Cross-Linked Gold Nanoparticle Composite Membranes as Highly Sensitive Pressure Sensors

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1. Introduction

Hybrid inorganic/organic nanoparticle composites exhibit unique characteristics making them highly interesting for various sensing applications. Due to their tunneling-based charge transport, substrate supported composite films of organically capped noble metal nanoparticles were extensively investigated as chemiresistors.[1–8] Here, sorption of chemicals leads to swelling of the organic matrix[9] with a concurrent change of the interparticle distances. Hence, the presence of the analyte can be measured by monitoring the film’s resistance.[9,10] Similarly, straining a nanoparticle composite directly affects the interparticle distances, and thus significant changes in the material’s resistance are observed.[11,12] This observation resulted in the investigation of substrate-supported gold nanoparticle (GNP) films as highly strain sensitive coatings. Gauge factors of up to ≈200 were observed by Herrmann et al. for spray-coated films of ≈18 nm sized GNPs that were capped with 4-nitrothiophenol ligands.[13] Similar gauge factors exceeding 100 were observed by Farcau et al. for highly ordered monolayered wires of GNPs.[13] Such strain-sensitive coatings can easily be deposited onto flexible substrates by ink-based procedures such as ink-jet printing, spin-coating, spray coating or drop-casting. Potential fields of application include monitoring fatigue of constructive parts and medical diagnosis. In the latter case they can act as sensing elements for motion, pressure or pulse-wave monitoring.[14–18]

More recently, nanoparticle composite films have been deposited onto three-dimensionally structured substrates to yield nanometer-thin freestanding membranes with lateral extensions in the micrometer range.[19] Noble metal nanoparticle membranes render a new material class. They enable addressing their unique optoelectronic properties (interparticle tunneling, plasmonics) originating from individual or collective characteristics of the incorporated nanoparticles directly, without substrate effects. Further, the lack of a substrate allows for coupling these properties to the mechanical characteristics of the membranes and enables new applications and fundamental studies of these interesting materials.

Even though their investigation is still in its infancy, some studies addressed the characterization and potential applications of such GNP membranes. Liu et al. investigated the plasmonic absorption features of so-called plasmen sheets,[20] that is, 2D assemblies of GNPs, and explored their potential application as optically transduced chemical sensors.[21] With respect to (electro-)mechanical systems, on the one hand, freestanding tense nanoparticle membranes were employed as actuators[22] and resonators.[23–26] Resonance shifts of such devices were used for chemical sensing,[27] or photodetection.[28] On the other hand, the mechanical properties of freestanding nanomembranes were probed by AFM nanoindentation experiments[29]
as well as micro-bulge testing with interferometric or AFM based deflection readout. In general, elastic moduli in the low GPa range were observed for composites of ligand-stabilized, polymer-grafted and organically cross-linked GNP s. Recently, we demonstrated the tunability of the elasticity of α,ω-alkanedithiol (ADT) cross-linked GNP membranes by adjusting the chain length of the ADT cross-linker.

Being comparable to polymers, the elastic modulus of GNP membranes is significantly lower than that of conventional strain sensing materials, such as metals or crystalline semiconductors, and of purely inorganic nanomembranes such as graphene or transition metal dichalcogenides (TMDs). This enables deflection and straining of nanometer-thin GNP membranes by only weak forces. Along with their high gauge factors, metal nanoparticle composite membranes can, hence, respond with strong resistance changes to slight perturbations and are, therefore, well suited as highly sensitive transducers in micro-/nanoelectromechanical systems (MEMS/NEMS). Recently, we presented the first resistive gauge pressure sensor based on a free-standing GNP membrane, sealing a rectangular cavity. Due to the evolving pressure difference with respect to the internal cavity pressure, the membrane was deflected upon changes of the environmental pressure and responded with pronounced resistance changes. Gauvin et al. characterized the electromechanical properties of freestanding GNP-monolayers using conductive AFM nanoindentation experiments.

In this paper, we report the fabrication of highly responsive resistive pressure sensors based on free-standing 1,9-nonanedithiol (9DT) cross-linked GNP membranes deposited onto silicon substrates with slit-shaped apertures. We demonstrate that the sensitivity of these pressure sensors can be tuned by reinforcement of the GNP membrane by an additional polymethylmethacrylate (PMMA) layer. Furthermore, the use of holey substrates for sensor fabrication allowed us to study the GNP membranes’ topography in situ by AFM during the application of pressure. The correlation of the AFM deflection data with the applied pressure and the measured resistance change enabled the direct electromechanical characterization of the free-standing membranes without the influence of an underlying substrate. Compared to nanoindentation-based methods, this approach has two significant advantages: First, due to the geometry of the bulged membranes, which can be approximated as a cylinder section, a rather homogeneous stress is applied to the membrane. Second, instead of measuring only a puntual deflection a rather large section of the membrane is sampled and the shape of the bulged membrane is recorded continuously. This ensures that the electromechanical responses are interpreted correctly by applying the simple cylinder model. Additionally, the precise topographic observation of the membrane’s surface by AFM ensures that the observed electromechanical responses are not influenced by crack formation, as discussed earlier.

2. Results and Discussion

Figure 1a illustrates the experimental configuration used in this work. First, 9DT cross-linked GNP films were deposited onto glass substrates following a layer-by-layer spin-coating procedure reported earlier. To this end, amine-stabilized GNP s with an average core diameter of 6.3–73 nm were used. Transmission electron microscopy (TEM) images of the GNP s and UV–vis absorbance spectra of GNP solutions used are provided in Section S1, Supporting Information. The thickness of the as-deposited GNP films was determined by AFM. For this purpose, sections of the films were scratched using a canula and AFM scans were performed at the edges of the scratches. An exemplary AFM scan is provided in Figure 1c. The film thickness was obtained as step height of the profiles extracted from the AFM data. The as-deposited GNP films had a thickness between 41 nm and 68 nm.

![Figure 1](image-url)
GNP multilayer composites commonly show ohmic conduction\cite{Abeles1981, Aizawa2003, Oka2004, Abeles2004} and their conductivity can be described following a thermally activated tunneling model.\cite{Abeles1981, Abeles2004, Abeles2006, Abeles2008} The GNP films used for sensor fabrication showed ohmic conductivities between 1 and 3 $\Omega^{-1}\text{m}^{-1}$, which is roughly one order of magnitude higher than values observed earlier for 9DT cross-linked GNP films consisting of significantly smaller particles.\cite{Aizawa2003, Aizawa2004, Aizawa2005}

As described by Abeles' granular metal theory\cite{Abeles1981} and further experimentally observed for GNP films\cite{Aizawa2003, Aizawa2004} a larger particle size results in a lower charge transport activation energy and hence an increase in overall conductivity. Also, composites consisting of larger GNPs contain a lower number of tunneling junctions per unit volume. Current-voltage data as well as absorbance spectra of the GNP films are provided in the Sections S3 and S2, Supporting Information, respectively. Figure 1e depicts a scanning electron microscopy (SEM) image of the GNP film used for the fabrication of device A3 (see below). The individual GPNs forming the granular film are clearly recognized.

Second, electrode microstructures featuring slit apertures were fabricated. A SEM micrograph of an exemplary substrate is shown in Figure 1d. Here, a deep-reactive ion etching process was utilized to emboss slit-shaped through-holes into a silicon wafer. Following thermal oxidation of the wafer a titanium/gold layer was deposited by means of thermal evaporation and electrodes terminated in proximity to the aperture were structured using direct-write photolithography and etching procedures.

Finally, free-standing GNP membranes were prepared by detaching the GNP films from their initial glass substrates and transferring onto the electrode microstructures. In the case of devices A1, A2, and A3 the transfer was performed via a flotation process.\cite{Abeles2005} Here, the glass substrates carrying the GNP films were floated on a water surface. After a while the GNP films were detached by immersing the glass substrate, leaving the GNP membrane floating at the liquid-air interface. Subsequently, as-fabricated microstructures were used to skim the floating GNP membranes from the water surface. While drying, the membranes settled onto the microstructures, remaining free-standing over the predefined apertures. An optical micrograph of device A1 is presented in Figure 1b. For the fabrication of device B a stamp-transfer process was used.\cite{Abeles2004, Abeles2005} For this purpose, the membrane was coated with a supporting PMMA layer and subsequently transferred from its original substrate to a polydimethylsiloxane (PDMS) stamp.\cite{Xu2017} Afterward, the GNP film was stamped onto a microstructure and released from the PDMS stamp by applying a temperature cycle.\cite{Xu2017} It is to note that in case of device B the PMMA layer remained on top of the GNP film. The overall thickness of the stack of 463 nm was measured using AFM and is the sum of the PMMA thickness (406 nm) and the thickness of the underlying GNP film (57 nm) measured before the deposition of PMMA. Optical micrographs of all investigated devices are provided in Section S6, Supporting Information. The membranes investigated in this study did not show any visible holes or cracks.

For performing AFM-bulge tests with in situ resistance measurements the devices were mounted onto a custom-built AFM sample holder that enabled connecting them to a gas inlet.\cite{Abeles2004, Abeles2005} A second port of the sample holder was connected to commercial reference pressure sensors. Positive differential pressure was applied using a nitrogen gas cylinder, while negative differential pressure were applied using a vacuum pump. Adjustment of the sample pressure was achieved using a cascade of needle valves. The resistance of the devices was measured between the two electrodes (cf. Figure 1a), which were contacted using wire bonding or silver paint, using a Keithley 2601a source measure unit. A detailed description of the setup is provided in Section S4, Supporting Information.

Figures 2a and 2b depict the resistive responses ($\Delta R/R_0$) measured between the terminals of devices A1 and B to differential pressure, respectively. A video recorded during a similar experiment is provided in the Supporting Information. It clearly shows the deflection of device A1’s GNP membrane during the application of negative differential pressure and the accurate replication of the applied pressure in the measured relative resistance change. As expected, the devices show an approximately symmetric response to negative and positive pressure. While the
latter lead to inward and outward deflection of the membrane, respectively, both deflections induce strain and consequently an increase of interparticle distances and membrane resistance. We note that a slight hysteresis can be observed, which we assign to retarded relaxation of the membrane upon removal of the pressure.\[32\] The data plotted in Figure 2a reveal changes in resistance of ≈6% when loading device A1 with ±6 kPa. The lower part of the plot shows the absolute of the sensitivity S, which is the derivative of the response curve:

\[
S = \frac{1}{R_0} \frac{d\Delta R}{d P}
\]

Here, \(P\) denotes the differential pressure. In order to smooth the derivative of the experimental data a Savitzky-Golay filter was applied. In the pressure range \(|P| < 2 \text{ kPa}\) the sensitivity considerably exceeds \(1 \times 10^{-3} \text{ mbar}^{-1}\). This sensitivity is approximately one order of magnitude higher than the sensitivity we observed for gauge pressure sensors reported in an earlier publication.\[34\] We attribute the higher value shown here to the optimized geometry, that is, the wider cavity, the smaller distances between the electrodes and the cavity edges, as well as the larger particle sizes.\[11\] The value is exceptionally high compared to sensitivities reported for other recent NEMS sensors (cf. Table 1). Approximately ten times higher sensitivities were reported by Chen et al.\[48\] for resistive pressure sensors employing palladium nanoparticles deposited onto polymer diaphragms as strain sensitive transducers. However, these sensors featured significantly larger diaphragms \((19.6 \times 10^4 \mu\text{m}^2)\) compared to approximately \(4 \times 10^4 \mu\text{m}^2\) membranes used in our study.

**Table 1.** Performance comparison table, listing the resistive sensitivities of different NEMS pressure sensors. Similar comparisons were reported by Wang et al.\[49\] and Wagner et al.\[50\]

| Device structure                          | Sensitivity S \([\text{mbar}^{-1}]\) | Reference |
|-------------------------------------------|-------------------------------------|-----------|
| GNP membrane diaphragm/transducer sensor | >1 \times 10^{-3}                    | This work |
| GNP membrane diaphragm/transducer gauge sensor | 1.01 \times 10^{-4}                  | Schlicke et al.\[34\] |
| Suspended graphene                        | 3.0 \times 10^{-6}                  | Smith et al.\[31\] |
| Graphene on suspended perforated SiN\(_x\) membrane | 2.80 \times 10^{-5}                | Wang et al.\[51\] |
| Graphene on suspended imperforated SiN\(_x\) membrane | 6.67 \times 10^{-6}                | Zhu et al.\[32\] |
| Graphene on fixed perforated layer on Si substrate | 0.88 \times 10^{-6}                | Hurst et al.\[52\] |
| Single-walled carbon nanotube on diaphragm | ≈1 \times 10^{-4}                  | Stämpfer et al.\[54,55\] |
| Multi-walled carbon nanotubes embedded into PMMA | ≈3.5 \times 10^{-5}                | Fung et al.\[56\] |
| PtSe\(_2\) covered with PMMA             | 1.39 \times 10^{-4}                | Wagner et al.\[50\] |
| Pd nanoparticles on 5 mm diameter PMMA diaphragm | 1.3 \times 10^{-2}                | Chen et al.\[44\] |

\(^a\) Exceptional device.

Figure 2b shows the response of device B, featuring the thicker, stacked GNP/PMMA membrane, as described above. Here, significantly higher pressures are required to achieve relative resistance changes in the percent range. The sensitivity of this device ranges around \(0.05 \times 10^{-1} \text{ mbar}^{-1}\). The lower sensitivity is due to the additional PMMA layer that has a similar Young’s modulus as the GNP film, while having a markedly higher thickness \((57 \text{ nm GNP film}/406 \text{ nm PMMA})\). This result demonstrates that the pressure sensitivity and the measurement range of such pressure sensors can be adjusted by adding a passive reinforcing PMMA layer to the device. In contrast to the response curve of device A1 the data of device B show a region of low sensitivity near zero differential pressure. As described in the Supporting Information, Section S8, this behavior can be explained by a higher pre-stress of membrane B (cf. Table 2).

| Device | Membrane thickness t\(_m\) [\text{nm}] | Sensitivity S \([\text{mbar}^{-1}]\) | Gauge factor g | Elasticity E [GPa] | Pre-stress \(\sigma_0\) [MPa] |
|--------|--------------------------------------|-----------------------------------|---------------|------------------|-----------------|
| A1     | 41                                   | 9.0 \times 10^{-4}               | 15            | 3.6              | 3.1             |
| A2     | 41                                   | 1.1 \times 10^{-3}               | 18            | 3.0              | 1.2             |
| A3     | 68                                   | 3.3 \times 10^{-4}               | 11            | 3.2              | 3.2             |
| B      | (57 + 406)                           | 6.9 \times 10^{-3}               | 15            | 2.9\(^a\)        | 7.4             |

\(^a\) Sensitivity estimated by linear fits to \(\Delta R/R_0(P)\) data over the complete bulge test pressure range (cf. Section S6, Supporting Information); \(^b\) Effective modulus of elasticity of the GNP/PMMA membrane stack.

In an earlier study we reported GNP membrane based gauge pressure sensors that consisted of a microcavity sealed by a GNP membrane.\[13\] Here, a pressure difference between the exterior and the interior of the closed cavity led to bulging. However, for testing such sensors by variation of the external pressure they had to be placed into a pressure cell. In this case monitoring the membrane deflection can hardly be achieved, as suitable measurement instrumentation would have to be incorporated into the cell. Also optical deflection measurements, such as interferometric measurements are difficult to perform because the refractive index of the cell’s atmosphere changes along with the cell pressure. In this study we solved these problems by using substrates with through holes. Thus, differential pressures bulging the membrane can be applied by adjusting the pressure acting on the back side. This eliminates the need of a pressure cell and enables to access the membrane’s upper side using topographic measurement techniques such as AFM (cf. Figure 1a) or interferometry.

Figure 1b exemplarily shows a topographic AFM scan of device A1 as an overlay on an optical micrograph. To decrease the scan time during the AFM-bulge experiments, the topography of this region \((100 \times 100 \mu\text{m}^2)\) was sampled by conducting 16 line scans with 512 samples each at varying applied pressures. The topographic data of scans of device A1 acquired at 0 and −5.7 kPa are depicted in Figures 3a and 3b, respectively. During the measurements a bias of 5 V was applied to the membranes to measure their resistance. To evaluate the deflection, stress and strain induced by the pressure loading, a cylindrical fit model was applied.\[38\] Cylinders, defined by a radius \(R_c\),
a support vector of the central axis $\vec{r}_0$ and an angle in the $xy$-plane $\theta$ for taking into account the orientation of the scanned membrane section (with respect to the direction of the slit aperture) were fitted to each set of AFM data acquired at different differential pressures using a custom algorithm. The evaluation process is outlined in Section S5, Supporting Information. The cylindrical fits are exemplarily depicted as false-colored surfaces in the respective figure parts 3a and 3b and underline the good agreement of the cylindrical model with the measured topographic data. The dependence of the cylinder radius $R_c$ on the applied differential pressure is depicted in Figure 3c. As expected, $R_c$ decreases significantly with increasing differential pressure acting on the bulged membrane.

From the cylinder radius $R_c$ the in-plane stress $\sigma$ of the membrane was derived using the model for a thin-walled cylindrical pressure vessel:\[36\]

$$\sigma = \frac{P R_c}{t_m} \quad (2)$$

Here, $P$ denotes the applied pressure, $R_c$ is the cylinder radius and $t_m$ the thickness of the GNP membrane. Further, the membrane strain was calculated from the aperture width $2a$ and the bulge arc length $s$ according to Equation (3).

$$\varepsilon = \frac{s}{2a} - 1 \quad (3)$$

The arc length was derived from the aperture width and the cylinder radius following a geometric model:\[31]\]

$$s = 2R_c \arcsin\left(\frac{a}{R_c}\right) \quad (4)$$

Using the obtained data the electromechanical properties of the GNP membrane could be derived. Figure 4a shows the relative resistance change $\Delta R/R_0$ measured between the terminals of device A1 as a function of imposed strain, corresponding to differential pressures between 0 and $-6$ kPa (light blue dots).

The resistance change measured between the device’s terminals is composed of the pressure-induced resistance change of the freestanding membrane section and a constant, parasitic parallel and serial resistance, which is governed by the surrounding substrate-supported membrane. To take this influence into account the electric currents traversing the membrane were simulated using a finite element model implemented by the COMSOL 5.4 software package. Figure 5a depicts a section of the simulation geometry for sample A1. A constant conductivity of $\sigma_{film}$ was attributed to the GNP film surrounding the freestanding membrane section. The latter was described using the same baseline conductivity $\sigma_{film}$, altered by $\left(\Delta R/R_0\right)_{membrane}$. A constant change of resistance was assumed for the whole freestanding membrane area.

Using a parametric sweep simulation $\left(\Delta R/R_0\right)_{membrane}$ was altered and the relative resistance change between the device’s terminals $\Delta R/R_0$ was computed for each device (cf. Figure 5b for device A1). Further details regarding the simulations are

Figure 3. a,b) The blue dots represent topographic AFM scan data of device A1 scanned at an applied differential pressure of a) 0 kPa and b) $-5.7$ kPa. The surfaces depict fits of a cylinder to the measured data. c) Radius $R_c$ of the fitted cylinders as a function of the applied differential pressure measured at descending and ascending pressure.

Figure 4. a) Relative resistance change measured between the terminals of device A1 $\Delta R/R_0$ (light blue dots) and calculated resistance change of the free-standing membrane section $\left(\Delta R/R_0\right)_{membrane}$ (dark blue dots) upon loading with negative differential pressure. The solid line depicts a slope fit to the data. b) Plot of the respective stress/strain data. The solid line depicts a linear fit to the data.
provided in Section S5, Supporting Information. Using the obtained relation, the relative resistance change of the free-standing membrane section \( \Delta R/R_0 \) was calculated based on the relative resistance change measured between the device terminals and is depicted as dark blue dots in Figure 4a.

Because of the high elastic modulus of the GNP films directly translates into changes of the interparticle distances. Hence, due to the tunneling-based transport an exponential increase of the GNP composites’ resistance in response to the applied strain is expected. This was observed by Farcau et al.\(^{[11]}\) and Herrmann et al.\(^{[14]}\) for substrate supported wires and films of larger (\( \sim 18 \) nm) GNPs. However, linear approximations apply very well within the low strain regime.\(^{[31]}\) Such linear relations are also commonly observed for disordered multilayer films of smaller GNPs.\(^{[12,14]}\) Here, reorganization of GNPs upon the application of strain can additionally contribute to result in the observed linear behavior. In accordance with these earlier studies the resistance change of the GNP composites observed in this work is approximately linear and the strain sensitivity can be described by the gauge factor \( g \).

\[
\left( \frac{\Delta R}{R_0} \right)_{\text{membrane}} = ge
\]

(5)

By fitting the data depicted in Figure 4a according to Equation (5) a gauge factor of \( g = 15 \) was extracted for the free-standing GNP membrane of device A1. This value is typical for disordered GNP films.\(^{[12,14]}\) It is higher than the value of \( g = 7 \) roughly estimated in our previous study.\(^{[14]}\) We attribute this deviation to the different experimental setup used in our earlier work, which only allowed a rough estimation of the membrane deflection and strain. The new experimental design employed in this work enables accurate monitoring of the bulged membrane and, hence, a straightforward derivation of the membrane strain. Further, in our current work we used larger GNPs for membrane preparation than in our previous study (6.3–7.3 nm vs 3.5 nm). It is well known that the gauge factor of GNP based resistive strain gauges increases with the GNP size.\(^{[11]}\)

From the stress–strain data depicted in Figure 4b, the Young’s modulus of the membrane material was derived by fitting a linear function according to Equation (6) to the data. Due to the high aspect ratio of the GNP membranes of \( >4 \) (cf. Section S6, Supporting Information), the axial strain can be neglected and a plane-strain state can be assumed. In this case, the measured circumferential (hoop) stress and strain are related by the plane-strain modulus \( E/(1-\nu^2) \).

\[
\sigma = \frac{E}{1-\nu^2} \varepsilon + \sigma_0
\]

(6)

Here \( \nu \) is the Poisson ratio. Taking into account a value of \( \nu = 0.33 \), which is commonly used for GNP composite materials,\(^{[28,57]}\) we obtain an elastic modulus of \( E = 3.6 \) GPa, which is in good agreement with values previously measured for 9DT cross-linked GNP membranes using bulge tests.\(^{[31,33]}\) The membrane further exhibits a pre-stress of \( \sigma_0 = 3.1 \) MPa. Such values in the low MPa range are also typical for nanoparticle composite membranes deposited onto microscale apertures.\(^{[27,31,33]}\)

The results of the electromechanical analysis of three devices (A1, A2, A3) consisting of free-standing 9DT cross-linked GNP membranes are summarized in Table 2. The data show a good agreement when comparing the individual devices. The electromechanical analysis of device B, consisting of the stacked GNP/PMMA membrane, yielded a gauge factor of \( g = 15 \) and an elastic modulus of \( E = 2.9 \) GPa. As expected, the gauge factor is within a similar range as a comparable strain-sensitive material (similar particle size, same linker molecule) was used for electromechanical transduction and the PMMA layer does not take part in charge transport. The elastic modulus is governed by the whole membrane stack, consisting of the GNP membrane and the PMMA layer. However, the similarity of this value to the moduli observed for the A-type devices is expected as PMMA has a similar elastic modulus (3 GPa)\(^{[58]}\) as the underlying GNP membrane.

Due to their nanoscale granular structure the GNP membranes investigated in this study are, to some extent, permeable for gases. This was observed in experiments described in Section S7, Supporting Information. Here, a GNP membrane was employed as diaphragm in a gauge pressure sensor, sealing a microcavity having a picoliter volume. We note that the observed permeability does not affect the measurements and sensor performances reported in our current study as the...
gas permeation through the membranes is slow and the differential pressure is kept constant dynamically. Still, permeation through GNP composite membranes is highly interesting and a subject of ongoing studies in our group. Controlling the permeability of freestanding nanoparticle membranes, for example, by adding additional polymer layers, or by varying the membranes’ granular structure, is of great interest with respect to various potential applications. For example, He et al. investigated molecular diffusion through ultimately thin GNP monolayer membranes for filtration purposes.[39] We are currently investigating the effect of molecular diffusion into GNP composites with respect to chemical sensing applications.

3. Conclusions

We demonstrated that the elasticity and pronounced resistive strain sensitivity of membranes consisting of molecularly cross-linked noble metal nanoparticles render them suitable for the fabrication of highly sensitive pressure/force sensors. Devices with freestanding membranes of only a few 1000 μm² and resistive sensitivities exceeding 1 × 10⁻¹ mbar⁻¹ were fabricated.

Moreover, we showed that AFM-bulge tests combined with in situ conductance measurements provide a powerful tool for the electromechanical characterization of nanoparticle composites.

4. Experimental Section

Synthesis of GNP: Three batches of GNPs, capped with 1-dodecylamine or oleylamine, were used for GNP membrane fabrication. The particles were synthesized according to methods by Peng et al.[38] and Wu et al.[39]. TEM micrographs of the GNPs and solution phase UV–vis absorbance spectra of the GNP solutions are provided in Section S1, Supporting Information.

Preparation of GNP Membranes: Glass substrates (Carl Roth, Manching, 22 × 22 mm²) were cleaned with acetone in an ultrasonic bath, immersed into demineralized water (18.2 MΩ cm), dried, and treated with air plasma. The deposition of 9DT cross-linked GNP films was conducted following a procedure published earlier[37] with slight modifications. For film deposition, the substrates were placed onto a spin-coater and constantly rotated at 3000 rpm. First, a solution of 9DT (7.4 mM in methanol for devices A, 2 mM in methanol for device B) was deposited two times onto the rotating substrate (2 × 100 μL). Subsequently, 10 μL of GNP solution in heptane (see the UV–vis spectra in Section S1, Supporting Information, for information on the absorbance of the GNP solutions) and 2 × 10 μL of methanolic 9DT solution (7.4 mM for devices A, 2 mM for device B) were dropped alternately onto the glass substrate. A ~30 s delay was kept after each deposition. The latter two steps represent one deposition cycle. By 3 to 5 repetitions of this cycle, the desired film thickness was obtained. Following deposition, the GNP films were immersed into the respective methanolic 9DT solutions overnight, rinsed with acetone, and dried under ambient conditions.

Preparation of Electrode Substrates: Electrode substrates were prepared by etching through-holes into a silicon wafer using a deep reactive ion etching process as described earlier.[40] Subsequently, the substrates were thermally oxidized to create an insulation barrier on the silicon. Further, a titanium/gold (~10/~40 nm) layer was deposited by means of thermal evaporation and structured to form the adjacent electrodes by means of direct-write photolithography and etching steps.

Flotation-Based Transfer of GNP Membranes: Segments of the glass-supported as-deposited GNP films were floated onto demineralized water. After a few days the films could be detached by immersion of the substrate and remained floating at the liquid air interface and were skimmed using the as-prepared microstructures.[24,31,33,34,37]

Stamping-Based Transfer of GNP Membranes: Stamp-based transfer of GNP membranes onto 3d microstructures was conducted as described earlier.[34,45–47]

In brief, substrate-supported GNP films were coated with an additional PMMA layer and transferred onto a PDMS stamp. Afterward, the membrane/PMMA stack was stamped onto a 3d electrode microstructure, pretreated in an air plasma. Finally, the PDMS stamp was removed by temperature cycling leaving the GNP membrane/PMMA stack on the microstructure.

Electromechanical Characterization: Electromechanical characterization of the GNP membrane pressure sensors was performed via AFM bulge testing with in situ charge transport measurements. Details on the experimental setup and the data acquisition and evaluation method are provided in Sections S4 and S5, Supporting Information, respectively.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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