Supporting Information

Solvent-Engineered Stress in Nanoscale Materials

Shaun Mills^{†, \perp}, Chiara Rotella^{†, \perp}, Eoin K. McCarthy^{\perp}, David J. Hill^{ϕ}, Jing-Jing Wang^{\perp}, John

F. Donegan^{§, \perp}, James F. Cahoon^{ϕ}, John E. Sader^{‡, \perp} and John J. Boland^{*, \dagger, \perp}

[†]School of Chemistry, Trinity College Dublin, Dublin 2, Ireland

[§]School of Physics, Trinity College Dublin, Dublin 2, Ireland

¹AMBER Research Centre and the Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN), Trinity College Dublin, Dublin 2, Ireland

[•]Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290, United States

^vARC Centre of Excellence in Exciton Science, School of Mathematics and Statistics, University of Melbourne, Victoria, 3010, Australia

*E-mail: jboland@tcd.ie

TEM images of AgNW and SiNW

TEM images showing (a) a AgNW surrounded by the PVP layer, (b) the presence of an oxide layer on a SiNW (b) and (c) a SiNW after the wire was coated with PVP showing the presence of both oxide and polymer layers



Figure S1. Nanowire TEM images. **a**, AgNW with a PVP coating **b**, SiNW with a native oxide outer shell and **c**, SiNWs with a native oxide layer and a PVP coating.

Stress state comparison in AgNWs when processed using polar and non-polar solvents

AgNWs are dispersed in a range of different solvents. Solvents are chosen depending on their ability to swell PVP. PVP is known to swell in polar solvents such as water and ethanol whereas it is non-swelling in non-polar solvents such as hexane and heptane. The aim of this measurement is to determine if the stress present in AgNWs varies depending on whether the solvent used to disperse them is capable of swelling the PVP surface layer. These NWs are dropcast over pre-defined trenches, mechanically clamped using Pt-EBID and measured using the 3-point bending technique. The *F*-*d* curves are then fit using the standard model. In Figure S2, a and b it can be observed that when AgNWs are dispersed in polar solvents such as water and ethanol they are subjected to stress due to the swelling of the PVP coating. In contrast, when they are dispersed in a non-polar solvent such as hexane or heptane they are not affected by stress and their *F*-*d* response is accurately described by the standard model as shown in Figure S2 c and d.



Figure S2. *F-d* curves of AgNWs processed using different solvents. *F-d* curves for AgNWs when deposited using different solvents and fit to the standard model. The solvents used are; **a**, Water, **b**, Ethanol, **c**, Heptane, **d**, Hexane.

Variation in adhesion of AgNWs when processed using polar and non-polar solvents

The adhesion of AgNWs dispersed in polar and non-polar solvents is investigated by dispersing AgNWs in various solvents, dropcasting them on a blank SiO₂ substrate and determining their adhesion by manipulation in air with an AFM tip. From Figure S3 b and d it is shown that when AgNWs are deposited in polar solvents such as water and ethanol, that the NWs are strongly adhered to the surface. NW fracture is generally observed. When deposited in non-polar solvents such as hexane and heptane, AgNWs adhesion to SiO₂ is reduced as the NWs are mobile on the surface as seen in f and g. The enhanced adhesion of the NWs when dispersed in polar solvents is due to the proposed softening of the polymer upon swelling which allows it to better conform to surface due to an increased contact area. In contrast, manipulations performed directly in the solvent caused the wires to become dislodged from the substrate due to poor adhesion.



Figure S3. Adhesion of AgNWs to SiO₂ when processed using different solvents. AFM images of AgNWs dispersed on SiO₂ before and after being manipulated with an AFM tip. NWs were deposited using both polar and non-polar solvents, **a**, Water, **c**, Ethanol, **e**, Heptane, **g**, Hexane. Images **a**,**c**,**e**,**g**, are wires before manipulation with the green arrows defining the loading path. The corresponding images after manipulation are shown in **b**, **d**, **f**, **h**, all scale bars $2\mu m$.

Enhanced adhesion and stress in AuNWs due to solvent deposition

AuNWs are deposited on a SiO₂ substrate using both solvent and dry-deposition methods. They are synthesised by Sigma-Aldrich in H₂O and so are dropcast in H₂O. As can be observed in Figure S4 b, when AuNWs are deposited in H₂O and manipulated they are strongly adhered to the SiO₂ substrate which results in wire fracture. When dry-deposited they are weakly adhered to the substrate as shown in Figure S4 d. Furthermore, when they are solvent-deposited over a trench, mechanically clamped with Pt-EBID and manipulated they are affected by stress. This can be recognised by the poor fit of the experimental data to the standard model as shown in Figure S4 e. Evidence of the CTAB surface coating on these AuNWs is shown in the TEM image in Figure S4 f.

AuNW – Solvent Deposited



Figure S4. AuNW experiment. AFM images of AuNWs deposited on SiO₂ **a**, solventdeposited, **c**, dry-deposited, with the resulting corresponding AFM images in **b**, **d** after AFM manipulation, all scale bars 1 μ m. **e**, *F*-*d* response of solvent-deposited AuNW in doublyclamped beam configuration fit to the standard (zero-stress) model. **f**, TEM image showing CTAB coating on the surface of the AuNW, scale bar 10 nm.

Raman Scattering Measurements on SiNWs

Raman measurements of SiNWs with PVP coating layer deposited on quartz substrate using dry-deposition methods and after the same wire is exposed to isopropanol (IPA) solvent. We use a wavelength of 488 nm, the spectrometer is a Renishaw Invia spectrometer with a 3000/mm grating, which has an instrumental resolution of better than 0.2 cm⁻¹. The probe size is about 0.5µm diameter and three measurements were performed on each wire.

	Dry transferred SiNW on Quartz	After exposure to IPA solvent		
	Centre (cm ⁻¹)	Centre (cm ⁻¹)	Shift (cm ⁻¹)	Average Shift (cm ⁻¹)
1	520.0	519.5	-0.5	
	520.0	519.5	-0.5	-0.5
<u>5 μm</u>	520.0	519.5	-0.5	
1	520.5	517.5	-3.0	
5 μm	520.5	517.8	-2.7	-2.7
	520.5	518.0	-2.5	
1	520.4	519.7	-0.7	
	520.0	519.6	-0.4	-0.6
<u>5 μm</u>	520.3	519.6	-0.7	
1	520.3	518.8	-1.5	1.4
1	520.3	518.9	-1.4	-1.4
<u>5 μm</u>	520.3	518.9	-1.4	

Table S1. Raman Scattering Measurements on SiNWs. Results show results for four different wires of different lengths before and after solvent exposure. For each wire three measurements are recorded at different positions along the wire length. The results are summarised in the inset of Figure 6 and show that shorter wires exhibit a greater Raman shift indicating a greater tensile strain in these cases.