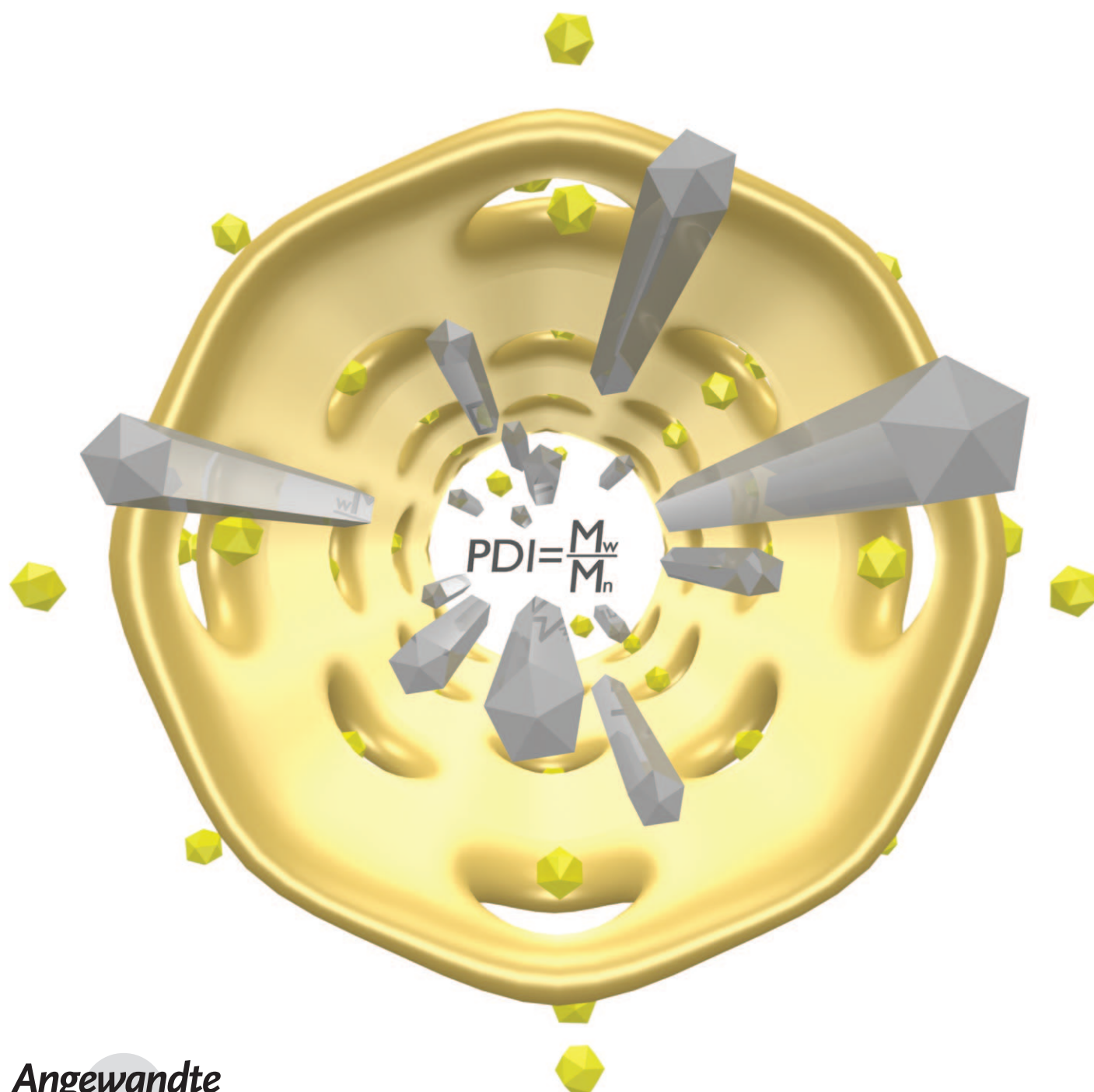


Cross-Flow Purification of Nanowires**

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Nanoparticles and other low-aspect-ratio shapes are a common byproduct from the solution chemical growth of nanowires.^[1,2] They are formed because nucleation is not instantaneous, and growth is diffusion-limited, causing particles to grow along multiple pathways. These unwanted morphologies can bring much difficulty to the subsequent material processing steps and degrade the material performance in device applications. For example, the presence of these short particles greatly affects the assembly of the nanowires. When making two-dimensional (2D) arrays of nanowires, the byproduct particles act as structural defects, disrupting the packing of the nanowires.^[3,4] Even a small number of particles can prevent the formation of a 2D lattice. On the other hand, as many properties of nanoparticles are highly size- and shape-dependent,^[2,5] such byproducts can have a detrimental effect on the quality of the final nanowire material. For example, metal nanowires, made for example of Ag, have rapidly attracted attention as an alternative material to indium tin oxide (ITO) for making flexible transparent conductor thin films.^[6–12] Although there has been great success in the synthesis of Ag nanowires, predominantly by the polyol route,^[2,13] the product is often contaminated by low-aspect-ratio particles and rods. The presence of these nanoparticle impurities in the nanowire network is highly undesirable because they would only have a marginal contribution to the electrical conductivity as they are too small to provide effective current pathways, but they will cause significant optical loss owing to their stronger light scattering properties.^[14] As the commercial production of a silver nanowire transparent conductor has emerged,^[6] there is a pressing need for a purification method that can meet the industrial scale of synthesis.

Nanoparticle purification can be achieved using common laboratory separation techniques, such as simple filtration, centrifugation, dialysis, and gel electrophoresis. However, these methods are generally limited to small-scale, batch-to-batch processing. There are the additional challenges of protecting the nanowires from deformation under the applied force field and keeping them dispersed in solvent after the sedimentation/precipitation steps during processing. For example, centrifugation is one of the most commonly used techniques for nanowire purification, but it can plastically deform high-aspect-ratio nanowires, making them less dis-

persible owing to aggregation and entanglement caused by sedimentation. Gel electrophoresis is capable of separating nanoparticle solutions by size and shape with great precision,^[15] but the materials need to be first processed through the gel, and then exchanged to a proper solvent, making it difficult to maintain the colloidal stability of the nanowires except at very low concentrations. Dialysis is non-destructive but requires extended processing time as determined by the diffusion rate of nanoparticles across the permeable membrane. Furthermore, most dialyzing membranes are designed to remove sub-10 nm substances, such as small molecules, polymer chains, and viruses, thus limiting their use for nanowire purification. Simple filtration (that is, dead-end filtration) is routinely applied to remove small particles from nanowire samples by passing the dispersion through size-selection membranes. The downward solvent flow could easily damage the nanowires, especially for those caught lying across the membrane pores. Another common problem is the reduction of flow rate and retention of particle impurities by the filter cake. For purification in large-scale production, a non-destructive, scalable method that allows continuous mode of operation is favored.

Herein, we present an effective nanowire purification method by cross-flow (that is, tangential flow) filtration^[16] using commercially available hollow-fiber membranes. We chose Ag nanowires synthesized by the polyol method^[13,17] as our model system as they are already produced commercially. To facilitate the measurement and counting of the particles and wires, we used the Langmuir–Blodgett technique^[3,4] to produce closed-pack 2D arrays, which allows for facile identification of impurities in the microscope images and measurement of the aspect ratio of the nanowires. To quantitatively describe the effect of purification, we borrowed the concepts of molecular weight distribution and polydispersity index (PDI)^[18] from polymer science and applied them to characterize the distribution of the nanowire aspect ratios. Finally, we demonstrated that purifying Ag nanowire samples indeed improves their performance as transparent conductor thin films.

Cross-flow filtration is a method that has been traditionally used for protein separation and other biological applications.^[19] In this method, the solution flow is perpendicular to the filtration direction (Figure 1). A major advantage of cross-flow filtration versus the conventional dead-end filtration is that it significantly decreases the degree of clogging as anisotropic shapes orient themselves along the flow direction as they are pumped through the filter. Cross-flow has recently been applied for size separation of spherical metal nanoparticles.^[20,21] When used for anisotropic nanostructures, there is the additional advantage that nanowires tend to align themselves with the flow direction,^[22] thus exposing their largest dimension to the separation membrane and lowering their chance of escape through the pores.

To directly visualize the separation effect, an Ag nanowire sample was blended with Au nanoparticles^[23] of comparable diameter as the starting mixture due to their distinctly different colors and the absorption bands. The diameters of the Ag nanowires and nanoparticles are around 80 nm, and the mixture was injected into a hollow fiber cross-flow filter

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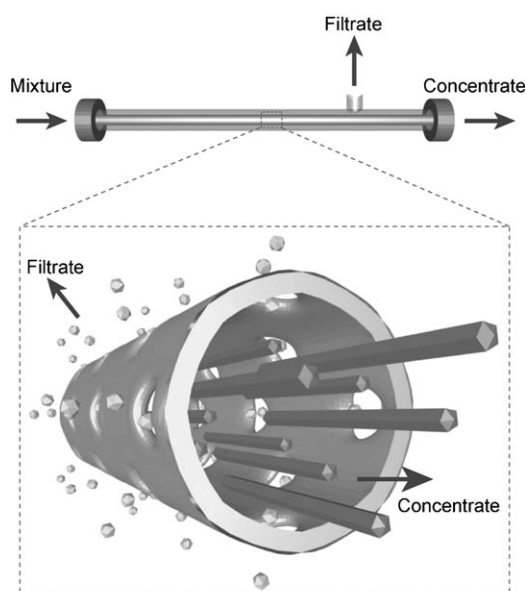


Figure 1. The cross-flow separation of nanoparticles and nanowires. When the mixture is passed through the hollow fiber filter, nanoparticles and low-aspect-ratio nanorods escape through the pores (inset) to the filtrate stream, resulting in highly purified nanowire product in the concentrate.

with 0.5 μm pores. As shown in Figure 2a, after cross-flow filtration, the pink-grayish mixture was separated into two portions: A pink colored filtrate and a gray-colored concentrate, which matches the colors of the original Au nanoparticle and Ag nanowire solutions, respectively. Materials in both of the resulting solutions were still well-dispersed without apparent sedimentation or aggregation. The color

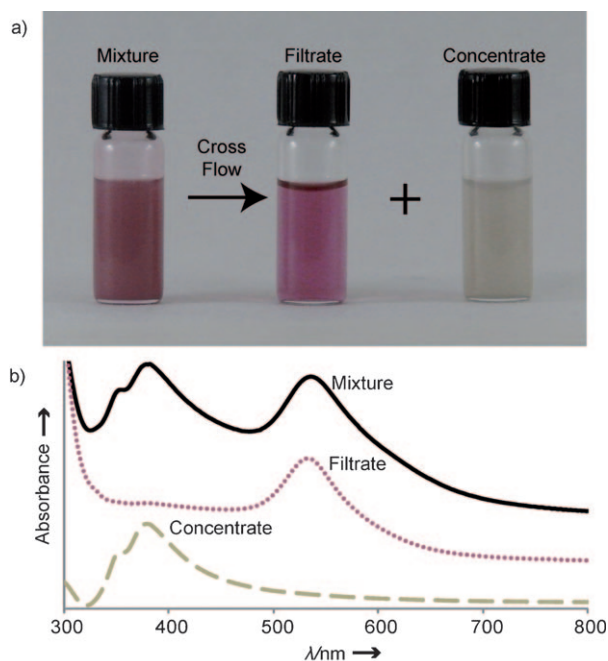


Figure 2. a) Photograph and b) UV/Vis spectra of a mixed dispersion of Au nanoparticles and Ag nanowires before and after cross-filtration.

change suggests effective separation, which was verified by spectroscopic studies. As shown in Figure 2b, a UV/Vis spectrum of the mixture has two bands at 380 and 535 nm corresponding to the plasmon bands of Ag nanowires and Au nanoparticles, respectively. After filtration, the 535 nm band disappeared from the spectrum of the concentrate, indicating that the concentration of nanoparticles has been successfully reduced to below the detection limit. In the spectrum of the filtrate, the 535 nm band is evident and there is a small shoulder at around 380 nm, corresponding to short Ag nanorods and nanoparticles. This proof-of-concept experiment suggests that cross-flow filtration is very effective for purifying nanowires.

Next, we applied cross-flow separation to prepare pure Ag nanowires. In a typical synthesis, the product contains long Ag nanowires with diameters of around 80 nm with low aspect ratio nanorods and polyhedral nanoparticles of diameters up to 150 nm. As the spectroscopic features of these nanostructures are not as distinguishable as those between Ag and Au, microscopy analysis is needed to quantify the effect of purification. To achieve this, the Ag nanostructures should be organized in arrays to minimize overlapping or entanglement, which greatly increase the difficulty of analysis. Therefore, a proper deposition method is needed to generate such arrays with representative collection of different morphologies present in the product. We discovered 2D monolayers prepared by Langmuir–Blodgett (LB) assembly^[3,4] are very suitable for this purpose. Figure 3a–c shows SEM images of the LB monolayers of the mixture, concentrate, and filtrate, and they indicate a great improvement in nanowire purity. The fraction of particles in the mixture (Figure 3a) was

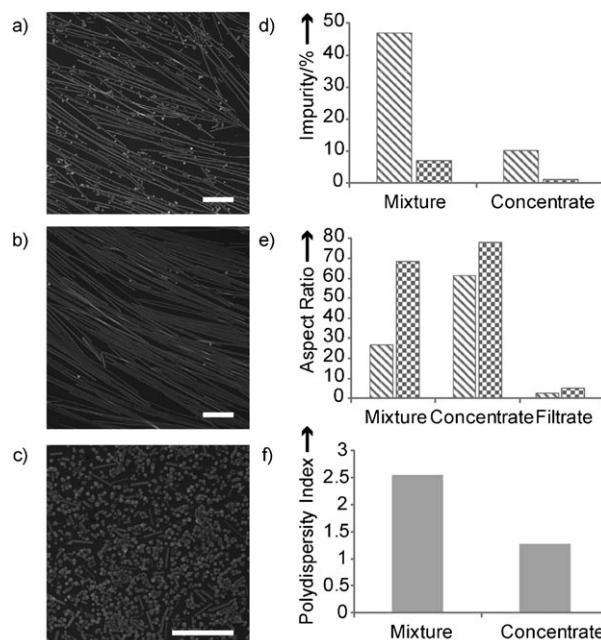


Figure 3. SEM images of a) the original mixture before filtration, b) the concentrate after filtration, and c) the filtrate removed by filtration. Scale bars: 2 μm . d) Number-average (diagonal shading) and weight-average (checked shading) percentage of impurities; e) aspect ratio; and f) PDI calculated from the aspect ratio of the three solutions.

greatly reduced in the concentrate (Figure 3b). In the filtrate (Figure 3c), only nanoparticles and nanorods with a low aspect ratio (<10) were observed. The presence of $1\text{ }\mu\text{m}$ nanorods in the filtrate despite the pores being $0.5\text{ }\mu\text{m}$ wide suggests that nanowires could pass through the smaller pores when they are orientated along the stream of the filtrate. If a wire is perpendicular to the pore, it will pass through no matter how long it is. On the other hand, if a wire is oriented parallel across the pores, it will not pass. Using simple trigonometry, we can see that the range of orientations where the projected wire length against the pore is less than the pore diameter (i.e. the probability of passing) increases with decreasing wire length. Furthermore, long wires can also better align themselves along the concentrate stream. Therefore, long wires have lower probability to flow through the pores. In principle, this can be used to separate nanowires of different lengths by optimizing the flow rate with different pore sizes.

Purification of nanowires by aspect ratio or length is conceptually similar to separating polymer chains by molecular weight. In polymer science,^[18] there are two common ways to define molecular weight distribution, namely by number (M_n) and weight (M_w), as shown in Equation (1), where N_i refers to the number of chains with molecular weight of M_i . The ratio of M_w/M_n gives the polydispersity index (PDI), the value of which is always ≥ 1 by definition. When the PDI approaches 1, the polymer molecular weight is completely monodisperse.

$$M_n = \frac{\sum M_i N_i}{\sum N_i}; M_w = \frac{\sum M_i^2 N_i}{\sum M_i N_i}; \text{PDI} = \frac{M_w}{M_n} \quad (1)$$

If an analogy is set up between polymer chains and nanowires, the molecular weight (or degree of polymerization) for a polymer chain would be the length (or aspect ratio) for a nanowire. Therefore, we can similarly define the number-based aspect ratio R_n of nanowires, the weight-based aspect ratio R_w , and the PDI [Eq. (2)].

$$R_n = \frac{\sum R_i N_i}{\sum N_i}; R_w = \frac{\sum R_i^2 N_i}{\sum R_i N_i}; \text{PDI} = \frac{R_w}{R_n} \quad (2)$$

As R_n is number-based, it is more suitable for microscopy analysis, where the number of objects with different aspect ratio can be counted. R_w is more useful in large-scale production, where the different fractions are measured by weight. The PDI characterizes the uniformity of the nanowire aspect ratio or length. The introduction of PDI now allows the polydispersity of a nanowire sample to be quantified and evaluated: the greater the PDI, the more polydisperse the sample; monodisperse samples should have a PDI value approaching 1. PDI is also a convenient index to evaluate the effectiveness of a separation technique as it is independent of the absolute value measured. The same idea was used to define the percentage of impurities. While the number-based impurity percentage I_n is simply the number fraction of particles observed (n_p), the weight-based average impurity percentage I_w is based on the weight (that is, the volume) of the particles and wires, respectively [Eq. (3)]. The wires were

modeled as cylinders with length l and radius r , and particles as spheres, also with a radius r .

$$I_n = \frac{n_p}{n}; I_w = \frac{\sum \frac{4}{3}\pi r^3}{\sum \frac{4}{3}\pi r^3 + \sum \pi l r^2} \quad (3)$$

For Figure 3a–c, the number and weight percentages of particle impurities were first calculated for the three samples (Figure 3d). Before separation, the number percentage of particle impurities was 47 % in the mixture, which decreased to 8 % in the concentrate. By weight, the percentage of impurities was decreased from 7 % to $<1\%$. These data are consistent with microscopy observations, suggesting successful purification. The weight-based percentage of particles are much lower than the number percentage owing to the wires being much larger than the particles. In Figure 3e, both R_n and R_w of the mixture, concentrate, and filtrate show effective removal of particle impurities, thus leading to an increase in aspect ratio in the concentrate. A greater change in R_n was observed as it is more sensitive to the fraction of low-aspect-ratio objects. Furthermore, the PDI decreased from 2.556 in the mixture to 1.277 in the concentrate (Figure 3f), showing an improvement in the monodispersity.

The effect of sample purity on the Ag nanowire performance in thin-film transparent conductors was investigated (Figure 4). Ag nanowire transparent conductors were created using samples before and after cross-flow filtration. As shown in the dark-field scattering images (Figure 4a,b), the nanoparticles can be clearly observed in the nanowire network, illustrating their strong light scattering properties, which cause significant optical loss of the thin film, as shown in the transmission measurement (Figure 4c). Owing to their isotropic shape, they do not form good connections in the percolating nanowire network. Therefore, they do not con-

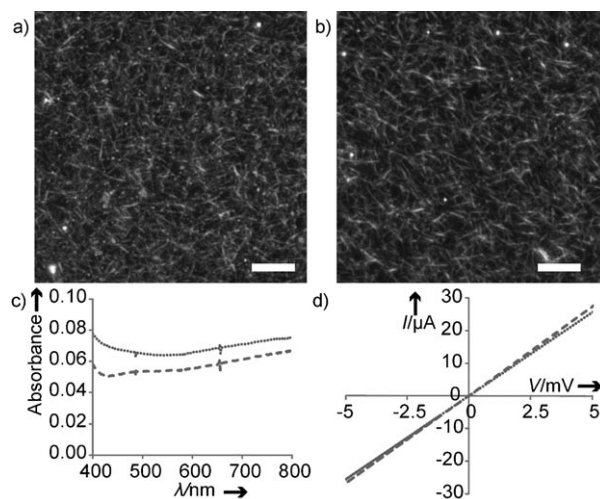


Figure 4. Dark-field scattering microscopy images of Ag nanowire transparent conductor films a) before and b) after the removal of low-aspect-ratio impurities. Scale bars: $20\text{ }\mu\text{m}$. c) Optical absorbance and d) electrical conductivity measurements for films with (•••••) and without particles (----) show that nanoparticle contamination only marginally decreases the conductivity but greatly increases the optical loss.

tribute to the overall electrical conductivity, even at high fraction (Figure 4d). If the particles are trapped between the nanowire junctions, they can even decrease the conductivity. The film made with unpurified nanowires (Figure 4a) had a slightly higher sheet resistance ($1650 \Omega/\square$) than that of the purified sample ($1565 \Omega/\square$), but 17.1 % more optical loss in the visible range from 400 to 800 nm (Figure 4c).

In conclusion, we demonstrated that cross-flow filtration is a viable method to purify nanowires. Furthermore, we borrowed concepts in polymer science and defined R_n , R_w , and PDI to characterize the aspect ratio of nanowire samples; the PDI can be used as an index to quantify the monodispersity of the nanowire sample. Cross-flow filtration can be readily adapted to other solution-grown nanowires. The continuous mode of operation makes it readily useful for industrial scale nanowire purification, and especially with large-size filters that can handle thousands of liters of solution. It could immediately benefit applications that use a metal nanowire network as a transparent conductor film.

Experimental Section

Ag nanowires synthesized by modified polyol route^[13,17] were chosen for our system as they can be made in high yield and are easily observable under an optical microscope. In a typical reaction, a solution of 55000 MW poly(vinylpyrrolidone) (PVP) in ethylene glycol (5 mL, 40 mg mL⁻¹) was refluxed at 170 °C in a hot oil bath with constant stirring. NaCl in ethylene glycol (150 μ L, 2.87 mg mL⁻¹) was added to the solution, followed by AgNO₃ in ethylene glycol (50 μ L, 25 mg mL⁻¹). The solution was heated to reflux at the same temperature for about 15 min. The solution then turned yellow, and AgNO₃ (1 mL) was then added and reacted for 12 more minutes, resulting in a gray dispersion containing nanowires and low-aspect-ratio nanorods and particles. The solvent was exchanged for redispersion in ethanol. Au nanoparticles were synthesized by reducing HAuCl₄ with pentanediol in the presence of PVP.^[23] 55000 MW PVP in pentanediol (5 mL, 40 mg mL⁻¹) was heated at 150 °C and of HAuCl₄ in pentanediol (50 μ L, 25 mg mL⁻¹) was added, instantly resulting in a ruby red solution of nanoparticles. The solution was then concentrated and redispersed in ethanol using centrifugation. The concentration was adjusted so that the intensity of the highest UV/Vis absorbance peak would match that of the Ag peak. The solutions were mixed together in equal volumes for the separation experiment shown in Figure 2.

For all filtrations, MicroKros hollow fiber modules with 0.5 μ m pores were used. For the proof-of-concept shown in Figure 2, 5 mL of a Au/Ag mixture was injected into the filter. The particles will go through the filter to be collected as the filtrate. The concentrate can be conveniently filtered again by reversing the flow, or looping it through the initial mixture port using a peristaltic pump. The flow rate was maintained at 1.5 mL s⁻¹. A clear filtrate suggests nearly complete removal of particles; the entire process took about half an hour to complete. The same filtration procedure was used to purify a Ag nanowire dispersion in ethylene glycol directly after synthesis. After filtration, the original mixture, filtrate, and concentrate underwent solvent exchange for dispersion in ethanol/chloroform mixture, which were assembled into monolayers using Langmuir–Blodgett (LB) technique^[3,4] for SEM imaging.

Ag nanowire transparent conductor films were prepared by drop-casting Ag nanowire samples dispersed in methanol on glass substrates. To improve the adhesion between the wires and the substrate, the glass was treated by H₂O₂/NH₃·H₂O and functionalized by (3-aminopropyl)triethoxysilane in methanol. Optical measurements were done with an Agilent 8453 UV/Vis spectrometer. Sheet resistance was measured using four-point probe methods with patterned electrodes.

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