Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supplementary Information

Ice-phobic gummed tape with nano-cones-on-microspheres

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The supplementary information is included as follows:

Supplementary Experimental Section

Treatment of micro-spheres:

To obtain hierarchical structure, micro-spheres need to be treated well for next growth of nanostructure before strong bonding on a substrate. Poly(vinylidene fluoride)(PVDF) micro-spheres with diameter about 100 μm purchased from Solvay China Ltd. The solution of crystal seed was prepared as follows: 2 g $Zn(Ac)_2 \cdot 2H_2O$, 20 mL ethylene glycol monomethyl ether (purchased from Zhongshan Xinxin Chemical Co., Ltd., China) and 0.6 g monoethanolamine (purchased from Shanghai Zhenpin Chemical Co., Ltd., China) were mixed and stirred with a magnetic stirrer for 30 min. And the cushioning material was prepared as follows: 5 g buffer layer material and 10 mL solution of crystal seed were mixed, and then put them into the muffle furnace and kept it at 300 °C for 1 hour. Micro-spheres and the cushioning material were mixed in a certain proportion, and then, the seed was absorbed on the micro-spheres surface. The aim of this special treatment was to solve the binding force between the inorganic material (ZnO nano-hairs) and the polymer substrate (PVDF micro-spheres).

Preparation of the flexible thin film with micro-/nanostructure:

Sticking the processed PVDF micro-spheres to the tape (27.0 cm ×6.0 cm, purchased from Zhongzheng Plastic Company Co., Ltd., China). Then the tape with micro-spheres was cleaned by deionized water for 2 min, and then dried it in a drying oven. The mother liquor was prepared as follows: 0.35 g hexamethylene tetramine (purchased from Beijing Lanyi Chemical Co., Ltd., China) was mixed into 100 mL deionized water and stirred to be transparent. And then put 0.74 g $Zn(NO_3)_2 \cdot 6H_2O$ (purchased from Beijing Lanyi Chemical Co., Ltd., China) into the solution under the stirring to be transparent. Put the solution into the reactor and kept it at 90 °C for 1-10 hours. We got different nanostructured morphologies. After that, removed the substrate from the reactor and washed it with deionized water for 5 min, dried in an oven. The growth of ZnO nano-hairs was realized by a simple method on the polymer (PVDF) surface. Next, the surface was cleaned with plasma cleaning (PDC-32G, HARRICK PLSMA) at middle power for 15 min and treated with Heptadeca Fluorodecyltri-propoxysilane (FAS-17) (purchased from Shanghai Sinofluoro Chemicals Co., Ltd., China). The low-surface-energy surface could be achieved. Alternative methods above were used to obtain the Tape-PVDF-ZnO micro-/nanostructured (MN) surfaces (NP, NC and NHR). To estimate the solid fraction, the intrinsic surface, e.g., smooth steel, PVDF and PDMS surface were prepared and treated by FAS-17 under the same experimental condition (see Fig. S3).

Measurement of water contact angles (CA) and sliding-off angle (SA):

A water droplet of 6 μL in volume was used in experiment. Water contact angles (CAs) and sliding-off angles (SAs) on all surfaces were tested by the optical contact angle system (Dataphysics SCA40, Germany) with cooling stage that temperature can be controlled precisely from −10 °C to 10 °C. The optical images of droplets and dynamic processes were captured by CCD camera of optimal contact angle system. In icing delay process, the CAs on surfaces were tested at initial time of ~ 5 min, subsequently at the moment that droplets frozen and that melted ones, respectively(see Fig. 2). As for surfaces in outdoor environment (with temperature −10 °C and −20 °C) for days, the CAs were tested timely (not more than 3 min) in the same cooling stage above (Fig. S4).

Experiment of ice-phobic property:

The IPGT were placed on the cold stage that the temperature was controlled down to −10 °C ~ −15 °C by Peltier cooling controller system and the humidity was ~ 80%. The reference water droplet (6 μL) was placed on the surfaces. When the drop turned to ice, the appearance of the drop would change into a peach shape (in visual observation, transparent one was changed into opaque one). We recorded the maximum icing delay time until droplet was frozen completely. As for recovery from icing, temperature of surface on the stage was gradually raised to 10 °C, we observed how non-transparent droplets on surfaces recovered completely into transparent ones.

Estimation of solid-liquid fraction on NC surface:

The solid-liquid fraction of surface can be estimated roughly. The f' of surface is defined with $f' = \frac{n\pi r^2}{S_t}$, where f' is the apparent fraction of solid/ water calculated by planar model, n is number of solid top in unit area, r is the average radius of the top of structure, and S_t is the total selected area. As for estimation on NC surface, the selected area $S_t \sim 100$ μm^2 (with the length and width of 10 μm, respectively), $r \approx 100$ nm, $n \approx 180$. It is estimated $f' \approx 0.056$. The ratio of micro-/nano-pocket is estimated with $\eta > (1-f') \times 100\%$.

Supplementary Figure Legend

Figure S1:

Figure S1. **The illustration of IPGT fabrication processes**. The poly (vinylidene fluoride) PVDF microspheres mixed with buffer layer materials together, and then bonded them to the tape via adhering. After ZnO crystal growth via hydrothermal method, the micro/nano-scale composite structures were fabricated successfully.

Figure S2:

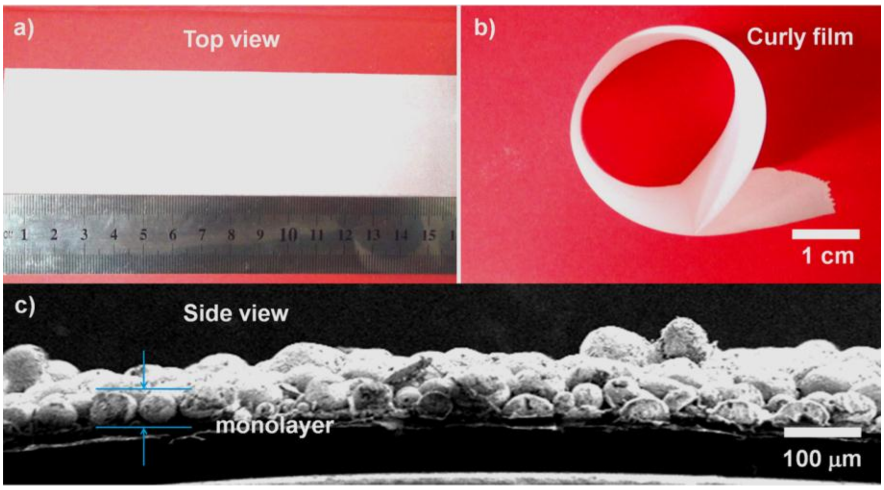

Figure S2. Photos and SEM images of IPGT. **a–b**) Photos of IPGT. IPGT has a large scale (a) and flexible property (b). **c**) SEM image of IPGT from side view. The micro-spheres are spread with monolayer on the substrate surface. The thickness of monolayer is not more than 200 μm.

Figure S3:

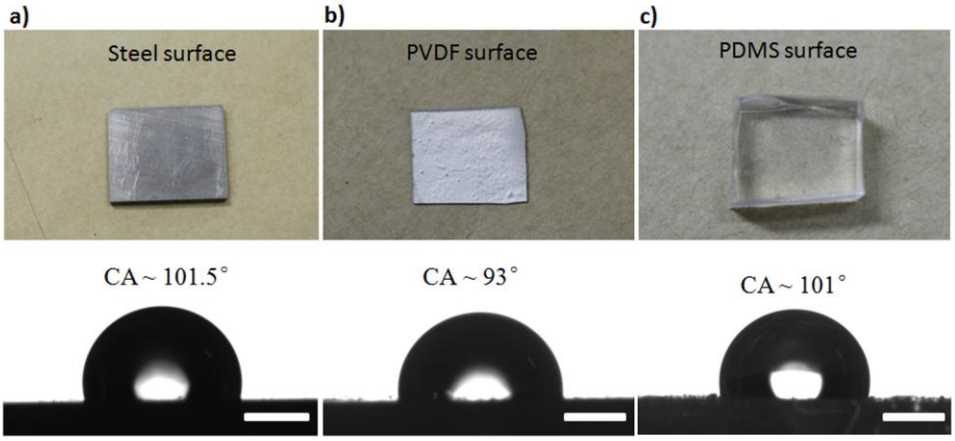

Figure S3 Optical images of droplet (~ 6 μL in volumes) on smooth surfaces (a) steel, (b) PVDF and (c) PDMS. There are contact angles (CAs) of (a) ~ 101.5°, (b) ~ 93° and (c) ~ 101°, respectively. The CA ~ 93° on smooth PVDF surface is used to estimate the solid fraction from Eq.(1). The scale bars are 1mm.

Figure S4:

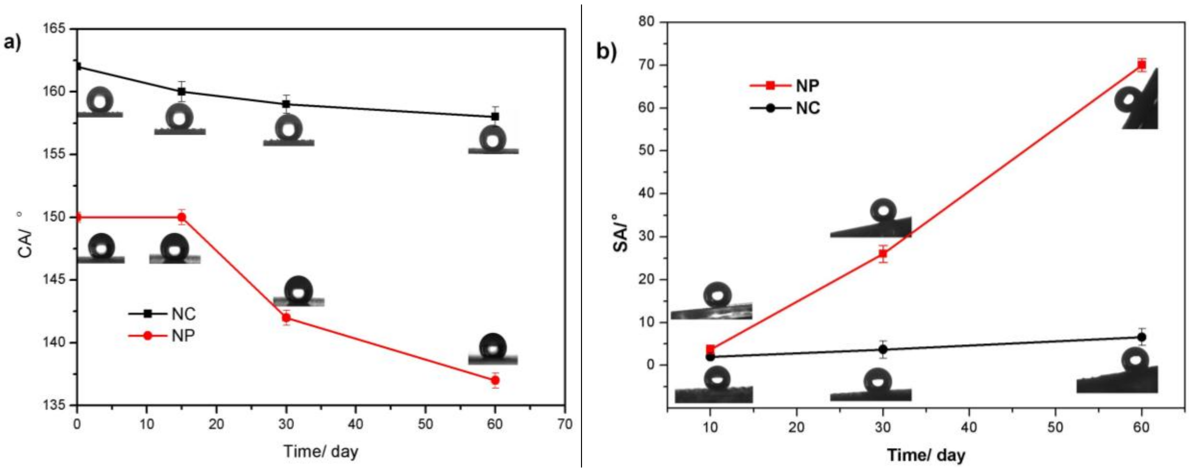

Figure S4. **Wetting properties on NC and NP surface**s. **a**) The changes of CAs after days in outdoor environment (between –10 °C and –20 °C). After 60 days, the CAs of NC surfaces decrease from ~ 162° to ~ 156°, but the CAs of NP surfaces decrease sharply from ~ 150° to ~ 137°. The insets are the optical images of water droplets. **b**) The changes of sliding-off angles (SAs) versus days. The SAs of droplets are all less than 5° at the initial state. After 60 days, the SAs change to ~ 6° on the NC surfaces, but the SAs increase rapidly and even pin on NP surface. The insets are the optimal images of droplet sliding-off. The droplets are ~ 6 µL in volumes.

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Figure S5:

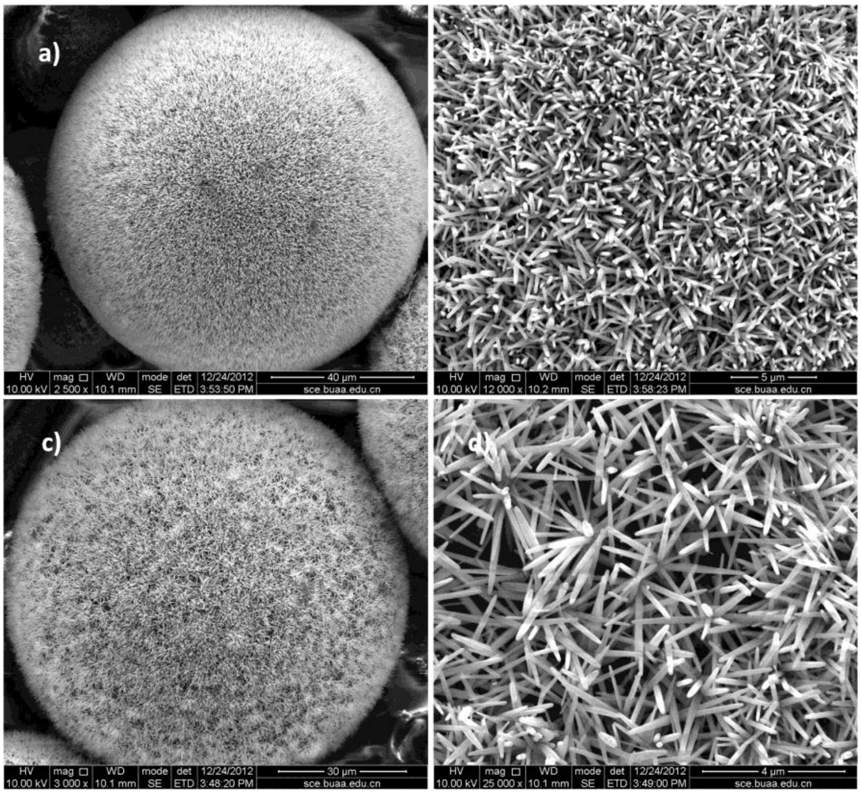

Figure S5. a-b) SEM images of the microsphere on NC surface after stayed in cold outdoor environment for 60 days, the single microsphere is surrounded with nano-cone structure (a) and nano-cone structure on microsphere (b). **c-d**) SEM images of the microsphere on NC surface repetitively used on icing/ melting process for 50 times. The microsphere is still surrounded excellently with nano-cone (c) due to the soft materials (belt and PVDF), and the nano-structures on microsphere are not broken (d), which is the mainly reason for durability in harsh conditions.