ADVANCED MATERIALS

Supporting Information

Gelatin–Graphene Nanocomposites with Ultralow Electrical Percolation Threshold

Hoda Nassira, Antoni Sánchez-Ferrer, Jozef Adamcik, Stephan Handschin, Hossein Mahdavi, Nader Taheri Qazvini,* and Raffaele Mezzenga*

Gelatin-Graphene Nanocomposites with Ultralow Electrical Percolation Threshold

Hoda Nassira[‡†], Antoni Sánchez-Ferrer[‡], Jozef Adamcik[‡], Stephan Handschin[‡],

Hossein Mahdavi[†], Nader Taheri Qazvini[†¶], Raffaele Mezzenga[‡*]*

‡ ETH Zurich, Department of Health Sciences and Technology, Food & Soft

Materials Science, IFNH, Schmelzbergstrasse 9, 8092 Zürich, Switzerland

E-mail: raffaele.mezzenga@hest.ethz.ch

† Polymer Division, School of Chemistry, College of Science, University of Tehran,

P.O. Box 14155-6455, Tehran, Iran

E-mail: ntaheri@ut.ac.ir

¶ Institute for Molecular Engineering, University of Chicago, Chicago

Illinois 60637, USA

E-mail: ntaheri@uchicago.edu

Materials: Gelatin (225 bloom, type B), was obtained from Sigma Aldrich. Graphite flakes with High-purity (RFL 99.5, 99.6% carbon content) were purchased from Graphit Kropfmühl. The particle size distribution was 7% for ≤100 μm, 20% for 160 μm, 48% for 200 μm and 25% for 315 μm.

Methods: The stock solution of gelatin was prepared by dispersing gelatin powder in milli-Q water at 50 ℃ and stirring for 1 h. GO was synthesized by the oxidation of graphite based on modified Hummers method.[1] In order to prepare GO dispersions, GO was dispersed and sonicated in deionized water in order to prepare a 0.5 wt% dispersion. The obtained dispersion was centrifuged at 3000 rpm for 30 min. The stable supernatant was purified by dialysis for one week to remove the remaining salts and acid. Calculated quantities of gelatin solutions at pH 3.0 were mixed with GO dispersion at pH 3 under vigorous stirring. After further stirring for 1 h, ascorbic acid (2 mM) was added. The reduction of GO to graphene was performed at 95 °C for 1 h under continuous stirring. The resulting black dispersions - with different weight ratios of 0.1, 0.2, 0.5, 1.0, 5.0, 10.0 and 15.0 wt% of GO -, were mixed with a freshly prepared gelatin dispersion (3 wt%) to the required ratio. After stirring for 2 h, films were fabricated by solvent casting and were dried at 37 °C under mild vacuum. Considering the weight ratios of solid GO to gelatin in the original mixtures, the films were labeled as 0.1, 0.2, 0.5, 1, 5, 10 and 15, respectively. For humidity sensitivity experiments, the films were equilibrated for 24 h in a closed glassware for different water activity values at 25 °C. To convert the loading of graphene (nanocomposite concentration) from weight to volume fraction, the density of both components were used, that is 1.27 g·cm^{-3} for gelatin and 2.2 g·cm^{-3} for graphene. For example, 0.96 wt% is equal to 0.56 vol%.

Characterization: Zetasizer Nano ZS dynamic light scattering analyzer (Malvern) was used to determine electrophoretic mobility. Each measurement was repeated 10 times, after which the average value was reported.

Atomic force microscopy (AFM) was performed by using Multimode VIII Scanning Probe Microscope (Bruker, USA) covered with an acoustic hood. AFM images were acquired in the tapping mode at ambient conditions using standard cantilevers with a typical tip radius <10 nm (Bruker, USA). A 20 μL aliquot of the dispersions was deposited onto freshly cleaved mica and incubated for 2 min. Samples were rinsed with Millipore water and gently dried with air. Derjaguin–Mueller–Toporov (DMT) out-of-plane modulus of the pure gelatin film and gelatin/graphene nanocomposites was obtained by AFM in peak force quantitative nanomechanical mode at a scan rate of 1 Hz. In order to calibrate the cantilever (Bruker, USA), calibrations samples including low-density polyethylene and polystyrene covering a broad range of moduli from 100 MPa to 2 GPa for low-density polyethylene and from 1 to 20 GPa for polystyrene were used. The analysis of DMT out-of-plane moduli was performed by Nanoscope Analysis software.

Transmission electron microscopy (TEM) images were obtained by using a FEI Morgagni TEM operating at a voltage of 100 kV. A drop of the dispersion was casted onto a carbon support film on a 400 mesh copper grid (Quantifoil). The excess solution was removed after 60 s by blotting using a filter paper. Samples were stained by adding a droplet of 2 wt% uranyl acetate solution (Sigma-Aldrich) onto the grid over a period of 15 s. Any excess of staining agent was removed again by a filter paper.

Scanning electron microscopy (SEM) was performed on a Zeiss Gemini 1530 SEM. A small piece of film was glued vertically in a sanded gap of an aluminium stub with

conductive silver paint (Plano) and manually cross fractured after drying. Following sputter coating with 2 nm of platinum (MED010, Bal-tec) imaging was done at 5kV using an in-lens detector.

Raman spectra were collected from 400 to 4000 cm^{-1} with a DXR Raman microscope (Thermo Fisher Scientific Inc.) at room temperature with 532 nm excitation laser (5 mW) under 10× objective of Olympus microscope. The Raman spectra for each sample were measured from different parts of sample.

Electrical Conductivity measurements were performed at room temperature by four-point probes with HMS-3000 Hall Measurement System. Current-voltage curves were obtained on 10 × 10 mm^2 films to extract the conductivity.

Small and wide-angle X-ray scattering (SAXS and WAXS) experiments were performed using a Rigaku MicroMax-002$^+$ microfocused beam (40 W, 45 kV, 0.88 mA) with the $\lambda_{CuK\alpha} = 0.15418$ nm radiation in order to obtain direct information on the scattering patterns. The scattering intensities were collected by a Fujifilm BAS-MS 2025 imaging plate system (15.2 cm 15.2 cm, 50 μm resolution) and a 2D Triton-200 X-ray detector (20 cm diameter, 200 μm resolution). An effective scattering vector range of 0.05 nm^{-1} < q < 25 nm^{-1} was obtained, where q is the scattering wave vector defined as $q = 4 \pi \sin \theta / \lambda_{CuK\alpha}$ with a scattering angle of 2θ.

Humidity sensing was electrically measured by Agilent Technology B1500A semiconductor parameter analyzer. The gelatin/graphene nanocomposite film was fixed on a circuit board and kept for more than one week before experiments. The sample was placed in a sealed box allowing the change in the relative humidity by changing saturated salt solutions.
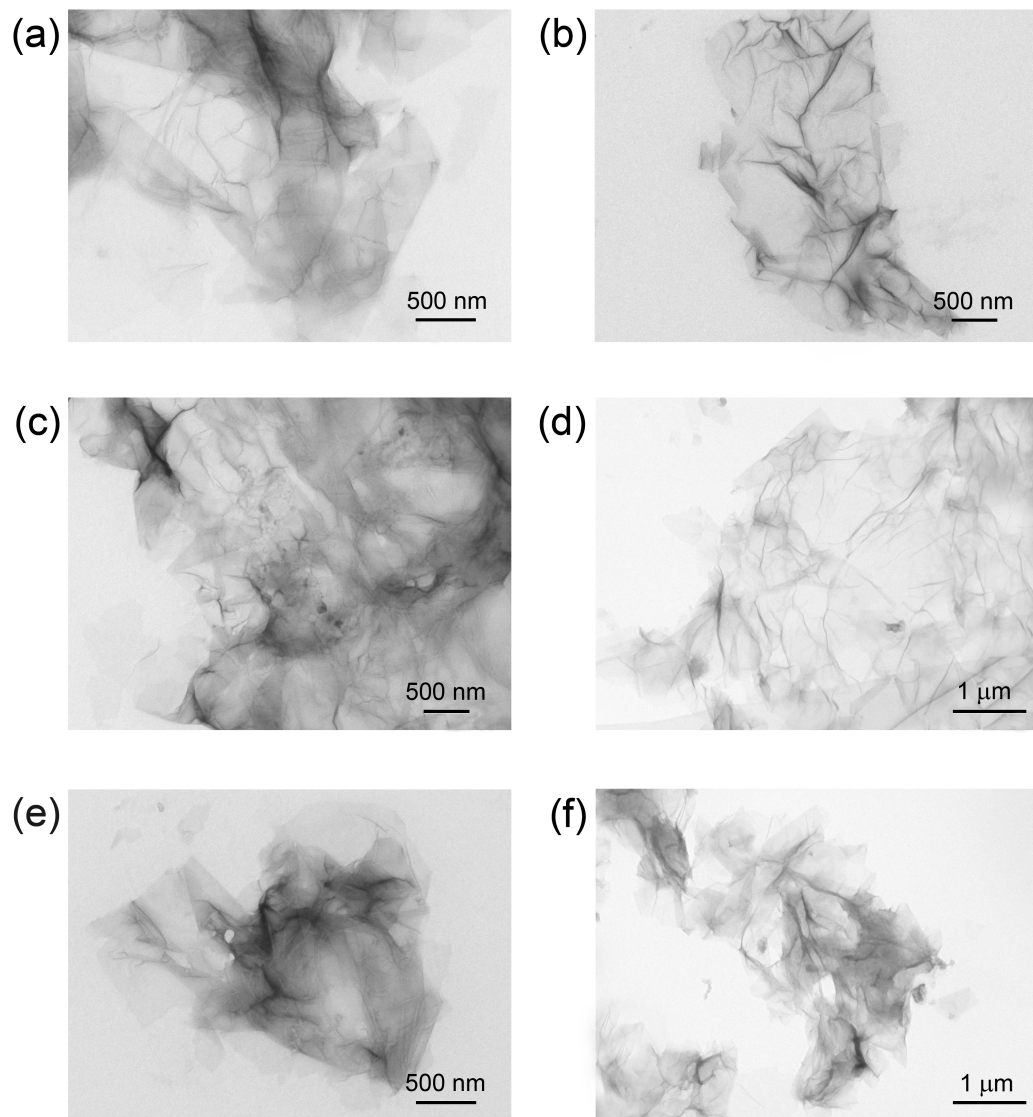
Figure S1. Morphology of the gelatin/GO dispersions before and after reduction. TEM image of gelatin/GO mixture with 1 wt% GO (a) before an (b) after reduction. TEM image of gelatin/GO mixture with 10 wt% GO (c) before an (d) after reduction. TEM image of gelatin/GO mixture with 15 wt% GO (e) before an (f) after reduction.

0.5wt% **1wt%** **5wt%** **10wt%** **15wt%**
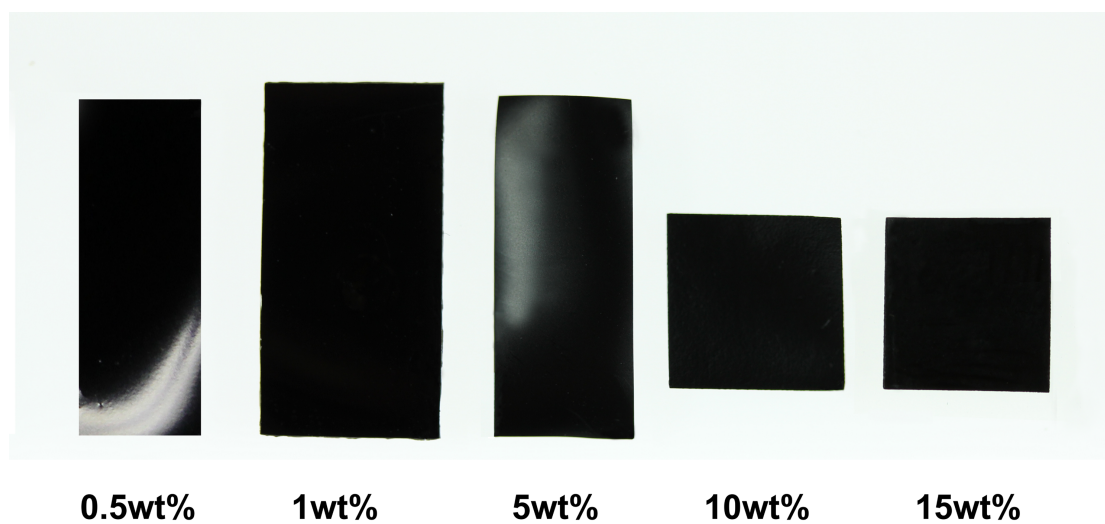
Figure S2. Optical images of the gelatin/graphene nanocomposite films (filler concentration 0.5, 1, 5, 10 and 15 wt%).

Table S1. Conductivity (σ) of the nanocomposites obtained by gelatin as reducing agent – no ascorbic acid added – in samples with different gelatin/GO ratio and pH ($T = 95$ °C, $t = 24$ h)

| Sample	Gelatin/GO (weight ratio)	pH (Gelatin : GO)	σ (S·cm^{-1})
1	100/1	5.2:5	Low*
2	100/1	5.2:3	Low*
3	100/1	3:3	Low*
4	1/1	5.2:5	Low*
5	1/1	5.2:3	3.1×10^{-7}
6	1/1	3:3	5.5×10^{-6}
7	0.5/1	5.2:5	Low*
8	0.5/1	5.2:3	0.31×10^{-7}
9	0.5/1	3:3	1.0×10^{-6}

* $\sigma < 10^{-8}$ S·cm^{-1}

Table S2. Conductance for some control samples

Sample	Conductance (mS)	Reducing agent T (°C) / t (h)	Appearance
Graphene	59	Hydrazine, 80/24	Precipitation
Graphene	low	Ascorbic acid, 23/48	Stable dark solution
Graphene	2.86×10^{-3}	Ascorbic acid, 55/48	Stable dark solution
Graphene	60	Ascorbic acid, 95/24	Precipitation
Gelatin	Insulator	Ascorbic acid, 95/1[a]	Stable light yellow solution
Gelatin	Insulator	Ascorbic acid, 95/1[b]	Stable light yellow solution

[a] Calculated quantities of ascorbic acid for 10 wt% GO. [b] Calculated quantities of ascorbic acid for 15 wt% GO.
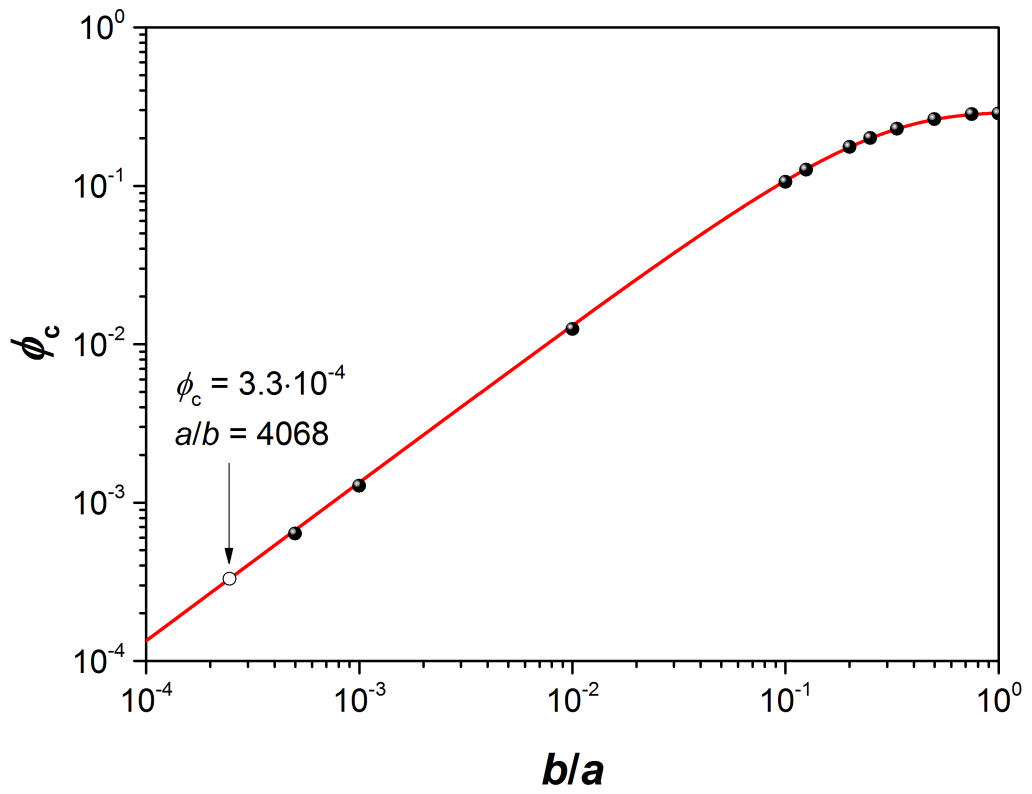
Figure S3. Percolation threshold vs. aspect ratio of oblate ellipsoids of revolution. Data has been taken from reference 2.[2]
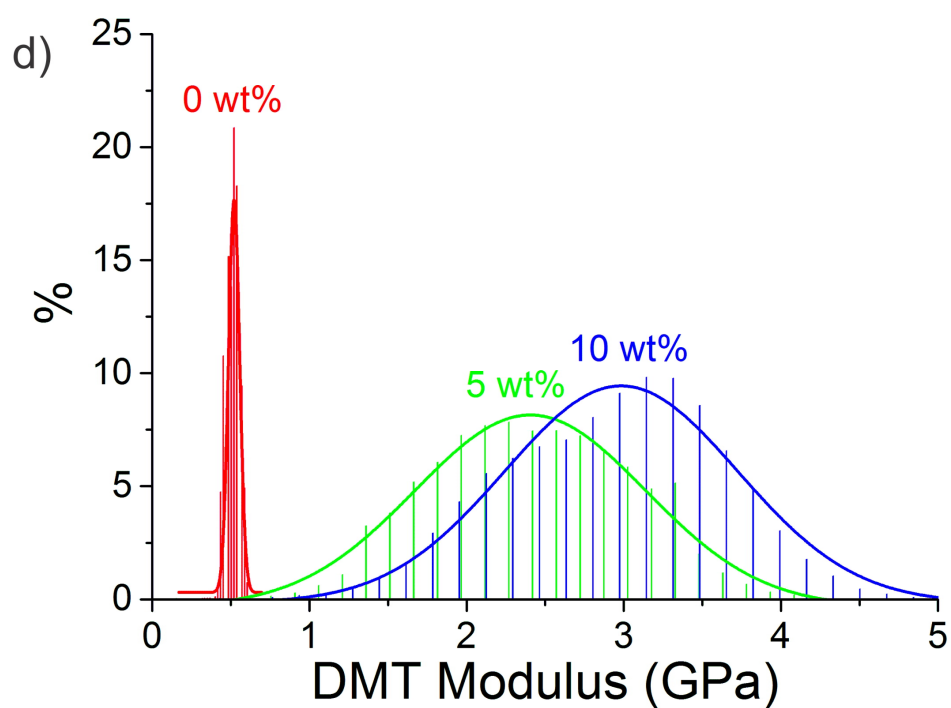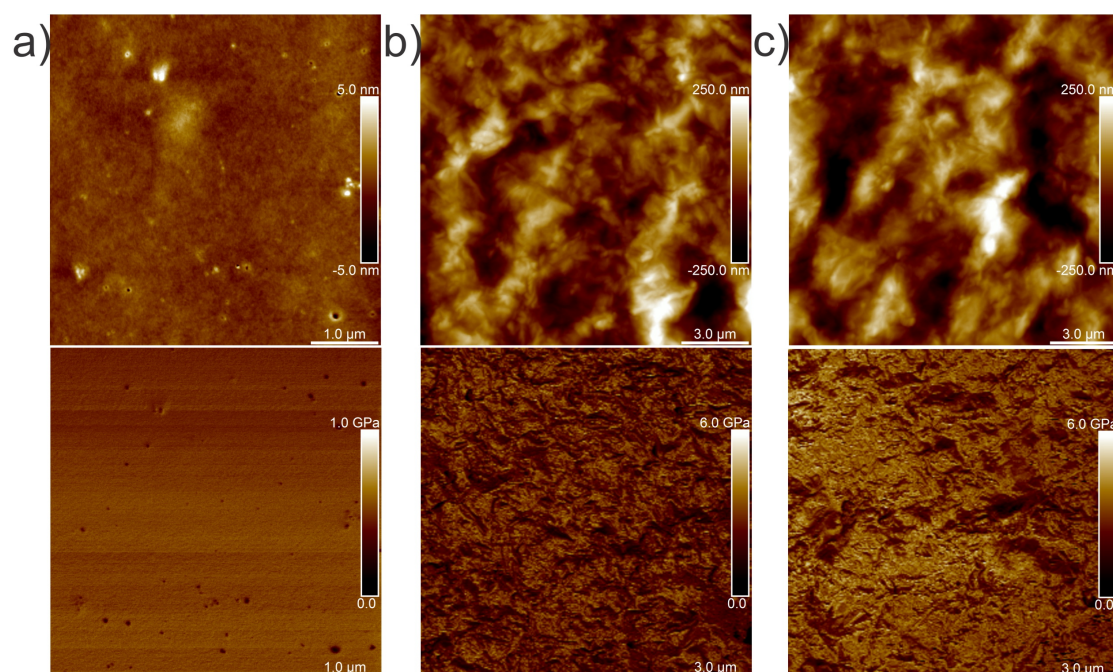
Figure S4. AFM topographic image with corresponding DMT modulus image of a) pure gelatin film, b) gelatin/graphene nanocomposite film with 5wt% graphene and c) gelatin/graphene nanocomposite film with 10wt% graphene. d) DMT modulus distribution of pure gelatin film (red), gelatin/graphene nanocomposite film with 5wt% graphene (green) and with 10wt% graphene (blue).
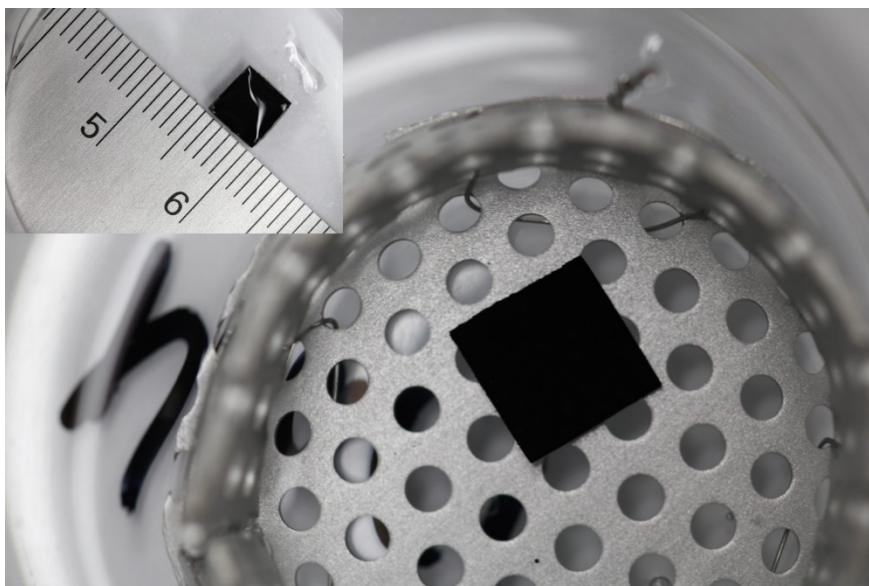
Figure S5. Stability of the gelatin/graphene nanocomposite (10wt% graphene) in PBS after 4 weeks at 37°C; Inset: The sample taken out of the media for size measurement.

References

[1]   D. C. Marcano, D. V Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu, J. M. Tour, *ACS Nano* **2010**, *4*, 4806.

[2]   D. Stauffer, A. Aharony, *Introduction to Percolation Theory*, London   : Taylor & Francis, **2003**.