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A brief review on plasma for synthesis and processing of electrode materials

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Abstract

Plasma, as an active, ionized and electrically neutral gas, consists of electrons, ions, molecules, radicals, photons, and other excited species. Due to its high activity, plasma can induce rapid and efficient reactions under relatively mild conditions. Hence, plasma has emerged as a powerful tool for material processing in both industrial and laboratory scale. This *Review* provides a timely summary of different plasma techniques and their application in electrode materials. We first provide a brief introduction to the nature of plasma and types of plasma technologies. Then we summarize the recent advance in material synthesis and processing (deposition, conversion reaction and surface modification) via plasma-assisted techniques with different feedstocks (C, H, N, O, Ar, S, P, etc.). Our focus is to put on electrode materials for energy conversion and storage devices, including batteries, supercapacitors, photo- and electro-catalysts. The advantages of plasma approaches over conventional technologies are discussed with examples.

Keywords: Plasma; Surface modification; Conversion reaction; Renewable energy; Electrode materials

1. Introduction

With increasing concern about environment and energy, a further expanding market for energy conversion and storage devices (ECSDs) has attracted considerable attention, within which electrode materials are the keystone and bottleneck of these devices [1, 2]. Herein, the exploitation of new materials and modification of existing materials at the atomic level become two meaningful and feasible strategies to meet the requirement of our society. However, researchers have suffered several challenges in traditional approaches for the fabrication of electrode materials with desirable structures, including sluggish reaction rates, high reaction temperature and long duration [3]. Hence, the innovation in preparation techniques is urgently needed. Recently, plasma-based methods have emerged, which delivers a unique environment, distinguishing from conventional physical and chemical processes [4]. Such strategy is expected to serve as a promising candidate in the preparation of advanced nanomaterials.

The concept “plasma”, first proposed by Irving Langmuir, is recognized as the fourth state of matters [5]. Unlike other three states (gas, liquid and solid), plasma is composed of a mixture of electrons, ions and neutral particles and most of these species in plasma preserve electronically excited states, exhibiting a highly reactive environment for physical and chemical reactions [6]. Hence, after almost one-century development from 1928, plasma-based techniques have evolved into an indispensable candidate in various applications [7]. Typically, non-thermal plasma has attracted considerable attention in material engineering because of its non-heating effect and relatively high reactivity, especially in the fabrication and modification of nanomaterials [8].

In this review, we briefly introduce the classification of plasma technologies and the principle of typical plasma-based strategies. Then, we will review recent advances of plasma-based techniques in material engineering based on different feedstocks (C, H, N, O, Ar, S and P). Typically, plasma deposition, conversion and modification are going to be illustrated with critical examples in recent literature. Representative instances applied in ECSDs will also be inventoried and discussed. Notably, this review mainly focuses on non-thermal plasma methods via electric activation in nanostructure processing as well as the predominance of experimental techniques for controllably achieving expected phase, morphology, and feature. Finally, we also propose the challenges and perspectives in the fabrication and surface modification of nanomaterials. Overall, this review devotes to highlighting the importance of plasma and proposing a more efficient approach to facilitate the development of advanced nanomaterials and their application in ECSDs.

2. Fundamental of Plasma

Figure 1: The classification of different types of plasmas. Top: Heat-generated and electric field generated plasma; Bottom: Hot plasma and cold plasma.

Plasma serves as a quasi-neutral gas of charged and neutral particles, which exhibits a collective behavior [9]. Here, two essential properties should be singled out and discussed in plasma: quasi-neutrality and collective behavior. Quasi-neutrality means that the density of electrons (n_e) is approximately equal to the density of ions (n_i), $n_e \approx n_i$. Hence, in a steady-state plasma, electrons and ions are created and lost from the plasma with equal rates. In addition, in plasma environment, the motion of species depends not only on micro-conditions (such as collisions), but on the macro-state of plasma (including electric and magnetic field), which is termed as collective behavior. There are two typical approaches to obtain plasma: thermal activation and electrical activation (Figure 1) [10]. For the former one, species are activated via absorbing sufficient energies from thermal sources, such as nuclear fusion [11]. For the later one, charged species obtain energies in electric field via continuous collision and oscillation to form plasma [12-14].

Electron temperature (T_e) and ion temperature (T_i) are two important parameters to characterize plasma. T_e is a quantitative reflection of thermal motion of the electron. Compared with electrons, heavy particles, ions and neutrals provide their own temperature, T_i . Herein, according to the difference between T_i and T_e , plasma can be classified to thermal plasma and non-thermal plasma (Figure 1). Thermal plasma delivers comparable temperature of electrons to that of heavy ions and neutrals ($T_i \approx T_e$), which means that all species have similar mobility behavior. In terms of non-thermal plasma, T_i is much lower than T_e ($T_i \ll T_e$), indicating that the electrons are energetically excited, while the heavy particles remain near room temperature, which is also named as cold plasma.

Since our concentration is plasma-based strategy on the synthesis and modification of materials, the plasma temperature, surface temperature and bulk temperature of target material should be identified and differentiated [7]. Plasma temperature is the average temperature in the center of plasma. In thermal plasma, such temperature is equal to T_e and T_i . In non-thermal plasma, even though T_e is quite high, the negligible weights of electrons compared with ions and neutrals cause little contribution towards plasma center. Thus, plasma temperature is similar with T_i , much lower than T_e . Surface temperature is the typical temperature of substrate surface and sub-surface. In thermal plasma, surface temperature is higher than T_i and T_e owing to collision of high-energy charged species based on electro-magnetic field. In comparison, although electrons with high energy continuously collide with substrate surface, their minimal masses deliver limited energy onto material surface. Hence, the surface temperature in non-thermal plasma is somewhat higher than T_i but much lower than T_e . Bulk temperature serves as the average temperature of bulk material. In thermal plasma, it is equal with T_i and T_e , while such temperature is almost same with T_i in non-thermal plasma due to the bare heating effect.

Because of the extraordinary kinetic features of ions and electrons, thermal plasma not only shows highly reactive behavior, but also exhibits considerably intense heating effect, which is sufficient to melt and even vaporize most materials, such as tungsten [15]. Hence, they are often used in melting of metals [16], ceramics sintering [17] and evaporation in materials-processing applications [18]. However, the heating effect is harmful to the fabrication of nanostructured materials. On the contrary, there is no apparent heating effect in cold plasma but high chemical activity, which is still preserved in mild condition. This unique property of cold plasma is very desirable for material

processing, especially for those sluggish reactions or materials sensitive to heat. So it is non-thermal plasma that has extensively been studied in preparation of nanomaterials. Here, we provide three common and typical plasma apparatuses to achieve non-thermal plasma.

2.1 Dielectric barrier discharge (DBD) plasma

DBD could produce homogenous discharge in a much simple way with low energy consumption [19]. As studied by Gibalov and Pietsch [20], DBD plasmas consist of a set of electrodes with at least one dielectric barrier between them (Figure 2a). To generate plasma, one electrode is connected to a high-voltage power supplier ($10^3 \sim 10^5$ V). The operated frequency is ranging from 50 Hz to ~ 10 MHz. The other electrode is grounded. Two electrodes produce a sufficient electrical field between them to form plasma when the gaseous molecules are passed through the dielectric surface. In general, the dielectric barrier is quartz, silica or alumina. Attributed to dielectric barrier, sparks inside the streamer channel could be avoided, which may lead to the serious overheating, local shock waves and noises. High discharge power is able to be achieved without employing extra power generator, such as bias voltage [21, 22]. Moreover, in DBD plasmas, the large volume excitation of glow discharge can be easily achieved. The flexibility of geometrical configuration, operating medium and parameters are also significant advantages of DBD plasma devices, which promotes researchers to apply them into various applications.

Figure 2: Three types of plasma setups to obtain non-thermal plasma: (a) Dielectric barrier discharge plasma, (b) Microwave plasma and (c) Radio-frequency plasma.

2.2 Microwave plasma

The generation of microwave plasma is specifically based on microwave frequencies, ranging from 300 MHz to 300 GHz. Since Bosisio et al. highlighted the superior behavior of microwave plasma in chemistry and spectroscopy in 1973, such kind of plasma has received numerous attention because of its high degrees of ionization and dissociation [23]. The schematic of microwave plasma is exhibited in Figure 2b. In microwave plasma, the energy transferred to charged species has a contrary tendency with the frequency of microwave [24]. Termly, lower frequency causes higher plasma temperature, while lower plasma temperature can be achieved with higher frequency. Herein, material fabrication and processing can be highly controlled via tuning the frequency of microwave. From last

two decades, various nano-sized materials such as ZrO_2 [25], Al_2O_3 [26], TiO_2 [27], and diamond-like carbon [28] etc have been successfully synthesized via microwave plasma. Simultaneously, the development of such apparatus has promoted microwave plasma to satisfy wide utilization in various fields.

2.3 Radio frequency (RF) plasma

RF discharge is produced by applying an alternating voltage to metallic or dielectric coated electrodes within the range of 1~100 MHz [29-31]. In terms of a conventional RF plasma (Figure 2c), two parallel disc electrodes are placed in a vessel. Since it is unnecessary for the ac circuit to be closed, the electrodes can be insulated from the conducting discharge plasma via dielectric material, avoiding the contamination from electrodes. To date, two major applications have stimulated tremendous interests in the study of RF plasma-based material processing: (i) etching effect with a moderate-pressure discharge (10~100 Torr) [32, 33], and (ii) conversion and deposition reaction with a low-pressure discharges (10^{-3} ~1 Torr) [34, 35].

3. The application of non-thermal plasma in material processing and fabrication

Compared to the ordinary chemical reaction media, non-thermal plasmas show distinct superiorities in the fabrication and modification of electrode materials [36-38]. Firstly, the presence of excited species in plasma results in an intrinsically high chemical reactivity even at ambient temperature. High reactivity leads to three typical consequences: high surface selectivity during processing [39], desirable production efficiency [40], and broad selection of starting materials [41-43]. Secondly, little heating effect is present in non-thermal plasmas, which is favorable for the preservation of nano-

framework [38, 44]. To date, here are three main categories of plasma reactions according to the interaction outcome: deposition, modification and etching (or ablation).

The typical candidate in plasma-assisted deposition is plasma enhanced chemical vapor deposition (PECVD). In traditional chemical vapor deposition (CVD), such process is always associated with high temperature, which is indispensable to promote the deposition reaction [45]. The high temperature may destroy the structure of temperature-sensitive substrates and resultant composites. Herein, plasma can be introduced to reduce the reaction temperature. According to average temperature in whole reaction system, PECVD can be divided as room temperature- and high temperature-processing. In room temperature, PECVD is mainly applied for polymer fabrication, also named as plasma polymerization [46]. Such method has received considerable attention because of the rapid conversion of reactive fragments from organic monomers within plasma condition. At high temperature, PECVD is typically used for fabricating carbon [47], silicon [48] and BN [49] etc. Based on electron impact dissociation of molecules for deposition processes, the introduction of plasma will largely decrease the required temperature as compared to that of CVD [50-52].

Plasma could also be applied in the modification of electrode materials [38, 53]. Plasma modification can be broadly classified as chemical and physical modification based on whether there are new chemical bonds formed. Chemical modification indicates that the species in plasma chemically react with material. Typically, there are three types of chemical modification: doping, conversion and etching [54, 55]. For example, under N-plasma environment, TiO_2 could be N-doped via the replacement of partial O atoms by N

atoms in TiO_2 lattice. As time goes on, when all O atoms are replaced by N-atoms, TiO_2 is converted into TiN [56-59]. In terms of chemical etching, volatile compounds are formed when elements on material surface react with species in plasma and then removed from the surface. For instance, oxygen-based ions in plasma react with carbon materials to achieve CO_2 , resulting in carbon removal from the surface of materials [60]. These three types of chemical modification can be either conducted separately or combined together according to different plasma parameters. Hence, by controlling plasma factors, products with specific requirement can be obtained.

For physical modification, there is no chemical reaction between charged species in plasma and target materials [61, 62]. In such process, charged species remove atoms or molecules physically and rearrange the configuration of material surface [54, 55]. Here, it should be noted that physical etching can also modify the chemical behavior of material surface although there are no chemical reactions during physical etching. For example, pure helium or argon discharges lead to the creation of free radicals on material surface [63]. These free radicals can subsequently be used for cross-linking or grafting of oxygen-containing groups when they expose to air. On the other hand, chemical modification is usually accompanied with plasma etching. Specifically, N-doping via N_2 plasma is also able to cause structural defects on graphene surface [64].

In plasma environment, above mentioned three interactions can take place separately as well as simultaneously [65, 66]. Here, integrating plasma with different gaseous feedstocks (C, H, N, O, Ar, S and P), we mainly discuss the above three plasma interactions in the following sections. Carbon plasma has mainly been applied into

deposition (such as graphene) and chemical conversion (typically carbidization). In terms of hydrogen-, nitrogen-, oxygen, sulfur, and phosphorus-based plasma, chemical doping and conversion serve as major candidates for material fabrication and processing. Due to its chemically-inert behavior, argon plasma is commonly used for delivering strong etching effect onto material surface. This section aims to provide the skeleton for researchers to understand the specific features, properties, and utilizations of cold plasma with different precursors.

3.1 Carbon plasma

Carbon plasma (C-plasma) is generated mainly from gas or liquid carbon-containing sources, such as CH_4 [67] and ethanol [68] etc., under specific environment. One of its major applications is to fabricate carbon-based materials, namely, carbon nanotubes (CNTs) [69], horizontal graphene (HG) [70] and vertical graphene [71]. Owing to its reducing behavior, C-plasma could also be applied in the modification (reduction and carbidization) of metal-based nanomaterials [72, 73].

3.1.1 Deposition

In the last two decades, carbon materials, especially graphene and CNTs have received considerable attentions in ECSDs because of their excellent conductivity, strong mechanical skeleton, and great chemical inertness [74, 75]. Generally, they are fabricated via traditional CVD method [45]. In PECVD, CNT growth mechanism is similar to the gas-solid interaction in CVD, during which plasma serves as a facilitating agent for nanotube fabrication [76]. Compared with traditional CVD method, there are some advantages of PECVD [37, 77]. Firstly, the lower reaction temperature: CNT growth in

CVD is controlled around 600-1000 °C and rare CNT can be observed below 500 °C. However, CNTs have been successfully fabricated via PECVD at 120 °C, which confirms that plasma can activate catalysts and facilitate the generation of carbon radicals at relatively lower temperature [78, 79]. Secondly, higher utilization of feedstocks: due to the abundance of active radicals, the concentration of carbon supply on catalyst surface is higher, leading to a rapid growth of CNT [51]. In addition, high concentration of H₂ is required to promote the formation of graphitic structures because of relatively low reactivity of H₂ in CVD method [80]. In comparison, H-species in plasma have high reactive behavior, so that small amounts of H₂ can facilitate the deposition of CNTs [81, 82]. Lastly, the presence of vertically-oriented electric field along substrate surface in plasma facilitates the growth of highly perpendicular CNT (Figure 3a), different from spaghetti-like films of CNT in CVD [51, 83]. These vertical nano-frameworks provide enhanced conductivity, high surface area and improved loading density, making it an ideal scaffold for electrode materials [84, 85].

Graphene could also be fabricated via PECVD, especially for vertical graphene nanosheets (VGSs), which could not be synthesized by traditional CVD [86]. VGSs have attracted huge research interests owing to their vertically-oriented structure, exposed reactive edges, high surface areas, great mechanical and chemical stability (Figure 3b) [87, 88]. These superior behaviors allow VGSs as a promising scaffold candidate in ECSDs. Until now, different plasma-based techniques have been reported for the fabrication of VGSs [89-92]. Distinct from the “dissolution-precipitation” growth model of HG during CVD process, VGS fabrication mainly depends on Volmer-Weber (VW) mechanism [93, 94]. In VW model, carbon radicals interact with each other rather than

with catalysts to achieve strong covalent bonding. With the effect of electromagnetic field in plasma, carbon radicals deposit perpendicularly onto substrate surface to finally achieve VGSs. Accordingly, no catalyst is required in the VGS growth process, leading to broad selection of substrates with various composition (such as Si [89], SiO₂ [95], Al₂O₃, [96], Ni [97] and stainless steel [98]) and different morphologies (foam-like [93], cylindrical shapes [99], micrometer- and even nanometer-sized structures [100]). So PECVD could be applied to fabricate high-quality carbon materials as an energy- and time-efficient strategy. Pure 3D vertical graphene sheets (3DVG) could also directly act as the anode for Li-ion battery (LIB). As shown in Figure 3c, they can deliver an enhanced performance as LIB anode compared with that of 3D horizontal graphene (3DG) [93].

Figure 3: The deposition function of C-plasma. (a) SEM images of CNT via PECVD approach [51] and CVD method (inset of a) [83]. (b) SEM image of vertical graphene sheets (VGS). (c) Electrochemical performance of VGS and horizontal graphene as anodes for Li-ion battery [93]. Structural characterization and performance evaluation of hierarchical vertical graphene nanotubes (hVGT) [100]. (d) TEM images of hVGT. (e) SEM images of MoS₂ coated hVGT (MoS₂@hVGT). (f) Rate stability of MoS₂@hVGT. Morphological characterization of hierarchical VGS coated SnS (hG@SnS) [101]. (g) SEM images. (h) TEM image. (i) Comparison of rate performance among different composites.

During the fabrication of VGSs, electrical field, feedstock, H₂ concentration and the temperature of substrate are all playing as important parameters to the growth of VGSs [102]. Within plasma environment, the existence of inductive electric field perpendicularly to the substrate surface facilitates the high mobility of carbon radicals,

causing vertically-aligned structure of carbon-based framework [94]. Since vertical electric field delivers an observable effect on the orientation of VGS, many attempts have been carried out for controllable growth [103-105]. By modulating the direction of electric field, graphene with specific angle to the substrate was obtained. The height and density could also be tuned via changing the electric field [106]. Furthermore, the growth rate of VGSs is closely related to the dissociation energy of feedstock [102]. With lower dissociation energy, more reactive carbon dimers C_2 can be formed, leading to faster growth rate of VGSs. For instance, it is easier to produce C_2 dimers by dissociating C_2H_2 than CH_4 molecules, because of the strong $C\equiv C$ bond in C_2H_2 molecules [107]. Consequently, VGSs grow much faster from C_2H_2 than from CH_4 in PECVD. Moreover, H-introduction is to promote the graphitization and prevent the formation of amorphous carbon [108]. With excessive H_2 , more disordered graphene would be fabricated due to etching effect of H-species as well as the decreased number of C atoms adsorbed on substrate surface. Less H_2 incorporation would cause the deposition of amorphous carbon. Taking CH_4 as carbon precursor, the optimum growth condition was related to the $H_2/(CH_4+H_2)$ ratio of 25% [108]. Furthermore, the temperature of substrate is directly proportional to the VGS nucleation [103, 109]. With increased substrate temperature, the density and diameter of VGS are also increased.

In the application of ECSDs, intrinsic CNTs and VGSs provide inferior performance. Specifically, these graphitic structures deliver a theoretical Li^+ storage behavior ($\sim 375 \text{ mA h g}^{-1}$) and usually negligible capacitance in supercapacitor devices, which are both much lower than those of metal-oxides ($800\text{-}1200 \text{ mA h g}^{-1}$ and $600\text{-}1300 \text{ F g}^{-1}$) [1, 110]. These drawbacks have limited their application in energy conversion and storage directly

acting as the electrode materials. However, due to the high conductivity, light weight and chemical stability, they could act as ideal substrates to improve the performance of other materials, typically metal-based compounds [111-113]. For example, Tay et al. fabricated the core-shell CNTs/NiCo₂O₄ as LIB anode [114]. Such anode displayed the specific capability of ~1031 mA h g⁻¹ at 200 mA g⁻¹. CNTs work as the scaffold to release the tension during charge-discharge process and offer highly sufficient active area for Li⁺ insertion and extraction. In addition, vertical CNTs supported MoS₂ exhibited enhanced HER performance [115]. With excellent electric conductivity of CNTs and more exposed active sites, the resultant composite delivered enhanced HER behavior than that of pure CNTs and MoS₂. VGSs have the same function as the scaffold [116-118]. Xia et al. achieved VGSs array on carbon cloth (CC) surface, followed by the deposition of MoO₂ film on VGS surface [119]. The obtained VG@MoO₂ core-shell structure exhibited higher capacity for sodium ion storage than that of electrode without VGSs. The VG@MoO₂ also showed good chemical and physical stability. After 500 cycles, VG@MoO₂ provided a capacity retention of 81.7% with well-preserved morphology.

According to the same growth strategy, it is also possible to deposit such VGSs directly on low-dimensional materials. Our group deposited such VGSs on CuO nanowires array followed by the removal of CuO, leading to the formation of hierarchical vertical graphene nanotubes (hVGT) [100]. TEM image of the obtained tubular graphene is depicted in Figure 3d. To demonstrate application in Na-ion storage, MoS₂ nano-crystals was further deposited via pulsed laser deposition technique to form a hierarchical array structure of MoS₂@hVGT (Figure 3e). Indeed this MoS₂@hVGT electrode exhibited relatively high discharge capacities of 535 and 314 mA h g⁻¹ at 0.5 and 20 A g⁻¹,

respectively (Figure 3f). Inspired by this, we deposited hierarchical VGS (hG) directly on battery materials, SnS nanowires in this case (hG@SnS) (see Figure 3g). In this configuration, the hGs densely cover the surface of each SnS nanowire, and function as both structural protector and conductive path for the SnS nanowires as anode for Na-ion battery [101]. What is unique here is that the SnS surface was partially reduced into metallic Sn owing to C-plasma reduction, and the achieved Sn catalyzed the growth of such hG (more discussion will be made in the next section). It is interesting that this hG@SnS electrode exhibited better capacity retention up to 1600 cycles, as compared to less than 500 cycles for the physical mixture of rGO/SnS and pristine SnS nanowire electrodes (Figure 3i). These results open the door to new applications of VGS in ECSD.

3.1.2 Carbidization and reduction

The other application of C-plasma is to reduce and carbonize metal-based materials [120, 121]. The work mechanism of C-plasma is similar with traditional carbothermal reaction, which takes place between active C-radicals and target materials. Due to the high activity, much lower temperature and shorter duration are required in plasma condition. Whitehead et al. studied the reduction of NiO via CH₄ plasma [120]. NiO was rapidly reduced to metallic nickel after C-plasma treatment at 330 °C, while no reaction has been observed in thermal condition. A layer of carbon would be deposited after the formation of metallic nickel based on VW growth model [122, 123]. Regarding this, we fabricated NiMo alloy nanoparticles on NiMoO₄ nanowire via C-plasma for enhanced HER performance (Figure 4a) [124]. Compared with hydrogen annealed samples, our C-plasma treated nanowires (C-30s) provided improved stability because of the protection of carbon shell (Figure 4b and 4c). Metallic Ni₄Mo nanoparticles could be observed,

indicating the successful reduction with short duration (30 s) and low temperature ($\sim 450^\circ\text{C}$) (Figure 4d). According to HER behavior (Figure 4e), NiMoO_4 with C-plasma treatment of 30 s delivered an overpotential of 76 mV at 10 mA cm^{-2} , slightly lower than that of Pt/C (45 mV) and much lower than that of H-treated NiMoO_4 (233 mV). The same phenomena were also observed on Co_3O_4 .

Figure 4: The reduction application of C-plasma. (a) The preparation of C-plasma treated NiMoO_4 . (b) TEM images of C-plasma treated NiMoO_4 (C-30s). High-resolution XPS for NiMoO_4 and C-30s (c) C 1s and (d) Ni $2p_{3/2}$. Electrochemical test of resultant samples (e) LSV curves [124].

Transition metal carbides (TMCs), typically tungsten carbide and molybdenum carbide, have attracted much attentions in electrocatalysis because of their Pt-like behavior [125]. Traditional approaches to achieve TMCs mainly depend on thermal treatment (above 800°C) of transition metal-based precursors in carbon-containing environment (such as CH_4 [126], ethylene [127], and ethanol [128] etc) with long duration (>0.5 hours). In comparison, C-plasma is capable of converting metal-based precursor into metal carbide

with a shorter duration (~10 min) and lower reaction temperature (below 650 °C). Such advantages further contribute to the prevention of structural agglomeration and excess carbon coating on material surface [129]. Wang et al. have ever achieved WC nanowires based on CH₄-H₂ plasma treatment of WO₃ nanowires [130]. The introduction of H₂ is to prevent the generation of amorphous carbon on nanowire surfaces, promoting the carbidization [131]. With C-plasma treatment, the surface of WC_x nanowire became much rougher as compared to pristine WO₃, within which W₂C and WC served as two major components. Acting as HER catalyst, the resultant nanowires delivered η_{10} of 118 mV and 122 mV in acidic and alkaline electrolytes, respectively. The capabilities of such catalyst in both environments still maintained with little degradation over 4000 cycles. Additionally, carbides could also be fabricated from corresponding pure metal. Lee et al. directly fabricated WC nano-wall based on the carbidization of metallic tungsten with solid carbon precursor, which also exhibited high catalytic activity and stable performance as HER catalyst [132]. Hence, C-plasma serves as an alternative for the carbidization and reduction for metal-based nanomaterials.

3.2 Hydrogen plasma

Hydrogen plasma (H-plasma) is commonly generated on the basis of H₂ feedstock. As mentioned in the last C-plasma section, H-plasma is able to be applied with C-plasma together for the deposition of graphitic carbon due to its etching effect on amorphous carbon [103]. In addition, a large number of active species including H, H⁺, H₂⁺ and H₃⁺ exist in H-plasma and these species deliver much higher oxygen-absorbing behavior than molecular hydrogen. Consequently, the other application of H-plasma is to serve a reducing agent for oxides [81, 133, 134]. Compared with long-term annealing within

hydrogen environment, H-plasma delivers the following advantages: (i) high reducibility at room temperature, (ii) rapid reaction process, and (iii) low destruction for the nanostructure of processed materials.

3.2.1 H-plasma on carbon materials

In addition to the assistance in synthesizing carbon materials, H-plasma is also introduced to remove O-species on carbon surface. In terms of chemical and thermal approaches to reduce graphene oxide (GO), chemical contaminants (such as hydrazine) and high-temperatures (1000~1100 °C) are usually required [135, 136]. In comparison, H-plasma offers another attractive strategy for controllable deoxygenation, defect elimination and restoration of graphene conductivity. For example, reduced graphene oxide (rGO) has been fabricated by Rahman et al. under H-plasma at room temperature for 40 s [137]. As confirmed by Raman and XPS spectra, H-plasma was capable of effectively removing oxygen-based functional groups from GO surface and simultaneously restoring sp^2 C=C bond. As is well known, GO is a class of active material or supporter for other materials owing to its high specific surface area [138, 139]. However, high O/C ratio leads to inferior electric conductivity, which is harmful for ECSDs [140]. Wang et al. reduced GO via H-plasma to acquire enhanced supercapacitive behavior [141]. The O/C ratio could be carefully tuned via controlling the duration and power of H-plasma. The obtained rGO with C/O ratio of 6.9 provided the optimum supercapacitive performance of 211.8 F g⁻¹ at 0.5 A g⁻¹, ~10 times higher than that of GO (22.7 F g⁻¹).

3.2.2 H-plasma on metal-based materials

Moreover, H-plasma offers reducing behavior towards metal oxides [142]. Wang et al. reported the successful reduction of NiO in H-plasma at room temperature [143]. The reduction was achieved within 10 min, much shorter than thermal reduction process over 10 hours. More importantly, the size and morphology were well preserved, indicating that the serious agglomeration in traditional thermal treatment could also be avoided via the H-plasma.

There are several metal oxides, such as ZnO and TiO₂, which deliver strong M-O bonds. So, the as-obtained O-H groups cannot be reduced further into H₂O and H-species will be binding on their surface. Such H-abundant layer also leads to the passivation of material surface. This phenomenon is termed as hydrogenation [144]. Specifically, when exposing indium tin oxide (ITO), F-doped tin oxide (FTO) and indium zinc oxide (IZO) films into H-plasma, both ITO and FTO were reduced to corresponding metal, while IZO was not reduced to elemental Zn. As analyzed by XPS results, hydrogen was to be bonded between two Zn or O atoms (Zn-H-Zn and O-H...O) [144]. Similarly, with H-plasma treatment, the surface of TiO₂ can only be partially reduced to Ti³⁺, along with the abundance of O-H groups on its surface [145]. Owing to the introduction of oxygen vacancy (Ti³⁺ sites) and hydrogenated shell, the resultant composite is expected to provide excellent capability in energy storage [146]. For example, Wu et al. ever reported the H-incorporation towards TiO₂ nanotube (ATO) surfaces for enhanced supercapacitance [147]. After plasma treatment at 320 °C, the obtained TiO₂ (ATO-H) exhibited rough and amorphous surface with a shell (1-2 nm) composed of the incorporated Ti³⁺ and -OH groups, which increased the carrier density of TiO₂ (Figure 5a-d). H-plasma preserved the toughness feature of TiO₂ nanotube. In comparison, the

annealed TiO₂ in hydrogen atmosphere (450 °C) became brittle after thermal treatment, which was ascribed to hydrogen embrittlement towards titanium at high temperature [148]. As the electrode of supercapacitor, the H-plasma treated TiO₂ nanotube exhibited a high specific capacitance of 7.22 mF cm⁻² at 0.05 mA cm⁻², which was 7 times higher than that of initial TiO₂ (Figure 5e).

In addition, the H-plasma treated TiO₂ also shows performance improvement as a photocatalyst. As reported by Mathur et al. [149], the formation of Ti³⁺ and disordered crystal after H-plasma treatment results in a broad spectrum of mid-gap states, which effectively shortens the bandgap to the visible range. As shown in XRD patterns (Figure 5f), peak intensities became weaker after H-plasma treatment, suggesting the formation of atomistic surface defects and hence crystal disorder. High defect concentration yielded a broad spectrum of mid-gap states, leading to the absorption of visible light (Figure 5g). This was also confirmed by the density of states (DoS) calculation that showed a transition from TiO₁₂₈O₂₅₆ to Ti₁₂₈O₂₅₆₋₁₂ (Figure 5h). As a result, plasma-treated TiO₂ provided larger photocurrent density as compared to untreated one under solar irradiation (Figure 5i). Rankin et al. further investigated the mechanism by means of neutron reflectometry [150]. As confirmed by simulation and experiment, H-species during treatment contributed to the generation of Ti³⁺ and doping effect into the lattice of TiO₂, resulting in the dramatic change of visible light absorbance. For photocatalytic behavior, the H-TiO₂ provided photocurrent 8 times higher than that of untreated TiO₂ under blue LED irradiation.

Figure 5: Metal oxides treated via H-plasma. (a) and (b) TEM images of TiO₂ (ATO) and H-plasma treated TiO₂ (ATO-H) nanotubes. The inset of (a) the corresponding FFT pattern. (c) and (d) Ti 2p and O 1s XPS spectra of ATO and ATO-H. (e) CV curves of ATO and ATO-H electrodes at a scan rate of 0.1 V s⁻¹ [147]. Characterization and photocatalytic behaviors of H-plasma treated TiO₂ at different temperatures [149]. (f) XRD patterns. (g) UV/vis/NIR reflectance spectra of the untreated and H₂ plasma-treated TiO₂. (h) Density of electronic states of TiO₂ for varying oxygen vacancy concentration. (i) Photocurrent density vs applied potential curves for TiO₂ before and after treatment.

3.3 Nitrogen plasma

As two critical nitrogen-containing feedstocks, NH₃ and N₂ have been widely applied to achieve nitrogen plasma (N-plasma) [30]. Ascribed to the stronger bond of N≡N in N₂ than that of N-H in NH₃, more energy is required to form N-based active species in N₂

plasma. Nonetheless, even with higher reactivity, no one could deny the excessive toxicity and high cost of NH_3 . Hence, N_2 plasma is a more economic and environmentally-friendly choice. In addition, introducing appropriate hydrogen is a feasible strategy to promote the activity of N_2 plasma [151, 152]. Of course, it also works on NH_3 plasma. In general, there are two major applications in material processing for the N-plasma utilization: (i) nitrogen doping, and (ii) nitridization.

3.3.1 N-doping in carbon materials

N-doping has received wide applications in carbon materials [153]. It has been demonstrated that heteroatom-doped carbon materials are capable of providing improved electrochemical behavior owing to their greater electron mobility and more exposed active sites [154]. Traditional approaches for achieving N-doped carbon usually depend on the decomposition of nitrogen-containing precursors or thermal treatment of carbon in NH_3 atmosphere [155]. Here, N-plasma offers another convenient choice to introduce N-atoms into various carbon materials at room temperature. Within plasma, nitrogen radicals are capable of substituting the carbon atom and then altering the overall electronic properties. With different doping positions onto graphene lattice, the resultant frameworks show different configuration. In N-doped graphene, three common bonding can be found, including quaternary N (or graphitic N), pyridinic N and pyrrolic N. Pyridinic N and pyrrolic N refer to N atoms which bond with C atoms at the edges or defects of graphene. Quaternary N substitutes for C atoms in the hexagonal ring. Among these N types, quaternary N and pyridinic N are sp^2 hybridized while pyrrolic N is sp^3 hybridized [153, 156]. By modulating plasma-based parameters, the bonding position is expected to be controlled. Typically, Lin et al. has achieved N-doping onto graphene

surface via N₂ plasma [64]. As indicated, N₂ plasma not only incorporated onto graphene plane, but also achieved N-bonding at edge sites and defects. As further reported by Lin et al., the N-bonding configuration in graphene can be controlled via selecting the reactive species [157]. Low-energy N₂ plasma exposure is inclined to introduce N-doping onto graphitic plane, while thermal treatment would only deliver nitrogen groups at edge sites. Their results indicated that nitrogen ions (N⁺, N₂⁺) were desired to substitute carbon atoms in graphitic lattice but thermal-activated neutrals (atomic N, molecular N) could only fill in pre-existing defects.

As discussed in H-plasma, H-species provide reducing effect onto oxide surface. Therefore, NH₃ plasma emerges as both doping and reducing agents on GO surfaces because of simultaneous presence of dissociated N- and H-species. For instance, Major et al. have treated GOs by NH₃ plasma [158]. With different processing duration from 1 to 20 min, the N/C ratio was continuously increased, indicating the successful doping of nitrogen content. In comparison, the ratio of O/C was firstly decreased, followed by an apparent growth with the minimum proportion at 5 min treatment. Such phenomenon was attributed to two crucial properties of NH₃ plasma: (i) the removal of O-groups to recovery sp²-C, and (ii) nitrogen incorporation into graphitic-N form. With shorter duration, numerous O-species were removed from GO surface while small amounts of N were introduced into graphitic lattice, causing the reduction of O/C ratio. With elongated processing, relatively low O-content led to an inferior removal rate of plasma. Hence, N-functionalization occupied the crucial part, resulting in continuous removal of atomic carbon on GO planes. This caused the increase of O/C ratio. Furthermore, Duesberg et al. also investigated the simultaneous reduction and doping with nitrogen of GOs via NH₃-

H₂ microwave discharge at room temperature [159]. After 1 h treatment, oxygen-containing groups were dramatically decreased, and N-doping was successfully achieved. Notably, the total number of defects on the surface of GO was reduced, due to more removed oxygen-groups but less introduced N-groups. No observable re-aggregation was observed after plasma processing, owing to the dry process. Such results were in agreement with that of Gomathi et al [160].

Unlike NH₃-based plasma, there is no reducing behavior for N-plasma based on pure N₂. Oppositely, it is able to accelerate the oxygen-absorbing capability of carbon materials, inducing the introduction of oxygen-based groups [161]. As reported by Lin et al., nitrogen was incorporated onto graphene surface after N₂ plasma processing. Simultaneously, oxygen content on graphene was also increased according to XPS results. This was attributed to the presence of unsaturated carbon atoms, created by ion bombardment of N-plasma. Consequently, once exposed to air, active carbon species react with oxygen to form polar groups on graphene surface [64]. Above all, N-plasma with different feedstocks may exhibit different properties, but there is no doubt that N-plasma is a promising method to modify carbon materials to meet specific requirement.

N-doped carbon materials, typically graphitic structures, have been applied as active electrode materials for ECSDs. Choi et al. [162] fabricated N-doped graphene via N-plasma processing, which provided a high specific capacitance of ~280 F g⁻¹ at 1 A g⁻¹, 4 times higher than that of pure graphene. The capacitance retention of N-doped graphene is 99.8% after 10000 cycles, indicating excellent cyclability. We also achieved hierarchical N-doped CC (hNCC) for enhanced LIB and supercapacitive behaviors [163].

After N₂ plasma processing, numerous nano-assemblies were formed on CC surface which were composed of N-doped graphitic structures (Figure 6a and 6b). The simultaneous N-introduction and surface nano-structurization were ascribed to doping and etching effect of N-plasma. In terms of its electrochemical performance, hNCC delivered 150 mA h g⁻¹ at 0.1 A g⁻¹, 3 times higher than that of pristine CC. Meanwhile, the capacitance of hNCC was 3 orders of magnitude as high as that of CC (Figure 6c). In addition to gaseous N-precursor, Guo et al. have applied plasma strategy to achieve nitrogen doped graphene oxide (N-PEGO) via treating GO/(NH₄)₂CO₃ mixed precursor for 10 min [164]. The N-PEGO displayed a more positive onset potential (0.89 V) than that of GO (0.65 V), which is quite close to that of commercial Pt/C (0.93 V).

In addition, N-plasma treatment of carbon materials could also benefit the further processing to form hybrid electrodes with metal-based materials [165]. Ramaprabhu et al. reported the fabrication of Pt loaded N-doped graphene nano-platelets for enhanced ORR performance [154]. As confirmed, the introduced defects and doping positions during N-plasma served as good anchoring sites for Pt deposition. Achieved polar groups also contributed to improved carbon-catalyst binding and increased conductivity, leading to an enhanced catalytic performance. Resultantly, Pt/N-G provided the maximum power density of 440 mW cm⁻², higher than that of Pt/G (390 mW cm⁻²). Additionally, Wang et al. have applied NH₃ plasma to realize doping and etching towards Co₉S₈-graphene [166]. They observed that NH₃ discharge not only doped graphene surface but also etched Co₉S₈ nanoparticles, generating sufficient active sites. The obtained composite provided an overpotential of 0.409 V at 10 mA cm⁻² in OER behavior, lower than that of untreated

sample (0.441 V). The N-treated composite delivered more positive onset potential (0.704 V) than that of unmodified sample (0.69 V) in ORR.

3.3.2 Nitridation

At the beginning, metal nitridation via plasma strategy has been applied mainly to improve their surface hardness, wear and corrosion resistance and fatigue life towards metal substrates such as titanium [167], copper [168], gold [169] and stainless steel [170]. Recently, metal nitrides have received considerable attention in the application of energy conversion and storage because of their quasi-metallic properties, high conductivity, and good chemical and physical stability [171]. The general choice to achieve metallic nitride is to anneal metal precursors in nitrogen-containing environment such as azides [172], hydrazine [173], and NH_3 [174]. Commonly, the nitridation requires high processing temperature (400~1000 °C) and long treatment duration (several hours) [175]. Incomplete nitrification reactions usually occur even after prolonged nitriding duration (6~10 h). Even worse, these nitrogen sources are environmentally hazardous [176]. Hence, N-plasma as an economic and environmentally-friendly method is proposed and applied to the fabrication of metal nitrides. Based on N_2 plasma, we successfully fabricated cobalt nitride nanowire arrays from corresponding Co_3O_4 nanowires at room temperature [177]. After 60 s treatment, Co_3O_4 nanowires were completely converted into CoN with well-preserved nanowire structures (Figure 6d). As OER catalyst, CoN nanowire arrays exhibited much lower overpotential of 290 mV (η_{10}) than that of Co_3O_4 (339 mV) and over 30 h electrolysis under different current densities (Figure 6g). Purified WN nanowires have also been successfully fabricated via N_2 plasma conversion towards WO_3 at room temperature [178]. The WN nano-framework delivered promising HER

performances of 134 mV (η_{10} , 10 mA cm⁻²) in acidic solution and 130 mV in alkaline solution with slight degradation over 40 hours.

Figure 6: The N-incorporation towards commercial carbon cloth (CC). (a) and (b) SEM and TEM images of hierarchical N-doped CC (hNCC). (c) The comparison of supercapacitive performance between hNCC and untreated CC [163]. The nitridation of metal oxides and metals via N-plasma. SEM images of (d) CoN-1 min, (e) NiMoN, and (f) hierarchical Ni₃N (hNi₃N) nano-coral. (g) Stability tests (voltage versus time) of the CoN-1min catalyst at current densities of 10, 30 and 60 mA cm⁻² overall 30 h [177]. (h) Polarization curves of NiMoN and reference samples [179]. (i) Cycling stability of hNi₃N and graphene quantum dot coated hNi₃N (GQD@hNi₃N) [180].

Apart from metal oxides, metals could also be converted into corresponding nitrides via N₂ plasma. We have successfully fabricated a series of highly-purified metal nitrides based on activating pure metal via N₂ plasma [179, 180]. For example, under N₂ plasma

treatment for 15 min, NiMo alloy as the starting material was completely converted into NiMoN with nano-coralline structure without oxide contamination (Figure 6e) [179]. Pure Ni could also be converted into corresponding nitride with even shorter duration (5 min). As a good HER catalyst, NiMoN provided a negative overpotential about 109 mV at 10 mA cm^{-2} and a large exchange current density of 0.92 mA cm^{-2} , which is comparable to commercial Pt/C catalyst of 43 mV and 0.72 mA cm^{-2} (Figure 6h). Coral-like nanostructure of Ni_3N can also be induced by N_2 plasma treatment of commercial Ni foam and shows functions in LIBs [180]. The initially smooth surface of the Ni foam turns into nano-coralline structure as seen in Figure 6f, exhibiting good capacity retention for Li ion storage up to 500 cycles (Figure 6i) [180]. A plausible growth mechanism of Ni_3N nano-coral was also proposed via controlling plasma duration. Within plasma environment, the rapid nitrification occurs on nickel surface. The lattice mismatch between Ni and Ni_3N layer causes the formation of vacancies. With elongated duration, vacancies accumulate to generate nano-pores. With the assistance of inward diffusion, continuously formed nano-pores interconnect to achieve nano-coralline structures. The thickness of porous Ni_3N is increased with prolonged processing, indicating the controllability of the obtained Ni_3N . Such growth mechanism is able to promote the generalization of N-plasma technique for developing nano-structured metal nitrides.

In short, N-plasma has received tremendous interest in N-doping of carbon and nitridization of metal-based materials for energy conversion and storage applications. It is noted that N-doping in metal-based composites via plasma techniques has also improved their performance in some other areas such as photovoltaic response, photoluminescence and electronics [42, 181, 182].

3.4 O₂ plasma

Similar with nitrogen plasma, oxygen plasma (O-plasma) has been largely used to process carbon and metal-based material [183, 184]. In terms of carbon materials, O-plasma is to introduce polar groups on their surface, due to its highly aggressive features. After the O-plasma treatment, the surface wettability of carbon materials can be largely improved [185]. Notably, excessive oxygen content on carbon surface can achieve volatile CO_x, resulting in the etching effect on carbon materials [186]. Hence, O-plasma can be used for the removal of carbon contaminants. Moreover, O-plasma usually serves as doping agent into metal-based compounds, typically metal sulfides [187]. With O-doping, defects and polar groups can be introduced into sulfides, leading to the modification of electronic structures. O-species in plasma condition also have strong capability in oxidizing metal-based materials [184]. In this section, we will apply typical examples to review the oxygen functionalization onto carbon and metal-based materials.

3.4.1 Oxygen doping in carbon materials

The introduced O-based groups on carbon materials via O-plasma act as active sites in the application of ECSDs. As reported by Liu et al., the OER behavior of O-doped CNT was improved with doping proportion of 8.2% based on O-plasma, in which the introduction of active sites served as the essential candidate for the performance enhancement [188]. However, the O-based groups slow down the charge transfer of carbon materials obviously, which is harmful to the electron conductivity. Hence, current researches usually apply O-doped carbon materials as skeleton for the growth of other materials [139, 189]. As reported by Wang et al., abundant hydrophilic groups were

introduced onto CNT surface via O₂ plasma treatment so that RuO₂ nanoparticles could be easily coated on CNT network by dip coating [190]. The resultant composite provided areal capacitance of 1.11 F cm⁻² at 1 mA cm⁻² with capacitance retention of ~106% after 8100 cycles.

3.4.2 Oxygen doping into metal-based materials

Figure 7: The applications of O-plasma. SEM images of (a) pristine MoS₂, (b) Ar-plasma treated MoS₂ (Ar-MoS₂), and (c) O₂-plasma treated MoS₂ (O-MoS₂) [191]. (d) SEM images of monolayer MoS₂ with 0, 10, 20 and 30 s O₂ plasma exposure. (e) Raman spectra before and after oxygen plasma treatment. (f) HER properties of MoS₂ before and after oxygen plasma treatment [192]. (g) SEM image of Nb₂O₅ nanowires. (h) Schematic

representation of the growth mechanism of Nb₂O₅ nanowires when exposed to O-plasma [193]. (i) SEM images of iron oxide nanowires grown on Fe bulk material [184].

O-doped metal-based materials have received considerable attention in ECSDs because of the introduction of active sites and defects [194]. Taking MoS₂ as an example, O-species substitute the S-position to achieve Mo-O bonding [191]. Atomic sulfur can react with O-species to achieve volatile SO_x, introducing S-vacancy on MoS₂ surface [195]. Meanwhile, ion bombardment from plasma etching also serve as an essential part for defect generation such as holes and cracks [192]. Specifically, Tao et al. reported the application of O₂ plasma to modify the surface properties of MoS₂ to improve its HER performance [191]. O₂ plasma delivered both doping and etching effect, while argon plasma was only favorable to etch MoS₂ surface to achieve sufficient defects. Smaller particles with sheet structures were formed after Ar- and O₂-plasma treatment as shown in Figure 7a-c. They conducted the XPS tests and found that there was almost no change after Ar-plasma treatment. After O-plasma processing, new oxygen-bonded peaks were observed, demonstrating O-incorporation into MoS₂. Interestingly, there was also a well-defined oxygen-based peak in Mo3d results after Ar-plasma activation, which was mainly attributed to strong absorption behavior of exposed defects towards air. This phenomenon is similar with the surface modification of materials after N₂ plasma processing. Hence, O₂- and Ar-plasma-treated MoS₂ both provided improved hydrophilic behavior, indicating polar functionalization on material surface. In terms of their performance, Ar plasma-treated MoS₂ for 720 s delivered improved HER performance of 16.3 mA cm⁻² at -350 mV, 11.7 times higher than that of pristine MoS₂. Further elongated treatment duration would reduce the HER activity. This was probably ascribed to the partial

removal of active sites (S-vacancies) via long-term etching effect. The similar results also occurred for MoS₂ thin film during O₂ plasma treatment. After treatment of 480 s, O-plasma activated sample provided a current density of 15.17 mA cm⁻² at -350 mV. With longer treatment duration, the catalytic activity also decreased due to over-doping of oxygen species as well as the removal of active sites (O-Mo-S and Mo-S-O).

Ajayan et al. have carefully studied the formation of defects on MoS₂ monolayer via O₂ plasma treatment and their HER performance [192]. Based on O-plasma, numerous cracks with certain angles and irregular shapes were formed in MoS₂ mono-layer, indicating that both Mo- and S-terminated edges substantially increased. Subsequently, large cracks and holes from intrinsic vacancies were achieved with longer exposure duration (Figure 7d). With elongated plasma processing, the ratio of A_{1g} to E_{1g} mode was increased with blue-shift of A_{1g} mode and red-shift of E_{1g} mode (Figure 7e), which confirmed that O-plasma caused strong lattice distortion via O-incorporation. Hence, the essential function of O-plasma was to provide cracks and edges by bombardment. With the introduction of numerous defects by O-plasma, the obtained MoS₂ exhibited enhanced HER performance (Figure 7f).

3.4.3 Oxidation of metal-based materials

As investigated for decades, O-plasma is favorable for the synthesis of metal oxides. Oxygen species (O, O⁺, O⁻) in plasma are mainly associated with the oxidation reaction via the recombination with metal along with heating up the surface [184]. Owing to the presence of electro-magnetic field, the oxidation process is usually accompanied with the fabrication of metal oxides with specific morphology. As reported by Sunkara et al.,

Nb₂O₅ nanowires have been achieved through directly exposing Nb foil to oxygen plasma for 90 s (Figure 7g) [193]. The Nb foil acted as the substrate and Nb source. The growth rate of nanowire was directly proportional to the density of O-species in plasma. A three-step interaction was involved during the fabrication (Figure 7h). First, O-species was dissolved and diffused into Nb surface. Afterwards, spontaneous nucleation of Nb₂O₅ nanocrystal took place on the surface of Nb foil, due to the super-saturation of the surface with oxygen. Finally, the Nb₂O₅ nanowires grew from the metallic surface because of the constant supply of O-species.

Nanostructured α -Fe₂O₃ was also successfully fabricated by Cvelbar on iron foil via O-plasma [196]. The diameters, densities and morphologies of α -Fe₂O₃ could be tuned via the plasma power. At lower temperature (450-780 °C), nuclei growth mainly took place at the base, leading to the nanostructural growth, while at higher temperature (>780 °C), the growth of nuclei occurred in any direction owing to enhanced mobility of iron atoms, causing the formation of oxide film. Nanowires with the optimum density formed at the surface temperature of 570 °C (Figure 7i). At higher temperature (~600 °C), nano-belts were formed as a result of the increased mobility of Fe atoms and further growth of nanowires in horizontal direction to become belts. When the temperature is over 780 °C, no nanostructure growth occurred and only oxide thin film was generated due to the temperature beyond Fe-O phase transition temperature, limiting the nano-structural formation. Based on the growth mechanism of α -Fe₂O₃ nanostructures, Varghese et al. fabricated the NiO nano-wall via O-plasma processing [197]. As the LIB anode, NiO nano-wall displayed capacity of 650 and 500 mA h g⁻¹ at 895 and 1343 mA g⁻¹. Other nanostructured metal oxides, such as CdO, were also prepared via the similar approach

[198]. Overall all, the above studies displayed the conceptual understanding of nano-structurization based on O-plasma oxidation, leading to a promising alternative for the fabrication of metal oxides.

3.5 Argon plasma

In argon plasma (Ar-plasma) environment, Ar-species (Ar^+ , Ar^* , e^-) are present, which delivers strong capability in etching effect. Different from O_2 and N_2 plasmas, Ar radicals are unable to directly introduce heteroatoms into target materials [199]. Ar-plasma can only be applied for plasma etching owing to its chemical-inertness. Therefore, the main application of Ar-plasma is to modify the surface of target materials via introducing defects and vacancies by means of its strong etching effect. However, similar with N_2 plasma, many dangling bonds will be formed after the treatment of Ar-plasma [200]. Hence, when treated materials are exposed to the air atmosphere, oxygen can react with these dangling bonds, forming oxygen functional groups. For carbon materials, this phenomenon will improve their hydrophilic behavior [201].

3.5.1 Ar-plasma in carbon materials

As reported, carbon-based materials are a class of important electrode materials for ECSDs, especially in electrolysis of water [153, 202, 203]. However, due to the limited number of exposed active sites for pure carbon materials, they exhibit an inferior electrochemical performance, which is far from meeting the requirement as electrode materials [204]. As we mentioned in N-plasma section, the introduction of heteroatoms as active sites is a feasible strategy to improve their performance. Additionally, topological defects can also act as active sites [205]. Tian et al. have employed Ar-plasma etching

strategy to achieve more topological defects on sulfur-doped graphene (Figure 8a) [206]. As shown in Raman spectra, Ar-plasma-treated S-doped graphene (SG-P) delivered enhanced I_D/I_G ratio as compared to that of pristine S-doped graphene (SG), demonstrating the introduction of abundant defects (Figure 8b). It has been discussed that more topological defects meant more active sites, allowing for the enhanced HER performance. As expected, such framework provided significantly enhanced HER activity with an overpotential of 178 mV at 10 mA cm^{-2} , which was ascribed to the synergetic coupling between S-doping and plasma-induced defects (Figure 8c). In comparison, S-doped graphene required a higher overpotential of 423 mV at the same current density. In addition, no obvious decay was observed after 3000 cycles, indicating great catalytic stability of SG-P. Furthermore, the HER performance of graphene samples with different level of doping were compared. It was observed that overpotential was gradually decreased with enhanced sulfur doping level. On the other hand, different topological defect levels could be obtained by varying plasma-etching duration. Modest plasma treatment could decrease the overpotential, but overlong plasma etching would cause serious damage of sp^2 graphitic structure and loss of S-dopants in graphene framework, largely decreasing the overall performance of the resultant graphene. A series of carbon materials, such as N-doped graphene [207] and N, S co-doped 3D graphene [208], were treated by Ar-plasma and exhibited improved HER performances, confirming that Ar-plasma with chemically-inert behavior can introduce controllable defects without the incorporation of polar groups, and enhance their catalytic performance.

Wang et al. have provided a facile plasma-etching approach to achieve graphene onto carbon cloth [201]. After Ar-plasma treatment, highly porous graphene nanosheets with

sufficient edges were formed on CC surface (Figure 8d). Notably, with increasing etching duration, the CC surface became rougher with more generated nanosheets. After 3 min treatment, the thickness of porous graphene nanosheets tended to be a constant due to the limited etching effect of Ar-species. When exposed into air, edge-dangling bonds induced by plasma interacted with oxygen, resulting in the formation of $\text{O}=\text{C}-\text{OH}$. Based on XPS results, bonded oxygen increased from 2.89% to 13.09%, indicating more defects and polar groups on CC surface (Figure 8e). Additionally, theoretical calculation indicated that introduced polar groups attracted electrons from atomic carbon, leading to carbon atoms with positive charges and hence enhancing adsorption of intermediate species in OER and ORR. This could improve the electrochemical property of as-obtained samples. As expected, plasma-etched CC (P-CC) reached 10 mA cm^{-2} at 1.68 V in OER behavior, lower than that of CC at 1.85 V. For ORR performance, the onset potential of P-CC was 0.76 V with a peak potential of 0.56 V, while the onset and peak potentials of CC were 0.69 and 0.47 V, demonstrating better electrocatalytic behaviors of P-CC.

Figure 8: Ar-plasma and its application in modification of electrode materials. (a) Schematic diagram of the preparation process of Ar-plasma treated S-doped graphene (SG-P) in the plasma system. (b) Raman spectra of S-doped graphene before and after Ar-plasma treatment. (c) Polarization curves for hydrogen evolution reaction [206]. (d) Schematic diagram of the preparation of plasma-etched carbon cloth (P-CC). (e) High resolution spectra of O 1s XPS peak of carbon cloth (CC) and P-CC. (f) Polarization curves for oxygen evolution reaction [201]. (g) and (h) SEM images of pristine Co_3O_4 and plasma-engraved Co_3O_4 . (i) Polarization curves as OER catalysts [209].

Qiu et al. achieved Ar-plasma treated GO for enhanced supercapacitive behavior [210]. With plasma processing for 2 min, the C/O ratio of GO rapidly increased from 1 to 4, which indicated the ion bombardment of Ar-species. The Ar-treated GO provided 210 and 185 F g^{-1} at 50 and 1000 mA g^{-1} , while intrinsic GO delivered negligible capacitance

because of the insulator property. In terms of that, Ar-plasma can serve as an alternative to remove O-species for these carbon-based active materials in ECSDs.

3.5.2 Ar-plasma in metal-based materials

The etching effect of Ar-plasma also works on metal-based materials [211]. During plasma processing, positive Ar species are inclined to provide energy to negative ions on the surface of metal-based materials, leading to the introduction of anion vacancies [212]. As demonstrated, the presence of oxygen vacancies (V_o) can significantly optimize their catalytic activity [209]. Herein, Ar-plasma currently serves as a promising candidate to achieve V_o with high stability. Wang et al. have successfully achieved V_o - Co_3O_4 nanosheets through Ar-plasma etching [209]. Highly porous nanostructures with amounts of nano-holes confirmed the strong etching effect of Ar-plasma (Figure 8g and 8h). By means of XPS spectra, the atomic ratio of Co^{2+}/Co^{3+} on treated Co_3O_4 surface was 1.2, higher than that on pristine Co_3O_4 of 1.0, indicating the production of oxygen vacancies. As the OER catalyst, the treated Co_3O_4 exhibited overpotential of 1.53 V at 10 mA cm^{-2} , lower than 1.77 V of Co_3O_4 (Figure 8i). No performance decay was found after 2000 cycles. The above results confirm that higher electro-catalytic behavior is obtained after the introduction of oxygen vacancy. Furthermore, theoretical study also indicated that the adsorption free energy of hydrogen of V_o - Co_3O_4 was -0.28 eV, lower than that of pristine Co_3O_4 (-0.23 eV), demonstrating the higher reactivity after Ar-plasma treatment.

3.6 Sulfur plasma

H_2S , a typical gaseous precursor for generating sulfur plasma (S-plasma), received considerable attention for the S-doping and sulfurization [213]. Within plasma

environment, excited radical (S^*) and ions (S^+ , S^-), dissociated by high-energy electrons, deliver high reactivity even in room temperature [214]. Reactive H-species are also present in H_2S plasma, which makes it exhibit reducibility. Compared to other S-containing precursors, such as sulfur, H_2S plasma displays superior behaviors of great controllability and little contamination. However, there is no doubt that H_2S is environmental-hazardous, so that there are only a few reports about H_2S -plasma for material processing. More environmentally-friendly S-source should be developed for plasma. To date, S-plasma is mainly applied as doping and sulfurizing agents.

3.6.1 S-plasma in carbon materials

S-doping can also tune the electronic structure in carbon materials, specifically graphene. Pumera et al. studied the fabrication of S-doped graphene via H_2S plasma [215]. Three types of graphene oxides were applied as starting materials, including Hummers (HU)-, Staudenmaier (ST)-, and Hofmann (HO)-graphite oxides. After plasma processing, these obtained graphene were termed as HU-MWS, ST-MWS and HO-MWS. According to SEM and Raman results, all of them have been doped with S. Among them, ST-MWS exhibits less S-doping content than that of HU-MWS and HO-MWS. Hence, ST-MWS displayed inferior OER performance than other two materials, indicating the promotion of electrocatalysis by S-doping. Furthermore, Hu et al. compared the difference between H_2S plasma and thermal treatment based on C_3N_4 as the precursor [216]. As shown in SEM images (Figure 9a-c), plasma-treated C_3N_4 at room temperature (PSN-40) exhibited a well-preserved morphology, while thermal-treated C_3N_4 after 2 h treatment at 650 °C (SN-650) had a serious aggregation. Moreover, PSN-30 showed comparable S-content to SN-650 (Figure 9d). Thus, compared with annealing method in H_2S ambient, H_2S plasma

could introduce S-content into C_3N_4 lattice efficiently and preserve their morphology well. These results confirmed that S-plasma served as a promising alternative for S-doping.

3.6.2 S-plasma in metal-based materials

Currently, transition metal sulfides also serve as important electrode materials in ECSDs. Accordingly, sulfurization has been largely applied based on metal oxides as precursors, which is easily to acquire with various nanostructure. Kumar et al. compared the sulfurization effect of MoO_3 among three different methods: sulfur vapor, H_2S -Ar gas, and H_2S -Ar plasma [214]. TEM images (Figure 9e-g) displayed that the thickness of as-obtained MoS_2 after H_2S -Ar plasma is much higher than that of other two approaches. Thermal treatment in S-ambient showed the lowest conversion efficiency due to it poor activity of S-species (3-4 MoS_2 monolayers) (Figure 9e). Normally at low temperature (~ 550 °C), sulfur powder sublimed in the form of S_2 and S_8 , offering an inferior reactive sulfurization environment. In comparison, the sulfurized layer was increased to 13-16 MoS_2 monolayers in H_2S -Ar atmosphere at 550 °C, indicating higher activity of H_2S (Figure 9f). In H_2S -Ar plasma environment, much more reactive species was present, delivering more reactive sulfurization ambience. As a result, the number of MoS_2 shell increased to 25-28 monolayers (Figure 9g). A conversion mechanism was also proposed. MoO_3 was firstly reduced to MoO_2 , followed by the subsequent conversion to MoS_2 from MoO_2 . In terms of H_2S annealing and H_2S plasma, reactive H-species served as reducing agent and S-content acted on sulfurizing candidate.

Furthermore, they also investigated the sulfurization effect of H_2S plasma as the function of temperature to confirm the above mentioned mechanism [217]. Notably, when temperature is lower than $350\text{ }^\circ\text{C}$, only H-species were active to reduce the MoO_3 into monoclinic MoO_2 . At higher temperature ($450\text{--}550\text{ }^\circ\text{C}$), S-species obtained sufficient energy to replace oxygen and convert more molybdenum oxide into MoS_2 . Such conversion model could serve as a guideline for other materials treated by S-plasma. Wolden et al. investigated the sulfurization effect of H_2S plasma onto WO_3 [213] and Fe_2O_3 [218], which showed the similar conversion mechanism. To obtain completely sulfurized FeS_2 , the required S-feedstock pressure was 4 orders of magnitude lower than that of typical thermal S vapor annealing, indicating the advantages of S-plasma.

Figure 9: The sulfurization of S-plasma. SEM images of (a) $\text{g-C}_3\text{N}_4$, (b) S-doped $\text{g-C}_3\text{N}_4$ via traditional annealing at $650\text{ }^\circ\text{C}$ (SN-650), (c) S-doped $\text{g-C}_3\text{N}_4$ via S-plasma at room temperature (PSN-40). (d) XPS S2p spectra of $\text{g-C}_3\text{N}_4$, SN-650 and PSN-40 [216]. TEM images of MoO_3 film treated in (e) sulfur vapors, (f) H_2S -Ar mixed gas and (g) H_2S -Ar plasma [217].

3.7 Phosphorus plasma

Similar with S-plasma, PH_3 has been mainly used for phosphorus plasma (P-plasma). Compared with other types of plasmas, P-plasma just emerged in recent years. Currently, P-plasma is usually applied for P-doping and phosphatization. Notably, the typical P source, PH_3 is dangerous and environmental-hazardous. To promote the application of P-plasma, it is urgent to develop economic and safety P sources.

3.7.1 P-plasma in carbon materials

In terms of P-doping, Arun et al. reported the fabrication of P-doped diamond-like carbon (DLC) via PECVD technique [219]. With increased P-incorporation, the band gap of as-obtained P-DLC decreased from 2.61 to 2.31 eV. Raman spectra indicated the blue shift of D-band with P-doping, which was ascribed to the conversion from sp^3 to sp^2 carbon. Regarding this, the P-doped DLC provided enhanced electrical conductivity as compared to un-doped one. Hence, P-doped graphitic structure may serve as a promising substrate for ECSDs.

3.7.2 Phosphatization

Recently, metal phosphides emerge as the essential electrode materials in ECSDs [220-222]. Phosphatization via P-plasma received tremendous research interest. As simulated by Alshareef et al., metal phosphides could serve as promising non-noble electrocatalysts for water splitting [223]. As calculated, NiCoP could deliver ΔG_{H^*} of -0.15 eV, higher than that of Ni_2P (-0.86 eV). Such value is close to that on Pt surface, suggesting its highly active electrocatalyst. Afterwards, NiCoP nanostructure was fabricated based on

PH₃ plasma with NiCo-OH as the starting materials (Figure 10a). As exhibited in Figure 10b, NiCoP nanosheets were well preserved. TEM images confirmed the complete phosphatization (Figure 10c). For HER performance, NiCoP provided a more positive overpotential of 32 mV at -10 mA cm⁻², compared with that of Ni₂P (93 mV), NiCo-OH (201 mV) and Ni foam (242 mV) (Figure 10d). In terms of OER behavior, NiCoP exhibited an overpotential of 280 mV at 10 mA cm⁻², more negative than that of Ni₂P (340 mV) and NiCo-OH (404 mV) (Figure 10e). The water electrolysis by using NiCoP as the bifunctional catalyst was further studied (Figure 10f). It took 1.58 V for this electrolyzer to reach the current density of 10 mA cm⁻². Alshareef et al. also investigated the energy storage performance of NiCoP nanoflakes as the anode for supercapacitor [224]. NiCoP electrode delivered a specific capacity of 194 mA h g⁻¹ at 1 A g⁻¹, higher than that of Ni₂P (166 mA h g⁻¹). In terms of rate performance, NiCoP provided 87% capacity retention from 1 to 10 A g⁻¹, compared with 50% retention of Ni₂P. The asymmetric supercapacitor was further assembled via NiCoP and graphene as positive and negative electrodes. The asymmetric devices could deliver excellent capacities of 43.8 and 28 mA h g⁻¹ at 2 and 10 A g⁻¹ with capacity retention of 64%. Overall, P-plasma strategy is expected to become an efficient route for the fabrication of metal phosphides at low temperature.

Figure 9: P-plasma for conversion reaction of nanostructured metal-based materials and their electrolysis of water. (a) Schematic illustration of the synthetic route for NiCoP nanostructure. (b) and (c) SEM and TEM images of NiCo-OH and NiCoP. (d) and (e) HER and OER in 1 M KOH. (f) Long-term stability of overall water splitting based on NiCoP electrocatalyst [223].

4 Conclusion & Outlook

In this review, we illustrate the recent progress of the fabrication and modification of materials via plasma-based strategies in ECSDs. Compared with conventional approaches, plasma techniques provide superior behaviors, including (i) relatively high reactivity, (ii) rapid reaction and weak heating effect, (iii) induced electrical field on material surfaces for the formation of unique structures, and (iv) various precursors and dry process to prevent the contaminant introduction. The recent progresses of plasma in the fabrication and modification of electrode materials have been summarized based on different feedstocks, including C, H, N, O, Ar, S and P. Among them, C-plasma serves as an important strategy in synthesizing graphitic structures with unique morphologies and

features, such as CNTs and VGSs. Such technique has also been applied for the carbidization and reduction of metal oxides. H-, N-, O-, S- and P-plasma have strong capabilities in reacting with material surface for doping and conversion. Ar-plasma, due to its chemical inertness, has been usually used in surface etching. As regards, plasma gradually serves as an indispensable candidate in numerous fields, especially ECSD field.

However, despite the above-mentioned advantages of plasma including high efficiency and environment-friendliness, some of main challenges are still urgent to be solved to enrich the plasma technology in short future. As discussed, although several types of plasmas (H-plasma, S-plasma and P-plasma etc) provide promising potentials in material synthesis and processing for ECSDs, only a few researchers have focused on them. This is mainly ascribed to (i) the intrinsically high toxicity of precursors in plasmas, especially H_2S and H_3P , and (ii) ambiguous mechanism of plasma treatment. For the former issue, alternative precursors with less environment-hazardousness are urgent to be explored. In terms of later one, in-situ plasma diagnostics has recently been introduced and would provide us deeper understanding of plasma. Moreover, different parameters have existed in plasma techniques, which causes the inferior controllability of the resultant materials. Specifically, etching effect usually occurs together with plasma surface modification of nano-materials. Hence, the controllability of plasma should be improved to accurately achieve the predesigned materials with desired structures and compositions. Furthermore, there are few theoretic researches on the plasma treatment of materials. Therefore, multidisciplinary efforts should be introduced. Last but not least, specific apparatus with additional energy resource is usually required to generate plasma, leading to a cost-consuming process. Such issue largely restricts the industrialization and popularity of

plasma technology. Accordingly, deeper investigation is demanded to simplify the manufacturing process to develop cost-effective and suitable plasma-based facilities.

Even with these aforementioned challenges, plasma has demonstrated its promise as a rapid, efficient and environment-friendly strategy for material fabrication and modification in energy conversion and storage devices. Yet, compared to more mature approaches including conventional physical and chemical approaches, plasma technology is still at a nascent state and lots of opportunities for further progress exists. We believe that the development of plasma strategy will attract more attention and be considerably enriched in ECSD field in short future.

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