

# TEMPLATED SYNTHESIS OF AGCN AND AG NANOWIRES

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## Introduction

Fabrication of one-dimensional metallic nanostructures is an important activity within nanoscience. Their ability to absorb and scatter light has led to numerous studies in plasmonics, spectroscopy and biosensing[1].

Silver is a low cost and highly conductive metal, well known for the intense and tunable optical properties of its nanostructures.

Unlike direct wet chemical methods which are usually complex, templating processes are versatile and have been shown to be particularly successful in nanocomposite synthesis.

We present here, a simple, reproducible, high yield and inexpensive route to produce silver nanowire arrays from AgNO<sub>3</sub> precursor and poly(styrene-alt-maleic anhydride; SMA) polymer. Recently it has been showed that SMA self-assembles to form nanotubes in aqueous media[2]. Our technique takes advantage of this property to guide silver cyanide (AgCN) growth into very high aspect ratio nanowires (5 to 100 nm wide, > 50 µm long) [3]. Subsequent chemical reduction of the composite with sodium borohydride leads to the formation of a conductive porous metallic silver nanowire network. It is the first time to our knowledge that such long AgCN nanowires have been synthesized.

## Experimental

### Materials

Poly(styrene-alt-maleic anhydride) was purchased from SP<sup>2</sup> Scientific Polymer Source(1.6 kDa and 50 kDa). Silver nitrate (>99%), sodium borohydride and cyanoborohydride were purchased from Aldrich, potassium cyanide was purchased from Anachemia, and used as received.

### SMA nanotube preparation

The SMA polymer nanotube preparation method (in deionized water) was the same for the two different  $M_w$  samples. An SMA solution of 0.1% wt. was prepared in deionized water. The maleic anhydride groups of SMA were hydrolyzed using an excess of NaOH, to obtain a pH beyond the second pKa. 3 mole equivalents of NaOH (by weight, relative to SMA monomer) was added. A 50% degree of protonation was achieved by dialysing the basic solution against 2 L of deionized water, using 1000 Da cut-off membranes (SpectraPore). When the solution inside

the dialysis bag reached pH 7.5 – 8, the dialysis was stopped.

### AgCN-SMA composite preparation

AgCN-SMA nanowires were prepared by dissolving AgNO<sub>3</sub> in deionized water, added dropwise to the SMA nanotube solution. NaBH<sub>3</sub>CN was dissolved in deionized water and added dropwise to the solution while stirring. The solution turned dark brown and opaque upon addition. During the course of 2 days, the bundles of nanotubes precipitated from solution as a white fibrous material.

### Molecular modeling

Hydrolyzed SMA polymers have an increased persistence length and are stiffer when 50% protonated. Molecular modeling of the association properties of SMA in this protonation state has shown that the polymers associate sideways to form rigid association complexes bent by 130 degrees[2]. Multiple rigid associations form a minimum energy closed tubular structure involving eight SMA polymers (see Figure 1).

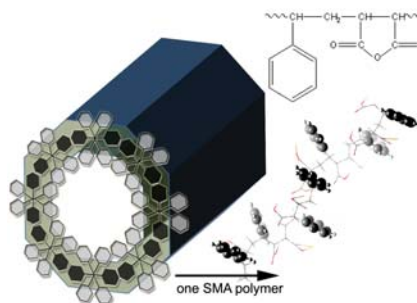


Figure 1: Schematic of the polymer nanotube formed by a process where 8 SMA polymer chains self-associate using  $\pi$ -stacking of the styrene groups.

The nanotube structure grows linearly by the addition of further polymers along the edges of the tube. Additional  $\pi$ -stacking at the periphery of the nanotubes drive sideways aggregation, giving SMA nanotube bundles. Modelling predicts that the SMA nanotubes have an outer diameter of 4.4 nm  $\pm$  0.2 nm and an inner diameter of 2.0 nm  $\pm$  0.2 nm.

### Results and discussion

SMA nanotubes prepared by dialysis were used to template the growth of silver cyanide via the reduction of silver nitrate with sodium

cyanoborohydride. A fibrous composite results. The nanowires precipitate in bundles with various aggregation numbers and lengths, dependant on the molecular weight of the SMA polymer and whether sonication was employed. Figure 2 is a SEM scan showing extremely long nanowires formed using 50 kDa SMA.

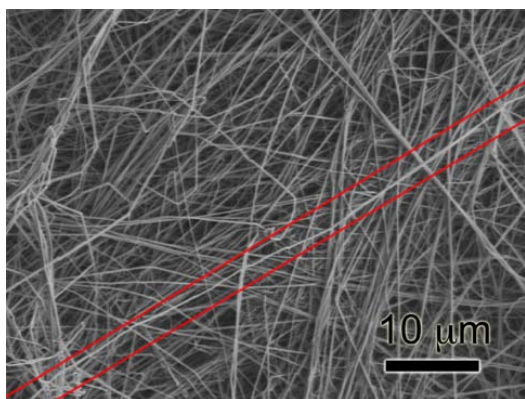


Figure 2: SEM scan of AgCN-SMA50K composite showing really long nanowires (up to 65 microns long)

1.6 kDa SMA forms bundles of 5-20 nanowires, which are joined together at one end. Performing the reaction while sonication leads to single nanotubes, as shown in figure 3.

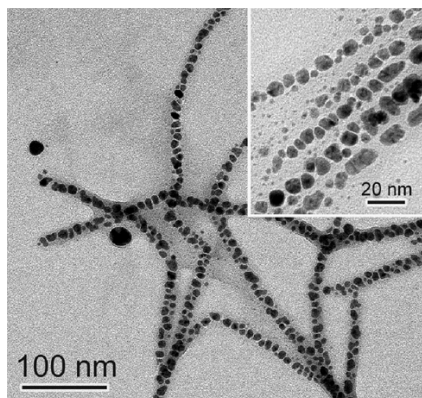


Figure 3: TEM scan of AgCN-SMA1.6K (reaction performed with sonication). Inset: High Resolution TEM showing single nanotubes.

A mechanism leading to the formation of these nano-composites can be described by a two step process. First, silver ions are quickly reduced to form silver nanoparticles (Ag NP), until the reducing power of  $\text{NaBH}_3\text{CN}$  is depleted, turning the solution into the characteristic orange color of Ag NP in water. This step is rapid and takes place in solution as typical for water phase nanoparticle synthesis.

The second step is slow and involves the growth of silver cyanide along the polymer nanotubes, forming AgCN-SMA nanowires that precipitate. Over the two day formation of the precipitate,  $\text{CN}^-$  is released, scavenging silver from the NP and reacting with free  $\text{Ag}^+$  ions to form AgCN with the SMA nanotubes. The

AgCN nanowire structure becomes insoluble and precipitates out of solution as a white yellowish fibrous aggregate. The yellowish tint disappears upon washing, and likely arises from adsorbed silver NP within the nanowire network.

$\text{CN}^-$  reacts with  $\text{Ag}^I$  and  $\text{Ag}^0$  forming different complex ions such as  $\text{Ag}(\text{CN})_2^-$ , and a silver cyanide precipitate in aqueous medium[4].  $\text{Ag}^0$  dissolution in an  $\text{O}_2$  containing  $\text{CN}^-$  solution is a 4 electron oxidation process, involving the reduction of  $\text{O}_2$  adsorbed on the metal surface. Reduction of silver nitrate with  $\text{NaBH}_3\text{CN}$  in presence of SMA in an Ar atmosphere did not form any wires after 4 days, in agreement with the proposed mechanism involving the oxidation of the Ag NP by  $\text{O}_2$  in presence of  $\text{CN}^-$ , to form AgCN.

Like the other metal cyanides AuCN and CuCN, AgCN forms infinite  $-\text{M}(\text{CN})-$  1D chains, packed through argentophilic interactions into a trigonal structure[4]. The presence of silver cyanide is verified by IR spectroscopy and X-Ray diffraction [4]. Moreover, selected area electron diffraction pattern and the absence of the SPR peak characteristic of Ag NP (ca. 400 nm) supports the case for formation of AgCN rather than Ag(0) at this stage.

Subsequent reduction of the composite deposited on a nylon filter forms a conductive network of silver nanowires. Two-point probe measurements were performed on the dried sample at multiple locations. The resistance measurements ranged from 100-300  $\Omega$  (distances from 1-10 mm) on the remaining pattern, and showed huge resistance outside the array.

## Conclusion

We have shown that SMA nanotubes can be used as templates to form stable networks of organic nanotubes with a high metal content. Lateral and longitudinal dimensions of the tubes can be tuned by modifying the  $M_w$  of the polymer and by sonication to prevent stacking between nanotubes. Silver cyanide is believed to occur along the length of the nanotubes and its reduction to metallic silver may be supported by the polymer scaffold of the SMA template.

Our work interest is three-fold: *first* it presents SMA as a new and an appropriate templating material, *secondly* it describes the synthesis of a new AgCN-SMA composite with genuine interesting geometry and *finally* it supports AgCN-SMA to be a suitable material for making silver nanostructures that would not be directly possible to make with pure AgCN.

## References

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