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Electronic Supplementary Information for

Bioinspired heterostructured bead-on-string fibers via controlling wet-assembly of nanoparticles

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This ESI contains:

Experimental Section

Supplementary Figures S1-S6

Supplementary Movie S1

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Experimental Section

Preparation of Materials: This electrospinning setup (Micro & Nano Technology Expert in Shenzhen, China) was used to fabricate the fiber. Firstly, the polymer solution was prepared by using an injected fluid of a 5% (w/v) PMMA (poly-(methyl methacrylate), Mw = 300000) solution in a solvent of N, N-dimethyl formamide (DMF) and then it was loaded into a 10 mL syringe, connecting a needle with its diameter of 0.9 mm by a poly-ethylene tube. The fluid was fed at a flow rate of 1 mL h^{-1}. An aluminum shelf (length×width×height of 2.5 cm ×1 cm × 1 cm) was used to collect sample with the distance from the needle to the shelf of ~ 20 cm. The voltage to make electrospinning fiber was set at 15kV. Secondly, the fog flow of hybrid nanoparticles can be made by the titanium tetrachloride ($TiCl_4$) hydrolysis as follows:

$TiCl_4 \cdot 5H_2O \rightarrow TiOHCl_3 \cdot 4H_2O + HCl\uparrow$

$\rightarrow Ti(OH)_2Cl_2 \cdot 3H_2O + HCl\uparrow$

$\rightarrow Ti(OH)_3Cl \cdot 2H_2O + HCl\uparrow$

$\rightarrow Ti(OH)_4 \cdot 3H_2O + HCl\uparrow$

The different concentration fog flows were realized by using with different volumes (e.g., 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, and 1.4 mL) of $TiCl_4$.

In addition, another pure nanoparticles as fog flow in control experiment were made by using TiO_2 nanoparticles (P25, Degussa-Huls) or ZnO nanoparticles (diameter of ~100 nm, Aladdin Industrial Corp.).

Thirdly, the electrospinning PMMA fiber was placed in the mist with above fog flows, e.g., $Ti(OH)_n^+$ nanoparticles, TiO_2 nanoparticles and ZnO nanoparticles. Thus nanoparticles-on-fibers with different densities were obtained for subsequent preparation of BHBFs.

Wet-assembly of BHBF: As for wet-assembly, relative humidity (RH) was controlled from 50% to 90% by Ultrasonic nebulizer NB-150U. The nanoparticles-on-fibers were placed

horizontally on holder in mist with fog flows in RH for a lasting wetting-period ranging from 2 s to 16 s. Subsequently, nanoparticles-on-fiber was assembled into nanoparticle-in-droplets-on-fiber during water condensation and water coalescence. After dried in ambient environment, "bead-on-string" structure was formed. By controlling the RH (from 60%, 65%, 70%, and 75% to 80%) and wetting times (from 6 s to 14 s), the volume and periodicity of bead-on-string were controlled easily. The multi-stage wet-assembly with repeated periods above was used to control the size of BHBFs. Thus excellent BHBFs were tailored successfully.

Water collection efficiency: Five kinds of BHBFs are placed horizontally in a vertical-down fog flow in a constant period. A scaling law of water droplet growth is used to estimate water collection efficiency η, i.e., $\eta=dV/dt=nSV_M$, where dV is volume of droplet, dt is wetting time S is effective collection surface of the droplet, V_M is molar volume of liquid and n is the number of moles of liquid. In our experiment, η can be characterized with the water volume V_w at maximum within a given wetting time, $\eta=V_w/t = 4/3\pi(r_w)^3/t$, where r_w is the radius of droplet and t is the wetting time.

Characterization: Structures of BHBFs were observed by scanning electron microscope (SEM, Quanta FEG 250, FEI) at 10 kV. Characteristic element mapping analysis were collected using an X-Max Silicon Drift Detector (Oxford Instruments) EDS detector. The signals of Ti in the spectra were used for EDS chemical mapping. The water collection of fibers was observed by an OCAmicro40 contact angle meter system (Data-Physics, Germany) at ambient temperature, utilizing an ultrasonic nebulizer. Water drops with a threshold volume just as detached off BHBF was recorded by CCD camera of OCAmicro40 contact angle meter system. Curves were plotted by originPro8 software. The linear fitting and statistics error were obtained by analyst of OriginPro8.

Supplementary Figures

Figure S1.

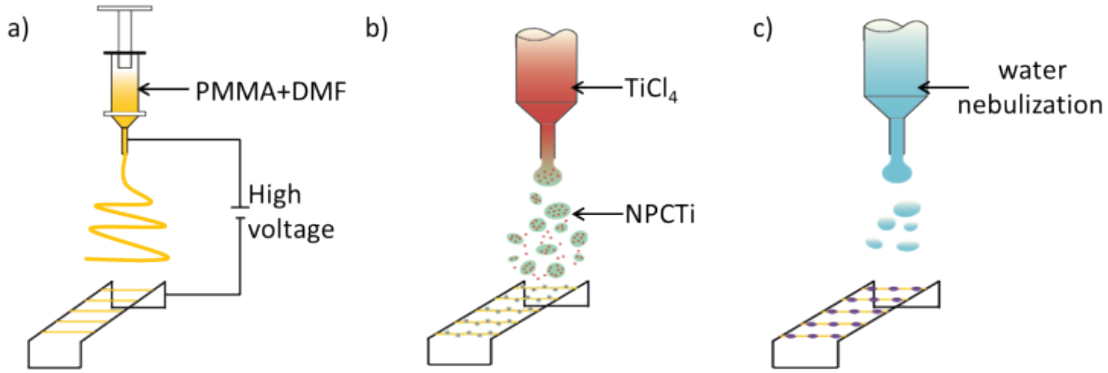

Figure S1. Schematic set-up of fabricating electrospun BHBFs. a) Schematic illustration of electrospun PMMA fibers. b) Schematic illustration of the hydrolysis of $TiCl_4$. Hydrolysis of $TiCl_4$ is expected to be quite fast and NPCTi are formed as white smoke in the hood which are modified as dust and smoke in the environment. c) Schematic illustration of wetting test. Relative humidity is adjustable by vapor pressure at a given temperature. The distance between the jet and shelf is 5 cm, and by tuning water vapor speed and volume, different RH can be achieved.

Figure S2.

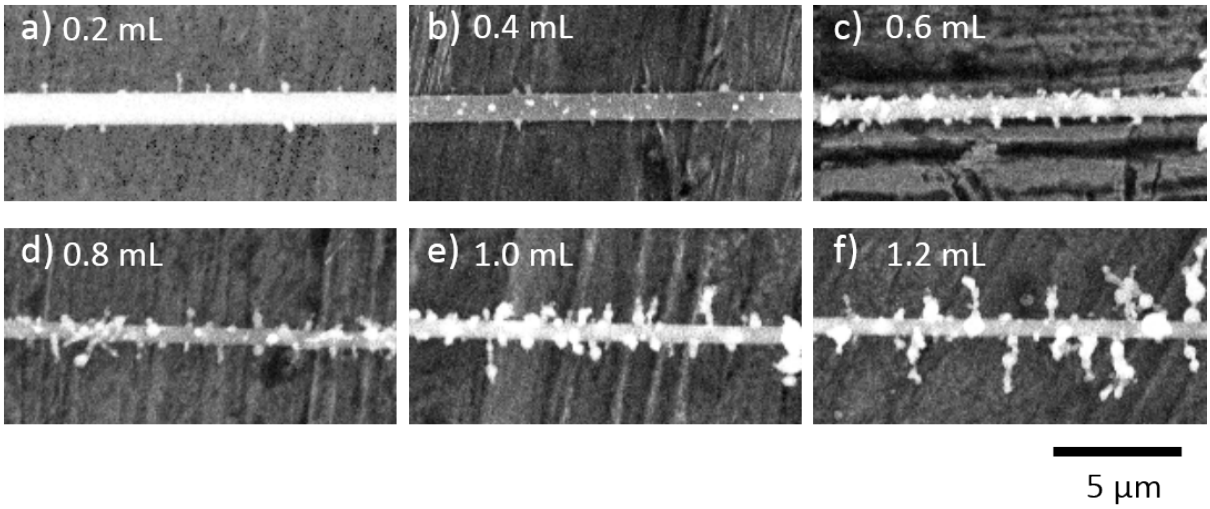

Figure S2. SEM images of nanoparticles on PMMA fibers via hydrolyzation of $TiCl_4$. Density of nanoparticle can be controlled by volumes from a) 0.2 mL, b) 0.4 mL, c) 0.6 mL,d) 0.8 mL, e) 1.0 mL to f) 1.2 mL of $TiCl_4$ to be hydrolyzed. The dense nanoparticle-coated fibers favor effectively formation of BHBF with excellent ″bead-on-string″ structures.

Figure S3.

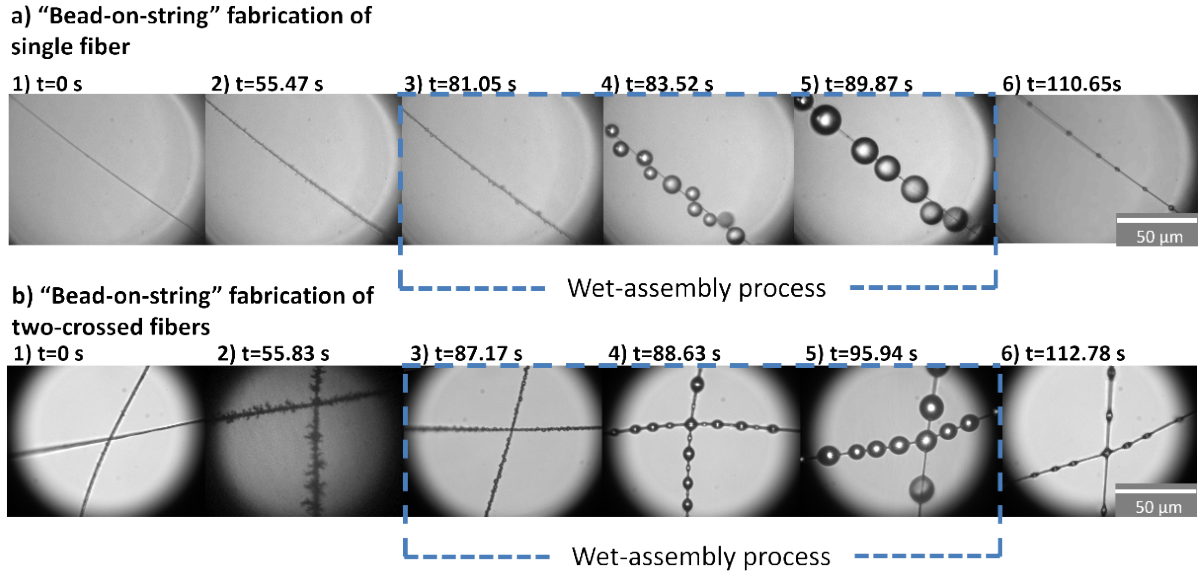

Figure S3. In-situ observation of "bead-on-string" fabrication on single and two-crossed fibers a) Observed on single fiber: 1) As-prepared electrospun PMMA single fiber is fabricated at ~0 s. 2) Nanoparticles are adsorbed on fiber at ~55.47 s. 3-5) Water condenses on PMMA-Ti fibers to form small droplets at ~81.05 s and water droplets coalesces into bigger droplets from ~81.05 s to ~89.87 s in a wet-assembly process. 6) A single fiber with "bead-on-string" structure is fabricated after drying at ~110.65 s. b) Observed on two-crossed fibers: 1) As-prepared electrospun PMMA contact fibers are fabricated at ~0 s. 2) Nanoparticles are adsorbed on fibers at ~55.83 s. 3-5) Water condenses on PMMA-Ti fibers to form small droplets at ~87.17 s and water droplets coalesces into bigger droplets from ~88.63 s to ~95.94 s in a wet-assembly process. 6) Contact fibers with "bead-on-string" structure are fabricated after drying at ~112.78 s. Images above illustrate the two-crossed electrospun fibers which exhibit correlate data compared with single fibers. RH of 70% and wetting time of 8 s is kept during wet-assembly.

Figure S4

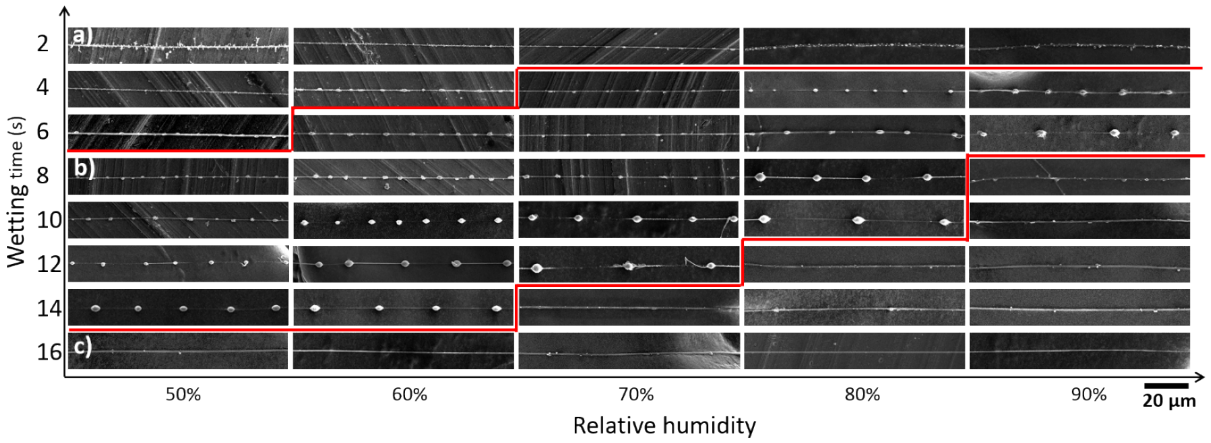

Figure S4. SEM images of "bead-on-string" structure at different conditions (humidity and wetting period) in single adsorption-wetting-drying process. The relative humidity increased from 50%, 60%, 70%, 80% to 90% versus wetting time 2 s, 4 s, 6 s, 8 s, 10 s, 12 s, 14 s and 16 s. In the images of a), where the humidity is too low or the wetting time is too short to form BHBF, nanoparticles are still scattered along fiber. In the images of c), where the humidity is too high or the wetting time is too long to form BHBF, no obvious "bead-on-string" structure appears on the fiber. The reason could be that during the droplet condensation process in a higher humid or longer wetting time, larger droplets containing nanoparticles may drop off fiber and little nanoparticles remain. In the images of b), where the wetting time and humidity are optimized, "bead-on-string" structure forms successfully.

Figure S5

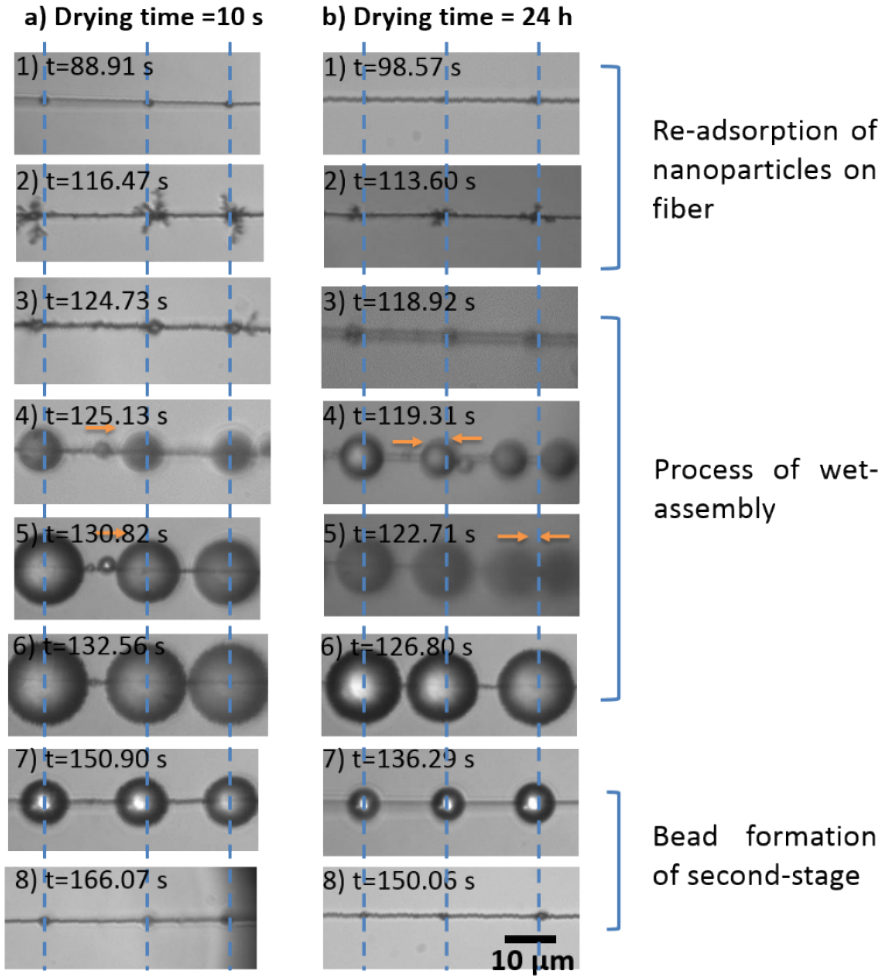

Figure S5 Optical images of second-stage adsorption-wetting-drying process on fiber via different drying times. a) The case on fiber with beads in drying time of 10 s. 1) Optical image is obtained after drying 10 s. 2) Nanoparticles are adsorbed at the water-air interface at ~116.47 s. 3-6) Water condenses and coalesces around bead from ~124.73 s to ~132.56 s. 7-8) There appears bead-on-string structure after water-evaporation at ~166.07 s. **b) The case on fiber with beads in drying time of 24 h.** 1) Optical image is obtained after drying 24 h. 2) Nanoparticles are adsorbed at the water-air interface at ~113.60 s. 3-6) Water condenses and coalesces around bead from ~118.92 s to ~126.80 s. 7-8) There appears bead-on-string structure after water-evaporation at 150.06 s. The hydrophility of NPCTi will accelerate wet-assembly due to the energy gradient arisen from a difference of Ti between "bead" and "string". It is supposed that the adsorption of nanoparticles on the water-air interface would act a significant and synergistic role during the wet-assembly. RH of 65% and wetting time of 8 s is kept during wet-assembly.

Figure S6.

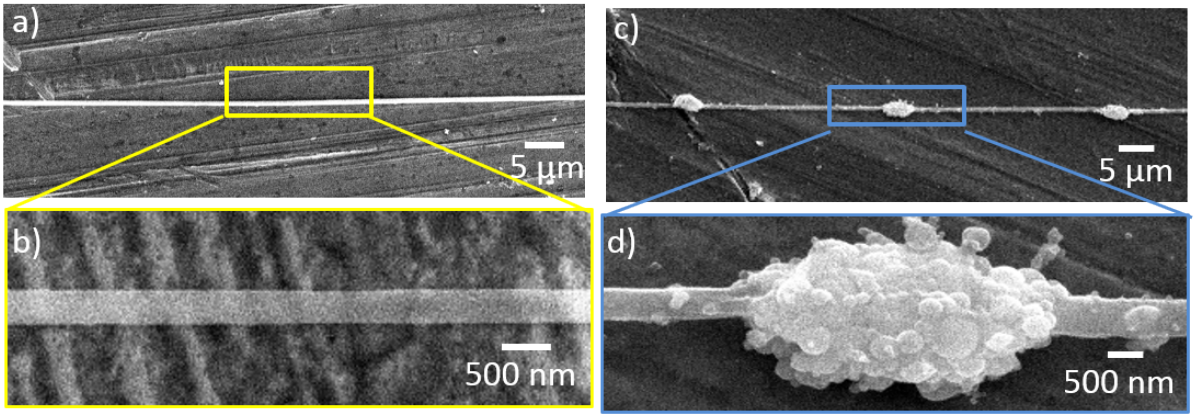

Figure S6. SEM images of bare PMMA fiber dealt by wetting for 10 s at the RH of 70%. a) SEM image of bare PMMA fiber after wetting. b) Magnified SEM image of bare PMMA fiber after wetting. c) SEM image of BHBF dealt by wetting for 10 s at the RH of 70%. d) Magnified SEM image of BHBF after wetting.

Figure S7.

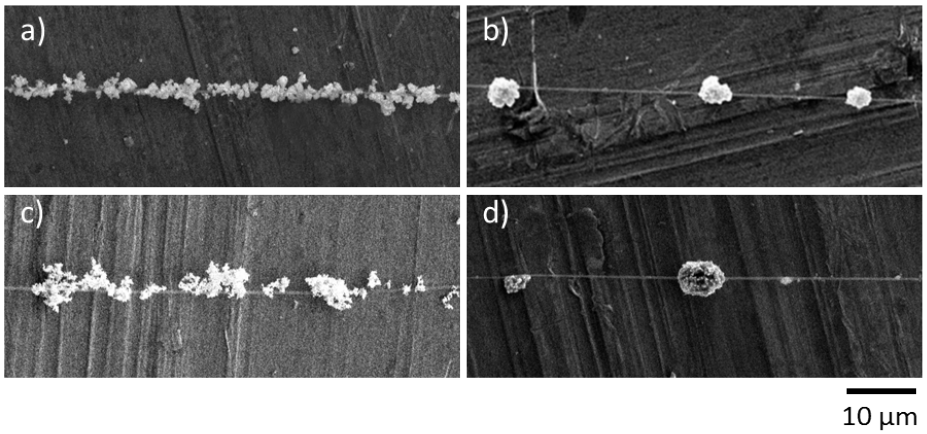

Figure S7. SEM images of bead-on-string formation via wet-assembly of TiO_2 and ZnO nanoparticles. Fog flows of TiO_2 (0.5 g) and ZnO nanoparticles (0.5 g) are maded by blowing N_2 gas. Wet-assembly is under humidity of 70% for 10 s. The unform fiber is PMMA electronspinning fiber. a) Nanoparticle TiO_2 is adsorbed on PMMA fiber. b) Bead-on-string is formed via wet-assembly during water condensation and coalescence. Bead is composed of nanoparticle TiO_2. c) Nanoparticle ZnO is adsorbed on PMMA fiber. d) Bead-on-string is formed via wet-assembly during water condensation and coalescence. Bead is composed of nanoparticle ZnO.

Supplementary Movie

Movie S1: The dynamic process of multi-stage wet-assembly for BHBF.