# Organic Solvent-Induced Crystallization of Water-Soluble Inorganic Salt of $Na_3Au(SO_3)_2$ into Ultralong Nanobelts on a Large Scale

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Since the discovery of carbon nanotubes by Iijima,[1] the research on one-dimensional (1D) nanostructures has received considerable attention by researchers and always been a hot research topic.[2–4] Indeed, in recent years the rapid development of the preparation of 1D nanostructures such as wires, rods, belts, and tubes of all kinds of materials made of metals, oxides, semiconductors, polymers, protein, DNA, and assemblies of nanoparticles has been witnessed;[4–8] however, the simple and effective synthesis of such 1D nanostructures on a large scale still remains a challenge for researchers. On the other hand, template-based synthesis of hollow structures via a layer-by-layer technique has also been another hot research topic,[9,10] and the preparation of tubular structures employing 1D nanostructures such as porous membranes, metal nanorods, nanowires, and carbon nanotubes as templates has also drawn a lot of scientific attention[11–14] because of the diverse applications of such tubular structures in drug delivery, catalysis, optics, electronic, and magnetic devices.[15,16] However, most of the template-based methods suffer from a tedious postsynthesis process where a base or acid medium or high temperature is usually required to remove the templates used and, therefore, considering safety and environmental hazards, an easily removable template is strongly expected. In this regard, water-dissolvable 1D nanostructure of water-soluble inorganic salts should be the best candidate because it can be easily dissolved and hence removed after exposure to water, making the postsynthesis process quite fast and also environmentally friendly. However, the preparation of such a kind of 1D nanostructures is still in its embryonic state, and only one study has been documented so far where water-dissolvable sodium sulfate nanowires were produced in an organic solvent of *N*,*N*-dimethylformamide (DMF) with the coexistence of $AgNO_3$, $SnCl_2$, dodecylsodium sulfate (SDS), and cetyltrimethylammonium bromide (CTAB); however, a high temperature of 160 °C and a long time 1 h were also involved in this preparation.[17]

In this communication we demonstrate the first example of the rapid formation of ultralong nanobelts of water-soluble inorganic salt of $Na_3Au(SO_3)_2$ on a large scale via organic solvent-induced crystallization, carried out by adding a diluted solution of commercial gold bath, an aqueous solution of $Na_3Au(SO_3)_2$, which has been largely been used for the fabrication of 1D gold structures by template-based electroless deposition of gold into polycarbonate membranes,[18] into an organic solvent DMF at room temperature. The 1D crystals growth process was also traced by in situ optical microscopy observation of the structures formed with different elapsed times after the mix occurs. Most importantly, it was found that the dimensionality of the nanobelts can be simply tuned by varying parameters such as the temperature and the relative amount of the components in the mixture including $Na_3Au(SO_3)_2$, DMF, and $H_2O$.

Figure 1A shows an optical microscope image of as-prepared precipitate (for the preparative details, see Supporting Information). It is clearly seen that the precipitate consists of a large quantity of ultralong 1D structures about several hundred micrometers in length, which is also confirmed by the corresponding low magnification scanning electron microscopy (SEM) image as shown in Figure 1B. The detailed morphology of such 1D structures was further examined by the high magnification SEM image as shown in Figure 1C. It can be clearly seen that these 1D structures are uniform and belt-shaped about 500 nm in width and 200 nm in height, demonstrating that they are nanobelts in nature. A transmission electron microscopy (TEM) image of a part of one single nanobelt shown in Figure 1D indicates that the nanobelts thus formed have an electromicroscopically smooth surface, and the corresponding selected area electron diffraction (SAED) pattern (inset) shows a hexagonal symmetry diffraction spot pattern revealing the single-crystalline nature of the nanobelt. It should be noted that these nanobelts have the following three features: (1) They are robust enough to stand a vigorous sonication process; (2) they can be dispersed in any organic solvent without any change; and (3) they are easily dissolved in water.

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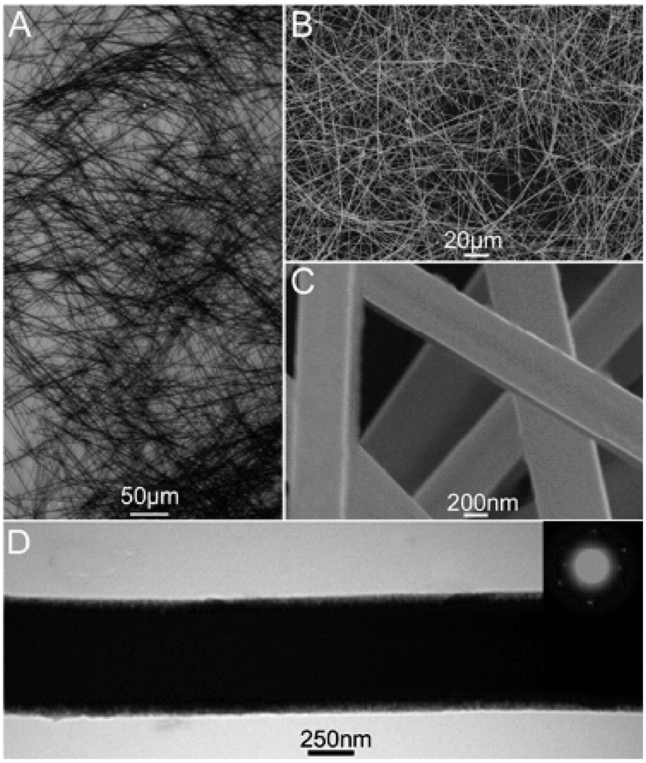

**Figure 1.** (A) Optical microscopy, (B) low magnification SEM, and (C) high magnification SEM image of the nanobelts obtained by adding a diluted solution of 5 $\mu$L of gold bath in 295 $\mu$L of $H_2O$ into 700 $\mu$L of DMF at room temperature. D is the TEM image of a part of one single nanobelt and the corresponding selected area electron diffraction (SAED) pattern (inset).

The chemical composition of as-formed nanobelts was determined by energy-dispersed spectroscopy (EDS) and X-ray maps analysis of the crystals coated on a glass slide. The EDS spectrum (Figure S1, Supporting Information) shows several peaks corresponding to Au, S, O, and Na elements (the peak of Si originated from the substrate used), indicating these belts are formed from gold bath salt. Further quantitative elemental analysis reveals that the atomic ratio of Au:S:O:Na contained in such nanobelts is 1:2:6:3, which is quite consistent with the chemical composition of the bath salt $Na_3Au(SO_3)_2$. The corresponding X-ray maps shown in Figure S2 (Supporting Information) further demonstrate that these four elements are relatively evenly distributed along the belts. All these observations clearly indicate that these nanobelts are crystals of inorganic salt $Na_3Au(SO_3)_2$. The crystal nature of such nanobelts was further confirmed by a bulk diffraction technique; the corresponding X-ray diffraction (XRD) pattern shows several peaks, and the strongest peak occurs at 10.8°, as shown in Figure S3, Supporting Information. However, owing to a lack of standard or referenced XRD data on these 1D structures, at present we cannot provide detailed information on the crystal nature.

It is thought that organic solvents generally have low capacity to dissolve electrolytes, since their dielectric constants are usually smaller than that of water, and as a result, it is usual that inorganic electrolytes are more likely to have lower solubility to organic solvents than in water. So it is not surprising to have found that the water-soluble inorganic salt of $Na_3Au(SO_3)_2$ is precipitated from the mixed solvents of DMF and water. It should be pointed out that organic solvent-induced crystallization and water solvent-driven dissolution of $Na_3Au(SO_3)_2$ compete with each other in our present study, as is evidenced by the experimental observation that adding a diluted solution of 5 $\mu$L of gold bath in 495 $\mu$L of $H_2O$ into 500 $\mu$L of DMF cannot lead to precipitate because the DMF-induced crystallization effect is not strong enough to compensate for the water-driven dissolution effect of $Na_3Au(SO_3)_2$.

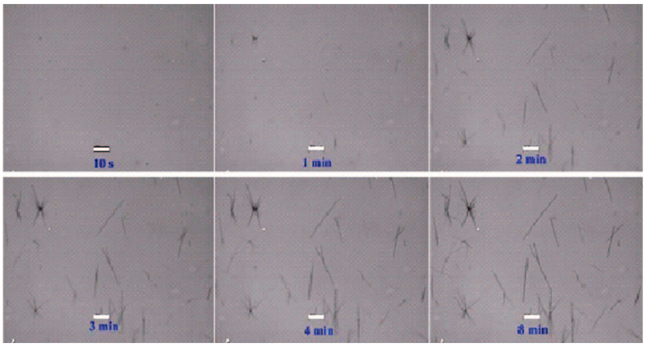

**Figure 2.** Time-dependent optical microscope images (scale bar, 100 $\mu$m) of the crystals formed with elapsed time in the range 10 s to 8 min after the introduction of a diluted solution of 5 $\mu$L of gold bath in 295 $\mu$L of $H_2O$ into 700 $\mu$L of DMF at room temperature.

The growth process of such 1D structures was also traced by in situ optical microscopy observation of the structures formed with different elapsed times after the mixing occurs. Figure 2 shows a a series of optical microscopy images of the structures with elapsed times of 10 s, 1 min, 2 min, 3 min, 4 min, and 8 min after a diluted solution of 5 $\mu$L of gold bath in 295 $\mu$L of $H_2O$ was added into 700 $\mu$L of DMF. With an elapsed time of 10 s, many small dots were generated. When the elapsed time was increased up to 1 min, these small dots were observed to evolve into 1D structures with low aspect ratios. When the elapsed time was further increased up to 2, 3, 4, and 8 min, it is clearly seen that the length of these 1D structures gradually increases. It is worthwhile to mention that there is no further observable change of the length of the 1D structures with an elapsed time of over 8 min, as is evidenced by the in situ images acquired with an elapsed time of 15, 30, and 60 min as shown in Figure S4 (Supporting Information). Such observation indicates that only 8 min is enough for the completion of the 1D crystallization of $Na_3Au(SO_3)_2$ from the mixed solvents of DMF and water. It is also very important to point out that the number of the structures remains the same; that is, no new nucleus forms during the 1D growth process of the structures. On the basis of the above observations, we suggest that the formation of the 1D nanostructures may involve the following two stages: an instant nucleation and a subsequent oriented 1D growth. However, at present the detailed mechanism involved is not entirely clear and requires further investigation.

The influence of the temperature on the formation of the 1D structures was also examined. Figure 3 shows a typical SEM image of the precipitate obtained by adding a diluted solution of 5 $\mu$L of gold bath in 295 $\mu$L of $H_2O$ into 700 $\mu$L DMF at 4 °C. Low magnification image shows that the precipitate thus formed also consists of a large quantity of 1D structures but with a decreased length (below 20 $\mu$m),

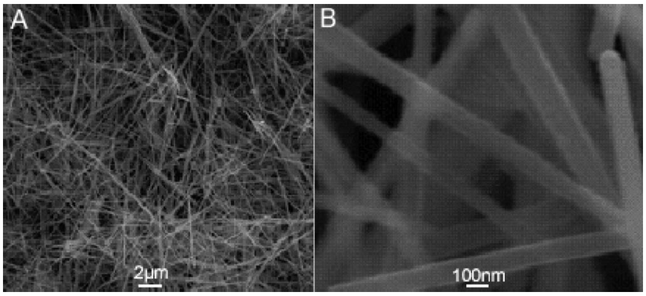

**Figure 3.** (A) Low and (B) high magnification SEM image of the precipitate obtained by adding a diluted solution of 5 μL of gold bath in 295 μL of $H_2O$ into 700 μL DMF at 4 °C.

as shown Figure 3A. The nanobelt nature is further evidenced by the corresponding high magnification image as shown in Figure 3B. It is found that the width of the nanobelts ranges from 80 to 150 nm. Furthermore, although the height information of the belt cannot be obtained from the SEM image, the observation that some of the belts are transparent reveals that these nanobelts should be smaller in height than those formed at room temperature. It is important to point out that a longer time of 20 min is required for the complete of the formation of the 1D structures at 4 °C. These observations demonstate that the temperature has strong influence on the growth kinetics as well as the dimensionality of these 1D crystals thus formed.

The influence of the relative amount of these three components including $Na_3Au(SO_3)_2$, DMF, and $H_2O$ contained in this system on the dimensionality of these 1D crystals was also investigated. First, the amount of $H_2O$ and DMF was changed, but the amount of gold bath was kept constant. When 300 μL of $H_2O$ and 695 μL of DMF was involved, nanobelts with widths ranging from 150 to 400 nm were obtained as shown in Figure 4A, and these nanobelts are found to be about several hundred micrometers in length (data not shown). However, the use of 290 μL of $H_2O$ and 705 μL of DMF leads to nanobelts with widths 1−1.5 μm as shown in Figure 4B. Again, the resulting belts are also several hundred micrometers in length. We also changed the amount of inorganic salt but kept the amount of $H_2O$ and DMF constant. When 10 μL of gold bath was used, nanobelts with a length below 50 μm and a width 100−400 nm were obtained, as shown in Figure 4C. A further increase of the amount of gold bath to 50 μL produced nanobelts with a length below 10 μm and a width of about 100 nm (Figure 4D). The above experimental observations clearly indicate that the dimensionality of these 1D crystals can be tuned in a controllable manner by simply changing the relative amounts of inorganic salt, $H_2O$, and DMF used in this preparation.

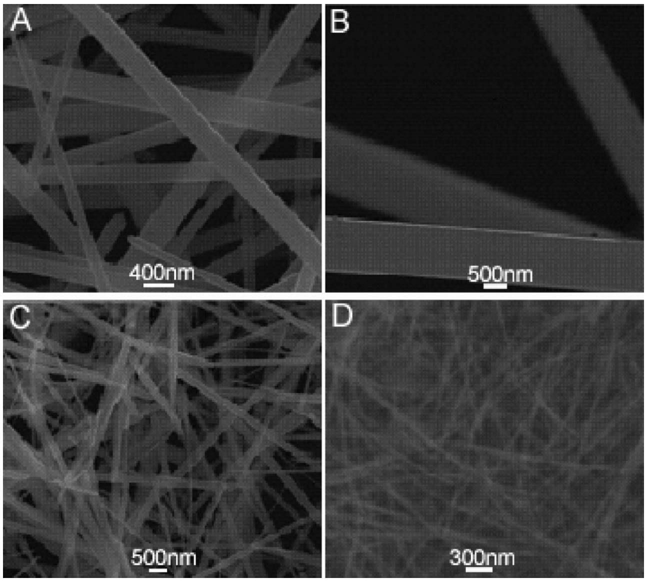

**Figure 4.** SEM images of the precipitate obtained at room temperature by adding the mixture of (A) 5 μL of gold bath and 300 μL of $H_2O$ into 695 μL of DMF, (B) 5 μL of gold bath and 290 μL of $H_2O$ into 705 μL of DMF, (C) 10 μL of gold bath and 290 μL of $H_2O$ into 700 μL of DMF, and (D) 20 μL of gold bath and 280 μL of $H_2O$ into 700 μL of DMF.

In conclusion, the first example of organic solvent-induced crystallization of water-soluble inorganic salt $Na_3Au(SO_3)_2$ into water-dissolved, single-crystalline, ultralong nanobelts on a large scale was demonstrated. Our present finding is significant for the following reasons: (1) It provides us a new and mild methodology for the convenient and rapid preparation of 1D nanostructures through organic solvent-induced crystallization of water-soluble inorganic salt in a controllable manner. (2) It provides us an ideal model system for the study of organic solvent-induced nucleation and growth of water-soluble inorganic salt in organic−water mixed solvents. (3) Such nanobelts are highly water-dissolvable and easily broken up by exposure to water, and therefore, they may hold great promise as easily decomposable 1D templates for the fabrication of tubular structures of other materials for a variety of applications.[10,16]

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**Supporting Information Available:** Experimental section, EDS elemental analysis and X-ray maps of the nanobelts, XRD pattern of the nanobelts, and time-dependent optical microscope images of the inorganic salt crystals formed with elapsed times of 15 min, 30 min, and 60 min (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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