

# Fabrication of Polymer Nanostructures via Maskless O<sub>2</sub> Plasma Etching

Ke Du, Yuyang Liu, Ishan Wathuthanthri, Wei Xu, Chang-Hwan Choi  
*Stevens Institute of Technology, Hoboken, NJ 07030*  
*cchoi@stevens.edu*

In recent years, the nanostructures of organic materials have drawn great interests because of their potential applications to polymer-based devices and systems, such as energy storage<sup>1</sup> and OLEDs<sup>2</sup>. Furthermore, there is an increasing interest in patterning functional organic nanostructures for 3D hierarchical architectures.<sup>3</sup> In this paper, we demonstrate that high-aspect-ratio organic nanostructures with sub-100 nm scale can be fabricated on UV-absorbing polymers via maskless O<sub>2</sub> plasma etching process. We further show that 3D hierarchical polymer nanostructures can also be conveniently fabricated by the method.

Figure 1 shows the fabrication results made on a planar polymer film of NR7-1500P (Futurrex) by O<sub>2</sub> plasma etching (Trion) in RIE mode with no aid of any mask layer. The etching times were modulated to study their effects on the structural dimensions of various polymer materials (Figure 2). In the O<sub>2</sub> plasma etching of polymer materials, nanoparticulate “inhibitors” form by the chemical reaction and deposit on the surface.<sup>4</sup> Because of the high etch selectivity, the inhibitors behave like etch mask and result in the self-formation of dense-array high-aspect-ratio polymer nanostructures in the etching. We have found that substrate temperature strongly affects the formation of inhibitors and hence the nanostructures; e.g. if the substrate temperature is increased from 20°C to 50°C, no nanostructure was formed. The result suggests that at higher temperature, the inhibitors possess higher kinetic energy and less probable to deposit onto the polymer surface. One of the advantages of the maskless etching process is that it can allow realizing 3D hierarchical nanostructures by additively forming the polymer nanostructures on a pre-patterned polymer film. For example, Figure 3 shows the hierarchical nanostructures designed on a nano-porous layer pre-defined by laser interference lithography.<sup>5</sup> By controlling the exposure dosage in preparing the nano-porous base layer at the interference lithography process, two-tier polymer nanostructures of various geometrical combinations, e.g., pillar-on-hole and pillar-on-pillar structures, were successfully fabricated.

Our results reveal that the maskless one-step O<sub>2</sub> plasma etching process can provide a simple route to fabricate 3D polymer nanostructures with great tunability of their nano-dimensions and hierarchy with no necessity of using expensive and complicated nanolithography techniques. Such a simple and efficient nanofabrication process can open a new application possibility to future polymer based devices and systems such as next-generation flexible electronics.

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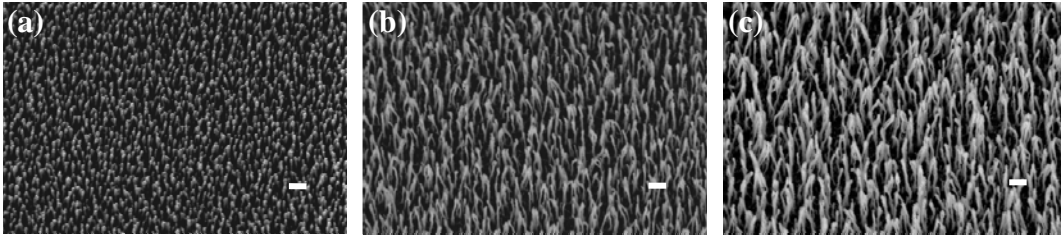
<sup>1</sup> K. Wang *et al.*, *J. Phys. Chem. C* **114**, 17 (2010).

<sup>2</sup> J. R. Morber *et al.*, *Adv. Mater.* **21**, 20 (2009).

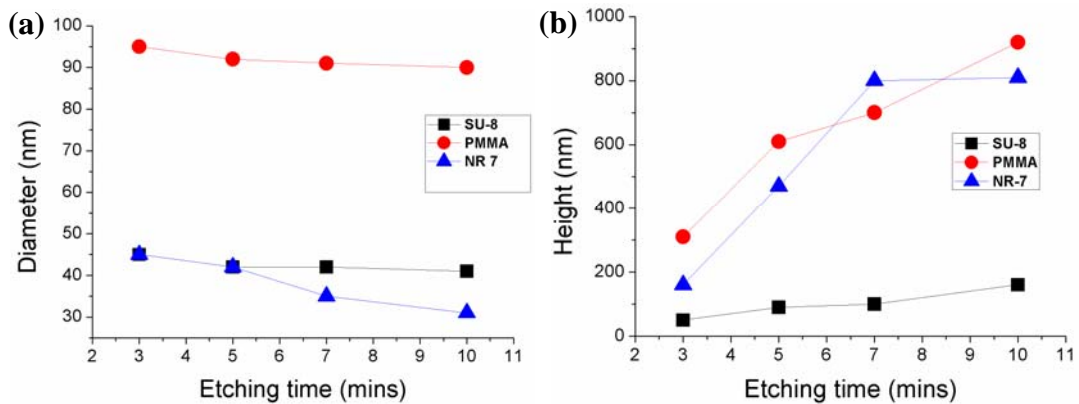
<sup>3</sup> H. Fang *et al.*, *ACS Nano* **5**, 1476 (2011).

<sup>4</sup> K. Tsougeni *et al.*, *Langmuir* **25**, 11748 (2009).

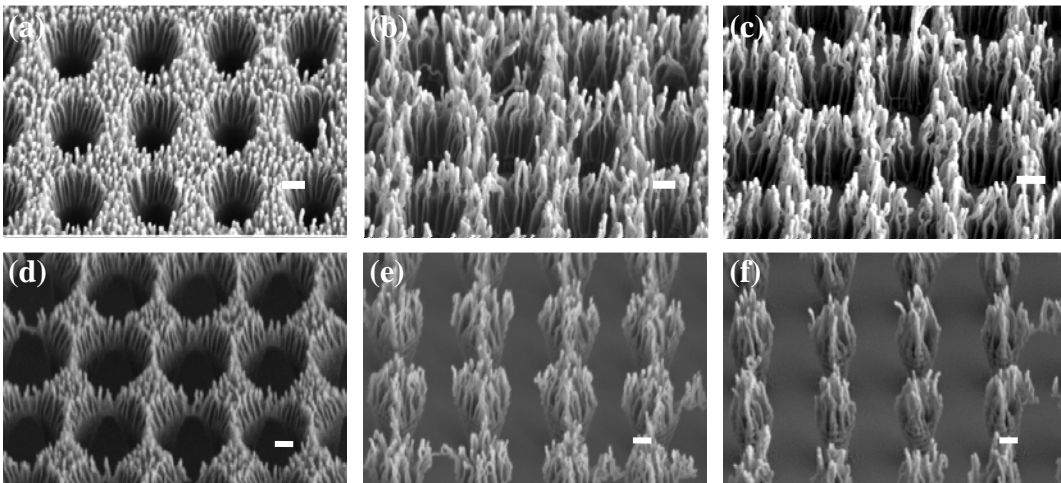
<sup>5</sup> W. Mao, I. Wathuthanthri, and C.-H. Choi, *Optics Lett.* **36**, 3176 (2011).



*Figure 1:* Polymer nanostructures created on planar NR7-1500P films (negative PR) by O<sub>2</sub> plasma etching for (a) 180 seconds; (b) 300 seconds; (c) 420 seconds. Each scale bar indicates 200 nm for all images.



*Figure 2:* Nanostructure etching characteristics for different polymers. (a) The diameters of nano-pillar structures were sub-100 nm. An increase of etching time did not affect the diameter significantly. (b) However, the nanostructure heights increase with etching time, resulting in aspect ratios greater than 20:1.



*Figure 3:* Hierarchical polymer nanostructures created on a pre-patterned (porous) NR7-1500P film by O<sub>2</sub> plasma etching for (a, d) 180 seconds; (b, e) 300 seconds; (c, f) 420 seconds. The initial pore sizes of the pre-patterns (a-c vs. d-f) were prepared to be different in the prior interference lithography step by controlling the exposure dosage. Each scale bar indicates 200 nm for all images.