Nonlithographic Fabrication of Nanostructured Micropatterns via Breath Figures and Solution Growth

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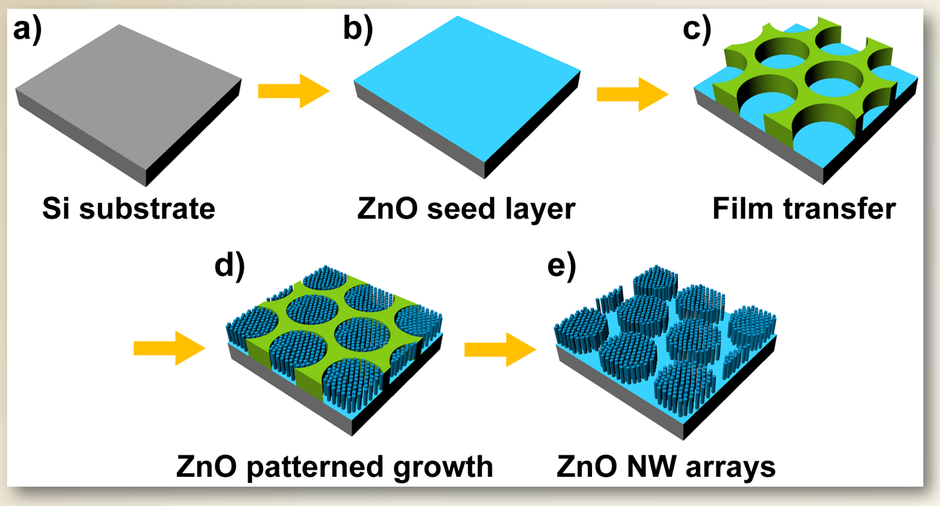
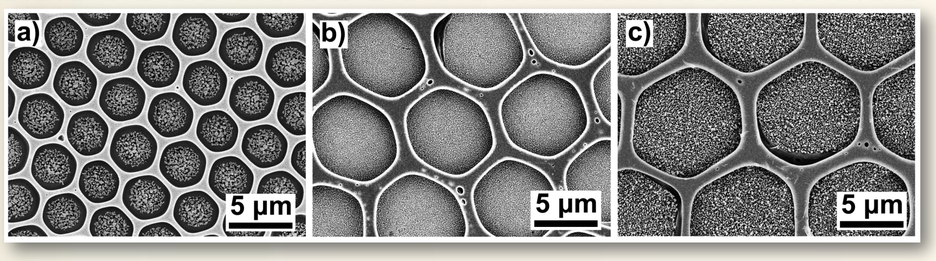
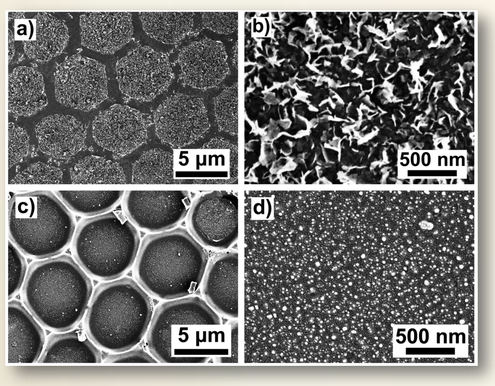
Breath figure (BF) method provides a simple, robust and efficient bottom-up strategy to fabricate hexagonally ordered two-dimensional films with a pore size in the range of micrometer and submicrometer. Using BF films as micropatterning templates has received great attention. However, non-through-pore BF films make it mandatory to introduce extra templating or pattern transfer procedures. In this work, we demonstrate a facile, versatile, nonlithographic one-step method to fabricate nanostructured micropatterns of ZnO nanowires (NWs), biomimetic hydroxyapatite and silver nanoparticles (Ag NPs). BF films with through-pore structures were prepared from a block copolymer at an air/ice interface and applied as templates on silicon substrate. ZnO NW micropatterns were obtained via confined solution growth, showing a significant intensity enhancement of near-band-edge exciton emission. This technique opens a novel alternative route to the fabrication of micropatterned surfaces.



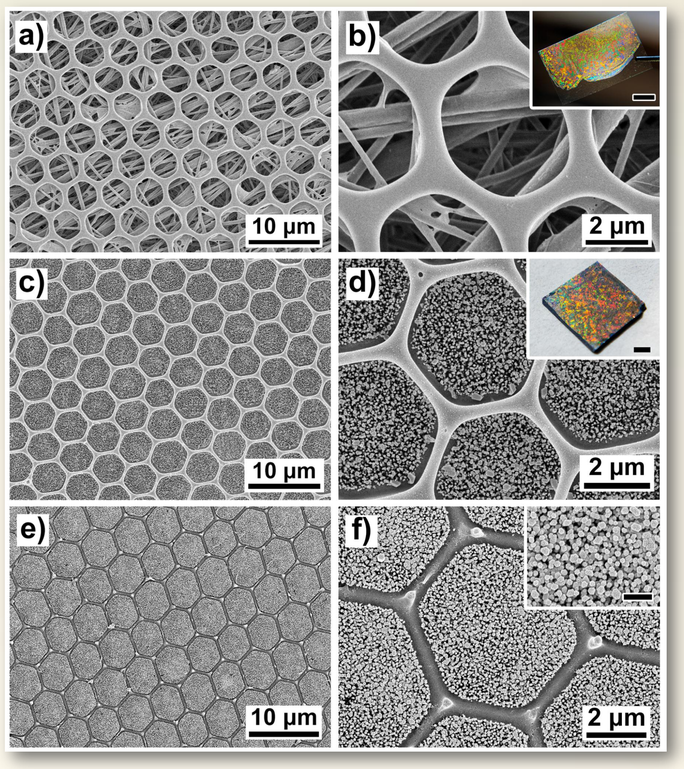
The solution of PS-*b*-PDMAEMA was cast at an air/ice interface under a humid airflow. A hexagonally ordered BF film with through-pore structures was formed and transferred onto a silicon substrate to template the low-temperature hydrothermal growth of ZnO NWs. A further removal of the honeycomb template gives a micropatterned ZnO NW surface.

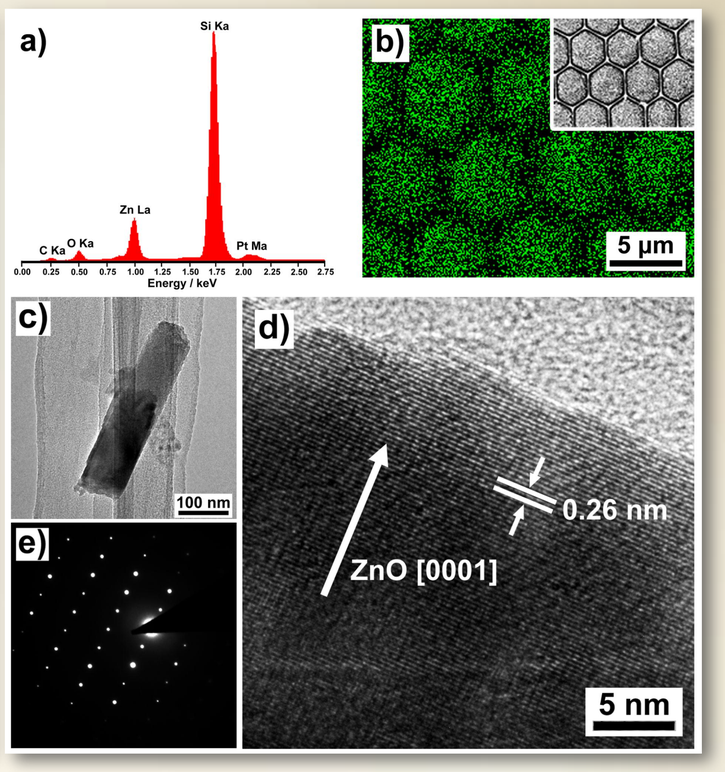


The scale of ZnO NW arrays can be facilely modulated in the range of 2-8 μm by tuning the period of BF templates via an appropriate dynamic control over the airflow speed in the film formation process.

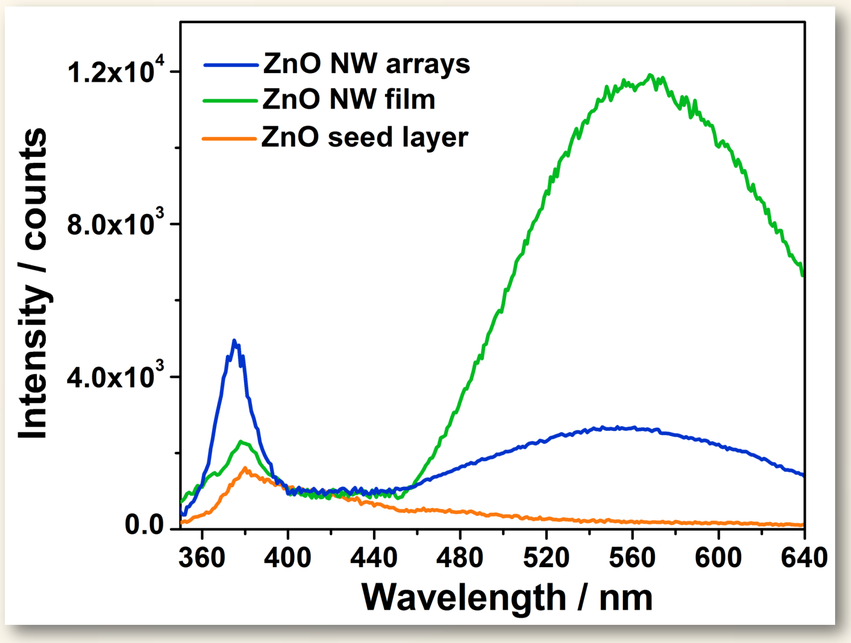


Through-pore BF films could also be templates for micropatterning of hydroxyapatite and Ag NPs, which may be applied in selective cell adhesion and surface enhancement of Raman scattering. This method provides an alternative approach for micropatterning in water phase.





Nanofibers underlying the BF film can be clearly seen through the pores. The growth of ZnO NWs was confined in the pores of the template, resulting in uniform microarrays in a large scale. Mapping of Zn displays a well patterned distribution in accordance with hexagonal shapes of the BF film. ZnO NWs grow along the ZnO [0001] direction, which are vertical to the Si substrate.



The micropatterned ZnO NW arrays exhibit a relatively much stronger band-edge UV emission and weaker broad defect-derived green-yellow peak than NW film, which reveals a higher optical excitement quality of ZnO NW arrays. The significant intensity enhancement of UV emission probably arises from the charge transfer of electron-hole recombination and a decrease in defect density due to the formation of microarrays. The micropatterned ZnO NW surface will be useful in applications of high-efficiency blue/near-UV light emitters.

Conclusions

- BF films with through-pore structures were prepared from a block copolymer, PS-*b*-PDMAEMA, at an air/ice interface.
- Through-pore BF films were applied as templates for micropatterning of ZnO NWs, hydroxyapatite and Ag NPs.
- ZnO NW microarrays show significant intensity enhancement of near-band-edge exciton emission.

References

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[2] S. Xu, Y. G. Wei, M. Kirkham, J. Liu, W. J. Mai, D. Davidovic, R. L. Snyder and Z. L. Wang, *J. Am. Chem. Soc.*, 2008, 130, 14958.

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