Supplementary Information

PANI Nanowire Film with Underwater Superoleophobicity a nd Potential-Modulated Tunable Adhesion for No Loss Oil Droplet Transpor

Chunmei Ding,[a] Ying Zhu,*[a] Mingjie Liu,[b] Lin Feng,*[c] Meixiang Wan,[b] and Lei Jiang[a,b]

[a] Key Laboratory of Bio-inspired Smart Interfacial Science and Technology of Ministry of Education, School of Chemistry and Environment, BeiHang University, Beijing, 100191 P. R. China. E-mail:zhuying@buaa.edu.cn

[b] Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences

[c] Department of Chemistry, Tsinghua University, Beijing, 100084 P. R. China. E-mail: fl@mail.tsinghua.edu.cn

Experimental Section

***Materials*:** Aniline (Beijing Chemical Co.) was distilled under vacuum before using. Perchloric acid ($HClO_4$) and other chemicals were commercially available analytical grade reagents (Beijing Chemical Co.) and were used without further purification. Ultrapure water (18.2 MΩ·cm) was acquired by using a Millie-Q water purification system from Millipore.

***Preparation of PANI nanowires film*:** Perchloric acid doped PANI films were synthesized using the electrochemical oxidative polymerization by a galvanostatic current procedure. The Au-coated silicon wafer was used as a working electrode to prepare aligned PANI film by Galvan static current procedure (0.01 $mA \cdot cm^{-2}$, an hour) in the electrolyte solution containing 0.1 $mol \cdot L^{-1}$ aniline and 1 $mol \cdot L^{-1}$ $HClO_4$. A platinum plate and saturated calomel electrode (SCE) were used as counter and reference electrodes respectively. After electrochemical polymerization, the working electrode was taken out from the electrolyte solution, washed with ultrapure water, ethanol and ether in turn and then dried under air for further characterization.

***Characterization*:** The morphology of the as-prepared film was investigated by field-emission scanning electronic microscope (SEM) (JEOL 6700F, Japan). A cyclic voltammogram (CV) measurement of the PANI film was carried out at the scan rate 30 $mV \cdot s^{-1}$ in 0.1 $mol \cdot L^{-1}$ perchloric acid ($HClO_4$) electrolyte, saturated calomel electrode (SCE) as reference electrode. Oil contact angles (CA) were characterized using a data-physics OCA20 contact angle system (Data-Physics, Germany) combined with the electricity workstation (State Key Laboratory of Electroanalytical

Chemistry, Changchun Institute of Applied Chemistry) in the electrolyte solution. Drops of 1.5 μL 1, 2-dichloroethane were used as the probe liquids for the CA measurements, and the values reported were the average of at least five drops per sample at different locations. Oil contact angles at applied potential were measured using three-electrode system consisting of the saturated calomel electrode and a platinum wire as reference and counter electrodes, respectively. The as-prepared PANI nanowire film was used as the working electrode and was mounted on the bottom of the reactor. The adhesive force that prevented the oil droplet being drawn away from the surface was measured by using a high-sensitivity microelectromechanical balance system (Data-Physics DCAT 11, Germany). The PANI film was a work electrode controlled by an electrochemical station. The dynamic force change was measured underwater environment. An oil droplet (1.5 μL) was suspended with a metal ring first, and PANI film was placed in an electrochemical cell. The PANI film was moved upward at a constant speed of 0.05 $mm \cdot s^{-1}$ until the PANI film contacted with the oil droplet. When the PANI film was moved down, the force increased and the shape of the oil droplet changed from spherical to elliptical. The contact force sharply reduced and the shape of the oil changed back to spherical, after the oil droplet left PANI film. The pH values were measured using pH meter (Mettler Toledo FE20K, Switzerland). *In-situ* Raman spectroscopy was conducted using a Jobin Yvon confocal micro-Raman spectrometer (Laboratory RAM HR800) combined with electricity workstation. The Ar^+ laser

emitting at a wavelength of 514.5 nm was used as a source of excitation, the laser power was 0.3 mW.

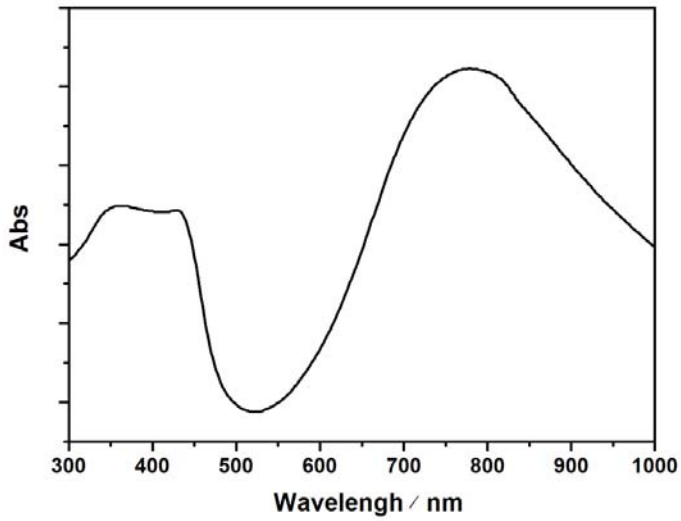

Figure S1. UV-vis spectra of the aligned PANI nanowire film in 0.1 mol·L^{-1} $HClO_4$ aqueous solution.

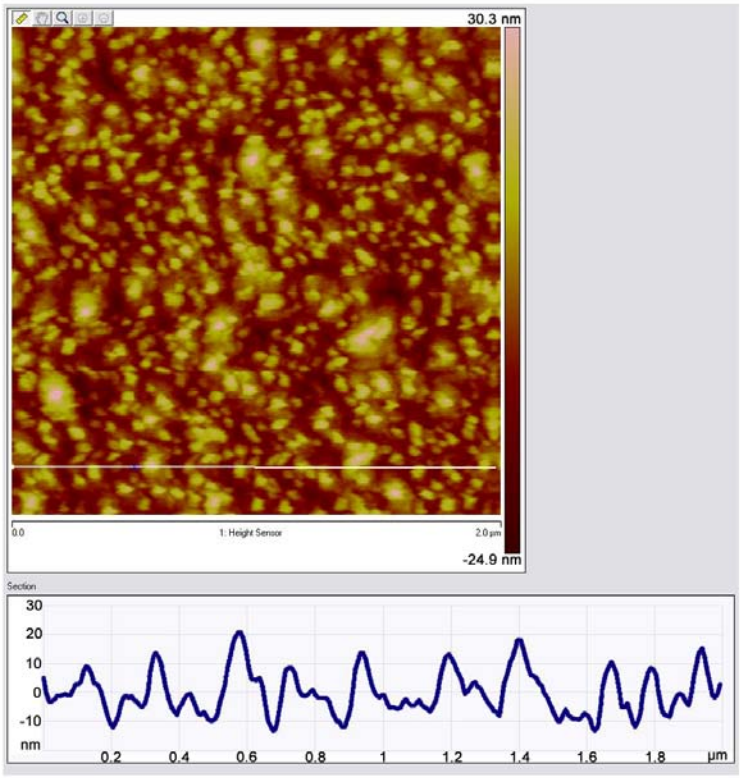

Figure S2. AFM images and corresponding height profiles of the aligned PANI nanowire film.

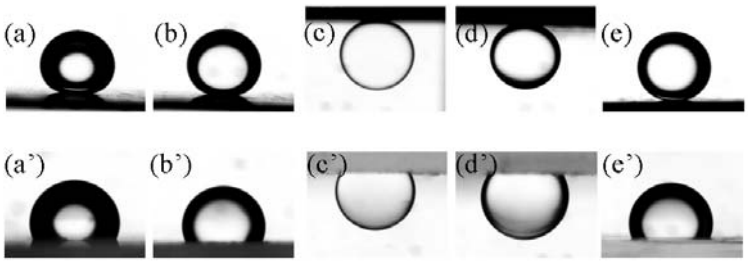

Figure S3. Contact angles of oil droplet on the aligned PANI nanowire film, a) 1,2-dibromoethane, b) chloroform, c) n-hexane, d), n-octane, e) 1, 2-dichloroethane; contact angles of oil droplet on the smooth PANI film a') 1,2-dibromoethane, b') chloroform, c') n-hexane, d') n-octane, e') 1, 2-dichloroethane.

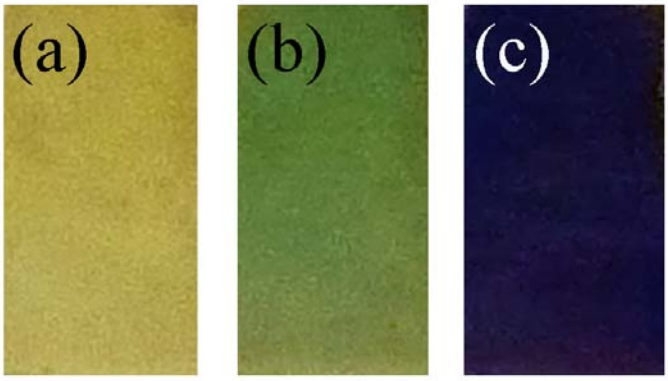

Figure S4. Photographs of the aligned PANI nanowire film at the applied potential of -0.2, 0.43, and 0.8 V (vs. SCE), showing the transparent yellow, green, and purple color, respectively.

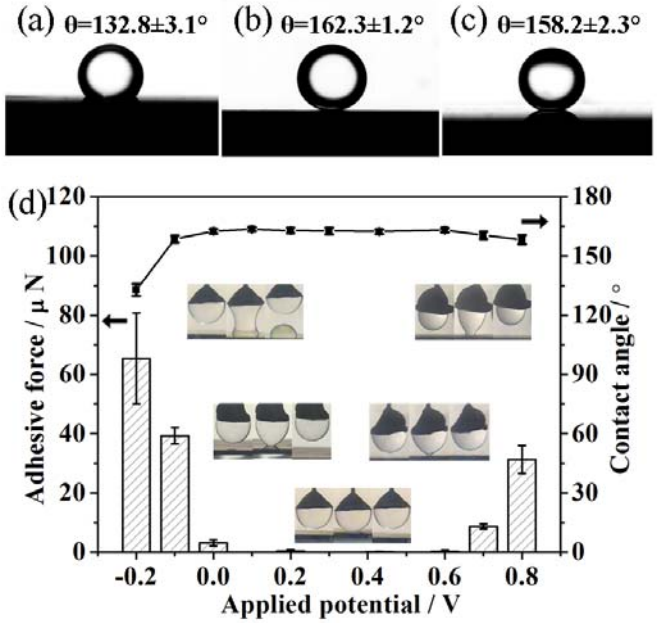

Figure S5. a), b), c) Oil droplets on the aligned PANI nanowire film in 0.1 mol·L^{-1} $LiClO_4$at the applied potential -0.2, 0.43, and 0.8 V, respectively; d) Oil droplet CA and adhesive force in 0.1 mol·L^{-1} $LiClO_4$ when PANI was at the potential ranging from -0.2 V to 0.8 V. The line graph stood for oil droplet CAs corresponding to the right vertical axis, while histogram exhibited adhesive forces corresponding to the left vertical axis. The inserted pictures are the shapes of oil droplet taken at -0.2, -0.1, 0.43, 0.7, 0.8 V during the adhesive force measurements respectively.

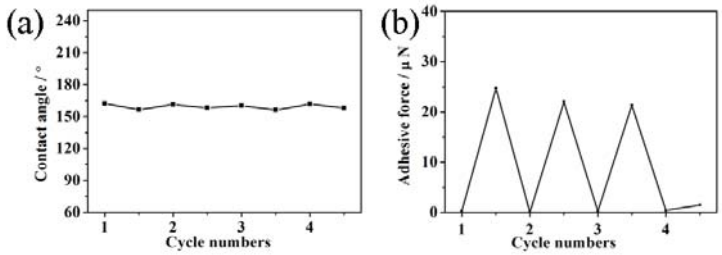

Figure S6. a) Oil contact angles and b) adhesive forces for the aligned PANI nanowire film at the applied potential of -.43 and 0.8 V.

Figure S7. Oil contact angle on the PANI nanowire film at the potential a) -0.2 V, b) 0.43 V, c) 0.8 V.

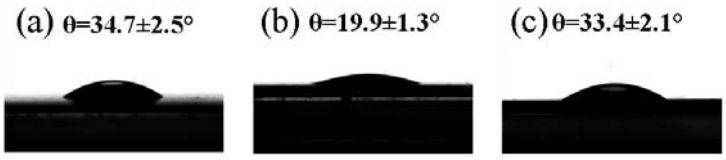

Figure S8. Water contact angles on the PANI nanowire film at the potential a) -0.2 V, b) 0.43 V, c) 0.8 V.

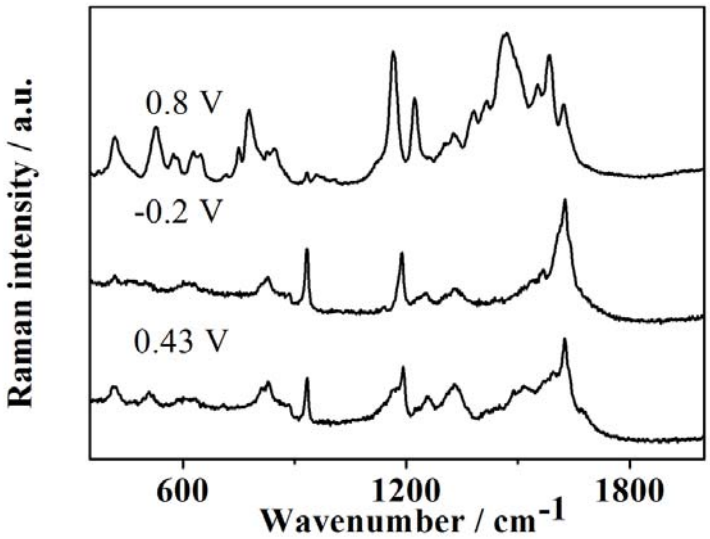

Figure S9. *In-situ* Raman spectra of PANI nanowires film by applying potential from 0.8 V to -0.2 V, in an electrolyte of pH 1.2.