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Functionalization of Silver Nanowire Transparent Electrodes with Self-Assembled 2-Dimensional Tectomer Nanosheets

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Here, we describe the unusual self-assembly of amine-terminated oligoglycine peptides into extended two-dimensional sheets in the presence of silver nanowires. The resulting tectomer sheets are shown to have a strong affinity for the nanowires through a charge-transfer interaction as evidenced by X-ray photoelectron spectroscopy. We show that extended assemblies of metalpeptide hybrids offer additional augmentative functionalities, for instance, the tectomer sheets are hydrophobic in nature and act as a protective layer preventing oxidation and degradation of the nanowires when exposed to atmospheric conditions. Moreover, for silver nanowire percolating networks the presence of the peptide markedly increases the overall electrical conductivity through mechanical squeezing of wire-wire junctions in the network. The peptide-metal interface can be controlled by pH stimulus thus potentially offering new directions where silver nanowire assemblies are used for transparent electrodes ranging from antimicrobial coatings to biosensors.

KEYWORDS: silver nanowires, peptides, peptide functionalization, protective coatings, transparent electrodes

INTRODUCTION

Silver nanowires (AgNWs) have recently attracted considerable interest in various fields of science and industry. Due to the nanoscopic diameter and high aspect ratio of the individual wires, films of AgNWs combine high optical transmission with low sheet resistance. These properties, together with their decreasing cost and large-scale manufacturing methods, make them perfect candidates as replacement materials of Indium Tin Oxide (ITO) for transparent electrode applications to name a few. $1-9$

In nature, the interactions between amino acids, peptides and proteins with metal ions have a fundamental role in many biological processes including oxygen transport and storage, enzyme inhibition, etc.¹⁰ Even though silver ions are not involved in metabolic pathways, they are highly important from a medical point of view.¹¹⁻¹² Also, peptides have the ability to spontaneously selfassemble into complex and sophisticated structures¹³⁻¹⁶ and can undergo structural changes based on changes in pH, temperature or ionic strength as well as electric/magnetic fields. Thus, they can act like smart building blocks in sensors, electronics and a range of stimuli-responsive materials.¹⁷⁻ 18

There is an increasing interest in controlling bio-interfaces for a range of medical and diagnostic device applications. The interplay of biological systems and nanomaterials can provide diverse functionality. For example, immobilisation of peptides on the surfaces of inorganic implants can aid their biocompatibility or enhance the sensitivity of bio-sensors.¹⁹ Covalently linking other peptide systems to metal nanowire-based sensors such as silicon nanowires has enabled the selective detection of small molecules.²⁰ However, as pointed out by Vallee et al., the interactions of proteins or peptides with solid oxide surfaces are still not fully understood¹⁹, and fundamentally, peptide-surface interactions are very substrate specific.²¹⁻²²

Silver-based nanomaterials have a high affinity for non-covalent binding to peptides^{[12,](#page-28-0) [23](#page-29-0)} normally mediated through Ag+ interacting with thiol, amino, cyanide and carboxylic acid groups. Such functionalization routes are crucial for efficient exploitation of the fascinating, physicochemical properties of AgNWs providing, amongst others, biocompatibility, antimicrobial, active wetting, cell attachment and molecular immobilization functionalities.²⁴⁻²⁸

Here we utilize the ability of amino-terminated oligoglycine peptides to self-assemble into unique two-dimensional (2D), smooth, rigid, nanosheets known as tectomers that resemble the structural features of graphene, $29-32$ to form hybrids with AgNWs. A 2D sheet-like morphology for an assembled peptide secondary structure is rarely available due to their inherent chirality and tendency for uni-directional growth;³³⁻³⁴ but would provide enhanced interfacial interaction features for functional devices. Tsygankova et al. have reported self-associating properties of different oligoglycines in aqueous medium, which depend on the aliphatic chain length and the number of glycines in the oligoglycine antennae.³⁰ Other oligopeptides are not known to form tectomers, as only oligoglycines are capable of forming polyglycine II-type structure, stabilized by a cooperative system of hydrogen bonds.³² Moreover, oligoglycine-based bolaamphiphiles with dicarboxylic head groups instead of amino terminal groups are not able to form tectomers, due to the electrostatic repulsion between the ionized carboxylic groups.²⁹

The exceptional structural and chemical features of tectomers have already been successfully utilized to coat negatively-charged surfaces, 30 biological membranes, 35 and polymer fibers, 36 and hold a promising potential in the field of antiviral applications.³⁷⁻³⁸ Previously we showed, for the first time, that tectomers effectively coat carboxylated carbon nanotubes (CNTs) and strongly interact with graphene oxide and can be used for scaffolds in tissue engineering³⁹ as well as pH responsive nanocarriers for theranostics.²⁹

This paper is focused on establishing a fundamental understanding of the interactions between AgNWs and tectomers. We also show that such hybridization leads to the formation of transparent hybrid electrodes with enhanced electrical conductivity and novel moisture protection functionalities, which creates opportunities in extending the applications of AgNW networks in new directions.

MATERIALS AND METHODS

Fabrication of silver nanowire networks. 5 mg mL⁻¹ AgNW dispersions in isopropyl alcohol (IPA) were purchased from Seashell Technologies (www.seashelltech.com) and used as received. The average diameter and length of the nanowires (as provided by the supplier and from AFM measurements) were 60 nm and 10 μ m respectively. Using transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) respectively, we confirmed that AgNW's surface was covered with a discontinuous residual layer of polyvinylpyrrolidone (PVP) of thickness ≤ 1 nm, presumably used in AgNWs synthesis (see Supporting Information). The initial AgNW dispersion was further diluted with IPA until a final concentration of 0.1 mg mL^{-1} was reached. A large number of samples of low, medium and high-density AgNW films were fabricated by spraying AgNW dispersions onto transparent electrode grade glass substrates with an airbrush. It is widely recognized that spray deposition directly onto a substrate is one of the most promising methods for assembling AgNWs from the liquid phase, as it requires no additional surface treatment whilst also enabling large-scale deposition on a variety of substrates (glass, plastic, fabric, to name a few). $6,40-41$ $6,40-41$

Preparation of oligoglycine solutions. Biantennary oligoglycine peptide C_8H_{16} (-CH₂-NH- Gly_5)₂* 2HCl, purity > 95%, was supplied by PlasmaChem GmbH (www.plasmachem.com) and used without further purification. This oligoglycine was dissolved in ultrapure water (pH 6.3) and the solution was bath sonicated for 2 min in a 100 W Branson 2510 bath sonicator (Branson Ultrasonics Corporation, Danbury, CT, USA) and then probe sonicated in a 500 W probe sonicator (Cole Parmer Ultrasonic Processor, Cole-Parmer Instruments, Vernon Hills, IL, USA) in pulsed mode (1 s "on", 3 s "off", amplitude: 21%) for 16 min (4 min of effective "on" sonication). The total energy transferred to the samples during this process was ~ 1000 J. Three oligoglycine

concentrations were prepared: 1, 0.5, and 0.01 mg mL^{-1} . pH values of solutions were measured using a Crison Basic 20 pH meter. pH values in water depend on oligoglycine concentration, due to the presence of HCl from oligoglycine synthesis^{31, 39}, thus, for the final 1, 0.5, and 0.01 mg mL⁻¹ 2T solutions, pH was 5.6, 5.8 and 6.3 respectively.

The same sonication procedure was used to prepare various aqueous oligoglycine dispersions in in buffer (pH 2.2 and 7.4). Buffer pH 2.2 and buffer pH 7.4 were prepared from citric acid and Na₂HPO₄ solutions, and from Na₂HPO₄ and NaH₂PO₄ solutions, respectively.

Fabrication of tectomer coatings on AgNW networks. To form AgNW/tectomer hybrids, drop-casting and dip-coating methods were used. During drop-casting, the tectomer solution was applied drop by drop on top of the AgNW networks until the whole substrate was covered with the solution and then left to dry at room temperature for 12 h. During the dip-coating process, the substrate with AgNWs coatings were vertically immersed in the tectomer solution at 1 mg mL^{-1} at a constant speed of 10 mm·min⁻¹ using an automated dipper attached to the Langmuir trough (NIMA technology, model 612D). The substrate remained fully immersed for 1 minute and the substrate was withdrawn, at a speed of 2 mm \cdot min⁻¹.

Characterization methods. Transmission electron microscopy (TEM) characterization of the oligoglycine assemblies was conducted using a TECNAI T20 microscope (FEI, USA). A drop of an oligoglycine solution was placed on a Cu grid coated with a holey carbon film, and most of the solution was then wicked away with a tissue paper. Topographic and phase-contrast imaging of the AgNW networks and AgNW/tectomer hybrids on glass substrates was performed using a commercial atomic force microscopy (AFM) system (Ntegra Prima, NT-MDT Co, Russia) in semi-contact mode with a standard Si cantilever (NSG10) having a spring constant of \sim 11.8 $N \cdot m^{-1}$.

The current–voltage characteristics have been obtained using a Keithley Model 4200 utilizing the two-point probe technique. To measure electrical properties of AgNW/tectomer hybrids, three types of AgNW networks with a sheet resistance $R_s \sim 50 \Omega$ sqr⁻¹, \sim 1 kΩ sqr⁻¹ and \sim 1 MΩ sqr⁻¹ were used respectively. All three types of electrodes were spray deposited on large glass substrates (touch screen grade glass), as described above, and divided into smaller electrodes of similar rectangular shape (~ 1 cm x 2 cm). Silver paint was applied along the width of the rectangle to act as contacts, and needle probes were placed on the contacts and connected to the conductivity measuring unit in order to obtain current-voltage (I-V) characteristics. Drops (0.05 mL) of the aqueous tectomer solution at oligoglycine concentrations ranging from 0.01 to 1 mg mL-1 were applied on top of AgNWs and I-V characteristics were obtained every couple of minutes for each sample until the droplets had completely evaporated.

The AgNW networks with and without tectomer coating where exposed to harsh atmospheric conditions of 85°C and 85% relative humidity (RH) by placing them in a custom-made humidity chamber. After 2 h the sheet resistance measurement was repeated to record a change in the R^s upon exposure to the harsh environment.

Optical transmission spectra were obtained using a Shimadzu 2501PC UV-vis spectrometer. Xray photoelectron spectroscopy (XPS) was performed using Theta Probe X-ray Photoelectron Spectrometer System. The spectra were energy referenced to the C1s signal located at a binding energy (BE) of 284.8 eV. A curve fitting of the spectra was performed using Void curves as fitting functions. Contact angle measurements were performed using a KRÜSS Drop Shape Analyzer DSA 100 system (Hamburg, Germany).

RESULTS AND DISCUSSION

Characterization of biantennary oligoglycine and tectomer assemblies. The biantennary oligoglycine C_8H_{16} (-CH₂-NH-Gly₅)₂ molecule is amphiphilic in nature: the alkyl -(CH₂)₁₀- center is hydrophobic, while both olygoglycine antennae are hydrophilic (Figure 1a and b). Such amineterminated antennary oligoglycines have the ability to spontaneously form tectomers in solution which consist of rigid, 2D, crystalline platelet-like structures,²⁹ stabilized by a highly cooperative system of hydrogen bonds between oligoglycine chains (Figure 1c). It was shown that the assembly process is even more rapid on negatively charged surfaces, such as mica, because of protonated amine groups assisting in the assembly on the substrate with opposite charge.³²

Figure 1. The structure of biantennary oligoglycine (a,b) and the schematic representation of the assembly in a tectomer platelet (c) consisting of three planes of oligoglycine assemblies on glass substrate, with the hydrophobic surface exposed to the air.

The interactions of amino-terminated tectomers with other surfaces will vary depending on the type. As we reported recently, carboxylated CNTs extensively interact with tectomers forming stable inks in aqueous solutions due to the favourable electrostatic interactions between them. In contrast, pristine un-functionalized CNTs are not able to form hybrids with the tectomer.³⁹ On the other hand, hydrogen bonding between oxygen functional groups in graphene oxide is responsible

for their strong interaction with tectomers. Additional control of the tectomer assembly on a supporting substrate can be achieved through covalent functionalization of the tectomers' terminal amino groups. $32, 37-38$ $32, 37-38$

Multilayered tectomer stackings together with individual plateles have been observed by AFM and TEM on dried samples prepared by drop-casting or spin coating. The tectomer platelets varied in size and thickness, showed sub-nanometre surface roughness, with no structural defects present. According to AFM studies (Figure 2 a and c), single-layered platelets had an average thickness of 5.7 nm (Figure 2b). This corresponded to three planes of oligoglycine assemblies – antennae, directed opposite to each other with the hydrophobic surface always exposed to air, as represented in Figure 1c, being the height of each plane \sim 2 nm.

Figure 2. (a) AFM topography image of platelets deposited on a glass substrate and (b) corresponding line profile showing single-layered platelets. (c) AFM topography image of 2 and 3 layered tectomers and (d) a corresponding line profile showing the thickness of these platelets. (e) TEM micrograph of the tectomer at a concentration of 1 mg mL^{-1} deposited on holey carbon film from solution. (f) AFM investigation of tectomer platelet thickness as a function of the number of layers (more than four layers being considered multilayers).

Thicker platelets consisting of additional layers (each additional layer consisting of 2 planes of \sim 2 nm each) were also found (Figure 2 c and d), ensuring that the hydrophobic surface was facing the air. The flake thickness as a function of layer number is plotted in Figure 2f. More than four layers are here considered as multilayers. The hydrophobic nature of the tectomer coatings was confirmed by contact angle measurements (Figure 9d-f).

AgNW/tectomer hybrids were formed by direct deposition of the oligoglycine solution via dropcasting onto spray-deposited AgNW networks on glass substrates. The morphology of pristine AgNW networks were described elsewhere. ⁶ The capillary forces induced by the evaporation of water forced the individual 2D tectomer platelets (Figure 3a), as well as larger aggregates (Figure 3b), to conform to the topography of the wires. A mixture of platelet sizes was present in the initial solutions (Figure 2e), while further aggregation took place on the substrate.

Figure 3. AFM 3D topography images showing tectomer platelets successfully conforming to the AgNW structure (a) individual platelets deposited from 0.01 mg mL-1 aqueous oligoglycine dispersions and (b) aggregates deposited from 0.5 mg mL-1 aqueous oligoglycine dispersions, respectively.

X-ray Photoelectron Spectroscopy (XPS) was used to understand the nature of interfacial interactions between AgNWs and tectomers. In order to obtain detailed XPS information, highresolution scans of the spectra of Ag3d, N1s and O1s with their respective deconvolutions are depicted in Figure 4. The AgNW Ag3d spectrum exhibits Ag3d_{5/2} and Ag3d_{3/2} featured at 368.9 eV and 374.9 eV respectively with a spin-orbit separation of 6 eV (Figure 4a). When the tectomer was deposited on to AgNWs, a significant shift to lower binding energy (BE) of 1.5 eV for the Ag3d peaks was observed which indicates strong donation of electron density towards the wires. From the above measurements, it is clear that Ag atoms strongly interact with tectomers and that this interaction is not effected or prevented by the presence of any residual PVP on the AgNW surface. The N1s peak at 399 eV for the pristine tectomer is attributed to the presence of amino groups (NH₂), which is in a good agreement with the literature.⁴² This N1s peak in the hybrid displays a shift to higher BE (399.4 eV) associated with a decrease in the electron density at N atoms due to electron donation to the Ag atoms of the nanowires (Figure 4b).

Figure 4c shows that the O1s peak in the hybrid is shifted to higher BE compared to its position in the pristine tectomer also indicating partial transfer of oxygen (O) lone pair electrons from the tectomer carbonyl groups to surface Ag atoms. This suggests that O atoms of carbonyl groups close to the amino terminal groups in the assembly are also able to interact with the surface. In fact, it is well known the O tendency to coordinate with Ag atoms, as evidenced by the preferential interaction of glycine with silver nanoparticles through the carbonyl site over the amino site.⁴³ Moreover, previous density functional theory (DFT) studies indicate that binding of silver clusters with simple amino acids, such as glycine, is dominated by the anchoring of N-Ag, O-Ag bonds and the non-conventional N-H \cdots Ag and O-H \cdots Ag hydrogen bonds.⁴⁴ O1s spectra for the AgNWs is included in Figure 4c together with the corresponding devolution analysis. The main O1s peak at 532 eV can be assigned to oxygen in SiO² from the glass support and the shoulder at lower energy to the presence of substoichiometric Si oxides (SiO_x) , both in good accordance with the literature.⁴⁵ These signals are significantly lower for the hybrids or tectomer only, which means that the tectomer layers efficiently coat the glass substrates in the studied samples.

Figure 4. (a) High resolution XPS spectra Ag 3d region of pristine AgNWs vs AgNW/tectomer hybrid. (b) N1s spectra of pristine tectomer vs AgNW/tectomer hybrid. (c) O1s spectra of AgNWs, tectomer and a hybrid of both. Fitted peaks (Voigt functions) are shown as dashed lines.

The strong interaction between both materials in the hybrid formation was further demonstrated by the fact that when the tectomers and AgNWs were mixed together in water, within two minutes hybrid particulates rapidly flocculated resulting in a clear supernatant (Figure 5a). The flocculated hybrid material was investigated using TEM. As can be seen in the Figure 5 b and c, the tectomer formed extensive coatings along and between wires. As a consequence of the strong interaction, the platelets simultaneously adsorbed to more than one wire, acting as a junction, leading to "bridging flocculation" in solution.⁴⁶ Additionally, immersing AgNWs deposited on a glass substrate into the tectomer solution at 1 mg mL^{-1} and then very slowly withdrawing the substrate (slow dip-coating process) led to the assembly/growth of the tectomer platelets on the surface of the wires (Figure 5d, e).

Figure 5. (a) A photograph of AgNW/tectomer hybrid mixed in solution showing spontaneous flocculation. (b, c) TEM micrographs corresponding to the flocculated hybrid material, showing that the strong interactions between tectomer and nanowires also occur in solution. (d) AFM topography and (e) phase images tectomer platelets crystallised on the wires via a very slow dipcoating deposition method.

pH –**responsive nature of tectomers.** Peptides can be designed to undergo self-assembly by applying an external trigger, for example $pH⁴⁷⁻⁴⁸$ By changing the pH of an oligoglycine solution towards acid or base, the state of the oligoglycine assembly can be significantly altered, since change in pH can make the amino terminal group of the oligoglycine chain be protonated or neutral.^{[31,](#page-30-2) [39](#page-31-1)} As shown in Figure 2, 1 mg mL⁻¹ oligoglycine solutions in ultrapure water comprised platelets of a few layers in thickness. The solution was visually clear, and the associated measured pH is 5.6 (middle solution shown in Figure 6b). In acidic conditions (pH 2.2) there was a strong protonation of amino terminal groups and electrostatic repulsion between neighbouring positive charges that triggered disassembly of the platelets as shown on the TEM micrograph in Figure 6a.

The deprotonation of amino groups by shifting the pH conditions to pH≥7.4, triggered massive aggregation of oligoglycine (Figure 6c), resulting in the solution becoming cloudy and the eventual settling of tectomer aggregates with time. This pH-dependent self-assembly and disassembly of the tectomer platelets was rapid and fully reversible and could be performed repeatedly.²⁹

Figure 6. pH-dependent assembly and disassembly of tectomer platelets in solution and on the AgNW network. (b) Optical images of oligoglycine solutions at different pH values. (a) TEM micrographs of 1 mg·mL-1 oligoglycine samples at pH 2.2 and (c) pH 7.4. (d) AFM topography images of AgNWs/tectomer hybrids on glass substrates exposed to solutions of different pH values.

Tectomers can reversibly be formed or destroyed in response to pH, and therefore this feature can be used to control the assembly process on AgNW networks. Thus, we exposed AgNW/tectomer hybrids to buffer solutions of various pH values. For this study, AgNW/tectomer hybrid electrodes prepared by depositing a 1 mg mL⁻¹ oligoglycine solution in ultrapure water were tested. As can be seen in the middle AFM image in Figure 6d, the AgNWs were covered with individual and few layer thick tectomer platelets. When such a sample was immersed for 5 seconds in a buffer pH 2.2 solution, the tectomer platelets disassembled and fully detached from the surface of the wires. However, when the hybrid sample was exposed to a buffer pH 7.4, the platelets assembled into a thick uniform coating on the wires (right image in Figure 6d).

The extent of interfacial interactions between AgNWs and tectomers is also pH-modulated. According to XPS results, the interaction involves donation of electronic density from nitrogen in the amino groups of tectomers, to the silver surface: thus, when the pH is increased toward alkaline conditions above pH 7.4, the number of protonated amino groups in the tectomers decreases, leading to a stronger AgNW-tectomer interaction. It has to be noted that the sensing capabilities of the tectomer/AgNW hybrids are not investigated here being beyond the scope of this paper.

Electrical performance of AgNW/tectomer hybrid structures. AgNWs were spray deposited on glass substrates at various densities, and a sheet resistance (R_s) versus transmittance (T) curve was obtained (Figure 7). The solid line represents a fit to the data using a model described elsewhere.⁴⁹ The choice of the deposition process was dictated by the fact that the spray deposition process is industrially scalable and can produce uniform, highly transparent films on large substrates. As can be seen in Figure 7, at low nanowire density the transmittance is above 92%, which gradually decreases as more AgNWs are added. It should be noted, that due to the large

diameter of AgNWs (~60 nm) the nanowire electrodes scatter a portion of the transmitted light. The 3D AFM topography image in the inset in Figure 7 shows a medium density AgNW network with $R_s \sim 10 \text{ k}\Omega$ and 91% transmittance, with 2-3 layers of AgNWs uniformly distributed on a substrate.

Several electrodes of low $(R_s \sim 1 \text{ M}\Omega \text{ sqr}^{-1})$, medium $(\sim 1 \text{ k}\Omega \text{ sqr}^{-1})$, and high $(R_s \sim 50 \Omega \text{ sqr}^{-1})$ density AgNW networks on glass substrates were fabricated that closely follow the transmittance vs. sheet resistance curve $(T \text{ vs } R_s)$ presented in Figure 7. Drops of tectomer solution, with oligoglycine concentrations ranging from 0.01 mg mL⁻¹ to 1 mg mL⁻¹ were deposited on the AgNW electrodes, and current-voltage (I-V) characteristics were obtained as a function of time for each sample. I-V characteristics of AgNW networks and hybrid structures exhibit excellent ohmic behaviour, regardless of the density of AgNWs and the concentration of tectomers. The schematic of the design of the device is shown in the inset in Figure 8a.

Figure 7. Left: Transmittance (@550 nm) plotted versus sheet resistance of AgNW networks of various densities with the theoretical fit of the data. The model fitted to the data has been described elsewhere.⁴⁹ The R-T curve shown is the aggregate data from three separate measurements. The small deviation of the data from the model fit indicates very good reproducibility. Right image: A representative 3D AFM topography image of a medium density AgNW network.

The change in R_s as a function of time, for one particular medium density AgNW network, with 0.5 mg mL $^{-1}$ oligoglycine concentration, is shown in Figure 8a. As can be seen, upon application of the tectomer solution (at t = 0 min), there is an increase in R_s from 1.25 k Ω ·sqr⁻¹ to 1.45 k Ω ·sqr⁻¹ ¹. It has been shown that AgNWs have poor adhesion to most substrates, including glass.² Since the nanowires are also hydrophilic, the water can easily access the spaces between the wires and consequently decrease the contact area between them. Such behaviour was also observed at other oligoglycine concentrations used, and the same trend was observed when pure water was placed on the pristine electrode. As the process of drying progressed, after approximately 10 minutes, the top of the droplet became flatter and the R_s approached the initial R_s of the electrode. After approximately 45 minutes the R_s drops sharply. At this critical point, the water is almost fully evaporated and the tectomer platelets are assembled on the wires. Once the water completely disappears from the electrode surface the R_s becomes constant. In this particular example shown in Figure 8a the R^s was reduced by almost 50%.

Figure 8b presents the percentage change in R_s as a function of oligoglycine concentration in the starting solution. If a drop of the solution is deposited at very low oligoglycine concentration (0.01 mg mL^{-1}) there is either an insignificant improvement, or a deterioration in R_s, for both medium and high density AgNW networks. For medium density films, there is a strong shift by 50 and 70% toward lower R_s , when the oligoglycine solution is deposited at 0.5 and 1 mg mL⁻¹, respectively.

Figure 8. (a) Measured sheet resistance (R_s) as a function of time for a representative medium density AgNW networks with tectomer solution (at 0.5 mg mL⁻¹ oligoglycine concentration) placed on top and dried at room temperature. Inset: Schematic of the device design used to obtain current-voltage characteristics. (b) Percentage change in R_s as a function of oligoglycine concentration in the initial aqueous solution.

In the case of the high density AgNW network, a small improvement in R_s (maximum 20%) is observed. The results for the lowest density AgNW electrodes are not shown here, since the electrode becomes non-conducting upon addition of the tectomer platelets on the wire surface. Also it has to be pointed out that for a very low oligoglycine concentration, not a decrease but an increase in R^s occurs for both medium and high density AgNW networks, therefore a linear trend is not followed for all the tectomer concentrations studied in this work.

During water evaporation, the overall concentration of tectomer increases and therefore we hypothesize that individual tectomer platelets and tectomer aggregates (Figure 9 a-c) start to mechanically press down on the AgNWs, thus increasing wire-to-wire contact. Such effect has been observed previously for AgNWs hybridized with pristine graphene or graphene oxide, leading to the enhanced electrical conductivity due to mechanical squeezing mechanism. ⁴⁷⁻⁵¹ At lower concentrations of tectomers $(0.01 \text{ mg} \text{ mL}^{-1})$ oligoglycine solutions), there are very few platelets, therefore only a small percentage of junctions can be successfully coated. Hence at this concentration, the tectomers are ineffective in terms of improving properties of the electrodes regardless of AgNW density.

When the concentration of tectomers in the starting solution was increased (0.5 or 1 mg mL^{-1}) oligoglycine concentration), significant reductions in R_s for medium density electrodes was observed. This is because the medium density AgNW network consists of 2-3 layers of wires, therefore tectomers can efficiently mechanically compress most junctions of the network.

For a high density network (consisting of 5 and more layers of wires) the tectomer/AgNW interaction only involves the outer AgNW layers of a multi-layered AgNW network resulting in only a minor R_s decrease.

For a very low-density, corresponding to a AgNW network structure (1-2 layers of wires) within the percolated regime, tectomers may electrically disconnect the network or enhance resistivity due to their dielectric nature. It has to be noted that the mechanism of enhancement of electrical properties of the tectomer/AgNW hybrid electrode is not the same as in the case of hybridising nanowires with pristine graphene, since in the former case it is most likely due to the mechanical compression of AgNWs that reduces the space between individual wires within the network.⁵⁰⁻⁵²

In the case of hybridization of nanowires with graphene, additional conductive pathways are created that further enhance the electrode performance.

Moisture barrier properties of tectomer coatings for AgNW networks. In the case of AgNW transparent electrodes, their performance is closely related to their degradation.⁵³ Under ambient conditions, AgNWs suffer from oxidation and sulfurization, therefore it is critical to protect the electrodes from harmful environmental factors such as humidity, oxygen/ozone, as well as gaseous sulphur-containing compounds. There have been a number of coatings developed and reported in the literature with the aim to protect nanowires from deterioration, based on coating individual wires, or overcoating the whole nanowire network.^{[7,](#page-27-1) [54-57](#page-33-0)}

Two AgNW networks with the R_s of \sim 2 kΩ/sqr were fully coated with the oligoglycine solution at 1 mg mL⁻¹ by drop casting. For comparison, two AgNW films with similar R_s were left uncoated. After complete evaporation of water, the R_s , of the fully coated by the tectomer, hybrid electrodes was significantly reduced from ~2 k Ω /sqr to 65 Ω /sqr, but with only 4% reduction in transmittance (from 91% to 87%) that was due to the deposited tectomer. Within 48 hours the R_s increased to 92 Ω /sqr. However, after that initial increase it stayed constant when measured a further 48 hours later.

Owing to the well-known oxidative nature of AgNWs, the R_s of the pristine AgNW networks increased by \sim 10% in 4 days after the initial spray deposition when kept at RT on the laboratory bench. After that initial time of 96 hours of keeping the samples at RT on open bench top, both types of electrodes were exposed to a humid and hot atmosphere using a built-in-house controlled humidity chamber. The R_s of hybrid structures exposed to such conditions for 2 hours increased by 10-14%, however the R_s of pristine AgNW networks increased by a significant 200%.

It is possible to control the coating's nature by changing the tectomer deposition method. For example, using a dip-coating process with a fast withdrawal speed extensive tectomer coatings over the entire AgNW network area can be formed, with a thickness of 1-2 tectomer layers (Figure 9 g and h) with the overall transmittance of the hybrids decreased by only 2% from 91% to 89% at 550 nm, but with a significant reduction of R_s by 95%. This is an indication that the tectomer coatings can potentially provide outstanding protective and moisture barrier properties.

Figure 9. AFM topography images and corresponding water contact angles of medium density AgNW networks covered with the tectomer platelets at an initial oligoglycine concentration of (a, d) 0.01 mg mL⁻¹, (b, e) 0.5 mg mL⁻¹ and (c, f) 1 mg mL⁻¹. (g) AFM topography and (h) phase images of ultrathin oligoglycine coatings formed on top of the AgNWs by dip-coating. (i) A photograph of the transparent electrode with the tectomer coating, showing self-cleaning functionality.

Owing to the way biantennary oligoglycine tectomer self-assembles (Figure 1c), it always exposes the hydrophobic face to the air.³⁶ Thus, the hydrophobicity of tectomer-coated AgNW networks was investigated by water contact angle measurements. It can be seen in the inset in Figure 9d that the contact angle of water on AgNWs deposited on a glass substrate is 33° . The presence of tectomer platelets at an initial oligoglycine concentration 0.01 mg mL⁻¹ on AgNW networks increases the water contact angle to 57° (Figure 9d). AgNW networks become significantly more hydrophobic (90 $^{\circ}$ and 84 $^{\circ}$) when the tectomer coating is deposited from 0.5 and 1 mg mL-1 oligoglycine solutions, respectively (Figure 9 e and f). The slight contact angle decrease measured when increasing the oligoglycine concentration to 1 mg mL^{-1} can be attributed to increased surface roughness and surface heterogeneity.⁵⁸

It is important to note, that when the droplet of water is left on the pristine AgNWs for 3 min the water contact angle decreases from 33° to 11° indicating significant water penetration into the network. The contact angle does not change with time for the hybrid structures. These results indicate that the tectomer coatings could serve as an alternative moisture barrier for the conductive films.

CONCLUSION

We have shown that the hybridization of 1D AgNWs with 2D peptide assembled nanosheets results in the formation of transparent hybrid nanostructures with enhanced electrical conductivity coupled with stimuli driven adaptive/smart features. Donation of electron density from peptide to silver atoms accounts for the strong interaction and the adsorption of tectomer platelets onto the nanowire surface. Tectomers platelets mechanically press down on the AgNWs, thus increasing wire-to-wire contact, and increasing conductivity of the AgNW network, which in turn enables the fabrication of low-cost transparent electrodes since lower amount of AgNWs are needed to attain a certain conductivity value. Also tectomer coatings can protect AgNWs against oxidation and sulfurization, which may be of interest at certain steps in the AgNW industrial production and processing, as well as to improve electrode durability. Water barrier properties can also provide self-cleaning functionality to AgNW transparent electrodes. AgNW/tectomer hybrid electrodes offer promise as an alternative material for flexible electronic devices to replace ITO films. On the other hand, adhesive properties of tectomers can be interesting to extend of the use of AgNWs to aqueous media, as AgNWs have poor adhesion to most substrates, including glass. In these situations the tectomer coatings prevent the detachment of the nanowire network when immersed in aqueous media, broadening their applications in new directions such as antimicrobial coatings or biosensors.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website at DOI: XX.XXXX/xxxxxxxx. Transmission electron microscopy and X-ray photoelectron spectroscopy images showing an insignificant present of PVP on nanowire surface. (PDF)

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Notes

The authors declare no competing financial interest.

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TOC Figure

