Supporting Information

Spray Processed Composites with High Conductivity and Elasticity

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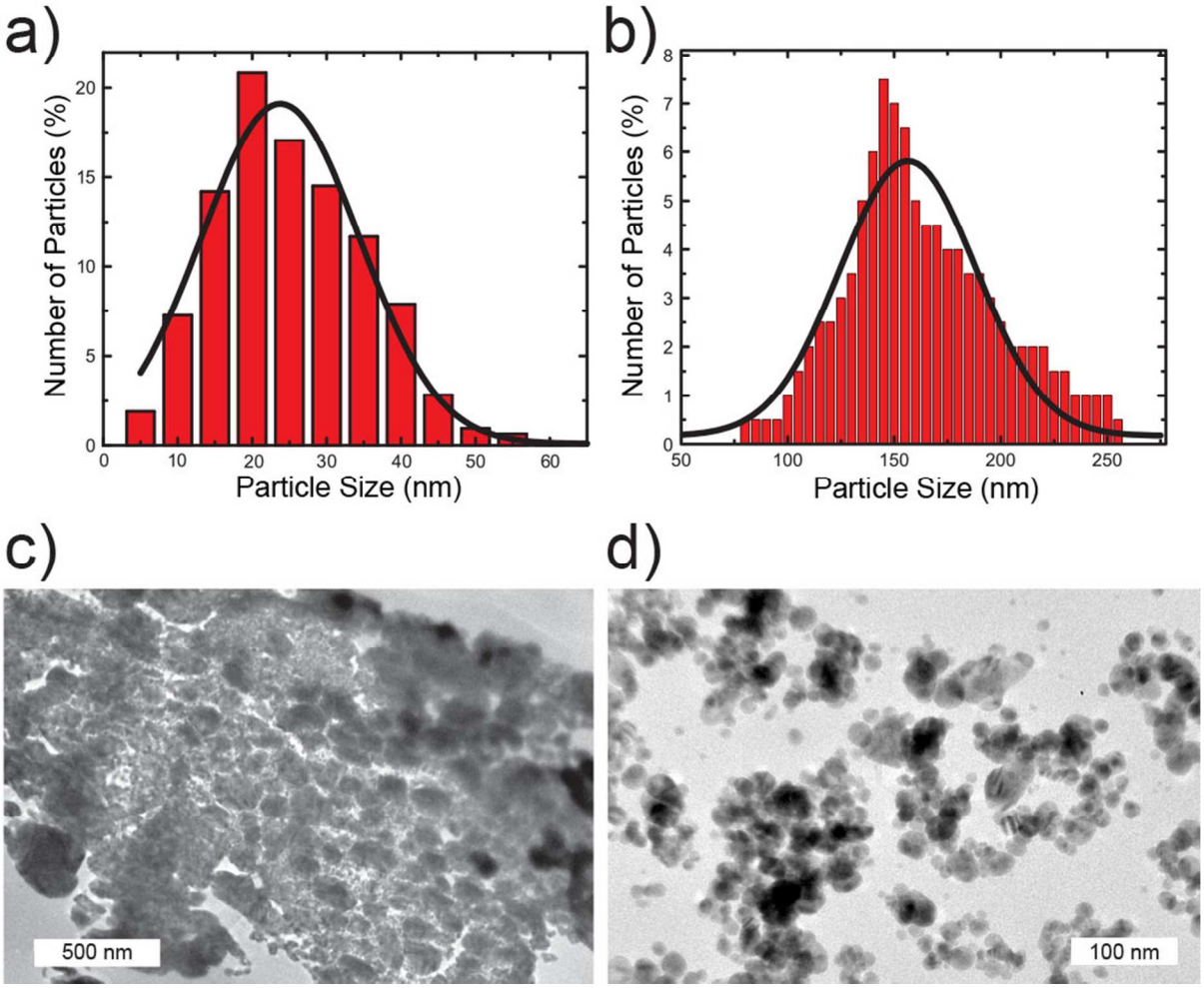

Figure S1 Nanoparticle size distributions of elastic conductors prepared a) without Ag-PAA nanoparticles and b) with Ag-PAA nanoparticles (35% (wt/vol) in spinning solution) as measured from cross-section TEM images (n=150). For elastic conductors with Ag-PAA, only the size distribution of large Ag-PAA nanoparticles was identified due to densely packed silver nanoparticle assembly. c, d) High resolution TEM images of stretchable conductors prepared with Ag-PAA (35% (wt/vol) in spinning solution).

Conductivity measurements of the composite fabric during tensile deformation

The change in electrical conductivity of the elastic conductors during tensile strain was measured with a 4 point-probe measurement system with precision motorized stages (± 0.254 mm translational resolution) (Figure S2). The resistivity (ρ) of the sample was calculated using the

simplified formula for resistivity, since the inter-probe distance (s = 1 cm) is significantly larger than the sample thickness (t = 0.25 mm):

$$\rho = \frac{\pi}{\ln 2} t \left(\frac{V}{I}\right) \quad (1)$$

The resistance (V/I) is measured from the 4 point-probe measurements, as the thickness was introduced as a function of applied strain using Poisson ratio of the samples corresponding to thickness (ν_t = 0.19):

$$t = t_0(1 - \varepsilon \nu_t) \quad (2)$$

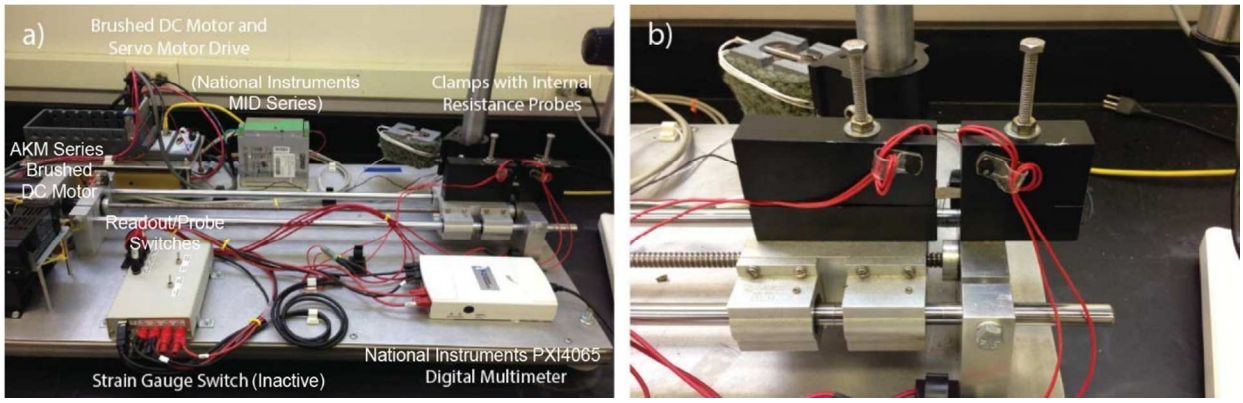

Figure S2: a) Custom-built 4 point-probe measurement system for tensile strain experiments. b) System applying strain while measuring electrical resistance using a 4 point-probe configuration.

The resistivity (ρ) values were then converted to conductivity (σ) values as a function of applied tensile strain (ε):

$$\sigma = \frac{1}{\rho} \quad (3)$$

Percolation theory model for elastic conductor fabrics with dual nanoparticle distribution:

The classical power law for percolation theory with the critical exponent (s) is given as [1]

$$\frac{\sigma}{\sigma_0} = (V_f - V_c)^s \tag{4}$$

The critical exponent is acquired for this composite system from the slope of the correlation between conductivity and nanoparticle volume fraction (Figure 4a). The Ag-PAA nanoparticle concentrations are converted to volume fractions using TGA data, and the resultant data is plotted on a log scale to calculate critical exponent value from the slope of the plot (Table S1). The volume fraction of the filler (V_f) changes with tensile strain [2]

$$V_f(\varepsilon) = \frac{V_{silver}}{V_2(\varepsilon)} \tag{5}$$

$$V_2(\varepsilon) = L_2(\varepsilon) w_2(\varepsilon) t_2(\varepsilon) \tag{6}$$

$$L_2(\varepsilon) = L_1(\varepsilon + 1) \tag{7}$$

$$w_2(\varepsilon) = w_1(1 - \varepsilon \nu_w) \tag{8}$$

$$t_2(\varepsilon) = t_1(1 - \varepsilon \nu_t) \tag{9}$$

$$V_1 = L_1 w_1 t_1 \tag{10}$$

$$V_f(\varepsilon) = \frac{V_{silver}}{V_1} \frac{1}{(\varepsilon + 1)(1 - \varepsilon \nu_w)(1 - \varepsilon \nu_t)} \tag{11}$$

The silver volume fraction at 0% strain (V_f^0) can be obtained by dividing the silver volume of the composite (V_{silver}) to the entire volume of the composite prior to tensile deformation (V_1). This corresponds to the strain independent expression in Equation 11 and was measured using TGA analysis (Figure S3).[3]

In the classical theory of the percolation for electrical conductivity of nanoparticle composites a strain-independent percolation threshold (V_c) is employed.[1-2] However, it has been recently demonstrated that polymer-nanoparticle systems with specific interactions (electrostatic, π electron interactions) can demonstrate an alignment along the direction of tensile deformation, which results in a change in percolation threshold.[3] A fibrous network can potentially enhance this effect, as the nanoparticles are already localized on a linear scaffold. The strain dependent percolation threshold is given with the formula:

$$V_c = \frac{V_c^0}{1 + \alpha\sqrt{\varepsilon}} \tag{12}$$

The initial percolation threshold (V_c^0) slowly drops with applied strain as the nanoparticles are being pulled in the direction of tensile deformation, while being attached to a linear scaffold (a fiber or a polymer chain). The parameter alpha (α) is employed to determine the impact of tensile deformation on percolation threshold, which was described recently for conductive polymer/nanoparticle composites.[3] Alpha parameter is used to refine the accuracy of the described percolation theory. A Levenberg-Marquardt algorithm is used to identify optimal alpha values from the data of conductivity as a function of strain (Figure 4b). The initial percolation can be calculated using a simple expression involving average nanoparticle diameter (D), and electric tunneling distance ($D_{tunneling} \approx 10$ nm)[2]:

$$V_c^0 = \frac{\pi}{6}\left(\frac{D}{D + D_{tunneling}}\right) \quad (13)$$

Equations 11 and 12 were combined with Equation 4 to develop a model for expressing the change in normalized electrical conductivity (σ/σ_0) in polymer-nanoparticle composites.[3] This model was slightly altered to develop a more accurate expression for the electromechanical characteristics of a fibrous polymer-nanoparticle composite with dual nanoparticle size distribution.

The presence of a larger nanoparticle distribution (150 nm ± 50 nm) alters the percolation threshold for polymer-nanoparticle composites. For elastic conductor fabrics, the volumetric filler contribution of larger Ag-PAA nanoparticles was too low ($V_f^{Ag-PAA} < 0.023$), since their major role is to facilitate nucleation of smaller silver nanoparticles (22.6 nm ± 14.2 nm) in higher volume concentrations. Due to the low volumetric contribution, it is possible to consider that these nanoparticles will act as small conductive volume contributions in an insulating polymer matrix, which will slightly reduce the effective percolation threshold ($V_c^{0,eff} = V_c^0 - V_f^{Ag-PAA}$). The second and more important modification on the model is to alter the onset strain for the conductivity expression (Equation 4), since the built-in strain originating from the fibrous network of conductive composites can mediate structural deformations for strain values up to 50% (Figure 4). For strain levels exceeding 50%, the elastic conductor fabric starts to demonstrate the electromechanical characteristics of a regular polymer-nanoparticle composite, as the fibers have limited space left to rearrange (Figure 4e). Consequently, 50% strain is defined as the onset strain (ε_0) for the percolation theory to accurately represent deformation mediated

changes in conductivity of composites. The parameters used to establish this model are presented in Table S1.

Table S1: Parameters for percolation model.

	25% wt/vol Ag-PAA	30% wt/vol Ag-PAA	35% wt/vol Ag-PAA
s (critical exponent)	1.1	1.1	1.1
ν_w (Poisson ratio width)	0.13±0.02 (5 Samples)	0.13±0.04 (5 Samples)	0.13±0.06 (5 Samples)
ν_t (Poisson ratio thickness)	0.19±0.03 (5 Samples)	0.19±0.05 (5 Samples)	0.19±0.05 (5 Samples)
α (fitting parameter)	0.3	0.5	0.6
V_f^{Ag-PAA} (Ag-PAA nanoparticle concentration, vol/vol)	0.0119	0.0179	0.023
V_c^0 (initial percolation threshold, vol/vol)	0.1595	0.1595	0.1595
$V_c^{0,eff}$ (effective initial percolation threshold)	0.1476	0.1416	0.1365
ε_0 (onset strain)	0.5	0.5	0.5

Table S2: Tensile modulus values conductive composites.

Ag-PAA concentration (wt/vol)	Sample 1 (MPa)	Sample 2 (MPa)	Sample 3 (MPa)	Sample 4 (MPa)	Sample 5 (MPa)	Sample 6 (MPa)	Average modulus (MPa)	Standard deviation (MPa)	Coefficient of variation (MPa)
0	1.46	1.33	1.34	1.54	1.44	1.48	1.44	0.07	0.05
10	1.82	1.30	1.74	1.51	1.50	1.45	1.55	0.19	0.12
15	1.99	1.80	1.70	1.94	1.67	1.96	1.84	0.14	0.08
20	2.50	1.87	1.99	2.30	1.90	2.02	2.05	0.17	0.08
25	2.36	2.15	1.96	2.35	2.56	2.45	2.29	0.24	0.10
30	1.98	3.02	2.01	2.80	2.92	2.95	2.74	0.42	0.15
35	3.8	3.27	3.00	3.46	3.32	3.53	3.40	0.27	0.08

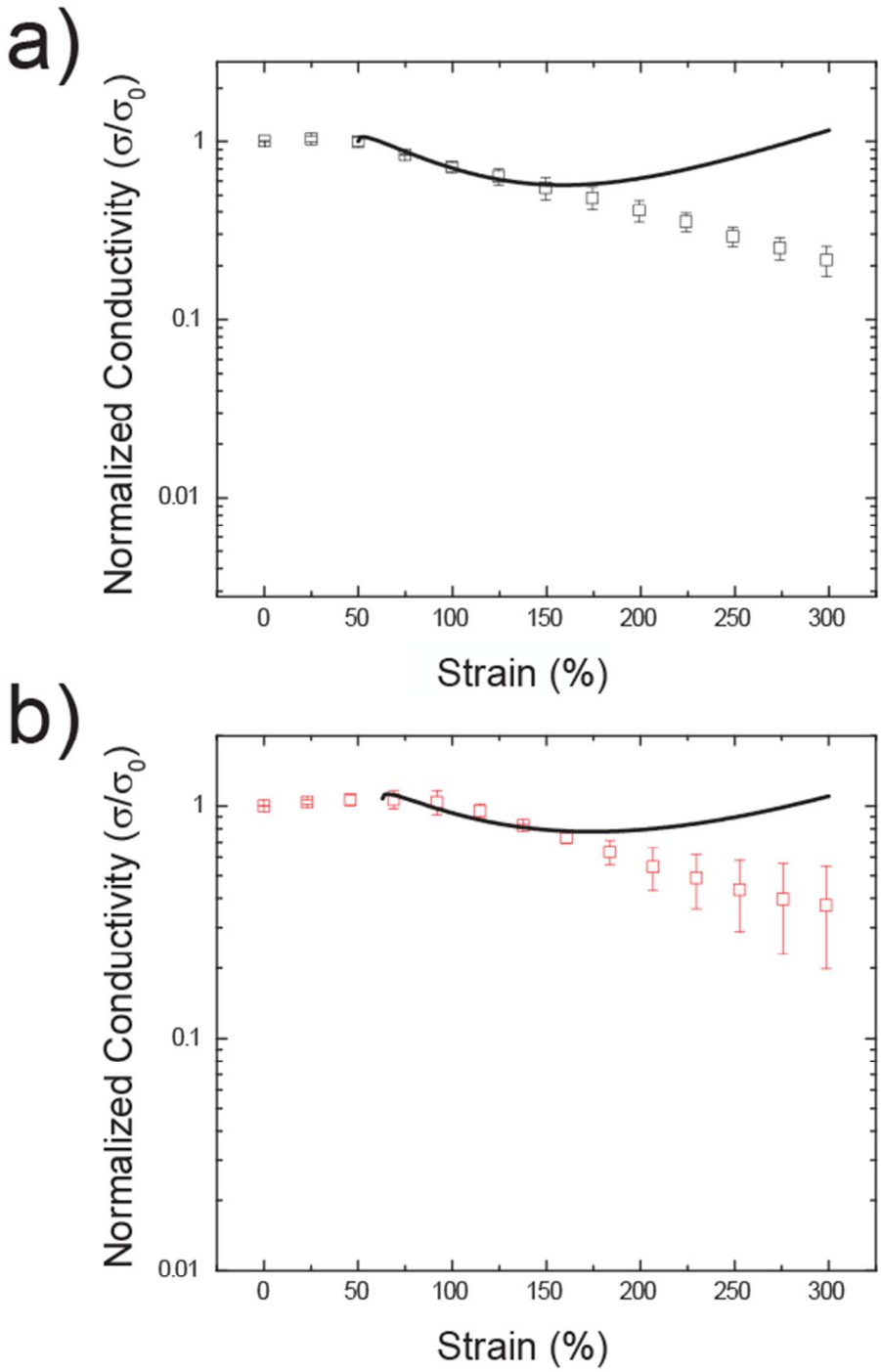

Figure S3: Experimental (data points) and theoretical (Equation 4) (black curves) normalized electrical conductivity (σ/σ_0) dependence on strain for elastic conductors prepared using spinning solutions with a) 25% (wt/vol), and b) 30% (wt/vol) nanoparticle concentration under uniaxial tensile strain. (number of samples is equal to 3 for all composites (n=3), error bars represent standard deviation)

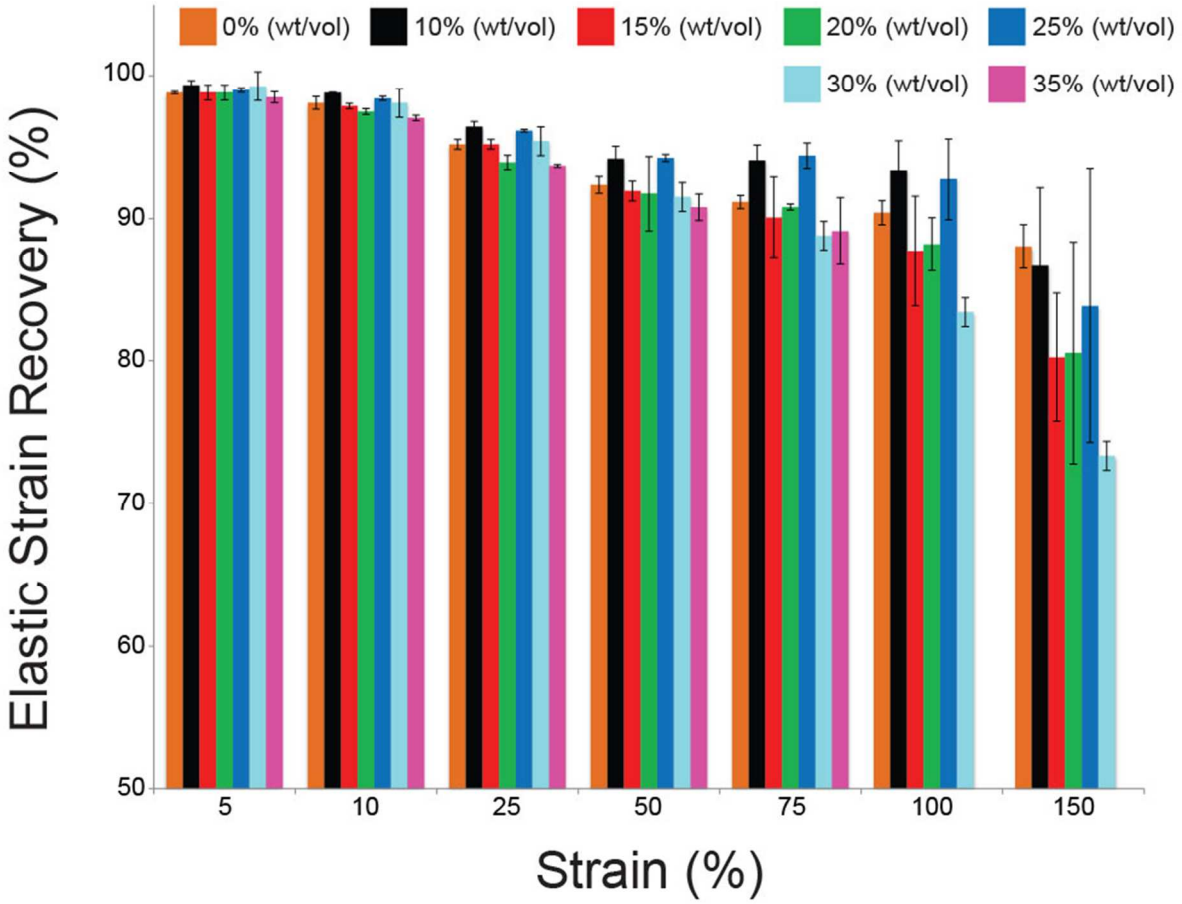

Figure S4: Elastic recovery of elastic conductors fabricated from block copolymer fiber mat (0%), and elastic conductors prepared from spinning solutions with different Ag-PAA nanoparticle concentrations after consecutive strain cycling to increasing maximum strain values. (number of samples is equal to 3 for all composites (n=3), error bars represent standard deviation)

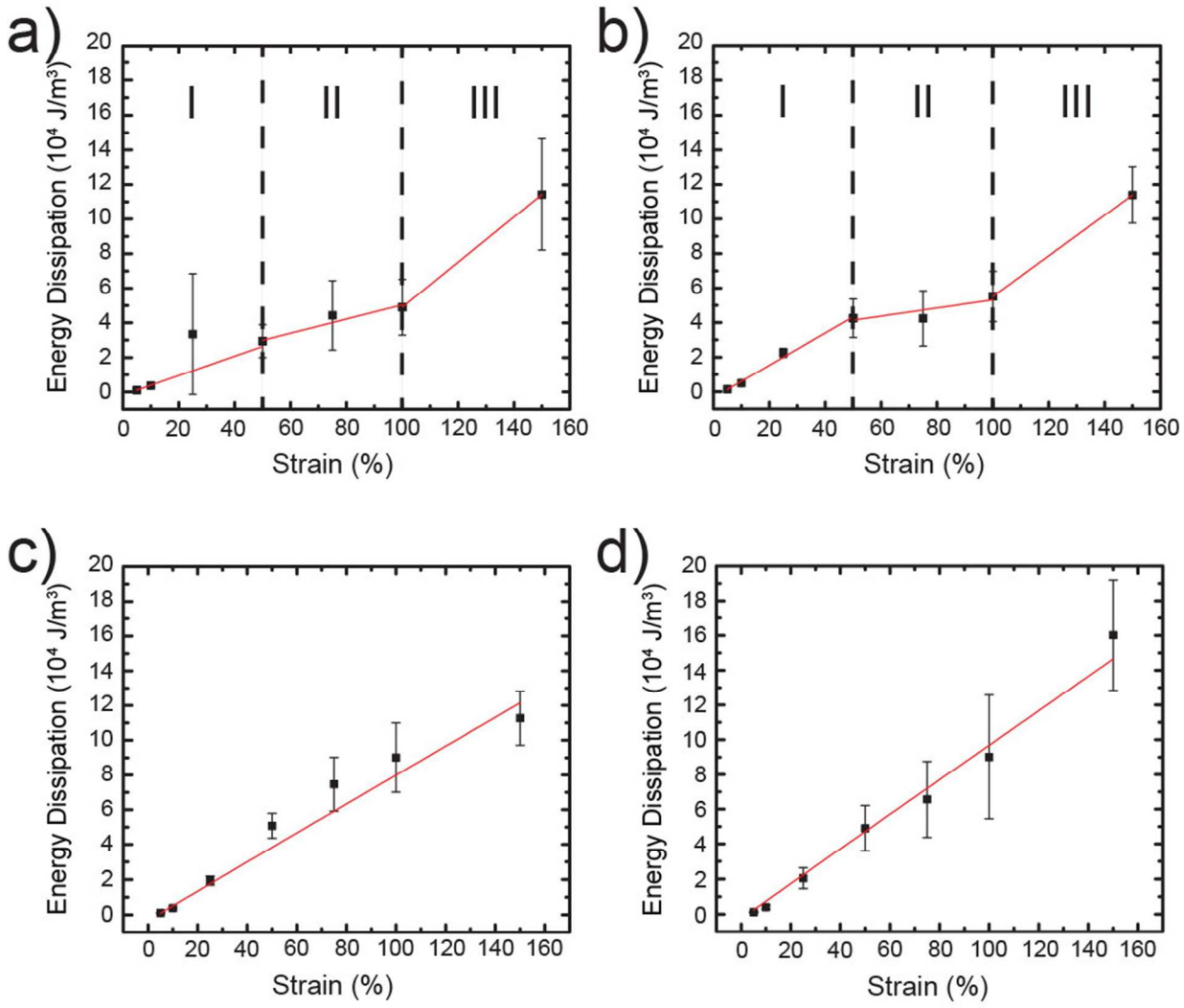

Figure S5: Average energy dissipation values and corresponding linear fits for elastic conductors prepared from spinning solutions with a) 15% (wt/vol), b) 20% (wt/vol), 25% (wt/vol), and 30% (wt/vol) Ag-PAA nanoparticle concentration. (number of samples (n=3) is equal to 3 for all composites, error bars represent standard deviation)

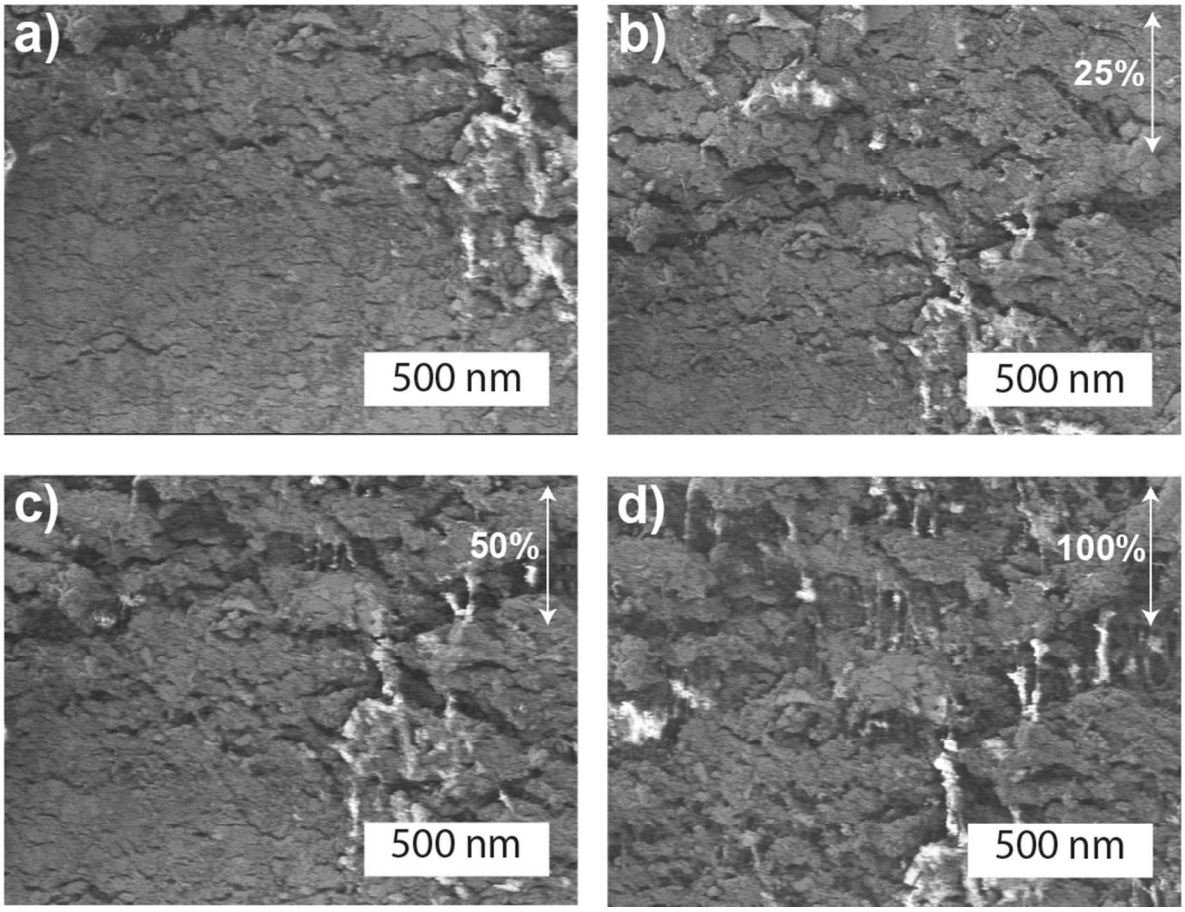

Figure S6: Low magnification SEM images of elastic conductors prepared from spinning solutions with 35% (wt/vol) Ag-PAA nanoparticle concentration under a) 0% strain, b) 25% strain, c) 50% strain, and d) 100% strain. The arrows indicate the direction of uniaxial tensile strain.

References:

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(3) Kim, Y.; Zhu, J.; Yeom, B.; Di Prima, M.; Su, X. L.; Kim, J. G.; Yoo, S. J.; Uher, C.; Kotov, N. A. Stretchable nanoparticle conductors with self-organized conductive pathways. *Nature* **2013,** *500* (7460), 59-63.