Supporting Information

Revelation of the Spatial Structure of Highly Crystalline and Conducting Polyaniline Membrane Constructed by Epitaxial Growth

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Supplementary experimental procedure:

1.1. **Reagents.** Water was purified using a Milli-Q (Millipore Corp., Bedford MA) purification system with a resistivity of 18 MΩ cm. Aniline (ACROS、ACS grade) was used after distilling over calcium hydride and stored in the dark under a nitrogen atmosphere. PhOH, $HCl_{(aq)}$, 0.1 M $NH_4OH_{(aq)}$, $(NH_4)_2S_2O_8$, and HFIP (hexafloro-isopropanol) were obtained from commercial resource (Aldrich Co. USA, reagent grade) and used without further treatment. HDPE (high density polyethylene) and Kapton (polyimide) substrates were obtained from Formosa Plastic Group, Taiwan. The crystallinity of the HDPE and Kapton was evidenced with XRD patterns as shown in Figure S1.

1.2. *In-situ* polymerization/deposition of polyaniline membranes on various polymer substrates. Polyaniline membranes on HDPE and Kapton were prepared using the method reported previously.^{S1} The polymer substrate (size of 1.0 cm x 1.0 cm, one side of the substrate was protected with a tape to avoid the deposition of polymer membrane on both side of the substrate) was put into the bottom of a reaction box. $(NH_4)_2S_2O_8/HCl_{(aq)}$ was first added slowly into the reaction box followed by aniline (containing 0.01wt% phenol)/$HCl_{(aq)}$ solution at 25 ^{o}C. The concentration of $HCl_{(aq)}$ solution is 1.2 M and the mole ratio of aniline to $(NH_4)_2S_2O_8$ is 1 to 1. Polyaniline membrane grew automatically on the surface of the substrate. The growth of the polymer membrane was terminated by taking the PANI coated substrate out of the reaction box and then washed with distilled water, followed by 0.1 M $HCl_{(aq)}$. Prior to analysis, each sample was first dipped in 0.1M $NH_4OH_{(aq)}$ for 5 minutes to insure that PANI is fully dedoped to emeraldine base (EB), washed with distilled water and dried under a stream of N_2 gas. The thickness of the membrane was determined by a Veeco Instruments Dektak3 surface profile meter and the absorption intensity at 600 nm. The doping (protonation) process was carried out by dipping the EB membrane into the 1.0 M $HCl_{(aq)}$ solution and the UV/Vis/NIR spectrum was used to monitor the doping levels. When the λ_{max} of ES stopped to red-shift, the PANI membrane is defined as fully doped/protonated. The formation of Polyaniline chains on the polymer substrates was identified with IR spectrum (displayed in Figure S2) and the reversible change of the absorption spectra (illustrated in Figure S3) upon doping/dedoping with $HCl_{(aq)}/NH_4OH_{(aq)}$.

1.3. C-AFM and AFM studies: Samples for C-AFM studies were mounted, via silver paste, to the AFM sample holder. Before imaging the PANI membrane, the surface of the membrane was purged by N_2 gas to minimize the effects of the moisture. The contact mode AFM with a current-sensing module (SPA400, SEIKO Inc., Japan) was used to simultaneously obtain the morphology and current images of the PANI membrane on polymer substrate. Topographical images were recorded using the height mode with the gold-coated Si cantilevers (spring constant 0.11 N/m) purchased from Nanosensor Co., Germany. The load force was maintained at ~ 0 N to avoid the damage of the tip and sample. A bias voltage (between the PANI membrane and conducting cantilever which is grounded) used for current images is 3 mV. The bias voltage between the substrate (ITO) and conducting cantilever (which is grounded) for measuring *I-V* curve were scanned from -1.6 to 1.6 V. The electrical conductivity of each tip was verified before and after each set of experiments by measuring the tip current that flowed when the probe was placed in contact with a gold film surface under an applied bias. The data were discarded whenever the images or the tip conductivities were different before, during, or after electrical measurements. Figure S4 displayed the AFM morphology and current images of thin (140 nm) PANI membrane deposited on Kapton.

1.4. TEM studies: The samples (free polyaniline membranes) for TEM studies were prepared as the following: Polyaniline membrane on polymer substrate was dipped into HFIP (hexafloro-isopropanol) for a couple of minutes. The membrane will come off the substrate and disperse in HFIP. A very small drop of the dispersion solution was dipped in a carbon coated copper grid (sample holder for TEM imaging), repeated for several times to insure sufficient sample was deposited on the copper grid. After drying the PANI loaded copper grid in a vacuum for an hours, the sample was mounted on the TEM instrument for imaging or measuring the electron diffraction patterns right after taking from the vacuum. EDS (Energy dispersive spectroscopic) spectrum was taken at the same areas as those for SAED study to prove that the sample is the doped PANI (ES) (Figure S5). A TEM image of PANI membrane peeled from HDPE at low magnification was also displayed in Figure S6 for reference. The SAED pattern and TEM image of PANI membrane peeled from Kapton are also displayed in Figure S4.

Supplementary Figures:

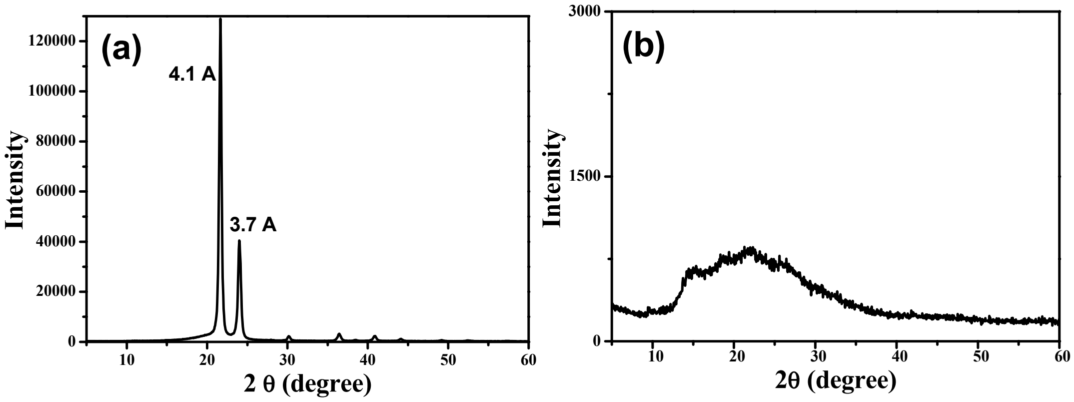

Figure S1: X-ray diffraction patterns of (a) HDPE film (b) Kapton film.

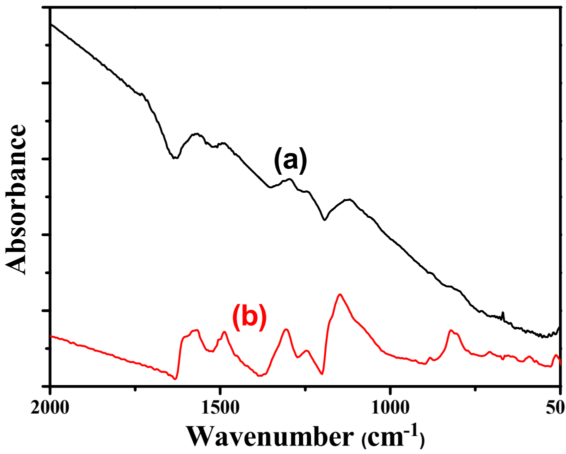

Figure S2: IR spectra of (a) PANI membrane peeled from HDPE substrate (b) PANI film on Si wafer as a reference.

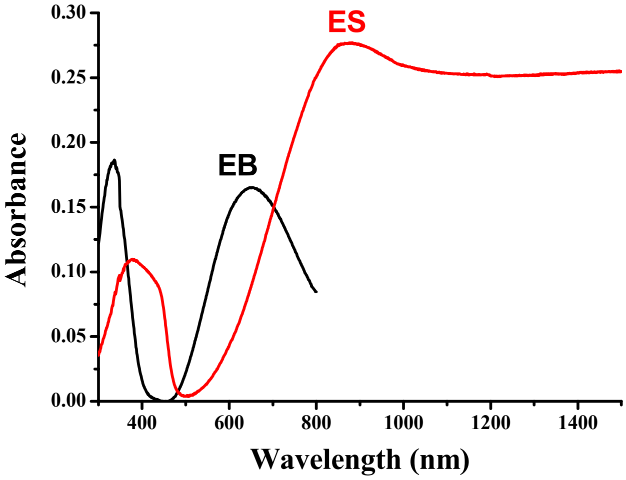

Figure S3: UV/Vis/NIR spectra of PANI membrane on HDPE at ES and EB forms.

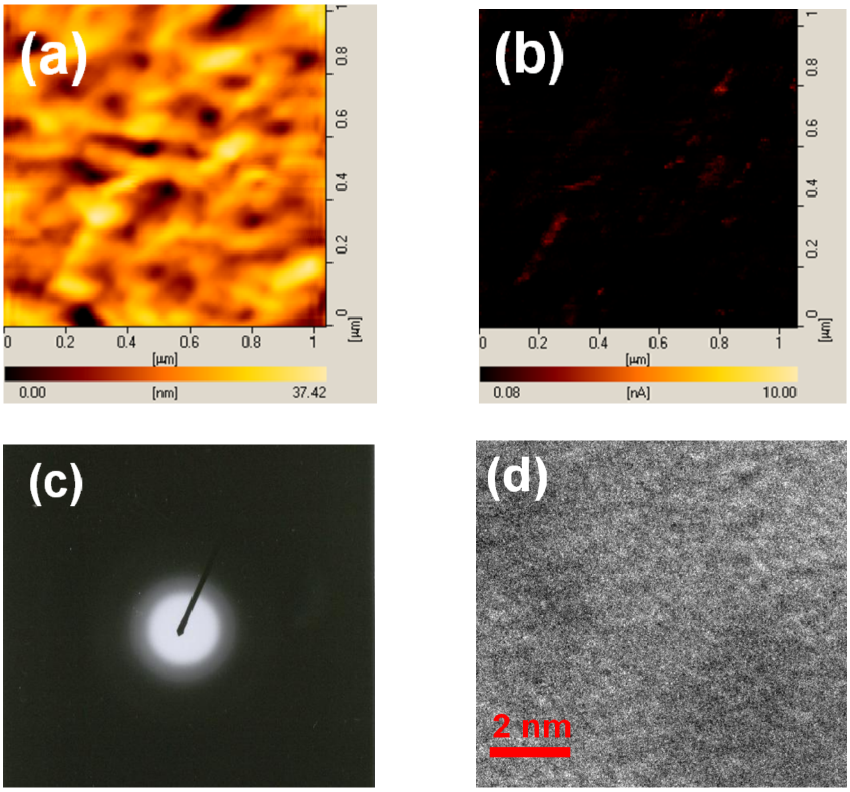

Figure S4: (a) AFM morphology (b) current image of PANI membrane deposited on Kapton, (c) SAED pattern (d) High resolution TEM image of PANI membrane peeled from Kapton.

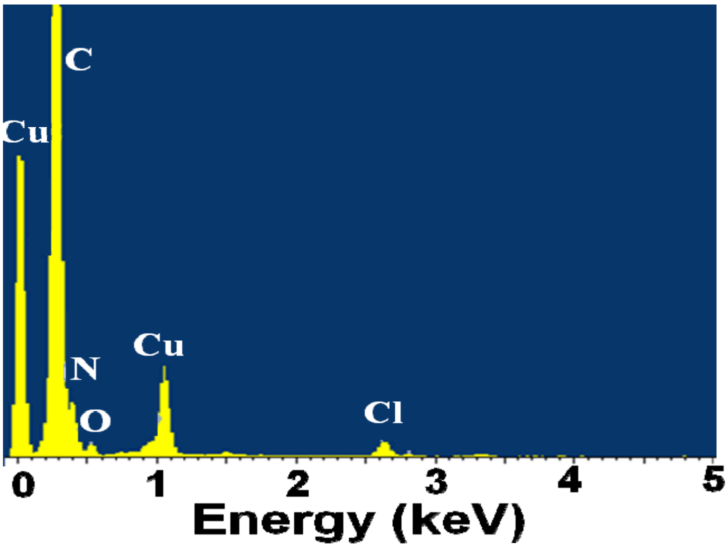

Figure S5: The (a) EDS spectrum of PANI membrane peeled from HDPE.

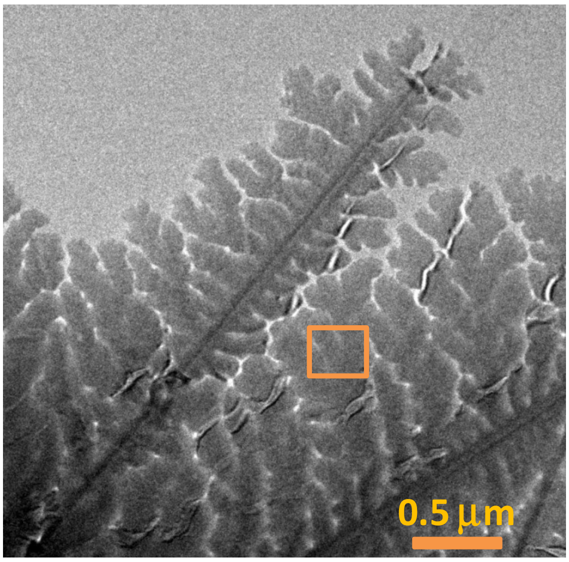

Figure S6: TEM image of PANI membrane at low magnification.

(The area inside the red square is the area where the high resolution TEM images were taken)

Reference:

S1. (a) C.-G. Wu, S.-S Chang, *J. Phys. Chem. B,* 2005, **109**, 18275. (b) C.-G. Wu, C. H. Chiang, U. S. Jeng, *J. Phys. Chem. B,* 2008, **112**, 6772.