

## Supporting Information

### Solid/Liquid Interfacial Synthesis of High Conductivity Polyaniline

Chingu Kim, Wangsuk Oh and Ji-Woong Park\*

Research Institute for Solar and Sustainable Energies (RISE), School of Materials Science and Engineering, Gwangju Institute of Science and Technology, 123, Cheomdan-gwagiro, Buk-gu, Gwangju, 500-712, Korea.

E-mail: [jiwoong@gist.ac.kr](mailto:jiwoong@gist.ac.kr)

#### Experimental Section

**Materials:** Aniline (99%, Acros) was freshly distilled under reduced pressure. D(+)-10-camphorsulfonic acid (CSA) (99%, Acros), ammonium persulfate (APS) (extra pure, Duksan), chloroform (anhydrous, 99%, Aldrich), meta-cresol (99%, Acros) and hydrochloric acid (HCl) (37%, Aldrich) were purchased and used without further purification.

**Solid/Liquid Interfacial Polymerization (SLIP) of aniline:** Aniline (3.725 g, 40 mmol) and CSA (18.584 g, 80 mmol) was dissolved in 80 ml chloroform. APS (2.282 g) was finely ground with a mortar and pestle just prior to use. The APS powder was added into the monomer solution all at once. Reaction mixture was vigorously stirred during polymerization. The molar ratio of aniline to APS, reaction temperature, and reaction time were 4 to 1, 25 °C, and 24 hours, respectively, unless otherwise mentioned. After 24 hours, the dark-green reaction mixture was washed and filtered. Polyaniline (PANI) was obtained using two different washing methods. In the first method, the mixture was precipitated into acetone, stirring for 10 min, and filtered, followed by washing with double-distilled (DI) water (SLIP-p).

In the second method, the mixture was washed several times with DI water using separatory funnel in order to extract unreacted monomer, APS, and by-products, followed by solvent evaporation. The extraction was done very quickly to prevent unwanted side-reaction. The resulting solid product was washed with acetone (SLIP-e). Dark purple emeraldine salt (ES) were obtained after drying at 60 °C for 24 hours in vacuum oven.

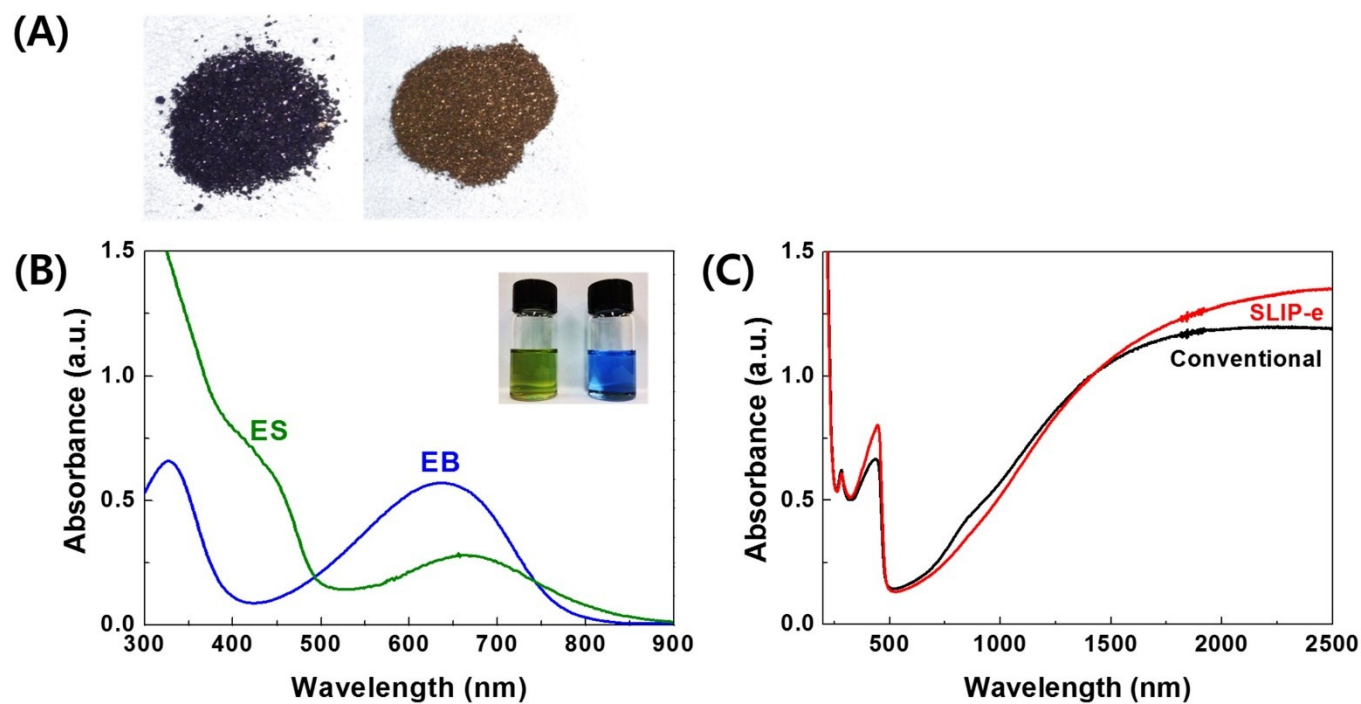
***Conventional polymerization of aniline:*** Aniline (3.725 g, 40 mmol) was dissolved in 40ml aqueous solution of 1.0 M HCl. 40ml of APS solution in 1.0 M HCl was added dropwise to the monomer solution for 10 ~ 20 min. Reaction mixture was vigorously stirred during polymerization. The molar ratio of aniline to APS and reaction time were same with SLIP method. We tried to keep the reaction temperature at 0 ~ 5 °C with ice bath, while it increased during the addition of oxidant solution. After 24 hours, the solid products was filtered, then washed with water and acetone. Dark green ES was obtained after drying at 60 °C for 24 hours in vacuum oven.

***Preparation of PANI-CSA solution:*** ES powders were dedoped with 0.1M ammonia by stirring for 24 hours. The dedoped powders were filtered, washed with DI water, acetone, and chloroform until filtrate solution was colorless, then dried at 60 °C for 24 hours in vacuum oven. The resulting emeraldine base (EB) form of PANI (0.030 g) and CSA (0.038 g) was mixed and thoroughly ground together with a mortar and pestle. The mixed PANI-CSA powder was slowly added into m-cresol to obtain 2 wt% PANI-CSA solution. The solution was vigorously stirred on hot plate at 60°C for 24 hours. Note that preparation of homogeneous solution is the most important to fabricate highly conductive PANI-CSA films with good reproducibility. The solution was filtered by syringe glass filter (Whatman, Glass Filter, pore size 2.7 µm) before use.

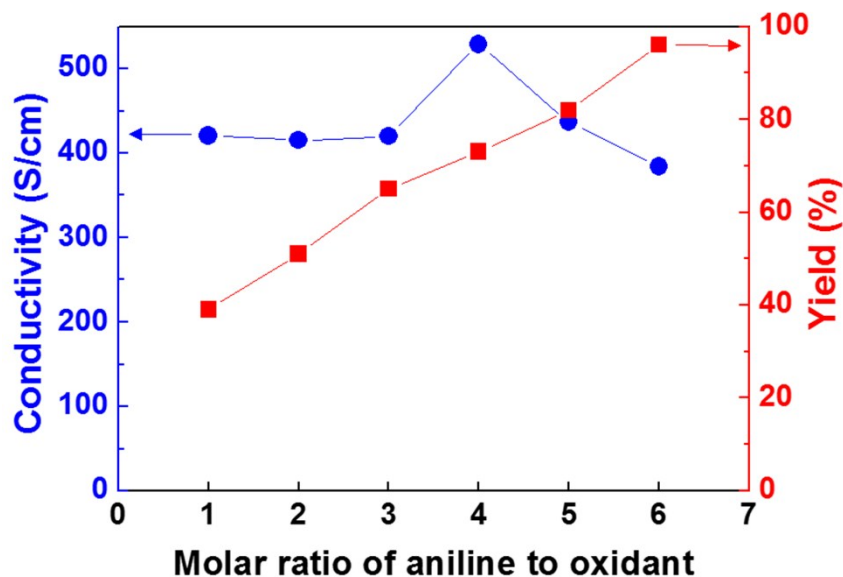
***Fabrication of PANI-CSA films:*** The PANI-CSA solution was drop-casted on the oxygen plasma

treated slide glass, and dried on hotplate (50 °C) for 12 hours, followed by drying at room temperature for 7 days in air.

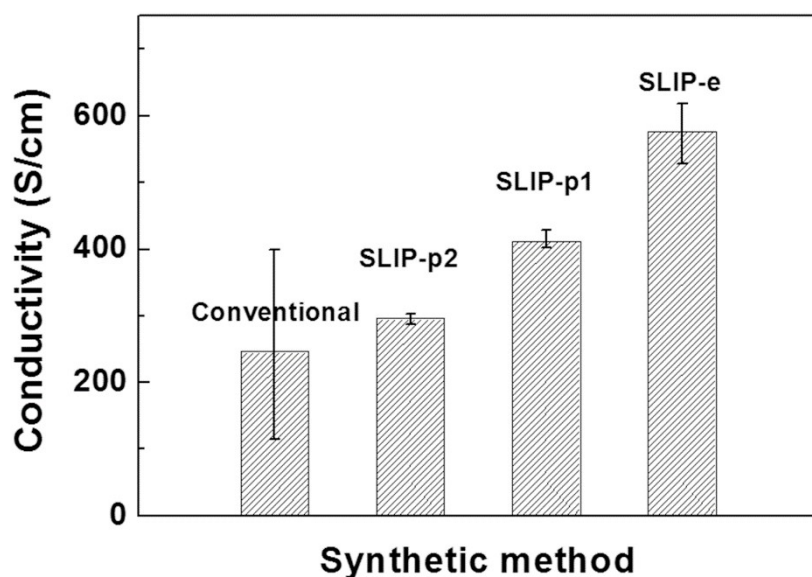
**Characterization:** Electrical conductivity was measured by using Hall measurements system with the van der Pauw configuration. (HL5500PC, Bio-Rad). Silver paste was used as electrodes on the PANI-CSA films (5 ~ 10 µm thick, 15 by 15 mm) for better electrical contact during the Hall measurement. Gel permeation chromatography was performed at 50 °C with an elution rate of 0.35 ml min<sup>-1</sup> on a system equipped with a column (Shodex, LF-804), a differential refractometer (Schambeck SFD GmbH, RI-2000), and a pump (ASI, Model 501). Fourier Transform infrared (FT-IR) spectroscopy was performed on a Perkin-Elmer 2000 Series FT-IR spectrophotometer. Small and wide angle X-ray scattering was measured by SAXSess system (Anton Paar). EB pellets (80 ~ 100 µm thick) and freestanding PANI-CSA films (~20 µm thick) were used for X-ray scattering measurements. The UV-Vis spectra was measured using a UV/Vis/Near IR spectrophotometer (Lambda 750, PerkinElmer).



**Fig. S1.** (A) Photographs of as-prepared SLIP-e PANI ES (left) and EB (right), (B) UV-Vis spectra of ES solution in m-cresol (green) and EB solution in NMP (blue), inset; photographs of each solutions. (C) UV-Vis-Near IR spectra of PANI-CSA films prepared by SLIP-e method (red) and conventional method (black) casted from m-cresol solution.



**Fig. S2.** Isolated yield of PANI EBs and conductivity of PANI-CSA films produced by SLIP-e procedure with various molar ratio of aniline to APS oxidant.



**Fig. S3.** Conductivity of PANI-CSA films of SLIP-produced and conventionally produced PANIs.

SLIP-p1 and SLIP-p2 represent PANIs prepared by the SLIP-p method with reaction time for 48 h and 24 h, respectively.

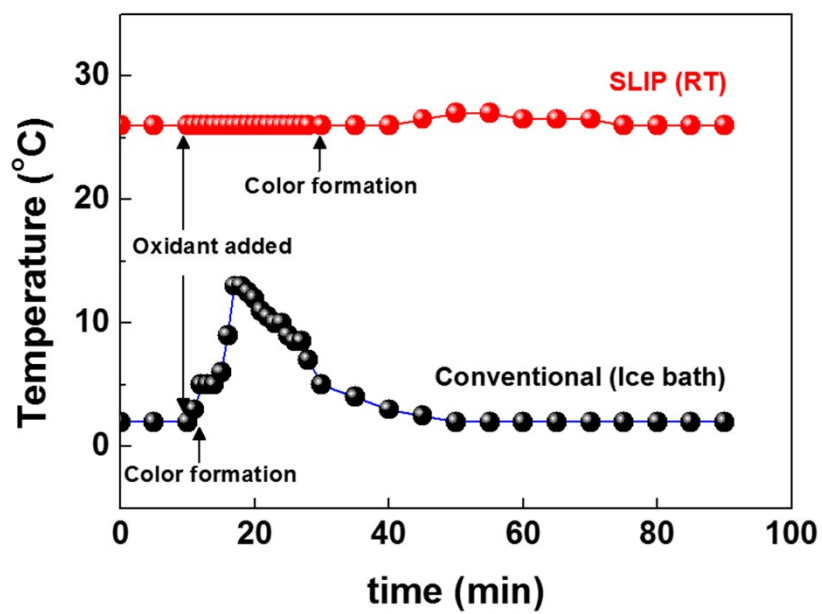


Fig. S4. Typical temperature profiles of SLIP and conventional polymerization.