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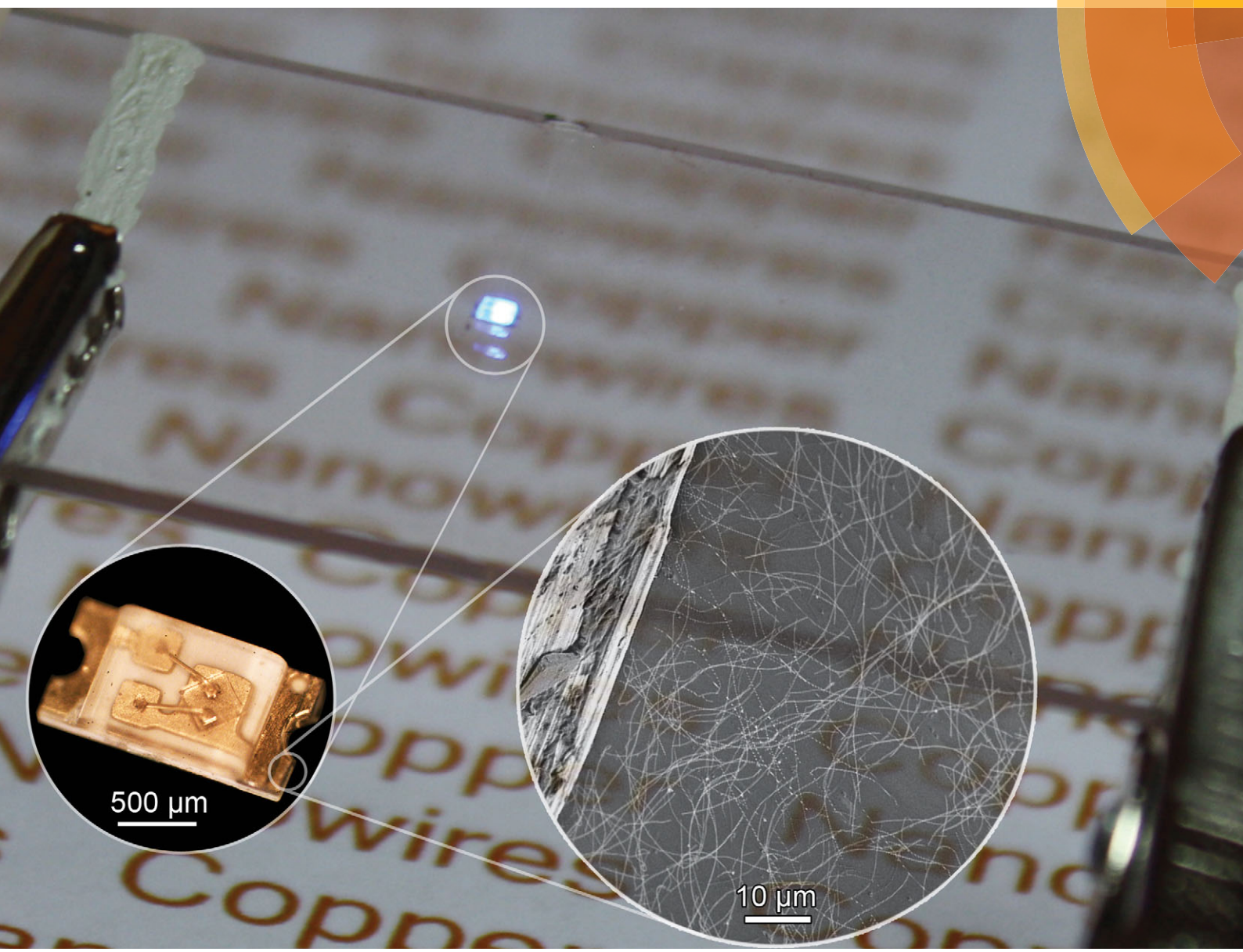

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This communication presents a way to produce copper nanowires with aspect ratios as high as 5700 in 30 min, and describes the growth processes responsible for their formation. These nanowires were used to make transparent conducting films with a transmittance >95% at a sheet resistance <100 Ω sq^{-1}.

Transparent conductors (TCs) are key components in solar cells, light-emitting diodes, flat panel displays, and touch sensors.[1,2] Indium tin oxide (ITO) is currently the most widely used transparent conductor due to its high optical transparency and electrical conductivity.[3] Metal nanowires are an attractive alternative to the high-conductivity ITO used in touch screens, OLED's, and organic solar cells because they can be deposited from solution at linear coating rates several orders of magnitude faster than ITO deposition, and, in the case of high-aspect ratio silver nanowires (Ag NWs), have demonstrated superior levels of performance.[4–13]

Copper is 6% less conductive than silver, but it is 1000 times more abundant and 100 times less expensive.[14,15] Thus, replacing Ag NWs with copper nanowires (Cu NWs) should offer comparable levels of performance at lower cost. Although great improvements have been made in the performance of Cu NW films, they still do not match the performance of ITO. One way to improve the performance of nanowire films is to use nanowires with higher aspect ratios.[16,17] Reduction of Cu(II) precursors in the presence of long-chain alkylamines produces high aspect ratio Cu NWs ($L/D = \sim 2500$), but this synthesis takes several hours and must be performed under pressure.[13,18–20] In comparison, production of copper nanowires by reduction of Cu(II) with ethylenediamine (EDA) as a capping agent is several times faster, and can be performed at atmospheric pressure, making it more attractive for commercial production and mechanistic studies.[8,10,21] However, the aspect ratio of Cu NW's produced with EDA are typically lower ($L/D < 650$) than those produced by the alkylamine-based synthesis. Here, we detail the processes that lead to low aspect ratio nanowires in the EDA-based synthesis, and how to circumvent these processes to obtain nanowires up to 200 μm in length, and 35 nm in diameter ($L/D = 5700$).

In a typical synthesis, 10.5–20 μL of 35 wt% hydrazine (N_2H_4, 5.7–10.5 mM in the final solution) is injected into a mixture containing 4.8 mM $Cu(NO_3)_2$, 14.3 M NaOH and 72–214 mM EDA preheated to 70 °C. When 10.5 mM N_2H_4 is present, the Cu NWs grow with a uniform thickness of 35 nm prior to 16 min (Fig. 1A). As the Cu NWs increase in length and yield, the solution becomes homogeneously dark red. The Cu NWs then spontaneously float to the air–water interface and start to turn pink at approximately 19 minutes. At this intermediate stage the surface of the nanowires becomes rough (Fig. 1B), presumably due to the nucleation and growth of Cu particles on the surface of

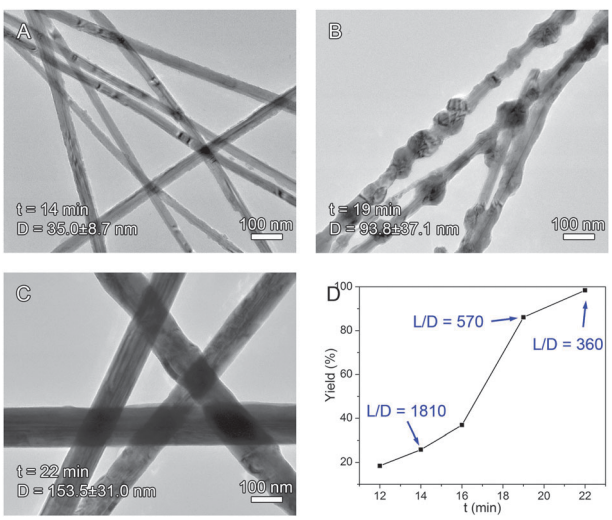

Fig. 1 TEM images of Cu NWs formed at the (A) early, (B) intermediate, and (C) final stages of a reaction. (D) Yield of reduced Cu as a function of reaction time. Note the average wire aspect ratio decreases over time.

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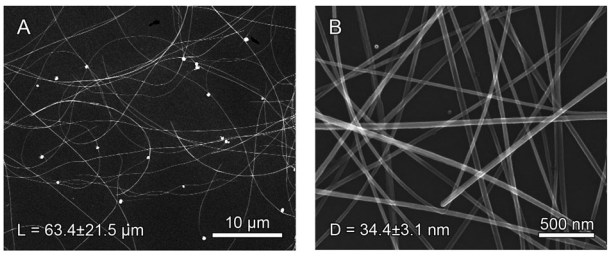


Fig. 2 Decreasing the concentration of N_2H_4 to 5.7 mM prevents thickening, resulting in nanowires (A) 63.4 ± 21.5 μm in length and (B) 34.4 ± 3.1 nm in diameter.

the nanowires. At ~22 minutes, the Cu NWs form a pink-coloured cake at the surface of the solution, and have an average diameter of 154 nm (Fig. 1C). The thicker NWs appear smoother than those at the intermediate stage. SEM images of nanowires at each stage of this process are given in Fig. S1 (ESI†). Fig. 1D shows that approximately 40% of the Cu(II) precursor is converted into thin nanowires at 16 min, and the remainder of the copper precursor adds to the sides of the nanowires over the next 6 minutes, resulting in a dramatic decrease in the nanowire aspect ratio.

The rapid conversion of the nanowires from thin to thick makes it impractical to obtain high aspect ratio nanowires by controlling the reaction time. Fortunately, this conversion can be prevented simply by lowering the concentration of N_2H_4. Fig. 2 shows that Cu NWs ~65 μm in length and ~35 nm in diameter (L/D = 1860) were obtained at 30 min by reducing the concentration of N_2H_4 from 10.5 to 5.7 mM. Running the reaction for longer times led to no appreciable increase in diameter (Fig. S2, ESI†). A slightly higher N_2H_4 concentration of 6.2 mM led to the formation of nanowires with particle-like structures along their length (Fig. S3, ESI†). Thus 5.7 mM represents the maximum concentration of hydrazine that does not cause the nanowires to increase in thickness. By lowering the reaction temperature to 60 °C, the average length of the Cu NWs can be increased to ~80 μm (L/D = 2280), with some wires as long as 200 μm (L/D = 5700), while retaining a diameter of ~35 nm (Fig. S4, ESI†).

Previous EDA-based Cu NW syntheses have led to the production of copper nanowires with a distinctive tapered structure, in which the diameter of the nanowire increases from one end to the other.[8,10] Fig. 3A shows a similar example of such a nanowire produced at an EDA concentration of 214 mM, for which the diameter increases from 32 nm near the seed to 155 nm at the end. This 6-fold increase in diameter over a length of 44 μm gives the nanowire an average L/D = 460. Thus, preventing the formation of this tapered structure is key to obtaining copper nanowires with high aspect ratios. Fortunately, simply reducing the EDA to a lower concentration (95 mM) results in Cu NWs with thin, uniform diameters along their entire length (Fig. 3B).

The tapered Cu NWs undergo a similar thickening process at higher N_2H_4 concentrations. Fig. S5 (ESI†) shows tapered nanowires with particles on their sides at a N_2H_4 concentration of 6.2 mM, and tapered nanowires that grew radially to an average diameter of 195 nm at a N_2H_4 concentration of 10.5 mM. These experiments show the tapering and thickening

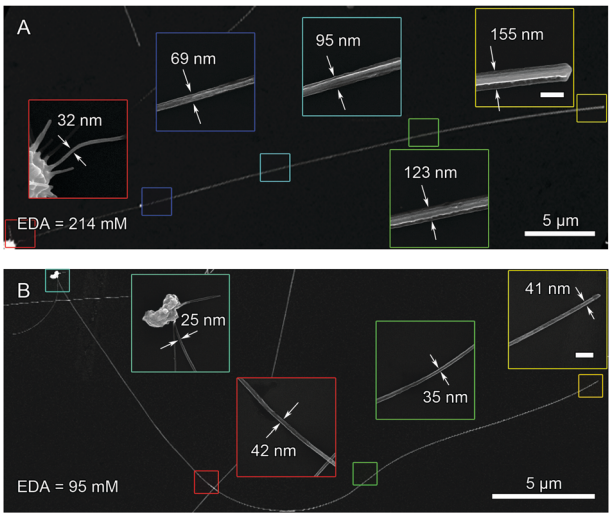
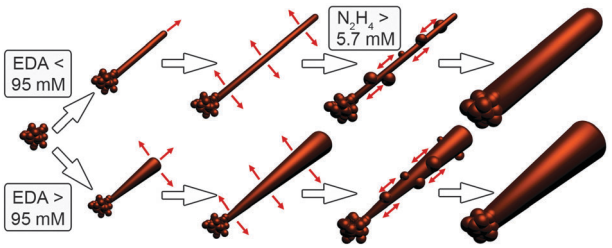


Fig. 3 SEM images of (A) a 44 μm-long tapered Cu NW grown with 214 mM EDA, and (B) a 33 μm-long taper-free Cu NW grown with 95 mM EDA. Insets (scale bars, 200 nm) show a closer view of the different parts of the nanowires.



Scheme 1 Nanowire tapering and thickening processes. Red arrows represent the growth direction.

phenomena are two independent processes. Scheme 1 summarizes the processes of nanowire tapering and thickening.

In order to gain additional insight into the reason for the formation of tapered nanowires, we monitored the growth of individual Cu NWs in real time with dark field optical microscopy. We note that this is the first real time observation of nanowire growth in solution. As shown in Fig. 4, all the Cu NWs grow out of the seed particles on the substrate. This is consistent with the situation for Cu nanowires grown in a flask.[8] When the concentration of EDA is low, the Cu NWs appear relatively long and thin (Fig. 4A–C). In contrast, the Cu NWs become shorter, thicker and more tapered at higher concentrations of EDA (Fig. 4D–F). Measurements of axial growth rates indicate that Cu NWs grow 3–4 times slower if the EDA concentration is increased from 95 to 214 mM (Fig. 4G and H). This experiment shows the presence of additional EDA suppresses the axial growth of the Cu NWs, leading to a relatively greater amount of Cu added to the sides of the nanowire, and more tapering.

To fabricate transparent conducting films of Cu NWs, we transferred the Cu NWs into a nitrocellulose-based ink solution and coated them onto a glass substrate with a Meyer rod. The plot of specular transmittance (%T) *versus* sheet resistance (R_s) for the Cu NW networks is shown in Fig. 5, along with some of the best previous literature results. The TCs made of long,

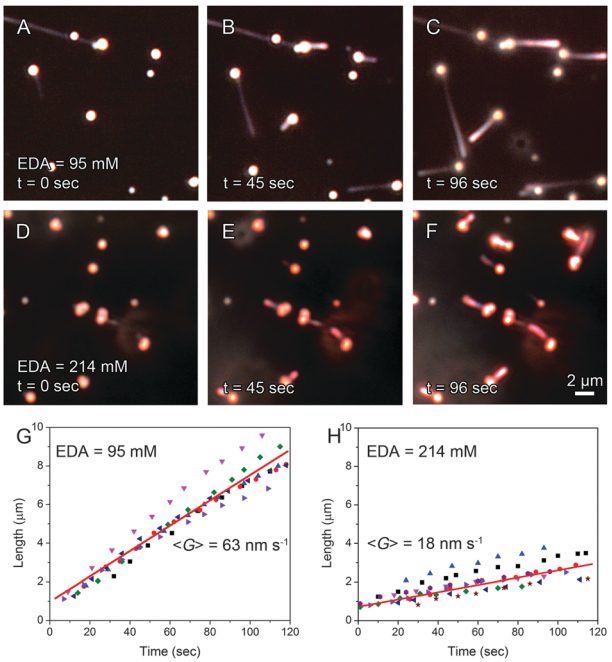


Fig. 4 *In situ* visualization of Cu NW growth in the presence of 95 mM (A–C) and 214 mM EDA (D–F). The growth rate, $\langle G \rangle$, of Cu NWs is (G) 63 ± 5 nm s^{-1} and (H) 18 ± 4 nm s^{-1}, respectively.

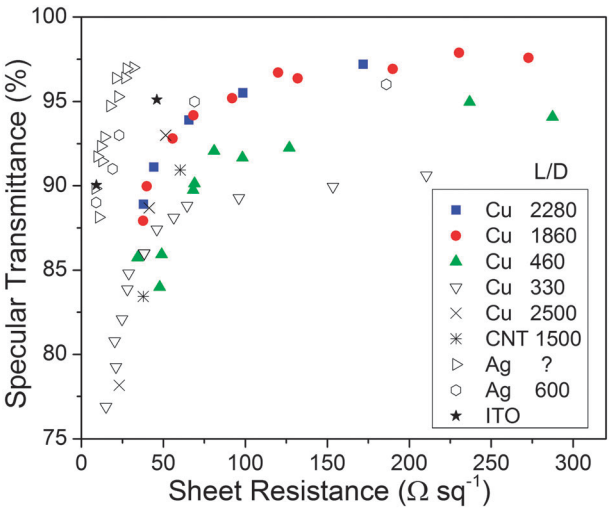


Fig. 5 *%T vs.* R_s of Cu NW networks based on high aspect ratio Cu nanowires (*L*/*D* = 2280, 1860) as well as tapered nanowires (*L*/*D* = 460). Comparison data are shown representing current state of the art TCs, including Cu NWs (*L*/*D* = 330,[10] 2500[13]), carbon nanotubes (*L*/*D* = 1500),[22] Ag NWs (*L*/*D* = ?,[23] 600[24]), and ITO.

thin Cu NWs (*L*/*D* = 1860) exhibit excellent performance in terms of transparency and conductivity. For example, at %*T* = 95%, the nanowire network has a R_s below 100 Ω sq^{-1}, and it is only 3% less transparent than ITO at a R_s of 50 Ω sq^{-1}. Films made of higher aspect ratio Cu NWs (*L*/*D* = 2280) do not exhibit better performance. This may be due to the poly-disperse distribution of nanowire lengths, or the fact that high aspect ratio nanowires behave more like flexible filaments than rigid rods; additional modeling efforts may shed light on this issue.[17] At R_s = 100 Ω sq^{-1}, the %*T* of films made of the tapered Cu NWs (*L*/*D* = 460) drops to 92–93%. This result confirms the importance of controlling the aspect ratio of the nanowires by minimizing tapering.[17,25]

We have shown how radial and tapered growth leads to the formation of Cu NWs with relatively low aspect ratios. Key to the production of high aspect ratio Cu NWs are the discoveries that (1) radial growth can be prevented by keeping the concentration of N_2H_4 below 5.7 mM, and (2) tapered growth can be prevented by keeping the concentration of EDA below 95 mM. We also demonstrated the first method to quantify the growth rate of individual Cu NWs, and use this method to show how high concentrations of EDA can decrease the axial growth rate. Improved understanding of the Cu NW synthesis enabled the production of Cu NWs with *L*/*D* > 5700, and the highest performance to date for a solution-coated, Cu NW-based transparent electrode.

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