

Wet-chemical templateless assembly of metal nanowires from nanoparticles†

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We describe a new, simple, room-temperature wet-chemical approach for assembling Au and Ag nanoparticles into nanowire networks, *without* the use of lithographic templates. Five to 35 nm-diameter nanowires passivated with a thin organic layer were synthesized by mechanically agitating a biphasic liquid mixture of an aqueous hydrosol containing the nanoparticles, and toluene. Nanowire structure and surface chemistry are discussed based on electron microscopy, UV-visible spectroscopy and thermogravimetric analyses.

One-dimensional nanostructures exhibit unique magnetic, optical, electrical and catalytic properties.^{1,2} In order to harness them for applications such as nanodevice components and interconnects^{3,4}, it is critical to synthesize nanowires with well-defined sizes, and configurations. A number of templating-based synthesis strategies to tailor nanowire aspect ratio and morphology have been reported. These methods typically rely on using porous,⁵ low-dimensional templates *e.g.*, zeolites,⁶ carbon nanotubes,⁷ DNA chains,⁸ micelles,⁹ and polymers.¹⁰ However, since template removal is often difficult, there is a great deal of interest in exploring templateless strategies.

We report a simple, scalable, templateless room-temperature approach to synthesize mesoscale networks of Au and Ag nanowires by agitating nanoparticles in biphasic liquid mixtures. While previous works have reported nanowire or nanomembrane formation by controlled removal of capping agents,^{11–13} here we demonstrate nanowire formation by coalescence of nanoparticles that are not capped by molecular ligands. Our strategy opens up new ways to tailor nanowire size and network connectivity, useful for forming self-supporting nanocatalysts, low-density high-strength foams for structural reinforcement, or interconnecting nanodevices.

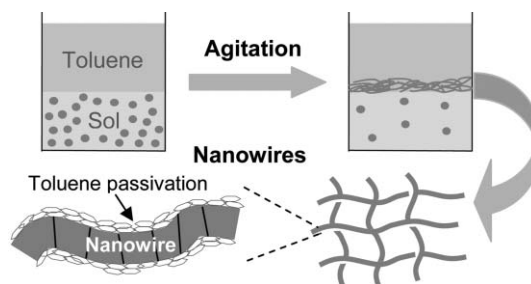
Hydrosols of Au and Ag were synthesized by reducing 500 mL of 1 mM of chloroauric acid and silver nitrate solution, respectively, with 7.4 mM sodium borohydride (NaBH₄), added drop-by-drop over 1 h at 5 °C. The solution transforms into a wine red color for Au, and dark brown for Ag, due to colloid formation. Toluene was added to the metal hydrosol in a 2 : 1 ratio and agitated vigorously with a magnetic stirrer at 600 rpm for 10 min. This depletes the nanoparticles from the aqueous layer, and results in the spontaneous formation of brown-colored

agglomerates that migrate to the toluene–water interface (see Scheme 1).

Transmission electron microscopy (TEM) images of the aggregates reveal 2-D networks of uniform diameter nanowires. Fig. 1A and 1B are from Au and Ag nanowire networks, respectively. Electron diffraction patterns (Below Fig. 1A and 1B) indicate that the nanowires are coalesced fcc nanocrystals. High-resolution TEM (Fig. 1C) reveals that each nanowire consists of randomly oriented grains. The grain boundaries (arrows in Fig. 1C) are close to a 90° ($\pm 20^\circ$) angle to the nanowire axis and do not show significant curvature, indicating that the nanowires are not merely linear aggregates of nanoparticles, but are welded through particle impingement and coalescence.

In contrast, agitating hydrosols *without* toluene result in aggregates whose smallest feature sizes of ~ 0.5 – $1 \mu\text{m}$, *i.e.*, more than 1000-fold larger than that of the nanowires. These aggregates, moreover, take 100-fold longer timeframes (*e.g.*, >10 h) to form, and precipitate at the container bottom in a lump. Increasing the ionic strength, a technique used in surface-enhanced Raman spectroscopy, results in similar structures without any control over the shape of the aggregates,¹⁴ suggesting the participation of toluene in nanowire formation in our synthesis.

The optical absorption signatures of Au and Ag nanowires are distinct from that of the as-prepared hydrosols. Strong surface plasmon peaks from Au (518 nm), and Ag (390 nm) hydrosols (see Fig. 2A), indicate average particle sizes of 5 and 7 nm, respectively. In contrast, Au nanowires (Fig. 2B) exhibit a broad longitudinal plasmon band in the 600–800 nm range,¹⁵ consistent with nanoparticle coalescence and aspect-ratio increase.¹⁶ This band overlaps with the transverse component in the 580–640 nm range, indicating networked nanowire segments of different lengths, unlike that expected from dispersed nanowires.¹⁵ Similarly, coalescence of Ag nanoparticles leads to a very broad band spanning 350–900 nm.¹⁷



Scheme 1 Templateless synthesis of noble metal nanowires from biphasic liquid mixtures. Not to scale. Vertical lines in the nanowire denote grain boundaries.

† Electronic supplementary information (ESI) available: Fig. 1S. UV-visible spectra from toluene compared with that of Au and Ag nanowires after vigorous washing and drying in N₂. Fig. 2S. Core level XPS spectra from the nanowires dispersed on a Si substrate. See <http://www.rsc.org/suppdata/cc/b4/b414447n/>

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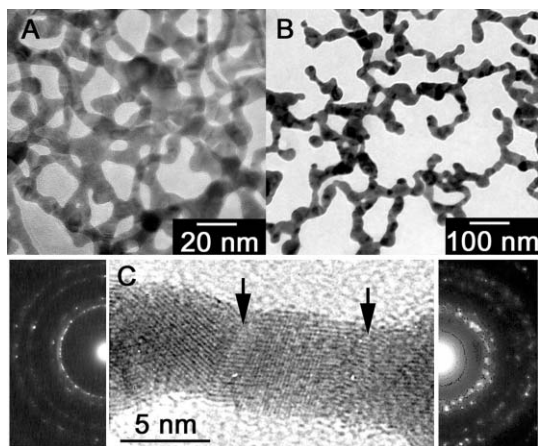


Fig. 1 TEM images of networks of (A) Au and (B) Ag nanowires. The respective electron diffraction patterns are shown below Fig. 1A and 1B. (C) A HRTEM image of a single Au nanowire. Arrows point to grain boundaries.

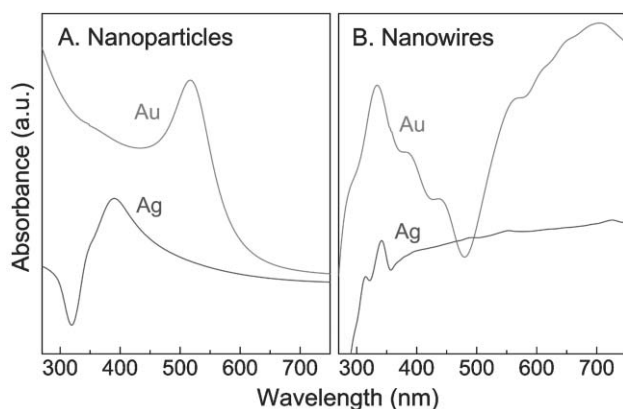


Fig. 2 Representative UV-Visible spectra from (A) as-prepared hydrosols and (B) nanowires drop coated on a quartz slide after vigorous washing with de-ionized water and drying in N_2 .

The nanowires show π - π^* transition signatures¹⁸ in the 300–400 nm range due to toluene. These are red-shifted by ~ 70 nm compared to that of pure toluene (Fig. 1S, see ESI†), suggesting toluene chemisorption on nanowires *via* π -cation interactions. XPS spectra (Fig. 2S, see ESI†) from the nanowires showing high energy 4f and 3d sub-bands centred at 85.6 eV, and 370.8 eV, corresponding to Au(III)¹⁹ and Ag(I)²⁰ states, respectively, confirm toluene chemisorption. Passivation *via* borates or chloride formation is unlikely because neither B nor Cl was detected by XPS. Thermogravimetry of the nanowires (Fig. 3) also verifies toluene chemisorption. The first sharp weight loss step, observed for both nanowires at ~ 300 – 400 °C—close to the boiling point of toluene—is due to physisorbed toluene. The subsequent plateau at 605 °C is likely due to desorption of toluene or aliphatic residues formed during heating. Infrared spectroscopy of Au nanowires showing chemisorbed toluene signatures, reported recently,¹⁶ support these results. The reason for the additional weight loss observed in Ag nanowires at 500–600 °C is not clear at present.

Salient aspects of nanowire formation can be understood as follows. Agitating mutually insoluble toluene–hydrosol mixture forms several toluene–water interfaces where toluene partially

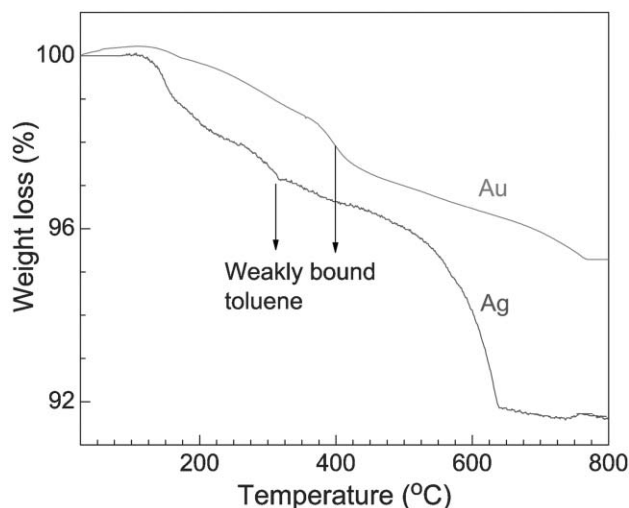


Fig. 3 TGA spectra of the nanowires obtained during heating at 10 °C min^{-1} in 50 mL min^{-1} N_2 .

passivates the nanoparticles *via* cation- π interactions. Toluene adsorption decreases electrostatic repulsion between nanoparticles, and promotes coalescence. Transport-limited aggregation of nanoparticles at the interfaces enables nanowire formation and networking.

In summary, we have demonstrated a new approach to assemble noble metal nanowire networks through nanoparticle coalescence by mechanical agitation of hydrosol–toluene mixtures. Such methods open up new possibilities for low-temperature synthesis of mesoscale structures from nanoscale units.

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