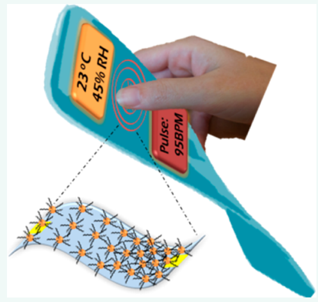
Flexible Sensors Based on Nanoparticles

Meital Segev-Bar and Hossam Haick*

The Department of Chemical Engineering and Russell Berrie Nanotechnology Institute, Technion—Israel Institute of Technology, Haifa 3200003, Israel

ABSTRACT Flexible sensors can be envisioned as promising components for smart sensing applications, including consumer electronics, robotics, prosthetics, health care, safety equipment, environmental monitoring, homeland security and space flight. The current review presents a concise, although admittedly nonexhaustive, didactic review of some of the main concepts and approaches related to the use of nanoparticles (NPs) in flexible sensors. The review attempts to pull together different views and terminologies used in the NP-based sensors, mainly those established *via* electrical transduction approaches, including, but, not confined to: (i) strain-gauges, (ii) flexible multiparametric sensors, and (iii) sensors that are unaffected by mechanical deformation. For each category, the review presents and discusses the common fabrication approaches and state-of-the-art results. The advantages, weak points, and possible routes for future research, highlighting the challenges for NP-based flexible sensors, are presented and discussed as well.



KEYWORDS: sensor · flexible · nanoparticle · strain · pressure · electronic skin · wearable · robotics

Future Applications Call for Flexible Sensors. Cost-effective, soft, transparent, lightweight, easy-to-fabricate, biocompatible and versatile sensing systems based on bendable and/or stretchable sensors will soon revolutionize the sensing technology. Figure 1 shows key applications of flexible sensors and examples of pertinent visions:

• *Flexible Panels*: Pliable transparent display panels and e-paper (Figure 1a), which use a simple mechanical switch mechanism to locate a touch in flat panel,[1] will soon replace analog resistive touch screens.

• *Electronic skin (e-skin)*: **A human-like**, highly pixelated **sense-of-touch** that translates miniscule deformation in spatial resolution into signals and has the capacity to withstand very large repeated deformation is currently at advanced stages of development.[2−8] This sensing platform is termed e-skin. It is anticipated that e-skin could equip inanimate objects with a sense of touch and with an ability to sense other environmental parameters.[2,9−11] For example, e-skin would allow dexterous robotic hands to perform complex tasks like tying a shoelace or pouring a drink, rather than binary touch sensing that can merely distinguish whether or not touch occurs (*cf.* Figure 1b; lower image).[9,11] E-skin would also endow surgical robots[12,13] (see Figure 1b; upper image) with tactile sensation, enabling improved minimal invasive surgery (MIS) as well as high-quality medical care in hard-to-reach areas in the human body.[14] E-skin based on high-lateral resolution arrays of flexible sensors could help restoring the natural sense of touch to people who use prosthetics (Figure 1c).[15−18]

• *Wearable sensors*: Flexible sensors in conjugation with efficient, wearable wireless recorders are anticipated to play a key role in future medical diagnostics and physiological monitoring, for early diagnosis through continuous monitoring of complex health conditions and for patients under treatment (Figure 1d).[19,20]

• *Structural Health Monitoring (SHM)*: Large-area, flexible sensing systems would allow monitoring a wide variety of loads during the lifespan of buildings, bridges, wind turbines, aircrafts, naval vessels and other types of large structures, due to routine operation, natural catastrophes (for example, earthquakes and hurricanes), long-term environmental corrosion, and unexpected severe incidents such as blast and impact.[21,22] One important example is sensing premature cracking in an aircraft body, enabling replacement of damaged parts before the possible occurrence of life threatening conditions (Figure 1e). Nevertheless, detecting and locating cracks in structural components and joints that have high

* Address correspondence to hhossam@tx.technion.ac.il.

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feature densities is a challenging problem and requires sensors with high gauge factors.

• *Space flight*: Flexible sensors that can easily be produced by printing could transform the way NASA builds spacecraft (see Figure 1f).[23,24] Printed flexible sensing technology on the spacecraft's exterior and interior would have a dramatic impact, considerably decreasing the mass, volume and total operation cost. Large, integrated, continuous areas of flexible sensors in a spacecraft would facilitate simple measurements of pressure, temperature, humidity, pH levels and surrounding gases, which are critically important for defining a new environment. In addition, these systems could monitor a pressurized tank or space station module and alert the crew to various hazardous conditions (Figure 1f).

Impressive proof-of-concept results have been achieved in each of the above-mentioned applications.[3−6,8,22,25,27−67] Nevertheless, the reliability, reproducibility, and the complexity to obtain integrated flexible systems are still major impediments to the realization of flexible sensors in real-world applications. For example, flexible sensors that are based on organic field effect transistors[55,64,68] are relatively inexpensive but might suffer from multistep processing[55,57] and high operation voltages.[8,57,59] Flexible sensors based on nanowire-array field effect transistors may offer

VOCABULARY: electronic skin – an array of flexible sensors that is able to imitate some of the skin sensing abilities such as the sense of touch and temperature; **wearable sensing technology** – sensors that are integrated in textile and fabrics. The main purpose of these sensors is for medical diagnostic and health monitoring; **strain gauge** – a device that measures the strain of an object attached to it; **gauge factor** – the response of a strain gauge divided by the strain applied on it, *viz.*, the sensitivity of a strain gauge; **fatigue test** – the reproducibility of a sensing signal after elastic deformation cycles; **strain-tunable sensitivity** – the response of the sensors toward a measurable property (*e.g.*, temperature) is altered when the sensor is under strain.

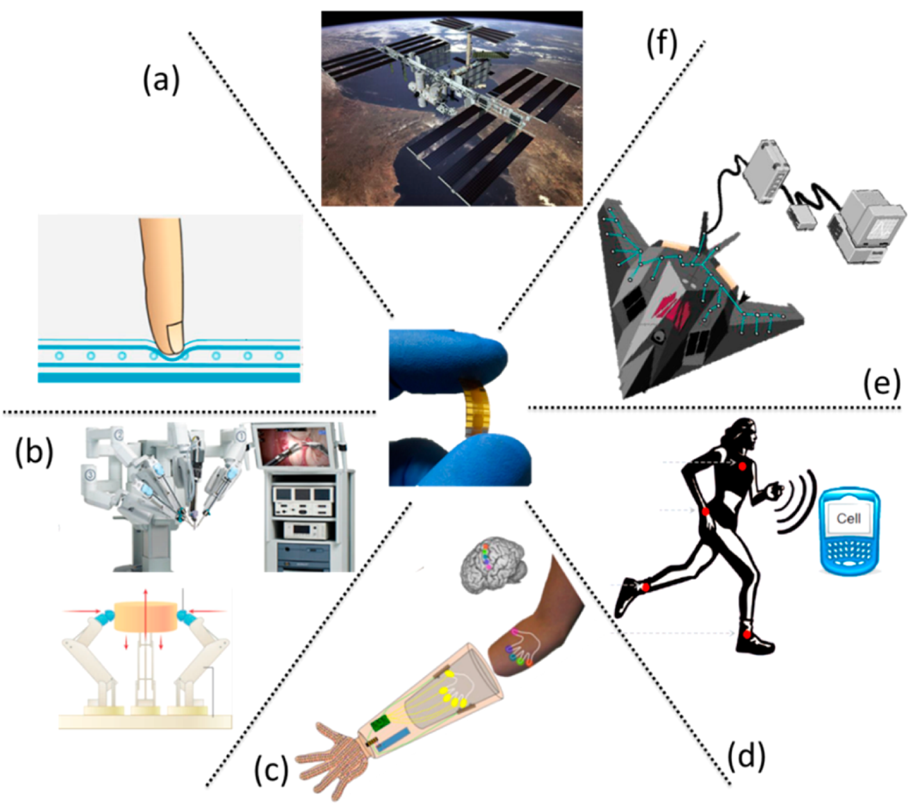

Figure 1. Present and future applications for flexible sensors; the middle image shows a flexible sensor. Adapted from ref 25. Copyright 2013 Elsevier. (a) An analog resistive touch screen with a simple mechanical switch mechanism to locate a touch. Adapted from ref 1. Copyright 2012 Society for Information Display. (b) E-skin based on flexible sensors for present robotic applications. The upper image shows the da Vinci Surgical System (Intuitive Surgical, Inc., Sunnyvale, CA), the most widely used robotic surgical system in the world. Adapted from ref 14. Copyright 2012 Springer. The lower image shows a three-fingered gripper. Adapted from ref 11. Copyright 2006 AAAS. (c) E-skin that could in the future provide a natural sense of touch to prosthetic limbs. Adapted from ref 15. Copyright 2012 IEEE. (d) Wearable sensors for monitoring an individual's physical parameters like movement, respiratory rate and heart rate while exercising. Adapted from ref 26. Copyright 2010 IEEE. (e) Large-area flexible sensing systems composed of a large number of individual sensors for early detection of cracks in large structures such as aircrafts or buildings. Adapted from ref 21. Copyright 2004 International Society for Optics and Photonics. (f) Printed sensors for future space applications.

good stability, but the fabrication process on flexible substrates might be expensive and involve multistep processing.[6,62,66,67] Additionally, there is a high potential for statistical fluctuations in the number of nanowires in the channel,[4] particularly at increased integration densities.[4] Flexible sensors based on carbon nanotubes or graphene can be fabricated through simple and inexpensive routes and can withstand extremely high strains of hundreds of percentages.[5,65] Nevertheless, this type of sensors exhibits a smaller gauge factor than that of conventional metallic strain gauges, making it unsuitable for sensing small strains or pressures.[5,56] Responsive photonic crystal structures have high potential to provide simultaneous sensing features including pressure, temperature, and vapor. Nevertheless, the bottom-up (self-assembly) techniques used for the fabrication of these devices are still premature for industrial implementation.[69]

Exploiting Nanoparticles for Sensing Applications. An emerging approach for robust real-world applications of flexible sensors relies on nanoparticles (NPs) with diameters that range from 10 to 100 nm.[70] Among the numerous reasons why exploiting (materials comprising) NPs for flexible sensors is promising, we note five main reasons. The first relates to the presumed ability to synthesize, if not at will, then with much control, nearly any type of NP. Several studies have shown the ability to control the NPs type,[71,72] starting with cores made of pure metal (*e.g.*, Au, Ag, Ni, Co, Pt, Pd, Cu, Al); metalalloys (*e.g.*, Au/Ag, Au/Cu, Au/Ag/Cu, Au/Pt, Au/Pd, and Au/Ag/Cu/Pd, PtRh, Ni−Co, Pt−Ni−Fe);[72] metal oxides, semiconducting materials (*e.g.*, Si, Ge),[73] and more.[36,40]

The second reason is the ability to cap the NPs with wide variety of molecular ligands, including alkylthiols, alkanethiolates, arenethiolate, alkyl-trimethyloxysilane, dialkyl disulfides, xanthates, oligonucleotides, DNA, proteins, sugars, phospholipids, enzymes, and more.[74−80] For sensing applications, this ability implies that one can obtain NPs with a hybrid combination of chemical and physical functions, which would have a great effect on the sensitivity and selectivity of the sensors.

The third reason is expressed in the ability to vary the NPs' size (1−100 nm) and shape (sphere-, rectangle-, hexagon-, cube-, triangle-, and star-, and branch-like outlines) and, consequently, the surface-to-volume ratio.[36,41,42] For sensing applications, these features would allow deliberate control over the surface properties and the related interaction "quality" with the physical parameters such as pressure, temperature, Plasmon resonance, and more.[81,82]

The fourth reason is attributed to the ability to prepare films of NPs with controllable porous properties. This allows control over interparticle distance as well as controllable signal and noise levels which, eventually, dominates the device sensitivity on exposure to either physical or chemical parameters.[76,83]

The fifth reason is the presumed ability of NPs to allow easier, faster, more cost-effective fabrication of flexible sensors compared to those currently in use, which mostly rely on complicated, multistep processes.[6,43,61,84]

Fabrication of NP-Based Flexible Sensors. NPs can either be deposited on flexible substrates at low temperatures as sensing cap-layers or they can be integrated into the composite of a flexible material. The common procedure for producing such NPs requires a (metal) salt as precursor, from which NPs are formed by elevating the temperature, leading to thermolysis of the pressures.[85,86] The distance between the encapsulated NPs are controlled by choosing the encapsulating molecules or the assembly/deposition procedure. The application of the NPs on a flexible substrate is achieved by a number of techniques such as layer by layer (LbL),[29] coating from suspension,[87] stamping methods,[33] drop casting,[3] inkjet printing,[38] stop-and-go convective self-assembly (CSA),[30,34,35,39] and electrodeposition.[51] Other production routes include deposition of NPs in a vacuum for strain and gas sensing, using a technique based on sputtering and condensation of atoms from a metallic target.[25,47]

Figure 2 illustrates four representative fabrication techniques for NP-based flexible sensors. Figure 2a shows a micromolding technique, using a polydimethylsiloxane (PDMS) stamp (upper image), in which Pd hexadecylthiolate in toluene serves as a precursor. Thermolysis at 195 °C leads to nanocrystalline Pd microstripes inside the microchannels (nanoparticle size, 8 ± 2 nm), as seen in the scanning electron microscopy (SEM) image of the NP stripes formed on a polyimide substrate (Figure 2a, lower image).[45] Figure 2b presents a CSA technique to fabricate highly ordered stripes of Au NPs.[30,34,35,39] The CSA technique allows deposition of NPs along the straight meniscus of the suspension drop due to particle flux toward the substrate−liquid−air contact line that is caused by solvent evaporation in this area. The width and the thickness of the NP wires obtained by CSA in the stick−slip mode are controlled by manipulating the substrate temperature and the meniscus translation speed.[35] Figure 2c presents an interesting electrodeposition method for creating NP-decorated nanostructures.[51] In this method, a drop of an aqueous solution containing Na_2PdCl_4 and NH_4Cl is deposited on the polyethylene terephthalate (PET) sheet with SWCNTs connecting the reference electrode, counter electrode, and working electrode to the potentiostat (Figure 2c, left side). Generation of Pd NPs on the surfaces of the SWCNTs is aided by the reduction of $PdCl_4^{2-}$ anions. The densities and sizes of the resulting Pd NPs are easily tuned by controlling the reaction time.[51] Figure 2d shows the integration of NPs into a polymer matrix to exploit the surface plasmon resonance (SPR) absorption of Au NPs.[22,27] The production of Au NP-

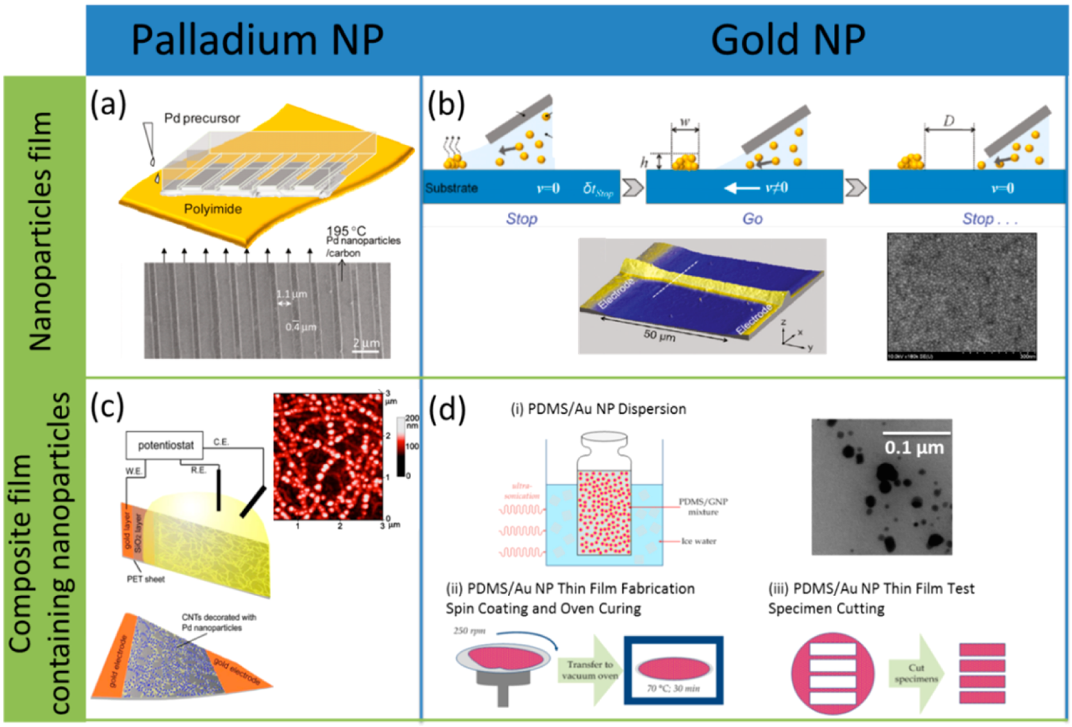

Figure 2. Representative examples of fabrication techniques for flexible sensors that are based on metal NPs. (a) The process of direct micromolding of Pd hexadecylthiolate onto a polyimide substrate; representative SEM image of micrometric Pd NP stripes that were formed by the method. Adapted from ref 45. Copyright 2011 American Chemical Society. (b) Stop-and-go convective self-assembly; atomic force microscopy (AFM) image of a characteristic NP film created by the CSA method (lower left image) and corresponding SEM image of the highly ordered NPs film. Adapted from ref 35. Copyright 2011 American Chemical Society. (c) Pd NP formation by electrodeposition on the surface of a random network of SWCNTs and AFM image of the resulting composite structure. Adapted from ref 51. Copyright 2007 American Institute of Physics. (d) Step-by-step representation of the fabrication process of PDMS-Au NP composite elastomers from PDMS-Au NP dispersion for sensing applications and SEM image of the Au NPs dispersed in the PDMS. Adapted from ref 22. Copyright 2011 Techno Press.

based composite starts with crushing gold salt and mixing it with PDMS by sonication in ice water. The homogenized solution is then spin coated on a silicon wafer. Afterward, strain sensing test specimens are cut and separated from the film on the silicon wafer.[22] Exploiting the piezoelectricity of ZnO NPs for dynamic strain sensing was achieved by using a similar fabrication method.[88] Additional fabrication methods that do not involve metal salts as precursors are also reported. For example, carbon NPs are fabricated by a simple flame synthesis process and then integrated into a PDMS substrate, providing a durable infrared sensor that also exhibited self-cleaning properties.[48]

For fabrication of flexible sensors, it is important to pay special attention to the way the NPs are incorporated on/into the flexible substrates. Several studies have shown that variation in thickness, morphology (continuous *vs* discontinuous *vs* perforated NP films)[34,89] and density[90] of the NP films affects the sensitivity, selectivity and the overall functionality of the NP-based sensors. Basically, these variations might raise concerns regarding the reproducibility of the fabricated sensors. Nevertheless, recent advances in the fabrication of NP films (*e.g.*, layer-by-layer[29] and stop-and-go convective self-assembly[34,35]) raise expectations that NP-based flexible sensors are likely to become a technological reality in the near future. Other studies have shown that the type and the thickness of the flexible substrates have a direct effect on the sensing signals obtained. In general, different substrates have different adhesion properties relative to the NP films. Additionally, the substrate's mechanical and geometrical properties affect the sensing signal[3] as well as the sensor's lifetime. Among the various materials used for flexible substrates, polyimide has excellent dielectric properties with a dialectic constant of ∼4, outstanding thermal stability of up to 200 °C without losing its flexibility, chemical stability (tensile retained of more than 96% for common organic solvents such as toluene and isopropyl alcohol), and low coefficients of thermal expansion (20 ppm/°C).[45,49] Polyethylene terephthalate (PET) exhibits almost no degradation in the fatigue performance, even after 2000 cycles of alternate squeezes to a curved profile and release to flat geometry. These results indicate that PET-based substrates for NP films possess excellent mechanical bendability and durability.[33,51] High density polyethylene (HDPE) provides a good substrate for the application of cross-linked metal NP-coatings as flexible chemiresistors, whereas low density polyethylene (LDPE) has drawbacks due to its higher vapor permeability.[29] Membranes[44] and elastomeric substrate of polydimethylsiloxane (PDMS) provide a platform for large strains up to 30%. When the strain is relieved, the PDMS substrate recovers, and the sensing signal returns to its original value.[22,27,31,40] When the sensor's components (the NPs and the polymer) are integrated to form a composite material, the mechanical, optical and/or other properties of the initial polymers would be modified due to association with the NPs. Subsequently, the properties of the final material could be tuned by tailoring the NPs type, coating and size.[91,92]

Figure 3 summarizes different types of sensors for various measured properties that were fabricated using a variety of NPs on different flexible substrates. Most of the sensors were deposited on polyimide (PI) and PET. The column height represents the number of deformation cycles. For Au NP sensors on polyimide, the response to load and strain remained similar after 10 000 bending cycles.[3] Pd NPs decorating carbon nanotubes as a sensing layer on flexible PET substrates

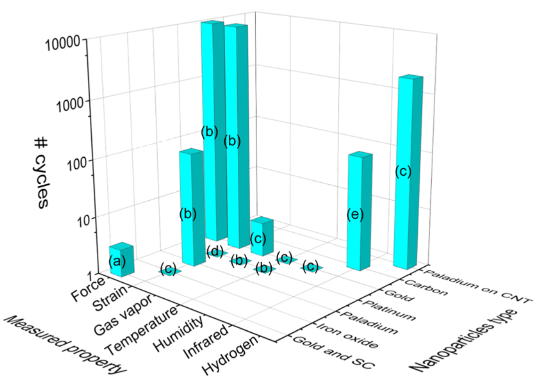

Figure 3. NP-based sensors on different substrates that were reported for sensing of different physical and chemical parameters. The columns height stand for the number of deformation cycles that the sensors were reported to withstand (*cf.* Table 1 for the applied strains). The deformation cycles were done on sensors fabricated on different substrates: (a) flexible plastic;[43] (b) flexible polyimide;[3,25,45] (c) flexible polyethylene terephthalate;[3,33,36,44,51] (d) rigid SiO_2/Si[47] that was strained up to 0.15% (Table 1); and (e) flexible polydimethylsiloxane.[48] Each substrate was subjected to different strains during the fatigue tests. NOTE: the value "1" on the *z*-axis (# cycles) stands for sensors whose reproducibility was not examined.

also exhibit outstanding properties—the response toward hydrogen remained similar after 2000 cycles of elastic deformation.[51] As understood from the figure, sensing different measured properties is done using a range of substrates. For example, sensing of strain is performed by using substrates such as polyimide,[3] PET[44] and even rigid SiO_2/Si that was strained up to 0.15% (Table 1).[47] Gas vapors and temperature, as well as strain, are sensed by using different substrates such as polyimide[3,25] and PET.[33,36] It seems that the impact of the substrate on the flexible sensors response is not yet fully understood and further research is required.

Classification of Flexible Sensors Based on NPs. Deliberate control of the substrate and NP properties provide sensors with different functionalities. These sensors are classified into three categories (Figure 4):

(i) **Stress-sensors for sensing deformation**: in these sensors, changing interparticle distance as a result of bending a flexible substrate (Figure 4a) changes, for example, the tunneling currents. Depending on the bending direction, a decrease or an increase in the sensing signal is obtained.[3] The gauge factor of the flexible NP-based sensor can be tuned by controlling a range of parameters in the sensors fabrication (Figure 4b).[47]

(ii) **Multiparametric NP-based sensors**: these sensors are responsive to volatile organic compounds (VOCs) as well as to ambient conditions (such as relative humidity and temperature), with sensitivities that are tunable by mechanical deformation (Figure 4c,d).[29] An individual sensor or an array of sensors is used to achieve multiparametric sensing in a single sensing platform.[3]

(iii) **Sensors that are not affected by the mechanical deformation**: these sensors are lightweight and simple-to-fabricate, but are not affected by the mechanical deformation of the flexible substrate (Figures 4e,f).

The current review attempts to pull together varying views and terminologies to provide an overview of

TABLE 1. Applied Strains in NP-Gauges

NP core material	sensor structure	applied strain range (%) (min−max)	reference
FeO	Film of colloidal NPs on mylar membrane	1.6−10.9	Siffalovic *et al.*[44]
Au	Wires of colloidal NPs on PET substrate	0.01−0.8	Farcau *et al.*[34,35]
	Wires of colloidal NPs on PET substrate.	0.15−0.6	Moreira *et al.*[30]
	Film of colloidal NPs on variety of substrates	0.05−0.5	Herrmann *et al.*[38]
	Film of colloidal NPs on variety of substrates	0.02−0.3	Segev-Bar *et al.*[3]
	Wires of colloidal NPs on PET substrate	0.2−0.6	Sangeetha *et al.*[39]
	Cross-linked NPs film on PE	0.25−3	Olichwer *et al.*[29]
Au and PDMS	Reduction of NPs in PDMS	10−30	Ryu *et al.*[22]
	Silica-coated NPs film on PDMS	6−30	Millyard *et al.*[40]
Pd	Micromolded Pd alkanethiolate on PI substrate	0.06−0.2	Radha *et al.*[45]
Pt	Bare sputtered NPs on silicon oxide substrate	0.06−0.15	Tanner *et al.*[46,47]

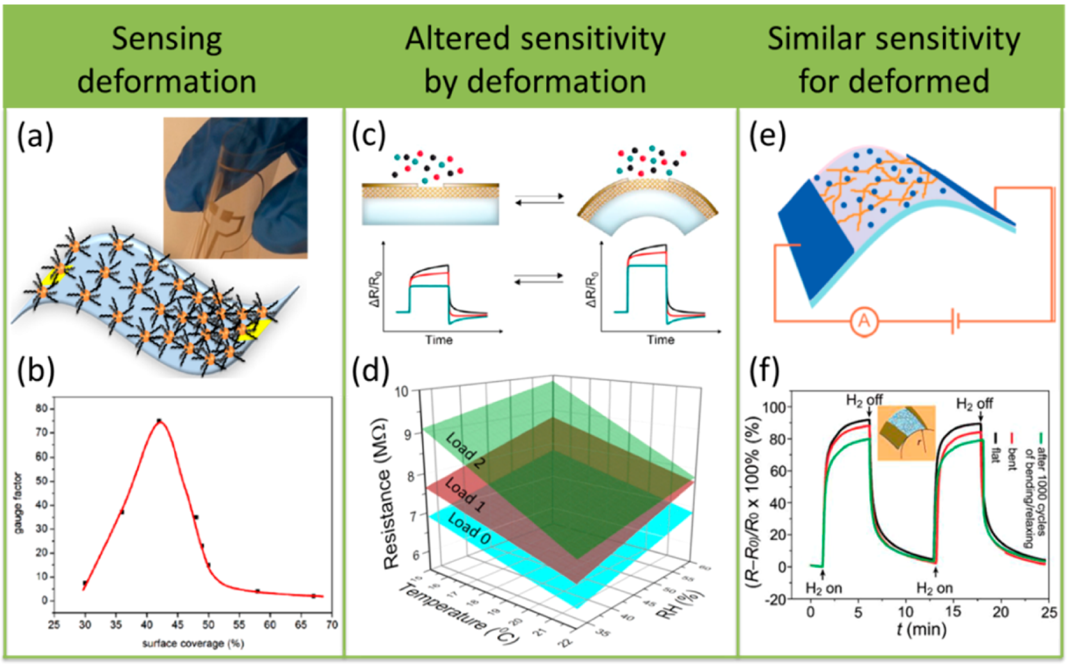

Figure 4. Classification of NP-based flexible sensors into three categories. (a) NP-based strain gauges for sensing mechanical deformation *via* the change in the interparticle distance during the deformation process. Adapted from ref 3. Copyright 2013 American Chemical Society. (b) Gauge factor tuning by changing the surface coverage. Adapted from ref 47. Copyright 2012 IOP Publishing. (c) NP-based flexible sensors for volatile organic compounds (VOCs) and/or ambient conditions such as relative humidity (RH) and temperature, with sensitivities that are tunable by mechanical deformation. Adapted from ref 29. Copyright 2012 American Chemical Society. (d) Tuning the sensitivity toward temperature and RH changes by applying different loads. Adapted from ref 3. Copyright 2013 American Chemical Society. (e) Flexible hydrogen sensor that is not affected by mechanical deformation. Adapted from ref 51. Copyright 2007 American Institute of Physics. (f) Stable and reproducible sensing signals under mechanical deformation, even after 1000 bending circles. Adapted from ref 51. Copyright 2007 American Institute of Physics.

the "real" and "ideal" in the field of NP-based flexible sensors.

Stress-Sensors for Sensing Deformation. Strain gauges (devices that measure the strain of an object attached to it) based on NPs are divided into two sub-categories. The first category relies on NP sensing layers deposited on top of flexible substrates (Figure 4a). These sensors are described as hybrid bilayer sensors.[3,30,34,35,38,39,44−46] The second category relies on NP-containing composite sensors, in which the NPs are integrated into the elastic substrate during the fabrication process. The substrate is usually an elastomer such as PDMS,[22,27] which is suitable for sensing large strains. In this category, the response of the sensors is often measured *via* optical changes such as small-angle X-ray scattering (SAXS).[44] Measuring large strains is important for the detection of cracking and damage in large structures such as maritime vessels, airplanes, buildings, bridges.[60,93] Small strain measurements are important for the delicate sense of touch in robots or health monitoring applications described in the introduction section dealing with future applications.

On the basis of the accumulated data in the literature, we propose a few possible mechanisms (*cf.* Figure 5) for strain sensing in NP-based sensors. One mechanism that controls the response of the NP's strain gauges relies on homogeneous changes in the interparticle distance (Figure 5a).[38] This may also explain the exponential dependence that has been observed for the response as a function of the applied strain.[34,35,38] An additional mechanism that could be responsible for nonexponential responses of the NP-strain gauges is the formation of cracks in the NP film during bending or stretching the sensor.[27] SEM images have reinforced this assumption (Figure 5b), and electrical measurements during tensile caused an irreversible increase in the resistance.[3,29] Cracking was also found to be the dominant mechanism for silica-coated Au NPs (Figure 5c).[40] In this study, combined SPR and AFM analysis showed that random formation of localized cracks in the NP-film acted as spacers between groups of NPs, in such a way that individual particles were not separated, but rather formed big agglomerates. The formation of these cracks in the NP film, after stretching of the PDMS elastomeric film, decreases the density of NPs in the examined area, thereby lowering the absorbance intensity of the gold SPR, which, in turn, is proportional to the stretching force.[27]

Table 1 summarizes the strain ranges reported for NP-based strain gauges while considering the NP core material and structure of the NP in the sensor. The majority of the NP cores reported in the literature

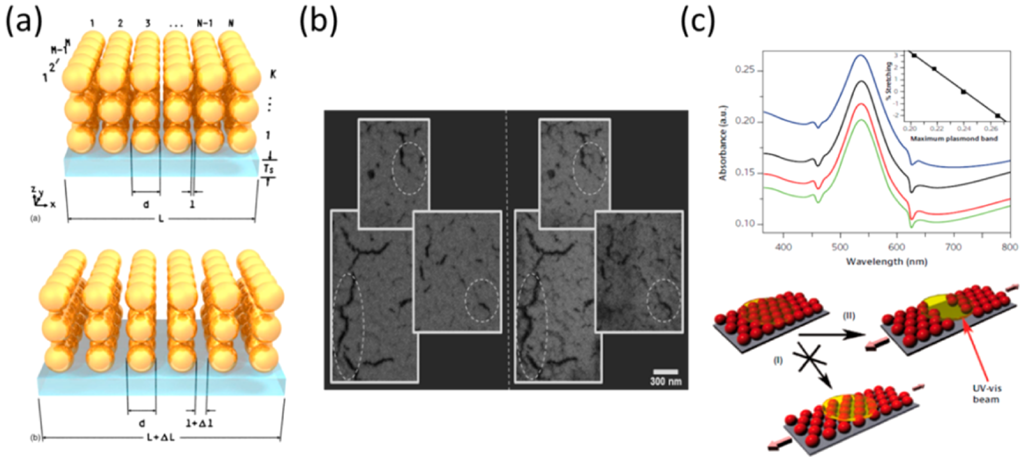

Figure 5. Possible response mechanisms for strain or touch sensing. (a) Schematic illustration of homogeneous changes in the interparticle distance due to deformation. Adapted from ref 38. Copyright 2007 American Institute of Physics. (b) SEM image showing evidence of crack formation in the NP film. Adapted from ref 29. Copyright 2012 American Chemical Society. (c) Change in the SPR peak upon deformation (upper image) and a schematic illustration of localized cracks as the main mechanism for deformation sensing (lower image). Adapted from ref 27. Copyright 2007 Springer.

focuses on Au. However, it seems that the differences in the NP arrangement on the flexible substrate create a range of strains that are measurable, from 0.01%[35] as minimal strain for highly ordered wires of Au NPs to 3% for crossed-linked Au NPs.[29] The dynamic range of the NP-based strain sensors can be controlled either by the substrate type and\or the signal transduction. As seen in Table 1, large (>1%) strains can be obtained by substrates based on membranes or elastomers (*e.g.*, PDMS) in conjugation with optical transduction of sensing signal.[22,40,44] On the other hand, small (<1%) strains can be measured by using substrates that are based on thermoplastic polymers and by tracking changes in the electrical characteristics (*e.g.*, the conductivity or the resistance of the NP film).[3,29,30,34,35,38,39,45,47] For this category of sensors, the data presented in Table 1 indicate that variations in the capping ligand,[30] the fabrication method,[3,29,45] and the NP film's density[47] (all of which affect the baseline resistance of sensors and cause for variations that range between kilo-ohms to giga-ohms) do not affect the measured strain signal. This finding makes this category of sensors relatively mature for technological applications.

Table 2 lists the gauge factors that were achieved by varying different parameters for sensors fabricated from different types of metal NPs, as well as by different arrangement of the NPs in the flexible strain gauges. As seen in the table, the reported gauge factors of NP-based flexible substrates compare favorably to commercial metallic strain gauges (gauge factors ∼2) and are equivalent to state-of-the-art semiconductor gauges (gauge factors ∼70−200). Additionally, it can be seen that the values of the gauge factors depend on the specifications used for the fabrication of the NP-based flexible strain gauges, thus providing a degree of freedom for manipulating the NP-based strain gauges. Nevertheless, such specifications induce also adverse effects on the performance of the constituent strain gauges. An important adverse effect originates from the interparticle distance and/or the film's morphology, which, in turn, is affected by the diameter and/or the capping ligands of the NPs and/or the deposition of the NPs films.[3,29,30]

Sangeetha *et al.*[39] have shown that increasing the diameter of the NPs[29,39] (from 5 to 97 nm) increases the disorder within the constituent NP assemblies and leads to an increment in the gauge factor (from 12 to 190) as well as in the hysteresis of the constituent electrical resistance (from 0.1% to 4.3%).[34] Moreira *et al.*[30] have reported that NPs capped with citrate create a perforated morphology, while other encapsulated ligands yield a compact NP film. The NPs encapsulated with the citrate ligand had smaller gauge factors by 1 order of magnitude compared to the other strain gauges. For NPs with defined diameter and capping layer, strain gauges that are based on single-monolayer assembly of NPs[34,46] yield optimal performances. For bare sputtered NPs, the gauge factor is attributed to the two-dimensional NP arrangement (*i.e.*, less than one monolayer), which is sensitive to interparticle spacing.[46] Tanner *et al.*[47] showed that there is an intermediate optimal surface coverage for which the gauge factor is maximal, while the thermally assisted transport is dominant in NP films with surface coverage less than 50%, above which a metallic behavior dominates (Figure 4b). However, this could also be a reason for a nonlinear relationship between the gauge factor and the strain.[45] For NP films having a specific thickness and morphology, strain gauges can be controlled through modulating the properties of the flexible substrates.[3] Under bending conditions, the strain is proportional to the substrate thickness; therefore, the gauge factor is proportional to the inverse of

TABLE 2. Gauge Factor Tuning in Flexible Sensors Based on Metal NPs

NP core material	tuning factor	sensor structure	tunable range of the gauge factor (min−max)	reference
Au	Film morphology	Wires of colloidal NPs on PET substrate	59−135	Farcau *et al.*[34]
	Ligands	Wires of colloidal NPs on PET substrate	26−47	Moreira *et al.*[30]
	Ligands, NP core diameter	Cross-linked NPs film on PE substrate.	18−24	Olichwer *et al.*[29]
	NP core diameter	Wires of colloidal NPs on PET substrate	12−190	Sangeetha *et al.*[39]
	Substrate thickness	Film of colloidal NPs on variety of substrates	35−250	Segev-Bar *et al.*[3]
Pd	Thermolysis conditions (temperature and time)	Micromolded Pd alkanethiolate on PI substrate	0−390	Radha *et al.*[45]
Pt	Deposition time, electrode gap	Bare sputtered NPs on silicon oxide substrate	2−75	Tanner *et al.*[47]
	Film coverage	Bare sputtered NPs on silicon oxide substrate	337−735	Tanner *et al.*[47]

the thickness.[3] Other mechanical properties of the substrate, such as the yield point, could also have an effect on the strain of the sensor, and consequently, on the gauge factor.

Recent studies have shown that a combination of several types of NPs also yield remarkable properties. For example, stress distribution with a resolution of 40 μm could be achieved by depositing a 100 nm-thick, large-area, thin-film device consisting of metal and semiconducting NPs.[43] In another example, Au NPs were shelled by 5 nm thick silica to ensure a distance of about 10 nm between the Au NPs. In this case, optical coupling interactions were avoided by the relatively large interparticle distance and a SPR band was maintained, increasing the sensor's ability to discriminate different strain levels.[27] Further, PdAu NP deposited on a microfiber induced scattering of the evanescent waves, easily detectable with a simple transmission measuring setup.[94]

Multi-Parametric NP-Based Sensors. Flexible sensors that provide multiparametric signals from complex samples under "harsh" conditions[29] have emerged as important tools for various applications, such as e-skin and wearable sensors for health monitoring.[95−103] The decoupling between the various stimuli (*e.g.*, pressure, temperature, humidity and physiological parameters)[7] that exist in a complex mixture and/or environment represents a critical challenge for these multiparametric sensors. Decoupling between the various stimuli can be achieved by one or a combination of the following actions: (a) choosing an appropriate substrate; (b) altering the capping ligands or the deposition parameters (*e.g.*, by employing a layer-by-layer deposition technique[104]) or controlling the layer's morphology (*e.g.*, perforated *vs* continuous morphology[89]); (c) controlling the protective material at the NP/air interface (*e.g.*, by employing a top protective layer on the NP film); and (d) using a postmeasurement algorithm.[3] Here we present three practical examples of decoupling-strategies. **Example 1:** Flexible substrates having negligible sensitivity to pressure but high sensitivity to humidity or temperature can be obtained by combining actions (a) and (b). For instance, one can use a substrate with a limited flexibility (*e.g.*, thick thermoplastic polymer), in which the pressure or strain play a negligible role. In a complimentary way, one can choose capping ligands for the Au NPs that would provide higher sensitivity toward humidity (*e.g.*, 2-nitro-4-trifluoro-methylbenzenethiol), compared to temperature, or ligands that provide higher sensitivity toward temperature (*e.g.*, 3-ethoxythiophenol), compared to humidity.[3] **Example 2:** Flexible substrates that have negligible sensitivity to pressure but high sensitivity to humidity or temperature can be obtained by combining actions (b) and (d); one can use a film of Au NPs with perforated morphology, which would provide reduced sensitivity toward strain.[30] Additionally applying an algorithm to a training set of "humidity *vs* temperature" calibrations would decouple the temperature and humidity responses.[3] **Example 3:** Flexible substrates that have high sensitivity to pressure but no (or negligible) sensitivity to humidity or temperature can be obtained by combining actions (a), (c) and (d). One can use a substrate with an optimized thickness, mainly because of the tight dependence of the strain response with the substrate thickness[3] and cover the NPs film with thermoplastic resins, which are known to eliminate humidity effects in NP-based sensors.[3] Finally, an algorithm can be applied to a training set of "humidity *vs* temperature" calibrations that would decouple the temperature and humidity responses.[3] Avoiding artifacts and overfitting during the "decoupling" is a top priority. The possibility of artifacts due to data-overfitting can be reduced by using blind validation tests with independent blind data sets: 60−80% of the data shall be used as a "training" set and the remaining 20−40% of the data can serve as "blind set". The training set allows building a sensing model, which will then be applied to the blind validation set. According to the results of the blind set, the accuracy of prediction of each specific response can be estimated.

A competitive approach which takes advantage of the signal change due to strain could be achieved by a deliberate deformation of the sensors substrate.[3] An elastic deformation of a specific (single) flexible substrate could provide a **virtual sensing** system that provides information from the deformation measurements and processes the parameters obtained to calculate the quantity of interest.[29] For a specific application that requires a sensor array,[33] this approach could potentially avoid the need for various sensors that rely on complicated synthesis of NPs and/or organic ligands.

Olichwer *et al.* enhanced the sensitivity of the chemiresistors by ∼30% by inducing 1% tensile strain, regardless of the analyte's polarity (Figure 4c).[29] In chemiresistors that sense VOCs, the substrate has a major effect on the sensitivity obtained and specificity of the device. This can be demonstrated by comparing similar Au NP films that are deposited onto LDPE and HDPE.[29] An additional example is the change in the response of a NP film to temperature and humidity, when the sensor is subjected to changing loads. When load is applied, the increased distance between the NPs changes the surface coverage and, in addition, changes the morphology. These changes affect the NP sensor's response in general (Figure 4d). The effect of load on the sensing of temperature and relative humidity (RH) is still subject to controversy, and a more thorough understanding is required.[3]

A "3 in 1" prototype array of sensors, based on Au NPs with abilities to sense temperature with resolution higher than 1 °C and average error of ∼5%, RH with resolution higher than 1% RH and average error of ∼9% and pressure/touch, was presented.[3] The prototype uses the post measurement algorithm to isolate load sensing from sensing temperature and RH. In general, the explorative "3 in 1" prototype demonstrates the feasibility of using a **single** (or similar) NP chemistry with various substrate structures/designs to achieve multiparametric sensing on the same platform, such as temperature, RH, and load. A step further will be the integration of VOC sensing in such a platform (referred to as "4 in 1").

An alternative approach for the electrical modulation of the NP-based flexible sensors is based on imaging. In this type of sensors, a CCD camera is integrated within/near the sensing device.[43] In these devices, the CCD camera monitors spatial vibration in electroluminescent light that is produced by the stress distribution.[43]

Sensors Not Affected by Mechanical Deformation. NP-based flexible sensors that are insensitive to strain are useful for sensing different properties such as infrared illumination[48] or VOCs[33] in lightweight, easy-to-carry applications that require flexibility, and low-cost fabrication (*e.g.*, printing on roll-to-roll flexible substrates).[105] Sensors of this type must remain unaffected during deformation if sensing during touch/strain is considered necessary.[50] Otherwise, they should have reversible properties after deformation cycles so the sensing signal will remain stable after a large number of deformation cycles. In this area, Sun *et al.*[51] have developed and tested Pd NP-based flexible sensors that provide high responses toward hydrogen but negligible responses toward other confounding factors, such as bending. As seen in Figure 4f, there is a slight decrease (by 4.7%) in sensitivity (red line). A fatigue test (green curve) over this device indicates that its sensitivity decreases by 13% after it is compressed to a curved surface followed by relaxing to a flat geometry for 1000 cycles.[52] Such hydrogen sensors would be essential and widely required as safety components in the anticipated future hydrogen-based economy. For extraterrestrial use, hydrogen-fueled space shuttles could be covered with large-area flexible hydrogen sensing systems on plastic sheets to reduce their overall weight and to detect any leakage of hydrogen prior to diffusion.[50] These flexible hydrogen sensors circumvent most of the problems associated with currently available metal oxide-based sensors that require high temperatures (over 400 °C) to maintain proper operation.[106]

Challenges and Open Questions. Which technologies will be able to satisfy the growing need for flexible sensors? Inexpensive and low-power touch-sensitive platforms of flexible sensors have been successfully demonstrated. However, the following targets must be met to make flexible sensors attractive for a wide range of real-world applications:

- Development of a sensing platform that measures a wide dynamic range of pressure, from low pressures (1−10 kPa), useful for small object manipulation,[110] up to high pressures (10−100 kPa), useful for lifting a person or a heavy object.
- Simultaneous[111,112] measurement of pressure (touch), humidity,[113] temperature and/or the presence of chemical agents.[32]
- Operation at low-voltage or low-power (below 5 V),[114] compatible with commonly used batteries of portable devices today.
- Development of printing techniques that allow high volume, low-cost manufacturing, and suitable for low-temperature manufacturing of flexible substrates.[62]
- Obtaining flexible sensors whose sensitivity/specificity is not affected across environmental variations. This is particularly important due to the fact that most currently available polymeric substrates are affected by environmental changes, such as spatial expansion or contraction due to temperature changes or absorption of humidity.
- Obtaining sensors whose sensitivity toward specific parameters is not influenced by the deformation of the sensor.[3]

An important limitation of today's printed flexible electronics is the lack of resolution due to the relative large pixel size of the state-of-the-art printing deposition techniques compared to microelectronic rigid technology (although costs are dramatically lower for printed technology).[115] On the other hand, in portable electronics that contain touch screens, the pixel size cannot be reduced below the size of a human finger and current touch screens have only on/off functionality. In response, NP-based strain gauges have an advantage as they measure the force applied by the finger enabling more potential touch screen applications. NP-based flexible sensors also allow multiparametric sensing, essential for many real-world applications. Various physical, chemical, and biological parameters can be detected from the ambient environment with mobile/autonomous/remote NP-based sensors on plastic substrates,[116] which could be useful for a variety of applications. Nevertheless, many issues that relate to large-scale production and integration with VLSI circuits must be solved before current limitations are overcome.

NP-based strain gauges should have a range of sensitivities and a detection limit toward load or strain that is suitable for the desired application. E-skin, for example, should have ~0.158 gr normal mean threshold value on the palm and about 0.055 gr on the fingertips in order to be comparable to human skin.[117] The properties of the NP-based flexible sensors are highly dependent on the substrate. Also, high strains of a few percent can cause irreversible changes both in the flexible substrate and in the NP layer when using thermoplastic polymers.[3] Strains smaller than 1% are practically invisible when using elastomers embedded with NPs.[22,27] Thus, high strains are sensed using elastomers and small strains are sensed using thermoplastic polymers substrates such as PI and PET. For real-world applications, the ability to tune the sensitivity over a large range of strains (or loads) should be considered. The effect of relative humidity and temperature on the NP-based flexible touch sensors and the integration of these sensing abilities are important for future applications and should be carefully considered.

Wearable sensors are anticipated to play a key role in future medical diagnostics and physiological monitoring.[20] To enable wearable sensing applications at a reasonable cost, sensors should ideally be integrated into the fabric/tag itself.[26] Alternatively, sensors on thin flexible substrates could be applied on top of the fabric/tag without compromising the material's flexibility. This cannot be achieved with conventional, rigid electronic components. In addition, adaptation of electronic circuits to wearable applications requires novel integrative production techniques.[58] For these sensory systems, mechanical design will be as important as circuit design.[84]

E-skin has a high potential for applications in robotics and prosthetics, all of which require exact measurement of the applied forces and close examination of the objects touched.[2,12,15,16] Ideally, e-skin for touch-sensitive artificial limbs should provide force sensitivity in the range of 5−100 mN, repeatability of the sensor output, monotonic sensor response, and a spatial resolution of 1−2 mm.[118] However, the advancement of tactile prosthetic limbs requires the development of novel electronic sensors that could connect the e-skin to the human nervous system. Until complete implementation of this vision, an intermediate development would be the integration of e-skin to a computer system.[17,18]

Conclusion and Outlook. Flexible sensors are expected to spur development of totally new, smart sensing applications in consumer electronics, robotics, prosthetics, healthcare, geriatric care, sports and fitness, safety equipment, environmental monitoring, homeland security and space flight.

NP-based flexible sensors are extremely promising for a wide variety of applications, but the necessary technology is still being developed. We have classified flexible NP sensors into three categories: (i) strain-gauges, (ii) flexible multiparameter sensors with strain-tunable sensitivity toward different parameters, and (iii) sensors that are unaffected by mechanical deformation. To date, most flexible sensors are based on metal NPs, but the future of these sensors could be in semiconducting NPs with quantum-dot properties. Incorporating NPs into flexible sensors will soon become one of the most important applications of nanotechnology. NP-based flexible sensors could help overcome the considerable technological challenges hindering development of real-world applications. These sensors are expected to provide a platform for future robust, simple, large-area, cost-effective and easy-to-fabricate bendable and stretchable sensing systems for a wide variety of applications.

Conflict of Interest: The authors declare no competing financial interest.

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