Hierarchical polymer micropillar arrays decorated with ZnO nanowires

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Abstract

We introduce a simple and robust method for fabricating hierarchical fibrillar arrays based on polymer micropillar (μ PLR) arrays decorated with ZnO nanowires (NWs) on mechanically flexible substrates. The hierarchical fibrillar arrays are fabricated by replica molding of polymer μ PLR arrays on microfabricated silicon templates and subsequent solution-based growth of ZnO NWs. Fine control over the dimensions and aspect ratios of both the microelements and the nanoelements is demonstrated. The hierarchical μ PLR/NW arrays show superhydrophobic surface properties, with the contact angle higher than that of planar surfaces and μ PLR arrays without nanostructures. The fabrication strategy suggested here may be potentially extended to fabricate other organic/inorganic hierarchical systems for different applications.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Nature provides impressive examples of nanostructured and microstructured systems with excellent optical and mechanical In particular, many biological systems functionalities. have evolved into multi-scale, hierarchical structures with sophisticated and smart functions. The strong adhesion abilities of gecko's foot [1], superhydrophobic surface of lotus leaf [2] and water strider leg [3], photonic crystal structures in butterfly wings [4], biomineralization of organic/inorganic structures [5] are just a few examples of hierarchical structures found in nature. These unique structure/function relations have motivated researchers to fabricate hierarchical microstructures and nanostructures that mimic the unique functionalities of biological systems [6, 7]. However, most of the man-made hierarchical structures are yet far from the sophisticated biological systems mainly due to the fabrication challenges. In the past, a number of methods have been explored to fabricate hierarchical structures including nanomolding and micromolding, direct growth of organic or inorganic structures, and lithography patterning of surfaces [8].

Extending on these works, here we introduce a simple and robust method to hierarchical fibrillar arrays based on hybrid organic/inorganic material systems on mechanically flexible substrates. The hybrid structures are beneficial for multifunctional materials due to the mixed and synergetic functionalities of organic and inorganic components. The structures consist of polymer micropillar (μ PLR) arrays decorated with ZnO nanowires (NWs). The polymer μ PLR arrays are fabricated by replica molding on microfabricated silicon templates containing hexagonal micropore arrays. Subsequently, the ZnO NWs are grown on the surface of μ PLRs by a low-temperature, solution-based growth method, resulting in hierarchical microfibrillar and nanofibrillar arrays. We demonstrate the superhydrophobic surface properties of hierarchical μ PLR/NW arrays with potential applications in self-cleaning smart surfaces, microfluidics, and biomedical devices. For these applications, the mechanical flexibility of the polymeric support substrate used here is advantageous over the traditional superhydrophobic surfaces with rigid silicon or glass support substrates.



Figure 1. (a) Schematic of the fabrication procedures for μ PLR/NW hierarchical structures achieved by molding of PC μ PLRs and a subsequent decoration of ZnO NWs by a solution-based growth method. (b) Top-view optical and (c) cross-sectional SEM images of a silicon micromold used for the fabrication of PC μ PLR arrays.

2. Experimental details

The fabrication process scheme for the μ PLR/NW hierarchical structures is shown in figure 1(a). For the formation of first-level microstructures, silicon micromolds (figures 1(b) and (c)) were prepared by standard photolithography and etching processes. Briefly, periodic circle arrays (1.5 μ m diameter, 4, 6, 8, and 10 μ m pitch, 1.5 \times 1.5 cm² area) are lithographically patterned on Si/SiO2 substrates (SiO2 thickness \sim 50 nm) followed by SiO₂ wet etch using 1% HF solution for ~ 5 min. Deep reactive ion etching (DRIE) was then carried out for 10 min, resulting in the formation of $\sim 40 \ \mu m$ deep micropores. For DRIE process, passivation and etching steps were alternately conducted to etch silicon. The passivation step was done for 5 s at 225 sccm C_4F_8 gas, 40 mTorr pressure, 0 W Bias, and 1200 W source power. The etching step was done for 7 s at 300 sccm SF₆ gas, 60 mTorr pressure, 6 W Bias, and 1200 W source power. Next, a polycarbonate (PC) film (thickness of 250 µm, McMaster-Carr) was cut into $\sim 2 \times 2 \text{ cm}^2$ size and placed on top of a silicon micromold and pressed by applying a normal pressure of \sim 3.5 N cm⁻² at a temperature of 190 °C for 30–120 min. Since the process temperature is over the PC glass transition temperature (T_g , 150 °C), PC polymer chains flow and partially

measured immediately after dropping a water droplet on the samples. The contact angles were estimated by analyzing the pictures of water droplet on the surface, which results in $\sim 5^{\circ}$ error in estimating the contact angle data.

fill the Si micropores as determined by the molding time. After the sample was cooled down, the PC film was peeled off

from the Si mold, resulting in hexagonal arrays of PC μ PLR

on flexible PC substrates. For the formation of second-level

nanostructures, we grew ZnO NWs on the PC μ PLRs by using

a hydrothermal growth method [9, 10]. Briefly, the substrates

with PC μ PLR arrays were dipped into the ZnO nanocrystal

solution (seed solution) for 20 s and blown dry with nitrogen

gas, resulting in the deposition of ZnO nanocrystal seeds on

the μ PLRs. The ZnO nanocrystal solution was prepared by

dissolving zinc acetate dihydrate (0.01 M) in methanol under

vigorous stirring at about 60 °C, adding a dropwise solution

of KOH in methanol (0.03 M) at 60°C, and stirring the

reaction mixture at 60 °C for 2 h [11]. Next, the PC μ PLR

substrate was placed inside an aqueous solution containing zinc

nitrate hydrate (25 mM), hexamethylenetetramine (25 mM),

and polyethylenimine (5 mM) at 85 °C, resulting in the growth

of ZnO NWs on the surface of μ PLRs. To compare the water

contact angles on different samples, static contact angles were



Figure 2. PC μ PLR arrays fabricated with a molding time of (a) 30, (b) 60, and (c) 90 min. (d) The lengths of μ PLR arrays as a function of \sqrt{t} , where *t* is the molding time. The best fit line is also shown. The pressure for the molding is fixed to ~3.5 N cm⁻² with a molding temperature of 190 °C.



Figure 3. Hierarchical μ PLR/NW structures achieved by ZnO NW decoration of the PC μ PLR backbones. Two different ZnO NW growth conditions resulted in (a) and (b) fine ZnO NWs (60 μ M seed solution, 1 h growth) with diameter of 20–30 nm and length of ~0.5 μ m or (c) and (d) large-diameter ZnO NWs (6 μ M seed solution, 1.5 h growth) with diameter of ~100 nm and length of ~1.5 μ m.

3. Results and discussions

Figures 2(a)–(c) show the scanning electron microscope (SEM) images of PC μ PLR arrays with diameter, d_{μ PLR} ~ 1.5 μ m as prepared by the described process (figure 1(a)) with different molding time of 30, 60 and 90 min, respectively. μ PLRs were found to maintain their structural integrity with hexagonal

ordering and vertical geometry for different lengths. One of the advantages of the thermal micromolding process is that the aspect ratio and dimensions of the μ PLRs can be easily tuned by controlling the molding temperature and time. For example, as can be seen in figure 2(d), the length of PC μ PLRs monotonically increases with the molding time. When the polymer is heated above T_g , as is the case here, it starts to flow and fill the Si micropores by a capillary force. The length of the obtained μ PLRs can be described by $z = C\sqrt{t}$ [12], where z is the length of an infiltrated polymer μ PLR in a micropore, t is the molding time, $C = \sqrt{\left(\frac{R\gamma}{4\eta}\right)\cos\theta}$ is the proportionality constant, R is the hydraulic radius, γ is the polymer/air interfacial tension, η is the viscosity of the polymer and θ is the contact angle of polymer melt on the micropore wall. From this expression, the length of PC μ PLRs is expected to linearly increase with \sqrt{t} , which is also confirmed from our experimental results in figure 2(d) with an observed $C = 0.84 \ \mu \text{m min}^{-0.5}$.

Hybrid organic/inorganic hierarchical structures are desirable for applications requiring the combined properties of organic and inorganic materials. To fabricate such structures, PC μ PLR arrays were used as the backbone for the growth of inorganic ZnO NWs. ZnO, a direct and wide band gap ($E_g = 3.37$ eV at 300 K) semiconductor, is a multifunctional materials with broad applications in photocatalysis, photovoltaics, lasers, energy harvesting, and sensors [13]. Figure 3 shows PC μ PLR arrays covered with ZnO NWs grown by a hydrothermal method. ZnO NWs were uniformly grown on the surface of PC μ PLRs with radial direction and dense coverage. The density and dimensions of ZnO NWs were readily tuned by the concentration of nanocrystal seed solution and the growth time, respectively. For example, two different growth conditions resulted in fine ZnO NWs (60 μ M seed solution, 1 h growth) with a diameter, $d_{\rm NW} = 20-30$ nm and length, $L_{\rm NW} \sim 0.5 \ \mu {\rm m}$ (figures 3(a) and (b)) or large ZnO NWs (6 μ M seed solution, 1.5 h growth) with $d_{\rm NW} \sim 100$ nm and $L_{\rm NW} \sim 1.5 \ \mu$ m (figures 3(c) and (d)) on the surface of μ PLR arrays.

One of the applications of hierarchical fibrillar structures is the design of superhydrophobic surfaces. It is well known that hierarchical microstructures and nanostructures composed of low surface energy materials can provide superhydrophobic behavior [14]. The superhydrophobic lotus leaf is one example of such a system, consisting of microscale bumps covered with nanoscale and low surface energy epicuticular wax [2]. Here, we demonstrate mechanically flexible (figure 4(a)) and superhydrophobic surfaces based on hierarchical μ PLR/NW structures. Figure 4 shows the water contact angle (CA) on planar, μ PLR, and μ PLR/NW structures coated with a low surface energy parylene-N layer (~10 nm thick). Parylene deposition was done in the gas phase, allowing for conformal coating to lower the surface energy of ZnO NWs and also to prevent the brittle breakage of ZnO NWs. As expected, the CA of μ PLR arrays with $L_{\mu PLR} = 10 \ \mu m$ and pitch, $P_{\mu PLR} = 6 \ \mu m$ (figure 4(c), ~130°) is higher than that of a planar surface (figure 4(b), $\sim 83^{\circ}$) due to the increase of surface roughness and thus the decrease of fractional solidliquid interfaces, resulting in the enhancement of hydrophobic properties. Most interestingly, the water CA on the hierarchical μ PLR/NW arrays (L_{μ} PLR = 10 μ m, P_{μ} PLR = 6 μ m, L_{NW} = 0.5 μ m) is ~150° (figure 4(d)), which corresponds to ~20° increase of CA as compared to μ PLRs.

The water contact angle on the rough surface can be related to the fractional area of solid and air in contact with the water droplet by using Cassie and Baxter equation [15],



Figure 4. (a) Optical image of a PC substrate with hierarchical μ PLR/NW arrays on the surface, showing its mechanical flexibility. Contact angle measurements for (b) planar PC substrate, (c) PC μ PLR arrays, and (d) hierarchical μ PLR/NW structures. The length and pitch of μ PLRs are L_{μ PLR} = 10 μ m and P_{μ} PLR = 6 μ m. In all cases, the surface is coated with a thin layer (~10 nm) of parylene-N by a gas deposition process.

 $\cos \theta_{\rm CB} = f_{\rm s} \cos \theta + f_{\rm a}$, where $\theta_{\rm CB}$ is the Cassie and Baxter apparent contact angle, θ is the Young contact angle, f_s is the area of solid-liquid interface, and f_a is the area of airliquid interface. The fractional area of top of micropillars (f_S) is calculated as $f_S = \pi (D/a)^2 / 2\sqrt{3}$, which gives fractional area change from 1 for 2D planar surface to 0.06 for 3D μ PLR surface. The f_S for hierarchical μ PLR/NW arrays can be estimated as 0.001-0.003 with the ZnO NW surface density of 50-80 NWs μm^{-2} and diameter of 20-Considering these fractional area of solid-liquid 30 nm. interface, the theoretical water contact angle from Cassie and Baxter equation is estimated as 160° for μ PLR arrays and 175° for hierarchical µPLR/NW arrays, which is higher than the experimental results with 130° for μ PLR arrays and 150° for hierarchical μ PLR/NW arrays. A possible reason for this discrepancy between theoretical and experimental contact angles may be due to the partial water penetration into the nanoscale and microscale grooves in real wetting situations, resulting in the increase of fractional area of solid-liquid interfaces. In the future, further exploration of this effect is needed. As previously suggested in several studies [14, 16, 17], the high CA of hierarchical

surfaces may be caused by the trapped air pockets in the apertures of micro/nanostructures which are responsible for the superhydrophobic wetting properties. However, the water droplet is more likely to penetrate into the grooves of μ PLRs without nanoscale surface roughness, resulting in lower CA. While most of previous superhydrophobic surfaces are based on hard and fragile substrates such as silicon or glass substrates [18–21], the flexible and superhydrophobic characteristics of μ PLR/NW arrays demonstrated in this study will be beneficial for applications requiring lightweight and bendable superhydrophobic substrates. In addition, the multifunctional properties of ZnO nanowires are expected to broad the applications to electronic and optical applications.

4. Conclusions

In summary, we demonstrate a simple and robust approach to fabricate mechanically flexible superhydrophobic surfaces based on hybrid organic/inorganic hierarchical structures. Our hierarchical structures containing piezoelectric ZnO NWs on PC μ PLR arrays may also find other applications such as generating electricity from vibrations and frictions [22]. In addition, the proposed process scheme can be applicable to other organic/inorganic materials systems, which may further expand the applicability of hybrid hierarchical structures to various fields in photonics, photovoltaics, and sensor devices.

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