Electronic Supplementary Information for

Multifunctional Ionomer-Derived Honeycomb-Patterned Architectures and Their Performance in Light Enhancement of Light-Emitting Diodes

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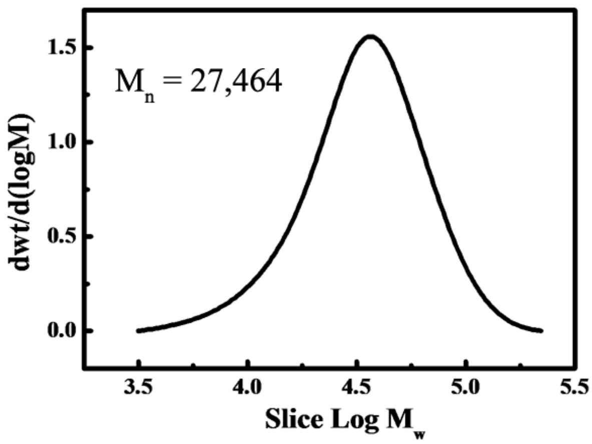

Fig. S1 GPC profile of PMMA/$Zn(AA)_2$ ionomer ($Zn(AA)_2$/MMA = 1:50 mol/mol).

Table S1. Molecular weight (M_n) of ionomers at different monomer molar ratios

	PMMA/$Zn(AA)_2$	PMMA/$Pb(AA)_2$
1 :100	27,081	--
1 :50	27,464	20,278
1 :25	31,644	---

As shown in Fig. S1, a typical PMMA/$Zn(AA)_2$ ionomer with M_n = 27,464 was successfully synthesized ($Zn(AA)_2$/MMA = 1:50 mol/mol). From Table S1, we learn that larger monomer molar ratios result in higher molecular weight of PMMA/$Zn(AA)_2$ ionomers (27,081 for the 1:100 case, 27,464 for the 1:50 case and 31,644 for the 1:25 case), and the molecular weight of PMMA/$Pb(AA)_2$ ionomer is 20,278.

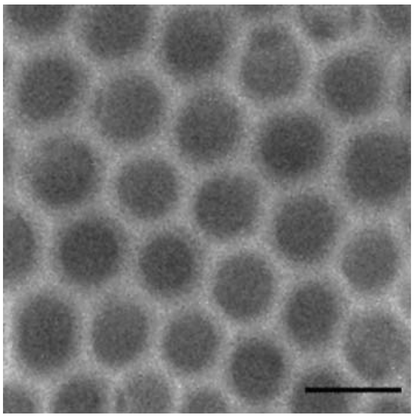

Fig. S2 SEM images of PMMA/$Pb(AA)_2$ film (monomer molar ratio: 1:50; ionomer solution concentration: 3 wt %; humidity: 85%; substrate: glass slide). Scale bar: 2 μm.

Fig. S2 demonstrates that the honeycomb-patterned PMMA/$Pb(AA)_2$ ionomer film can also be obtained *via* BF, with their average pore sizes of *ca.* 1.0 μm.

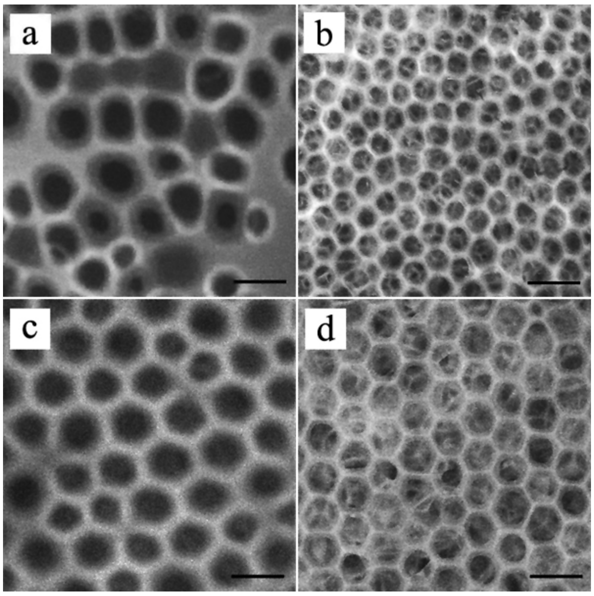

Fig. S3 SEM images of PMMA/$Zn(AA)_2$ films of (a-b) $Zn(AA)_2$/MMA = 1:50 mol/mol, ionomer solution concentration (a) 1% and (b) 6%; (c-d) ionomer solution concentration: 3%, (c) $Zn(AA)_2$/MMA = 1:100 mol/mol and (d) $Zn(AA)_2$/MMA = 1:25 mol/mol (substrate: glass slide; humidity: 85%). Scale bar: 2 μm.

Tuning pore diameters of ordered porous materials for different applications is necessary in technological areas. In this case, we also investigated the effect of ionomer solution concentrations and monomer molar ratios on the morphologies of these ionomer films. As shown in their SEM images, disordered holes are observed for the 1 wt % ionomer solution (Fig. S3a), and regular honeycomb structures with rather small pore sizes for the 6 wt % ionomer solution (Fig. S3b) (the monomer

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molar ratio of the PMMA/$Zn(AA)_2$ ionomer solutions is 1:50). We consider the ionomer solution concentration of 1 wt % is too low for ordered hexagonal arrays. When raising the ionomer solution concentration to 3 wt % and 6 wt %, the pore structures become more organized with average diameters reduced from 1.2 μm to 0.7 μm (Fig. 1b and S3b). According to Stenzel,

$$PS = k/c$$

where PS is pore size on the membranes, k is a constant dependent on the polymers used, and c is the concentration of the ionomers, higher ionomer concentration engenders smaller pore sizes. Actually, more concentrated ionomer solutions may contribute to faster evaporation of the volatile solvent, which effectively hinders the water droplets from packing into larger ones during the BF process and gives smaller pores. It should be noticed that the ionomer solutions are too viscous to realize honeycomb patterns *via* BF when the solution concentration is over 6 %.

In addition to the ionomer solution concentration, molar ratios of the two monomers can also influence the pore sizes in our case. As seen in Fig. S3c and S3d, the pores are closely packed in ordered arrays with their sizes declining from 1.5 μm to 1 μm when enhancing the $Zn(AA)_2$/MMA molar ratios from 1:100 to 1:25 mol/mol (ionomer solution concentration: 3 wt %). In this respect, higher molecular weight leads to smaller pore diameters, which seems inconsistent with previous reports where the pore sizes of honeycomb structures are found to increase with molecular weight of polymers, like polysulfone or polyphenylene oxide (PPO). [1,2] We attribute this to the different and more complicated ionomer systems, because higher $Zn(AA)_2$ content can promote the crosslinking behavior of PMMA chains and provide abundant zinc ion clusters in the ionomer matrix, which may prevent water coalescence more effectively. Therefore, decreased pore sizes are observed, revealing that appropriate molar ratio of monomers is also important in controlling pore sizes.

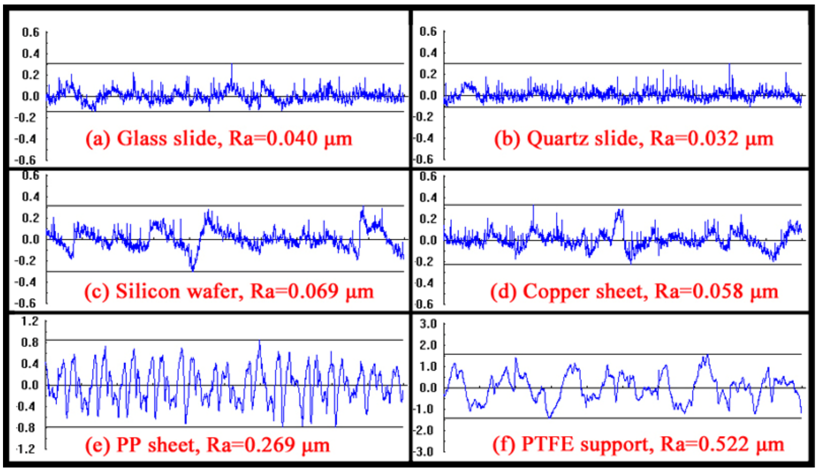

Fig. S4 The surface roughness of the six substrates of (a) glass slide, (b) quartz slide, (c) silicon wafer, (d) copper sheet, (e) PP sheet and (f) PTFE support.

Fig. S4 shows the surface roughness of six substrates including glass slide, quartz slide, silicon wafer, copper sheet, PP sheet and PTFE support. The inorganic surfaces are relatively smooth with their surface roughness below 0.07 μm, whereas the organic surfaces are much rougher (*R*a of PP sheet and PTFE support is 0.269 μm and 0.522 μm, respectively). The smooth surfaces may benefit for the adsorption of water droplets onto the substrates during the BF process.

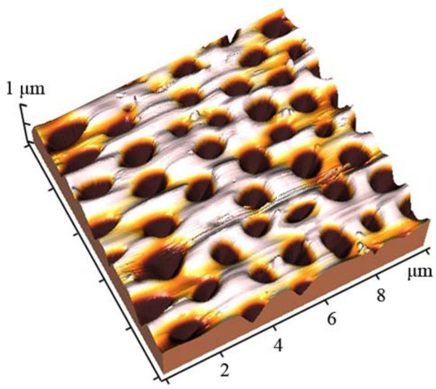

Fig. S5 Three-dimensional (3-D) AFM image of the as-prepared PMMA/ZnS hybrid films (solvent: chloroform; monomer molar ratio: 1:50; hybrid solution concentration: 3 wt %; humidity: 85%; substrate: glass slide).

The three-dimensional (3-D) AFM image clearly exhibits hierarchical pore structures of the as-prepared PMMA/ZnS hybrid films, confirming these honeycomb-patterned films are rough enough for hydrophobicity enhancement.

1. Y. Xu, B. Zhu and Y. Xu, *Polymer*, 2005, **46**, 713-717.

2. Y. Tian, Q. Jiao, H. Ding, Y. Shi and B. Liu, *Polymer*, 2006, **47**, 3866-3873.