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Microwires

Freeze-Align and Heat-Fuse: Microwires and Networks from Nanoparticle Suspensions**

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The use of a simple freezing technique to produce microwires from a wide range of materials is demonstrated. Freezing has been used previously to prepare porous materials with new structures and useful properties.[1–3] For example, Deville et al. have shown how to replicate the nacre structure of shells by using a simple freezing path.[4] Also, highly porous fibers were synthesized by electrospinning into a cryogenic liquid.[5] Hierarchical biohybrid materials were prepared by an ice-segregation-induced self-assembly process.[6] We have demonstrated the synthesis of three-dimensional aligned porous materials by directional freezing of aqueous/organic solutions and emulsions,[7] and liquid CO_2 solutions.[8]

Microwires can be produced by electrospinning[9] but this requires the use of soluble or fusible polymers in solution. Silicon and silica microwires were synthesized using a vapor–liquid–solid process.[10,11] In addition, capillaries,[12,13] fungi,[14] and porous membranes/plates[15] have all been used as templates to produce microwires. A self-seeding technique was adopted to prepare single-crystal polythiophene microwires on a silicon substrate,[16] and a photolithographic route was applied to fabricate micro/nanowires of semiconductors.[17] An external perpendicular magnetic field was applied to a $CoPt_3$-nanocrystal sol to drive the formation of microwire structures.[18] Electrically functional microwires were also assembled from metallic nanoparticles by dielectrophoresis.[19,20]

Herein, we show that directional freezing is a simple and flexible method that can be applied to a range of particulate materials (metal nanoparticles, metal-oxide nanoparticles, polymer colloids) with diameters ranging from 10 to 500 nm. The scope of the approach encompasses materials such as metals, metal oxides, and polymers. The method is also easy to scale up for bulk-quantity microwire synthesis, and the aggregated nanoparticles may in some cases be fused together by heat treatment.

To produce gold microwires, a concentrated suspension of gold nanoparticles (GNPs; 15 nm in diameter[21]) was injected dropwise into liquid nitrogen. The GNP sol droplets were observed to float for a few seconds at the liquid surface before freezing and sinking into the liquid nitrogen. Porous bead structures were produced after freeze-drying. Figure 1a shows the porous structure of a sectioned surface of a single gold-microwire bead. The bead consists of a randomly oriented porous shell surrounding radially aligned microwires, focusing at the center of the bead.

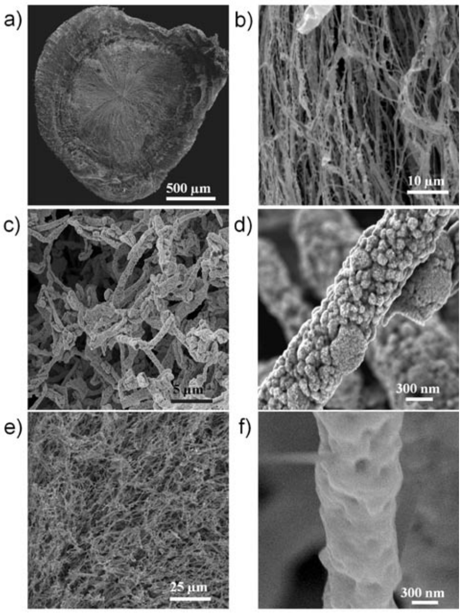

Figure 1. Microwires produced by freezing/freeze-drying of a concentrated GNP solution (average particle diameter: 15 nm). a) A cross-section of a gold bead shows its porous structure; b) aligned gold microwires; c) disordered microwire network in the shell of the bead; d) a single microwire imaged at higher magnification; e) calcined porous gold structure; f) a single gold microwire after calcination imaged at a higher magnification (see (d)).

Freezing a solution or suspension concentrates and then excludes solute molecules or particles from the freezing front if the freeze rate is below a critical freeze velocity.[22,23] Thus, the GNPs were aggregated and assembled into microwire structures during freezing. The relatively weak particle aggregation and attraction is believed to be a result of the breakdown of the charged layer around the particles and the high surface energy of these nanoparticles. Figure 1b shows one area of the radially aligned microwires. Junctions are observed between the interconnected aligned microwires.

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When the temperature gradient is high and hence the freezing rate is above the critical velocity, the GNPs would be expected to be encapsulated into the freezing front,[22,23] and this explains the randomly porous shell structure that was formed (Figure 1 a,c). A single microwire is shown in Figure 1 d; it has a diameter of about 700 nm and is composed of aggregates of the original 15-nm GNPs.

Previously, GNPs were assembled into a 3D fibrous network by a site-exchange reaction using thiol-terminated gelators[24] or a branched-chain network by controlled ligand exchange of surface-adsorbed citrate ions.[25] In our study, simple freezing of a bulk GNP suspension gave rise to a uniform porous network (Figure 1 c) without the need to use gelators. The average size of the pores between the interconnected microwires in these networks was around 5 μm. All of the freeze-dried GNP samples were black, which is consistent with the highly aggregated state of the GNPs.

When the freeze-dried sample was placed in an oven at 300 °C in air, the resulting calcined sample turned yellow and resembled metallic gold. Slight shrinkage was observed after the heat treatment but, remarkably, the porous network structure was completely retained (Figure 1 e). The microwires appeared smoother after calcination (Figure 1 f) which, in combination with the metallic luster of the sample, is consistent with fusion of the metal nanoparticles to form a porous interconnected bulk gold network. This technique represents a very simple and effective method for preparing porous metallic gold, without the use of organic templates[24–26] or complex dealloying processes.[27]

The method is readily extended to inorganic nanoparticle suspensions. A range of metal-oxide nanoparticle materials (iron oxide, titanium dioxide, indium tin oxide, and zinc oxide) were suspended in water with poly(sodium acrylate) (PSA) as stabilizer. These suspensions did not have very good long-term colloidal stability in the absence of stirring, but this was not critically important given the rapid freezing that occurred while the samples were lowered into the liquid nitrogen. In all cases, aligned microwire structures were observed after freeze-drying (Figure 2).

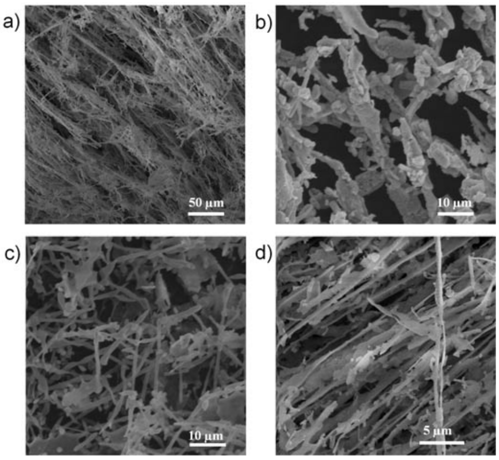

Figure 2. Microwires formed from various metal-oxide nanoparticles. a) 26-nm Fe_2O_3 nanoparticles; b) 21-nm indium tin oxide nanoparticles; c) 34-nm titanium dioxide nanoparticles; d) ZnO nanoparticles.

Figure 2 a shows the aligned iron oxide microwires which were formed with an average diameter of approximately 3 μm. When indium tin oxide nanoparticles were used, larger micrometer-sized rods with diameters of around 5 μm were obtained (Figure 2 b). These microrods were less smooth than the other microwires. Micrometer-sized rods with diameters of around 2 μm were produced when TiO_2 nanoparticles were used; these materials were less aligned than other samples (Figure 2 c). Well-defined aligned microwires composed of ZnO nanoparticles were produced with average diameters of around 2 μm (Figure 2 d). It was observed that some wires were not very smooth and homogeneous. This may be improved by better control of the freezing process, and particularly by utilizing nanoparticles with narrow size distributions and controlled shapes.

In all cases, the average diameters of these metal and metal-oxide nanoparticles were less than 50 nm. It was interesting to see whether aligned microwire structures could also be formed by directional freezing of larger organic-polymer colloids. Polystyrene (PS) colloidal suspensions were prepared (average diameter 450 nm) for this purpose. First, poly(acrylic acid) (PAA)-stabilized PS colloids were prepared at a solids concentration of 11 wt %. When this suspension was diluted six times, a few assembled PS colloid microwires were formed by directional freezing but these coexisted with irregular aggregates. When the suspension was diluted 60 times, powders of irregular aggregates were produced exclusively after freeze-drying.

In the case of the GNPs, the colloids were negatively stabilized by surface charge (zeta potential −45.2 mV) and it was thought that this negative surface charge might play a role in forming the aligned microwires. A methacrylic acid (MAA)-stabilized PS colloid suspension (average diameter around 450 nm) was therefore used to produce aligned microwires. MAA was copolymerized onto the surface of these PS particles, which exhibited a negative charge density of 160 $\mu C\,cm^{-2}$ as measured by conductometric titration. By comparison, the PAA stabilizer was physically adsorbed on the surface of the PS particles. In strong contrast to the PAA-stabilized system, well-defined aligned microwires were formed across the whole sample after directional freezing and freeze-drying of the MAA-stabilized colloids.

Figure 3 a shows these microwires at a high magnification and illustrates the relatively close-packed assembly of the PS colloids. The microwires were aligned, as shown in Figure 3 b and c. After heating the freeze-dried samples in an oven at 150 °C, the PS colloids were fused together to form smooth microwires (glass transition temperature for PS: 107 °C[28]), as shown clearly in Figure 3 d, and the aligned structure was retained (Figure 3 e,f). As such, this “freeze-align and heat-fuse” strategy seems to be quite generic and is applicable to polymers as well as metals such as gold.

A mixture of PS colloids and GNPs was also investigated. The PAA-stabilized PS colloidal suspension was mixed with an as-prepared sodium citrate-stabilized GNP sol at a volume ratio of 1:1. Composite microwires were formed with significantly better degrees of alignment than those observed without the addition of the GNPs (see the Supporting Information). MAA-stabilized PS colloids were also mixed

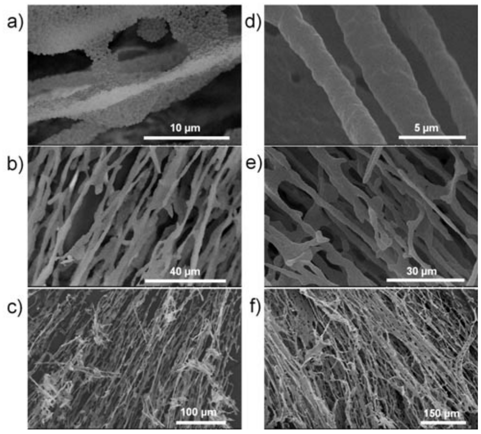

Figure 3. Aligned microwires prepared from MAA-stabilized PS colloids. The as-prepared PS suspension was diluted six times before processing. a–c) Aligned microwires after freeze-drying; d–f) the same sample after heating at 150 °C overnight.

with GNPs at volume ratios of 1:1, 1:2, and 1:5. In all cases, aligned composite microwire structures were formed. Images of a freeze-dried sample of MAA-stabilized PS colloids and GNPs at a volume ratio of 1:5 are shown in the Supporting Information.

The in situ directional freezing process was observed directly using an optical microscope equipped with a freezing stage by which the movement rate of the sample could be controlled very precisely. When the native ZnO suspension was used, it was difficult to produce aligned wires irrespective of the freezing rate. When PSA was added (0.13 w/v %) to make the suspension more stable, aligned structures could be observed (Figure 4 a) when the sample was moved at a rate of 30 $\mu m\,s^{-1}$. The zeta potential of the PSA-stabilized suspension was −23.0 mV (Figure 4 c), whereas the original ZnO suspension had a zeta potential of −3.4 mV. This suggests again that aligned structures are more readily produced from stable suspensions with higher negative surface charges. This suggestion was corroborated by the formation of aligned structures from other PSA-stabilized inorganic nanoparticle suspensions (see the Supporting Information).

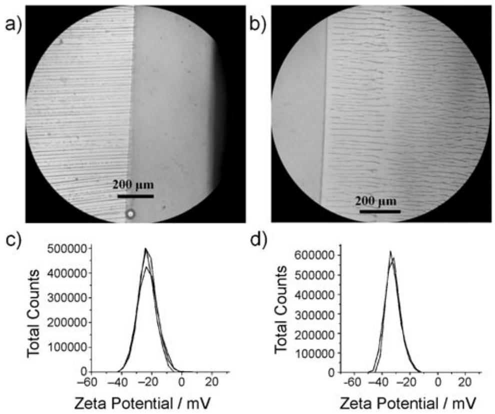

Figure 4. Optical images of the directional freezing of a) PSA + ZnO and b) MAA-stabilized PS colloidal suspensions. Zeta potential distributions for c) PSA + ZnO suspension and d) MAA-stabilized PS colloids.

Figure 4 b shows a comparable optical image of 2D aligned patterns of MAA-stabilized PS colloids; these resemble the aligned microwires formed in the respective freeze-dried 3D samples. The zeta potential of the MAA-stabilized PS colloids was −32.1 mV (Figure 4 d).

In conclusion, the directional freezing of aqueous colloidal suspensions is a generic method for the preparation of aligned microwires and networks from a broad range of organic and inorganic nanoparticle materials in the diameter range of 10 to 500 nm. Moreover, materials such as gold and polymers can be fused together by heat treatment with essentially complete retention of the microwire structure and, in the case of gold, formation of an interconnected porous bulk metallic network. Given the simplicity and diversity of the method, we envisage potential applications in a wide range of areas, such as sensors, tissue scaffolds, separation media, and electronic/optoelectronic components.

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