Young-Laplace Equation

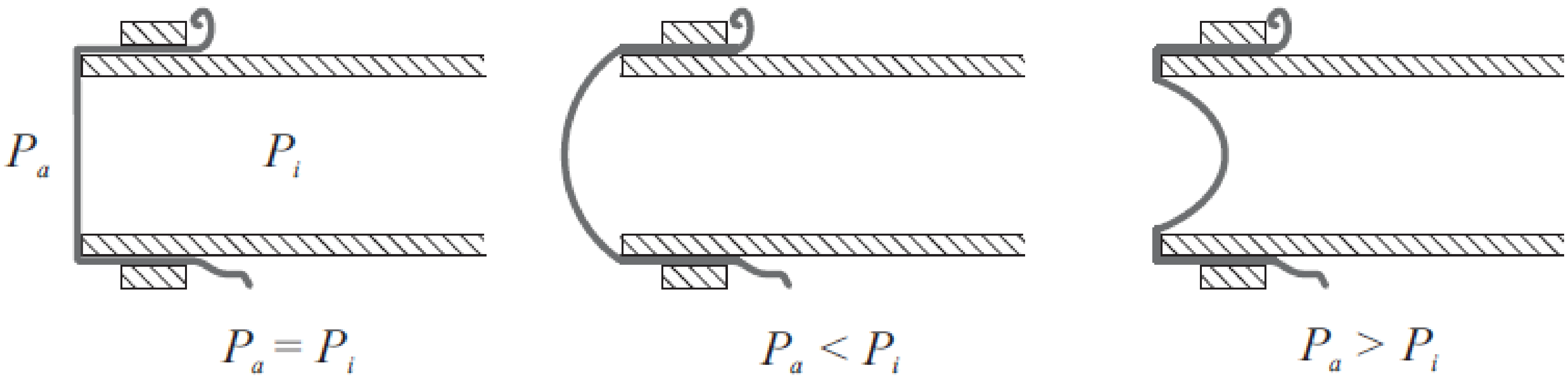


Figure 2.4: Rubber membrane at the end of a cylindrical tube. An inner pressure P_i can be applied, which is different than the outside pressure P_a.

Young-Laplace Equation

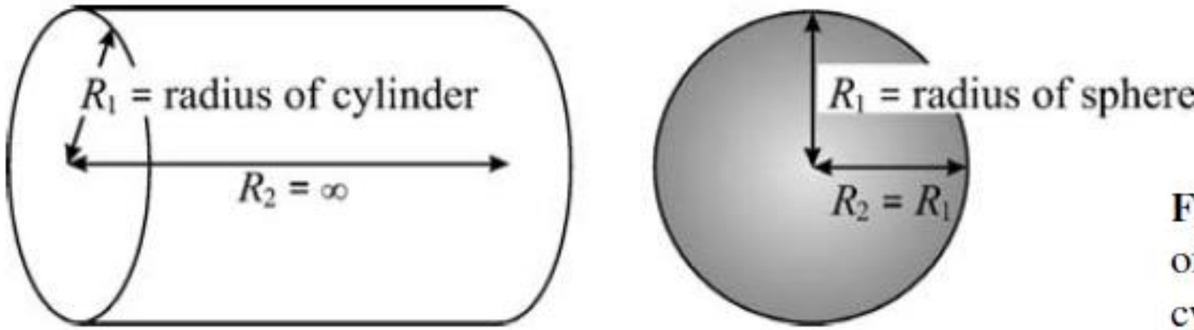


Figure 2.5: Illustration of the curvature of a cylinder and a sphere.

Young-Laplace Equation

■ **Example 2.4.** How large is the pressure in a spherical bubble with a diameter of 2 mm and a bubble of 20 nm diameter in pure water, compared with the pressure outside? For a bubble the curvature is identical to that of a sphere: $R_1 = R_2 = R$. Therefore

$$2\gamma$$

Young-Laplace Equation

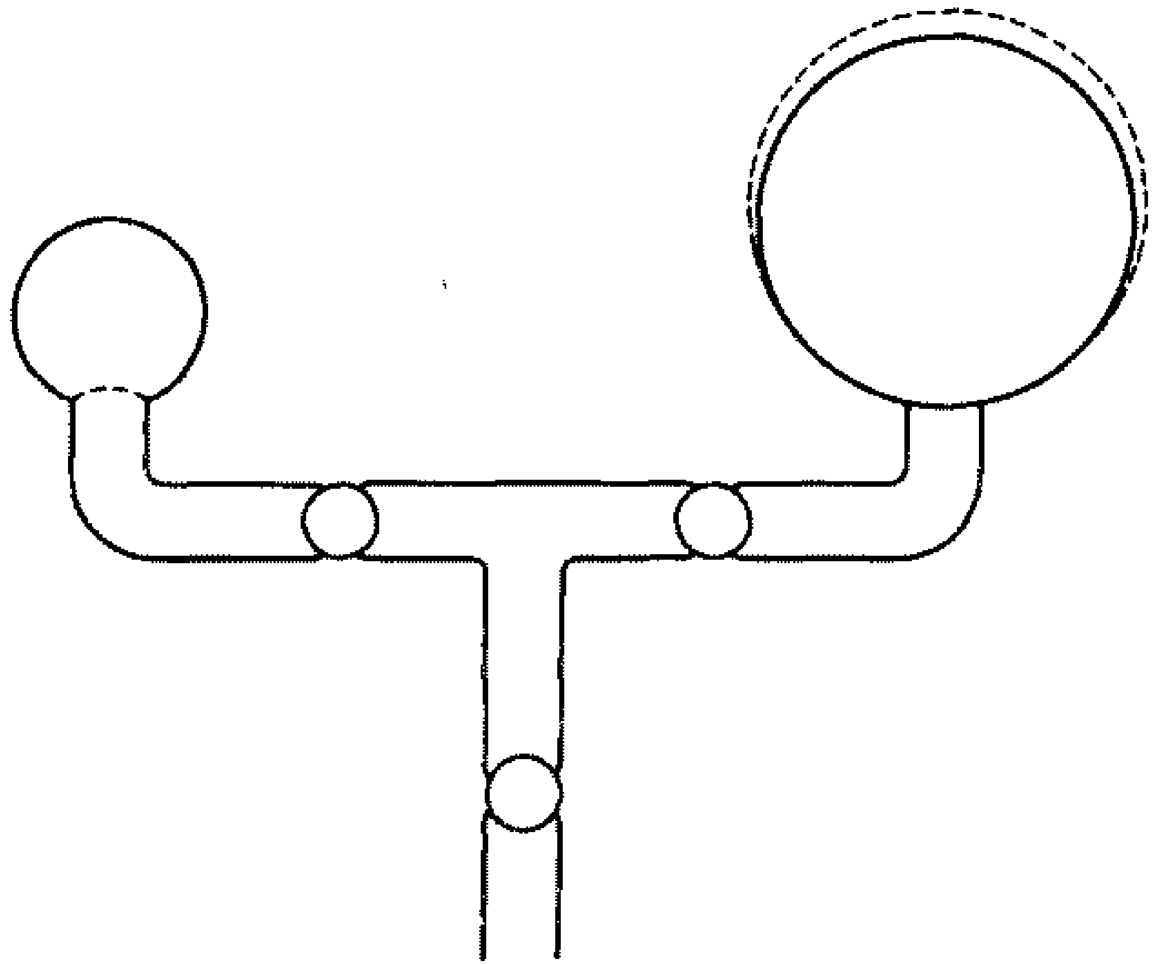


Fig. II-2. Illustration of the Young–Laplace equation.

Capillary Rise

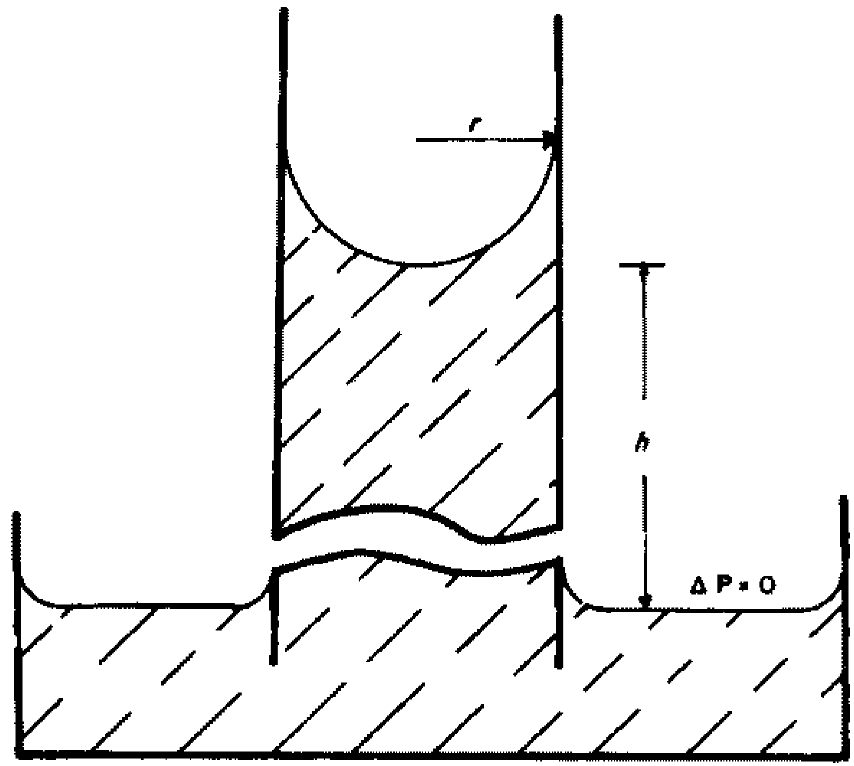
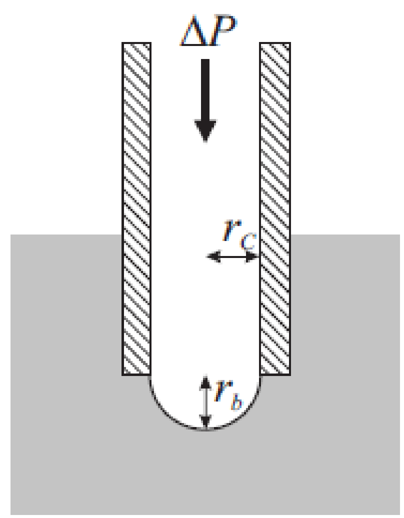


Fig. II-6. Capillary rise (capillary much magnified in relation to dish).

Maximal bubble pressure method



Capillary condensation

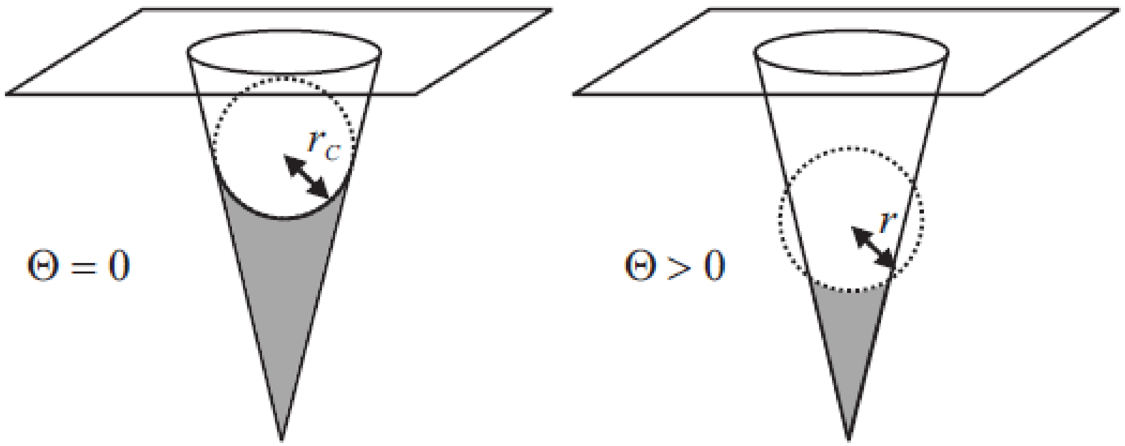


Figure 2.12: Capillary condensation into a conical pore with wetting and partially wetting surfaces.

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Room-Temperature Chemical Welding and Sintering of Metallic Nanostructures by Capillary Condensation

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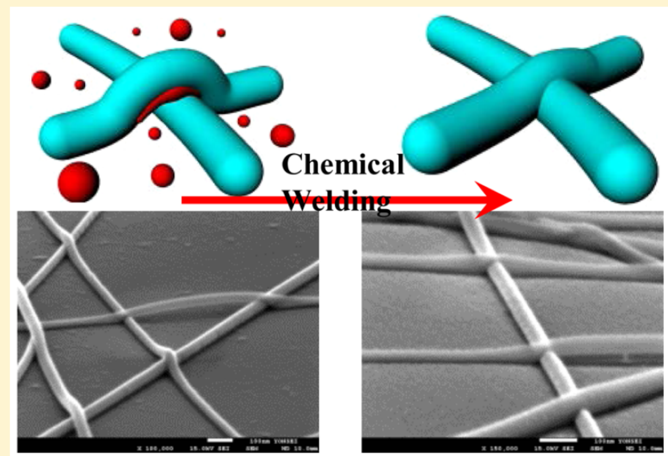
Supporting Information

ABSTRACT: Room-temperature welding and sintering of metal nanostructures, nanoparticles and nanowires, by capillary condensation of chemical vapors have successfully been demonstrated. Nanoscale gaps or capillaries that are abundant in layers of metal nanostructures have been found to be the preferred sites for the condensation of chemically oxidizing vapor, H_2O_2 in this work. The partial dissolution and resolidification at such nanogaps completes the welding/sintering of metal nanostructures within ~10 min at room-temperature, while other parts of nanostructures remain almost intact due to negligible amount of condensation on there. The welded networks of Ag nanowires have shown much improved performances, such as high electrical conductivity, mechanical flexibility, optical transparency, and chemical stability. Chemically sintered layers of metal nanoparticles, such as Ag, Cu, Fe, Ni, and Co, have also shown orders of magnitude increase in electrical conductivity and improved environmental stability, compared to nontreated ones. Pertinent mechanisms involved in the chemical welding/sintering process have been discussed. Room-temperature welding and sintering of metal nanostructures demonstrated here may find widespread application in diverse fields, such as displays, deformable electronics, wearable heaters, and so forth.



KEYWORDS: *Capillary condensation, metal nanostructures, welding, sintering*

Room-Temperature Chemical Welding and Sintering of Metallic Nanostructures by Capillary Condensation

- Capillary condensation, a premature condensation of vapor into liquid even at vapor pressures lower than its thermodynamic saturation vapor pressure, is a ubiquitous phenomenon in our daily life.
- The phenomenon can easily occur especially under geometrical confinement, such as divided media, cracks, contacts, or nanoscale gaps between surfaces, when the mutual interaction (van der Waals interaction, in general) among vapor molecules exceeds a certain limit.
- It has been found to play an important role in a wide variety of science and engineering fields that involve small gaps or capillaries, such as scanning probe microscopy (SPM), micro- or nanoelectromechanical system (MEMS/NEMS), porous media and oil recovery, and colloidal and sol−gel based film formation.

Room-Temperature Chemical Welding and Sintering of Metallic Nanostructures by Capillary Condensation

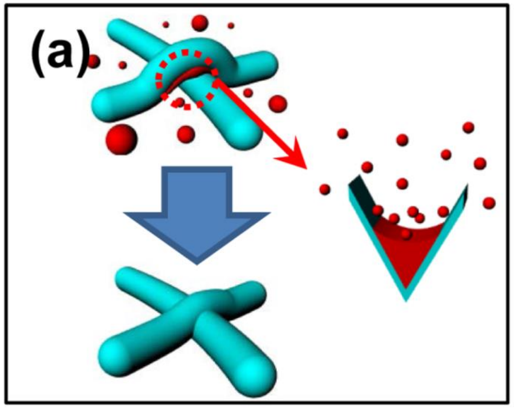
- We demonstrate in this work that the capillary condensation can be used as a valuable tool in welding and sintering of metal nanostructures chemically at room temperature.
- The nanoscale gaps abundant in the network or film of metallic nanostructures have been found to be the preferred locations of capillary condensation.
- When chemical vapors of highly oxidizing agents, hydrogen peroxide (H2O2) in this work, condense at such nanogaps, welding and sintering can be accomplished at room temperature due to dissolution and redeposition of materials at such gaps only.

Room-Temperature Chemical Welding and Sintering of Metallic Nanostructures by Capillary Condensation

- Welding or joining of material pieces together has long been practiced in history.
- Contrary to the welding of bulk materials, which is now a mature technique, joining of nanoscale counterparts imposes significant barriers not seen in the bulk
- Traditional thermal welding is not compatible with low thermal budget substrates such as flexible polymers.
- The room-temperature chemical welding and sintering of metal nanostructures by capillary condensation is a simple and readily scalable approach and thus may find a wide range of applications, especially for transparent electrical conductors in highly bendable or stretchable forms.

Approach

- When deposited on a substrate, metal nanowires form percolating thus electrically conducting network.
- Here, the physical contacts between nanowires form a nanogap or capillary.
- Upon exposure to oxidizing vapor of H2O2, condensation occurs preferentially at such nanogaps, leading to dissolution and joining of nanowires altogether.



$$\frac{P_{\mathrm{v}}}{P_{\mathrm{sat}}} = \exp\left\{-\frac{2\gamma V_1}{rRT}\right\}$$

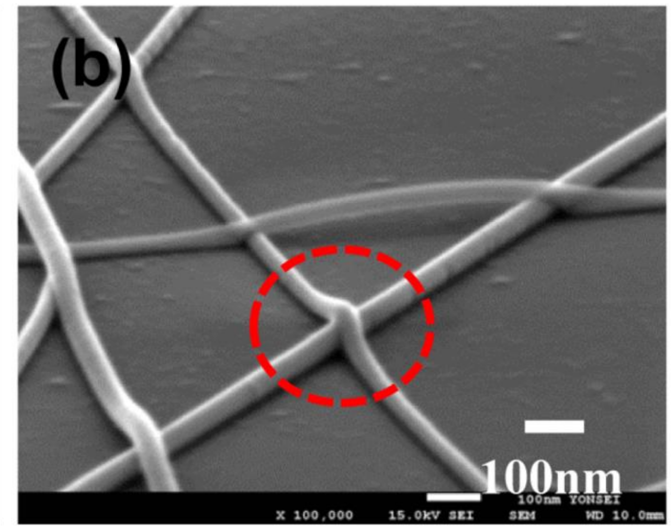
- The capillary condensation phenomenon is explained by the following Kelvin equation
- All things being constant, the mean radius of curvature of meniscus governs the condensation.
- It can easily be verified that the smaller the radius of curvature (or nanoscale gap), the earlier the vapor condensation occurs at such spots compared to areas having large radius of curvature.

Structural Characterization

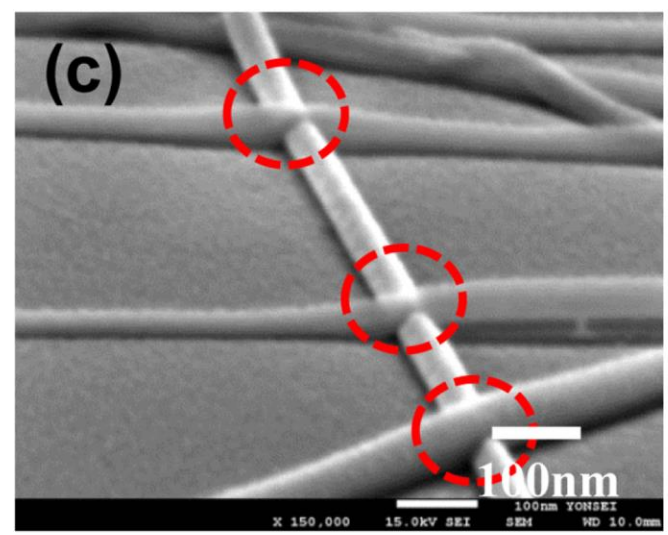
- **Indeed, the exposed nanowires' surface remains almost intact while the junctions between them are welded together.**

- Before the welding by capillary condensation, the overlying nanowire bends conformally along the contour of bottom-lying one at the physical junction
- After the chemical welding by exposing the sample on the vapor of H2O2, however, the junction seems to be flattened by partial sinking of the overlying nanowire
- Note here that there is no noticeable change in nanowire morphology under the scanning electron microscopy (SEM) observation after the welding process except for the junctions.

Before H2O2



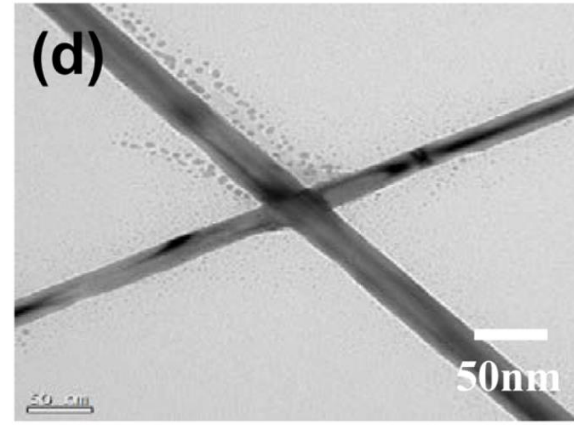
After H2O2



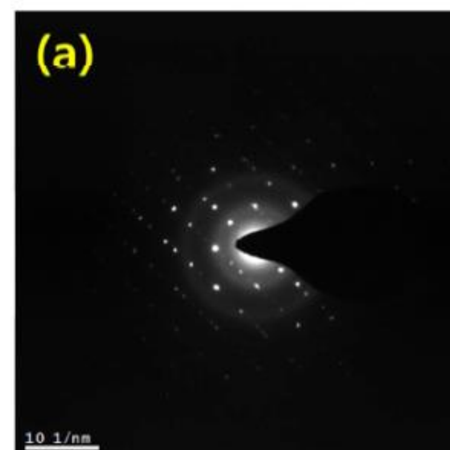
Structural Characterization

- The nanowire morphology, especially in the neighborhood of the welded junctions, showed slight change upon high resolution transmission electron microscopy (HR-TEM) observation
- The outer surface of the nanowires became wobbly and there were very small (<∼10
- nm) particulates around the nanowires.
- Contrary to thermal based welding processes, each AgNW retains their own crystallinity or crystalline direction even after the chemical welding

TEM



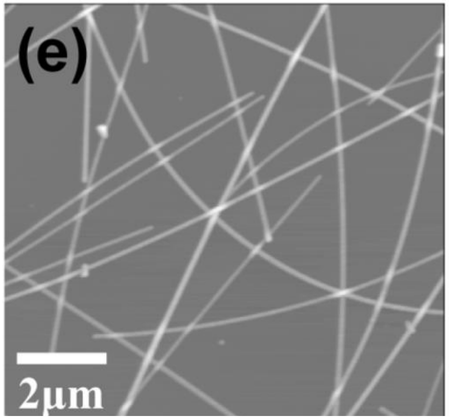
Selective area diffraction pattern

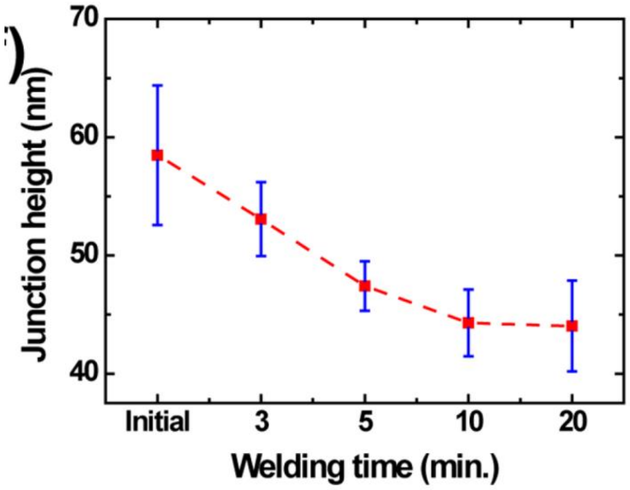


Structural Characterization

AFM

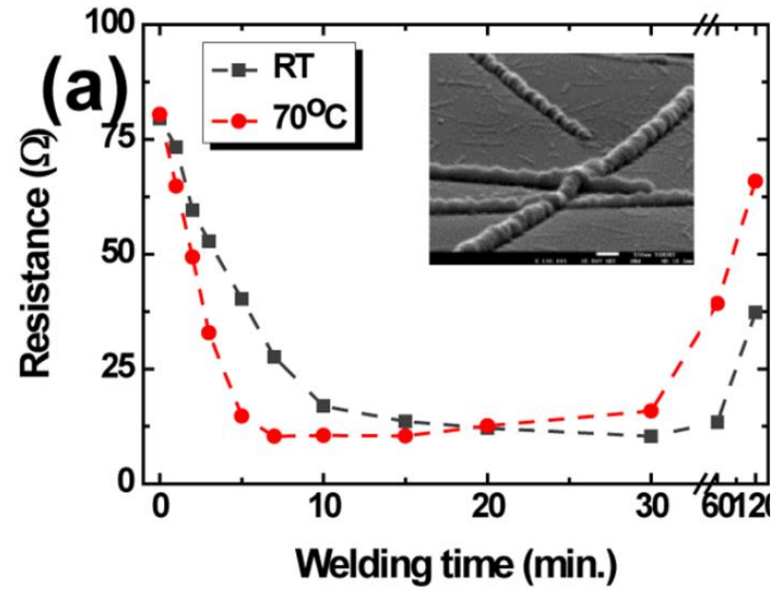
- Figure 1e shows a representative atomic force microscopy (AFM) height image of the welded AgNWs network.
- The junction height, obtained from section analysis of the AFM image, decreases gradually up to ∼10 min of chemical welding
- The reduction in junction height signifies the progression of chemical welding.
- Prolonged (20−30 min) exposure to chemical vapor, however, does not reduce the junction height any further, which means now the vapor condensation is not preferential at junctions but occurs everywhere.





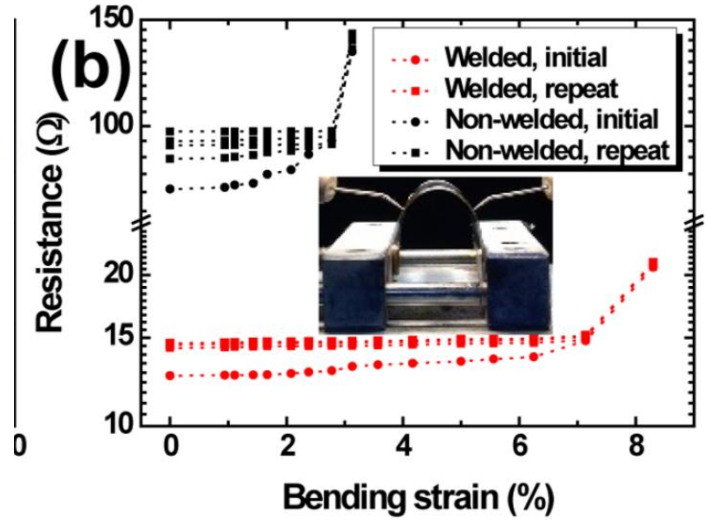
Other properties

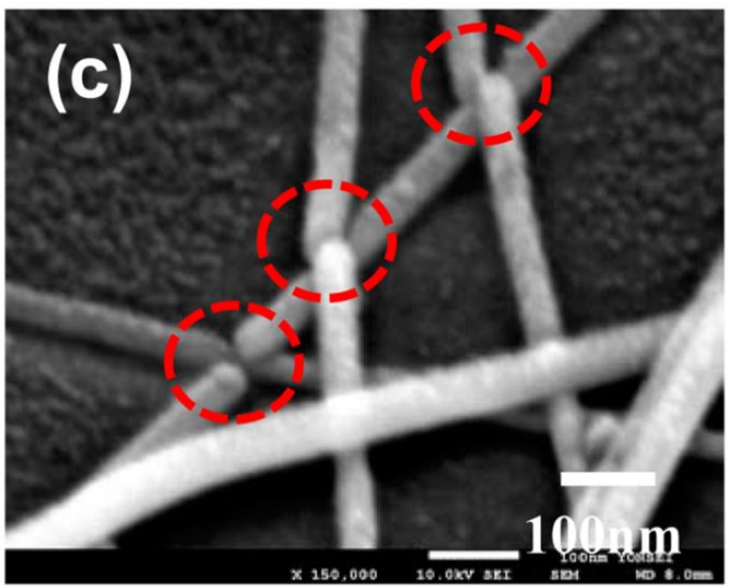
- As expected, the chemical welding of junctions in AgNWs network has led to great enhancement in its electrical and mechanical characteristics.
- As the welding time increases, the resistance decreases down to a minimum value, at 20−30 min for room temperature and at ∼5 min for high temperature (70 °C) vapor treatments
- Then the resistance starts to increase again upon further increase of H2O2 vapor exposure due to damage or chemical dissolution of nanowires, as shown in the inset SEM image of Figure 2a



Other properties

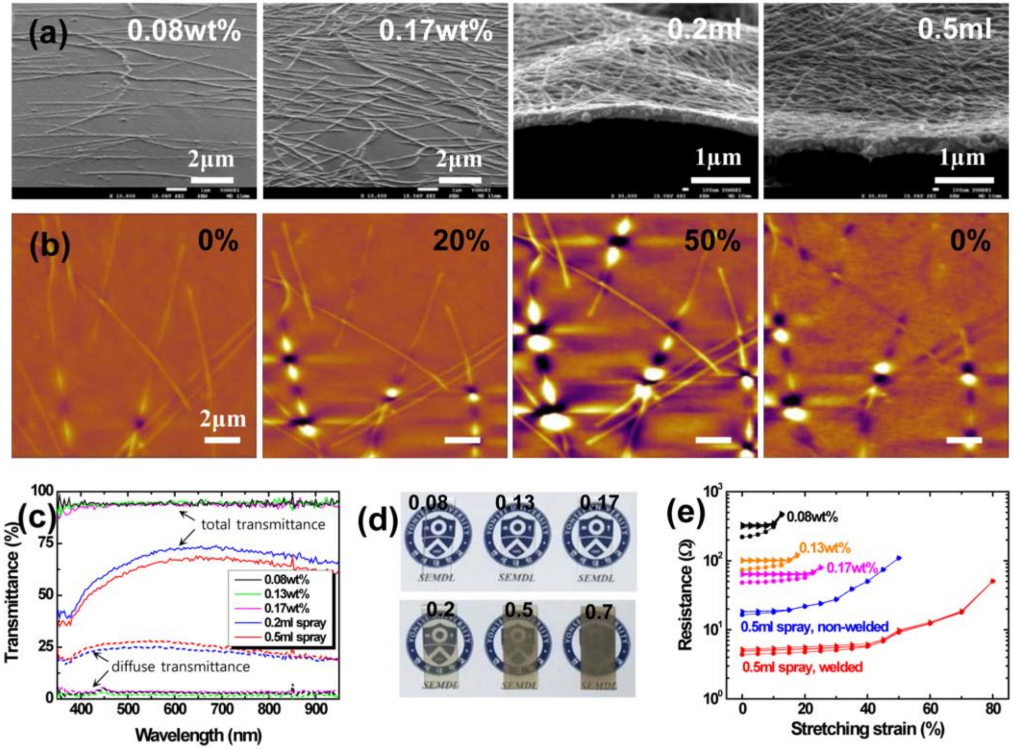
- The welded network of AgNWs on a flexible polymer substrate (polyethylene terephthalate, PET) showed greatly enhanced bendability, almost constant resistance values up to ~7% tensile strain, while the nonwelded one maintains its resistance only up to ~3%, as shown in Figure 2b
- Upon applying external tensile strain by bending the substrate, the mutually connected network of nanowires now can distribute the applied strain evenly out over the whole sample.
- On the contrary, the nonwelded network of nanowires easily fractures upon applying external tensile strain due to stress localization, as shown in Figure 2c





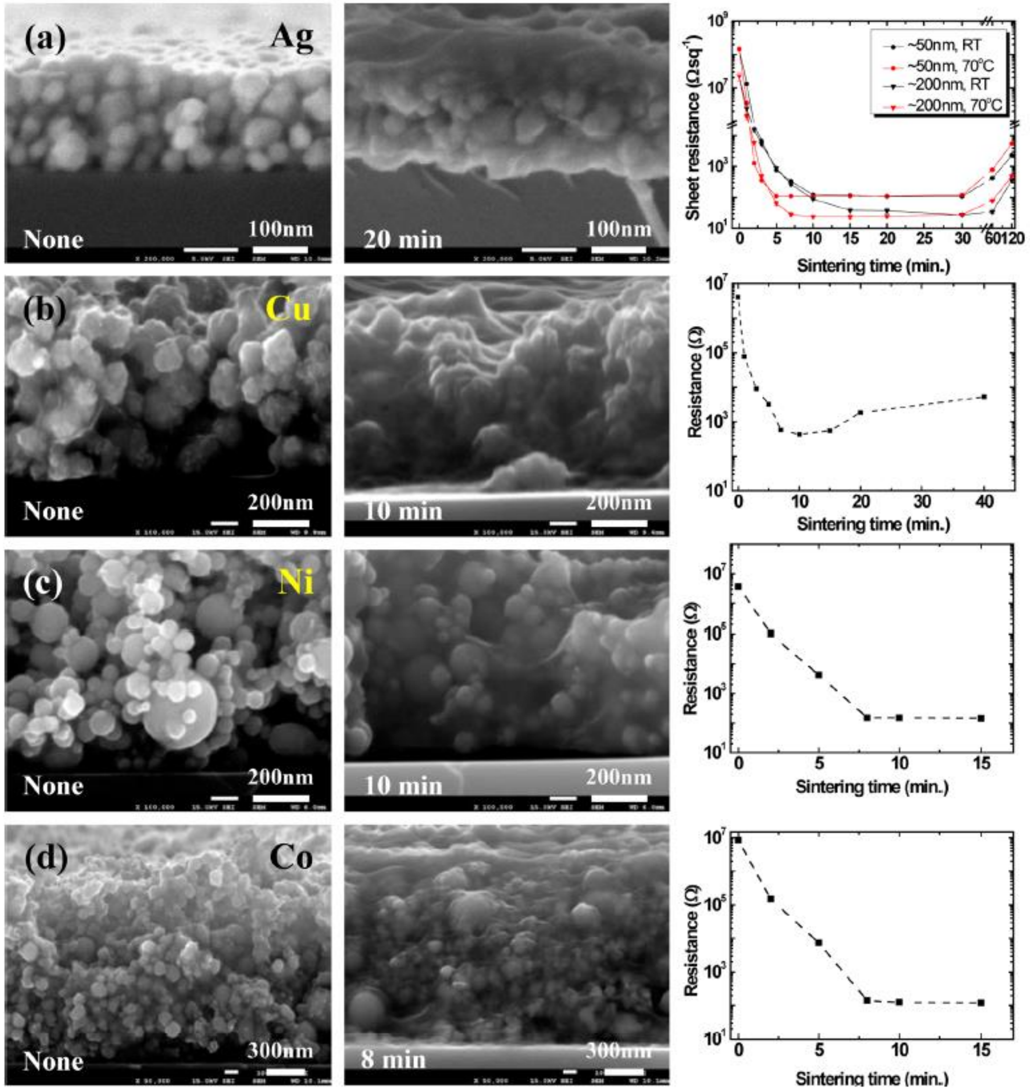
Transparent and strechable conductors

- Transparent and stretchable conductor by employing the same chemical welding approach.
- As shown in Figure 3a, the welded network of AgNWs could indeed be partially embedded into an elastomeric substrate surface, namely polydimethylsiloxane



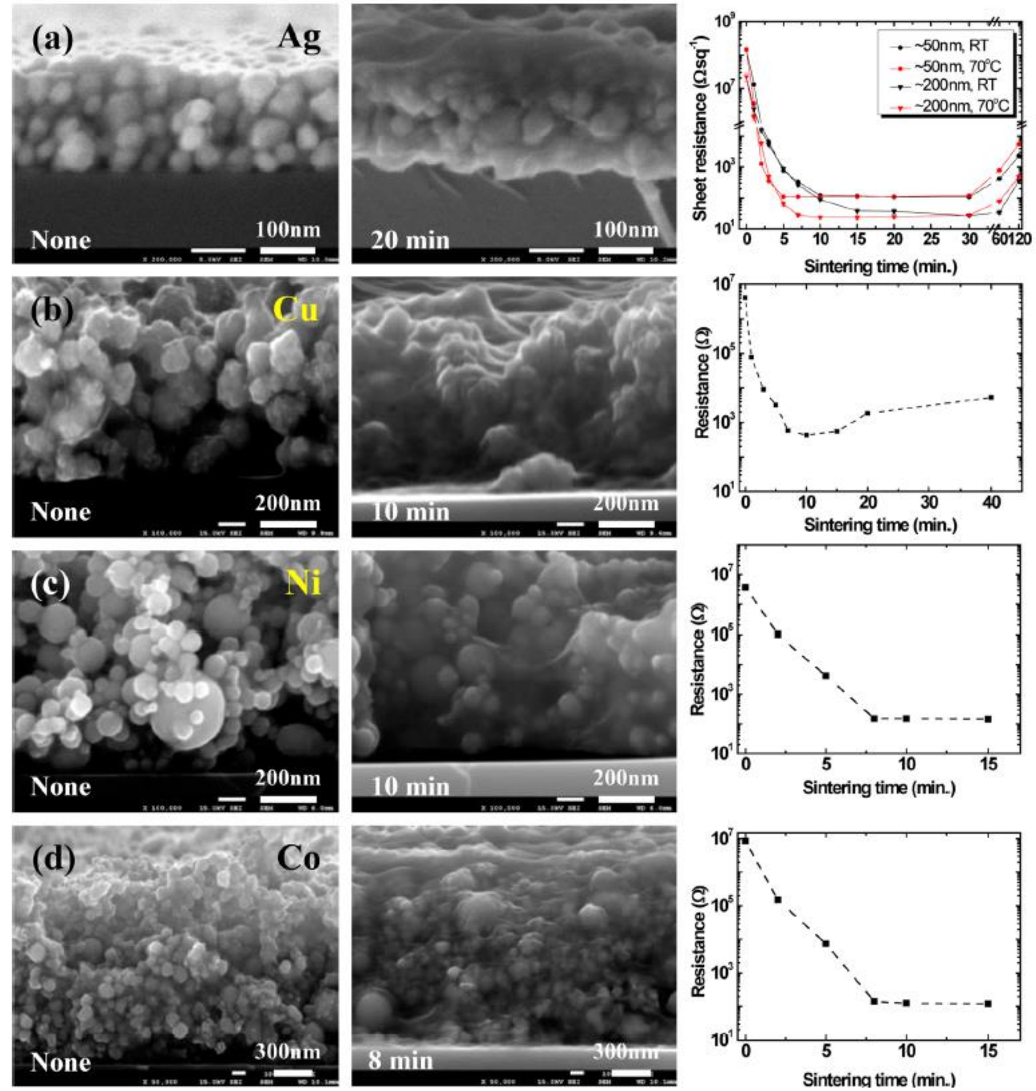
Other metallic nanoparticles

- All the physics and chemistry discussed for AgNWs have been found to be equally applicable in chemical sintering of other metal nanoparticles at room T.
- In fact, the nanoparticles layer has numerous contact gaps among particles, which greatly facilitate the capillary condensation of oxidizing H2O2 vapor.
- Shown in Figure 4a is the ~200 nm-thick layer of Ag nanoparticles, before and after the room-temperature chemical sintering by capillary condensation.
- The individual nanoparticles are hard to discern after the chemical sintering

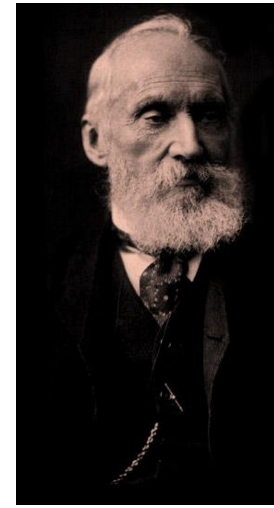


Other metallic nanoparticles

- At the same time, the sheet resistance of the layer decreased ∼7 orders of magnitude upon chemical sintering.
- Similar results were obtained for ∼700 nm thick Cu nanoparticles film, as shown in Figure 4b.
- The chemical sintering or fusion among metal nanoparticles has led to ∼5 orders of magnitude reduction in electrical resistance, too.
- Ni and Co nanoparticles showed similar sintered morphology and orders of magnitude reduction in electrical resistance upon ∼10 min of exposure to H2O2 vapor



Lord Kelvin (1824-1907)



- Devising the absolute temperature scale, now called the 'Kelvin scale'
- Formulating the second law of thermodynamics
- Working to install telegraph cables under the Atlantic
- Lord Kelvin's father became Professor of Mathematics at Glasgow University. Kelvin attended university classes from the age of 10.
- He wrote his first scientific paper, under the pseudonym 'PQR', aged only 16.
- In his teens he learned French well enough to read the work of eminent French mathematician Jean Baptiste Joseph Fourier.
- Philip Kelland, Professor of Mathematics at Edinburgh University, had criticised Fourier's work on the theory of heat. Kelvin boldly stated that Kelland was wrong – and later scientists agreed with him.