Microengineered hollow graphene tube systems generate conductive hydrogels with extremely low filler concentration

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**Experimental Details**

**Fabrication of microchannel-containing PAM-EG networks.** The tetrapodal zinc oxide (t-ZnO) was produced via a simple flame transport synthesis, described in detail elsewhere.[1,2] Briefly, zinc oxide powder (1-5 μm grain size) was mixed with poly(vinyl butyral) in a mass ratio of 1:2 and then heated in a furnace up to 900 °C for 30 min with a heating rate of 60 °C min⁻¹. The harvested powder of t-ZnO microparticles was pressed into sacrificial templates of cylindrical shape (6 mm height, 6 mm diameter), possessing a density of 0.3 g cm⁻³ (94 % porosity). The porosity of the scaffolds is obtained as follows: A defined amount of tetrapodal ZnO powder (here: 0.051 g) is pressed into a cylindrical shape (6 mm diameter; 6 mm height). The resulting volume is ~0.170 cm³ and leads to a density of around 0.3 g cm⁻³. Since the bulk density of ZnO is 5.61 g cm⁻³ the porosity is ~94 % for the ZnO template. By increasing the density of the sacrificial t-ZnO by using more tetrapodal ZnO powder, the free volume is decreased and thus, the porosity of the conductive sample is increased.

The prepared templates were then sintered at 1150 °C for 5 h to obtain a network of interconnected ZnO tetrapods. To coat the ZnO tetrapods with exfoliated graphene (EG) a wet-chemical infiltration process was applied.[3] An aqueous dispersion of EG (1.7 or 1.9 mg mL⁻¹), provided kindly by Sixonia Tech GmbH and used without further purification, was drop-cast onto the template until its entire free volume was filled. The solvent was then allowed to evaporate at 50 °C for 4 h, resulting in the deposition of EG onto the ZnO tetrapods. For the hydrogel precursor, acrylamide (Bio-Rad, 40 %, 1250 μL), N,N'-methylenebis(acrylamide) (Bio-Rad, 2 %, 1000 μL), HEPES buffer (Sigma-Aldrich, pH 7.5, 50.0 μL), 2625 μL ddH₂O and ammonium persulfate (APS, Sigma-Aldrich, 10%, aq., 75.0 μL) were mixed and degassed for at least 10 min in a desiccator. Afterwards, N,N,N',N'-tetramethylethylenediamine (TEMED, Sigma-Aldrich, 10 %,
20.0 µL) was added and the hydrogel precursor solution was drop-cast onto the t-ZnO templates until their entire free volume was filled. The hydrogel was allowed to polymerize for 90 min followed by wet-chemical removal of the ZnO with 0.5 mol L⁻¹ hydrochloric acid. Before measurements, the samples were washed extensively with double distilled water.

**Biocompatibility of microchannel-containing PAM with different carbon fillers.** To determine the cytotoxicity of the microchannel-containing polyacrylamide composites an indirect MTT extraction test was performed according to ISO-10993-5. In brief, extractions were prepared by incubating hydrogel samples at 37 °C in culture medium for 24 h (Dulbecco’s modified Eagle’s medium (DMEM) supplemented with 10 % fetal bovine serum and 1 % penicillin/streptomycin). 10⁴ rat embryonic fibroblasts (REF52-wt) are cultured in 100 µl of medium in 96-well plates for 24 h. Afterwards, the medium is replaced with the original extraction medium, as well as with a dilution series of the extract medium. Cells are incubated for another 24 h. The number of viable cells was measured by adding 50 µL of methylthiazolyldiphenyl-tetrazolium bromide (MTT; Sigma-Aldrich, Germany) solution. After 2 h of incubation the absorbance was measured at 570 nm. Fresh culture medium was used as a negative control and culture medium supplemented with 10 % dimethyl sulfoxide as a positive control. The results were normalized to the absorbance measured in the controls (Figure S1). PAM network samples show a high biocompatibility above 90 % for undiluted extracts. PAM-EG samples show a decrease in fibroblast proliferation but values for undiluted extracts are still above 70 %, which is according to the ISO norm regarded as biocompatible.
Figure S1. Cell viability of rat embryonic fibroblast cells (REF52wt) treated with extraction medium of polyacrylamide (PAM) and microchannel-containing PAM with exfoliated graphene (EG, 0.32 vol%). Fresh culture medium served as a control. Error bars depict standard deviations, N = 3.

Raman Spectroscopy. Raman spectroscopy was used to investigate the potential chemical bonding between PAM and EG. An alpha300 RA (WITec) microscope with a triple grating spectrometer (600 gmm⁻¹) and a charge-coupled device detector was applied. The laser had an excitation wavelength of 532.2 nm and the spot size on the sample was 1.41 μm with a maximum power of 52 mW. Spectra were recorded of PAM-EG (0.16 vol.%) and network PAM samples and are shown in Figure S2. In comparison to the network PAM sample the PAM-EG sample revealed additional bands at ~1350 cm⁻¹, ~1580 cm⁻¹ and ~ 2700 cm⁻¹ corresponding to the D, G and 2D band of graphene.[6,7] As no further additional bands were observed no covalent bonds between PAM and EG formed and the bonding is based on structural attachment and van der Waals forces.
**Figure S2.** Raman spectra of network PAM and PAM-EG samples. The PAM-EG sample shows additional bands at ~1350 cm⁻¹, ~1580 cm⁻¹ and ~2700 cm⁻¹ corresponding to the D, G and 2D band of graphene.

**Microscopy.** SEM analysis of the ceramic templates was performed with a Zeiss Supra 55VP. PAM hydrogel samples stored initially for a few weeks in water were dehydrated using a graded ethanol series with a final exchange to acetone followed by air drying. Thin slices were prepared using an RMC powertome PC ultramicrotome and imaged in a ZEISS Ultra 55. In **Figure S3** SEM images of PAM-EG network samples are shown, where it is clearly visible that the non-conductive polyacrylamide matrix is charging under the electron beam (bright spots) whereas the exfoliated graphene-coated channel is not affected. Interference patterns were imaged using a ZEISS AxioImager light microscope.
Figure S3. SEM images of PAM-EG network sample. The non-conductive polyacrylamide matrix is charging under the electron beam (bright spots), whereas the exfoliated graphene-coated channel is not affected.

**Electrical conductivity measurement.** The electrical conductivity was determined by the two-wire sensing method. To obtain sufficient electrical contact the t-ZnO templates infiltrated with EG were contacted in a sample holder between two brass rods using silver paste. The subsequent fabrication steps to achieve PAM-EG networks were performed with the samples inside the sample holder. The current-voltage curves were recorded via a Keithley 6400 sourcemeter and a customized LabView program while the samples remained in water. Voltage was increased from -1 V to +1 V in 0.05 V steps while measuring the current. All samples showed ohmic behavior and the specific electrical conductivity $\sigma_s$ is further calculated with $\sigma_s = \frac{I}{\rho}$. A representative example of a current-voltage curve with linear fit is shown in Figure S4. The change of resistance during compression was measured on a customized micromanipulator set-up. The current-voltage curves were recorded via a Keithley 6400 sourcemeter and a customized LabView program while the samples
were compressed (~35%) in water. To ensure good electrical contact, the samples were fixed with silver paste in the set-up. The change of resistance was calculated as \( \frac{\Delta R}{R} = \frac{R_0 - R}{R_0} \).

**Figure S4.** Exemplary determination of the specific conductivity of PAM-EG (0.16 vol%). The measured current was plotted as a function of the applied voltage and fitted linearly. The sample shows ohmic behavior and the specific conductivity was obtained from the linear fit.

**Mechanical testing.** Mechanical properties were determined using a ZwickRoell 2.5 kN Zwicki machine in compressive mode with a Xforce P 5 N force sensor. Samples were compressed by 33% with 10 mm min\(^{-1}\) for 100 consecutive cycles in water to avoid altering and drying of the matrix when water is squeezed out during compression. To determine the ultimate compressive stress-strain curves samples were compressed with a speed of 10 mm min\(^{-1}\) until they collapsed. Compressive stress \( \sigma \) and strain \( \varepsilon \) were calculated from the obtained force-distance curves. The Young’s modulus of a sample was determined by linear fitting up to a strain rate of 5% for every cycle and taking the mean value. Representative linear fits for the 2\(^{nd}\) cycle for every sample type
are shown in Figure S5a-d. The recovered height in percent was determined by

\[ \text{recovered height} (\%) = \frac{h_0 - d_{F=0}}{h_0} \times 100 \]

where \( h_0 \) is the initial height of the sample and \( d_{F=0} \) is the distance at \( F = 0 \). Representative curves are shown in Figure S5e-h. Figure S6a-d show representative stress-strain curves of all sample types until they break. Figure S6e shows an overview of ultimate compressive stress and strain values, respectively, of all sample types.

To restore the mechanical properties of PAM-EG (0.32 vol%), the initiator-catalyst system consisting of APS and TEMED was adapted. For that, a 20% APS and TEMED solution was used, respectively. In addition, the amount of TEMED added to the hydrogel precursor solution was doubled. In summary, the hydrogel precursor consisted of acrylamide (Bio-Rad, 40 %, 1250 µL), N,N’-methylenebis(acrylamide) (Bio-Rad, 2 %, 1000 µL), HEPES buffer (Sigma-Aldrich, pH 7.5, 50.0 µL), 2625 µL ddH₂O, ammonium persulfate (APS, Sigma-Aldrich, 20%, aq., 75.0 µL) and TEMED (Sigma-Aldrich, 20 %, 40.0 µL).
Figure S5. a-d) Representative linear fits for the 2nd cycle for every sample type up to a strain rate of 10 %. The slope of the linear fit equals the initial Young’s modulus. For a typical
application, a strain rate of 5 % is sufficient and thus Young’s moduli determined from a 5 % strain rate are discussed in this paper. e-h) Representative graphs for the relative recovery (%) as a function of the cycle number for every sample type. After an initial deformation during the first few cycles, the deformation remains at a constant level (higher than 95 % for all sample types) indicating high mechanical stability with a compression strain of 33 %.

**Figure S6.** a-d) Representative stress-strain curves of a) bulk PAM, b) network PAM, c) PAM-EG (0.16 vol%), d) PAM-EG (0.32 vol%) until they break. e) Overview of ultimate compressive
stress and strain values for all sample types. Error bars depict standard deviation, \( N \geq 3 \). All samples show ultimate compressive strain values around 67 % and ultimate compressive stress values of approximately 0.1 N mm\(^2\).

**Swelling tests.** Water contents and mass swelling ratio of hydrogel samples were determined by the weight of the samples in their hydrated and dried state. Samples in a hydrated state were blotted with paper to remove excess water and weighed (= initial weight \( W_i \)) and then dried in an oven at 50 °C until there is no further change in weight (= \( W_d \)). For studying swelling behavior at 37 °C, the samples were hydrated in water at 37 °C for 24 hours and weighed afterwards. Water contents \( W_c \) of the hydrogels was determined by \( W_c = \frac{W_i - W_d}{W_i} \cdot 100\% \). The mass swelling ratio was calculated with \( \frac{W_i - W_d}{W_d} \cdot 100\% \).

**Micro-CT.** One sample of type t-ZnO-EG and network PAM each were imaged in the P05 microtomography beamline operated by Helmholtz-Zentrum Geesthacht at the PETRA III storage ring at Deutsches Elektronen-Synchrotron (DESY), Hamburg. A photon energy of 34.6 keV was selected. The field of view was 7.2 x 5.4 mm with an effective pixel size of 0.9 µm. The t-ZnO-EG sample was placed into a PEEK cylinder to avoid sample movement. To achieve the best image quality in attenuation contrast, the sample-to-detector distance was set to 15 mm, and 4000 projections (with 20 dark and 900 flat field images) were obtained at an exposure time of 120 ms. The PAM sample was placed in an Eppendorf tube with water to avoid dehydration of the sample and fixated with paper tissue. The sample-to-detector distance for the PAM sample was set to 500 mm to obtain edge enhancement for better visualization of the low attenuating sample. A flyscan with 2000 projections (with 20 dark and 300 flat field images) and an exposure time of 100 ms was performed to ensure that sample movement was minimal. The overall scan time for
the PAM sample was approximately 4 minutes. Both scans were tomographically reconstructed with bin 2 using a customized reconstruction tool[8] utilizing the Astra Toolbox[9,10] in Matlab R2020a (The MathWorks Inc., USA).

Following reconstruction, the PAM sample displayed movement and beam profile variation artefacts, and the image noise was high due to the short imaging time. The image was filtered using an iterative non-local means filter[11] with in isotropic search radius of 6 voxel and 4 iterations. Subsequently, a region-of-interest (ROI) of 1.6 x 1.2 x 0.36 mm$^3$ was selected for analysis. The pores in the ROI were segmented using the trainable WEKA plugin[12] in Fiji/ ImageJ[13]. Avizo 2020 (FEI SAS, Thermo Scientific, France) was then used for a connected component analysis allowing for a minimum component size of 27 voxels and corner connectivity. For the t-ZnO-EG sample a ROI of 3.1 x 3.1 x 2.2 mm$^3$ was selected, thresholded and analysed for its connected components in Avizo. The connectivity of both samples was computed as the fraction of the volume of the largest connected component divided by the overall component volume, where a component designates a pore or ZnO tetrapods, respectively.

**Diffusion.** Diffusion experiments were performed to investigate the diffusion through bulk PAM samples and network PAM samples based on a sacrificial t-ZnO template with 0.3 g cm$^{-3}$ and 0.9 g cm$^{-3}$, respectively. For this, a set-up consisting of two half-cells separated by a wall was used. The samples were placed inside a hole in the wall to act as a diffusional membrane. The half-cells were filled with distilled water and an aqueous methylene blue solution (MB, Eydam, 2.5 mM), respectively. After certain time periods approximately 1 ml of the solution inside the water-filled half-cell was analyzed using a UV-Vis spectrometer Lambda 9000 by Perkin Elmer. Absorption spectra were recorded in a range of 550 to 750 nm. After the measurement the solution was put
back into the water-filled half-cell. The values of the absorption maximum at 662 nm were extracted from the spectra and are shown in Figure S7 for bulk PAM, network PAM (0.3 g cm$^{-3}$ t-ZnO template) and network PAM (0.9 g cm$^{-3}$ t-ZnO template) samples for different time points. The absorption values are normalized to the absorption value of bulk PAM. Although methylene blue also diffuses through the polyacrylamide matrix the results clearly indicate that the microchannel network enhances the diffusion as the values of network PAM samples are twice as high as that of bulk PAM after 30 hours.

![Figure S7](image)

**Figure S7.** Absorption values ($\lambda = 662$ nm) normalized to the values of bulk PAM measured with UV-VIS for different time points for bulk PAM, network PAM (0.3 g cm$^{-3}$ t-ZnO template) and network PAM (0.9 g cm$^{-3}$ t-ZnO template) samples.
### Table S1. Data and references of electrically conductive hydrogels from Figure 3.

| Hydrogel                  | Filler material | Preparation method       | Filler concentration (wt%) | Conductivity (S m⁻¹) | Reference             |
|---------------------------|-----------------|--------------------------|----------------------------|----------------------|-----------------------|
| Chitosan–lactic acid      | graphene        | solution mixing          | 3.0                        | 0.133                | Sayyar et al. [14]    |
| PAM                       | graphene        | *in-situ* polymerization | 4.0                        | 20                   | Didehban et al. [15]  |
| PAM                       | graphene        | *in-situ* polymerization | 3.0                        | 3.56 x 10⁻⁶          | Alam et al. [16]      |
| PAM                       | graphene        | *in-situ* polymerization | 2.0                        | 1.02 x 10⁻⁶          | Das et al. [17]       |
| PAM                       | rGO             | *in-situ* polymerization | 1.2                        | 9.1 x 10⁻⁵           | Li et al. [18]        |
| PAM                       | MWCNTs          | *in-situ* polymerization | 40.0                       | 120                  | Awasthi et al. [19]   |
| PAM                       | MWCNTs          | *in-situ* polymerization | 15.0                       | 3.48 x 10⁻⁴          | Awasthi et al. [19]   |
| PAM                       | CNTs            | solution mixing          | 1.0                        | 0.085                | Chen et al. [20]      |
| Poly(AAm-co-AAc)           | graphite        | solution mixing          | 9.0                        | 9.2                  | Boruah et al. [21]    |
| PVA                       | graphene        | solution mixing          | 10                         | 1.33 x 10⁻⁶          | Alam et al. [22]      |
| PVBA                      | CNT-CNFS        | *in-situ* polymerization | 0.3                        | 0.8                  | Han et al. [23]       |
| PVBA                      | CNT-CNFS        | *in-situ* polymerization | 0.5                        | 8                    | Han et al. [23]       |
| PVBA                      | CNT-CNFS        | *in-situ* polymerization | 0.7                        | 10                   | Han et al. [23]       |
| Methacrylated chitosan     | graphene        | solution mixing          | 3                          | 0.25                 | Sayyar et al. [24]    |
|                          |                  |                  |     |     |                              |
|--------------------------|------------------|------------------|-----|-----|-------------------------------|
| Methacrylated chitosan   | graphene         | solution mixing  | 1.5 | 0.02| Sayyar et al. [24]           |
| OPF                      | rGOa/CNT pega    | solution mixing  | 1.1 | 3 x 10^{-3} | Liu et al. [25]             |
| Sodium alginate          | graphite         | solution mixing  | 30.0| 0.17| Qu et al. [26]                |
| This work                |                  |                  |     |     |                               |
| PAM                      | Exfoliated graphene | Microengineered graphene tube system | 0.06 | 0.012 | -                              |
|                          |                  |                  | 0.12| 0.08 | -                              |
|                          |                  |                  | 0.20| 0.34 | -                              |
|                          |                  |                  | 0.47| 1.8  | -                              |

CNTs = carbon nanotubes; CNT-CNFS = carbon nanotube cellulose nanofiber; MWCNTs = multi-walled carbon nanotubes; OPF = Oligo(poly(ethylene glycol)fumarate); rGO = reduced graphene oxide; Poly(AAm-co-AAc) = poly(acrylamide-co-acrylic acid); PAM = polyacrylamide; PVA = poly(vinyl alcohol); PVBA = polyvinyl alcohol-borax
Table S2. Data and references of electrically conductive hydrogels from Figure 5.

| Hydrogel                  | Filler material | Preparation method            | Filler concentration (wt%) | Normalized conductivity (S m⁻¹ wt%⁻¹) | $E$ at 0 wt% (kPa) | $E$ at x wt% as given (kPa) | increase by factor | Reference          |
|---------------------------|-----------------|--------------------------------|---------------------------|----------------------------------------|--------------------|----------------------------|--------------------|--------------------|
| Chitosan–lactic acid      | graphene        | solution mixing                | 3.0                       | 0.044                                  | 5.8 x 10⁶          | 1.4 x 10⁷                   | 2.35               | Sayyar et al. [14]  |
| PAM                       | graphene        | *in-situ* polymerization       | 3.0                       | 1.19 x 10⁻⁶                            | 1.8 x 10³          | 4.4 x 10³                   | 2.44               | Alam et al. [16]    |
| PAM                       | graphene        | *in-situ* polymerization       | 1.68                      | 9.29 x 10⁻⁶                            | 1.6 x 10⁴          | 1.9 x 10⁵                   | 10.3               | Alam et al. [27]    |
| PAM                       | rGO             | *in-situ* polymerization       | 1.2                       | 7.58 x 10⁻⁵                            | 700                | 1.5 x 10³                   | 2.14               | Li et al. [18]      |
| PAM                       | CNTs            | solution mixing                | 1.0                       | 0.085                                  | 1.1 x 10³          | 3.2 x 10³                   | 2.91               | Chen et al. [20]    |
| PVA                       | graphene        | solution mixing                | 10                        | 1.33 x 10⁻⁶                            | 1.1 x 10⁵          | 1.2 x 10⁶                   | 11.6               | Alam et al. [22]    |
| Methacrylated chitosan    | graphene        | solution mixing                | 1.5                       | 0.02                                   | 1.8 x 10⁴          | 4 x 10⁴                    | 2.22               | Sayyar et al. [24]  |
| OPF                       | rGOa/ CNTpega   | solution mixing                | 1.1                       | 2.7 x 10⁻³                            | 1.8 x 10³          | 5.4 x 10³                   | 5.35               | Liu et al. [25]     |

This work

| Hydrogel | Filler material | Preparation method            | Filler concentration (wt%) | Normalized conductivity (S m⁻¹ wt%⁻¹) | $E$ at 0 wt% (kPa) | $E$ at x wt% as given (kPa) | increase by factor | Reference          |
|----------|-----------------|--------------------------------|---------------------------|----------------------------------------|--------------------|----------------------------|--------------------|--------------------|
| PAM      | EG              | Microengineered graphene tube system | 0.20                      | 1.7                                    | 45                 | 91                         | 2.02               |                    |

CNTs = carbon nanotubes; EG = exfoliated graphene; OPF = Oligo(poly(ethylene glycol)fumarate); rGO = reduced graphene oxide; PAM = polyacrylamide; PVA = poly(vinyl alcohol)
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