Supporting Information

Entropy can bundle nanowires

in good solvents

Hongyu Gao,[†] Simon Bettscheider,[‡] Tobias Kraus,[‡,¶] and Martin H. Müser[∗,†]

†*Department of Materials Science and Engineering, Saarland University, Campus C6 3,*
66123 Saarbrücken, Germany

‡*INM - Leibniz Institute for New Materials, Campus D2 2, 66123 Saarbrücken, Germany*

¶*Colloid and Interface Chemistry, Saarland University, Campus D2 2, 66123 Saarbrücken,*
Germany

E-mail: martin.mueser@mx.uni-saarland.de

Phone: +49 681 302 57452. Fax: +49 681 302 57454

Contents

S1 Experimental methods

S1.1 Synthesis of ultrathin gold nanowires

Ultrathin AuNWs were prepared using an adapted protocol originally developed by Feng et al.[1] Gold(III) chloride hydrate (CAS number 7440-57-5; InChI and PubChem CID of all chemicals can be found in Table S1) was prepared by dissolving a gold ingot (99.99 %, Degussa, Munich, Germany) in aqua regia. An amount of 39 mg $HAuCl_4 \cdot xH_2O$ (degree of hydration $x \approx 3$) was dissolved in a mixture of 6 mL n-hexane (99 %, ABCR, Germany, CAS number 110-54-3) and 1.8 mL oleylamine (technical grade, 70 %, Sigma-Aldrich, Steinheim, Germany, CAS number 112-90-3). Subsequently, 2.6 mL triisopropylsilane (98 %, ABCR, Germany, CAS number 6485-79-6) were added as reducing agent. The solution was flushed with argon, vortexed for 5 min, and left undisturbed to react at room temperature for 16 h. The as-synthesized AuNWs were purified twice by adding an excess of ethanol (99.8 %, Sigma-Aldrich, Germany, CAS number 64-17-5), carefully removing the supernatant, and re-dispersing in 6 mL n-hexane. Finally, the AuNWs were redispersed in their final solvent (n-hexane or ethanol).

Table S1: Chemical identifiers of the substances used to synthesize ultrathin gold nanowires.

Name	PubChem ID	CAS Number	InChI Key
Gold	23985	7440-57-5	PCHJSUWPFVWCPO-UHFFFAOYSA-N
Chlorauric acid	28133	1303-50-0	VDLSFRRYNGEBEJ-UHFFFAOYSA-K
Aqua regia	90477010	8007-56-5	NICDRCVJGXLKSF-UHFFFAOYSA-N
n-hexane	8058	110-54-3	VLKZOE-OYAKHREP-UHFFFAOYSA-N
Oleylamine	5356789	112-90-3	QGLWBTPVKHMVHM-KTKRTIGZSA-N
Triisopropylsilane	6327611	6485-79-6	ZGYICYBLPGRURT-UHFFFAOYSA-N
Ethanol	702	64-17-5	LFQSCWFLJHTTHZ-UHFFFAOYSA-N

S1.2 Characterization by transmission electron microscopy

In order to observe AuNWs by transmission electron microscopy (TEM), an amount of approximately 1 µL of dispersed AuNWs was dried on a 400-mesh carbon coated copper

grid (Plano, Germany), which was then introduced into a JEM 2010 microscope (JEOL, Germany) operated at an acceleration voltage of 200 kV.

S1.3 Characterization by small angle X-ray scattering and data analysis

The arrangement of AuNWs in different solvents was observed via small angle X-ray scattering (SAXS) 24 h after redispersion in the respective solvent. Samples were introduced into a glass capillary with an inner diameter of 1.5 mm. The XEUSS 2.0 (XENOCS SA, France) SAXS setup was equipped with a Cu K-α X-ray source and a PILATUS3 R 1M (DECTRIS, Switzerland) X-ray detector. The sample to detector distance was 560.07 mm and the setup was calibrated by measuring a glass capillary filled with silver behenate.

All samples were measured five times for a period of 300 s. The diffraction patterns were integrated with the software Foxtrot[2] and the resulting two-dimensional patterns were averaged over the five measurements. To correct for the background, the solvent signal was subtracted from the sample signal.

Wire-wire distances d were determined from the q-vector of Bragg peaks using the Miller indices h and k of a two-dimensional, hexagonal lattice according to

$$q_{hk} = \frac{4\pi}{\sqrt{3}d}\sqrt{h^2 + hk + k^2},$$ (1)

as proposed by Förster et al.[3]

S2 Simulations methods: OPLS-AA force field parameters

Table S2: OPLS-AA non-bonded parameters

Mat.	Type	12-6 Lennard-Jones		Charge (e)
		σ (Å)	ϵ (Kcal/mol)	
oleylamine	CT_{CH_3}	3.50	0.066	-0.222
	CT_{CH_2}	3.50	0.066	-0.148
	CM_{CH}	3.55	0.076	-0.160
	HC_{CH_3}	2.50	0.030	$+0.074$
	HC_{CH_2}	2.50	0.0263	$+0.074$
	HM_{CH}	2.50	0.030	$+0.160$
n-hexane	CT_{CH_3}	3.50	0.066	-0.180
	CT_{CH_2}	3.50	0.066	-0.120
	HC	2.50	0.030	$+0.060$
ethanol	CT_{CH_3}	3.50	0.066	-0.180
	CT_{CH_2OH}	3.50	0.066	$+0.145$
	OH	3.12	0.170	-0.683
	HC	2.50	0.030	$+0.060$
	HO	0.0	0.0	$+0.418$
gold	Au	2.934	0.039	0.0

Table S3: OPLS-AA bonded parameters

	Type	K_s (Kcal/mol-Å^2)	r_0 (Å)
	CT-CT	268.0	1.529
	CT-HC	340.0	1.090
	CT-CM	317.0	1.510
stretching	CM-CM	549.0	1.340
	CM-HC	340.0	1.080
	CT-OH	320.0	1.410
	OH-HO	553.0	0.945

	Type	K_b (Kcal/mol-rad^2)	θ_0 (degree)
	CT-CT-CT	58.35	112.7
	CT-CT-CM	63.0	111.1
	CT-CT-OH	50.0	109.5
	CT-CT-HC	37.5	110.7
	CT-CM-CM	70.0	124.0
bending	CT-CM-HC	35.0	117.0
	CT-OH-HO	55.0	108.5
	HC-CT-CM	35.0	109.5
	HC-CT-OH	35.0	109.5
	HC-CT-HC	33.0	107.8
	HC-CM-CM	35.0	120.0

	Type	K_{t1}	K_{t2}	K_{t3}	K_{t4}
				(Kcal/mol-Å^2)	
	CT-CT-CT-CT	1.3	-0.05	0.2	0.0
	CT-CT-CT-CM	1.3	-0.05	0.2	0.0
	CT-CT-CT-HC	0.0	0.0	0.3	0.0
	CT-CT-CM-CM	0.346	0.405	-0.904	0.0
	CT-CT-CM-HC	0.0	0.0	0.468	0.0
	CT-CT-OH-HO	-0.356	-0.174	0.492	0.0
	CT-CM-CM-CT	0.0	14.0	0.0	0.0
torsional	CT-CM-CM-HC	0.0	14.0	0.0	0.0
	CM-CT-CT-HC	0.0	0.0	0.366	0.0
	CM-CM-CT-HC	0.0	0.0	-0.372	0.0
	OH-CT-CT-HC	0.0	0.0	0.468	0.0
	HC-CT-CT-HC	0.0	0.0	0.3	0.0
	HC-CT-CM-HC	0.0	0.0	0.318	0.0
	HC-CT-OH-HO	0.0	0.0	0.352	0.0
	HC-CM-CM-HC	0.0	14.0	0.0	0.0

S3   Supporting experimental results: nanowire spacing in different solvents

The quality of AuNWs synthesized in *n*-hexane was controlled by TEM by drying the nanowire suspension on a carbon-coated copper grid. Fig. S1a shows a TEM micrograph of AuNWs that are homogeneous and monodisperse in diameter and almost perfectly aligned. Individual wires follow nearly straight lines with only small degrees of curvature. A small fraction of spherical nanoparticles formed as a side product during the synthesis can also be seen in the upper right part of Fig. S1a.

AuNWs precipitated when a volumetric 4:1 mixture of ethanol and methanol was added to the dispersion as shown in the photograph in Fig. S1b. Here, filament-like structures can be observed by bare eye, indicating that the nanoscale-size AuNWs have agglomerated into micrometer-scale structures.
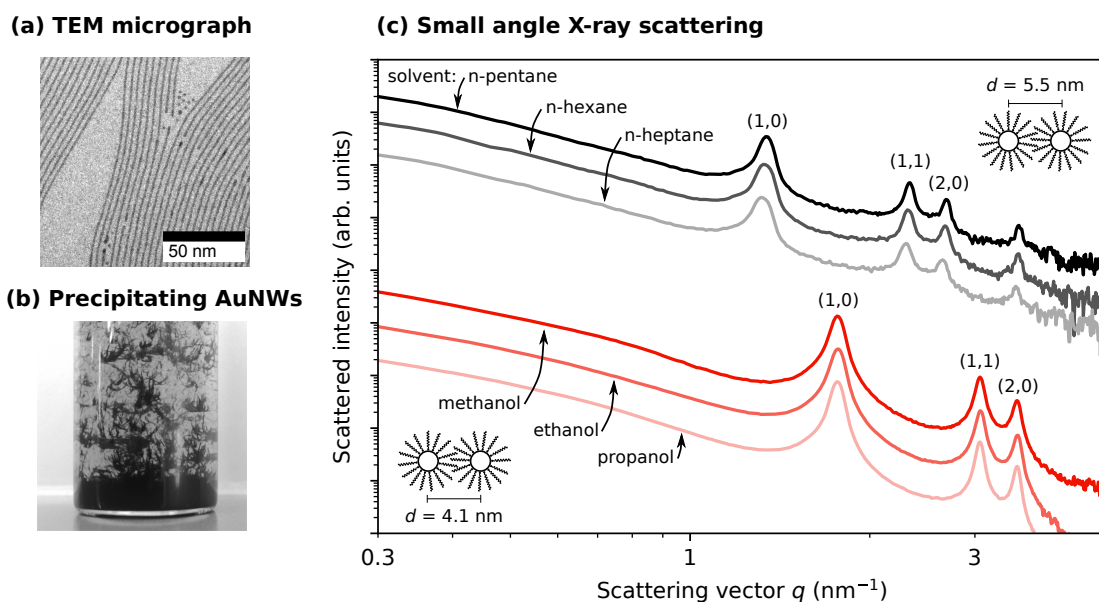

Figure S1: (a) TEM micrograph of bundled AuNWs. (b) Photograph of a beaker containing AuNWs in dispersion after precipitation with a mixture of ethanol and methanol. (c) SAXS signals for AuNWs dispersed in alkanes (upper, gray curve) and alohols (lower, red curve) with the lattice indices indicated above the corresponding Bragg reflection peaks. A wire-wire distance of 5.5 nm and 4.1 nm is found for the alkanes and alcohols, respectively.

In order to qualitatively assess the structure of AuNWs in the two solvents, SAXS measurements were performed 24 h after redispersion in the desired solvent. Given the results of Reiser et al.,[4] this period is sufficient for the AuNWs to reach their equilibrium arrangement. All SAXS curves shown in Fig. S1 show distinct Bragg reflection peaks. The relative position of these reflection peaks reveal that the wires pack in a hexagonal lattice. We calculate the lattice parameter, i.e. the wire-wire distance, by extracting the q-vector of the local maxima in the SAXS curves and then applying Eq. (1). In alkanes, wire-wire distances of 5.42 nm, 5.47 nm, and 5.52 nm arose for n-pentane, n-hexane, and n-heptane, respectively. For alcohols, we found identical 4.11 nm for methanol, ethanol, and 1-propanol*.

A comparison with the size of the AuNWs can help to interpret this result. The AuNW have a core diameter of approximately 1.7 nm and a shell of oleylamine molecules that have a length of ca. 2 nm in their fully stretched configuration (see introduction). Two layers of fully extended oleylamine between the gold cores yield a wire-wire distance of 5.7 nm, which is close the value measured in alkanes. A single layer of oleylamine would give a wire-wire distance of 3.7 nm, which is close to the result that we find for the alcohols. This suggests that the oleylamine ligands barely interdigitate when in contact with n-hexane but almost fully interdigitate when dispersed in ethanol. The degree of interdigitation in linear alkanes depended on the alkane length and increased by about 1 Å from n-pentane to n-heptane. This is on the order of magnitude of a C-C bond, for a solvent length increase by two C-C bonds. Further experiments and simulations are planned to investigate this interesting trend.

---

*Measurements of AuNWs in ethanol were already performed in earlier work.[5] The SAXS data that we report in here match the previously published data. Note, however, that the analysis of the SAXS data in [5] of the wire-wire distance in ethanol contains a typo and was incorrectly stated as 3.5 nm, where the correct value is 4.1 nm, consistent with the analysis reported here.

S4 Supporting simulation results: Radial probability density distribution of ligands

To demonstrate that the increase of distance between NW in good solvents is not predominantly caused by a swelling of the ligands, we measured the probability density $\text{Pr}(r)$ of ligand carbon atoms for a single immersed NW. Here, $2\pi\, r\, \text{Pr}(r)\Delta r$ denotes the probability of a ligand carbon atom to be within a distance of $r \pm \Delta r/2$ from the NW's symmetry axis. Analysis of the resulting probability densities, which are shown in Fig. S2, reveals that the tail of the probability distribution in n-hexane are shifted slightly above 1 Å to the outside compared to ethanol.
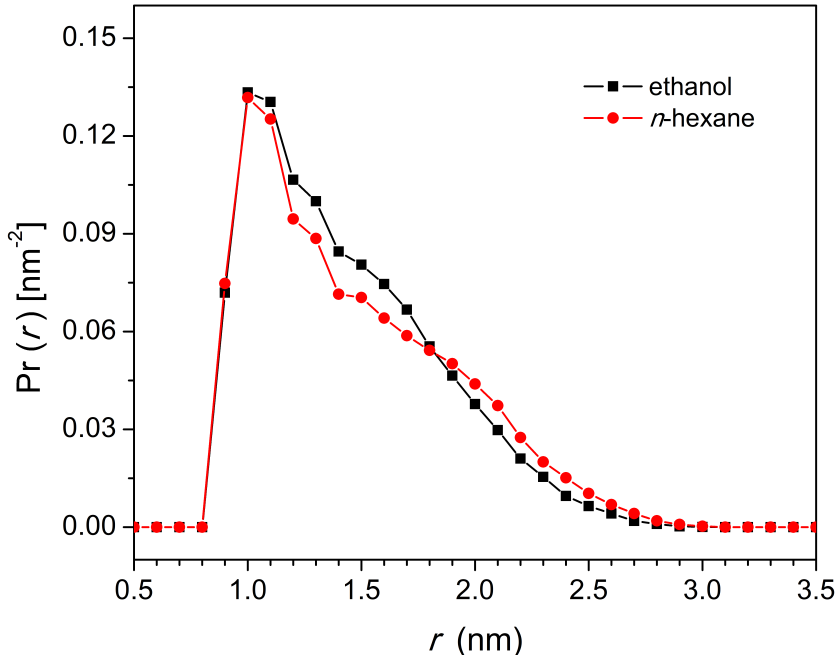

Figure S2: Radial probability density $\text{Pr}(r)$ of ligands in ethanol and n-hexane. Inset shows a schematic of how the parameters are defined.

To quantify the swelling induced by good solvents in terms a number of unit length rather than with a distribution function, we computed the root-mean square distance d of an end-group from the surface of the NW gold core and found values of $d = 12.7$ Å for ethanol and

9

14.5 Å for n-hexane.

References

(1) Feng, H.; Yang, Y.; You, Y.; Li, G.; Guo, J.; Yu, T.; Shen, Z.; Wu, T.; Xing, B. Chemical Communications **2009**, 0, 1984–1986.

(2) Girardot, R.; Viguier, G.; Pérez, J.; Ounsy, M. FOXTROT: A Java-based application to reduce and analyse SAXS and WAXS piles of 2D data at synchrotron SOLEIL. canSAS-VIII. Japan, 2015.

(3) Förster, S.; Timmann, A.; Konrad, M.; Schellbach, C.; Meyer, A.; Funari, S. S.; Mulvaney, P.; Knott, R. Journal of Physical Chemistry B **2005**, 109, 1347–1360.

(4) Reiser, B.; Gerstner, D.; Gonzalez-Garcia, L.; Maurer, J. H. M.; Kanelidis, I.; Kraus, T. Physical Chemistry Chemical Physics **2016**, 18, 27165–27169.

(5) Reiser, B.; Gerstner, D.; Gonzalez-Garcia, L.; Maurer, J. H. M.; Kanelidis, I.; Kraus, T. ACS Nano **2017**, 11, 4934–4942.