Plasma surface modification of polymers for sensor applications

Carlos Alemán,[1,2,*] Georgina Fabregat,[1,2] Elaine Armelin,[1,2] Jorge J. Buendía,[1,2] and Jordi Llorca[1,2,3,*]

[1] *Departament d'Enginyeria Química, EEBE, Universitat Politècnica de Catalunya, C/ Eduard Maristany, 10-14, 08019, Barcelona, Spain*

[2] *Barcelona Research Center in Multiscale Science and Engineering, Universitat Politècnica de Catalunya, C/ Eduard Maristany, 10-14, 08019, Barcelona, Spain*

[3] *Institut de Tècniques Energètiques, EEBE, Universitat Politècnica de Catalunya, C/ Eduard Maristany, 10-14, 08019, Barcelona, Spain*

* carlos.aleman@upc.edu and jordi.llorca@upc.edu

Abstract

Polymeric sensors play an increasingly important role in monitoring the environment we live in, providing relevant information for a host of applications. Among them, significant efforts have been made to fabricate polymeric sensors useful for healthcare-related application fields, such as the sensitive detection of biomolecules and cellular interfacing. Within the well-stablished field of biomedical polymeric sensors, surface modification and/or functionalization using plasma is just emerging as a technology to improve the selectivity and sensitivity in the biodetection process. Treatments based on plasma irradiation on polymer surfaces, which have been traditionally applied for cleaning, etching, activating or cross-linking, are currently being used to induce the formation of electrocatalytic species able to promote the oxidation of, for example, bioanalytes and/or gas molecules harmful for human health. Here, we summarize the main advances on the utilization of plasma technologies for the fabrication of polymeric sensors for advanced biomedical applications (*e.g.* humidity, temperature, pH, neurotransmitters, and glucose sensors).

Introduction

Since the earliest systematic research during the sixties, the field of materials surface modification by plasmas has undergone an enormous expansion. Much of this expansion has taken place in the last decade, particularly in the surface modification of polymeric materials. Thus, among the almost 26000 references under the heading “Plasma + Polymer + Surface” appeared in the Web of Science from 1963, more than 52% have been published after 2008 (Figure 1a). Although numerous industrial applications have been developed for plasma-treated polymers (*e.g.* enhancement of paint adhesion and improved bonding in polymer matrix composites), biomedical applications have become a topic of growing interest. Thus, 1794 of the 3047 entries found for “Plasma + Polymer + Surface + Biomedical” in the Web of Science were published after 2011 (Figure 1b). Similar progress is observed when citations are analysed (not shown).

Although plasma irradiation on polymer surfaces is the most widely used technique for cleaning from adsorbed contaminants and effective modification of material surfaces, it is also applied for other purposes, as for example etching, activation and cross-linking.[1-7] This is because plasma exposure activates polymer surfaces by creating new polar functional groups including carbonyl, carboxyl, ether, amine and hydroxyl; thus markedly increasing the free polymer surface energy and reactive capacity. Other well-known advantages of plasma treatment in polymer chemistry are the control (*e.g.* short-time plasma irradiation allows to alter surface properties, up to a few nanometers deep, without affecting the characteristics of the bulk polymer), the speed, the exclusion of the need of solvents, and the practical scalability.[8-10]

In recent years the attractiveness of plasma treatment has been extended to the biomedical field. For example, polymer surface functionalization by plasma has been used for drug delivery[11-15] (Figure 2a), antimicrobial applications[16-18] (Figure 2b), and tissue regeneration[19-23] (Figure 2c). However, in last few years development of sensors using plasma-treated polymers has emerged as a very promising technology for biomedical devices with multiple applications. In this mini-review we have focused on these very recent achievements.

The review is organized in several sections, which are briefly described in Table 1. In the first two sections, we briefly discuss the plasma concept and the effect of plasma on the polymer surface. After this, the most recent achievements on sensors for biomedical applications prepared using different plasma treatments have been discussed. Table 2 summarizes and compares the most relevant characteristics of the plasma treatments used to achieve such biosensors, as for example, kind of biosensor, plasma treatment conditions (*i.e.* type of plasma, power and application time), and purposes of usage. Finally, conclusions and future applications of biosensors based on plasma-treated materials are summarized.

The plasma concept

A plasma is originated when energy is applied to a gas resulting in the formation of a mixture of electrons, ions, radicals and neutral species. This energy can be directly thermal or derived from an electric current or electromagnetic radiation. In the chemical laboratory, most plasmas are generated from electrical energy. The electric field transmits energy to the electrons, which in turn transmit part of this energy to the neutral gas molecules by collisions. If this collisions are elastic the energy transmitted results only in an increase of the kinetic energy of the neutral molecules. If they are inelastic then the electronic structure of the gas molecules changes and excited species such as radicals and ions are created. Usually these excited species have a very short lifetime and relax by emitting a photon, which gives the characteristic colour of plasmas. The electron impact ionization is the major source of charged species in the electrical discharge. Plasmas are categorized as equilibrium and non-equilibrium depending of the temperature difference between ions and electrons in it. Thermal plasmas of about 4000 K or higher are considered to be in equilibrium (regarded as ‘hot’ plasmas), whereas in non-equilibrium plasmas only electrons are kept at high temperature; they are referred as ‘cold’ plasmas.[24,25] For polymer application, cold plasmas are preferred with a degree of ionization less than 1%, which can be sustained at room temperature with inexpensive equipment and prevents thermal degradation of thermosensitive materials.[26]

There are various possible set-ups for plasma generation and some of them are already developed for industrial use. If the plasma is not confined it is called plasma plume or plasma jet. These devices are an ideal solution for large and/or geometrically complex surfaces since the plasma is generated and launched outside the physical boundaries of the plasma as far as a few centimetres,[27,28] although different chemical zones form in a radial fashion starting from the central point, where the plasma jet hits the surface, and then spread outwards creating a spatial distribution of active species.[29] More often, the sample to be plasma treated is placed between electrodes in a confined space to better control the physics and chemistry of the process. This is normally accomplished by a corona discharge or by a dielectric barrier discharge both at low pressure and under atmospheric pressure. In a corona discharge a lighting crown is build out of many streamers by applying a DC electrical source in a pulsed mode, whereas in a dielectric barrier discharge a high frequency AC source, a radio frequency source or microwave fields are employed.[30,31] In a corona discharge reactor there is a cathode wire and the anode is normally the sample to be treated. A dielectric barrier discharge reactor for surface treatments usually consists of two parallel metal electrodes separated by few millimetres and covered with a dielectric material and the sample is placed between them; the plasma generated contains many micro-streamers that are homogeneously distributed across the electrodes. Low-pressure discharges are the most common methods used for plasma modification of polymers but, recently, there is an effort to replace them with methods utilizing atmospheric pressure discharges because they not require expensive vacuum systems and the modification process becomes faster because of higher concentration of active species (from minutes to seconds).

The effect of plasma on a polymer surface

Plasma activation has demonstrated to be very promising in a plethora of processes which allow the modification of the surface of polymers. These processes include cleaning and etching for the removal of contaminants and polymer material, cross-linking and branching for the deposition of polymer and/or hybrid organic/inorganic multicomponent thin films, and surface treatment for the modification of the outermost layers of the polymer through chemical grafting of specific functional groups. Plasma etching is routinely used in microelectronics. More recently, controlled surface modification, deposition of films irrespective of the surface geometry, intrinsic sterility and the prospect of scaling-up make the plasma treatment of polymers suitable for tissue engineering and biomedical applications, such as the creation of scaffolds on body implants (prostheses, catheters and intraocular lenses), biosensors, etc. Also, plasma treatment favours cell growth and adhesion, which improve biocompatibility.[32,33]

Plasmas are probably the most widely used method for surface modification of polymers. Exposition of a polymer to plasma results in the immediate formation of radical active sites on its surface, typically up to a depth of a few nanometres, and in the increase of roughness and formation of nano-sized pores.[34] The plasma has sufficiently high energy to break the covalent bonds of polymers exposed to it. Depending on the gas used to generate the plasma, active sites can be different and react and/or recombine into a broad variety of chemical functional groups, which in turn will have a strong impact on the surface properties of the polymer. In industry this is commonly performed to clean components, to activate plastics before gluing and painting and to change the hydrophobic/hydrophilic character of surfaces, among many other uses. For instance, commonly used hydrophobic polymers like polyethylene (PE) and polyethylene terephthalate (PET) can be treated effectively with plasma to increase their surface energy and, therefore, to strongly enhance the wettability of their surface as well as their adhesion to inks, glues, adhesives and metal coatings (Figure 3).[35-39]

The effect of the plasma changes by varying the process parameters such as pressure, power, process time, gas flow and composition and distance from the substrate surface. Plasma treatment also leads to a variation of the zeta potential. The detailed mechanisms of plasma processes are very complex because they are governed by various simultaneous surface reactions among the particles, ions, electrons, photons and radicals interacting at the surface of the polymer.[40] Surface treatments of polymers by plasma technology are fast and easily adaptable to on-line production protocols with low running costs; in addition they are environmental friendly processes.[41,42] For industrial application, the less expensive option are plasma processes performed using air or nitrogen atmospheres, but the use of noble gases with eventual admixture of reactive gases (O_2, steam, NH_3, etc.) is also reported.

While wettability, lubricity and adhesion enhancement of polymers represents a well-established application of plasmas, its use in the preparation of polymer-based sensors, flexible electronics and batteries represent a recent field of study.[43-45] In fact, many sensors are based on surface modifications that specifically measure the concentration of a bio-molecule through the surface attachment of a chemical group able to recognize it. The use of polymers as sensors, however, is very limited because their surface properties are correlated to their bulk properties, and most polymers are inert. Plasma processing allows tailoring the surface properties of a polymer independent of its structure and bulk properties and, for this reason, the surface modification of polymers by plasma has gained interest in sensor technology.[46,47] Particular attention needs to be given to the aging of the treated surfaces. This involves the reorientation of plasma-grafted reactive groups into the bulk of the polymer during air storage, which may cause a progressive passivation of the surface imparted by the plasma treatment.[48]

Plasma treatments are able to alter the surface characteristics of polymers by substitution of chemical groups present on the polymer chain being modified. In addition, the different process atmospheres can incorporate different types of chemical groups such as hydroxyl (O–H), alcohol (C–O), carbonyl (C=O), carboxylic (O–C=O) or amino (N–H) on the polymer surface and/or implant reactive oxygen and/or nitrogen species. The addition of O_2 to the gas atmosphere facilitates the generation of polar, oxygen-containing groups on the treated surface, although some etching and damage of the surface layer also occur. In particular, for polymers with oxygen-containing functionalities in the backbone, etching, rather than oxygen incorporation, is observed. In contrast, aromaticity within the polymer backbone favours the incorporation of oxygen-containing species, as corroborated by high resolution X-ray photoelectron spectroscopy (XPS).[49,50]

In inert gas plasmas, the dominant process is hydrogen abstraction and exposure to the laboratory atmosphere leads to functionalization. However, in polystyrene, the addition of hydrogen in nitrogen plasma increases the reactivity toward the attachment of amine groups.[51] These functional groups anchored on the surface of polymers may enable covalent bonding for fixation of biomolecules, which may be used as receptors in biosensor applications. Examples in the literature include sensors for DNA and urea detection.[52,53] In the latter case, urease was linked to the surface of polypropylene treated with NH_3 plasma. Carbonyl groups introduced employing an O_2 plasma can serve as linker groups for protein immobilization through the formation of Schiff bases with the amine groups of proteins to fabricate biosensors.[54,55]

Pressure, temperature and humidity sensors

Touch sensors have received a great deal of attention in electronics. Indeed, capacitive touch sensors are commonly used in touch screens for many mobile devices, such as smart phones and tablets. However, recent work on touch sensors has been also aimed at developing biomedical applications, as for example robotic for medical procedures, such as surgery and catheter radio-frequency ablation, prosthetics and artificial skin.[57] Microfabrication technologies used to develop touch sensors destined to the medical field couple characteristic technological features, as for example small size, sensitivity and low power consumption, with the chance of providing a better outcome for the patients.

In a recent study, Lee and co-workers[58] prepared stretch-unresponsive stretchable and transparent sensors, thus avoiding the most frequent drawback of capacitive touch sensors: capacitance changes upon stretching. Such capacitance variation is usually induced by dimensional variations in the elastomeric dielectric, limiting the stability of the sensor under large strains. The key parameters for the new sensors were a selective plasma-based patterning process and the choice of dielectric and substrate materials with low strain responsivity. For this purpose, thin polyurethane (PU) dielectric was sandwiched between two transparent and stretchable electrode lines, made of silver nanowires (AgNW) / reduced graphene oxide (rGO), on polydimethylsiloxane (PDMS) substrate. The selective patterning of the PDMS substrate using a shadow mask, which was performed using an O_2 plasma treatment in a microwave plasma reactor, converted the hydrophobic polymeric surface into hydrophilic. After removing the PMDS shadow mask, solutions of AgNW, rGO and PU were coated in sequence. Thin films were formed only in the plasma-treated regions of the substrate due to the surface energy difference with respect to the non-treated regions.

Wang *et al.*[59] prepared a pressure-sensing device by combining two parts, a plasma modified poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) film and a patterned interdigitated ITO electrode (Figure 4a). The surface of the PEDOT:PSS film, which was spin-coated onto PET-ITO substrates, was treated for 3 min with a N_2 plasma to enhance its piezo-resistive sensitivity and response. Specifically, the water contact angle of PEDOT:PSS increased from 88º to 95º after N_2 plasma surface modification for 3 min (Figure 4b), this value decreasing dramatically after such time of plasma exposition (*i.e.* the film became more hydrophilic due to plasma damage). The increment of hydrophobicity reached after 3 min was attributed to a change in the chemical structure (Figure 4c) that affected the conventional core-shell structure of micelles in PEDOT:PSS films (*i.e.* PEDOT as the core and PSS as the shell).[60] More specifically, the conjugation at PEDOT chains was altered by the apparition of thiocyanate groups, which reduced the horizontal carrier mobility (*i.e.* the horizontal resistance increases), while the formation of sulfamate (SO_2–NH_2) affected the electrostatic bond at PEDOT:PSS micelles improving the conductivity when force was applied (*i.e.* the vertical resistance decreases). These changes in the piezo-resistance characteristics explained the sensitivity enhancement experienced by the plasma modified pressure sensor.[59]

On the other hand, temperature and moisture are critical factors for living systems. Temperature and/or humidity sensors have been integrated into biomedical devices, as for example artificial skin for body temperature regulation and moisture sensation resembling human skin,[61,62] and applied as imaging bioplatforms, for example to identify the biological status of the human body and of the individual tissues.[63]

In response to the demands of high-accuracy and high-stability temperature sensors for biomedical applications, Aliane *et al.*[64] described enhanced printed temperature sensors on large area and flexible foils made of polyethylene naphthalate (PEN) and PET. Two different sensitive inks were screen printed onto the PEN or PET substrates: a positive temperature coefficient layer, which acted as a resistive paste, and a negative temperature coefficient sensitive layer made of a metallic oxide based on antimony tin oxide (ATO). The resistance temperature coefficient of the ATO was enhanced by applying an O_2 plasma treatment (power= 120 W,O_2 flow= 50 cm^3/min) for 1 minute. This short time interval precluded the damage of the plastic flexible substrate while the sensitivity increased up to 0.025 V/ºC at 37ºC, evidencing the utility of the sensor for human body temperature detection.[64]

More recently, a flexible simultaneous temperature and humidity sensor was prepared from graphene woven fabrics (GWF) by chemical vapour deposition.[65] Figure 5a shows the key steps to fabricate the sensor. Initially, GWF was transferred to a flexible PDMS substrate. After O_2 plasma treatment, the resulting temperature sensor was spin-coated with a PDMS layer, flipped over and, subsequently, another GWF was transferred onto the top side. Finally, a solution of cellulose acetate butyrate (CAB) was spin-coated on the GWF to form a humidity-active film, which was coated with another layer of GWF to achieve the humidity sensor. It is worth noting that the latter essentially consisted in a sandwich-like capacitor formed by to GWF electrodes separated by a CAB layer that acts as a dielectric. Although the O_2 plasma-treatment was not required for the humidity sensor, the sensitivity of the temperature sensor increased significantly with plasma treatment time (Figure 5b). This was attributed to at least one of the following three factors: (1) the formation of oxygen functional groups on the graphene; (2) the plasma-induced interactions between the GWF and the PDMS substrate, improving the contact between the two components of the assembly; and/or (3) the inhomogeneity of the PMDS treated surface due to the formation of microcracks. In any case, the temperature sensor exhibited very good sensibility and stability in the 20-55 ºC temperature range (Figure 5c).

In spite that Zhu and co-workers used plasma treatment for the temperature sensor but not for the humidity one,[65] plasma technologies can be very valuable for the latter.[66,67] In a pioneering work, Gangal and co-workers[66] reported for the first time humidity sensing by applying Ar plasma treatment to polymethyl metacrylate (PMMA). More specifically, after spin coating a PMMA solution onto a glass substrate, the resulting films were exposed to Ar plasma in a dc plasma reactor. The capacitive response of the sensor was taken over saturated salt solution, changing the relative humidity from very low to ~90%. Unfortunately, the sensitivity was not linear through such wide relative humidity range, the usable range of the sensor being 0-40% for which sensitivities of nF were determined.[66]

More recently, Kim and co-workers[67] developed a humidity sensor by dry etching and residue removal of functional polymer mixed with TiO_2 microparticles *via* inductively coupled CF_4/O_2 plasma. Inductive coupled plasma micro-patterning is a time efficient, clean and solvent-free process, which is precisely controlled through the corresponding processing parameters (*i.e.* power, chamber pressure, discharge gas, time, etc). The sensor fabrication process, which is schematically depicted in Figure 6a, consisted in a four-step process: (1) a polymer was spin-coated on the surface of a silicon wafer; (2) a negative photoresist patterning was spun onto the surface of the polymer layer; (3) the polymer was etched by applying the inductively coupled CF_4/O_2 plasma; and (4) the residue was removed with deionized water and chemical treatments. Interestingly, the surface roughness was regulated through the percentage of CF_4 in O_2 (Figure 6b). Although at low CF_4 concentration etching was not aggressive enough to roughen the surface, the surface roughness increased with CF_4 concentration in O_2 up to a percentage of 20%, at which the maximum roughness was achieved. Above this concentration, the roughness was reduced as a balance reached between the concentration of fluorocarbon compounds and the protection of the surface by the etching products. On the other hand, the roughness increased with both the plasma power and chamber pressure, which was also good for the adsorption of moisture. The best capacitive humidity sensor application was obtained a plasma power of 900 W, a chamber pressure of 450 mTorr, and 10% of CF_4 in O_2.[67]

Hybrid capacitive humidity sensors with a wide sensing range were prepared combining two different plasma treatments.[68] The sensor was composed of three elements: 1) a porous top electrode obtained by combining polyamic acid and oxydianiline with TiO_2 microparticles; 2) a bottom electrode; and 3) a glass substrate. The two plasma treatments were applied to the top electrode and consisted of an O_2 inductively coupled plasma that was applied to increase the contact between the TiO_2-containing functional polymer and water vapour, and a reactive-ion etching to increase the roughness of the functional polymer surface. The fabricated sensors exhibited ultralow hysteresis, high sensitivity, fast response time, good temperature dependence and stable capacitance.[68]

These recent contributions on pressure,[58,59] temperature[64,65] and humidity[66-68] sensors exemplify the importance and high potential of conventional plasma technologies as strategies for the functionalization and activation of polymeric substrates. In all studies plasmas technologies have been applied within the framework defined by their traditional usages. More specifically, for the pressure, temperature and humidity sensors developed by Choi *et al.*,[58] Abou *et al.*[65] and Liu *et al.*,[67] respectively, plasma treatments were used to etch the surface for selective patterning or to prepare the surface for additional coating. Besides, plasma technologies were used by Wang *et al.*,[59] Aliane *et al.*[64] and Dabhade *et al.*[66] to modify and regulate the surface properties of polymers (*i.e.* wettability, thermal resistivity and capacitive response, respectively), which were subsequently employed as pressure, temperature and humidity sensors, respectively. Thus, activation with O_2 or N_2 plasmas induced the transformation of functional groups into other oxygen- or nitrogen-containing groups, which were used to regulate such properties and, therefore, the sensitivity of the sensors. Finally, the humidity sensor developed by Qiang *et al.*[68] merges the two approaches. These authors combined two plasma treatments: the first one was used as an etching tool while the second one increased the contact area between the polymer and water vapour. Because O_2 and N_2 plasmas are simple to use, dry and one-step method, these surface treatment technologies will undoubtedly play a crucial role in next years for the development of sophisticated pressure, temperature and humidity sensors with practical biomedical applications.

pH and UV-responsive sensors

Hydrogen ion is a ubiquitous species found in most chemical reactions. It is quantified in terms of pH –the negative logarithm of its activity. The pH sensors are widely used in chemical and biological applications such as environmental monitoring (water quality), blood pH measurements and laboratory pH measurements amongst others.

The most common systems for pH sensing are based on electrochemical measures, either potentiometric or amperometric, using for example glass electrodes, which exhibit high selectivity for hydrogen ions in a solution. Ion selective membranes, ion-selective field effect transistors, two terminal microsensors, fibre optic and fluorescent sensors, metal oxide and conductometric pH-sensing devices have also been developed,[69,70] even though they often suffer from instability or drift (*i.e.* constant re-calibration is required). In the last decade, considerable research interest was focused on the development of chemical or biological sensors using functional polymers.[71,72] Within this context, both conducting polymers and non-conducting polymers are being employed for adequate sensitivity, accuracy and rapid potentiometric and spectroscopic detection of pH.[73-75]

In a recent work, Catalina and co-workers[76] proposed a new methodology for the functionalization of polymers using microwave radiation. This technique was applied to poly(ethylene-butyl acrylate) copolymer superficially functionalized with a fluorescent dye attached to the surface, the response of both the untreated and plasma-treated materials being evaluated as pH sensors by determining the change in the spectroscopic properties of absorption and fluorescence with pH. A crucial step in this new approach was the improvement of polymers surface wettability through an oxidation treatment. Specifically, after 30 min of O_2 plasma treatment, the contact angle for water decreased from 92.6º to 41.0º while the average roughness increased from 12.5 to 35.5 nm. This was attributed to the generation of free radicals and oxygen-containing functionalities at the polymer surface, together with the subsequent re-arrangement of the modified chains. The O_2 plasma substantially decreased the response time of the dye fluorescence in strong acid media (from 80 min to 30 min) and induced a large decay of fluorescence in the treated polymer film.[76] Changes in the fluorescence properties were observed in HCl solutions with concentrations ranging from 1 to 12 M. Furthermore, the plasma treated film was also sensitive to extremely acidic environments in the vapour phase, even though this phenomenon was only observed after 1 hour. Overall, results evidenced that the oxidative effects caused by the O_2 plasma on the polymer surface facilitated the penetration of protons into the regions in which the fluorescent dye was anchored.

On the other hand, UV radiation is dangerously increasing because of the decrease of ozone in the stratosphere.[77] Thus, exposure to UV radiation is the main factor that causes skin cell to become cancer cells (*i.e.* 99% of non-melanoma skin cancer and 95% of melanoma are due to too much UV radiation from the sun or other sources, such as solariums and sun lamps).[78] Consequently, different UV light detectors have been proposed, many of them being based in the phase change experienced by photochromic dyes when exposed to UV radiation.[79,80] The latter causes a change from colourless to coloured, reverting to the original state when the source of UV radiation is removed. In a very recent study, the surface of PET fabric was treated with O_2 and NH_3 plasma to increase the embedment of UV-responsive microcapsules that were deposited by pad-dry curing.[81] The plasma gas (*i.e.* one gas or the combination of both) and treatment times affected considerably the reactivity of the PET fabric. The O/C ratio of untreated samples, which was 0.31 as expected from the chemical composition of PET, increased upon the application of O_2, evidencing the saturation with oxygen-containing polar functional groups at a treatment time of 100 s (Figure 7a). Besides, treatment with only NH_3 containing plasma did not significantly alter the surface composition, while the combination of O_2 and NH_3 resulted in an enhancement of both O/C and N/C ratios (Figure 7a). Both FTIR and secondary ion mass spectrometry showed that NH_3 plasma induced the apparition of CN^- and OCN^- fragments with a OCN^-/ CN^- ratio of 0.57 (Figure 7b). Plasma treatment of PET fabric with O_2 and NH_3 gases caused higher reactivity of the substrate and, consequently, higher uptake of UV-responsive microparticles, colour strength increasing up to 75% (Figure 8).[81]

These works represent very different degrees of innovation from the point of view of the objective of using plasma. The pH sensor manufactured by Fernández-Alonso *et al.*[76] was based on a very conventional utilization of O_2 plasma (*i.e.* increase the wettability by modifying the surface roughness), while Gorjanc *et al.*[77] proposed a more innovative application combining the action of two plasmas, which were applied consecutively to independently control the concentration of O- and N-containing species. Specifically, the regulation of the surface composition through the sequential application of O_2 and NH_3 microwave discharge plasmas resulted in a much more efficient uptake of photochromic dye and, therefore, in a very remarkable improvement in colour depth and the colour difference.

In any case, development of pH- and UV-responsive functionalized polymeric surfaces by applying simple plasma treatments represents a fast, low-cost and, therefore, valuable alternative to tedious chemical methods. Although it frequently allows a very precise control on both the kind and degree of functionalization, post-modification of polymeric surfaces by chemical functionalization involves specific costly multiple-step processes that potentially limit the application in commercial sensors. In contrast, plasma functionalized treatments are more efficient, versatile and cheap but less controllable in the synthesis and for the chemical structure of the chemical groups. However, the latter drawbacks are not particularly relevant for the development of pH and UV sensors, which are mainly based on the formation of free radicals and oxygen-containing functionalities at the polymer surface for reaction or formation of physical interactions.

Gas sensors

In the area of volatile organic chemical (VOC) and simple gases detection and identification, polymeric sensors can be used independently for detection and measurement of individual vapours or jointly in the form of arrays for measurement of complex odours and gases. Polymeric gas sensors are typically based on electrically-responsive materials, so that the electrical conductivity of the polymer film changes when exposed to analyte vapours.[82] The changes can be correlated quantitatively to the concentration of the vapours and can be readily reversed when the vapours are removed. This technology has resulted in the development of sensors with very different applications as for example the environmental monitoring in chemical and biomedical electronics and diagnosis. For example, human olfactory receptor-conjugated polypyrrole nanotubes were recently integrated into a field-effect transistor sensor platform for the fabrication of bioelectronics noses,[83] while chemical electro-responsive sensors able to detect traces (in the order of ppm) of gaseous agents with biomedical implications, such as acetone[84] and ammonia,[85] have been constructed combining conducting polymers with different materials.

Gas sensing composites were prepared by dielectrophoretic assembly (Figure 9a) of a nanostructured PEDOT:PSS layer and O_2-plasma treated single-walled carbon nanotubes (SWCNTs).[86,87] The O_2 plasma was used to functionalize the SWCNTs surface by grafting oxygen-containing functional groups, improving the aqueous solubility, while PEDOT:PSS was used as dispersant to enhance the dispersion of SWCNTs. Simultaneously, the dielectrophoreric process was utilized to align the functionalized SWCNTs enhancing the electrical and mechanical properties of the resulting composite, which depended on the orientation of the nanotubes. Also, the formation of compact and large congregated PEDOT-rich grains separated by SWCNTs facilitates the nearest-neighbour electron tunnelling between conducting polymer chains. This particular structuration allowed the selective and sensitive response to ppm-level NH_3 and ppb-level trimethylamine (TMA) vapours (Figure 9b).[86,87]

Plasma treatments have been recently applied to complex polymeric composites designed to be potential sensing materials in gas sensors. For example, the chemiresistive properties of polyaniline (PAni)/multi-walled carbon nanotubes (MWCNT) doped with anionic biopolymer ι-carrageenan, were tuned by treating the surface with Ar non-thermal plasma.[88] The increment in the conductivity caused a change in the response to H_2 gas. Thus, in dry environments the sensitivity of plasma-treated samples to H_2 gas was ~5 folds higher than that of untreated PAni/MWCNT. This response was even better than that earlier reported by Yoo *et al.,*[89] who studied the effects of radio frequency O_2 plasma treatment on the gas sensing characteristics of PAni/MWCNT composite films deposited onto a MEMS micro-hotplate. Oxygen-containing defects at the surface of plasma-functionalized MWCNTs were found to improve the binding with PAni, promoting the conductivity between the two species. As a result, the sensitivity of plasma treated PAni/MWCNT was about three times higher than that obtained for the untreated sensor for NH_3 concentrations ranging from 0 to 100 ppm. This result was explained by the formation of hydrogen bonds between polar NH_3

molecules and the oxygen-containing functional groups created on the surface of MWCNTs.

Simple O_2 plasma post-treatment for electrospun polyacrylonitrile nanofibers have been recently used to fight against air pollution,[90] which is serious human health issue. Thus, it is well-known that exposure to particulate matter pollution has a growing impact on public health and, therefore, filter technologies to improve the air filtration efficiency are required.[91,92] Application of the plasma treatment to the surface of polyacrylonitrile nanofibers induced the formation of function groups as $–CONH_2$, –COOH and –COOR, resulting in high-performance particulate matter removal compared to commercial filters.[90] Although in this case the plasma surface modification was not directly applied in the particulate matter sensor but on the coupled polymeric filter, improvement of air pollution represents a great advantage of undeniable biomedical importance.

Plasma modified carbon nanotubes have been used in absence of any polymeric matrix to detect different toxic gases, as for example CO, NO_2, H_2S, SO_2 and ethanol vapors.[93--97]. Among such studies, one deserves special attention since it reported a new method for uniform functionalization of powdery materials, achieved by repetitive circulation of the latter within the plasma reactor.[93] This consists in a plasma reactor equipped with a porous metallic filter electrode that increases both homogeneity and degree of functionalization by capturing and circulating powdery materials via vacuum and gas-blowing (Figure 10a). Although this method was applied to carbon nanotubes, it can be also applied to powdery polymers or powdery polymer/carbon nanotubes composites. Plasma activation with 1:1 O_2:air created oxygen-containing functionalities (*i.e.* hydroxyl and carboxyl groups) on the surface of the nanotubes, while nitrogen functionalization was performed on O_2:air plasma-treated samples through an NH_3

plasma. The resulting sensors were tested on dimethyl methylphosphonate (DMMP) vapors, a stimulant for G-type nerve agents. Figure 10b compares the change in the resistance of pristine and plasma-treated carbon nanotubes upon exposure to DMMP vapors. As it can be seen, the signals, which depended on the concentration of DMMP, were partially irreversible and greater for the plasma-treated sensor (Figure 10b, left). The detection limits were 120 ppb and 180 ppb for pristine and plasma-treated sensors, respectively (Figure 10b, right).

Continuous monitoring of gases concentration is crucial for many different healthcare-related application fields, ranging from medical ventilation devices to environmental monitoring. For example, in the field of medical ventilation devices for emergency treatment, intensive care or home use, gas sensors should detect not only the gas concentration but also the gas flow. Also, the diagnostics of gaseous issue in relation with concentration of chemical in human body and their monitoring (*i.e.* chemical activities in the body) is performed by gas sensors implemented in biomedical devices.[98] Functionalized polymer-based gas sensors have been found to exhibit higher sensitivity and selectivity than non-functionalized one. Thus, the creation of active polar groups in the polymer surface favors the formation of stable interactions with gas molecules. Polymers functionalization using plasma treatments presents significant advantages with respect other methods, such as low cost, easy production and compact size. Although, gas sensors based on plasma treated polymers exhibit high sensitivity, selectivity and response speed, more work is still necessary for optimizing such characteristics through the enhancement of both the degree and uniformity of functionalization. Within this context, the pioneering contribution of Lee *et al.*[93] represents a very significant advance in the field. These authors developed a methodology for uniform plasma functionalization of powdery materials, achieved by repetitive circulation the materials within the plasma reactor. The new approach was successfully applied to CNTs for detection of toxic gases, which is a very attractive utilization from the perspective of biomedical devices. This pioneering plasma treatment is cost effective, environmentally friendly, and applicable to a broad range of powdery micro/nanomaterials.

Sensors for biomolecules and living systems

A number of sensors utilizing organic semiconducting polymers have been developed for the detection of biochemical molecules (*e.g.* simple electrolytic salts, neurotransmitters and enzymes).[99-101] Among these sensors, one architecture family is the organic electrochemical transistor, which can be used for enzymatic sensing using dedoping mechanisms and/or field effect transistor (FET) principles.[102] This strategy has been combined with plasma techniques to prepare flexible and optical transparent biosensors. For example, Werkmeister and Nickel[103] used an O_2 plasma treatment to improve the FET response of a flexible parylene dielectric substrate in presence of simple electrolytes.

Sensitive detection of the physiologically important chemicals involved in the brain function has drawn much attention for the diagnosis and treatment of brain diseases and neurological disorders.[104] For example, glucose monitoring is not only important for medical diagnosis and management of diabetes, which is a major health problem for most developed societies around the world, but also to improve diagnosis and treatment of brain tumours.[105,106] To date, the most common glucose biosensors, which are based on amperometric detection, achieve specific recognition by immobilizing an enzyme called glucose oxidase (GOx) that catalyzes the oxidation of glucose to gluconolactone.[107] Following this approach, in an early study Maekawa *et al.*[108]

developed a glucose-sensing electrode based on the cathodic detection of the O_2 consumed with the GOx reaction in presence of glucose. The sensor was prepared by immobilizing the enzyme on a poly(dimethylsiloxane) layer treated with O_2 plasma to replace silane groups by silanol groups at the surface, which were employed to fix the GOx by cross-linking chemical processes. Thus, plasma-treatment allowed to solve the problems typically associated to enzyme-based sensors (*e.g.* poor reproducibility, complicated immobilization processes and high cost), facilitating the integration of the GOx layer. The resulting biosensor measured glucose in the concentration interval comprised between 0.02 and 1.8 mM without the error caused by interferents, such as L-ascorbic acid and uric acid.[108]

In recent studies we proposed a completely new approach devoted to transform low density polyethylene (LDPE) into an electroactive material able to detect selectively dopamine and glucose using an air-corona discharge cold plasma treatment.[46,47] LDPE is an inert and insulating low commodity plastic with null capacity for electrochemical detection. However, plasma exposure promotes the formation of a large variety of reactive species at the surface (*e.g.* N, O, N_2^+, O_2^+ and O^+). A three-step mechanism was proposed:[46] 1) plasma activates hydrogen separation from polymeric chains, forming free radicals; 2) radicals react with the reactive species previously mentioned and/or components from air; and 3) the functional groups resulting from such reactions remain at the polymer surface, which becomes very active. XPS results clearly indicated that the nature of reactive species formed upon exposure of the polymer to the plasma depends on both the chemical structure and the duration of the treatment. The high reactivity of the excited species formed on the surface of LDPE had direct electrocatalytic effects in the oxidation of dopamine, an important neurotransmitter associated to different neurological disorders (*e.g.* Parkinson and schizophrenia),[109] to dopamine-*o*-quinone. Thus, application during 1-2 min of air-plasma to LDPE films resulted in sensors (Figure 11a) with resolution and sensitivity similar to those achieved through sophisticated chemical modifications, as for example the incorporation of AuNPs to conducting polymers.[110]

Identical cold plasma treatment was applied to other electrochemically inert plastics as well as to selected conducting polymers.[46] Plasma treated polypropylene, polyvinylpyrrolidone, poly(4-vinylphenol), polycaprolactone and polystyrene transformed into electrochemical sensors for dopamine detection by applying a simple cold plasma treatment (Figure 11b), as occurred for LDPE. The implications of this approach were very significant since the utilization of conventional commodity polymers can cause not only a very significant reduction in the economic cost of the detection devices but also opens a new door for the technological reuse of recycled polymers. Regarding to conducting PEDOT and poly(*N*-cyanoethylpyrrole) (PNCPy), which already were reported to detect dopamine without any treatment (Figure 11c),[111,112] application of corona discharge at 0.5 J cm^{-2} in ambient atmosphere during 2 min improved the resolution, sensitivity and selectivity, especially for PNCPy that is unable to discriminate dopamine from interferents without plasma treatment (Figure 11d).

In a very recent study it was found that plasma-treated LDPE acts as mediator in enzymatic glucose biosensors based on GOx and glass carbon substrate.[47] Results indicated that plasma-induced changes facilitate the electrocommunication between the enzyme and the substrate. The chronoamperometric response of these sensors prove their bifunctionality since the oxidation of glucose to gluconolactone, which is catalysed by the GOx, coexists with the oxidation of dopamine that is electrocatalytized by the plasma activated LDPE surface. Thus, glucose and DA, which exhibit very different electron transfer rates, were clearly differentiated from the rest of interferents (Figure 11e).

The application of plasma for transforming electrochemically inert polymers into compounds able to electrocatalyze the oxidation of dopamine and to act as electrochemical mediators able to detect the enzymatic oxidation of glucose, should be defined a paradox-based paradigm for the fabrication of electrochemical sensors by using inert and cheap plastics. Thus, in these cases, the objective of using plasma is very far from what are the traditional uses of plasma technologies directed simply to introduce certain surface modifications to achieve changes in some properties. Indeed, such studies opened a facile, simple and rapid way for the fabrication of sensitive biomolecule detectors that can be implemented as a very cost-effective diagnostic test.

Alocilja and co-workers[113] developed an electrospun biosensor of nitrocellulose based on capillary separation and conductometric immunoassay to detect bacterial and viral pathogens. The capillary performance was enhanced by treated the electrospun nitrocellulose nanofibers with an O_2 plasma. Removal of the surface nitrate groups increased the hydrophilicity of the material, the contact angle between the water droplet and the nanofiber mat decreasing from 135º to 56º. After this, the nanofibrous mat was functionalized with antibodies for application to bacterial and viral pathogen detection. Due to the unique structure and biocompatibility of the electrospun nitrocellulose mats, the antibody-functionalized sensor had linear detection response for *Escherichia coli* O157:H7 and bovine viral diarrheal virus. The detection time of the sensor was 8 min and the detection limit was 61 CFU/mL and 10^3 CCID/mL for microbial and virus samples, respectively.[113] The utilization of plasma-treated electrospun nitrocellulose fibres as biosensors can be extended to other antimicrobial and viral organism by appropriately changing the antibodies.

Overall, the most popular field implementing the use of biosensors is the biomedical sector, as for example to keep a check on molecules that are relevant for metabolic and heart diseases, to control neurological disorders facilitating the application of appropriated treatments, to detect processes associated with the microbial and virus invasions at the early stages, and to enable in vivo monitoring of cellular processes. Electrochemical sensors are also playing a vital role in cancer. The emerging extrapolation of well-known plasma technologies for the treatment of materials represents a significant improvement in the detection of biomolecules and living organism, opening a new door in the clinical field. As the level of functionalization achieved in plasma-treated materials is similar or even higher than that achieved using untreated sophisticated materials, advantages can also result in less favored countries where the use of expensive sensors is very restricted.

Conclusions

Rapid diagnosis of medical conditions is the goal for high healthcare standard for the society. Within this context, the design of sophisticated materials to achieve extremely sensitive detection of target biological parameters has originated the convergence of various research domains ranging from life science, chemistry, biosensor design, microfabrication and more. Electrochemical biosensors have been worked on for a long time and in recent years design of devices based on sophisticated electroactive materials have already been realized as a commercial product. The evolution of the electrochemical glucose sensors into a viable commercial product, ever since its inception in the second half of the last century, is an example of the success of electrochemical techniques. Therefore, electrochemical techniques for biosensors applied now, among others, to environmental, biomolecule and cytometric detection applications are being researched for application in the area of point of care testing systems. Recent examples are blood analysis monitoring systems, like the commercial i-STAT from Abbott Point of Care, USA.[114]

An alternative approach to the development of increasingly sophisticated electroactive materials, in terms of supramolecular organization and/or number of components, is the extrapolation of plasma technologies to biomedical sensing. In the last years, electrochemical biosensors based on plasma-treated polymeric materials have proved to be good and precise, to present reduced costs, and to exhibit high specificity. In this mini-review we have shown that biosensors based on relatively simple plasma-treated biosensors are useful for the detection of the broad spectrum of agents and biomolecules that are crucial to human health, showing excellent responses and success against humidity, pH, glucose, neurotransmitters bacteria and pollutants, among others.

In general, the incorporation of plasma technologies to biomedical sensors has occurred at three different levels. The first corresponds to that in which plasma treatment has been used to clean or to prepare the surface for additional coatings. The second is based on the utilization of plasma to regulate the physical properties of polymers surfaces through their functionalization. Finally, the most outstanding level is the transformation of electrochemically inert plastics, such as LDPE, in electroactive compounds able to electrocatalyze the oxidation of biomolecules.

Other applications that are expected to involve in a near future plasma-modified biosensors are food industry to keep a check on its quality and safety and to help distinguish between the natural and artificial, and the fermentation industry for continuous monitoring of the glucose level. All in all, “plasma-treated materials for biosensing” is a new area of research and can be a potential alternative to existing strategies due to the several advantages described in this work. However, there are several challenges that need to be surpassed in order to establish plasma technologies as a standard alternative approach in biosensing.

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Table 1. Brief description of the content of sections presented in this review.

Section	**Content**
The plasma concept	Basic technical information on plasmas categorization and generation
The effect of plasma on a polymer surface	Background on the effects of plasmas when used for surface modification of polymers.
Pressure, temperature and humidity sensors	Plasma processes to active polymeric surfaces during the fabrication of touch, temperature and humidity sensors.
pH and UV-responsive sensors	Plasma technologies to change the composition of polymeric surfaces and, therefore, to regulate properties like the wettability and the reactivity, which are fundamental for sensors of pH and UV.
Gas sensors	Plasma-based tools for the preparation of sensors with selective and sensitive response to organic and toxic vapours, air pollution or nerve agents.
Sensors for biomolecules and living systems	Plasma processes used to transform polymers into materials able to electrocatalyze the oxidation dopamine, promote the enzymatic oxidation of, or detect bacterial and viral pathogens.

Table 2. Summary of the most important characteristics of sensors prepared using a plasma treatment: detected analyte; plasma treatment conditions, such as type of plasma, power and time of treatment; and role of the plasma treatment in the sensor.

Sensor	Plasma treatment	Role of the plasma treatment	Ref
Pressure	O_2 plasma (500 W for 5 min) in a microwave plasma reactor	Selective patterning to transform the hydrophobic polymeric surface into hydrophilic	58
Pressure	N_2 plasma (50 W for 3 min) in a chemical vapour deposition system	Reduce the wettability to enhance the piezo-resistive sensitivity	59
Temperature	O_2 plasma (120 W for 1 min)	Enhance the resistance temperature coefficient	64
Temperature	O_2 plasma (1.5 min)	Prepare the surface of graphene woven fabrics for coating with polydimethylsiloxane	65
Humidity	Ar plasma (5 W for 5 min) in a dc plasma reactor	Regulate the capacitive response of the polymeric surface	66
Humidity	Inductively coupled CF_4/O_2 plasma (10% of CF_4 in O_2; 900 W for 3 min)	Controlled etching to modify the polymer surface roughness	67
Humidity	O_2 inductively coupled plasma (900 W for 1-3 min) and O_2 reactive-ion etching (100 W for 2 min) treatments	Successive treatments for polymer etching and further increase the surface roughness and the contact area between the polymer and water vapour	68
pH	O_2 plasma (30 W for 30 min)	Increase the surface wettability to decrease the response time	76
UV radiation	O_2 plasma (150 W for 200 s) and NH_3 plasma	Enhance the embedment of UV-responsive microcapsules,	81

	(150 W for 243 s) from a microwave source	which were deposited onto a polymeric substrate with pad-dry-cure process	
NH_3 and TMA vapours	Inductive coupled O_2-plasma (30 W for 3 min)	Functionalize the SWCNTs surface by grafting oxygen-containing functional groups to improve their solubility	86,87
H_2 gas	Ar gas plasma beam (30 short pulses, ~10 μs, with a discharge voltage of 500 V)	Increase the conductivity of PAni/MWCNT doped with anionic biopolymer ι-carrageenan	88
NH_3 gas	O_2 plasma (30 W for 60 s)	Functionalize MWCNTs by creating oxygenated groups on the surface, which facilitates the preparation of PAni/MWCNT composite films, to promote hydrogen bonds with NH_3 molecules	89
Air pollution	O_2 plasma (50 W for 90 s)	Modify the surface of electrospun polyacrylonitrile nanofibers for generating polar functional group, increasing the wettability.	90
Toxic gases	1:1 O_2:air plasma (50 to 100 W for 40 min) using a a plasma reactor equipped with a porous filter electrode	Very efficient and homogeneity functionalization of powdery materials, such as CNTs, using a vacuum-assisted sample circulation technique	93
Glucose	O_2 plasma (unknown power for 90 s)	Replace the silane groups by silanol groups at the surface of a poly(dimethylsiloxane) layer to immobilize the GOx enzyme by cross-linking chemical processes	108
Dopamine	Cold plasma in ambient atmosphere (discharge of 45000 V at 4.5 MHz for 1-2 min	Transformation of electrochemical inert LDPE into an electroactive polymer able to electrocatalyze the oxidation of	46

		dopamine to dopamine-*o*-quinone	
Dopamine and glucose	Cold plasma in ambient atmosphere (discharge of 45000 V at 4.5 MHz for 1-2 min	Transformation of electrochemical inert LDPE into an electroactive polymer able to both electrocatalyze the oxidation of dopamine to dopamine-*o*-quinone and fix GOx for glucose detection	47
Pathogens	O_2 plasma (120W at 13.6 MHz for unknown time)	Enhance the capillary performance of electrospun nitrocellulose nanofiber mats by decreases the water contact angle.	113

CAPTIONS TO FIGURES

Figure 1. Evolution of (a) the number of papers published every year in the field of plasma treated polymer surfaces and (b) the number of such papers related with biomedical applications. The searches were carried out using the Web of Science (Thompson Reuters) combining (a) "*Plasma + Polymer + Surface*" and (b) "*Plasma + Polymer + Surface + Biomedical*" as keywords.

Figure 2. (a) Scheme displaying how plasma treatment is used as a postproduction method of tuning drug release and bioadhesion of poly(lactic-co-glycolic acid) (PLGA) thin films. Reprinted and adapted with permission from *ACS Appl. Mater. Interfaces*, 2014, **6**, 5749. Copyright 2016 American Chemical Society. (b) Top: Surface topographies of the untreated and metal (Cu and Ag) plasma treated implanted polyethylene. Bottom: Bacterial infection conditions of bone tissues surrounding untreated and plasma treated implants with pre-injection of bacteria. Reprinted and adapted with permission from *ACS Appl Mater Interfaces*, 2011, **3**, 2851. Copyright 2016 American Chemical Society. (c) Plasma plasma treatment is an effective method to immobilize growth factors on scaffolds for tissue engineering. Left: Binding efficiency of basic fibroblast growth factor (bFGF) to plasma treated microtubuleorientatated PLGA scaffold without interconnected pores (MONIP-PLGA) and plasma treated PLGA scaffold with interconnected pores (MOIP-PLGA). Right: Cumulative release of bFGF from the MONIP-PLGA and MOIPPLGA scaffolds. Reproduced from Ref. 22 with permission from The Royal Society of Chemistry.

Figure 3. Example the influence of plasma treatments in the physical and chemical properties of polyethylene. Two different atmospheric plasma torches with different configurations (linear and showerhead supplied with He and Ar, respectively, as carrier gas) and different treatment times have been considered. The variation of the (a)

advanced water contact angle (aWCA), (b) the O/C ratio, (c) the mass loss, (d) the root-mean-squared roughness, and (e) the surface topography as observed by AFM exposed to plasma torches with different configurations and treatment time are displayed. Reproduced from Ref. 35 with permission from John Wiley and Sons.

Figure 4. (a) Schematic diagrams of PEDOT:PSS pressure sensor after N_2 plasma modification: different elements (left) and cross-sectional view of the final device (right). (b) Variation of the contact angle of PEDOT:PSS against the surface treatment time using N_2 plasma. (c) Molecular structure of PEDOT:PSS before and after surface modification using N_2 plasma. Reprinted and adapted with permission from *J. Phys. Chem. C*, 2016, **120**, 25977. Copyright 2016 American Chemical Society.

Figure 5. (a) Schematic diagram of the assembly steps of the flexible temperature and humidity sensor. (b) Evaluation of the temperature sensing performance with different plasma treatment times. (c) Cyclic temperature tests. Adapted and reprinted with permission from *ACS Appl. Mater. Interfaces*, 2017, **9**, 30171. Copyright 2017 American Chemical Society

Figure 6. (a) Schematic diagram showing the fabrication process of polymer dry etching by inductively coupled CF_4/O_2 plasma: (1) polymer deposition; (2) photoresist patterning; (3) polymer dry etching; and (4) residue removal and photoresist strip. (b) Surface roughness of the polymer film measured using AFM relative to the different percentages of CF_4 in O_2 used for the inductively coupled plasma treatment. Reproduced from Ref. 67 with permission from The Royal Society of Chemistry.

Figure 7. (a) Variation of the composition (in atomic %) and atomic ratios (×100) of the untreated and plasma-treated PET fabrics as determined by XPS (represented data taken from reference 81). (b) Negative time-of-flight secondary ion mass spectroscopy

spectra of untreated (top) and O_2 and NH_3 plasma-treated (bottom) PET fabrics. Reproduced from Ref. 81 with permission from Elsevier B. V.

Figure 8. a^* (green-to-red) b^* (blue-to-yellow) colour values of untreated and plasma-treated microcapsule-coated PET fabrics, before and after illumination with UV light source. Reproduced from Ref. 81 with permission from Elsevier B. V.

Figure 9. (a) Scheme and SEM micrograph showing the structuration of PEDOT/PSS-SWNCTs composited by dielectrophoretic assembly. The SEM image of the structure was taken from reference 87. SEM image reproduced from Ref. 87 with permission from The Royal Society of Chemistry (b) Selective responses of the dielectrophoretically assembled composite films with PEDOT/PSS and SWCNTs to various vapours of 10 ppm. Graphics reproduced from Ref. 86 with permission from Elsevier B. V.

Figure 10. (a) Scheme illustrating the repetitive circulation and plasma treatment of powdery materials (green) in a plasma reactor. The fed materials are attached onto porous filter electrodes by simultaneous vacuum and gas blowing, plasma treated (pink), and detached from the electrodes by back-blowing. The cycle can be repeated until desired materials properties are obtained. (b) Comparison of the responses curves to DMMP of pristine and plasma-treated sensors based on carbon nanotubes. Graphics reproduced from Ref. 93 with permission from Elsevier B. V.

Figure 11. (a) Control of 100 µM dopamine (DA), 100 µM uric acid (UA) and 100 µM ascorbic acid (AA) in 0.1 M phosphate buffer solution (PBS) at plasma-functionalized LPDE pressed onto a bare untreated glass carbon electrode (GCE). (b) Control voltammogram of 10 µM DA in 0.1 M PBS at plasma-functionalized polypropylene pressed onto a bare GCE. Voltammograms recorded using untreated electrodes (dashed lines) and cold-plasma treated electrodes (solid line) are displayed.

The same behaviour was observed for plasma-functionalized polyvinylpyrrolidone, polycaprolactone and polystyrene. (c) Control voltammograms of DA, UA and AA (100 µM each) in 0.1 M PBS at untreated PNCPy- and PEDOT-modified GCEs. (d) Control voltammograms of DA, UA and AA (100 µM each) in 0.1 M PBS at plasma-functionalized PNCPy- and PEDOT-modified GCEs. Grey arrows in (d) indicate secondary oxidation processes. (e) Control voltammogram of 10 mM glucose (Glu) in 0.1 M PBS with 0.1 mM DA, 0.1 mM AA and 0.1 mM UA at plasma-functionalized LPDE pressed onto GCE. In all cases, scan rate: 100 mV/s; initial and final potentials: -0.40 V; reversal potential: +0.80 V.

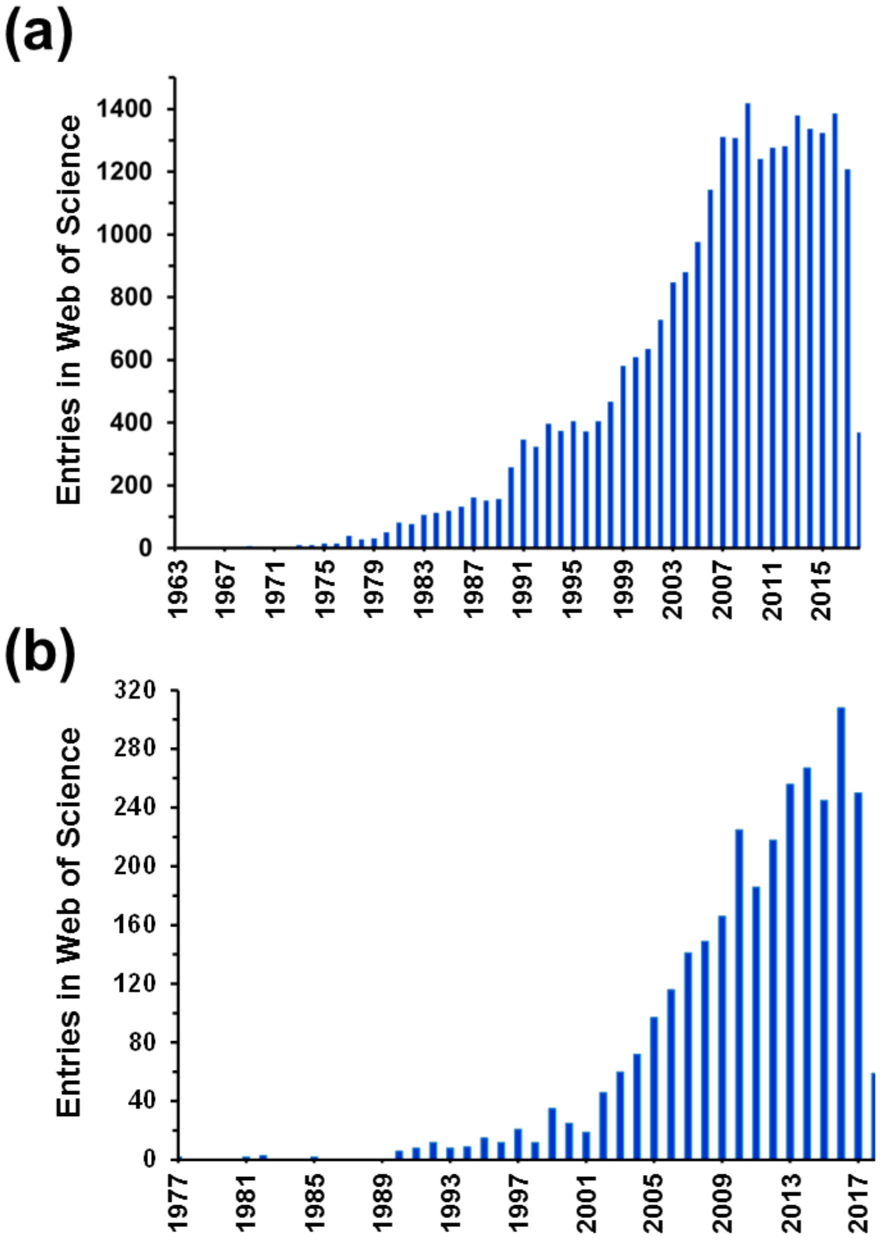
(a)
Entries in Web of Science
1400
1200
1000
800
600
400
200
0
1963
1967
1971
1975
1979
1983
1987
1991
1995
1999
2003
2007
2011
2015
(b)
Entries in Web of Science
320
280
240
200
160
120
80
40
0
1977
1981
1985
1989
1993
1997
2001
2005
2009
2013
2017

Figure 1

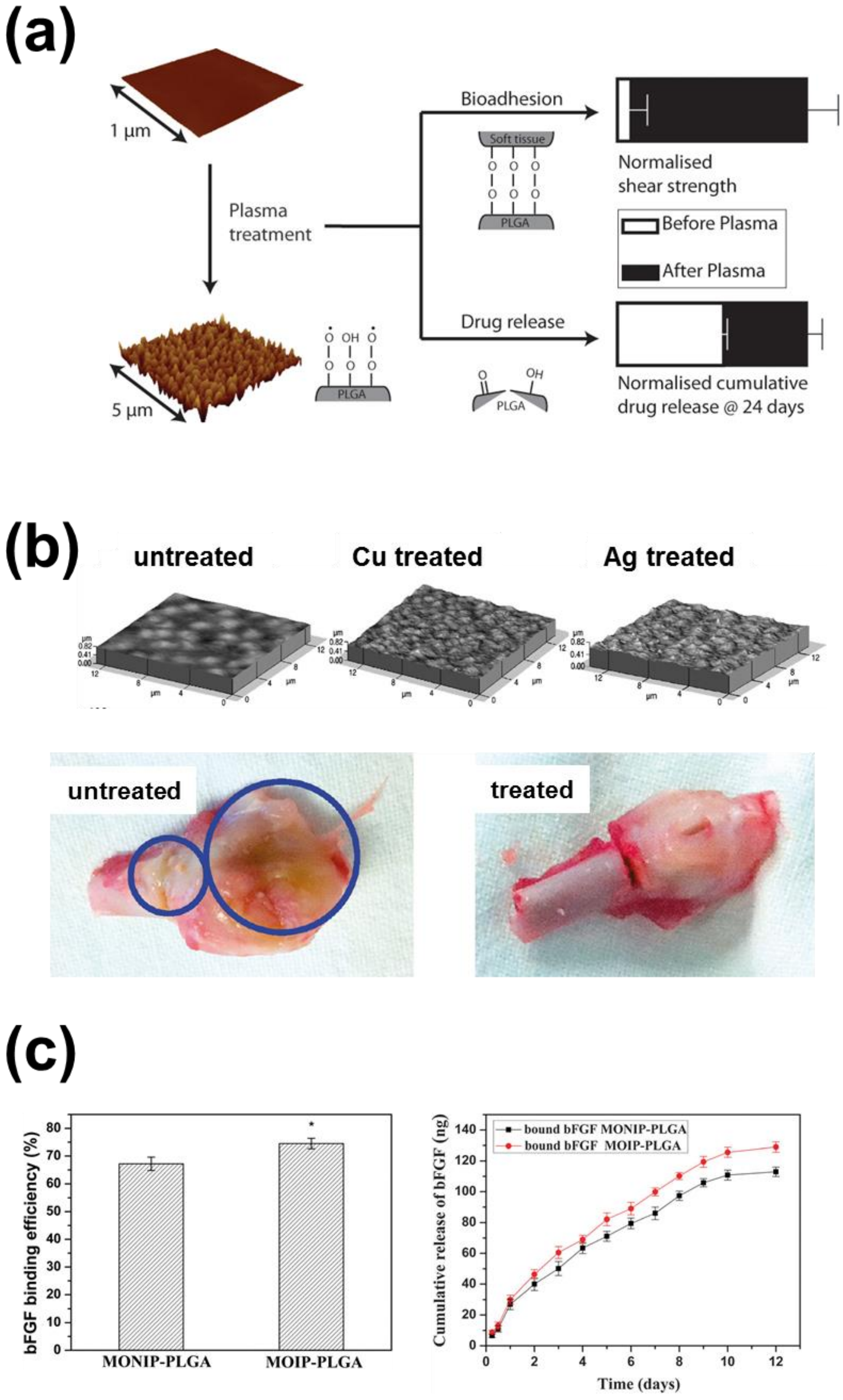
(a)
1 µm
Plasma treatment
5 µm
O OH O
PLGA
Bioadhesion
Soft tissue
Normalised shear strength
Before Plasma
After Plasma
Drug release
O OH
PLGA
Normalised cumulative drug release @ 24 days
(b)
untreated
Cu treated
Ag treated
µm 0.82 0.41 0.00
12 8 µm 4 0
untreated
treated
(c)
bFGF binding efficiency (%)
0 10 20 30 40 50 60 70 80
MONIP-PLGA
MOIP-PLGA
*
Cumulative release of bFGF (ng)
0 20 40 60 80 100 120 140
bound bFGF MONIP-PLGA
bound bFGF MOIP-PLGA
Time (days)
0 2 4 6 8 10 12

Figure 2

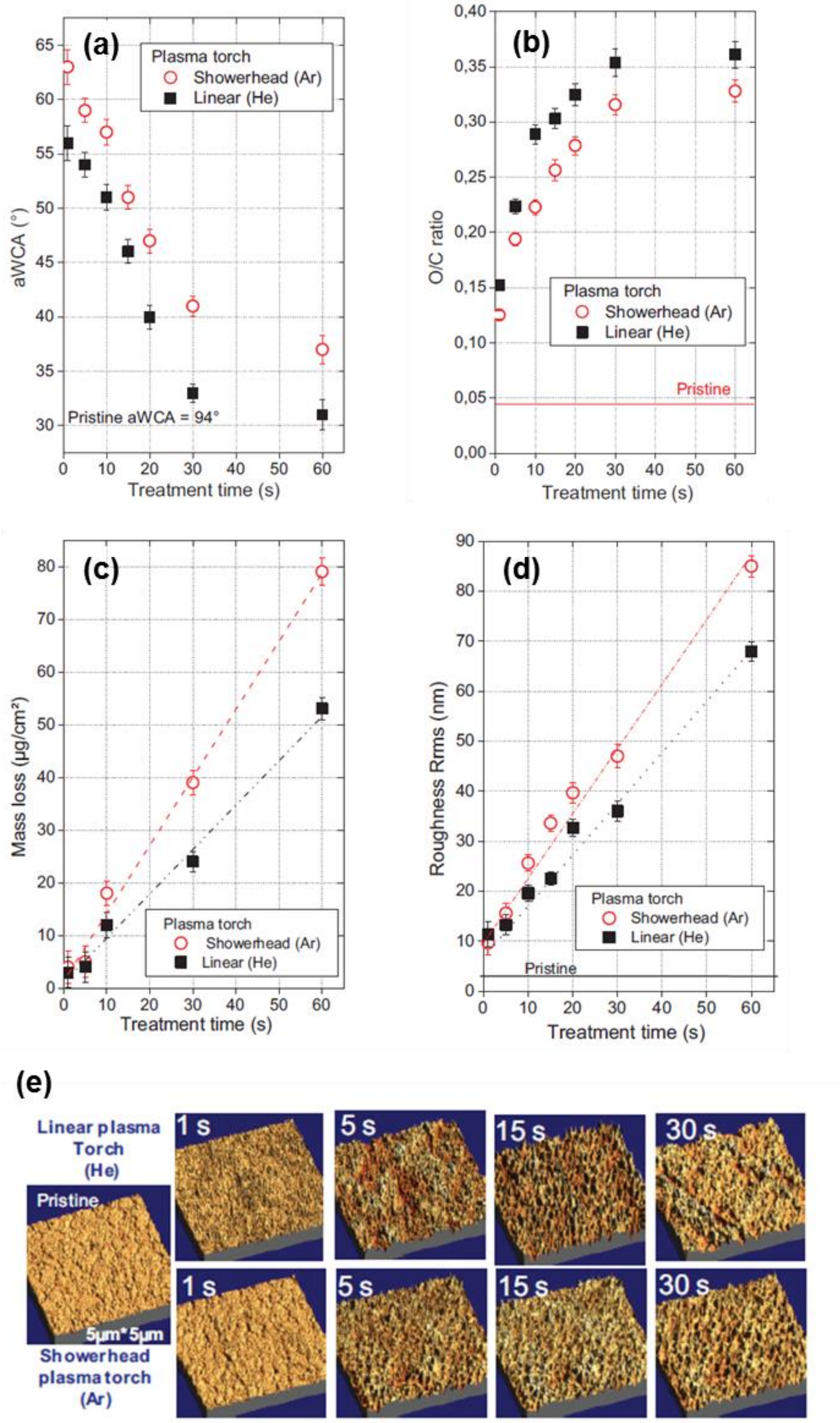
(a)
aWCA (°)
Treatment time (s)
Plasma torch
Showerhead (Ar)
Linear (He)
Pristine aWCA = 94°
(b)
O/C ratio
Treatment time (s)
Plasma torch
Showerhead (Ar)
Linear (He)
Pristine
(c)
Mass loss (µg/cm²)
Treatment time (s)
Plasma torch
Showerhead (Ar)
Linear (He)
(d)
Roughness Rrms (nm)
Treatment time (s)
Plasma torch
Showerhead (Ar)
Linear (He)
Pristine
(e)
Linear plasma Torch (He)
Pristine
5µm*5µm
Showerhead plasma torch (Ar)
1 s
5 s
15 s
30 s
1 s
5 s
15 s
30 s

Figure 3

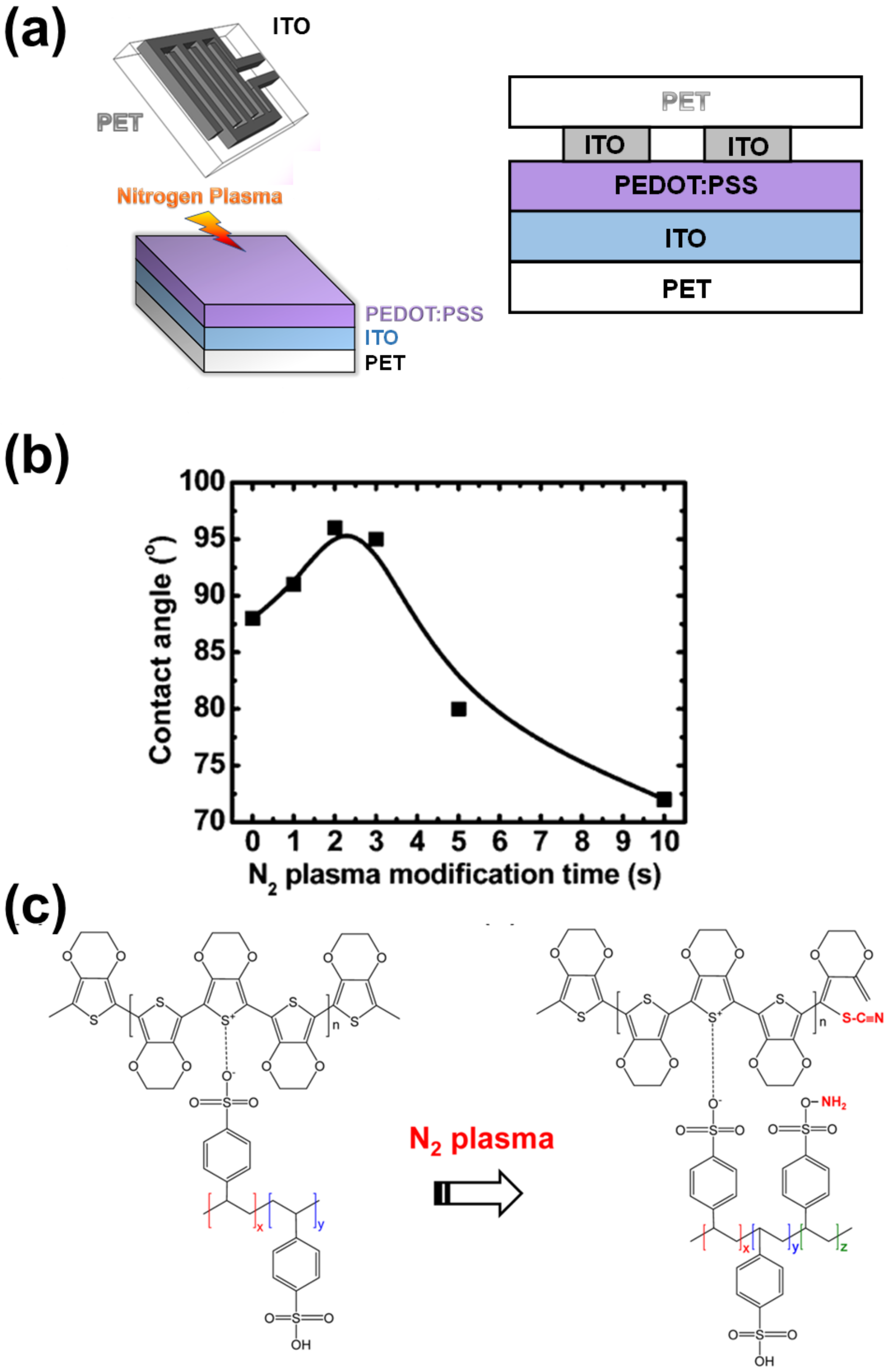
(a)
ITO
PET
Nitrogen Plasma
PEDOT:PSS
ITO
PET
PET
ITO
ITO
PEDOT:PSS
ITO
PET
(b)
Contact angle (°)
100
95
90
85
80
75
70
0 1 2 3 4 5 6 7 8 9 10
N2 plasma modification time (s)
(c)
N2 plasma
S-C≡N
O-NH2
OH
x
y
z
n

Figure 4

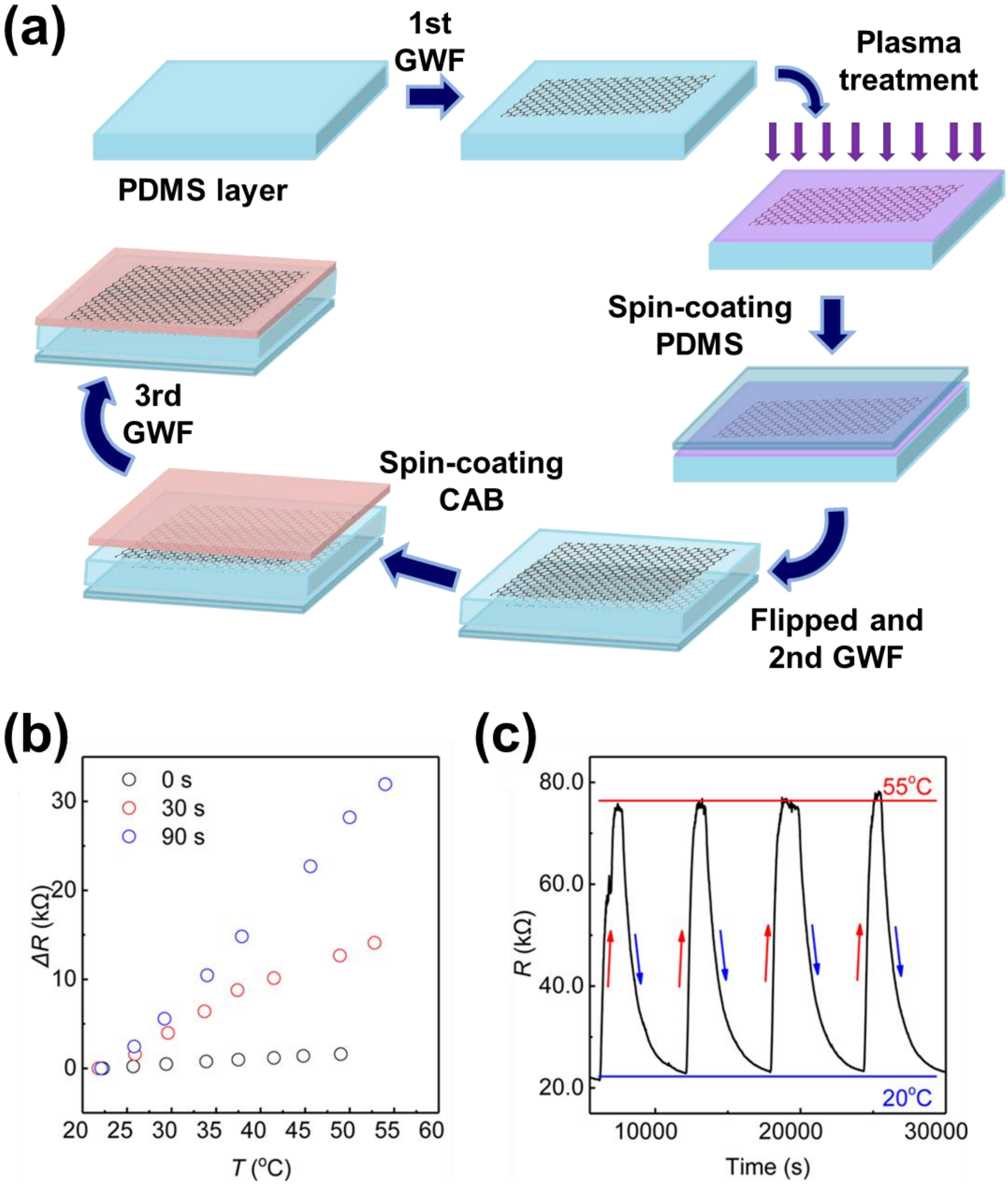
(a)
1st GWF
Plasma treatment
PDMS layer
Spin-coating PDMS
Flipped and 2nd GWF
Spin-coating CAB
3rd GWF
(b)
0 s
30 s
90 s
ΔR (kΩ)
0
10
20
30
20 25 30 35 40 45 50 55 60
T (°C)
(c)
80.0
60.0
40.0
20.0
R (kΩ)
55°C
20°C
10000 20000 30000
Time (s)

Figure 5

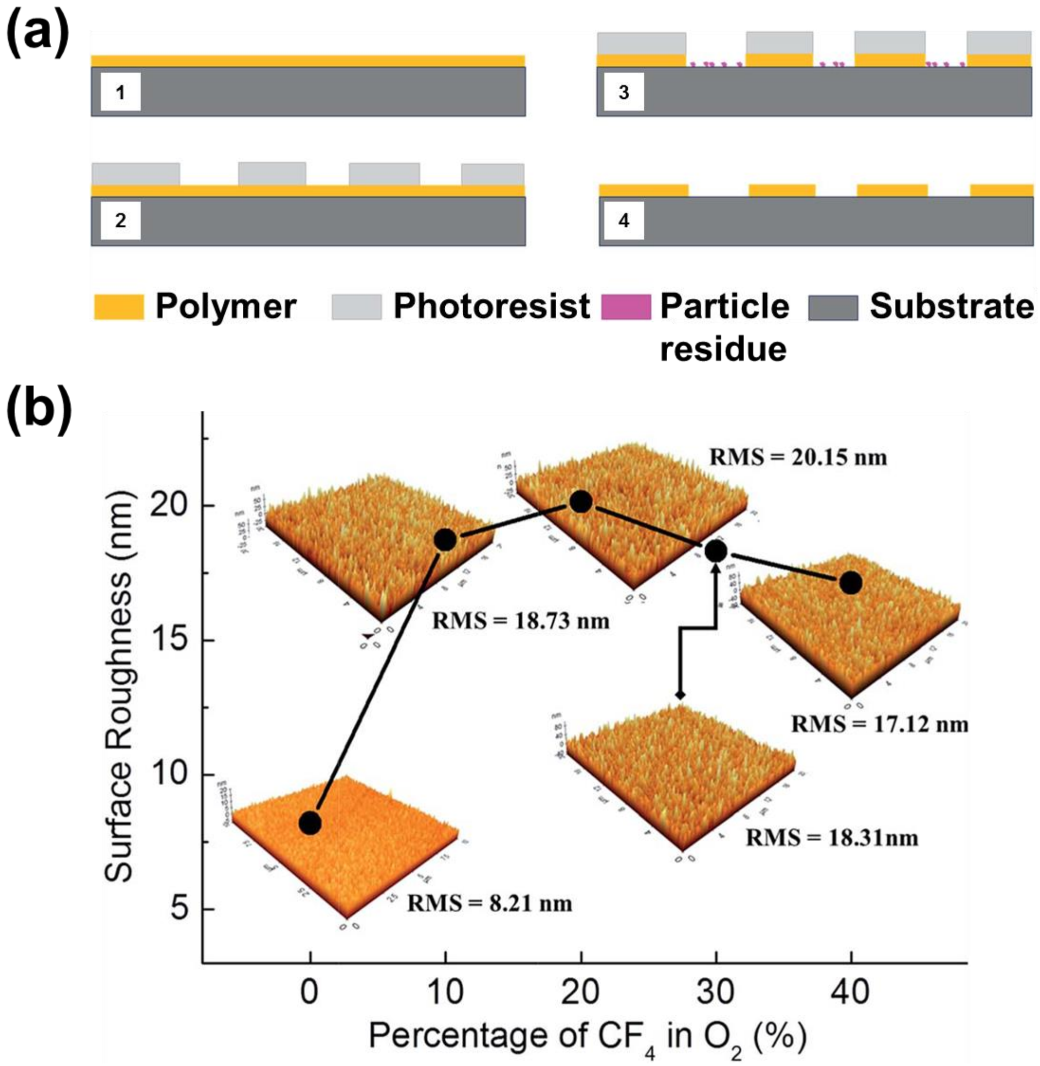
(a)
1
2
3
4
Polymer
Photoresist
Particle residue
Substrate
(b)
Surface Roughness (nm)
5
10
15
20
0
10
20
30
40
Percentage of CF_4 in O_2 (%)
RMS = 8.21 nm
RMS = 18.73 nm
RMS = 20.15 nm
RMS = 18.31nm
RMS = 17.12 nm

Figure 6

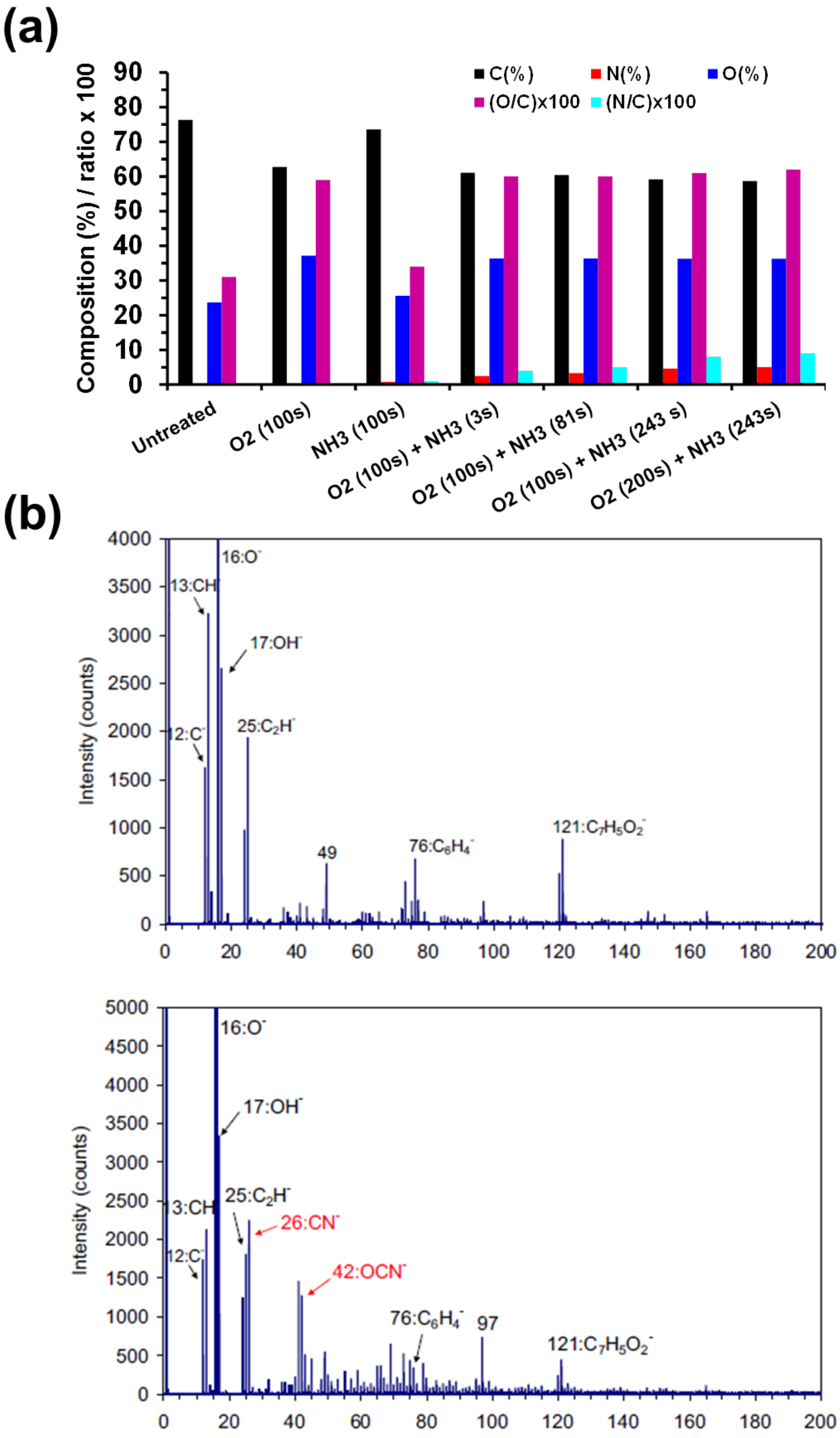
(a)
Composition (%) / ratio x 100
■ C(%)
■ N(%)
■ O(%)
■ (O/C)x100
■ (N/C)x100
Untreated
O2 (100s)
NH3 (100s)
O2 (100s) + NH3 (3s)
O2 (100s) + NH3 (81s)
O2 (100s) + NH3 (243 s)
O2 (200s) + NH3 (243s)
(b)
Intensity (counts)
16:O⁻
13:CH⁻
17:OH⁻
12:C⁻
25:C2H⁻
49
76:C6H4⁻
121:C7H5O2⁻
26:CN⁻
42:OCN⁻
97

Figure 7

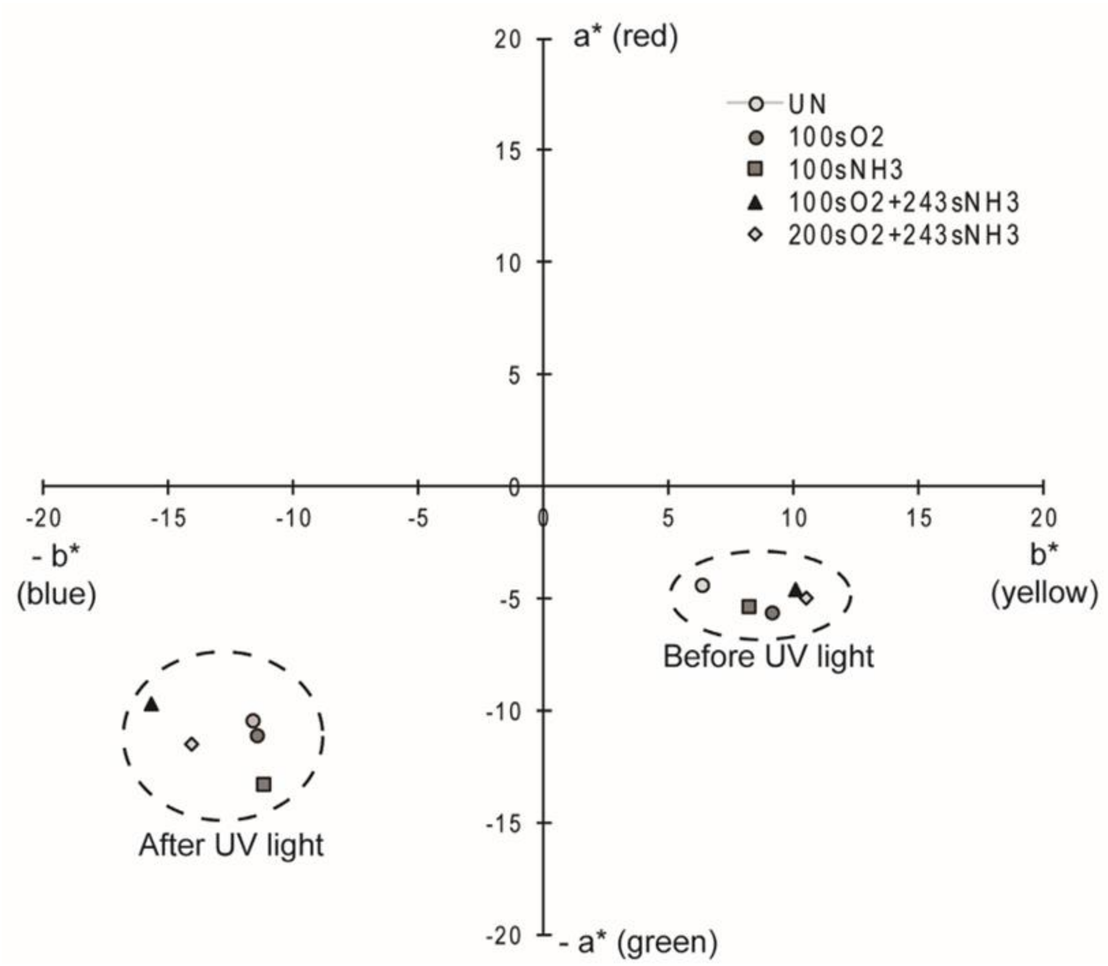
a* (red)
- a* (green)
- b* (blue)
b* (yellow)
20
15
10
5
0
-5
-10
-15
-20
UN
100sO2
100sNH3
100sO2+243sNH3
200sO2+243sNH3
Before UV light
After UV light

Figure 8

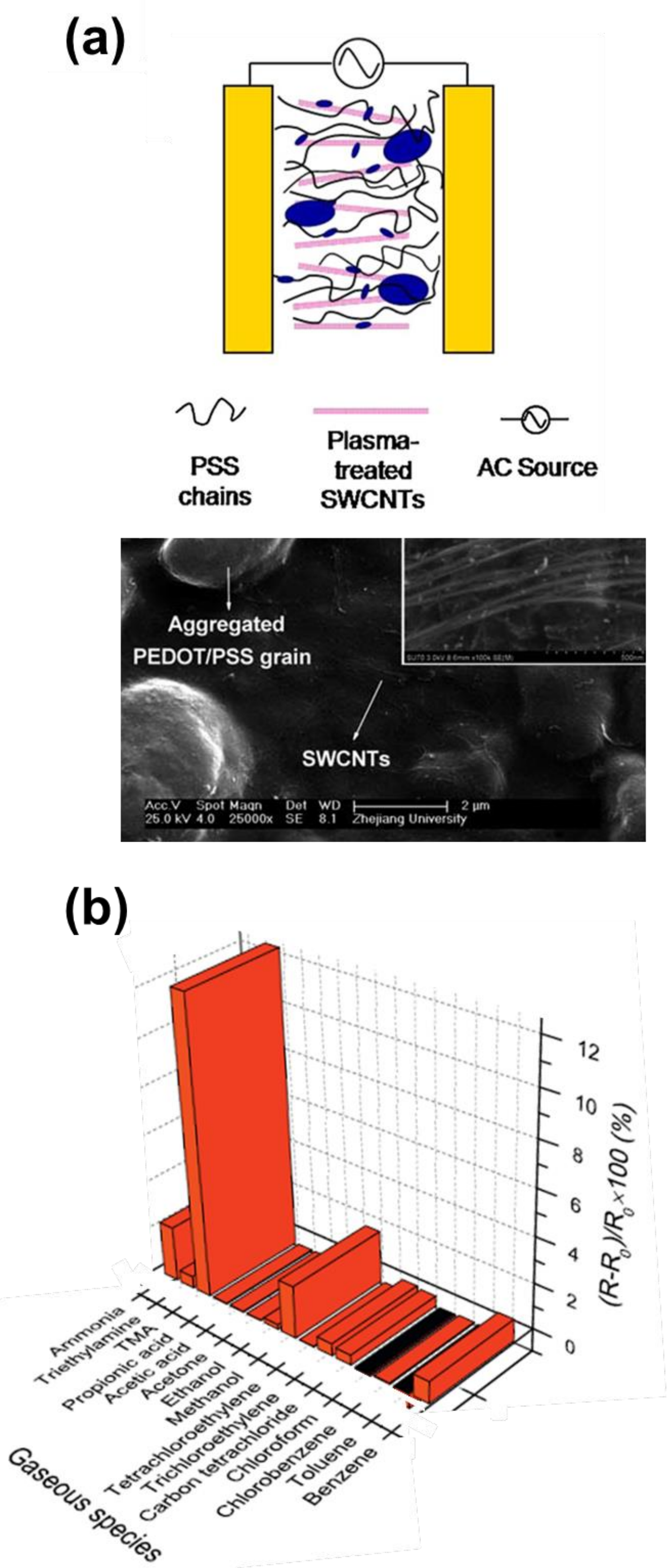
(a)
PSS chains
Plasma-treated SWCNTs
AC Source
Aggregated PEDOT/PSS grain
SWCNTs
Acc.V Spot Magn Det WD 2 µm
25.0 kV 4.0 25000x SE 8.1 Zhejiang University
(b)
12
10
8
6
4
2
0
(R-R0)/R0×100 (%)
Ammonia
Triethylamine
TMA
Propionic acid
Acetic acid
Acetone
Ethanol
Methanol
Tetrachloroethylene
Trichloroethylene
Carbon tetrachloride
Chloroform
Chlorobenzene
Toluene
Benzene
Gaseous species

Figure 9

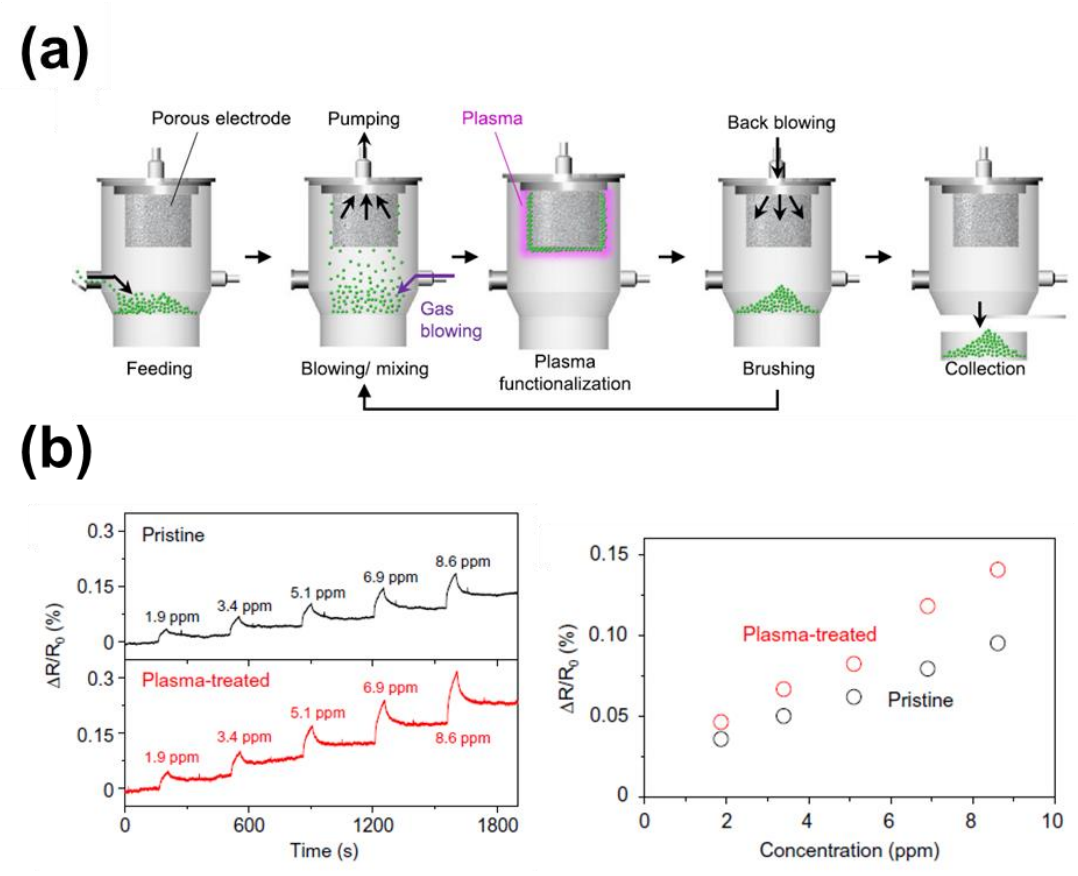
(a)
Porous electrode
Pumping
Plasma
Back blowing
Gas blowing
Feeding
Blowing/ mixing
Plasma functionalization
Brushing
Collection
(b)
Pristine
Plasma-treated
1.9 ppm
3.4 ppm
5.1 ppm
6.9 ppm
8.6 ppm
ΔR/R0 (%)
0
0.15
0.3
Time (s)
0
600
1200
1800
0.05
0.10
0.15
Concentration (ppm)
2
4
6
8
10

Figure 10

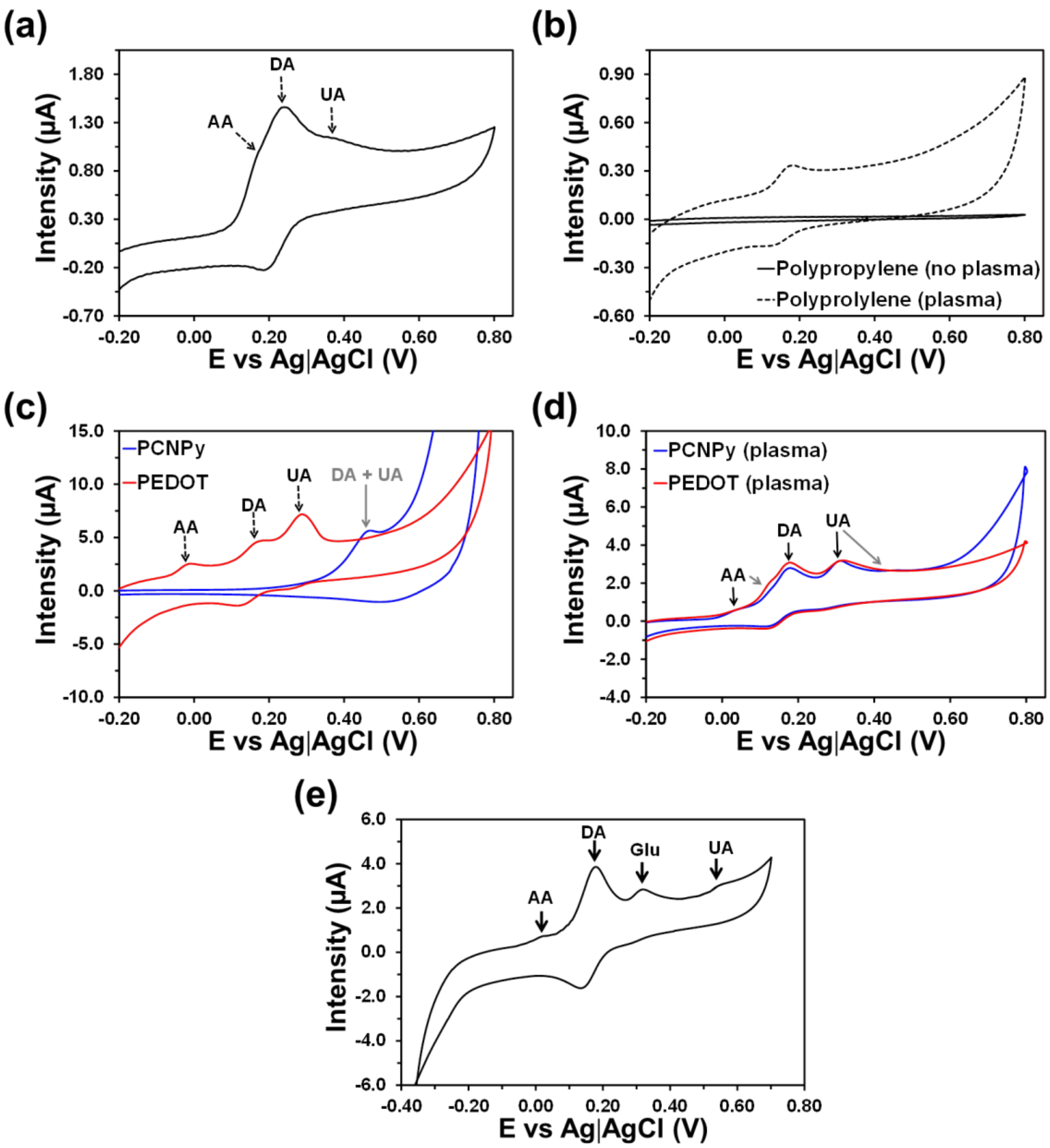
(a)
Intensity (μA)
1.80
1.30
0.80
0.30
-0.20
-0.70
AA
DA
UA
-0.20
0.00
0.20
0.40
0.60
0.80
E vs Ag|AgCl (V)
(b)
Intensity (μA)
0.90
0.60
0.30
0.00
-0.30
-0.60
Polypropylene (no plasma)
Polyprolylene (plasma)
-0.20
0.00
0.20
0.40
0.60
0.80
E vs Ag|AgCl (V)
(c)
Intensity (μA)
15.0
10.0
5.0
0.0
-5.0
-10.0
PCNPy
PEDOT
AA
DA
UA
DA + UA
-0.20
0.00
0.20
0.40
0.60
0.80
E vs Ag|AgCl (V)
(d)
Intensity (μA)
10.0
8.0
6.0
4.0
2.0
0.0
-2.0
-4.0
PCNPy (plasma)
PEDOT (plasma)
AA
DA
UA
-0.20
0.00
0.20
0.40
0.60
0.80
E vs Ag|AgCl (V)
(e)
Intensity (μA)
6.0
4.0
2.0
0.0
-2.0
-4.0
-6.0
AA
DA
Glu
UA
-0.40
-0.20
0.00
0.20
0.40
0.60
0.80
E vs Ag|AgCl (V)

Figure 11

GRAPHICAL ABSTRACT