Transparent, conductive gold nanowire networks as assembled from soluble Au thiocyanate†

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Extremely long gold nanowires spontaneously assemble in a water–dimethylsulfoxide (DMSO) solution of Au(SCN)$_4$. The Au nanowires were crystalline, exhibited a very high aspect ratio, and, importantly, were produced without co-addition of reducing agents. Transparent conductive films were formed by surface deposition of the nanowires and plasma treatment.

Fabrication of thin transparent conductive electrodes (TCEs) which would be inexpensive, robust, and exhibit scalable surface areas is a highly sought albeit challenging goal in optoelectronics, photovoltaics, and nano-photonics research and development.1,2 While most currently fabricated micro- and nano-electronic devices are produced via “top-down” lithography methods,3 “bottom-up” approaches have emerged as promising alternatives for generation of organized nanostructures and electronic components.4 Bottom-up techniques generally rely upon molecular self-assembly phenomena to produce defined structures that could be practically utilized.5–10 Here we describe a new approach for construction of thin-film TCEs through deposition of extremely long nanowires which self-assemble from water–DMSO solutions comprising the complex gold thiocyanate.

The experimental scheme is depicted in Fig. 1A. Water-soluble Au(SCN)$_4$ was prepared through mixing of chloroauric acid and potassium thiocyanate.11 The complex was then incubated for 24 hours in a solution comprising water and DMSO (the volume ratio providing the most optimal results was 1:4, although other mixtures of the two solvents gave rise to nanowire formation). Upon gradual drying of the solvent, films comprising a network of nanowires were obtained. Further plasma treatment of the Au nanowire films was carried out, resulting in enhanced electrical conductivity (Fig. 1A).

Fig. 1 Generation of a nanowire network. (A) Schematic depiction of the nanowire formation method; (B) SEM image of a typical nanowire network before plasma treatment, scale bar is 1 μm; (C) SEM image of a single wire before plasma treatment, scale bar is 5 μm; the inset shows a magnified region within the wire, underscoring its uniform, smooth appearance. Scale bar 500 nm.

Scanning electron microscopy (SEM) analysis, presented in Fig. 1B and C, highlights the film configuration and nanowire morphology. The SEM results highlight the formation of extremely long nanowires in the water–DMSO solution (up to hundreds of microns, see Fig. S1, ESI†), resulting in an interspersed network following solvent evaporation. The nanowires exhibited smooth surfaces and a relatively uniform diameter of around 300 nm (Fig. 1C).

Fig. 2 presents microscopic and spectroscopic analyses of the nanowires, illuminating their structural features. The transmission electron microscopy (TEM) image and the associated diffraction pattern of as-synthesized nanowires before plasma treatment shown in Fig. 2A underscore the crystalline nature of the individual nanowires. In particular, the diffraction pattern in the inset of Fig. 2A reveals crystal spacings of 3.61 Å, 6.11 Å, and 9.23 Å corresponding to Au(SCN)$_4^−$ crystalline domains. The nanowires contained also metallic gold [Au(0)], evidenced by energy dispersive spectroscopy (EDS) analysis (Fig. S2, ESI†).

The powder X-ray diffraction (XRD) data in Fig. 2B confirm the crystalline nature of the nanowires and shed light on the
The effect of plasma reduction. The powder XRD pattern of the as-prepared nanowires (Fig. 2B, top) attests to the presence of abundant Au(SCN)$_4^-$ crystallites, giving rise to major peaks at 8.34 Å, 6.11 Å, and 2.90 Å. The powder XRD pattern in Fig. 2B (bottom spectrum) underscores the dramatic impact of plasma treatment on the gold nanowires. Essentially, the diffraction peaks assigned to the Au(SCN)$_4^-$ crystalline species are significantly diminished in intensity following plasma application (e.g. peaks at 8.34 Å and 6.11 Å), while the XRD peaks ascribed to crystalline Au(0) become the prominent spectral features (Fig. 2B, bottom). Overall, the powder XRD analysis indicates that plasma treatment promoted reduction of the Au(III) species to Au(0), essentially transforming the nanowires into an almost fully metallic phase.

X-ray photoelectron spectroscopy (XPS) experiments are presented in Fig. 2C. While we previously reported that Au(III)(SCN)$_4^-$ is reduced to Au(I)(SCN)$_2^-$ in aqueous solutions, the XPS result in Fig. 2C suggests that DMSO stabilized the Au(III) state (peaks at 87.2 eV and 90.8 eV), promoting self-assembly of the nanowires.

Examination of the XPS peak areas indicates that the as-prepared nanowires comprise Au(III) and Au(0) at an approximately 1:1 ratio (Fig. 2C, top spectrum). However, application of plasma treatment gave rise to transformation of the nanowires into a metallic Au phase (Fig. 2C, bottom spectrum). Previous studies have reported reduction of Au ions following application of plasma treatment, SEM data presented in Fig. S3, ESI† indicate that the plasma reduction process gave rise to pronounced morphological changes within the nanowire surface, which are consistent with the spectroscopic results in Fig. 2.

The formation of interspersed metallic Au nanowire networks, apparent in Fig. 1, opens the way for varied practical applications. Fig. 3 depicts the transparency and conductivity profiles of a Au nanowire film deposited on a glass substrate after plasma treatment (yielding nanowire morphology as shown in Fig. S3, ESI†). The transmittance spectrum in Fig. 3A underscores excellent transparency ~ almost 80% of the incident light was retained after passing through the nanowire film. Considerable electric conductivity was similarly recorded for the glass-supported nanowire film (Fig. 3B). The current–voltage (I/V) curves, depicted in Fig. 3B, recorded for 100 μm and 1 mm electrode spacings, respectively, display linear appearance, e.g. Ohmic behaviour. Importantly, the calculated sheet resistance was ~ 70 Ohm sq$^{-1}$ which is comparable to those of the previously reported transparent conductive electrode designs.

In summary, we have described a new method for producing elongated Au nanowires. The synthetic scheme involves spontaneous, single-step crystallization and reduction of Au(SCN)$_4^-$ in a DMSO–water mixture, followed by conventional plasma treatment. The new Au nanowire production approach is very
easy to implement, particularly compared to previously-reported methodologies, and constitutes a useful platform for assembly of transparent conductive films. Importantly, the nanowire formation process we reported here does not require addition of reducing agents - the almost universal precondition for current Au nanowire synthesis. The Au nanowire network is stable for long time periods and exhibits excellent transparency and electrical conductivity, pointing to its potential uses in electro-optic and photonic devices.

Financial support provided by the Ministry of Trade and Industry, Infrastructure Grant.

Notes and references