A direct synthetic approach to vanadium pentoxide nanofibres modified with silver nanoparticles

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Small amounts of silver ions have been found to significantly enhance the growth rate of vanadium pentoxide (V_2O_5) nanofibres in aqueous solution at room temperature, yielding fibres with lengths of several micrometers within a few days; the V_2O_5 fibres are decorated with silver nanoparticles with sizes in the range of 5–15 nm, which opens perspectives for applications in chemical sensors.

V_2O_5 nanofibres are moderate electrical conductors that have found application as charge storage materials in batteries, as well as antistatic coatings in the photographic industry.[1] Moreover, their use as components of gas sensors has been proposed.[2] In this context, the electrical transport mechanism in V_2O_5 fibres has been studied in detail.[3,4] The commonly used synthesis method comprises the poly-condensation of vanadic acid prepared from different precursors in aqueous solutions.[1,5,6] Their extraordinarily regular structure (~ 1.5 nm $\times$ 10 nm cross section)[3,7] is an outstanding property which distinguishes V_2O_5 fibres from other nanowires and nanotubes. In contrast to the crystalline architecture of bulk V_2O_5 compounds, which has been modified by a wide variety of organic components,[8] only a few attempts have been reported to alter the chemical composition of isolated V_2O_5 fibres. These involved reaction with reducing agents like aniline, whereby the ratio between V^{5+} and V^{4+} centres is decreased.[9] However, the possibility to chemically tailor the V_2O_5 fibre surface would be highly desirable, *e.g.*, for the development of highly sensitive and selective chemical sensors. Preliminary studies have shown that the sensitivity of V_2O_5 fibres upon interaction with ammonia can be significantly enhanced *via* their post-synthesis modification with noble metal clusters, for instance *via* evaporation of nominally 1 nm of gold.[2] Here we report an easy method allowing for the *in situ* attachment of silver nanoparticles to the V_2O_5 fibres during synthesis, which furthermore offers the advantage of a substantially increased growth speed of the fibres.

The nanoparticle-modified V_2O_5 fibres were synthesised by adding 100 µl (420 µmol) of vanadium-oxytriisopropoxide, $OV(OC_3H_7)_3$, to a solution of 15 mg (90 µmol) silver acetate in 80 ml H_2O, followed by stirring the mixture for 5 min at 70 °C. The resulting orange solution was then kept at ambient conditions, yielding fibres denoted as "Ag–V_2O_5". A reference sample without silver acetate was prepared by the same procedure. However, the concentration of the vanadyl ester was increased by a factor of four, as no nanofibres were obtained at lower concentrations in the absence of silver ions.

In order to evaluate their dimensions after different periods of ageing, the V_2O_5 fibres produced by the two methods were deposited on SiO_2/Si-wafers, which were previously amino-silanized by immersion in a 4.6 mM aqueous solution of *N*-[3-(trimethoxysilyl)-propyl]ethylene diamine for 2 min at room temperature. In Fig. 1, the average length of the Ag–V_2O_5 fibres determined from tapping-mode atomic force microscopy (AFM) images is plotted as a function of ageing time (full squares). The growth characteristic displays two well-distinguished regimes. Up to an age of 5 days, a fast growth regime with a rate of ~ 0.5 µm d^{-1} is recognised, which is followed by a slower regime with a rate of ~ 0.08 µm d^{-1}. In

comparison, the growth of the reference V_2O_5 fibres is characterised by a constant rate of ~ 0.043 µm d^{-1} (open triangles), which is slightly lower than in the slow regime of the Ag–V_2O_5 fibres, despite the higher concentration of the vanadyl precursor. With the increased speed of growth it is possible to obtain fibres with lengths exceeding 1 µm within only one day, whereas in the absence of silver this length is approached after two weeks. The high rate within the initial phase of Ag–V_2O_5 fibre growth provides clear evidence that the silver ions promote the growth. The subsequent slow growth regime may be explained by the consumption of the limited amount of Ag^+-ions within the solution. It is worthy of note that the fast growth regime can also be induced at later growth stages of the pure V_2O_5-fibres. This conclusion is drawn from experiments in which silver ions were added to a reference sample with an age of at least 5 days.

The Ag–V_2O_5 fibres were further examined by scanning transmission electron microscopy (S-TEM), operated with a high-angle annular dark-field (HAADF) detector,[10] and complemented by energy dispersive X-ray (EDX) analysis. From the S-TEM image (Fig. 2), it follows that the Ag–V_2O_5 fibres have widths between 8 and 15 nm, in reasonable agreement with the value of 10 nm reported for pristine V_2O_5 nanofibres.[7] Furthermore, bright dot-like features become visible on top of the fibres. The size of these nanoparticles is found to fall in the range of ~ 5–15 nm. On the basis of EDX spectra, which indicate the presence of V, O, and Ag, the dots are assigned to metallic silver. This conclusion is solidified by the high silver signal at the location of the clusters, as apparent from the two energy-selective line-scans presented in Fig. 3b. It is noticed that for a freestanding nanoparticle (location B) no V-signal is detected, demonstrating that the dots are exclusively composed of Ag. Conversely, at a position comprising a pure fibre (location A), a strong V-signal is measured.
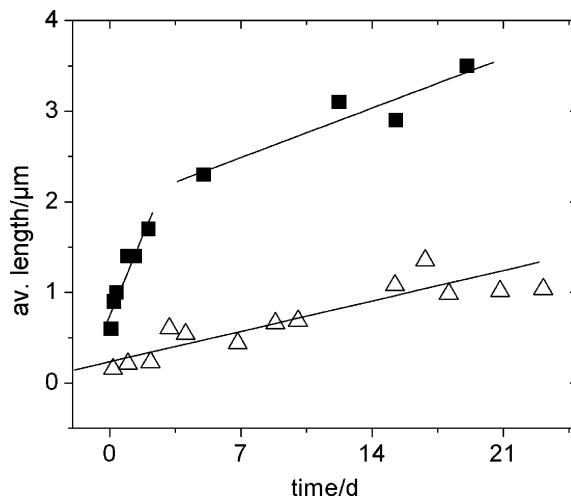

Fig. 1 Average length of Ag–V_2O_5 fibres as a function of sample age (closed squares), in comparison to V_2O_5 fibres grown without Ag-ions (open triangles).
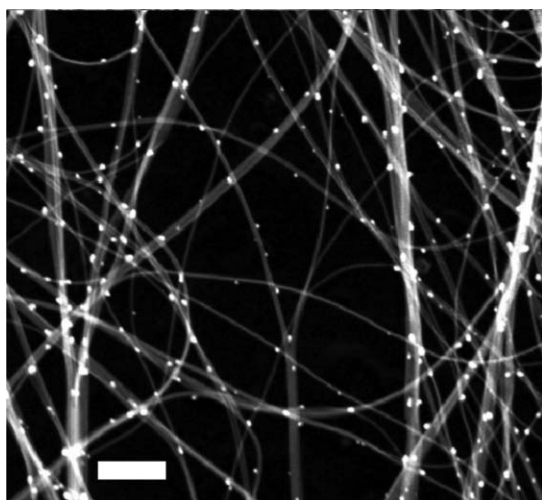
Fig. 2 S-TEM image of Ag–V$_2$O$_5$ nanofibres (scale-bar = 100 nm).
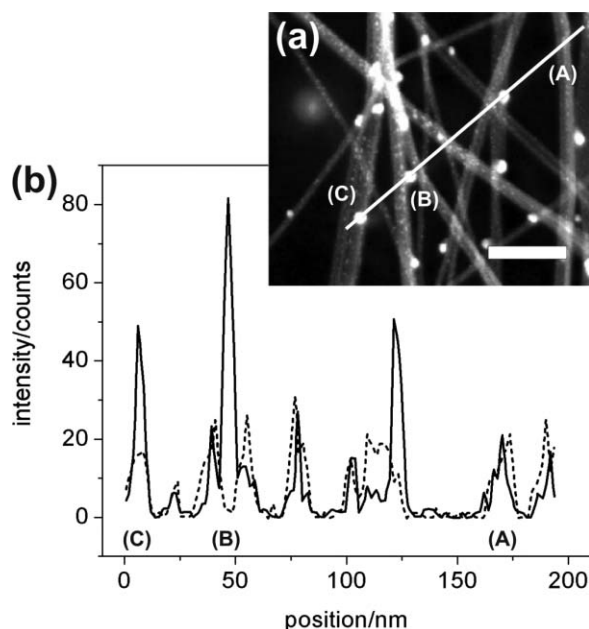

Fig. 3 (a) S-TEM image of Ag–V$_2$O$_5$ nanofibres (scale-bar = 50 nm) identifying the line-scan direction. Various positions are marked: isolated fibres (A), freestanding clusters (B), and clusters on top of fibres (C). (b) Two EDX line-scans along the line indicated in (a). The energy-window was adjusted to 2.8–3.7 keV and 4.8–5.6 keV, to be element specific to Ag-atoms (solid line) and V-atoms (dashed line), respectively. The markers (A–C) correspond to positions marked in (a).

In addition, a non-vanishing signal of Ag is detected, indicating a small amount of silver incorporated into the fibres. The formation of silver nanoparticles provides a further hint for the above suggested mechanism of the transition from a fast to a slow growth regime, since the silver of the particles should no longer be available for a promotion of the fibre growth.

It is an intriguing issue by what extent the attached silver particles modify the electrical transport properties of the V$_2$O$_5$ fibres. Towards this end, electrical measurements were performed on a dense network of Ag–V$_2$O$_5$ fibres at different temperatures under ultrahigh vacuum conditions. As apparent from the inset of Fig. 4, the low-bias resistance (V_{SD} = 100 mV) follows the dependence $R = R_0 \exp\{(T_0/T)^{1/(d+1)}\}$, where T_0 is a characteristic
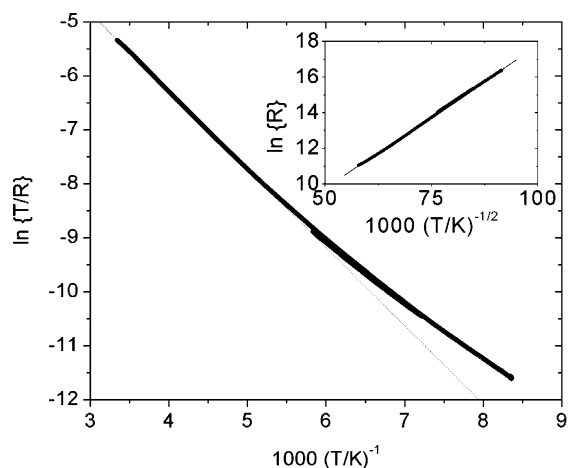

Fig. 4 Temperature dependence of the network resistance at small bias voltage. Inset: validation of one-dimensional conductivity in accordance with the variable range hopping model.

temperature, and d characterises the dimensionality of the system.[4] A best fit was obtained with $d = 1$, in accordance with the dimensionality of the fibres. The same dependence was found for the pristine V$_2$O$_5$ fibres, which exhibit variable range hopping between V^{4+} and V^{5+} centres,[5] described in terms of the small-polaron model.[11,12] From a plot $\ln\{T/R\}$ vs. T^{-1} (Fig. 4), an energy-barrier of E_a = 125 meV can be extracted for the hopping process at higher temperature.[3,12] At lower temperatures, the activation energy decreases, which could be attributed to a disorder-energy incorporated in the (total) activation energy at higher temperatures.[3,13] The obtained activation energy is in good agreement with 92–180 meV reported for unmodified V$_2$O$_5$,[4] further testifying that the conduction properties of the V$_2$O$_5$ fibres are not significantly affected by the presence of Ag.

To summarise, we have demonstrated that the decoration of V$_2$O$_5$ fibres with silver nanoparticles can be achieved under mild conditions in the presence of silver ions. The electrical conduction mechanism in the resulting nanowires is only slightly affected by the attached nanoparticles. Nonetheless, the Ag-particles could act as mediators between fibres and analytes, due to an enhanced interaction of the analytes with the noble metal.

Notes and references

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