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Self-Formation of Polymer Nanostructures in Plasma Etching: Mechanisms and Applications

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In recent years, plasma-induced self-formation of polymer nanostructures has emerged as a simple, scalable and rapid nanomanufacturing technique to pattern sub-100 nm nanostructures. High-aspect-ratio nanostructures (>20:1) are fabricated on a variety of polymer surfaces such as poly(methylmethacrylate) (PMMA), polystyrene (PS), polydimethylsiloxane (PDMS), and fluorinated ethylene propylene (FEP). Sub-100 nm nanostructures (i.e., diameter \leq 50 nm) are fabricated in this one-step process without relying on slow and expensive nanolithography techniques. This review starts with discussion of the self-formation mechanisms including surface modulation, random masks, and materials impurities. Emphasis is put on the applications of polymer nanostructures in the fields of hierarchical nanostructures, liquid repellence, adhesion, lab-on-a-chip, surface enhanced Raman scattering (SERS), organic light emitting diode (OLED), and energy harvesting. The unique advantages of this nanomanufacturing technique are illustrated, followed by prospects.

1. Introduction

Polymer nanostructures have been widely used in the fields of mass data storage [1, 2], energy storage [3, 4], photovoltaic [5, 6], biomedical sensing [7, 8], and drug delivery [9, 10]. Conventional bottom-up fabrication techniques for polymer nanostructures include electrodeposition [11, 12], electro-spinning [13, 14], and DNA-assisted assembly [15, 16]; however, the uniformity, orientation and alignment of polymer nanostructures are difficult to control by the bottom-up approaches. Top-down approaches such as electron-beam lithography [17, 18], nanoimprint lithography [19, 20], laser interference lithography [21, 22], stencil lithography [23, 24], dip pen lithography [25, 26], and nanosphere lithography [27, 28] provide high uniformity and controllable feature sizes, but all have their own limitations. Electron-beam lithography is a serial type process which is slow and expensive thus not ideal for large-scale fabrication. Nanoimprint lithography requires the fabrication of nanoimprinting molds and careful characterization of heat/pressure parameters. Laser interference lithography is a parallel and scalable process but is normally used to produce periodic nanostructures. Stencil lithography

requires the fabrication of stencil masks by using other types of nanolithography techniques. Dip pen lithography has a slow scanning speed and requires expensive instruments such as atomic force microscopy. Nanosphere lithography requires the fabrication and assembly of nanoparticles, whose uniformity is difficult to control. In addition, fabricating high-aspect-ratio polymer nanostructures by the top-down approaches is very challenging because of collapsing issues [29].

In recent years, a simple and one-step etching process has been introduced to pattern polymer nanostructures in a large area with a feature size less than 50 nm [30, 31]. Oxygen or fluorine plasma is generated in reactive ion etching (RIE) or inductively coupled plasma (ICP) and used to etch polymer surfaces [32]. First, the sample with polymer coated is loaded in the etching chamber and the chamber is pumped to low vacuum. Then, gas molecules are filled in the chamber and plasma is initiated by applying a strong radio frequency (RF) electromagnetic field to strip the electrons. The positively-charged ions drift toward the bottom substrate where they collide with the polymer surface. The polymer surface is then removed by physical knock-offs and chemical-etching with vertically accelerated ions, as illustrated in Fig. 1a. With this one-step process, nanostructures can be created on various polymer surfaces. Figure 1b shows the scanning electron microscopy (SEM) images of high-aspect-ratio polymer-nanostructures of various polymer materials including PMMA, PS, PDMS, PEDOT/PSS, PEN, PET, Durafilm, and Kapton [33]. The nanostructures are uniform and cover a large surface area. In addition, the polymer nanostructures have a sub-50 nm feature size regardless of the polymer types. Such small dimension is difficult to achieve even with most conventional nanolithography techniques.

In this review paper, we present the formation mechanisms of the polymer nanostructures including surface modulation, crystalline, and impurities. Then, we illustrate the advantages of such polymer nanostructures in the applications of hierarchical nanostructures fabrication, wetting, adhesion, microfluidics, biomedical sensing, surface-enhanced Raman scattering (SERS), organic light-emitting diodes (OLED), and energy harvesting. These applications illustrate the versatility of high-aspect-ratio polymer nanostructures in order to improve the performance of micro-and nano-systems and move the micro-and nano-devices toward the market. Whereas a recent review paper by Phan et al. [34] also presented several applications of polymer nanostructures including wettability, bio and energy areas, the discussion of the formation mechanisms more extensively, including surface modulation and crystalline, and introduce broader application potentials.

2. Formation Mechanisms

2.1. Surface Roughness

Polymer nanostructures can form during plasma etching with the presence of surface protrusion or surface concave [35]. During the interaction of charged ions with polymer surfaces, physical sputter-off and local ionization were observed. The interaction between incoming ions and the polymer is confined within a "cone-shaped" space. The volume of the "cone-shaped" structure is related to the incident angle of the ions. Deepest penetration of the ions occurs when the ions are normal to the polymer surface. Suppose a protrusion is present on the polymer

 surface (Fig. 2a-1), three possible incident ion locations are shown: ion I is a normal incident on a flat area, ion II is on the sidewall of the protrusion, and ion III is at the top of the protrusion. Both ions I and III are normal to the surfaces so that the paths of the penetration for ions I and III are longer than that of ion II. After sputtering off the "cone-shaped" space, a polymer nanostructure, typically polymer nanowire (PNW) is formed. Further etching of the polymer surface results in the formation of a polymer nanostructure with a dip on top. In an alternative case that the polymer surface has a concave (Fig. 2a-2), ions IV and VI are normal to the surfaces, whereas ion V is off the normal. The penetration paths for ions IV and VI are longer than that of ion V, resulting in a nucleation of a ring pattern on the surface. Further etching of the polymer surface results in along polymer nanostructure, i.e., polymer nanotubes (PNT). Experimental observations of formed nanostructures are shown in Fig. 2b. Morber et al. found that polymer nanostructures would tend to form at the areas where tens of nanometer wide wrinkles were present (Fig. 2b-2). A dip on top of the polymer nanostructures was observed (Fig. 2b-3). As shown in Fig. 2b-4, tracks of ions were observed on the sidewalls of the polymer nanostructures.

2.2. Crystalline Structures

Semicrystalline morphology can affect the geometry and dimensions of the polymer nanostructures due to thermal and mechanical history [36]. Fernández-Blázquez et al. studied the polymer nanostructures morphology with different mechanical treatments [37]. PET films with different mechanical pretreatment etched by oxygen plasma are shown in Fig. 3a. Differential scanning calorimetry (DSC) was used to analyze the melting enthalpy, crystallinity, and melting temperature (Fig. 3b). The crystallinity and melting temperature can be changed with mechanical loading history and result in different morphology after plasma etching. A significant weight loss was detected after etching for amorphous and semicrystalline PET films. A greater weight loss rate was observed on amorphous samples, indicating a higher etching rate of polymer chains (Fig. 3c-1). After 24-hour exposure to the ambient environment after plasma etching, a significant weight increase of the sample was detected, indicating that the polymer surface remains reactive after plasma treatment (Fig. 3c-2) [38]. The nanostructures formation mechanism has been explained by the models developed by Peterlin [39] and Elias [40]. Stretching polymer films result in the formation of second "shish"-like structures (Fig. 3d). A network of linked "shish"-like structures could result in "kebab"-like structures. "Shish"-like structures have a higher crystallinity and are more resistant to etching. Small and imperfectly folded lamellar structures are filled between "shish"-like structures and etched away during plasma treatment[37]. High-aspect-ratio nanostructures are formed with a long etching time.

2.3. Impurities

During plasma etching, impurities such as dust can deposit on the sample surface and act as micromasks [41]. Spikes could form after prolonged directional etching. This phenomenon has been observed in silicon etching, which is known as "black silicon". Black silicon covered with a thin passivating silicon oxyfluoride skin becomes higher with an increase in etching time [42, 43]. Because of the high-aspect-ratio and sharp-tip morphology, black silicon has been widely used in photovoltaics [44], liquid repellence [45], and anti-bacteria applications [46]. A similar mechanism has been introduced to explain the formation of plasma-induced polymer nanostructures.

2.3.1. Impurities from Etching Chamber

Impurities such as metal or silicon have a high etching selectivity over polymer materials when exposed to oxygen or fluorine plasma [47]. The presence of such impurities could lead to the formation of polymer nanostructures during long-time plasma etching. Metal impurities originated from plasma etching of chamber walls [31] and steel electrodes [48] can be accumulated on the sample surface. Zhang et al. used bright field transmission electron microscopy images, scanning transmission electron microscopy images, and energy dispersive X-ray spectroscopy mapping to study the metal impurities on the formation of PET nanostructures. Elements including Cu, Fe, Cr, Mn, Zn, and O were detected on the polymer nanostructures. These metal elements are the major composition of the electrode material in the etching chamber (Fig. 4a) [48]. This indicates that metal or metal oxide could deposit on polymer nanostructures during the plasma etching process [49].

2.3.2. External Impurities

Impurities can also be introduced from external sources. Chen et al. used a dummy material (cover glass) to introduce self-formed nanomasks on polymer surface during plasma etching [50]. The fabrication process is shown in Fig. 4b. A glass slide covers a part of a Parylene C film and nanomasks originated from the cover glass were sputtered and deposited onto the polymer surface. Polymer nanostructures were formed after a designated etching time period. X-ray photoelectron microscopy (XPS) was employed to examine the etched Parylene C film and showed the presence of sodium (Na) and potassium (K). In addition, Auger electron microscopy (AES) showed that elements of Na and K appeared only on top of the nanostructures. In recent work by Jiang et al., a silicon substrate was added into the etching chamber to create nanostructures of conjugated polymer dodecylbenzenesulfonate doped polypyrrole (PPy(DBS)) [51]. The XPS data showed that silicon was deposited on the polymer surfaces during the formation of nanostructures. In addition, the atomic compositions of silicon increased with the increase in etching power, indicating more silicon particles were sputtered off from the silicon substrate. These findings support the mechanism that impurities can serve as random etching masks for the formation of polymer nanostructures.

2.3.3. Impurities from Polymeric Chemicals

Photoresist, such as SU-8, containing some amount of antimony (Sb) could be the source of metal impurities itself. De Volder et al. found out that Sb could accumulate at the substrate surface due to plasma etching and reached up to 19% of the surface composition after plasma etching [52]. In the work by Du et al., Sb was also detected after oxygen plasma etching for negative-tone photoresist materials such as NR-7 and SU-8 (Fig. 4c); however, no Sb was detected for PMMA samples. Since Sb is one of the components for negative-tone photoresist, the results indicate that metal impurities originated from photoresist or other polymeric chemicals can also appear as etching masks to influence polymer surfaces and form polymer nanostructures [31].

2.4. **Dimensions of Formed Nanostructures**

Table 1 summarizes the lateral dimensions, i.e., period and diameter of the polymer nanostructures reported in the literature. Even though etching gas and etching power vary and the

true formation mechanism is still unclear, oxygen is used for all the protocols regardless of the formation mechanisms. Taking PMMA as an example, the reported period ranges from 300 to 80 nm and the diameter ranges from 150 to 35 nm with the different protocols and formation mechanisms. It strongly suggests that more experiments and modeling efforts are needed to further understand the large variation in the lateral dimensions depending on the formation mechanisms [53, 54].

3. Applications

3.1. Hierarchical Nanostructures

Three-dimensional (3D) hierarchical nanostructures for the applications such as biochemical sensing [55], drug delivery [56], water treatment [57], fuel cells [58], and solar energy conversion [59] have drawn great interests. The surface properties of micro- and nano-devices can be tuned with 3D hierarchical nanostructures to enhance the performance [60]. Several fabrication techniques were explored to fabricate high-aspect-ratio hierarchical nanostructures. Uniform hierarchical nanostructures can be patterned by using advanced nanolithography techniques such as dual-scale electron beam lithography [61], nanoimprint lithography [62], and stencil lithography [63]. However, all these nanolithography techniques require the creation of nanoscale templates which increase the cost and fabrication complexity.

Alternatively, uniform hierarchical nanostructures can be created by using a one-step plasma etching process. Fang et al. utilized the laser interference lithography in conjunction with ICP etching to demonstrate large-area and well-ordered polymer nanostructures [64]. A 266-nm wavelength laser was split to two coherent beams interfering with each other on the polymer surface (Fig. 5a). After that, ICP etching was used to pattern well-ordered hierarchical nanostructures. Both UV-absorbent polymers (PET and Dura film) and UV-absorbing polymers (PVA and PP) could be patterned with this technique. The results of Dura hierarchical nanostructures with different exposure dosage (40-110 mJ/cm²) are presented in Fig. 5b.

In the work by Wathuthanthri et al., a Lloyd-mirror configuration was used with the combination of ICP etching to create large-scale hierarchical nanostructures. The interference was achieved by the reflection of one beam by a flat mirror. The patterning period can be easily tuned by adjusting the angle between two interference beams [21]. The aspect-ratio of the nanopatterns can be controlled by adjusting the film thickness. Additionally, the sidewall profile of the nanostructures can be adjusted by the underlying anti-reflective coating (ARC) (Fig. 5c) [65-68]. The laser interference lithography patterning is followed by a one-step oxygen plasma etching process. Both "pillar-on-pore" and "pillar-on-pillar" hierarchical nanostructures were created by controlling the interference lithography exposure condition and the plasma etching time (Fig. 5d). The plasma etching with longer duration formed the nanostructures with higher aspect ratio. In addition, the isotropic oxygen plasma etching resulted in the increase of pore size of photoresist patterns and transformed the "pore-on-pore" hierarchical nanostructures to "pillar-on-pillar" hierarchical nanostructures (Fig. 5d-b-v) [31, 69, 70].

3.2. Wetting

Superhydrophobic surfaces have drawn much attention due to their broad promising applications, such as biotechnology [71], microfluidics [72], thermal system [73], drag reduction

(1)

[74], self-cleaning [75], anti-icing [76], anti-fouling [77], and "smart" coating [78]. The hydrophobicity of a surface can be characterized by the classical Cassie-Baxter equation [79], which is given as,

$$\cos \theta_I = \phi \cos \theta_i - (1 - \phi)$$

 where θ_I , θ_i , and ϕ represent the apparent contact angle on a structured surface, that on a flat surface, and the solid fraction (solid-liquid contact area normalized by the 2-D projected area), respectively. According to this equation, there are two typical routes to enhance the surface hydrophobicity (i.e., increase the apparent contact angle). One is to decrease the solid fraction by physically engineering the surface structures and the other is to increase the surface intrinsic water repellency (increase the apparent contact angle on the flat surface) by chemically modifying the surface.

Plasma etching process can fabricate high-aspect-ratio and discrete pillar-like nanostructures on polymer surfaces, which is a promising candidate to decrease the solid fraction and enhance the surface hydrophobicity. Several works have been conducted to demonstrate the applications of oxygen-plasma etched surfaces regarding their hydrophobicity of various polymers (PMMA, PEEK, PDMS, and cyclo-olefin polymer). Ebert et al. fabricated nanostructures on PDMS by the O₂/CF₄ plasma etching process [80]. At the region of small surface RMS roughness (short etching time), both the apparent contact angle and contact angle hysteresis increase with the RMS roughness. It indicates that the surface is completely wetted (Wenzel-state droplet [81]) because the short structures cannot sustain the suspended liquid-gas interface due to the short etching time. In contrast, at the region of larger surface RMS roughness (longer etching time), the contact angle is greater and the contact angle hysteresis is smaller than that on short-timeetched surfaces, respectively. It indicates that droplets on such surfaces are in Cassie-Baxter state [82].

In practical applications, such as biotechnology, drag reduction, self-cleaning, anti-icing, and anti-fouling surfaces, the surface hydrophobicity is required to endure harsh operating conditions (high pressure, mechanical wears, aging, underwater environment) for various liquids, including the liquids with low surface tensions (superamphiphobic) [83]. Therefore, hierarchical nanostructures with re-entrant tip profiles are desired for the broader applicability, which is also attainable by the oxygen plasma etching process. Ellinas et al. showed that high-aspect-ratio polymer (PMMA) nanostructures with re-entrant tip profiles could be fabricated by adopting microparticle colloidal lithography in conjunction with two-step O_2 plasma etching processes [84]. First, PS colloidal particles were uniformly deposited (spin-coated) on a PMMA flat surface. Then, the surface was treated by oxygen plasma with a bias voltage (anisotropic etching) to induce high-aspect-ratio nanostructures. Subsequently, the surface was treated by oxygen plasma without a bias voltage (isotropic etching) to make the re-entrant profile. By adjusting the size of deposited particles and the etching recipes, the optimized re-entrant structures were prepared, as shown in Fig. 6b. The hydrophobic robustness of the surfaces with re-entrant structure profiles has been corroborated as shown by the increment of apparent contact angles of droplets with various surface tensions (decane, hexadecane, soya oil, diiodomethane, and water) compared with those on surfaces without re-entrant structure profiles (Fig. 6a). In addition, by incorporating such structured polymer surfaces with a layer of low surface energy chemical (PFOTS), these surfaces demonstrated a robust superamphiphobic property (droplet impacting pressure as high as 36 atm for a liquid with surface tension of 66 mN/m) compared to the

 surfaces without re-entrant profiles or chemical coating (~5 atm) [85] (Fig. 6c). Moreover, the optimized surfaces (inset in Fig. 6c) stood the ultrahigh impact pressure of droplets with low surface tension (7 atm for 36 mN/m) (Fig. 6d). Nanostructured PEEK surfaces demonstrated excellent stability (still sustaining large-contact-angle and low-hysteresis droplets with various surface tensions) after immersed in water or hexadecane for 14 days [86]. The cyclo-olefin polymer, which is a popular material for microfluidics due to its good chemical resistance against various organic liquids, has demonstrated excellent robustness of superhydrophobicity (without noticing the decrease of droplet contact angle) against the environmental aging(continuously wetting-drying) test for 60 cycles [87]. All these results indicate that plasma etching is an effective technique to fabricate liquid-repellent surfaces of various polymers.

3.3. Adhesion

The interactions between multiple materials are critical to the mechanical properties of composite materials [88]. Thus, surface modification is needed in order to enhance the chemical bonding and improve the overall interfacial strength [89]. The maskless oxygen plasma etching process is a technique that can be applied to enhance the adhesion between the polymer fibers to the epoxy resins. For instance, Fernández-Blázquez modified the polymer fiber surface morphology by etching the fibers with a fixed power at100 W with different durations (0.5, 1, 2, 5, 10, and 20 min) [37]. Then, epoxy resin droplets were deposited on the treated fibers and cured, followed by measuring the force (F) required to pull the polymer droplet out of the fibers (Fig. 7f). Then, the Interfacial Shear Strength (IFSS, defined as $F/\pi D_r L$ where F is the force,

 D_f is the average diameter of fibers, and *L* is the length of fibers) was calculated and plotted with respect to the duration of plasma treatment (Fig. 7a). There is no significant difference in surface morphology observed by SEM when the durations of plasma treatment were less than 2 min (Fig. 7b), which explains the constant IFFS is among those samples with plasma treatment shorter than 2 min. In contrast, the IFFS increased significantly with the increase in plasma treatment duration because the PET fiber-epoxy resin interfacial areas were greatly enhanced by the fabricated lamellae (Figs.7c and 7d). However, it was reported that the increase of IFFS was saturated as the duration of plasma treatment was above 10 min (Fig.7e) because the further treatment cannot affect the surface roughness anymore due to the collapse of lamellae. This study demonstrated that the maskless oxygen plasma etching process can be used to significantly enhance the fiber-matrix adhesion of various combinations of materials.

On the other hand, high-aspect-ratio polymer nanostructures can modulate cell adhesion [90, 91]. Cells tend to grow on the tip of nanostructures and have weak adhesion to the substrate so that they can be easily removed from the surface [92]. Serrano et al. also showed that plasmatreated polymer surface can improve bacterial repellence [93]. Interestingly, the polymer nanostructures do not increase the frictional forces between the polymer surface and an artificial skin [93]. Such polymer nanostructures are useful to improve the healing process by preventing infection [94].

3.4. Microfluidics

Microfluidics devices have been widely used for biomedical applications [95]. Because the flow channels and reactors are in micrometer scale, microfluidics show many advantages such as low volume consumption and low costs. However, due to the low specific Reynolds number, mixing is limited in microfluidics devices [96]. For example, conventional microarrays are used

 to capture biomarkers by immobilizing the capture probes on a flat surface [97]. Thus, the capture efficiency is typically low because the bind sites are limited. On the other hand, microbeads are used to improve the capture efficiency by providing a high concentration of capture probes on 3D surfaces. However, microbeads are hard to incorporate into the microfluidics devices [98].

Tsougeni et al. demonstrated a sample preparation module which was used for bacteria cell capture and thermal lysis functions on a chip (Fig. 8a) [99]. In the microfluidic chip, PMMA surface was treated with plasma and used for immobilizing antibodies. Because the solid surface area was significantly improved by plasma etching, more binding sites were provided. The chip exhibited 100% capture efficiency with a cell concentration of 10⁵/mL or below. The work shows the potential for developing an integrated microfluidic chip for cell capture. Such nanostructures-based microfluidic chip has also been used for DNA purification [100]. Kastania et al. designed a PMMA microfluidic chip with zig-zag shaped microchannels (Fig. 8b) [101]. The bottom surface of the microchannels was treated with oxygen plasma for the creation of high-aspect-ratio nanostructures. Carboxyl groups (-COOH) was generated by oxygen plasma and combined with buffer containing poly-ethylene glycol (PEG), NaCl and ethanol for DNA binding. The chip showed a DNA recovery efficiency of 96±11% for Salmonella DNA and was not affected by the flow rate (Fig. 8c). In addition, polymer nanostructures have also been used for protein immobilization [102, 103]. The large surface area of the polymer nanostructures provides more binding sites than conventional microarrays [104]. For example, Tsougeni et al. found that the adsorption of proteins increased up to 6-fold with polymer nanostructures compared with untreated flat surface [102]. This will improve the target capture efficiency and extend the detection limit [105].

In recent years, automated transportation of fluids in the microfluidic devices has been achieved by integrating pneumatically controlled micropumps [106-108]. The micropumps control the opening and close of the microchannels and the automated microfluidic chips allow precise and multiplexing handling of reagents in microliter and nanoliter scales without using pipettes and microtubes [109]. Such automation can also be achieved by modifying the surface properties of the microfluidic chip [110]. The fluidic resistance of the microchannels can be controlled by varying the plasma treated polymer surfaces. For example, plasma treated high-aspect-ratio PMMA surfaces are superhydrophilic and the fluids are easily filled (open state) [111]. On the other hand, coating the plasma treated PMMA surfaces with a hydrophobic coating makes the microchannel superhydrophobic and it closes the microchannel (close state). Tsougeni et al. demonstrated such a "smart" microfluidic device (Fig. 8d) for dye transportation [112]. Because the automation was achieved by simply adjusting the surface properties, no additional components were needed. This improvement is very helpful to develop portable and low-cost point-of-care (POC) detection systems.

3.5. Surface-Enhanced Raman Spectroscopy

Compared with traditional Raman spectroscopy, surface-enhanced Raman spectroscopy (SERS) technique dramatically increases the Raman intensity by several orders of magnitude from molecules that are attached to rough surfaces of plasmonic metals such as copper, silver, and gold nanostructures or their nanoparticles [113]. Many physical effects could contribute to the enlargement of effective SERS cross-sections per molecule (10¹⁷-10¹⁶ cm²/molecule) in order to observe such strong SERS phenomena. It has been reported that SERS phenomena are

 generally interpreted by two major effects: (1) electromagnetic and (2) chemical effects [113-115]. The electromagnetic SERS enhancement is caused by the excitation of electromagnetic resonances in the metallic structures, that can be physically explained by the collective theory based on Maxwell's equations by F. J. Garcia and J. B. Pendry [114]. On the other hand, chemical SERS enhancements due to a metal-electron mediated resonance Raman effects via a charge transfer intermediate state at the active sites can be interpreted by a physical model established by A Otto and others [115]. Overall, the SERS enhancements provide high sensitivity to structural detection of trace amount of chemical species, even for single chemical molecules. This breakthrough was first achieved by K. Kneipp et al. as they observed a strong SERS signal as the fingerprint of Raman features between 700 and 1700 cm⁻¹ originated from single crystalline violet molecule in the silver aqueous colloidal solution [116]. In order to utilize the great potential of SERS phenomena in the fields of chemistry, biology, medicine, pharmacology, and environmental science, there are a variety of SERS active substrates that have been engineered, such as metal substrates with rough surfaces, metal nanoparticle films, and metallic nanostructures, and 3D nanostructured Raman active substrates. The formation of 3D nanostructured Raman substrates with enhanced light scattering effects based on the collective theory mentioned above is an important parameter to enhance SERS signals for various sensing applications [116-119]. Recently, Shin et al. reported a 3D nanostructured SERS substrate fabricated by very dense and vertically aligned graphene/magnetite nanostructures which exhibits highly enhanced Raman scattering effects resulting in the enhancement factor of 7.0×10^4 due to significant trapping of the absorbed light in this nanostructure forest [120]. Those nanostructures were essentially fabricated by oxygen plasma treatment without using any artificial mask. The method reported in that study provides a simple, cost-effective, maskless top-down fabrication technique for well-controlled hematite nanostructures.

The schematic fabrication process of hematite nanostructures is shown in Fig. 9b. The mixture solution of all chemicals described in Fig. 9a was spin-coated to form a homogenous polymer film. The polymer film was then polymerized on a hot plate at 80 °C for 2 h. With anisotropic oxygen plasma treating (5–30 min, 250 W, 80 sccm and 270 mTorr), the iron precursor was converted into iron oxide, serving as an etch mask, and organic parts without this oxide passivation layer was etched away. The vertically-aligned iron oxide/organic nanostructures could be transformed into two types of iron oxide nanostructures, hematite and graphene-coated magnetite, according to different annealing conditions.

A TEM image of multilayer graphene is shown in Fig. 9c. Polymer nanostructures were successfully converted into graphene/magnetite nanostructures. The graphene/magnetite nanostructures exhibited remarkable enhancement of the Raman signal of dye molecules, compare to the Raman signal of CVD-grown monolayer graphene, as shown in Fig. 9d. The SERS enhancement is strongly attributed to the 3D forest structure of the graphene/magnetite nanostructures [117]. As shown in Fig. 9e, the graphene/magnetite nanostructures exhibited about 20 times higher diffuse reflectance in the whole spectrum region at the visible wavelength of 532 nm, compared to the small scattering of light on the single layer graphene/Si substrate. The incident light was effectively absorbed and scattered with an SERS enhancement factor of 7.0×10^4 observed in the 3D forest structure of the vertically-aligned graphene/magnetite nanostructures fabricated via a cost-effective etching process.

3.6. Organic Light-emitting Diodes (OLEDs)

Recently, vertically-aligned nanostructures of inorganic semiconductor materials have been widely used in areas spanning from optoelectronics, photovoltaic, and their related lighting device applications [121-123] because they exhibited enhanced performance on physical properties intrinsically associated with low dimensionality and size confinement [124]. In order to fully exploit the special feature of nanostructures, the intensive studies have been focused on nanowire (NW) synthetic process of these nanoscale building blocks with a preference of costeffectiveness, simplicity, and scalability. Up to now, the preparation of well-aligned NW arrays, however, is often done through vapor-liquid-solid (VLS) or vapor-solid-solid (VSS) techniques with assistance of metal catalysts at high temperature around 500 °C or higher. Although either VLS or VSS methods at high temperature is very reliable currently to prepare nanostructured materials on silicon or silica-based substrates. However, their use will be hindered in the emerging flexible electronic and photonic devices [125, 126] since several common flexible substrates currently applied in flexible electronics, such as polymide (PI) or polyethyleneterephthalate (PET), can only withstand the temperature around 250 °C or lower. Simple, scalable, and low-temperature techniques for producing high-quality and controllable polymer nanostructures on a large scale is highly demanded [127-132] in the field of flexible electronics including wearable devices, curved TV screens, foldable monitor and so on.

To response to the problem mentioned above, Morber et al. reported on a simple, one-step method for fabricating wafer-scale aligned PNWs by employing the ICP or RIE processes [35, 133]. The success in fabricating PNW arrays from conductive and semiconducting polymers fosters the development of high-performance nanostructured polymer optoelectronics, due to more superior charge transport ability from the larger contact area as compared to the conventional polymer thin-film based devices [134]. In this case, OLEDs based on PEDOT:PSS NWs were fabricated and demonstrated as shown in the inset of Fig. 10b. A layer of PEDOT:PSS was spin-coated onto an ITO substrate and baked for 10 min at 120 °C, followed by ICP RIE treatment to form vertically-aligned NWs with typical lengths of ~5 mm and diameters of ~400 nm. MEH-PPV and an Al electrode was then coated onto the PNWs successively. Under the same testing conditions, ~40 times greater current density is transported by the PNW-based OLEDs as compared to conventional thin film devices, shown in Fig.10b-2. As applying a DCbias between anode and cathode electrodes, every single PNW OLED creates a small light spot $(\sim 1 \text{ } \mu\text{m} \times 1 \text{ } \mu\text{m})$. By bundling multiple PNWs, LEDs will lead to bigger and brighter light emission. The demonstration illustrated in Fig. 10b-3 is to pattern the PNW OLEDs into a "US map" where the bright border is composed of those high-performance PNW OLEDs.

3.7. Energy Harvesting

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59 60 Another strong interest of PNW films is in harvesting sustainable energy [135, 136]. Water waves are considered as one of the sustainable energies from the blue ocean, which is abundant (70% of Earth's surface), and environmentally friendly [137]. Traditionally, electromagnetic generators have been widely used to convert water motions into electricity. However, it faces many engineering difficulties. For example, they are bulky and not easy to scaleup [138]. In addition, they need other accessories to support the energy conversion such as an absorber that collect ambient water, and a turbine that drive the generator in order to deliver a decent power output. As a consequence, those additional equipment raise the total cost and make this

technology at low exploiting level. On top of that, there are various types of natural water motions, and only specific types can compatibly drive the turbine. Therefore, this limitation significantly reduces the efficiency of this sustainable wave energy.

Zhu et al. developed a liquid-solid electrification enabled generator (LSEG) that is all-in-one, low-cost, extremely light-weight, and portable (Fig. 12a) [139]. This LSEG device consists of fluorinated ethylene propylene (FEP) film with two parallel electrodes attached on one side of this FEP film, and the surface of the other side has a hydrophobic treatment that is modified by vertically-aligned PNWs. This single-component LSEG device with nanostructured FEP surface can generate electricity from ambient water waves or water drops via the triboelectric effect. To further explain this phenomenon, the FEP surface is initially negatively charged as it has an interaction with ambient water, and those negative charges do not dissipate for a long time although the water is repelled by those hydrophobic FEP nanostructures. Once the electrode 'A' is partially submerged by the rising water wave that is normally positive charged (e.g., hydroxonium), those positive charge screens the negative triboelectric charges on the FEP surface by forming an interfacial electrical double layer. Thus, the unbalanced electric potential between two electrodes drives free electrons flowing from electrode 'B' to 'A' until water covers the half of the device. When the rising water partially overlaps the electrode 'B', the same mechanism occurs and drives free electrons flowing in the opposite direction until the device is entirely covered by water. Thus, triboelectric energy is obtained via the repetition of rising/descending water motion. The kinetics of the charge-generation process is illustrated in Fig. 12b [139]. Those vertical PNWs that feature 2 µm in length and 100 nm in diameter, play a critical role to increase the liquid-solid surface, which lead to enhanced surface charge density, and also repel the water immediately during every repetitive emerging-submerging process. Those polymer nanostructures increase the amount of induced charges by 50 % as compared to those without the modification, and the electric output from the device reaches the efficiency of 7.7 %, showing a potential application of simple energy converter offshore, onshore, or in the rainy area.

Another interesting research regarding TENG devices is to harvest human biomechanical energy (Fig. 11c-1) [140]. For example, the device that consists of Al, Cu electrodes and a nanostructured FEP layer illustrated in Figs. 11c-2 and 11c-3 can be installed in the running shoes in order to convert such low-frequency biomechanical motion into a DC electricity of 1.044 mW (7.34 W/cm³), which is sufficient to charge other small electronic devices such as thermometers, heart rate reader, pedometers, wearable watches and radio-frequency communication device shown in Fig. 11c-4 [140]. Recently, Xu et al. developed a TENG array devices, which enable to integrate a series of 38 sub-TENG units simultaneously [141]. The device consists of the inner oscillator connected with the outer shell with elastic bands, which forms a spring-levitated oscillator structure. The oscillator is composed of upper and lower air chamber walls made of a soft polymeric membrane (20 % nylon and 80% polyethylene) that endures the high pressure up to 80 kPa. While the device is operated in the water wave at low frequency, which is near its resonant frequency of 2.9 Hz, the oscillator converts mechanical energy from the water wave into electricity. The stability of this device relies on elastic bands that provide the elastic force isotropically toward the center of the oscillator and ensure the

oscillator is seated firmly in the proper position. This TENG array device was tested in the water tank with a simulated water wave, and it was able to output transferred charges per cycle of 15 μ c, short-circuit current of 187 μ A, and the optimized peak power density of 13.23 W/m³. This performance can light up 600 LEDs floating on the water simultaneously. Those LEDs powered by the electricity that is generated by the TENG array device is illustrated in Fig. 11d [141].

Furthermore, Xi et al. recently revealed the structure of their multifunctional triboelectric nanogenerator (TENG) device illustrated in Figs. 12e-1 to 12c-4 [142]. This device consists of two parts: a rotation TENG (r-TENG) and a cylindrical TENG (c-TENG), as shown in Figs. 12e-2 and 12e-3 in order to fully exploit a variety of sustainable vibration energies including wind and water. The r-TENG is designed for harvesting water/air flow energy, and the c-TENG aims to harvest wave energy based on the conjugation of the triboelectric effect and electrostatic induction. It is noteworthy that the group also employed FEP nanostructure (~1 μ m in length, and 100 nm in diameter) film made by a one-step plasma reactive ion etching process on the patterned copper electrode. This FEP nanostructure film significantly enhances the surface charge density as well as the device performance. Overall, r-TENG and c-TENG have the maximum output of 490 V and 100 V, the open circuit current of 24 μ A and 2.7 μ A at the water wave frequency of 3.0 Hz, respectively. The energy converted from mechanical vibration by TENG devices have demonstrated a great potential to replace traditional heavy electromagnetic generators and harvest sustainable energy including water wave, flow, and wind in a more efficient way.

4. Conclusion and Outlook

Over the past ten years, remarkable progress has been made in the fabrication and application of polymer nanostructures. Using a one-step plasma etching, high-aspect-ratio polymer nanostructures are fabricated enabling applications such as hierarchical nanostructures, liquid repellence, improved interfacial adhesion, microfluidics, enhanced Raman scattering, OLED, and energy harvesting. In this review, we have summarized the possible formation mechanisms and discussed different kinds of applications. We point out that this technique overcomes the scalability issues and is a key step toward a commercially scalable and economically sustainable manufacturing of such devices [143].

Current challenges for the polymer nanostructures in real applications include improving the mechanical strength of the nanostructures, reducing the dimension of the nanostructures, and tuning the period of the nanostructures. For example, the mechanical strength of the polymers can be increased by changing the chemical composition but it can also change the etching properties. We also anticipate more efforts to be made on explaining and understanding the formation mechanisms of the polymer nanostructures. For example, molecular dynamics modeling can help us to better understand how ions interact with the polymer surface [144, 145]. This development will allow us to control the period and dimension of the nanostructures and extend this technique for more applications such as semiconductors manufacturing. Another challenge for plasma induced nanostructures is how to further reduce the feature size to sub-10 nm. This challenge could be addressed by the emerging sub-10 nm lithography techniques [146, 147].

 The continued development of the polymer nanostructures to a higher level of maturity will enable its usage in nanotechnology in the coming years. The key advantages of this method is that sub-50 nm nanostructures are achieved without lithographically patterned nanomasks. The high aspect ratio of the nanostructures significantly increases the surface area and improves the surface properties. With the technological developments described here, we are reaching the long-held dream of a simple and powerful technique for nanostructures manufacturing with versatile functions. This said, we hope that this review will motivate colleagues to explore more applications with plasma induced polymer nanostructures.

Table 1. Comparison of lateral dimensions of polymer nanostructures fabricated by different formation mechanisms reported in the literature.

Mechanism	Materials	Etching gas	Power	Period (nm)	Diameter (nm)
			(W)	P	
Surface roughness	PMMA [35]	Ar, O_{2} , and CF_4	400	~300	~150
	PPy [35]	Ar, O_{2} , and CF_4	400	~500	~300
	PET [33]	Ar, O_2 , and CF_4	400	N/A	~100
	PS [35]	Ar, O ₂ , and CF ₄	400	~400	~200
	SU-8 [35]	Ar, O_{2} , and CF_4	400	~600	~300
Crystalline structure	PMMA [36]	O _{2,}	100	~80	~40
	PET [38]	O ₂	100	~50	~30
	PS [36]	O ₂	100	~50	~20
lucrossitics		0	400	N1/A	~25
Impurities	PIVIIVIA [148]	02	400	N/A	-35
	PMMA [31]	O ₂	50	~200	~100
	PPy [51]	O ₂	50	~50	~30
	SU-8 [31]	O2	50	~100	~40
	SU-8 [50]	CF_4 and O_2	150	~200	~150
	PET [149]	O 2	N/A	~250	~110 and ~40



Figure 1. (a) Schematic of the plasma-induced formation of polymer nanostructures. Plasma is generated in the etching chamber (left) and accelerated to the polymer surface with RF power (right). (b) SEM images of fabricated polymer nanostructure arrays: (1) PMMA, (2) PS, (3) PDMS, (4) PEDOT/PSS, (5) PEN, (6) PET, (7) Durafilm, and (8) Kapton film. (b-9) Optical image of 4 cm × 4 cm Kapton film covered with uniform array of polymer nanostructures. Reprinted with permission from [33]. Copyright (2009) American Chemical Society.



Figure 2. (a) Schematics of the nanostructure formation mechanisms of (1) PNW (polymer nanowires) and (2) PNT (polymer nanotubes) arrays on a polymer surface that has a protrusion and concave morphology, respectively. (b) Observations of PNWs and PNTs that formed due to surface modulation: (1) PS film surface showing wrinkles/ridges prior to plasma etching. (2): PS film surface showing the formation of PNWs along the wrinkles/ridges on the surface. (3): Presence of dips at the top ends of PEDOT NWs. (4): MEH-PPV PNT arrays formation due to plasma etching [35]. Reprinted with permission.



Figure 3. Surface nanostructures formation mechanisms due to mechanical and thermal treatment. (a) PET nanostructures formed by different mechanical pretreatment. (i) Isotropic film. (ii) Uniaxially oriented fiber. (iii) Extruded and drawn fiber. (iv) Biaxially oriented film [37]. Reprinted with permission from. Copyright (2012) American Chemical Society. (b) Summary of melting enthalpy, crystalline, and melting temperature of the polymer samples due to mechanical pretreatment [37]. Reprinted with permission from. Copyright (2012) American Chemical Society. (c) Weight loss measured on amorphous and semicrystalline PET samples and biaxially oriented semicrystalline PET immediately after plasma etching (above). Weight gain of the same plasma-treated samples after 24-hour exposure to ambient conditions (below). Reprinted with permission from [38]. Copyright (2010) American Chemical Society. (d) Structural model for a biaxially oriented samples according to Elias model. Reprinted with permission from [37]. Copyright (2012) American Chemical Society.



Figure 4. Surface nanostructures formation mechanisms due to impurities. (a) Metal impurities from the etching chamber (above). Bright field transmission electron microscopy (BFTEM) image (I), STEM image (II), and EDX mapping images (III-VIII) of a single PET nanostructure. The red arrow shows the orientation of the nanostructure from the top to the bottom (below) [48]. Reproduced from with permission of The Royal Society of Chemistry. (b) Impurities from external sources. A glass slide was used to deposit nanomasks on polymer surface during plasma etching [50]. Reprinted with Permission. (c) Metal impurities as a polymer content. Metal impurities antimony (Sb) exposed on the polymer surface due to plasma etching. Antimony is used in the manufacturing of negative-tone photoresist [31]. Reprinted with permission.



Figure 5. Hierarchical nanostructures patterning with laser interference lithography and plasma etching. (a) Schematic and SEM images of the experimental setup with two coherent beams and excitation wavelength of 266 nm. Reprinted with permission from [64]. Copyright (2012) American Chemical Society. (b) Nanostructures patterning on dura film with laser interference lithography and plasma etching. Reprinted with permission from [64]. Copyright (2012) American Society. (c) Schematic of Lloyd-mirror system for wafer-scale nanopatterning [21]. Reprinted with permission. (d)



Figure 6. (a) Contact angles of various liquids with different surface tensions on nanostructured PMMA surfaces fabricated by one-step (black) and two-step (red) O_2 plasma etching process. Reprinted with permission from [84]. Copyright (2011) American Chemical Society. (b) Morphologies of PMMA surfaces etched by one-step (top) and two-step (bottom) processes, where the scale bar is 1 μ m. Reprinted with permission from [84]. Copyright (2011) American Chemical Society. (c) Impact threshold pressure of the droplet on surfaces with different morphologies and chemical modifications, where the insert (c-i) refers the optimized surface (anisotropic 60 s, isotropic 15 s etching, coated with PFOTS) and the scale bar is

500 nm [85]. Reprinted with permission. (d) Impact threshold pressures of droplets with various surface tensions on the optimized surface [85]. Reprinted with permission. (e-f) Shapes of droplets on superamphiphobic surfaces [80, 84]. Reprinted with permissions.



Figure 7. (a) Interfacial Shear Strength (IFSS) of oxidative plasma treated PET fiber-epoxy resins interface is plotted with respect to the plasma treatment time. SEM images of the surfaces treated with oxygen plasma for (b) 0, (c) 5, (d) 10, and (e) 20 min. (f) The image of the cured epoxy droplet on the PET fiber [37].



Figure 8. Nanotextured surfaces for microfluidics applications. (a) PMMA-based cell capture module patterned with lithography and oxygen plasma etching [99]. Reproduced from with permission of The Royal Society of Chemistry. (b) Plasma micro-nanotextured polymeric micromixer for DNA purification. Reprinted from [101], Copyright (2016). (c) High recovery efficiency (~96%) of eluted DNA versus DNA entrance flow rate by using the micromixer shown in (b). Reprinted from [101], Copyright (2016). (d) Successive snapshots of a red dye–water solution in a PMMA microchannel with integrated superhydrophobic, hydrophobic and superhydrophilic stripes. The filling of fluids is controlled by surface wettability. Dye spontaneously fills in superhydrophilic areas while high pressure is needed to cross over the superhydrophobic areas [112]. Reproduced from with permission of The Royal Society of Chemistry.



Figure 9. Nanotextured surfaces for surface enhanced Raman scattering (SERS) applications. (a) List of chemicals used to synthesize hematite nanostructures. (b) Schematic illustration of the fabrication of vertically-aligned iron oxide nanostructure arrays using a simple maskless etching approach: (I) hematite nanostructures under calcination at 500 °C under air conditions and (II) graphene/magnetite nanostructures under 700°C under H₂/Ar conditions.(c) TEM images of graphene/magnetite nanostructures. (d) Raman spectra of R6G on graphene/magnetite nanostructures (red line) and single layer graphene (black line). (e) Diffuse reflectance spectra of graphene/magnetite nanostructures (red line) and single layer graphene (blue line) on a Si substrate [120]. All the figures reproduced from with permission of The Royal Society of Chemistry.



Figure 10. Nanotextured surfaces for organic light-emitting diode (OLED) applications. (a) Photograph of a large-area flexible OLED (50 mm × 50 mm) working at high luminance (>5,000 cd m⁻²) [150]. Reprinted by permission from Macmillan Publishers Ltd: [Nature Photonics], copyright (2011). (b) Nanostructure-based OLED device. (1) Small and large dots of bright yellow light are likely to be emitted from single nanostructures and nanostructure bundles, respectively. A schematic of the device is shown in the inset. (2) The nanostructured OLED device demonstrated a significantly lower turn-on voltage and higher current-density capacity compared to a thin film control fabricated under the same conditions. The film OLED curve is magnified 15 times to emphasize the difference in turn-on voltage compared to the nanostructured device. (3) Patterned light output from the OLED showing the outline of a "US map." The OLED data recorded at 3.5 V were clearly visible to the naked eye [35]. Reprinted with permission.



Figure 11. Nanotextured surfaces for energy harvesting applications. (a) Structural design of the liquidsolid electrification-enabled generator (LSEG). (1) Schematic of the bent electrification layer with two electrodes on one side. (2) SEM image of the polymer nanostructures on the opposite side of the polymer layer. The scale bar is 1 μ m. (3) Schematic of a substrate-supported LSEG positioned in water waves. The up-and-down movement of the surrounding water body induces electricity generated between the two electrodes [139]. (b) Electricity-generating process of the LSEG [139]. (c) Design of a multilayered triboelectric nanogenerators (TENGs) self-powered system [140]. Reproduced from Nanture Publishing Group. (d) TENG used to light up 600 LEDs floating on water. Reprinted from [141], Copyright (2017), with permission from Elsevier. (e) A multifunctional TENG used for water waves, air flowing, and water flowing energy harvesting [142]. Reprinted with permission.

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