

## Electronic Supplementary Information

### **Superhydrophobic Polyaniline Hollow Spheres with Mesoporous Brain-like Convex-fold Shell Textures**

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## Experimental Section

**Materials:** The aniline monomer, ammonium persulfate (APS), perfluorooctanoic acid (PFOA), chloroform and ethanol were purchased from Sigma Aldrich. All reagents were used as received. Deionized water was applied for all experimental process.

**PANI synthesis:** PANI materials were prepared by three different polymerization approaches, namely micelles-mediated phase transfer (MMPT) method, interfacial polymerization and emulsion polymerization method.

The typical MMPT polymerization process is as follows: PFOA was firstly dissolved in 4 mL chloroform, and 3.5 mL aniline solution dissolved in chloroform was added under ultrasonic stirring to form a uniform emulsion of PFOA/aniline salt. 7.5 mL aqueous solution of APS was then added. The mixture was vigorously up and down shaken for 5 min and ultrasonic stirred for 30 min. Finally the reaction was left at room temperature ( $20\pm 2$  °C) for 20 h.

For the interfacial route, 7.5 mL APS in aqueous solution was carefully added to chloroform solution of PFOA/aniline (7.5 mL) without disturbing the interfacial. The interfacial polymerization was allowed to stand at room temperature ( $20\pm 2$  °C) for 20 h without disturbing.

Emulsion polymerization was performed by mixing PFOA, aniline and APS in aqueous phase. The solution was allowed to stand at room temperature ( $20\pm 2$  °C) for 20 h.

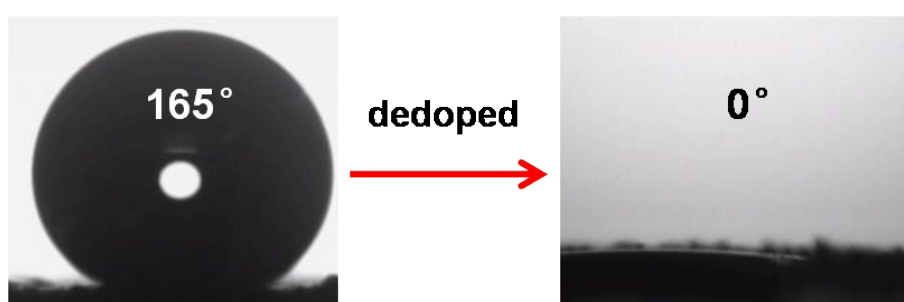
The resultant PANI precipitate was washed with water and ethanol to remove aniline oligomers and monomers, and dried in a dynamic vacuum at 60 °C for 48 h.

The yield of PANI was obtained by the ratio of PANI (after dedoped by ammonium hydroxide) to the initial aniline weight.

**Characterizations:** The morphologies of as-prepared PANI were characterized by a field-emission scanning electron microscope (SEM, JEOL-7401) with a sputter-coated gold layer on the sample surface. The statistical analysis of SEM image was performed with ImageJ software. Transmission electron microscopy (TEM) samples were prepared by placing a drop of sample suspended in ethanol on carbon-coated copper TEM grids and further characterized by FEI scanning TEM with an accelerating voltage of 120 kV. The elemental composition of PANI was inspected by energy dispersive X-ray spectrometer (EDX) and X-ray photoelectron spectroscopy (XPS). XPS was carried out on a PHI VersaProbe II Scanning XPS Microprobe using Al K $\alpha$  line excitation source. The Fourier transform infrared (FT-IR) spectra were collected on a Digilab Excalibur FTS 3000 series FT-IR spectrometer with a resolution of 1 cm<sup>-1</sup> using KBr pressed disks. The UV-vis spectra of PANI spheres in ethanol were measured on a Hitachi 4100 UV-vis spectrophotometer. The contact angles of distilled water and glycerin were determined by the sessile drop technique on a Rame-Hart contact angle goniometer. At least five samples were measured in order to obtain the average values of contact angles.

The cyclic voltammogram tests were carried out in 1 M H<sub>2</sub>SO<sub>4</sub> on an electrochemical workstation (METEK VersaSTAR 4) with a scan rate of 0.05 V/s in the potential range from -0.2 V to 1.0 V. The working electrode of PANI-deposited glass carbon electrode with a geometric area of about 0.72 cm<sup>2</sup> was measured in a one-compartment cell equipped with a platinum wire counter electrode and saturated calomel electrode (SCE) reference electrode. Thermal analysis was performed using a TA Q500 thermal gravimetric analyzer. Samples were heated under N<sub>2</sub> from 50 °C to

800 °C at a rate of 10 °C/min. Specific surface areas and pore-size distributions were measured by N<sub>2</sub> adsorption at 77.4 K with an automatic adsorption system (TriStar II). Prior to each measurement, samples were degassed at 90 °C for 12 h under high vacuum (<0.01 mbar). The pore size distribution was calculated by the Barrett-Joyner-Halenda (BJH) method using desorption isotherms.

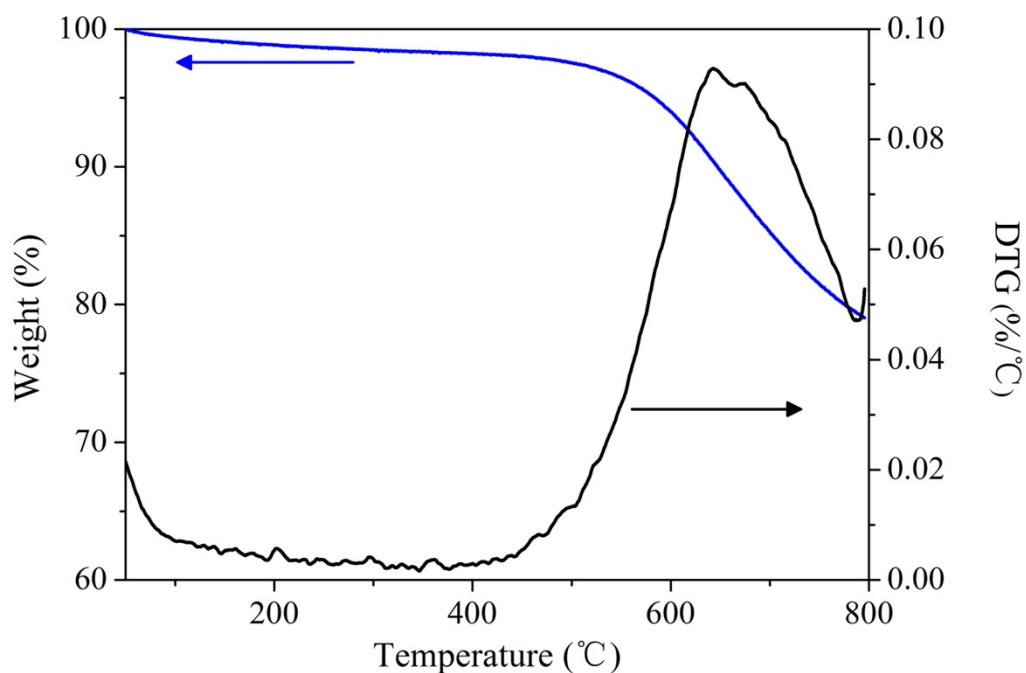


**Figure S1.** Photographs of the water droplet shape on the PANI surface before (left) and after (right) de-doping treatment.

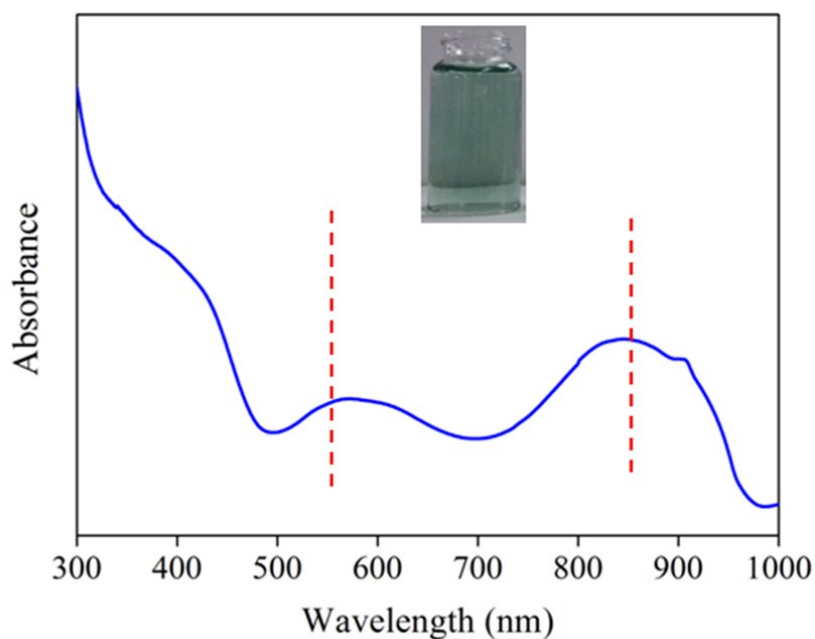
**Table S1.** Specific surface areas reported for porous polyaniline with various morphologies<sup>a)</sup>

Morphology	Surface area (m <sup>2</sup> /g)	Sources
Mesh-like	630	Ref. 1
Hollow spheres	385	Ref. 2
Nanofibers	55	Ref. 3
Nanofibers	49	Ref. 4
Urchin-like microspheres	24.5	Ref. 5

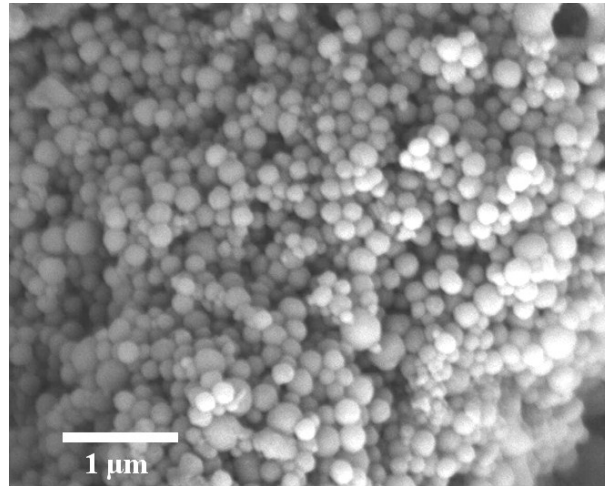
<sup>a)</sup> The polyaniline using porous material as template is not considered since the majority of the resulting material is not polyaniline.



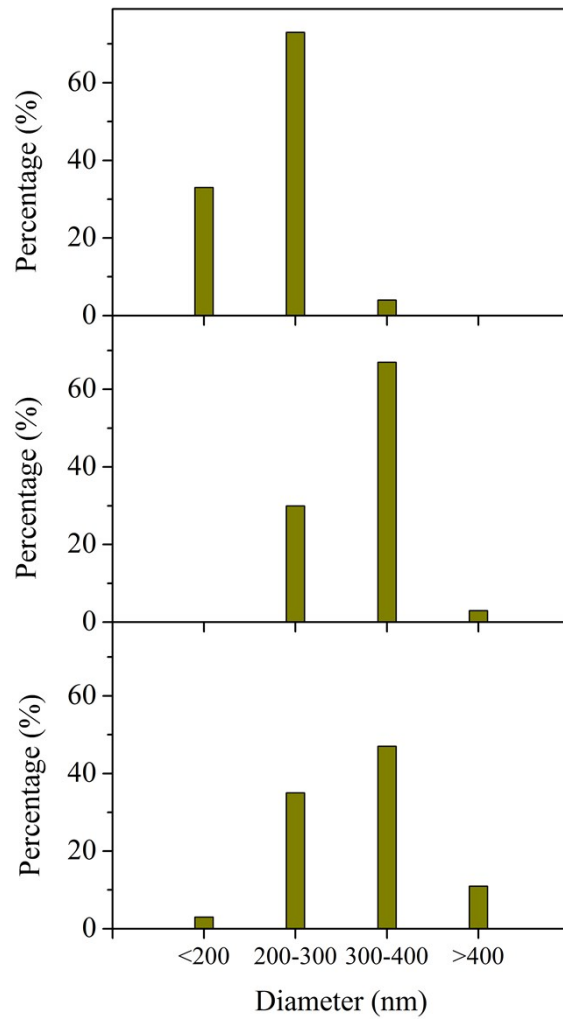
**Figure S2.** TG (thermogravimetry) and DTG (derivative thermogravimetry) of brain-like PANI hollow spheres. Conditions: PFOA:aniline:APS=1:1:1, PFOA=10 mM, polymerization time=20 h.



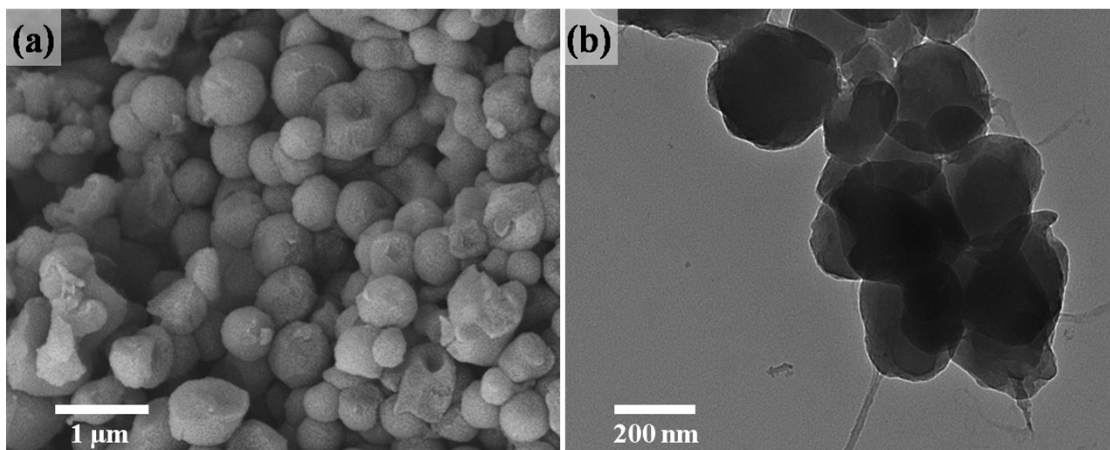
**Figure S3.** UV-vis spectrum and photo (inset) of the brain-like PANI hollow spheres in ethanol. Conditions: PFOA:aniline:APS=1:1:1, PFOA=10 mM, polymerization time=20 h.



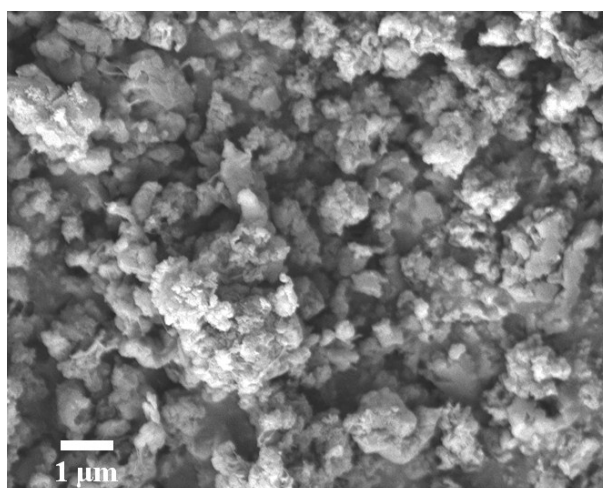
**Figure S4.** SEM image of the brain-like hollow PANI spheres. Conditions: PFOA:aniline:APS=1:1:1, PFOA=10 mM, polymerization time=5 h.



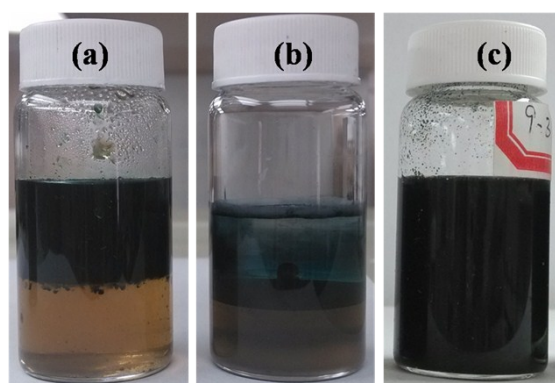
**Figure S5.** Particle size distribution of PANI spheres after 5 h (a), 12 h (b) and 20 h (c). Conditions: PFOA:aniline:APS=1:1:1, PFOA=10 mM.



**Figure S6.** (a) SEM and (b) TEM images of PANI spheres. Conditions: PFOA:aniline:APS=0.25:1:1, PFOA=2.5 mM, polymerization time=20 h.



**Figure S7.** SEM image of PANI materials. Conditions: PFOA:aniline:APS=2:1:1, PFOA=20 mM, polymerization time=20 h.



**Figure S8.** Photos of PANI via (a) micelles-mediated phase transfer method, (b) interfacial polymerization method and (c) emulsion polymerization method. Conditions: PFOA:aniline:APS=1:1:1, PFOA=10 mM, polymerization time=20 h.



**Figure S9.** SEM image of PANI spheres via interfacial polymerization route. Conditions: PFOA:aniline:APS=1:1:1, PFOA=10 mM, polymerization time=20 h.

**References:**

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