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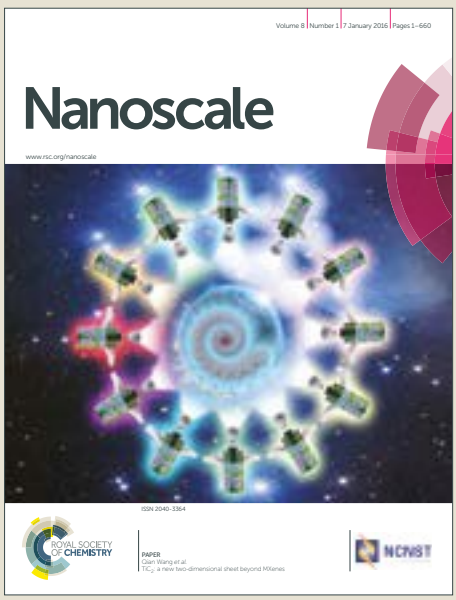

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Oxygen plasmas: a sharp chisel and handy trowel for nanofabrication

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Although extremely chemically reactive, oxygen plasmas feature certain properties that make them attractive not only for material removal via etching and sputtering, but also for driving and sustaining nucleation and growth of various nanostructures in plasma bulk and on plasma-exposed surfaces. In this minireview, a number of representative examples is used to demonstrate key mechanisms and unique capabilities of oxygen plasmas and how these can be used in present-day nano-fabrication. In addition to modification and functionalisation processes typical for oxygen plasmas, their ability to catalyse the growth of complex nanoarchitectures is emphasized. Two types of technologies based on oxygen plasmas, namely surface treatment without a change in the size and shape of surface features, as well as direct growth of oxide structures, are used to better illustrate the capabilities of oxygen plasmas as a powerful process environment. Future applications and possible challenges for the use of oxygen plasmas in nanofabrication are discussed.

1. Introduction

Oxygen plasmas are a truly unique tool in nanofabrication[1,2]. Being primarily oxidative in nature, active oxygen ions could perform two distinct functions, namely the *removal of material* from the surfaces through the formation of gaseous oxides , and *building of new structures* through the formation of stable oxides, and eventually, oxide-based nanoparticles.[3,4,5] Moreover, these two functions could be applied within the same process, thereby selectively removing some materials and synthesizing others within a single processing step.[6] Removal of carbon in the form of CO and CO_2 gases, and formation of metal oxides, such as MoO_2, illustrates this capability. Moreover, in the oxygen plasma environments, same materials could be transformed into gaseous (CO_2) or solid (graphene oxide) forms.[7,-9]

These unique features of oxygen plasmas can be used to promote and sustain self-organization and self-assembly. Indeed, the complexity of oxygen-driven reactions implies the formation of dynamically open systems far from thermodynamic equilibrium,[10-13] leading to realization of complex nanoarchitectures and metamaterials[14,15] where the self-assembly processes are governed by the laws of statistical physics. Self-organized processes are currently attracting considerable attention due to their ubiquitous nature spanning complex physical systems,[16,17,18] biological systems[19,20] and medical applications,[21,-23] and significant benefits that they can deliver in surface modification,[24,25] e.g. at plasma-surface interfaces,[26,27] and in the nanotechnological systems.[28,29,30] Oxygen plasmas are a processing medium that features a large variety of processing conditions,[31,32] some of which cannot be reached by the use of other techniques because of the dissipation processes.[33,34] Moreover, oxygen plasmas have the potential to enable new stages for a processing system on its path to thermal equilibrium, and as such can serve as a foundation for the entire family of essentially new technological processes.[35,36]

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✓ *A general purpose of this review is to demonstrate a unique capability of oxygen plasmas to be a key processing tool for both subtractive (etching etc.) and additive (building) technologies, thus enabling self-organization of various nanostructures via quite different routes. We will also illustrate a framework for self-organisation that takes into account the spectrum of physical processes and driving forces on a surface under the action of the plasma particles, and bulk plasma parameters, which are associated with various plasma sources.*[37,38,39]

The paper is organized as follows:

- In **Section 2**, we introduce a rich plethora of capabilities intrinsic to oxygen plasma-based process environments; then, we briefly outline specific processes and processing routes in oxygen plasmas, illustrated by several unusual structures grown directly in oxygen plasmas.[40,41,42] Without going into excessive detail which may be found in the referenced literature, we emphasize the uniqueness of the oxygen plasma as a flexible tool for nanofabrication;
- In **Sections 2**, we also briefly outline processes and routes pertinent specifically to oxygen plasmas, answering the central question of *Why oxygen*? Using several illustrative diagrams, a brief overview of theoretical basics and a table that summarises the chemistry of charged and neutral species in oxygen plasmas, this section will show why oxygen plasmas are a highly useful tool in nanotechnology;

Next, sections 3 and 4 illustrate the efficient use of oxygen plasmas in in *subtractive processes* (plasma as a "sharp chisel") and *additive processes* (plasma as a "handy trowel"):

- In **Sections 3** we outline the application of oxygen plasmas in the *subtractive processes*, i.e. for the oxygen-enabled selective etching, sputtering, as well as treatments that do not lead to reshaping yet still rely on selective removal of material;
- In **Sections 4** we outline the application of oxygen plasmas in the *additive technologies*, where plasma environment is used to generate and deliver construction material as well as active process media for material growth and activation and functionalization of surfaces, respectively;

And finally,

- **Summary and outlook** section brings some thoughts and ideas on the possible future trends and current challenges facing the use of oxygen plasmas in nanotechnology.

2. Oxygen plasmas: key advantages and a range of capabilities

The majority of examples discussed so far referred to interfacial synthesis and processing.[24-27] Are oxygen plasmas able to sustain nucleation and grow of nanostructures directly within the bulk plasma environment, similar to the case of plasma-produced graphene[43,44]? Indeed, bulk plasmas created in *continuously flowing* oxygen-containing processing media are well suited for production of engineered nanoparticles of complex architecture and morphology. Furthermore, such oxygen-containing plasmas could be produced by a variety of means, i.e. not only by using electric discharges but also through application of laser and microwave energies.[45] **Figure 1a** shows a schematic of oxygen-plasma-enabled production of nanoparticles in a continuous plasma setup, where the synthesis of larger structures takes place downstream from the active plasma region. In this configuration, the precursor in combination with O_2 and Ar is introduced into the top part of the reactor. The presence of oxygen in this process is critical, as will be seen later. As the precursor and processing gas molecules move into the active plasma region, the concentration of charged carriers increases drastically, leading to ionization and dissociation processes and ensuing generation of large quantities of highly reactive particles, such as electrons, ions, and radicals. The concentration of charge carriers continues

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to increase until a point when an equilibrium is established between their generation and consumption.

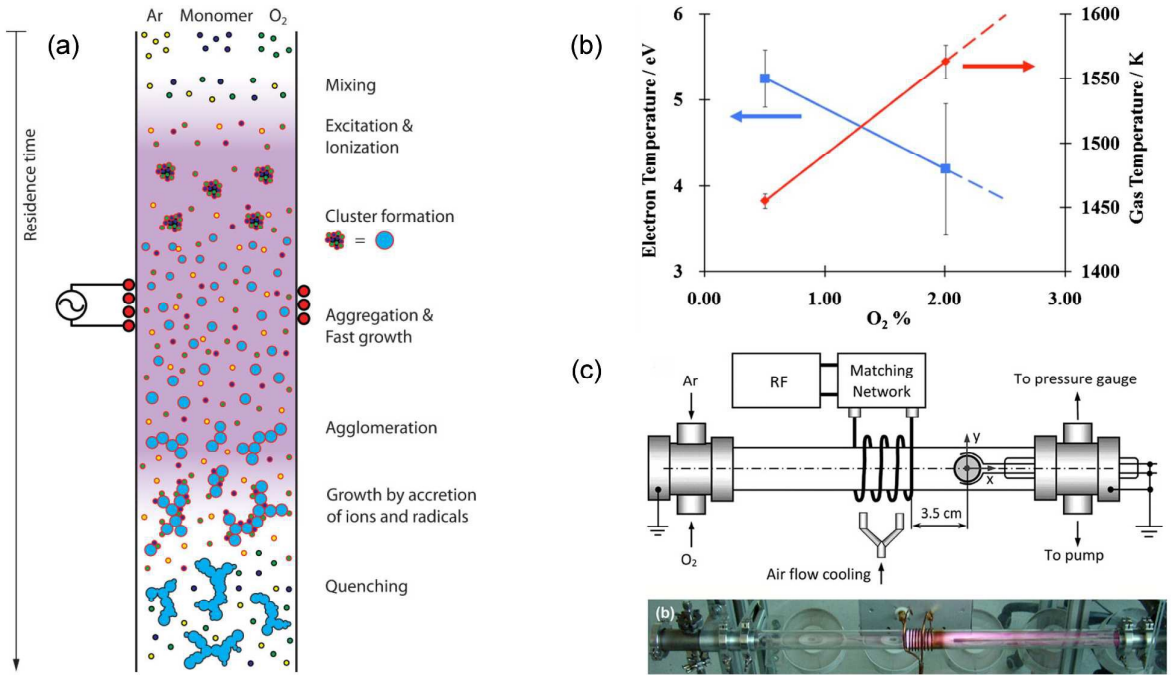

Fig. 1 (a) A schematic of nanoparticle synthesis in a continuous plasma setup, downstream from the active plasma region. The molecules of the precursor interact with oxygen ions and radicals, as well as with other precursor molecules to produce stable chemical substances and cluster-type structures. Reprinted with permission from [47]. Copyright 2012, Wiley. (b) How oxygen works in plasmas: Changes in effective electron and gas temperatures under varying oxygen concentrations in an Ar background gas at the total gas flow of 20 sccm; 450 MHz power supply at 3 W; the capillary was situated at 0.3 mm above the substrate. Reprinted with permission from [55]. Copyright 2008, AIP. (c) Typical setup for a radio-frequency (13.56 MHz) powered nanosynthesis in the oxygen plasma. Reprinted with permission from [46]. Copyright 2014. AIP.

The exposure of precursor molecules to the highly reactive oxygen-containing environment results in their ionization and fragmentation. Subsequent interaction of thus-formed precursor-derived particles with oxygen ions and radicals, as well as with each other results in the formation of chemically-stable molecular structures and cluster-like structures. In cases where a critical number of the latter cluster-like structures is attained, their aggregation ensues, leading to the formation of nanometre-sized primary particles. Given the configuration of the experimental set-up with respect to reactor geometry and inductively coupled plasma (ICP) coil, the ion density shows an axial profile, where the location beneath the coil corresponds to the maximal charge carrier density and, likely, the region where fast cluster growth and aggregation is at the peak intensity.[47] For optimum efficiency in such processes, metal and oxygen atoms should be generated and subsequently utilized in a stoichiometric manner. To some degree, this could be achieved by, for example, introducing an electric current between two metal electrodes via a gas discharge in the space between the electrodes, where metal atoms originate from the surface of the electrodes through evaporation and oxygen atoms are produced by gas-phase break down of O_2.[48]

✓ *Why oxygen?*

Indeed, how do oxygen plasmas ensure diverse ways of nanosynthesis and support self-organization? Fundamentally, interactions of active oxygen radicals with surfaces, e.g. formation of Si–O and Si–OH bonds, is one of the key mechanisms that allows for tailoring of the properties of oxygen plasma-grown nanostructures. For example, in silicon nanocrystals these bonds are characterized by significantly lower energy bandgaps than those of the equivalent hydrogenated Si nanocrystals. Furthermore, it was demonstrated that there was a dif-

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ference in the bandgap values of different Si–O bond arrangements,[49] with that of sub-nanometre sized OH-terminated silicon clusters becoming greater once even a single OH-termination was substituted with a Si–O–Si bridge bond.[50] A large set of stable molecular configurations can be nucleated in the presence of oxygen radicals.[51,52] A very high chemical activity of oxygen radicals in plasmas provides a sophisticated control mechanism over the chemical composition and structure of plasma-nucleated oxide nanoparticles and clusters.[53,54]

Moreover, the content of oxygen in the plasma-forming gas also serves as a powerful control that allows for adjustment of key parameters of the process environment, including gas and electron temperatures. **Figure 1b** shows the experimentally measured dependencies of the electron and gas temperature on O_2 concentration in Ar. In general, the temperature of electron becomes lower with an increasing concentration of O_2. A typical reactor for the oxygen plasma-enabled synthesis is illustrated in **Figure 1c**.

The reduction in the temperature of electrons with increasing oxygen content is attributed to the fact that some of the electron energy previously available for ionization of Ar is now being diverted to electron-mediated reactions with oxygen, in a similar way to that observed in CH_4/Ar mixtures.[55] Furthermore, the processes involving oxygen in its atomic and molecular states have an activation energy in the range of 4.5-14.7 eV, lower than that of many other processes. It should be noted, however, that the ionization and dissociation of oxygen leads to the formation of numerous ions, including positive O^+, O^{2+}, O^{4+} and negative O^{3-}, O^{2-}, and O^- [56], which could contribute to an increase in an overall temperature of the gas.

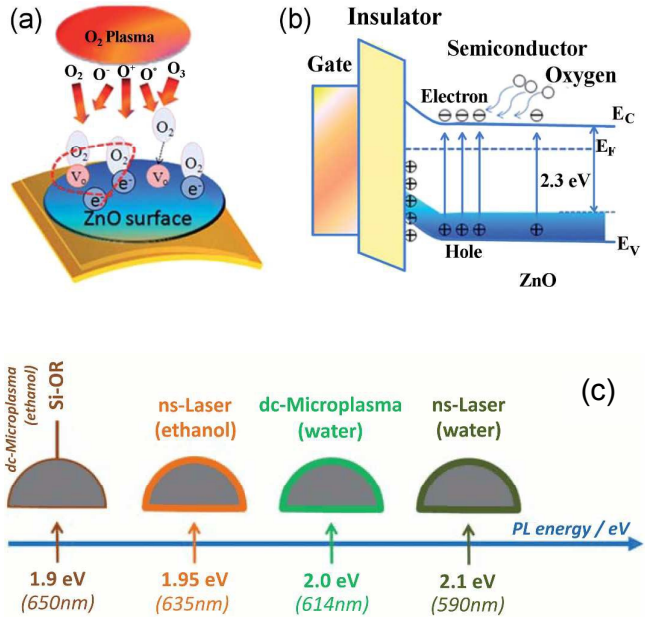

Fig. 2 (a) Oxygen plasmas are capable of shifting the threshold voltage, and (b) Energy band diagram illustrating the photo-electric process under the action of an oxygen plasma. Reprinted with permission from [57]. Copyright 2013, RCS. (c) Schematic diagram depicting the range of outcomes of oxygen-based surface engineering of materials illustrated by the change in the photoluminescence properties of silicon nanocrystals. Reprinted with permission from [50]. Copyright 2013, RCS.

However, surface modification with oxygen plasmas is the most powerful tool that enables an extensive modification of properties of a wide range of materials. **Figures 2a, b** illustrate the effect of an oxygen plasma-enabled treatment on the energy band diagram of a material,[57] while **Figure 2c** shows the extent of possible changes in photoluminescence properties of nanocrystals that could be attained using oxygen-based surface engineering.

Figure 3 summarizes the fundamental processes associated with oxygen plasma fabrication of complex architectures, and presents the entire spectrum of oxygen plasma-based technologies used for material treatment. Depending on the manner in which plasma is generated, the chemistry of the carrying gas and specifically its oxygen content, the plasma will possess varying concentrations of such species as electrons, ions and neutrals, dust particles, clusters, and even droplets. Hence, the reactions could be differentiated and used in accordance with the particular requirements for the treatment. Presence of electrically charged particles in the bulk plasma provides a considerable advantage since it opens up a possibility of using *electric* and *magnetic fields* to separate, guide, and accelerate the charged species, thus enabling better selectivity and efficiency of the treatment process and facilitating multiple processes within a single environment. The entire system could be characterized as an ensemble of five main constituents: a *surface, plasma, sheath, controls, and drivers*. External electric and magnetic fields, gas flows, pressure gradients, and applied power are the main controls of the process, influencing the *surface defects, stress and temperature gradients*, and *local electric fields*. The resultant effect of the exposure of a material to oxygen plasmas could be described in terms of the processes that transform an initial state into another state, the latter being in thermal equilibrium.

Within the formalism of the bottom-up approach, the main steps in surface-based material synthesis include the generation of adsorption sites on a specified surface area, growth of nanostructures on a base of the adsorption sites, and trimming of the developed structures. Subsequently, the surface of thus-grown nanostructures is considered as the basic platform for the next stage of processing, where some of its areas serve to providing the site for the new production cycle of preparation, growth and trimming, as shown in **Figure 3**. From this perspective, during the *first stage*, the substrate is treated to lay a base pattern for the following growth. Ion bombardment of

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the surface by high energy ions generates a large number of defects such as vacancies, interstitial atoms, cascades of shifted atoms. An intense bombardment results in mixing of the substrate material and results in surface chemical composition that is substantially different to that obtained under equilibrium conditions, where the latter is greatly limited by solid solubility. Furthermore, the ion flux increases the surface temperature due to the ion kinetic energy and heat released in the process of dissociation of oxygen molecules on the surface. Ion bombardment also stimulates the dissociation.[58] Eventually, enhanced surface temperature results in segregation of the reactive components.[59]

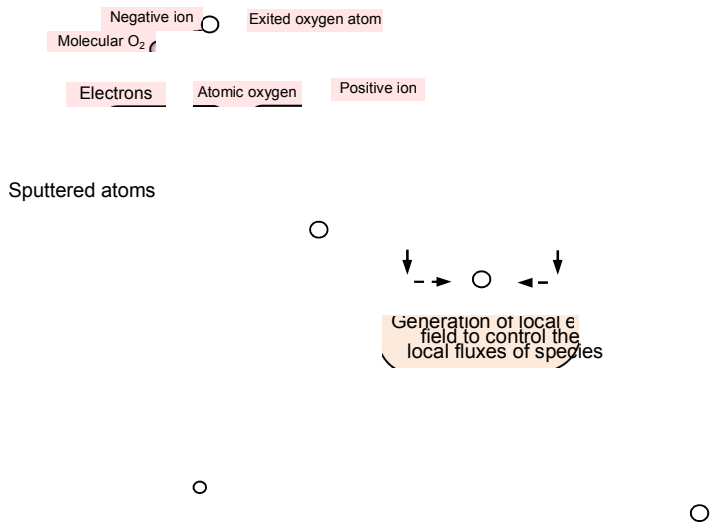

Fig. 3 Oxygen plasmas control the stages of fabrication of complex architectures: ions control the generation and distribution of the specified defects that serve as the adsorption sites; molecules and atoms in excited states provide the building blocks and heat necessary to conduct plasma-based che-mical reactions; while the electrons are responsible for the local electric fields. Finally, the surface processed and trimmed by the use of the process drivers. The mutual influence of the drivers and the surface makes the treatment process complex yet versatile.

The *second* stage is an additive process, which is characterized by a directed and controlled growth of new structures on the basis of the already-developed base platform, i.e. the generated layout of the seeds, so the rate of the geometry change is positive ($V_g > 0$). Here, the deposited droplets coalesce into nuclei, and nanowires, nanosheets, nanocones, and nanotubes grow from the clusters or surface defects. In oxygen plasmas, the energy released from the ion-induced dissociation of the oxygen molecules is the main source of the heat used as the driving force behind surface diffusion of the adsorbed species. The rough pattern formed during the initial stage of plasma processing is used during the seeding to fix the specified pattern of the deposited species, and to control the growth processes. As the nuclei grow, the effect of the electron bombardment becomes dominant: the surface exposed to the electron flux redistributes the strength of the local electric field generated as a result of the interaction of plasma with the substrate. The electric field generated on the topmost part (i.e. the tip) of the surface pattern feature can be estimated by considering an electric contact of nanometre-size object with a micrometre-size feature of the surface pattern. Microscopic fields increase from 10^5 to 10^7 V/m, while at the prominent features with a nanoscale dimensions, the field can reach a value of 10^{11} V/m. Values for the fields similar to these were demonstrated experimentally.[60] Besides, the stress gradients generated as a result of formation of a continuous oxide layer also act as the driving force that guides the formation of the next layer of nanostructures growing on the oxide film.[61,62]

Then, during the *third stage*, the finishing treatment should be applied to thus-grown structures to trim them in accordance with the specified requirements, typically through the removal of excess structures, and correction of their shape and size. As such, this trimming stage is characterized by a negative rate of the geometry change ($V_g < 0$). Sputtering and etching are the main processing tools during this stage. Sputtering is guided by the energy supplied to the surface by ions.[63] The interaction of the oxidant with the surface material can decrease the energy of the atomic bonding to intensify this process, which as a result is transformed from sputtering to etching.

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✓ *Which plasma parameters affect subtractive and additive processes?*

Neutrals, radicals, and species in excited states are the main building blocks during the growth stage, since these species are deposited on the preliminary layout of the precursors settled on the surface as the latter is bombarded by ions and heated by electrons. The species can diffuse along the surface until they find an energetically beneficial place determined by the precursor, at which point they attach and as such facilitate the growth of the nanostructure. **Table 1** illustrates the diversity of the plasma-enabled chemical processes conducted during the etching of MoS_2 two-dimensional crystals in an O_2/Ar inductively coupled plasma.[64] *Plasma density* and *electron temperature* determine intensity of a flux of the plasma species. Strictly speaking, the electron temperature is another parameter that should be taken into an account; however, the electron temperature could be changed within a range of 1 to 10 eV, while the plasma density could be varied by six orders of magnitude. *Chemical composition of a gas-plasma mixture* determines the nature and relative abundance of the species and as such the nature of the non-equilibrium plasma chemistry; *partial gas pressures* determine density and fluxes of the species. *Total gas pressure* determines transport properties of the plasma gap and energy of ions. While the density and hence the flux of the neutral species to the surface is proportional to the partial pressures, the total gas pressure determines the transport properties of the gap between the source and substrate. The *stress and temperature gradients* generated by treating the surface with a strongly non-uniform plasma flux can also be used as driving forces, as was shown during the growth of copper nanostructures of various dimensionalities.[65]

Sheath potential determines the ion energy and hence the ballistic processes in the material, while the *sheath thickness* determines a maximal size of an object that could be uniformly treated by a plasma flux. The sheath can be a matrix, transient, or steady-state sheath. This option is accessible starting from the micrometre-size objects, since for the nanometer-size objects the anisotropy of treatment is determined by a direction of an incident ion flow.

Table 1. Selected reaction set for charged and neutral species in O_2/Ar plasma.[66,67,68,69]

Process	Energy ε_{th}, eV
Chemistry of charged species:	
$O_2 + e \rightarrow O_2^+ + 2e$	12.06
$O_2(a^1\Delta) + e \rightarrow O_2^+ + 2e$	11.08
$O_2(b^1\Sigma) + e \rightarrow O_2^+ + 2e$	10.43
$O + e \rightarrow O^+ + 2e$	13.62
$O(\,^1D) + e \rightarrow O^+ + 2e$	11.65
$Ar + e \rightarrow Ar^+ + 2e$	15.60
$Ar(\,^3P_{0,1,2}) + e \rightarrow Ar^+ + 2e$	4.49
$O_2 + e \rightarrow O^- + O$	4.20
$O^- + O_2^+, O^+, Ar^+ \rightarrow$ neutral products	
Chemistry of neutral species:	
$O_2 + e \rightarrow O + O + e$	6.40
$O_2 + e \rightarrow O + O(\,^1D) + e$	8.57
$O_2 + e \rightarrow O_2(a^1\Delta) + e$	0.98
$O_2 + e \rightarrow O_2(b^1\Sigma) + e$	1.63
$O_2(a^1\Delta) + e \rightarrow O_2 + e$	–
$O_2(a^1\Delta) + e \rightarrow O + O + e$	5.42
$O_2(a^1\Delta) + e \rightarrow O + O(\,^1D) + e$	7.59
$O_2(a^1\Delta) + e \rightarrow O_2(b^1\Sigma) + e$	0.65
$Ar + e \rightarrow Ar(\,^3P_{0,1,2}) + e$	11.6

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Below we examine several characteristic examples of the two main routes for the application of oxygen plasmas in nanosynthesis discussed with respect to their effect on surface geometry, namely:

- *Subtractive and geometry-unaltering oxygen plasma-based techniques, i.e. those that imply material removal or a treatment that largely preserves original feature geometry – oxygen plasma as a cutting tool; and*
- *Additive oxygen plasma-based techniques, i.e. those that imply nucleation and growth – oxygen plasma as a building tool.*

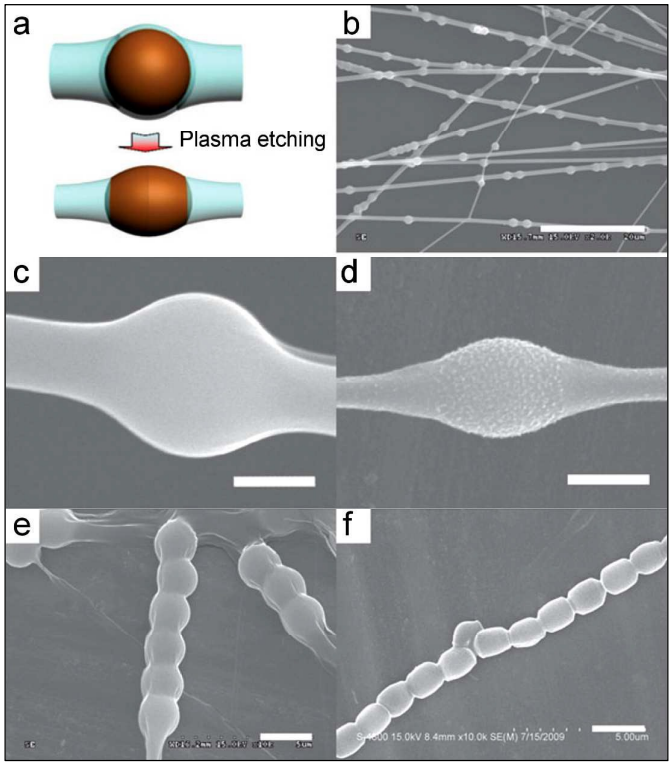

Fig. 4 (a) Plasma-enabled transformation of composite fibres comprising polystyrene particles (brown) embedded into electrospun polyvinyl-pyrrolidone threads (blue). (b)-(c),(e) SEM images of fibres prior to and (d),(f) subsequent 10 min plasma treatment. Scale bars are 20 mm for (b), 2 mm for (c) and (d), and 5 mm for (e) and (f). Reprinted with permission from [70]. Copyright 20112, RCS.

3. Sharp chisel: oxygen plasmas as a shaping tool

Since oxygen is a very reactive element, it is quite natural to examine specific examples of the oxygen plasma-based material processing techniques that take advantage of processes of etching and oxygen-enabled material removal. Indeed, various useful material characteristics can be gained and enhanced by such a treatment via selective, precise removal of atoms from the surface, with *selective etching* being one of the most prominent examples of the use of oxygen plasmas.

3.1 Selective etching in oxygen plasmas

Selective, anisotropic oxygen plasma etching was successfully utilized to produce a complex nanomaterial by transforming embedded polystyrene spheres into barrels attached to the electrospun fibres,[70] as illustrated in **Figure 4**. Anisotropy of the O_2 etching was the main feature of this process, resulting in the fabrication of a fascinating nanomaterial. Indeed, the process was designed to enable careful removal of material along the direction orthogonal to that of the polyvinyl-pyrrolidone fibre. Initially, the etching leads to the collapse of the thin shell that encapsulates the polystyrene sphere, leading the underlying sphere to become exposed to the plasma-generated particles while their caps remain protected by the fibre. Upon further treatment, the etching of the exposed area leads to a continuous removal of polystyrene and

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directional reduction in the sphere volume at a rate that is much greater than the etching rate along the length of the fibre. By using this simple but efficient anisotropic etching technique, it is possible to transform nanospheres into barrels and spindles in a highly controllable process, without detaching them from the string. This technique could also be used to fabricate other similar multi-material structures that require anisotropic oxygen-enabled processing. For example, inorganic silica microspheres partially encased by polymeric patches at their caps could also be produced. These polymeric patches can then be linked by other organic molecules to produce intricate patterns with controlled interparticle distance and morphology. The size of the particles processed in this manner can range 100 nm to several micrometres depending on the diameter of the fibre used for particle entrapment.

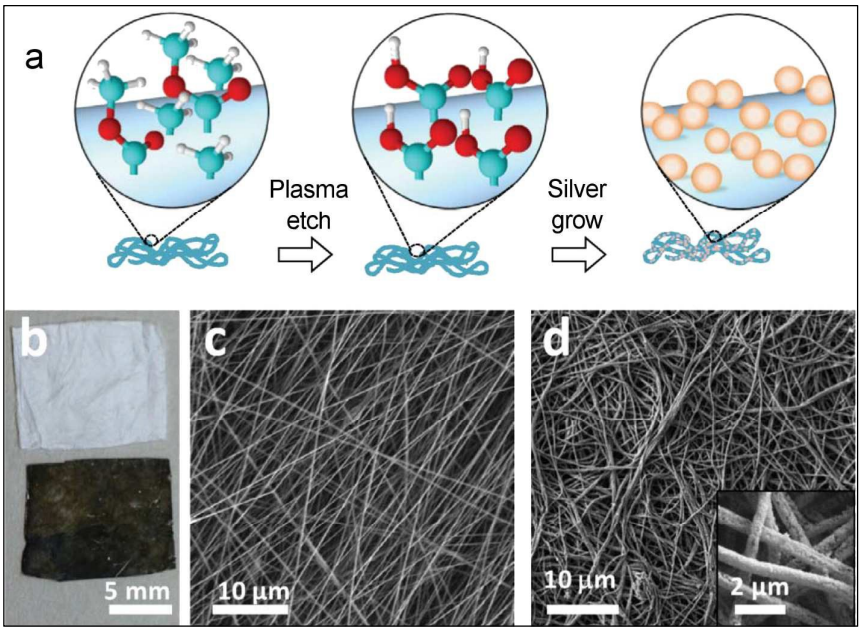

Fig. 5 (a) Concept of plasma-enabled immobilisation of silver nanoparticles on the surfaces of poly(methyl methacrylate) nanofibers. Blue, red, grey and orange spheres correspond to carbon, oxygen, hydrogen and silver, respectively. (b) Photographic images of the polymer film prior to (top) and subsequent to (bottom) decoration with silver nanoparticles; SEM images of fibres before (c) and after (d) plasma-assisted nanoparticle immobilisation. Reprinted with permission from [71]. Copyright 2013, RCS.

Another characteristic example of the fabrication of complex, hierarchical nanomaterials through sophisticated applications of an anisotropic oxygen plasma-based etching is shown in **Figure 5**. Here, plasma treatment enabled modification of electrospun polymethyl methacrylate nanofibers to promote the growth of silver nanoparticles on their surfaces. The mats of thus-functionalised polymethyl methacrylate nanofibers showed promising strong surface-enhanced Raman scattering behaviour, and as such can be potentially used as active substrates for rapid trace detection and identification of toxic, explosive and narcotic substances at ultra-sensitive levels. This work demonstrated that such approach can control interfacial interactions within multi-material systems and produce composite structures with well-resolved hierarchical features and outstanding Raman scattering performance .[71]

Similar etching procedures were successively applied to develop a two-dimensional array of nanobowls by exposing SiO_2/poly(methyl methacrylate) particles to the oxygen plasma flux.[72] Plasma treatment was performed in an atmosphere of oxygen at a quite low absorbed power of 10 W, followed by hydrogen fluoride etching to remove the SiO_2 cores. Due to the *anisotropy* of the plasma flux, after being treated with the oxygen plasma for only 1.5 min, the PMMA shells at the top of the spheres were removed thus exposing the SiO_2 cores to the highly reactive atmosphere of the plasma. During the process, the cores were gradually exposed by etching, as evidenced by the growth of an open size diameter up to the treatment time of 1.5 min, until the half of the external shell is removed. The nanobowl height decreased monotonically during the processing while the observed projection of the external diameter stayed constant. Then, both the open size and external diameters decreased due to the etching of the lower half-sphere of the bowls. Moreover, the nanobowls were used to demonstrate a possibility to obtain a hydrophilic outer side and a hydrophobic inner side of

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the nanobowls. After the oxygen plasma treatment, the nanoparticles of calcium carbonate were grown by a vapour diffusion technique on the outer side of the nanobowls, thus creating the raspberry-like nanostructures. In the absence of oxygen plasma treatment, no particles would grow on the initially hydrophobic surface of PMMA.

Selectivity of etching with the oxygen plasmas is an important parameter that could be easily controlled by the content of oxygen in plasma. For example, PMMA was selectively etched by changing the percentage of oxygen in Ar plasma in a study by Satake and colleagues. Specifically, their study showed that the etching depth dependent linearly on treatment time when processed in either pure

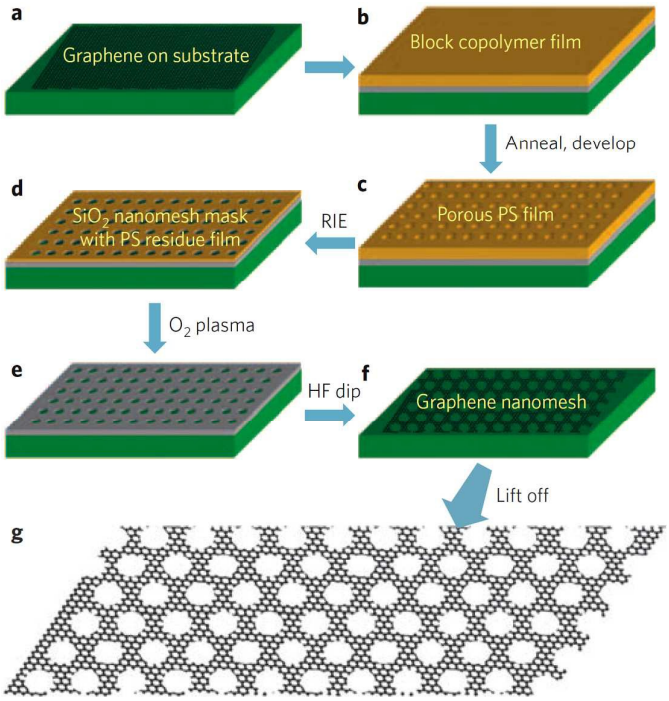

Fig. 6 Schematic of graphene nanomesh fabrication with oxygen plasma etching (e) utilized to define surface morphology. Reprinted with permission from [77]. Copyright 2010, 2010 Macmillan Publishers Limited.

oxygen or Ar/O_2 plasmas. This trend was observed even for etching depths exceeding 50 nm, suggesting that introduction of minute amounts of O_2 to Ar plasmas has the capacity to limit the variability in etching rate that results from the reduction in oxygen concentration during plasma etching.[73]

Efficient synergistic oxidation and detachment of graphene via plasma etching was demonstrated recently. Interestingly, the extent of damage to the graphene network as a result of exposure to oxygen plasmas varies dramatically between free-standing and surface bound graphene, arising from the differences in interactions between oxygen ions, graphene and substrate material (in this case, copper).[74]

When graphene is not firmly attached to the surface, the oxygen ions interact solely with the carbon bonds, leading to the destruction of the carbon network and evolution of CO_2 from the surface. In the case of substrate-bound graphene, the oxygen ions interact with the substrate, e.g. Cu, leading to its oxidation and promoting graphene anchoring at the sites of thus-formed cuprous oxide (i.e. the sites of defects in graphene). The oxygen content in graphene oxide is important for many practical applications.[75,76]

An important graphene-based structure, namely graphene nanomesh, potentially applicable for the fabrication of field-effect transistors was recently demonstrated, with the oxygen plasma etch being a key process in its fabrication due to the ability of the etch to punch holes in the graphene layers (**Figure 6**). This intrinsically scalable process could pave the way to an industry-scale graphene-based electronics fabricated by the processes widely used in the present-day semiconductor industry. The nanomesh with the feature size of about 5 nm can be prepared using convenient block copolymer lithography followed by etching in reactive oxygen plasma environment (see the detailed description of the process and all stages elsewhere[77]).

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Oxygen plasma etching was also successfully applied to form nanopatterns on solid surfaces. For example, tall and slender protrusions were fabricated on the surface of polypyrrole doped with dodecylbenzenesulfonate using a single-step oxygen plasma etching treatment. The method was highly efficient, applicable for large scale processing, and did not necessitate the use of a mask. The absolute and relative dimensions of the features were controlled by adjusting the applied power and treatment duration. It was found that while the aspect ratio and the length of the features became greater with increasing the length of processing or the applied power, the pitches and feature diameters did not change significantly. The self-driven production of such features was associated with the presence of impurities, deposited on the polymer surface via sputtering of material from the holding substrate.[78,79]

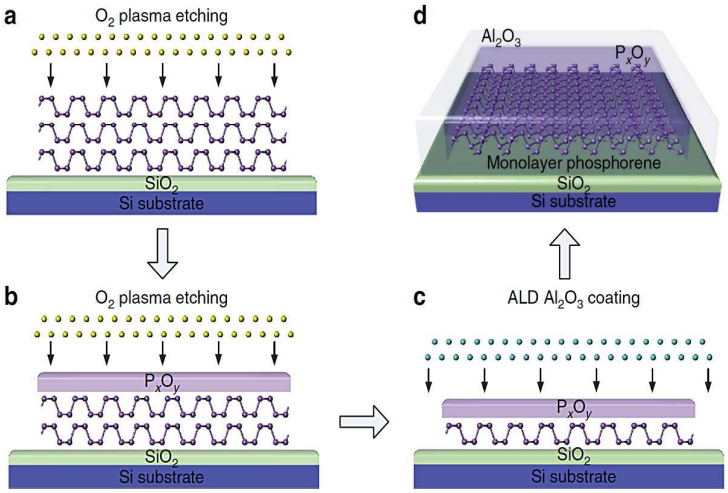

Fig. 7 Fabrication of air-stable mono- and few-layer phosphorene samples via the dry oxygen plasma etching process. Reprinted with permission from [81] under the terms of under a CC BY Attribution 4.0 International License.

Oxygen plasma etching was also successfully used to fabricate air-stable phosphorene films[80] with a designated number of layers, down to a monolayer system. The dry oxygen plasma etching allowed to thin pristine exfoliated phosphorene flakes with atomic precision, eventually obtaining the targeted structure with the highest level of controllability (**Figure 7**).[81] Moreover, not only structure but also the defect concentration in the phosphorene films could be efficiently controlled by the duration of etching. As a result, many practical properties of this important material may be directly managed by the application of the oxygen plasma-based process, including intensity of photoluminescence, as well as the concentration of oxidation-induced defects, the latter being critically important for tuning the key characteristics of such materials, including the band gaps.[82]

3.2. Sputtering in oxygen plasmas

Sputtering, i.e. a process of material removal that is driven by *physical action rather than chemical reactions*, also could be an important mechanism of nanoprocessing in the oxygen plasma. Sputtering of a surface due to the action of the high-energy ion flux generated in glow discharge in pulsed mode (matrix sheath) is a physical effect that can be effectively used over various spatial scales. In macroscopic treatment (up to a few cm), the ions accelerated by the electric field are applied to clean the surface for the subsequent technological stages. In general, the gas pressure should be kept as low as possible so as to prevent the contamination of the treated surface, and to exclude the

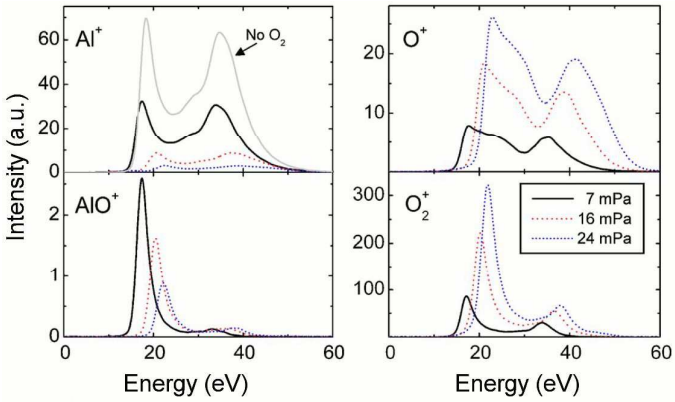

Fig. 8 Energy distributions of the main film-forming ions during RF magnetron sputtering for three different O_2 partial pressures at a total pressure of 0.33 Pa. For Al+ the distribution recorded in a pure Ar discharge is shown. Reprinted with permission from [83]. Copyright 2017, AIP.

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interactions of the ions with the background gas atoms to decrease the ion energy loss in the plasma sheath. However, when dealing with the microscale objects, the pressure should be increased greatly to preserve pressure × distance value necessary to ignite the discharge.

High efficiency of oxygen plasma environments is mainly due to high energy of oxygen ions that may be generates in these technological setups. Indeed, direct measurements show that the significant fraction of the ions in the oxygen-containing mixtures could reach considerably high levels of 20–40 eV.[83] As a result, O_2 sputtering-based processes find broad applications in synthesis and property tuning of novel materials.[84] **Figure 8** shows the experimentally measured distributions of various oxygen ions in plasma.

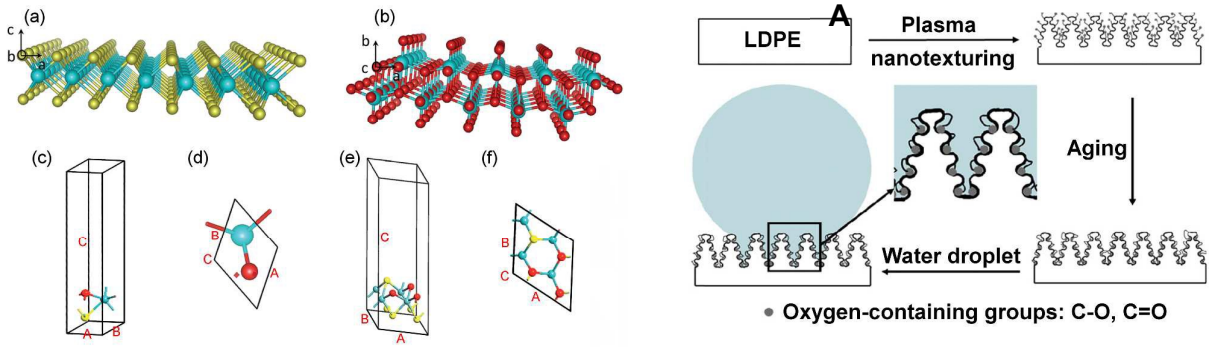

Fig. 9 Panel A: Single sheets of MoS_2 and MoO_3 (a,b) and side views of the optimized structures of MoS_2 (c-f). Reprinted with permission from [88]. Copyright 2017, ASC. **Panel B:** Schematic of the development of superhydrophobicity by oxygen plasma nanotexturing, where the surface is characterised by high water adhesion on the post-aged low density polyethylene. Reprinted with permission from [85]. Copyright 2012, Elsevier.

Numerous noticeable examples of this technology were demonstrated. The oxygen plasma sputtering was used to change the electrical conductance in carbon nanotubes.[86] The nanotubes were deposited during fabrication of the field effect transistor (FET), and they bridged the gap between the source and drain electrodes. Then, the gap was exposed to the oxygen plasma to perform partial removal of the nanotubes with a purpose to tune the conductance between the electrodes. Oxygen plasma processing was performed for 5, 10, and 15 s with 100 W of plasma power, 90 sccm of O_2 gas flow rate, and 300 mTorr of pressure, and the conductance was tuned from 47 μS to zero, which was attributed to the decrease in the number of the CNTs in the source-drain gap.

The oxygen plasma-based material processing techniques that do not change the surface geometry but tune the surface chemistry, particularly surface hydrophilicity, were also demonstrated.[87] Among other examples, defect engineering in various nanostructured materials, such as single-layered molybdenum disulphide (MoS_2) is an important, sophisticated application of the reactive oxygen plasma treatment. It is possible to notably tune the electrical characteristics of these systems through selective treatment by oxygen plasmas, switching the behaviour of the materials between semiconducting and insulating states. It was suggested and subsequently supported by the analysis and numerical simulation that the mechanism behind such a change in electrical behaviour was associated with the oxygen plasma-generated emergence of dielectric MoO_3-rich disordered regions within the semiconducting MoS_2, with the treatment time defining an exponential change in carrier mobility and material resistance (see **Figure 9A**).[88]

In the experiments on plasma treatment of polymer microfibrillar structures with a purpose to improve their surface wettability[89] and adhesion, oxygen plasmas proved to be a versatile tool for the development of hydrophilic properties.[90,91] Polyurethane (PU) and polydimethylsiloxane (PDMS) surfaces were exposed to oxygen plasma treatment for 1–5 min at 1000 mTorr and an oxygen flow rate of 18.3 ml/min using a Harrick Plasma Cleaner. After the oxygen treatment, a coating of a thin layer of polyethyleneimine (PEI) was applied. The water contact angle of PDMS microfibrils reached 10° after 5 min oxygen plasma treatment. However, the hydrophobic recovery commonly observed in polymers also took place; the con-

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tact angle subsequently increased from 10º to 36º after 72 h of storage, and eventually to 95º after seven days. In the experiments, the combination of molecular dissociation and tailored surface morphology can be used to explain the improved adhesion capacity of treated fibrillar arrays. Self-assembly of thin layers of selected polyelectrolytes on treated surfaces can hinder hydrophobic recovery, and thus stabilize the hydrophilic surface of plasma-treated fibrillar arrays.

Importantly, control of the hydrophilic and hydrophobic properties usually require a complex treatment that involves both material-removing routes to fabricate special surface textures, and processing that changes the active states of the surface. In this case, complex technologies that include several steps (and utilize different plasmas) can be used, as shown in **Figure 9B** (see details elsewhere).[85,92]

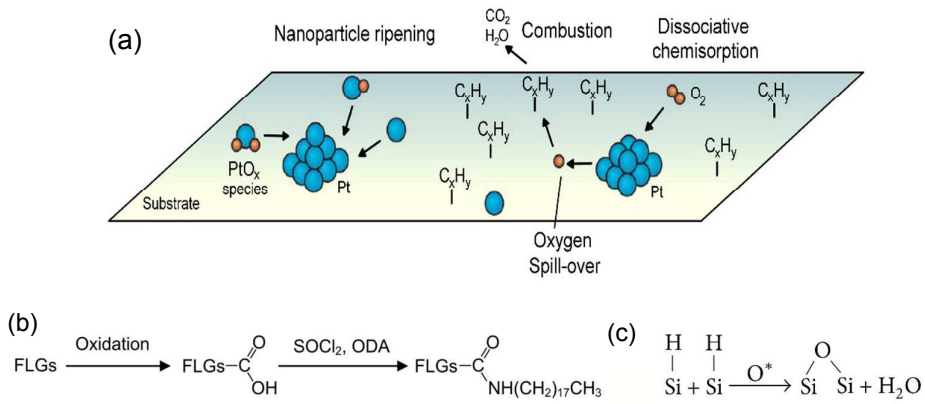

Fig. 10. (a) Surface reactions during the O_2 pulse of atomic layer deposition of thin platinum films on an oxide substrate. Oxygen promotes nucleation and ripening of Pt particles, primarily through the generation of PtO_x species that are capable to more rapid surface diffusion compared to metallic atoms. Reprinted with permission from [93]. Copyright ACS, 2013. (b) A schematic of chemical functionalisation of few-layer graphene nanosheets via oxidation. Reprinted with permission from [94] under a Creative Commons Attribution-NonCommercial-NoDerivs 3.0 Unported License. (c) Oxidation of silicon. Reprinted with permission from [95] under the Creative Commons Attribution License.

4. Handy trowel: oxygen plasmas as a building tool

Being highly chemically reactive, oxygen plasmas are typically associated with material removal via etching and formation of volatile gaseous fractions. Oxygen plasmas are nonetheless capable of efficiently supporting material synthesis, nucleation and growth. In the processes designed for *building* of nanostructures, oxygen plasmas could play two distinct roles, namely

- *Plasma could be employed in the capacity of an intermediary agent which a function similar to that of a catalyst, and*
- *Plasma could be used directly for the fabrication of oxide materials, nanomaterials and nanostructures.*

4.1. Oxygen plasmas as an intermediary agent

In these applications, oxygen in the plasma is not used as a building block for the new nanostructure (as a rule, an oxide), but is directly involved and plays a key role in the chain of reactions that result in the fabrication of this new material. **Figure 10a** shows a characteristic example of this application, when an oxygen plasma is used in the atomic layer deposition of Pt films. Oxygen radicals are directly involved in the process, and are critical to ensure the final result, i.e. a highly controllable Pt film structure.[93] Specifically, the presence of O_2 during the oxygen pulse is a critical control for nucleation of Pt on the surface. The nucleation depends on oxygen density, since oxygen positively contributed to the diffusion of platinum species along the surface. The exposure to oxygen plasma during deposi-

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tion could achieve several practical aims, including *fabrication of very thin metallic layers* with a minimal nucleation delay, synthesis of core/shell nanoparticles, and nanostructuring of metallic surfaces using area-selective deposition. Another important example is the application of O_2 plasma for the shape-preserving control of surface wettability. The great potential of oxygen plasmas in controlling wettability was successfully demonstrated for graphenes,[94] silicon,[95] polyvinyl chloride[96] and other polymers.[97] Superhydrophobic and superhydrophilic properties of chemically-modified graphene have been achieved by a simple chemical oxidation (**Figure 10b**). The oxygen plasma treatment can also modify chemical bonds on silicon surface, eventually changing the contact angle. In a typical reaction illustrated in **Figure 10c**, O_2^- and O^- species from plasma first attach to the silicon surface and then form Si–O–Si bonds via reaction with the Si–H groups on the silicon surface.

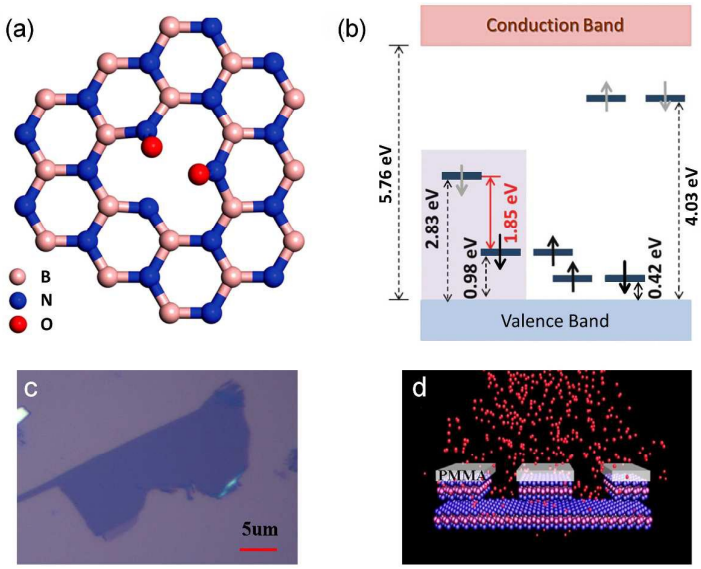

Fig. 11 (a) Illustration of the introduction of a boron vacancy by oxygen atoms and (b) Numerical simulation of electronic structure of the resulting material. Arrows represent occupied (black) and unoccupied (grey) impurity states, with spin corresponding to an up or down arrow direction. Reprinted with permission from [101]. Copyright 2018, RSC. (c, d) Optical images of a pristine bilayer MoS_2, and schematic fabricating the heterostructure. Reprinted with permission from [98]. Copyright 2013, ACS.

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Oxygen plasmas can also be used for a quick and efficient tailoring of hydrophobicity of various materials, such as porous silicon, which represents a type of very important and useful nanoporous platforms.[99,100] Pore diameter determines the penetration of oxygen ions into the material, and thus influences the resultant surface chemistry. In addition to the properties of the material, the *parameters of the plasma* also influence the penetration dynamics, and hence, the final result of the treatment (i.e. hydrophobicity of the treated surface). Indeed, at a fixed oxygen flow rate and working pressure, the penetration of oxygen radicals deep into the pores of the material are influences by the dimensions of the pore, e.g. its diameter, with smaller pores having lower oxygen radicals than larger pores or the gas bulk. Upon penetration into channels and bonding to the external surface of the silicon, oxygen radicals form Si–O–Si bonds. Upon exposure to aqueous media, these bonds spontaneously transform into polar Si–OH bonds, rendering the surface highly hydrophilic. As the number of Si–O–Si bonds tends to increase with the length of the oxygen plasma treatment, so does the resultant hydrophilicity to the extent of reducing the water contact angle below the detection limit of ≤0.5°.[95]

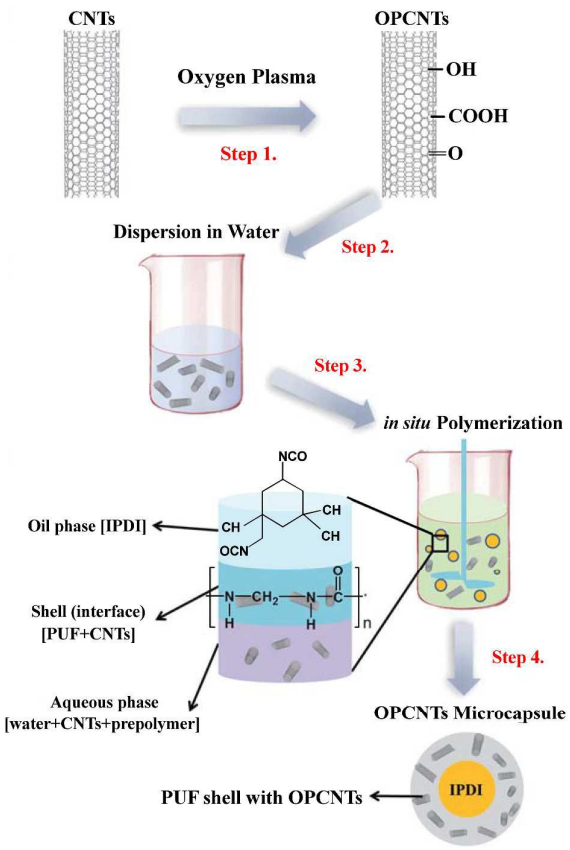

Fig. 12 Schematic representation of oxygen plasma treatment and isocyanate microcapsules fabrication technique. Reprinted with permission from [104]. Copyright 2018, RSC.

Oxygen ions could be used as a control mechanism for tailoring photon emission in various two-dimensional materials, such as hexagonal boron nitride[101] and graphene.[102] Experiments and density functional theory simulations have demonstrated that the level of emission may be affected by the presence of oxygen-containing defect complexes. The maximum penetration lengths of argon and oxygen ions from the plasma environment are about several nanometres below the surface, thus evidencing the under-surface action required for tuning the photoluminescent properties of the two-dimensional materials.[103] The schematics of the boron vacancy generation by oxygen atoms, and the simulated electronic structure of the resultant material are shown in **Figure 11a** and **11b**. Moreover, plasma-assisted fabrication of important oxygen-containing MoS_2 2D material with highly controllable thickness down to monolayer is also possible (**Figure 11c**, **d**).[98]

One more important example of the oxygen plasma treatment without the change of nanostructure size, i.e. for activation and modification of the surface properties, was demonstrated by the fabrication of isocyanate microcapsules with the improved properties using oxygen plasma-treated carbon nanotubes (**Figure 12**).[104] The experiments have demonstrated that the introduction of oxygen plasma-treated nanotubes into microcapsule shells had significantly improved their hardness and increased their Young's modulus.

4.2. Oxygen plasmas as a source of construction material

When oxide nanostructures are nucleated and grown in an oxygen plasma, the active oxygen radicals and ions perform a twofold function. Firstly, they ensure intense chemical reactions (often not possible at all outside of the plasma environment, or necessitating the use of extremely high temperatures

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which could be absolutely impractical for the real industrial processes), and secondly, they can directly incorporate into the growing oxide structure and thus serve as physical building blocks for the new structure.[105] Importantly, their role as an intermediary agent catalysing and activating the key reactions is still vital in these technologies.[106]

A typical outcome of the oxygen plasma-driven nanosynthesis of metal oxide nanowires usually represents a dense forest, or a brushe of very long (with the aspect ratio reaching 100–1000) and sharp nanostructures (sometimes called nano-needles). Let us first briefly outline some examples of novel nanostructures fabricated by oxygen plasmas, when the plasma-supplied oxygen was used as a building block (a construction material). **Figure 13** illustrates several quite diverse examples of metal oxide structures. Even with the same starting metal (in this case, molybdenum), an oxygen-containing process environment could produce amazingly different materials.

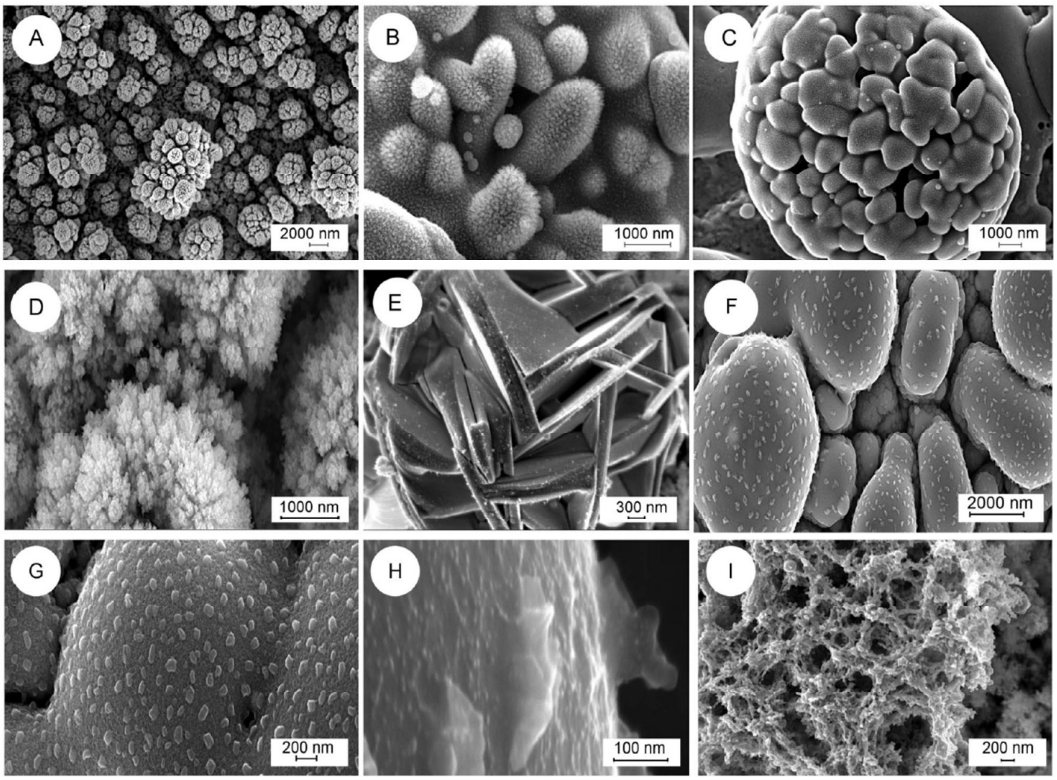

Fig. 13 SEM images of MoO_3 nanostructures. (a–e) Deposited in the pin-to-pin electrode configuration, (f–h) deposited in the pin-to-plate electrode configuration; (i) porous networks of MoO_3 deposited in the pin-to-plate configuration. Reprinted with permission from [48] under a Creative Commons Attribution-Non-Commercial 3.0 Unported License.

Indeed, a spark discharge at 5 kV in air led to the formation of multi-tier structures, where sub-micrometre sized features were decorated with nanometre-sized flakes. The former features were themselves organized into micrometre-sized cluster formations, see **Figure 14(a-d)**. This image shows several SEM images of the arrays grown on copper foils in the reactors similar to that depicted in **Figure 1c**. This typical radio-frequency setup, where the metal nanowires could be grown in an Ar + O_2 mixture, is a simple and convenient device.[46]

Nucleation and growth of metal oxide nanowires from an oxygen plasma is another characteristic example that illustrates the ability of oxygen plasmas to form unique structures that cannot be produced by other routes. Not surprisingly, the growth of metal oxide nanowires involves a significantly

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larger chain of reactions. The exact routes for the nucleation and growth of metal oxide nanowires in oxygen plasma remains not fully understood. It is often suggested that initially, the formation of seeds (which serve as a source of Cu atoms and have a relatively low initial density) takes place through the entire process of the plasma treatment.[107] The Cu atoms are subject to chemical interactions with the atoms of oxygen generated in the plasma discharge as well as on the nanowire surface, the latter being the result of the ion bombardment of the O_2 adsorbed on the nanowire surface. This ensures the growth of copper oxide.

Increasing the voltage to 12 kV led to the synthesis of distinctly different features that resembled nanowalls, as illustrated in **Figure 14**. Using a pin-to-plate configuration, it was possible to fabricate multi-tier architectures composed of micrometre-sized protrusions decorated by nano-sized dots, as shown in **Figure 14**(f)–(h) that feature structures grown under 7.7 kV and a pulse width of 45 ns. The location of the substrate in relation to the location where the plasma discharge comes into direct contact with the cathode also was shown to play a role in determining the resultant morphology of the architecture. For example, by placing the substrate ~100 mm away from the said location, it was possible to fabricate a network of nanoscale pores shown in **Figure 14**(i). Importantly, under all fabrication conditions used in this study, the architectures has high feature resolution, clearly-defined tier structure and a relatively uniform distribution of features across nano- to micrometre length scales.[48]

When considering the growth of nanowires, two possible mechanisms could be distinguished. The first one is the basal growth model, which largely relies on thermally-activated processes that take place between the atoms of oxygen adsorbed on the surface in the proximity of the nanowire base and the copper atoms. The second mechanism is based on a tip nanowire growth driven by thermal- and plasma-activated processes, such as bombardment of copper and oxygen compounds on the nanowire surface by plasma-generated ions. Furthermore, the thermal activation considers the heat that is delivered to the surface through ion and electron bombardment, as well as exothermic chemical reactions between oxygen atoms as they recombine to O_2 on the surface of the nanowire. Indeed, modelling has demonstrated that > 90% of the generated heat could be attributed to the latter. The bombardment of the adsorbed O_2 by plasma-generated ions leads to their dissociation, and production of oxygen atoms. Where oxygen is adsorbed on the surface of the nanowires, the activation processes result in oxidation of unreacted copper, however the growth of copper oxide that results from this oxidation process is not directed. Nevertheless, it is important to consider that the electric field in the plasma will direct the flux of ions, and as such the growth of copper and other oxides.[108 - 112]

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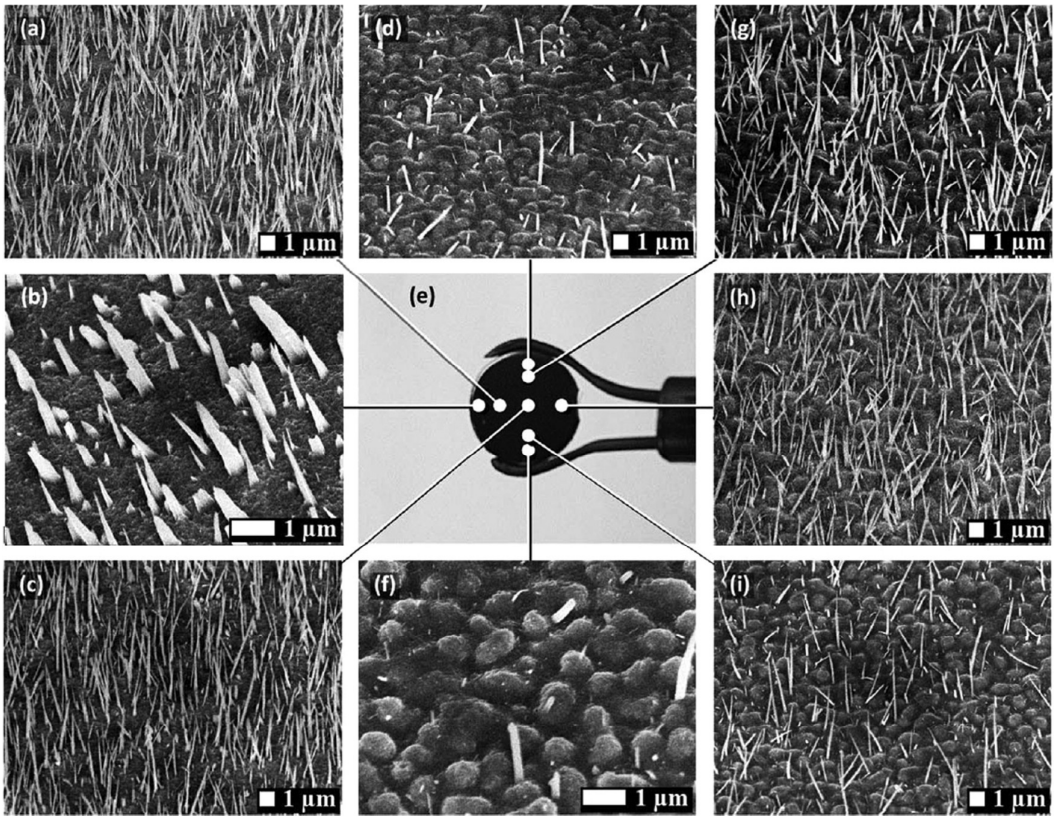

Fig. 14 SEM images of copper oxide nanowires grown in a radio-frequency oxygen plasma. Central photo (e) shows the positions of the specific samples on the table installed in the reactor. Quite different densities of the copper oxide nanowires (nano-needles) were obtained for different localizations of the samples. Reprinted with permission from [46]. Copyright AIP, 2014.

5. Summary and outlook

Future development of oxygen plasma-based technologies and applications may be related to two major directions.

- ✓ Novel processes and roadmaps for oxygen plasmas

An exhaustive review of the existing schematic solutions and plasma generating capabilities is beyond the scope of our work which is mainly focused on the capabilities of oxygen plasmas as a concept processing environment and its unique features that are applicable to the fabrication of novel materials.[113] However, here, we will briefly point out that in addition to a large amount of various plasma systems and process reactors such inductively- and capacitive-coupled setups, arc discharge, atmospheric-pressure, microdischarges, Townsend type and many other,[114,115,116] novel systems capable of addressing pressing challenges of nanoscale fabrication and assembly of complex hierarchical structures with high resolution will be in high demand. Among others, novel design solutions for the future plasma-based systems could explore the modular structural approach and the use of strongly concentrated energy fluxes to enable process flexibility and efficiency.[117,118]

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- ✓ Novel applications for oxygen plasma-synthesised materials

Although nanostructured and nanoscale materials fabricated with the use of oxygen plasmas have already gained a considerable interest from many industrial fields[119,120], future development of energy conversion systems and space exploration technologies may call for many novel, presently unavailable materials.[121] Some unique material systems, e.g. oxidized graphenes, have the potential to deliver significant benefits to existing and emerging devices and applications.[122,123,124]

- ✓ Novel level of understanding – how does oxygen plasma work?

Finally, as a prerequisite for the future successful development of oxygen-based plasma technologies, a much deeper level of understanding is required to properly design and control processes that govern the interactions between oxygen plasmas and different types of matter.[125,126] Excitation of metastable states in plasmas and on surfaces, the influence of strong UV and other radiation fluxes that could be present at the nanoscale level, and other fast processes that are extremely challenging for the direct experimental measurements should be carefully examined by novel experimental techniques and powerful numerical methods.[127,128]

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