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Surface-Stabilization of Ultrathin Gold Nanowires for Capacitive Sensors in Flexible Electronics

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ABSTRACT: Ultrathin gold nanowires (AuNWs) have shown great potential towards flexible electronics applications. However, they suffer from high surface instability that consequently limits their applicability for solution-processed composite materials. To overcome this limitation,

we show for the first time how a synthetic thiolated small molecule ligand such as ethyl 11-(4-mercaptobenzamido) undecanoate can stabilize the AuNWs surface enabling their manipulation in solution-processed composite manufacturing techniques. As a proof of concept, we show how such stabilized NWs can be formulated into a PDMS matrix and spin-coated to afford stretchable elastomeric strips able of sensing mechanical deformation with loading as low as 0.03 wt.%.

Polymer-based nanocomposites can combine the mechanical properties of inert polymers that act as a matrix with the peculiar and outstanding properties (conductivity, piezoelectricity, fluorescence, ...) of nanostructured materials.¹ Amongst these, carbon nanomaterials are indeed the most widely used.² Both graphene and carbon nanotubes have been employed for realizing capacitive strain sensors for application in flexible electronics.³ Unfortunately, high production costs and the impossibility to functionalize their surface without affecting the conductivity graphene and carbon nanotubes have strongly hindered the market application of carbon nanomaterials.^{4,5} Conductive metal NWs have found extensive applications for the preparation of conductive nanocomposites in flexible electronics.⁶ In the majority of applications, they represent a valid solution, as they combine conductivity and good mechanical properties, without relevant drawbacks as the production costs. Indeed, silver NWs (AgNWs) are a well-known and reported class of conductive nanostructures that have found several applications in flexible electronics.⁷ Often AgNWs up to 10–20 μm in length with diameters higher than 20 nm are obtained: the elongation can be easily tuned by adjusting synthetic parameters, while diameter reduction remains challenging even if extremely promising. Sorel et al. in 2012 synthesized AgNWs with various diameters (reaching down to 25 nm) and demonstrated that the ratio of Direct Current (DC) to

optical conductivity, often taken as a figure of merit for transparent electronics, scales approximately as length/diameter ratio, suggesting the importance of having long and ultrathin metal wires for application in electronics devices and sensors.⁸ Even though well-described, low-diameter AgNWs are prepared by the polyol reduction method which involves the anisotropic reduction of silver nitrate by means of polyols at high temperatures, with drawbacks related to the thermal degradation of the solvent and nitrate ions that cause the release of toxic vapors of NO_x and polyols.⁹ In addition, small diameters are obtained by applying high pressures.¹⁰

In light of these aspects, AuNWs whose diameter does not exceed 10 nm, and preferably remains in the 2-3 nm range,¹¹ are much easier to synthesize and have shown very interesting electrical properties combined with easy manufacturing and outstanding mechanical performances.¹² The most commonly employed synthetic approach for their synthesis relies on the reduction of Au-oleylamine polymeric complexes in hexane using triisopropylsilane as a reducing agent and leads to the obtainment of NWs in hexane solution.¹³

Although the synthetic approach described for the formation of such NWs is easy and easily scalable, their high aspect ratio (>1000) makes AuNWs extremely unstable and causes them to collapse into nanospheres quite easily, thus a great effort still needs to be directed towards the stabilization and manipulation of ultrathin AuNWs for more sophisticated manufacturing techniques.

With the aim of durable stabilization, surface modification of gold nanostructures with thiol functional group has been identified as being the best. A long aliphatic chain ending with a thiol group remains the best choice to allow self-assemblies onto the surface, whereas the presence of intermolecular hydrogen-bonding guarantees stability to the final architecture.¹⁴

For instance, for AgNWs, even if having diameters easier to handle higher than 100 nm, the stabilization via surface coating allowed great improvement in their final manufacturing, thanks to a better interaction between nanostructures and solvent and to a decreased wire-to-wire junction resistance.¹⁵ Ultrathin AuNWs stabilization was recently performed by entrapping them in phospholipid micelles¹⁶, but only two examples of organic coatings on ultrathin AuNWs have been reported, presenting non-neglectable drawbacks and no reported application: trioctylphosphine-coated AuNWs were manufactured in protected atmosphere to avoid oxidation of the ligand, and amino-based surfactants have been employed to synthesize water-soluble AuNWs which have been entrapped in dielectric silica shells, limiting their electronic properties.¹⁷ Finally, there is no example of successful surface stabilizations performed employing thiols-based ligands, therefore coating of ultrathin NWs is a chemical challenge because AuNWs clearly represent promising candidates for the preparation of conductive nanocomposites for flexible electronics.

The demand for stretchable strain sensors has increased exponentially due to their application in human motion monitoring, prosthetic devices and soft robotics.¹⁸ However, developing stretchable strain sensors with optimal properties such as easy fabrication, low cost and good response linearity remains challenging. Recently, self-assemblies of AuNWs on polymeric substrates have been widely explored as sensing elements for flexible and transparent electronics.¹⁹ AuNWs-based pressure sensors have demonstrated to be able to efficiently detect pressing, bending, and twisting of the flexible device, enabling its employment as wrist motion and vibration sensors that requires low input powers ($< 30 \mu\text{W}$) at low operating voltages (1.5 V), even if at the very high Au loadings, that made the impregnated sheet appears completely black.²⁰

We describe for the first time the surface stabilization of ultrathin AuNWs using organic ligand and their subsequent permanent entrapment in polydimethylsiloxane (PDMS) matrices showing

preliminary results of their impedentiometric characterization as transparent strain sensors at very low Au loadings (0.03 wt%).

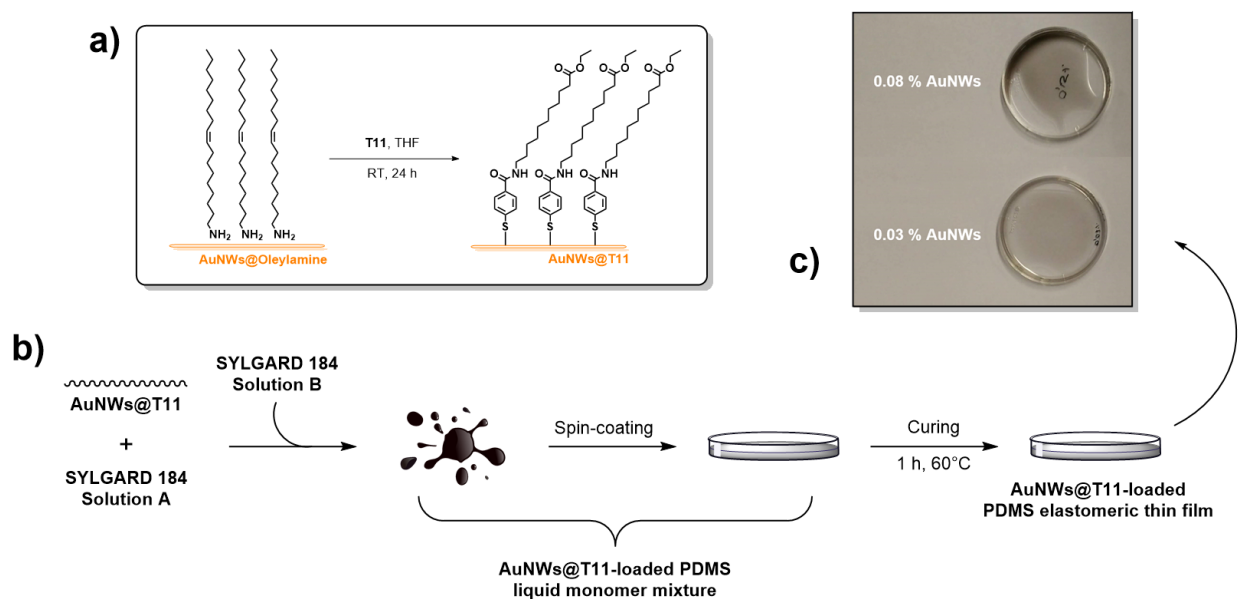
AuNWs have been synthesized according to the procedure reported by Feng, but in more concentrated conditions.²¹ This allowed for a reduction of the total reaction volume without any variation in the quality of the prepared nanostructure or in the yield, which was measured via atomic absorption spectroscopy (AAS) to be as high as 71% (Supporting Information).

Due to their high aspect ratio, and therefore the related high surface energy, the surface tension of AuNWs tend to reshape them into rounder nanostructures, associated with a much lower surface-to-volume ratio (Rayleigh-Plateau instability). A thiol-based organic ligand can be employed to reduce gold surface energy better than other functional groups, forming stronger and more stable interactions due to “hard” vs. “soft” acid-base chemistry.²² Both gold and sulfur fall in the “soft” category, while amine and phosphines are considered as “hard”.

Stabilization of AuNWs with long-chain thiols was already attempted without being successful.¹⁷ This was probably due to the employment of aliphatic thiols, which can form a self-assembled monolayer onto the surface of the wire, but not to stabilize the same against Rayleigh-Plateau instability.²³ We decided to exploit the thiolated ligand ethyl 11-(4-mercaptobenzamido) undecanoate (T11, **Scheme S1**), which has demonstrated to be able to efficiently form lipophilic self-assembled monolayers onto gold surfaces thanks to its ability to establish hydrogen bonds, π -stacking and Van der Waals interactions (**Scheme 1a**), therefore it is believed to be able to further decrease the free surface energy at the metal-shell interface.^{24,25}

Regarding the instability of AuNWs towards agglomeration, it has been discussed how oleylamine-coated AuNWs tend to buddle in solution by establishing weak interactions between

the alkyl chains.²⁶ This phenomenon varies as a function of the concentration of the free ligand and the type of dispersant solvent. However, no discussion is yet reported regarding thiolated ligands.



Scheme 1. Preparation of AuNWs-loaded thin PDMS films for stretching sensing applications. a) Ligand exchange reaction. Since the interaction of gold with sulfur is much stronger than that with nitrogen, oleylamine is easily replaced. b) The so-obtained AuNWs@T11 are then dispersed into solution A of SYLGARD 184 PDMS elastomer kit and mixed with a 10% of solution B to afford a liquid PDMS monomer mixture, which is then spin-coated on Petri dishes and heat cured leading to thin elastomeric films which are cut into small strips for testing their sensing ability. c) Optical camera picture of the obtained PDMS films.

After surface stabilization, a solution of AuNWs@T11 in chloroform was obtained and characterized by gravimetric analysis and flame absorption spectroscopy to estimate the AuNWs

coverage. Total dry content of 4.0 mg/mL and gold content of 3.2 mg /mL were determined, suggesting that the nanomaterial was composed of 80% gold and 20% organic material.

The nanostructure was further characterized via TEM, which revealed an average diameter of 2 nm and length up to 5 μ m. (**Figure 1**). The nanostructure was demonstrated to be unstable when exposed to the 200 keV electron beam of the microscope, which led to a fragmentation of the NWs overtime during the analysis (**Figure S1**).

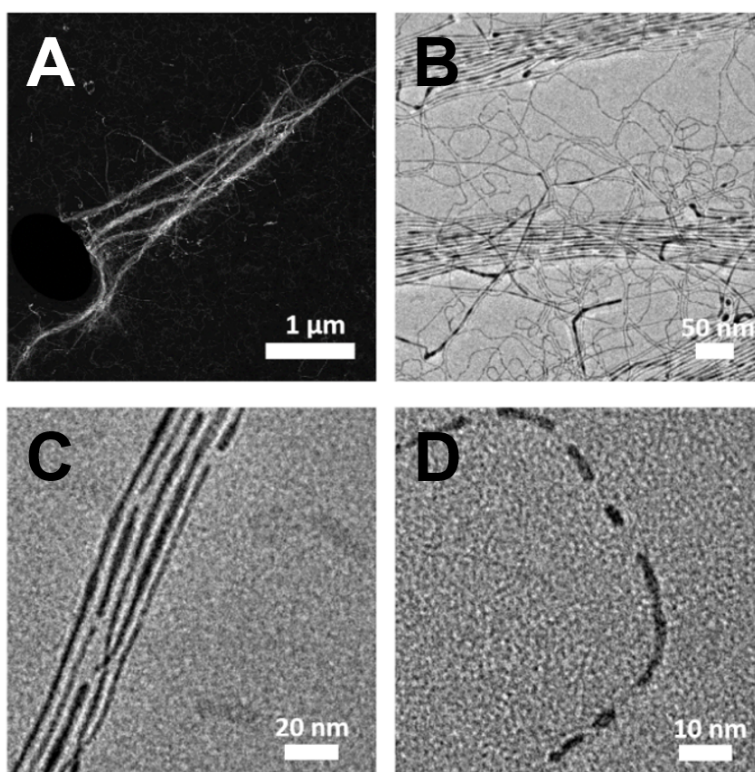


Figure 1. TEM images of AuNWs@T11. **A)** Low-magnification STEM-HAADF image of AuNWs@T11. **B,C)** Higher magnification TEM images showing partial wire alignment. **D)** NWs appear to be fragmented under high magnification, but this is due to the highly focused electron beam damaging the thin nanostructure.

For this reason, AuNWs appear to be broken in multiple locations, a phenomenon that is known to frequently happen under exposure to the highly energetic TEM electron beam.²⁷ The different contrasts come from the fact that single, isolated nanowires are very thin and do not block a lot of the electron beam that is employed in TEM, therefore they appear as grey. The darker ones are regions in which no single nanowire can be observed but shows two or more layers of nanowires that dried on top of each other on the TEM grid.

Energy dispersive x-ray spectroscopy (EDX) and electron diffraction (SAED) analyses revealed that the nanostructure is mostly composed of gold atoms with the characteristic FCC crystal cell structure (**Figure S2**). The effectiveness of the ligand exchange was confirmed by ¹H-NMR (**Figure S2**), no residual oleylamine peak can be noticed in the ¹H-NMR spectrum of AuNWs@T11. The effects of the thiol binding onto the gold surface are reflected in the NMR spectrum of the bound ligand; as expected, the SH proton signal of T11 (at 3.55 ppm) disappears after ligand exchange, and the aromatic signals get deshielded due to the electron attracting features of the Au surface. This is consistent with previously NMR of small thiols conjugated to the surface of gold nanoparticles.²⁸ The surface stabilization of AuNWs related to surface coating was demonstrated by recording the UV-VIS spectrum of oleylamine-coated AuNWs compared to AuNWs@T11 over a period. The stabilizing effect of T11 on the morphology of the nanostructure is shown in **Figure 2**. Without the thiolated ligand, an absorption maximum between 500 and 600 nm appears and gets more intense as time passes, suggesting the formation of round nanoparticles. On the other hand, T11-coated NWs display complete stabilization and the absence of spherical impurities over a wide period, maintaining their UV-VIS features for several weeks of storage at room temperature.

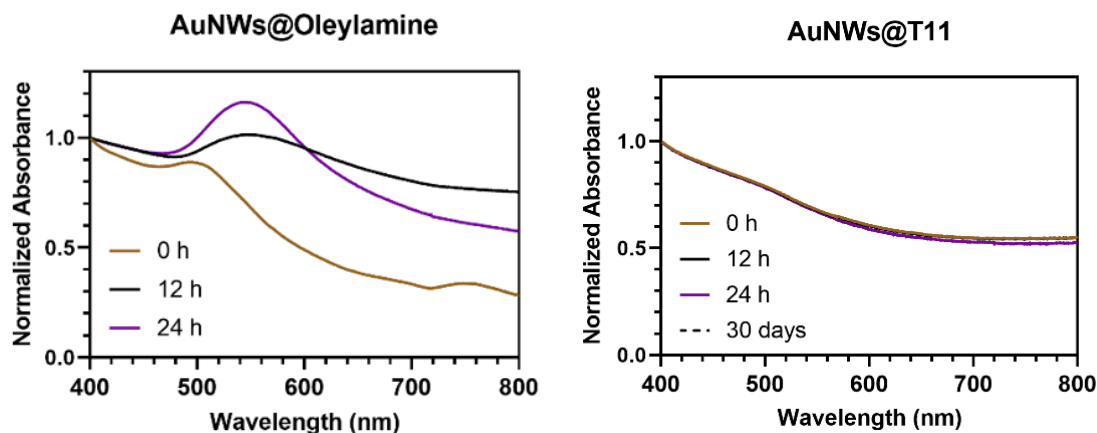


Figure 2. Visible spectrophotometric analysis of AuNWs solutions (THF, 25°C) recorded at different time steps after their purification.

Additionally, the surface stabilization of AuNWs by the thiolated ligand was confirmed by comparing TEM images of AuNWs@Oleylamine and AuNWs@T11 at 2 and 4 weeks after purification (**Figure S4**), showing no morphological changes in the T11-coated structure and the extensive presence of bigger and rounder particles in the non-stabilized specimens. No appreciable differences in stability were observed changing the solvent (chloroform, THF and hexane).

The characterized AuNWs were then formulated in a polymer matrix to test their electrical properties. PDMS (SYLGARD 184) was selected as the polymer matrix thanks to its flexibility and easy manufacturing, and AuNWs@T11 were added in defined amounts to achieve gold concentrations in the composites equal to 0.03 wt.% and 0.08 wt.% (30 ppm and 80 ppm). The preparation is summarized in **Scheme 1b**: AuNWs@T11 in chloroform are mixed with an appropriate amount of component A of the SYLGARD 184 elastomer kit and, after evaporation of the organic solvent, component B is added, leading to a thick homogeneous dispersion of AuNWs in the PDMS monomer mixture, with no observable sedimentation of the nanostructure over 5

days. Then, thin films are produced by spin-coating on Petri dishes and cured in an oven at 60°C for 1 h to achieve polymerization of PDMS. Even though stabilized AuNWs tend to form strongly brownish-black solutions, such low concentrations allowed for the preparation of transparent elastomeric strips (**Scheme 1c**). The film transparency has been quantified by measuring the optical transmittance of the films throughout all the visible wavelength range, revealing transmittance above 80% even for the highest AuNWs concentration. (**Figure S5**). Higher NWs loadings interfere with the polymerization of PDMS and increasing AuNWs concentration above 0.5% causes a significant loss in the transparency of the composite.

The nanocomposites were firstly characterized in terms of their dielectric properties by measuring their impedance at rest by varying applied AC frequency (**Figure S6**). Impedance resulted inversely proportional to the frequency (capacitive behavior) and that there is an effect on the overall impedance of the film (measured applying the electric field along the longitudinal direction) due to the AuNWs; however, there is no substantial variation of the measured impedance with the different concentrations.

Characterization of the impedance variations with the elongation applied through a dynamometer has been done on films with different concentrations of AuNWs (**Figure S7**). Before this characterization, a pure PDMS film was also measured. **Figure 3A** shows an impedance vs frequency graph measured with different applied elongations that does not show a definite trend. When inserting AuNWs in the PDMS matrix, the film starts to show an impedance that does not depend on the frequency and depends on the applied strain (**Figure 3B,C**). As shown in **Figure 3D**, the slope of the curve impedance vs strain increases if the concentration of NWs increases, i.e., the film becomes more sensitive to elongation.

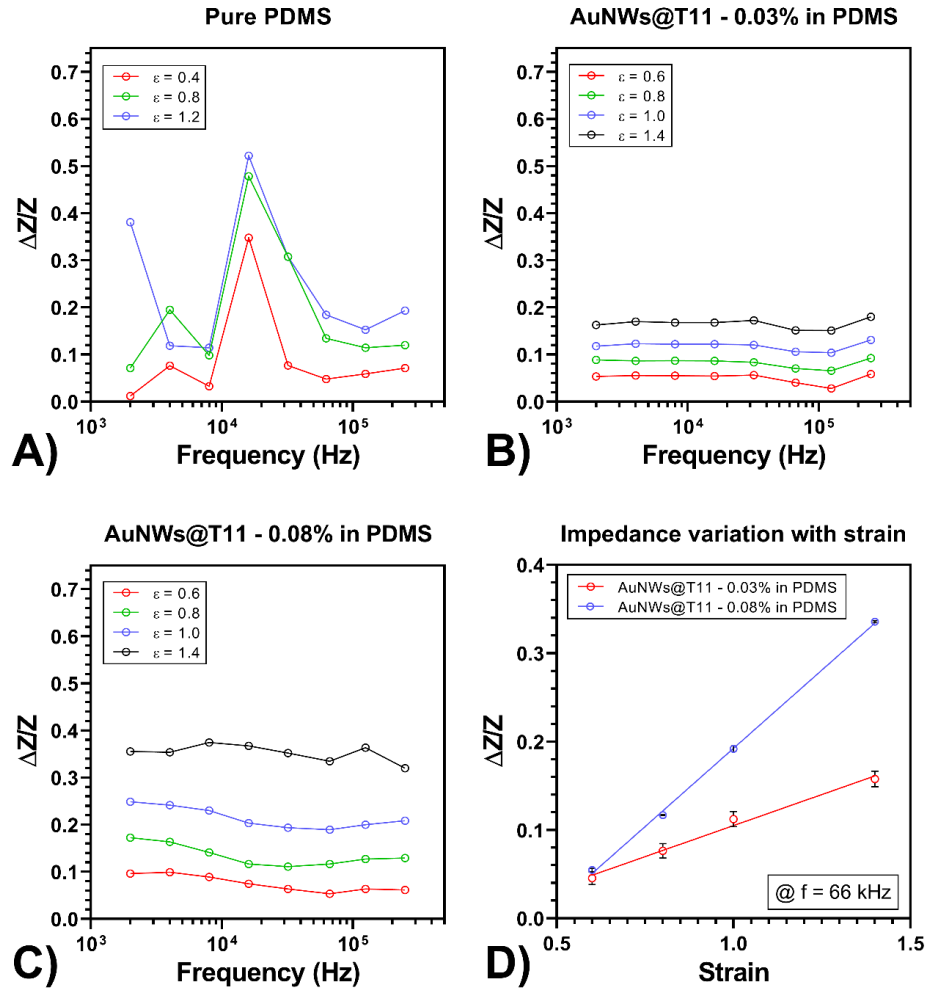


Figure 3. Results on impedance vs. strain measurements made on elastomeric films containing AuNWs. (A) Relative variation of impedance vs frequency in pure PDMS films; (B) and (C) Relative variation of impedance vs frequency in PDMS films containing different concentrations of AuNWs at different strain values (ε); (D) comparison between PDMS films containing different concentrations of AuNWs in terms of sensitivity to strain (the error bars refer to 2 different measurements on the same sample).

These observations seem to indicate that the embedded conductive NWs add a resistive component, which is frequency-independent, to the observed impedance. However, the measured impedance is affected by many effects (for instance those related to the contacts between the film and the copper surface of the sample holder), not easily distinguishable. At a first approximation, AuNWs may be modelled as purely resistive filaments embedded in an insulating PDMS matrix: therefore, not considering the parasitic components possibly due to the contacts, the equivalent circuit of the device can be modelled as a parallel of a resistor R_{Au} and a capacitance C_{PDMS} , whose global impedance is given by:

$$Z(\omega) = \frac{R_{Au}}{1 + (\omega C_{PDMS} R_{Au})^2} - i \frac{\omega C_{PDMS} R_{Au}^2}{1 + (\omega C_{PDMS} R_{Au})^2}$$

Comparing the experimental curves, we derive that the impedance Z is independent of the frequency and we may assume that the observed phenomenon is mainly due to the variation of the NWs resistance with elongation. When a strain is applied, AuNWs embedded in the film should possibly align with the strain direction. The increase of the impedance with elongation seems to indicate that their resistance increases, whilst the increase of the slope of $\Delta Z/Z$ vs $\Delta L/L$ with the AuNWs concentration must be further investigated to elucidate the exact mechanism behind the observed sensitivity.

In conclusion, ultrathin AuNWs have been prepared with a fast, easy, and reliable methodology: surface coating was attempted for the first time and successfully obtained with thiol-ending ligand T11. The so-coated AuNWs demonstrated high stability during the manufacturing process such as incorporation in PDMS matrix keeping transparency. The behavior of the nanostructured materials showed appealing electrical properties, with films impedance which does not depend on the frequency but depends on the applied strain even at very low Au payloads (0.03%).

ASSOCIATED CONTENT

Supporting Information. Experimental section and ^1H -NMR spectra. Additional TEM analysis and pictures of the impedance measurement setup.

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Author Contributions. The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

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