Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Silver nanowires for highly reproducible cantilever based AFM-TERS microscopy: towards a universal TERS probe

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Long Nanowire formation

Attachment of long nanowire assembles could be promoted by using higher concentrations or longer dipping times (Fig S1a). However, relatively longer tips were found to be unstable for scanning in tapping- and/or contact-mode, as evidenced, for example, by the sharp temporal changes in the amplitude of oscillation when in tapping mode (Fig S1b).

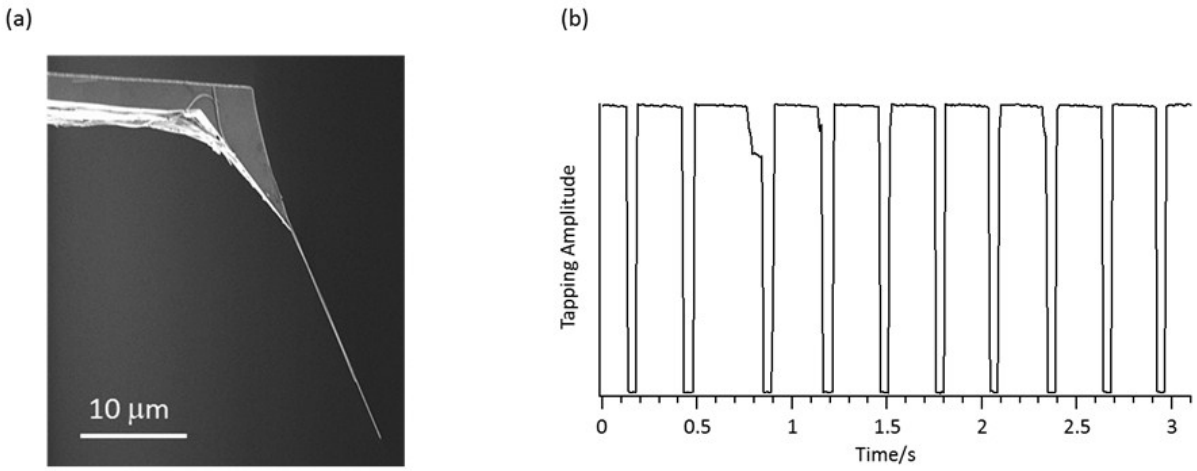

Fig S1. (a) SEM image of a long nanowire assembly (approx. length ~20 µm) formed using the AC-DEP process. (b) Plot of tapping mode amplitude against time for an unstable tip.

Resolution comparison between functionalised and unfunctionalized tips

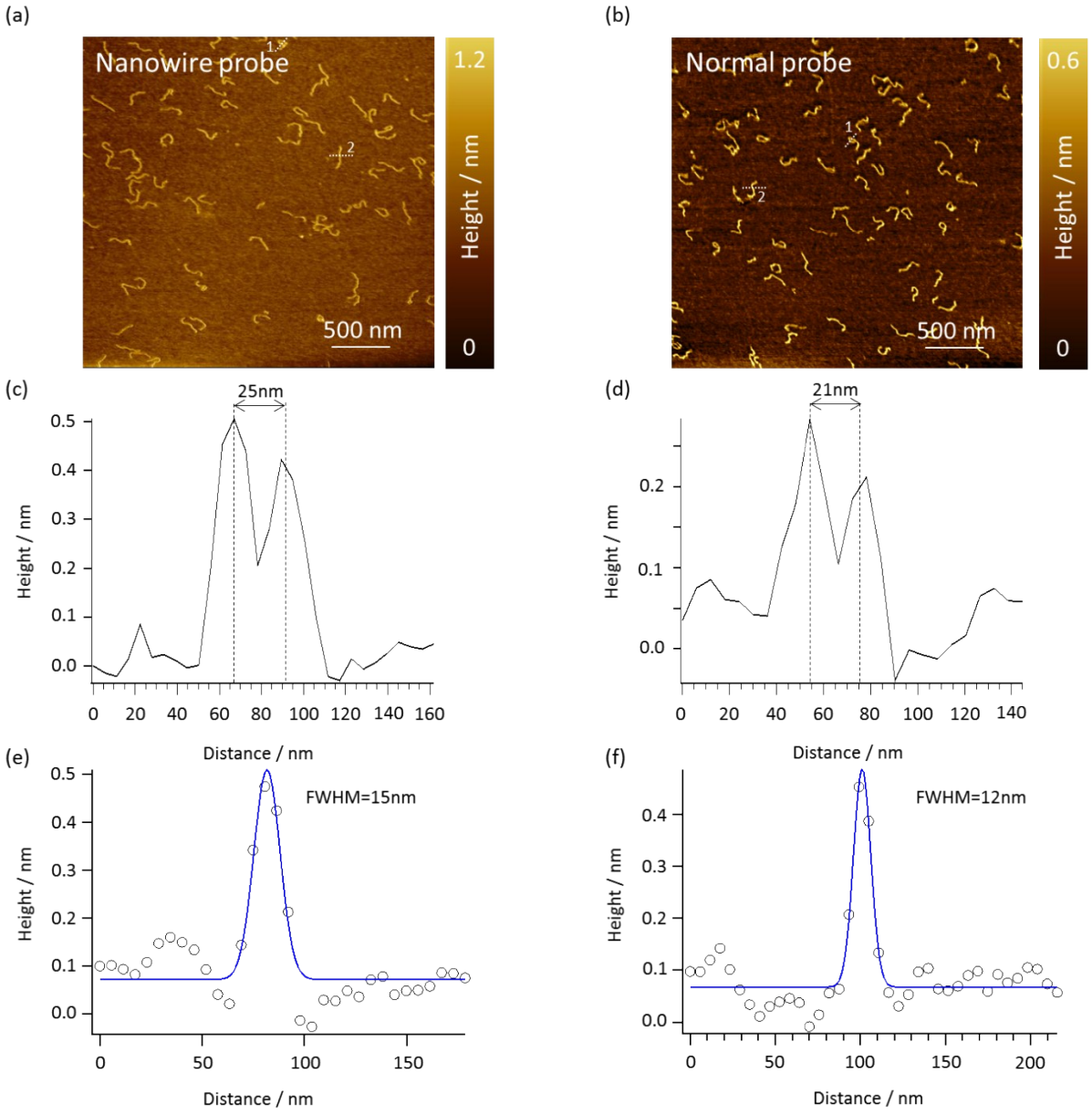

Fig S2. (a, b) AFM height images of single DNA molecules taken with a AgNW and unfunctionalized tip. (c, d) Line profiles represented by the number 1 in a and b, showing the distance between two approximately parallel DNA strands. (e, f) Line profiles designated by the number 2 in a and b along with fitted Gaussian profiles, used to determine the FWHM of a DNA strand for the AgNW and unfunctionalized tips. The raw data is displayed as points with the Gaussian fit in blue.

Side and top-illumination configurations

The TERS setup used in this study could be operated in either top or side-illumination modes with the same optical pass. In top-illumination, light impinges on the tip apex parallel to the surface normal and is polarised parallel to the tip long axis. The tip is tilted forwards by an angle of approximately 10° with the ACCESS-NC-A cantilevers used in this study.

Side-illumination is achieved by tilting the sample stage by approximately 60° using a home-built stage. In such a configuration light is directed at an approximate angle of 60° to the tip long axis and 30° to the surface plane.

Side illumination allowed direct comparison to the electrochemically-etched Au tips also used in this study, as well as giving greater optical access to the tip apex and thereby simplifying alignment. Top-illumination was in turn implemented due to the reduced far-field contributions expected and the empirical observation of greater optical/mechanical stability in this configuration.

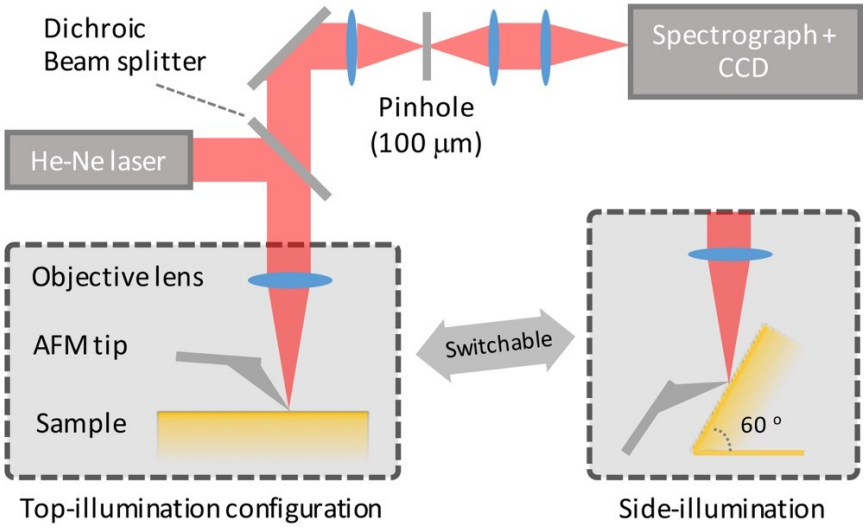

Fig S3. Schematic representations of the setup in top- (left) and side-illuminations (right).

Additional information figure 4

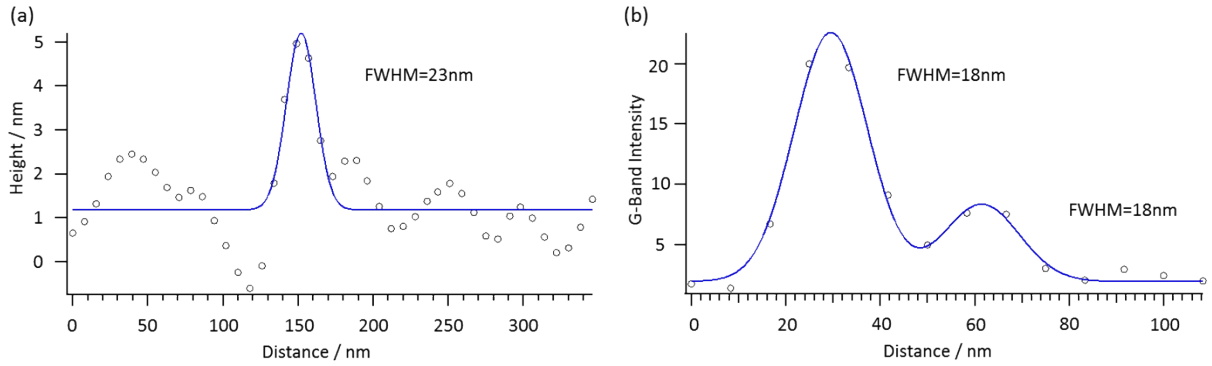

Fig S4. (a, b) Topographic and TERS line profiles generated from Figure 4a and c. In each case the raw data is displayed as points along with a Gaussian fit in blue. Based on the images in figure 4, a single Gaussian was employed for the topographic line profile, whereas a double Gaussian was used in the case of the TERS profile.

Choice of excitation wavelength

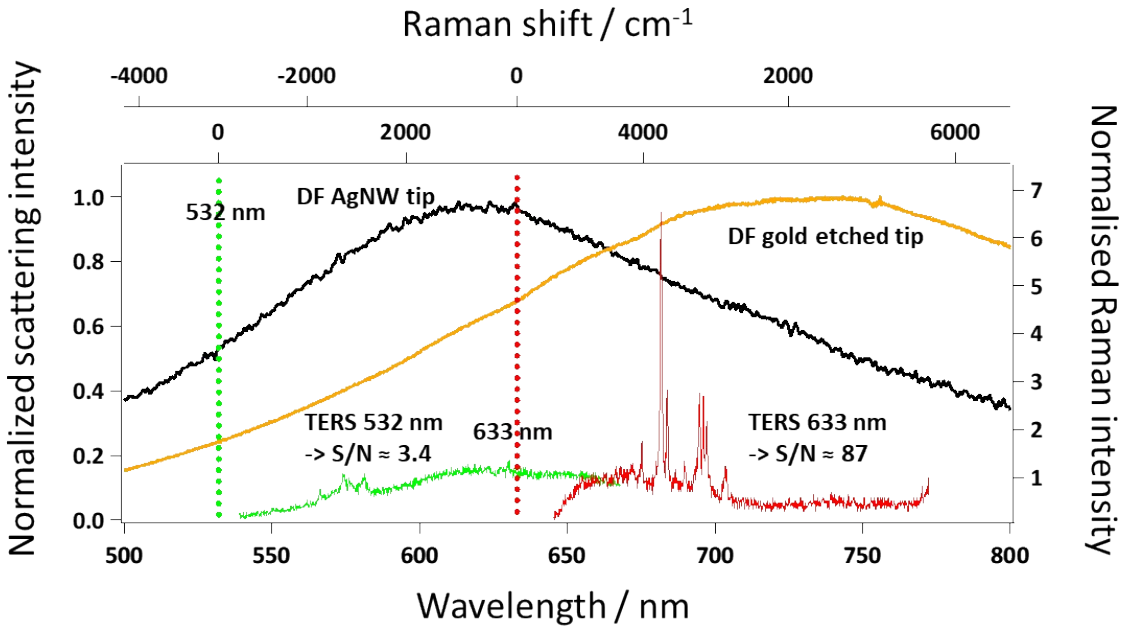

Fig S5. Example dark-field and TERS spectra obtained under 532 and 633 nm excitations. Dark-field spectra were obtained with a method presented in ref 45. Both TERS spectra were obtained on an Azobenzene thiol on gold sample with the same AgNW tip (contact mode feedback). Both TERS spectra were normalized to the background intensity at 650 nm. The laser power was set to approximately 200 µW for both excitation conditions.