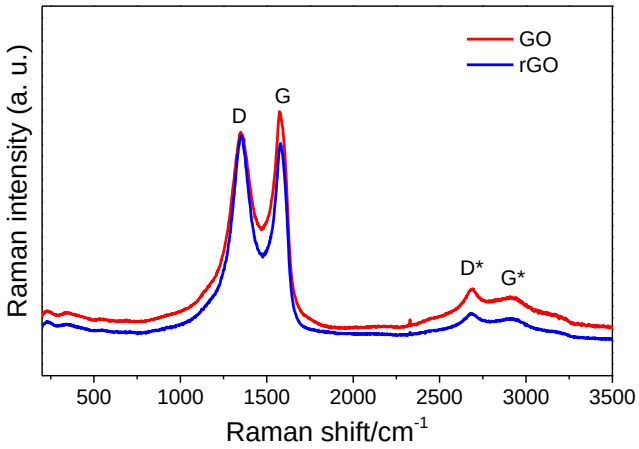

Figure S1. Raman spectra of GO and rGO.

FTIR Spectroscopy

FTIR spectroscopy was conducted on Spectrum One FTIR Spectrometer (PerkinElmer, Massachusetts, USA) at room temperature (RT) between 4000 and 600 cm^{-1} with a resolution of 4 cm^{-1}. Scans of 32 were accumulated. The spectra were baseline-corrected with 20

iterations and 200 statistical baseline points using OPUS Ver. 6.5 (Bruker Optics, Ettlingen, Germany).

Based on FTIR spectrum of BC/rGO after different reduction times, it is obvious that the maximal was reached after 4 h reduction.

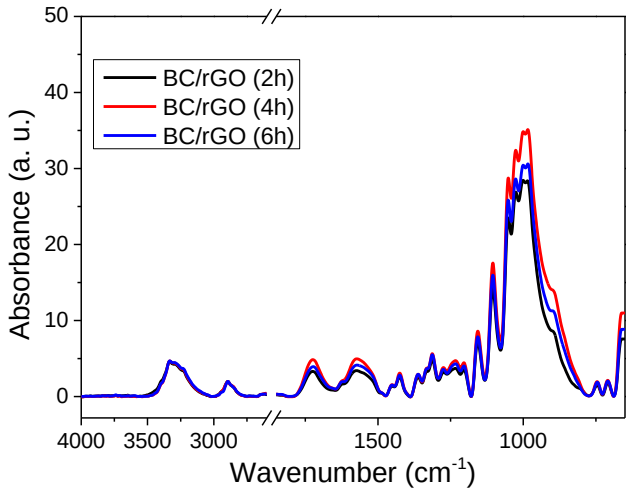

Figure S2. FT IR spectrum of BC/rGO after the reduction for 2, 4, and 6 h.

Figure S3. GO aerogel and GO aerogel in cyclohexane. Scale bar: 4 mm.

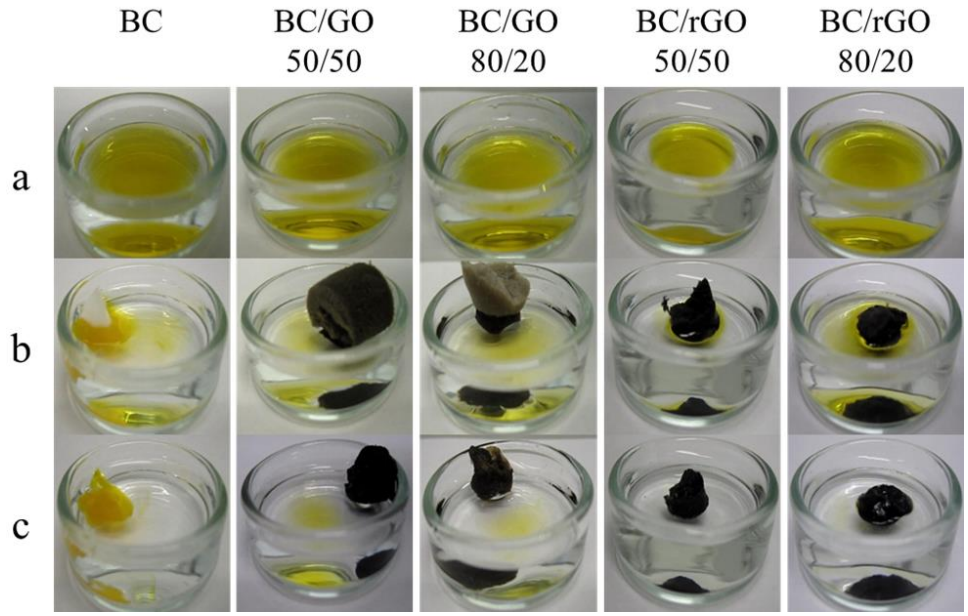

Figure S4. Representative images showing the absorption of cyclohexane (dyed with Sudan I) from water surface with a: dyed cyclohexane on water surface in petri dishes; b: placement of aerogel onto the surface of the mixture and begin of the absorption; c: end of the absorption.

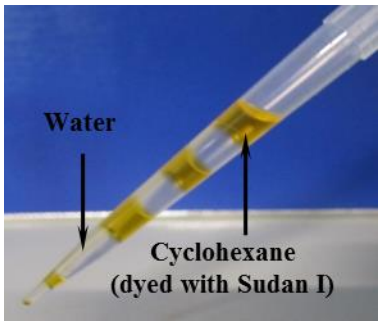

Figure S5. Representative image of added mixture of water and cyclohexane (dyed with Sudan I) for the separation experiment.

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2. D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu and J. M. Tour, *ACS Nano*, 2010, **4**, 4806-4814.
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