Functionalised Silver Nanowire Structures

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Abstract. Crystalline silver nanowires 60-100 nm in diameter and tens of micrometres in length have been fabricated using a low temperature, solution synthesis technique. We explore the potential of this method to produce functional nanowire structures using two different strategies to attach active molecules to the nanowires: adsorption and displacement. Initially, as-produced silver nanowires capped with a uniaxial-growth-inducing polymer layer were functionalised by solution adsorption of a semiconducting conjugated polymer to generate fluorescent nanowire structures. The influence of nanowire surface chemistry was investigated by displacing the capping polymer with an alkanethiol self-assembled monolayer, followed by solution adsorption functionalisation. The success of molecular attachment was monitored by electron microscopy, absorption and fluorescence spectroscopy and confocal fluorescence microscopy. We examined how the optical properties of such adsorbed molecules are affected by the metallic nanowires, and observed transfer of excitation energy between dye molecules mediated by surface plasmons propagating on the nanowires. Non-contact dynamic force microscopy measurements were used to map the work-function of individual wires, revealing inhomogeneity of the polymer surface coverage.

1. Introduction
Nanowire structures have intrinsic properties which differ significantly from those of the bulk material as a result of their low-dimensionality and have potential for miniaturizing device structures. Silver is an ideal candidate for incorporation in nanowire structures; its high electrical conductivity gives excellent electrical transport, and the low optical absorption (for a metal) and negative real component of the dielectric constant confer interesting optical properties. These include supporting localized and/or propagating surface plasmons, depending on the structure, and exhibiting Surface Enhanced Raman Scattering when the metal surface is nanostructured [1].

In this study we fabricated extremely high aspect ratio silver nanowire structures (60-100 nm diameter, length up to 90 µm) using a low-temperature solution technique and functionalised them with fluorescent molecules using two different strategies, producing hybrid structures that exploit and enhance the optical properties associated with the nanostructured Ag.

2. Synthesis and functionalisation strategies
Ag nanowires were synthesized using the polyol technique, which produces nanowires of excellent uniformity in good yield [2]. The polyol technique is a soft (low temperature) solution synthesis where a silver salt is reduced by ethylene glycol (EG) in the presence of a capping polymer, poly(vinylpyrrolidone) (PVP). The ethylene glycol acts as both solvent and reducing agent, whilst the
PVP caps nascent Ag particles, simultaneously preventing aggregation and directing the anisotropic growth of particles into wires. Sun proposes a mechanism commencing with the formation of thermodynamically stable decahedral multiply-twinned Ag nanoparticles (MTPs) through Ostwald ripening [3]. Ag preferentially attaches at the high energy surface sites at twin boundaries, accretion elongating the MTPs into rods. PVP is critical to uniaxial growth as it preferentially adsorbs on and passivates the \{100\} side facets of the growing wires and only weakly interacting with the \{111\} end facets.

Silver seed nanoparticles were produced by reducing AgNO$_3$ with EG by refluxing at 160°C in a argon atmosphere, the barrier gas ensuring high nanowire yield and reproducible results [4]. Slow addition of PVP and further AgNO$_3$ to the reflux formed Ag nanowires, with reaction completion at 60 minutes. Progress was monitored by observing the evolution of the plasmon resonances of the developing Ag nanomaterial by UV-Vis spectroscopy. Ag nanowires were purified by suspension in ethanol, vortexing and centrifuging five times, removing residual EG as well as Ag nanoparticles.

After purification, functionalisation was carried out using two different strategies. Initially as-synthesized Ag nanowires (with PVP capping layer) were functionalized by adsorbing a semiconducting conjugated polymer, poly[2-methoxy-5-(2’-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) onto the wire from solution. Ag nanowire solutions in tetrahydrofuran (THF) were prepared by concentrating nanowires through centrifugation, ethanol removal and resuspending at a concentration of 1mg/ml. Such solutions were mixed with equal volumes of MEH-PPV dissolved in THF (concentration 0.4mg/ml or 0.01mg/ml), sonicated for 3 min to thoroughly mix nanowires and MEH-PPV, and incubated for 72 hrs to allow MEH-PPV adsorption onto the wires. The nanowires were washed to remove free and unbound MEH-PPV by centrifugation and resuspension in THF followed by vortexing, a process repeated five times.

As an alternative strategy, Ag nanowires were functionalized by displacing the PVP layer with an alkanethiol self-assembled monolayer (SAM). The PVP layer, estimated to be a monolayer thick, is only weakly attached to the nanowire through a coordination bond between the PVP and nanowire Ag atoms [5] and is easily displaced by molecules with thiol functionality, as the thiol sulfur forms a strong chemical bond with Ag. Equal volumes of a 1mg/ml ethanol solution of Ag nanowires and a 100 µM solution of 1-undecanethiol in chloroform were mixed and sonicated for 5 mins. The resulting solution was left for 20hr allowing a thiol SAM to form on the nanowires, which were recovered and purified by centrifugation, precipitate extraction and resuspension in chloroform. This process was repeated five times to remove unreacted thiol and displaced PVP. Thiolated nanowires were further functionalized with MEH-PPV to see whether MEH-PPV adsorbed onto the alkane-terminated nanowire surface more effectively than onto the PVP termination.

### 3. Characterisation and properties of functionalised wires

Samples of each batch of functionalized nanowires were dispersed onto clean Si from solution and imaged using SEM. Figure 1 shows representative images for as-synthesised Ag nanowires, nanowires with adsorbed MEH-PPV and thiolated nanowires; all three batches having a mean wire diameter of ~100 nm with ~30 µm length. The as-synthesised wires present a smooth featureless surface, figure 1(a), whereas after adsorption of MEH-PPV, figure 1(b) shows that the wire surfaces become decorated with “chains” of small particles <10 nm in size, wrapping around the wire. We assume these indicate the inhomogeneous adsorption of MEH-PPV onto the PVP surface. In contrast, the thiolated wires of figure 1(c) are smooth, the faceted structure of the nanowires being clearer than for the PVP-capped nanowires. Changes in contrast visible on the nanowires perhaps indicate domains created by the incomplete displacement of the PVP capping layer by the thiol SAM. SEM images of thiolated nanowires after MEH-PPV adsorption (not shown) reveal wires with very similar appearance to 1(c).
To confirm MEH-PPV adsorption on the nanowires, confocal laser-scanning fluorescence microscope imaging was carried out on MEH-PPV-functionalized Ag nanowires dispersed onto silica. Figure 2(a) shows the absorption and emission spectra measured for a 0.4mg/ml solution of MEH-PPV in THF. Samples were excited in the MEH-PPV absorption band by λ=457 nm light, and the resulting red-shifted fluorescence imaged through a λ=505-550 nm band-pass filter. The confocal fluorescence image, Figure 2(b), clearly shows MEH-PPV emission emanating from the nanowires.

Fluorescence spectra measured for Ag nanowires in THF solution functionalized with different concentrations of MEH-PPV are given in figure 3(a), together with those for just MEH-PPV, and for unfunctionalised wires. This data confirms that the fluorescence emission from the coated wires is that of MEH-PPV, though the wire spectra are blue-shifted by ~5 nm w.r.t. the MEH-PPV:THF solution spectrum. The nanowire emission intensity is lower than for the initial MEH-PPV solution, and decreases with the initial MEH-PPV concentration, whilst the unfunctionalised wires merely exhibit a scattered light background. Figure 3(b) shows the equivalent data measured for the thiolated Ag nanowires after MEH-PPV adsorption, this time from chloroform. Here the blue-shift for the MEH-PPV adsorbed on the wires is greater, at ~9 nm, and only the wires functionalized at the highest MEH-PPV concentration (0.4mg/ml) show emission, suggesting that MEH-PPV adsorption is less efficient for the thiol-terminated wires. This is confirmed by the optical absorption data: only Ag nanowires functionalised with the highest concentration MEH-PPV display the MEH-PPV absorption peak at 550 nm, all other spectra exhibited only the peaks at 350 nm and 400 nm associated with the “bulk” and transverse surface plasmon modes of the Ag nanowires respectively. The conclusion from the spectral data is that MEH-PPV does adsorb onto Ag nanowires, but at a low density since blue-shifted emission spectra usually indicate low-self quenching, and thus greater emitter separation.

It appears that MEH-PPV adsorbs best on PVP-coated wires, presumably due to the very different surface chemistry and morphology of the two surface terminations. Adsorption is likely to occur through the van der Waals interaction between the alkyl side chains of the MEH-PPV and the organic surface layer. The thiol SAM is presumably more ordered and densely packed than the displaced PVP film and this perhaps hinders MEH-PPV attachment by reducing the penetration of the MEH-PPV alkyl side chains into the organic layer, decreasing the interaction.
Figure 3 Fluorescence spectra of solutions of (a) MEH-PPV coated Ag nanowires together with controls, (b) Thiolated Ag nanowires coated with MEH-PPV together with controls and (c) Absorption spectra of MEH-PPV coated Ag nanowires in solution.

Non-contact atomic force spectroscopy (NC-AFM) is used to map the nanowires’ work function, allowing assessment of the uniformity of the native PVP coating, as well as modifications introduced by functionalization. Measurements were performed in ultra-high vacuum on as-synthesized nanowires dispersed on a Au(111) substrate. A PtIr coated Si cantilever was driven at resonance and its frequency shift due to interaction with the surface was measured while the cantilever was scanned over the surface. Work function maps were constructed from frequency shift-voltage spectroscopic curves. Figure 4 shows such a map taken over a PVP capped wire. The work function is about 0.9 eV lower on the wire than on the Au(111) substrate, and varies up to 0.1 eV over the top surface of the wire. Comparison with values for clean metals (~ 4.64 eV for Ag(100), ~ 5.3 eV for Au(111)) shows that the PVP layer lowered the work function of the Ag(100) faces of the wire by about 0.1-0.2 eV, and that this coating is not entirely homogeneous.

Figure 4 Work function map of a PVP-capped Ag nanowire on an Au(111) surface, derived from NC-AFM frequency shift-voltage spectroscopic curves. The mapped area is 800 nm × 300 nm, the work function measured with 5 nm spatial resolution.

4. Excitation energy transfer via Surface Plasmon

Surface plasmons (SPs) are electromagnetic waves coupled to longitudinal charge oscillations which are bound to, and propagate along metal/dielectric interfaces [6]. Surface localisation means that they have highly enhanced optical fields and strongly couple with materials placed in close proximity: fluorescent molecules within ~100 nm of metals are readily excited through SP evanescent fields, and primarily de-excite by exciting SPs [7]. Ag nanowires act as SP waveguides [8]; we demonstrate that SPs propagating on such wires can mediate the transfer of excitation energy from donor dye molecules to acceptor molecules near to the metal, figure 5(a). Ag nanowires were dispersed on a silica surface and microcontact printing (µCP) used to pattern donor dyes, Fluorescein isothiocyanate (FITC), and acceptor dyes, Rhodamine B (RB) on top. Figure 5(b) shows the absorption and emission spectra measured for µCP layers of FITC and RB indicating the overlap between the FITC emission and the RB absorption spectra necessary for energy transfer. Fluorescence microscopy using dye-specific filter
sets, figure 5(c-e), was then used to image the fluorescence emitted by the dye/nanowire system. The transmission image in Figure 5(c) clearly shows the nanowire locations, which can be clearly correlated with the absence of FITC donor emission in figure 5(d) and enhanced RB acceptor emission in figure 5(e). The decrease in FITC emission on the Ag nanowires is due to enhanced quenching of the FITC through generation of nanowire SPs and subsequent excitation of the RB acceptors followed by red-shifted remission. This leads to enhanced emission from the nanowires in the RB fluorescence image, indicating that excitation energy has been transferred from FITC to RB via the SPs of the nanowire.

![Figure 5](image_url)

**Figure 5** (a) Schematic of SP-mediated energy transfer on Ag nanowires, (b) the absorption and emission spectra of the donor (FITC) and acceptor (RB) dyes and optical microscope images of Ag nanowires in (c) transmission, (d) FITC fluorescence and (e) RB fluorescence (60 µm x 160 µm).

5. Conclusions
We have synthesized Ag nanowires with diameters 60-100 nm and lengths up to 90 µm and functionalized them using either thiol displacement of the PVP capping layer, or by adsorption of a luminescent polymer. Electron microscopy shows that the polymer wraps around the nanowires inhomogeneously, and the resulting nanowire fluorescence is blue-shifted from the polymer emission spectrum in solution, suggesting non-interacting polymer excitons. NC-AFM measurements show that the PVP capping layer on the wires lowers the work-function by ~0.2 eV w.r.t. Ag (100), and shows a degree of inhomogeneity. Finally, we have demonstrated the enhanced transfer of excitation energy from donor to acceptor dyes, mediated by the SP modes of the Ag nanowires.

References
[1] Kneipp K, Kneipp H, Itzkan I, Ramachandra R D and Feld M S 2002 *J. Phys: Condens. Matter* **14** R597-R624
[2] Wiley B, Sun Y, Mayers B and Xia Y 2005 *Chem. Eur. J.* **11** 454-63
[3] Sun Y, Mayers B, Herricks T and Xia Y 2003 *Nan Lett.* **3** 955-60
[4] Chen C, Wang L, Jiang G, Yang Q, Wang J, Yu H, Chen T, Wang C and Chen X 2006 *Nano Technology* **17** 466–74
[5] Gao Y, Jiang P, Liu D F, Yuan H J, Yan X Q, Zhou Z P, Wang J X, Song L, Liu L F, Zhou W Y, Wang G, Wang C Y, Xie S S, Zhang J M and Shen D Y 2004 *J. Phys. Chem. B* **108** 12877-81
[6] Raether H 1988 *Surface Plasmons* (Berlin:Springer)
[7] Weber W H and Eagen C F 1979 *Opt. Lett.* **4** 236-8
[8] Graff A, Wagner D, Ditlbacher H and Kreibig U 2005 *Eur. Phys. J. D* **34** 263-9