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2 Plasma surface activation and functionalization of carbon-based materials

2.1 Introduction

Carbon-based materials have been extensively researched for an increasing number of applications because of their abundance and low cost, ease of processability, high-temperature stability and corrosion resistance, high electrical conductivity and good mechanical properties, particularly in the microscopic and nanoscopic scale [1]. The uses of carbon-based materials are very diverse, going from mechanical reinforcement in polymer matrix composites [2] to electrodes in supercapacitors and fuel cells [1]. However, their chemical inertness poses a common challenge in most applications, and several surface activation and surface functionalization methods have been developed to improve their performance, their compatibility with other materials or their interaction with the service environment [3].

The chemical inertness of carbon-based materials is attributed to the presence of graphene planes on the surface, having a low density of dangling bonds [5]. Graphene, carbon nanotubes (CNTs) and buckyballs are extreme examples of this microstructure, as they are composed of a single or a small number of graphene layers with a regular arrangement [6]. On the other hand, carbon fibers and amorphous carbon exhibit a turbostratic structure, with a higher degree of disorder and a larger number of dangling bonds on the surface (Figure 2.1). Several surface engineering techniques have been developed to activate and/or functionalize carbon-based materials [7]. These processes aim at increasing the number of dangling bonds and attaching functional groups to them to make the carbon-based material more compatible with the polymeric matrix in a composite, or to improve the wettability by an electrolyte in a supercapacitor and increase the charge exchange rate at the electrode.

The conventional surface engineering methods include wet chemical processes [8, 9], thermochemical [10] or electrochemical treatments [11]. Even though these methods are effective, they can be difficult to control and, in some cases, they raise environmental concerns. Therefore, recent studies have focused on the development of plasma processes for surface activation and functionalization of carbon-based materials [12, 13]. Plasma processes are conducted under vacuum or at atmospheric pressure and use highly reactive ionized gas molecules to create active sites and

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Figure 2.1: Turbostratic microstructure of carbon fibers, with inert graphene basal planes on their surface. Reprinted with permission from [4].

attach functional groups on the surface of carbon-based materials. In general, these processes are easier to control than conventional treatments, and they offer technical and environmental benefits.

2.2 Active screen plasma surface engineering

Active screen plasma (ASP) is a low-temperature and low-pressure plasma technology of surface engineering, which was developed at the University of Birmingham in the early 2000s [14–16]. The technology was initially applied to the thermochemical treatment of steels, but its potential for the functionalization of other materials was recognized immediately [17]. The schematic diagram in Figure 2.2 illustrates the main features of the ASP reactor in contrast to a conventional DC plasma reactor. The benefits of the ASP technology are mainly attributed to the creation of ions and active species on an auxiliary surface, the so-called *active screen*, as opposed to the surface of the treated material [18]. This allows more control over the type of plasma–surface interactions and the severity of the physical and chemical processes [3].

The active screen is a metallic mesh negatively biased to form ions and other active species from gas molecules, most typically N_2 , H_2 , Ar, CH_4 . The surfaces to be treated can be simply left at floating potential¹ and exposed to the flow of active

¹ Floating potential is the electric potential that an insulated object develops when exposed to the plasma. An object immersed in the plasma will be exposed to ions and electrons, but the electrons move much faster than the ions because of the difference in mass, so the number of electrons arriving at the surface of the object is higher than the number of ions. If the object is electrically insulated, the negative charge of the electrons accumulates, developing a self-induced bias that attracts positive ions and repels the less energetic electrons, until an equal number of ions and electrons arrive at the surface at any given time, that is, zero net current.

Figure 2.2: Schematic diagram of an active screen plasma reactor. Reprinted with permission from [19].

species, in which case the plasma–surface interactions are mainly of chemical nature, for example, attachment of functional groups. In other cases, a moderate bias is applied on the treated surface in order to attract the active species with increasing energy, making the physical action of the ions more pronounced. This ion bombardment can create new active sites and change the surface roughness. Alternatively, the material from the active screen can be sputtered² and deposited on the surfaces exposed to the plasma. This approach is particularly useful to functionalize surfaces with metallic materials.

In summary, the ASP technology has an additional degree of freedom compared to other plasma reactors, making it possible to create highly reactive ions and excited species on the *active screen*, and attracting them toward the work table with varying levels of energy (bias) to control the type of plasma–surface interaction, thus favoring physical or chemical phenomena. The following sections illustrate some of the recent

² Sputtering refers to the ejection of material from a solid surface by the physical action of impacting ions.

uses of the ASP treatments to activate and functionalize carbon-based materials with a wide range of microstructures, from the highly ordered structure of graphene to the disordered microstructure of carbon paper.

2.3 Reduction of graphene oxide for optoelectronic devices

Graphene has attracted significant attention for optoelectronic devices, and graphene oxide (GO) is an interesting precursor for graphene coatings of high-quality and over large-surface areas [6, 20]. GO has a nanosheet-layered structure similar to graphene but contains different oxygen groups [21, 22]. The GO coatings can be produced by chemical methods [23], dissolving graphene powder and other salts in sulfuric acid, subsequently dispersing and exfoliating the GO nanosheets by sonication, and finally casting it onto the substrate. A reduction process is then required to remove the oxygen functionalities and obtain a graphene coating of high quality, and the ASP technology was used for this purpose [24]. The ASP treatments were conducted at 400 Pa in pure H_2 or N_2-H_2 mixtures, at temperatures between 100 and 200 °C for 1 h.

The appearance of coatings changed from a light brown color to silver-gray after the plasma reduction in pure hydrogen and nitrogen–hydrogen mixtures, and this change was accompanied by a decrease in optical transparency and electrical resistance of the coating (Figure 2.3). The reduction process with the plasma technology was more effective than the heat treatment of GO in a reducing atmosphere, and the results varied with the treatment temperature (100–200 °C) and the gas mixture (H_2 or H_2-N_2). The X-ray diffraction (XRD) traces revealed that the GO peak disappeared after the reduction process, and the Raman spectra indicated an increase in the ratio of disordered to graphitic bands (D/G), which was attributed to the introduction of defects in the graphene planes during the reduction process. The X-ray photoelectron spectroscopy (XPS) data showed a marked decrease in oxygen functional groups attached to the carbon network, with the carboxylic oxygen ($O-C=O$) being the most unstable functional group compared to other oxygen bonds. The XPS data also revealed the presence of Fe, Cr and Mo doping elements in a partially oxidized state. These metallic dopants are transferred from the mesh of the active screen equipment to the GO-coated substrates, particularly when using nitrogen containing gas mixtures. A small amount of nitrogen was also incorporated into the coatings.

The oxygen to carbon ratio (O/C), reported in Table 2.1, reflects the efficiency of each process to reduce the GO coating. The plasma treatment in pure hydrogen was the most effective, resulting in an extensive decomposition of carboxyl functionalities and the creation of carbonyl groups. On the other hand, the use of nitrogen in the gas mixture increased the doping of the GO coating with metal atoms from the active screen, with a marked drop in electric resistance. The level of doping can be

Figure 2.3: Properties of the untreated and reduced GO coatings: (a) optical transparency and (b) electrical resistance. Reprinted with permission from [24].

PET: poly(ethylene terephthalate) substrate; GO: graphene oxide coating; ASP: active screen plasma surface treatment.

controlled by varying the processing conditions (composition of the active screen, gas mixture, electric bias applied on the treated surface and duration of the process), opening new pathways to reduce and functionalize GO coatings.

Table 2.1: Chemical analysis from XPS: O components and O/C ratio. Reprinted with permission from [24].

Sample	Treatment	Gas	Temperature	O—Si	O—Me	O—C=O	O—C	O/C
GO	Untreated	N/A	N/A	2.6	0.0	9.2	9.0	0.235
HT200	Heat treated	H ₂	200 °C	4.3	0.0	7.4	5.7	0.154
ASP150	ASP	H ₂	150 °C	5.6	6.7	6.9	1.5	0.122
ASPN150	ASP	H ₂ –N ₂	150 °C	2.1	7.4	7.4	1.3	0.125
ASP200	ASP	H ₂	200 °C	1.7	6.2	6.2	1.1	0.102
ASPN200	ASP	H ₂ –N ₂	200 °C	2.4	6.8	6.8	1.1	0.115

2.4 Functionalization of carbon nanofibers for supercapacitors

Carbon nanofibers (CNF) are good candidate materials for electrodes in energy storage devices because of the intrinsic properties of carbon (thermal and chemical stability, electric conductivity) and the ability to form controlled porous structures with the nanofibers [1]. This combination allows researchers to create stable electrodes with a very large surface area, and recent efforts have focused on increasing the surface conductivity and the charge exchange efficiency with the electrolyte. Silver and nickel are among the proposed electroactive materials, capable of increasing the pseudocapacitance and double-layer energy storage mechanisms,³ and the ASP technology was used for this purpose [25]. CNFs were dispersed in isopropanol, the suspension was placed in Petri dishes and the solvent was left to evaporate before the plasma treatments.

The ASP treatments did not change the size or the structure of the CNFs, but their surface was covered with nickel and silver nanoparticles, respectively. The metal nanoparticles were approximately 10–50 nm in diameter (Figure 2.4), and their size and density increased with the ASP treatment time, which was reflected on the nickel and silver contents detected by energy-dispersive X-ray spectroscopy and XRD. The ASP functionalization with silver produced a rough surface, even after 120 min of plasma treatment, which is beneficial to increase the surface area. On the other hand, nickel tended to form a continuous coating on the CNFs after only 45 min of ASP treatment, thus limiting the amount of material and the morphology of the particles that could be deposited on CNFs.

³ Electrical double layer capacitors are based on non-Faradaic mechanisms, in which the electric charge is stored in the double layer formed at the interface between the inert electrode material and the electrolyte, without involving redox reactions. On the other hand, the pseudocapacitors rely on reversible redox reactions (Faradaic), which take place on the surface of the active electrode material in contact with the electrolyte [1].

Figure 2.4: Surface morphology of carbon nanofibers: (a) untreated and (b) ASP functionalized with nickel. Reprinted with permission from [25] Copyright (2017) American Chemical Society.

The cyclic voltammetry (CV) tests conducted in 1 M sodium sulfate solution revealed a significant increase in the loop area after the ASP treatments, particularly with silver (Figure 2.5). More importantly, the CNFs functionalized with silver retained the rectangular shape of the CV curves, which was attributed to the high surface conductivity and ion transport efficiency. On the other hand, the nickel-functionalized CNFs showed severe distortions, particularly at higher scan rates, between 100 and 200 mV/s. The differences were also observed in the cyclic charge–discharge curves, with the nickel-functionalized CNF electrodes showing a twofold increase in capacitance and the silver-functionalized CNF electrodes exhibiting a fourfold increase in capacitance compared to the untreated CNFs. The electrochemical impedance spectra indicated that the increase in capacitance was mainly due to the double layer mechanism, rather than pseudocapacitance. However, recent reports have indicated that vanadium and other transition metal nitrides can improve both Faradaic and non-Faradaic charge storage mechanisms, which make them promising electrode materials for supercapacitors. This finding opens good prospects for the ASP technology, considering that it has been extensively used to form nitrides and carbides for surface functionalization and hardening.

2.5 Surface activation of carbon paper gas diffusion layers in fuel cells

Carbon paper is used as gas diffusion layer (GDL) in direct methanol fuel cells [26]. The electrocatalysts, which consist of reaction layers of precious metals with nanometer-size features, are frequently deposited directly on the GDL. These deposition processes are typically conducted in an aqueous environment and the poor

Figure 2.5: Cyclic voltammetry of carbon nanofibers functionalized with silver (a) and capacitance (b) calculated from charge–discharge experiments. Reprinted with permission from [25] Copyright (2017) American Chemical Society.

wettability of the hydrophobic carbon paper results in aggregation and uneven growth of the electrocatalyst, which reduces efficiency and increases cost [27, 28]. Therefore, the ASP technology was used to activate the surface of Sigracet®

GDL 35BC carbon paper [19]. The activation treatment was conducted in a gas mixture of 25% N_2 and 75% H_2 at a pressure of 400 Pa. The temperature ranged from 100 to 210 °C and the duration of the treatment was between 10 and 30 min. After the activation treatment, the carbon papers were rinsed in ethanol and immersed in an aqueous solution of H_2PtCl_6 and formic acid to grow the platinum nanowires (2 mg/cm^2), and finally rinsed in water/ethanol/water and dried at 40 °C for 24 h. These carbon papers were then used as integrated cathodes in single cell tests, with a Nafion 117 membrane and the commercial JM anode ($PtRu\ 4\text{ mg/cm}^2$). The electrodes were then hot-pressed against the Nafion 117 membrane at 135 °C for 2 min under a constant pressure of 5 MPa. The reference cells were fabricated with Nafion 117 membrane, commercial JM cathode ($Pt\ 4\text{ mg/cm}^2$) and JM anode ($PtRu\ 4\text{ mg/cm}^2$). These electrode assemblies were sandwiched between two graphite flow field plates to form a single cell with an active electrode area of 5 cm^2 .

The CV tests conducted on a single cell revealed that all the carbon papers activated with the ASP technology for 10 min had higher electrochemical surface area (ECSA) than the untreated carbon paper. What is more, the ECSA increased with the ASP treatment temperature up to 150 °C, and then decreased with further temperature increments (Figure 2.6). The maximum ECSA value of $25.8\text{ m}^2/\text{g}$ corresponded to the carbon paper activated at 150 °C with the ASP technology, which was 65% higher than the ECSA value of the untreated carbon paper. The polarization curves also revealed maximum power densities for moderate ASP treatment temperatures in the order of 120 and 150 °C. The highest power density measured in these experiments was 63.9 mW/cm^2 , which was three times higher than the power density obtained with the untreated carbon paper.

This remarkable improvement in the performance of the single cells was attributed to the different surface morphology observed at high magnification. The surface of the untreated carbon paper was only partially covered by Pt nanowires, and they formed rather large cubic-shaped clusters. The uneven surface morphology was a result of the super hydrophobic nature of the untreated carbon paper and its poor wettability (Figure 2.7). In contrast, the surface of the ASP-activated carbon paper showed a more uniform distribution of the Pt nanowires, with a decreasing number of aggregates as the ASP treatment temperature increased up to 150 °C. At temperatures higher than 150 °C, the morphology of the Pt nanowires changed, becoming shorter and, consequently, reducing the ECSA and the cell performance. Longer ASP activation times, that is, 30 min, had a detrimental effect on the surface morphology of the catalyst layer and, consequently, on the cell performance. In summary, the ASP activation at moderate temperature (120–150 °C) and for a short time (10 min) can effectively promote the growth of the electroactive layer of Pt nanowires on the carbon paper, improving the utilization of this expensive catalyst and, ultimately, increasing the ECSA and the power density of the fuel cell.

Figure 2.6: (a) Electrochemical surface area (ECSA) and (b) power density from polarization tests. Reprinted with permission from [19].

2.6 Improving the bond strength of carbon fibers in composite materials

Carbon fibers are exceptional reinforcements for polymer matrix composite materials, particularly because of their high strength, high stiffness and lightweight [29].

Figure 2.7: Surface morphology of the electrocatalyst layer deposited on the (a) untreated and (b) ASP functionalized carbon paper (ASP treatment conducted at 120 °C for 10 min) [19].

However, the graphitic basal planes present on the surface of the carbon fibers make them relatively inert and this reduces the wettability and the bond strength with the polymeric matrix, frequently an epoxy resin [3]. Plasma treatments have been used to introduce polar functional groups on the surface of carbon fibers. These functional groups help to modify the bond strength with the polymeric matrix and to tailor the mechanical properties of the composite material, particularly the strength and toughness [30, 31]. The ASP technology offers good control over the treatment conditions to avoid damaging the fibers, thus retaining their strength.

Carbon fibers were ASP treated in a gas mixture of 75% H₂ and 25% N₂ at a pressure of 50 Pa. This atmosphere was selected to introduce –NH_x functional groups on the surface of the carbon fibers [32]. These functional groups are known to create strong chemical bonds with the epoxy resins used in these composites, and the physical etching creates a microroughness on the carbon fibers, which increases the mechanical interlocking with the matrix. Optical emission spectroscopy studies conducted during the ASP treatments revealed NH_x species in the plasma phase, and NH groups were also identified on the surface of the functionalized carbon fibers using XPS (Figure 2.8). The relative intensity of the NH species in the plasma decreased with increasing applied power, and this change correlated with a reduction in the nitrogen content on the surface of the functionalized fibers. A similar trend was observed on the contact angle of glassy carbon disks, functionalized alongside with the carbon fibers. All the ASP-treated carbon disks showed contact angles significantly lower (<60°) than the untreated disks (80°), but the lowest contact angle (40°) corresponded to the disk treated at low power and for short time.

Further wettability measurements were conducted on carbon disks immediately after the ASP treatment and over the subsequent 4 weeks. It was found that the contact angle dropped remarkably after the plasma treatments to values as low as 10°. However, the contact angle increased rapidly over the subsequent 7 days

Figure 2.8: Correlation of active species in the plasma phase with functional groups on the surface of the carbon fibers as a function of the ASP treatment conditions (potential). Reprinted with permission from [30]. Copyright 2017, American Vacuum Society.

and remained relatively constant for the remaining 3 weeks (Figure 2.9). The chemical analysis by XPS showed a small but consistent reduction in the nitrogen content (from 5.8 to 5.1 at.%) over a period of 28 days. However, the initial XPS analysis was only conducted 3–4 weeks after the ASP treatment, so the wettability measurements could not be correlated with the XPS data. The change in the nitrogen content and in the wettability was consistent with an exponential decay, which could be attributed to a degradation of the nitrogen functionalities by oxidative scissions and evaporative loss upon their exposure to air. The elucidation of the degradation mechanism requires further study.

Figure 2.9: Evolution of the contact angle of an ASP-treated carbon surface with time. Reprinted with permission from [30]. Copyright 2017, American Vacuum Society.

2.7 Synthesis and deposition of carbon nanotube films

CNTs exhibit extraordinary electrical, thermal and mechanical properties, similar to CNFs. CNTs are frequently synthesized by arc discharges, laser ablation or chemical vapor deposition (CVD) [33–35]. The latter method is capable of producing vertically

aligned CNT (VACNT), but the process requires prior deposition of metal nanoparticles on the substrate to act as catalysts and nucleation sites. In addition, the high temperature required for conventional CVD processes can be detrimental for the substrate. It is known that plasma-enhanced CVD (PE-CVD) can reduce the deposition temperature, but the energy of the ions needs to be carefully controlled to enhance rather than suppress the growth of CNT [36]. A multistep process to deposit metal nanoparticles and grow CNTs at low temperatures has been recently developed based on the ASP technology [33].

Silicon wafers (100) were used as substrates for the PE-CVD process with RF excitation (13.56 MHz, 30 W) and a modified active screen experimental setup (Figure 2.10). Metal nanoparticles with different compositions were deposited on the silicon wafers by changing material of the active screen, in this case nickel and stainless steel. The size, morphology and uniformity of the metal particles were critical for the success of the process, the density and vertical alignment of the CNTs. VACNTs were grown in the same active screen experimental arrangement using a gas mixture of acetylene, argon and hydrogen at 100 Pa (Figure 2.11). Transmission electron microscopic observations revealed a tip-growth mode, in which the metal nanoparticles were detached from the silicon wafer and remained at the tip (growing front) of the CNTs. For a given treatment time (100 min), the length of the CNTs increased with the processing temperature from 0.6 μm at 400 $^{\circ}\text{C}$ to 6 μm at 500 $^{\circ}\text{C}$, and their diameter decreased from 28 to 16 nm, respectively (Figure 2.11). The structure of the CNTs did not change significantly with

Figure 2.10: Schematic diagram of the active screen setup used for PE-CVD of vertically aligned carbon nanotubes. Reprinted with permission from [33].

Figure 2.11: SEM images of CNTs grown at (a) 400 °C and (b) 500 °C. Reprinted with permission from [33].

the deposition temperature, but the ratio of D and G bands (I_D/I_G) in the Raman spectra changed from 0.7 to 0.97 with increasing content of acetylene in the gas mixture.

The multistep PE-CVD process, based on the ASP technology with RF excitation, could successfully deposit a layer of metal nanoparticles on a silicon wafer and subsequently grow vertically aligned CNTs. The size, morphology and microstructure of the VACNTs could be controlled by changing key processing parameters, such as size, distribution and uniformity of metal nanoparticles, gas mixture and processing temperature. This process represents a simple and cost-effective method to functionalize the surface of a wide range of substrates with CNTs.

2.8 Summary and future perspectives

This chapter presents a summary of the research undertaken at the University of Birmingham on the functionalization of carbon-based materials using the ASP technology. This research exploits the typical physical and chemical phenomena associated with the plasma technology, further optimized by the additional control and degrees of freedom offered by the ASP technology. In this way, the highly reactive species in the plasma were used to reduce GO films, activate the surface of carbon paper membranes or functionalize the surface of carbon fibers. In addition, the sputtering of material from the active screen and its deposition on the surfaces exposed to the plasma was used to increase the conductivity and surface area of CNFs and to create nucleation sites for CNTs. In all cases, the treatment conditions could be optimized, targeting specific plasma–surface interactions, to achieve the desired properties.

Future efforts will focus on expanding the range of gases and active screen materials used to functionalize temperature-sensitive substrates, as well as combining the ASP technology with pre- and post-treatments. There are also challenges related to the

uniformity of the ASP treatment of porous and three-dimensional structures due to shadowing effects that need to be addressed. In addition, the interaction between active species in the plasma and different microstructures of carbon-based materials deserves further study, together with the evolution of the ASP functionalized surfaces over time. Lastly, there seem to be good opportunities to create patterned surfaces using the ASP technology, in combination with other processes with potential application in multiple fields such as functional materials, sensors and biosensors, electrical, electronic and optoelectronic devices. Without question, the ASP technology remains to be a valuable enabling technology for the surface functionalization of engineering materials, showing broader prospects of practical applications than ever before.

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