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

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Chemicals:

HAuCl₄, sodium acrylate, poly(sodium acrylate) (Mw 2,100 g/mol), methacrylic acid, potassium persulfate, polyacrylic acid (50 wt % in water), and ethyl alcohol were purchased from Aldrich and used as received. Styrene was obtained from Aldrich and distilled under the reduced pressure of nitrogen and stored in a refrigerator. Inorganic nanoparticles (NanoTek® Indium Tin Oxide, NanoTek® Titanium Dioxide, NanoGard® Iron Oxide, and NanoTek® Z1121W zinc oxide suspension) were purchased from NanoLab (Nanophase Technologies Corporation) and were used without further purification. Ultrapure water with a resistivity of 18.2 MΩ/cm was used as solvent for the synthesis of gold nanoparticles. Distilled and deionized water was used for all the other experiments.

Preparation of poly(acrylic acid)-stabilized polystyrene colloids

The dispersion polymerization was performed in a double-wall glass reactor equipped with stirrer, thermometer, condenser, and nitrogen gas inlet. Styrene monomer (84 g) was dissolved in the mixture of ethyl alcohol and water (520 g H₂O + 213 g ethyl alcohol). 20.2 g poly(acrylic acid) solution was then added. The reactor was left for 30 min for the contents to attain the reaction temperature 70 °C. During this period, the contents of the reactor were stirred and flushed with nitrogen. The initiator potassium persulfate (1.41 g) was dissolved in 20 g water and then added into the reactor. Polymerization was conducted under a nitrogen atmosphere for 24 h at 70 °C with stirring at 60 rpm.

Preparation of methacrylic acid-stabilized polystyrene colloids

A two-stage shot growth polymerization was carried out in a double-wall glass reactor equipped with stirrer, thermometer, condenser, and nitrogen gas inlet. The stirring rate was maintained at 250 rpm. The reactor was initially charged with styrene (60 g), methacrylic acid (0.6 g), and water (580 g). The reactor was left for 30 min for the contents to attain the reaction temperature 70 °C. During this period, the contents of the reactor were stirred and flushed with nitrogen. The initiator potassium persulfate (0.24 g) was dissolved in 20 g water and then added into the reactor. After 6 h reaction (about 90% conversion), 9 g styrene, 6 g methacrylic acid, and 0.048 g potassium persulfate were added into the reactor. The polymerization was continually conducted for 24 h under nitrogen atmosphere until the reaction was completed.

Processing gold nanoparticles

The gold nanoparticles were prepared with sodium acrylate (SA) or sodium citrate (SC) as stabilizers as described in ref [21]. SA-stabilized GNPs suspensions (0.15 g/L) were concentrated 300 times by
centrifugation and then be frozen and freeze dried to produce aligned microwires or foamed structure. The freeze dried GNPs structure was placed in an oven (Carbolite CWF 12/13) in air in order to produce porous metallic gold structures. The heating procedure was: heating at 0.5 °C.min\(^{-1}\) to 350 °C, hold for 240 minutes, then cool down at 2 °C.min\(^{-1}\) to room temperature. SC-stabilized GNPs were mixed with PS colloidal suspension in order to produce well-aligned microwires.

**Processing inorganic nanoparticles**

Nanoparticle powders (iron oxide, titania, indium tin oxide) were suspended in water with poly(sodium acrylate) (PSA). A stock PSA aqueous solution at a concentration of 0.145 wt. % was prepared. The nanoparticle suspensions were formed by stirring and sonification of: (1) PSA solution 10 ml + iron oxide powers 0.2418 g; (2) PSA solution 9.0 ml + 1.0 ml ZnO suspension; (3) PSA solution 5.0 ml + indium tin oxide powers 0.1648 g; (4) PSA solution 5.0 ml + titania powders 0.1525 g.

**Preparation of aligned microwires:**

Only gold nanoparticles suspensions were injected into liquid nitrogen using a syringe to produce the radially-aligned microwires. For all the other suspensions, 1 ml of the suspension was added into a glass tube of diameter 5 mm which was then lowered into liquid nitrogen at a rate of 3 mm/min using the movement mechanism of a syringe pump. When the suspension was completely frozen, the samples were transferred into a freeze dryer (LyoLab 3000 Heto) to be dried. It should be noted that gold nanoparticle suspension was also directionally frozen by lowering a glass tube into liquid nitrogen. In this case, aligned microwires were also produced.

**Characterization**

The morphologies were characterized using scanning electron microscope (SEM, S-4800 Hitachi). The GNP and metal oxide samples were stuck to aluminium stubs using double-sided carbon tapes while the PS colloidal samples were fixed using an Araldite resin. The GNP samples were observed directly without gold coating. Other samples were coated with gold using a sputter-coater (EMITECH K550X) for 1.5 minutes at 40 mA. The in-situ directional freezing was investigated using an Olympus CX41 microscope equipped with a digital camera and a computer-controlled freezing stage. The directional freezing was carried out by moving a glass slide which contained a liquid sample and was placed on two temperature-controlled metal plates separated by a distance of 2 mm in the horizontal axis. Zeta potentials of colloidal suspensions were measured using Malvern Zetasizer Nano ZS at 25 °C. The measurements were also carried out at temperature 2 °C and 12 °C. There was no effect of temperature on the values of zeta potentials observed.
Figure S1: PAA-stabilized PS particles/GNPs 1:1 showing uniform aligned structure across the sample.
**Figure S2:** MAA-stabilized PS particles /GNPs 1:5 showing aligned microwires across the sample.
Figure S3: Optical images for directional freezing of various systems on a controlled freezing stage. (a) Fe$_2$O$_3$ suspension stabilized by PSA. (b) Indium tin oxide suspension stabilized by PSA. (c) Titanium dioxide suspension stabilized by PSA.