Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Flexible and printable dielectric polymer composite with tunable permittivity and thermal stability

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Methods

Protonic doping of commercial PANi (HPANi) and preparation of PVDF-TrFE/HPANi composite. Typically, 0.5 g of PANi powder was dispersed in 50 mL, 1 mol/L of HCl solution following by sonication of 2 h. Then, the protonic doped PANi was centrifuged and dried at 60 °C oven for overnight. The as-prepared HPANi powder was mixed with PVDF-TrFE powder with a different weight ratios and well blended using a mortar. Then, 0.1 g of the mixture was pressed by a mold with a pressure of 20 MPa for 5 min to form a polymer composite with a diameter of 1 cm and a thickness of around 0.8 mm.

In-situ synthesis of acid doped PANi (s-HPANi). Briefly, 0.192 mL of aniline and 0.683 mL of HCl solution (35%) were added into 51 mL of H_2O following by stirring for 10 min at 0 °C. Then, 2 mL, 0.854 mol/L of ammonium persulfate (APS, $N_2H_8S_2O_8$) aqueous solution was added. The solution was left for stirring at 0 °C for 6 h with the formation of acid doped PANi. The product was collected by centrifugation and washed by H_2O, ethanol, and DMF. The as-formed s-HPANi was finally redispersed in DMF for further use.

Synthesis of s-HPANi-MTM heterostructures. The exfoliated 2D MTM nanosheets were obtained by dispersing 1 g of gelwhite-GP powder into 50 mL of H_2O following by a probe sonication for 2 h. The formed milky solution was centrifuged by 6000 rpm for 10 min to remove the aggregates. The clear supernatant containing atomic layered 2D MTM nanosheets was stored. For the synthesis of s-HPANi-MTM heterostructures, 1 mL of MTM nanosheets with a concentration of 20 mg/mL was added into 39 mL of H_2O containing 40 mg of PVP (MW = 40,000) to form a uniform dispersion under stirring. Then, a mixture of 0.192 mL of aniline, 0.683 mL of HCl (35%) solution, and 11 mL of H_2O was added into the above dispersion. After the stirring for 0.5 h at 0 ºC, 2 mL, 0.854 mol/L of $N_2H_8S_2O_8$ aqueous solution was added. The reaction was extended for 6 h to form the s-HPANi-MTM heterostructures with a green color. The product was collected by centrifugation and washed by H_2O, ethanol, and DMF and finally redispersed in DMF.

Preparation of PVDF-TrFE/s-HPANi and PVDF-TrFE/s-HPANi-MTM composite. The suspension containing PVDF-TrFE and s-HPANi or s-HPANi-MTM was dried in oven with a temperature of 100 ºC. Then, 0.1 g of dried sample was hot pressed by a mold with a pressure of 20 MPa for 5 min to form a polymer composite.

Screen printing of PVDF-TrFE/s-HPANi-MTM composite dielectric films. The direct writing apparatus consists of Ultimaker^2 Go, an air compressor along with a pressure multiplier (Nordson EFD). A syringe of 3 mL in volume with a nozzle size of 200 microns is utilized for printing the s-PVDF-TrFE/s-HPANi-MTM suspension. The distance between the nozzle and the substrate is 0.5mm. Pressure for material deposition is around 25 psi. The print speed is 500 mm/min. Multiple passes are used for obtaining variable thickness of the print. The printed samples were post-treated by heating for 60-70°C.

Characterization. The scanning electron microscopy (SEM) images and element analysis were taken on the Carl Zeiss AURIGA Cross Beam Focused Ion Beam Electron Microscope with an accelerating voltage of 200 KV, and a point resolution of 0.19 nm. The transmission electron microscopy (TEM) images were taken on a high-resolution electron microscope-JEOL JEM 2010. X-ray diffraction measurement was conducted on the Rigaku Ultima IV with operational x-ray tube power of 1.76 kW (40 kV, 44 mA). The DSC curves were obtained from a differential scanning calorimeter (TA Instruments DSC Q20). Silver electrodes (silver epoxy) and aluminum foil were coated on the both sides of the PVDF-TrFE and composite sheets for the measurement of dielectric performance. The dielectric constant and dissipation factor were determined from a LCR meter with a frequency from 100 Hz to 1 MHz (Agilent E4980A).

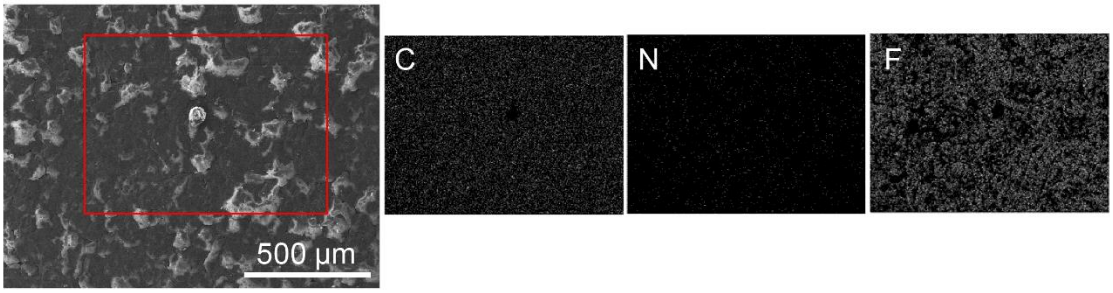

Figure S1. SEM image and EDS mapping of PVDF-TrFE/HPANi composite containing 1 wt% of HPANi.

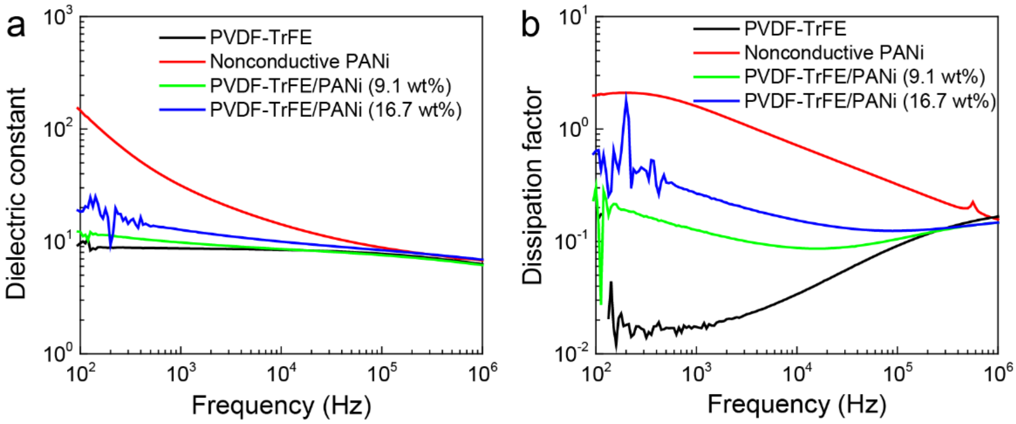

Figure S2. a) Dielectric constant and B) dissipation factor of PVDF-TrFE, PANi, and PVDF-TrFE/PANi containing 9.1 wt% and 16.7 wt% of nonconductive PANi.

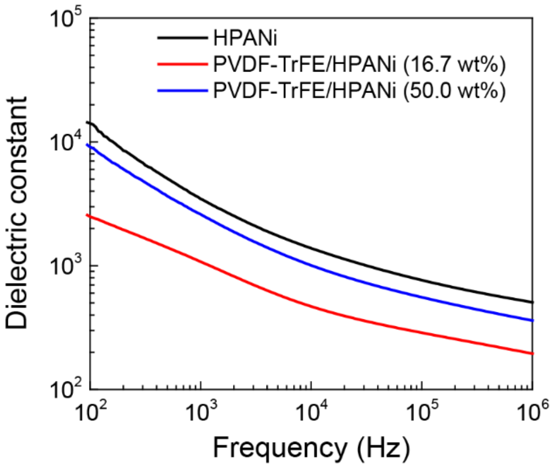

Figure S3. Frequency dependent dielectric constant of HPANi and PVDF-TrFE/HPANi composites containing 16.7 wt% and 50.0 wt% of HPANi.

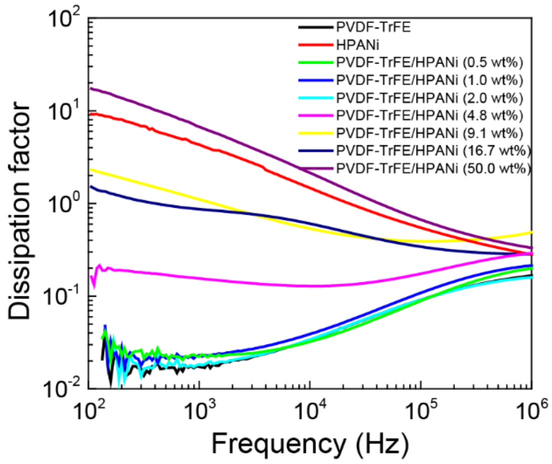

Figure S4. Dissipation factor of PVDF-TrFE, HPANi, and PVDF-TrFE/HPANi containing different concentrations of HPANi.

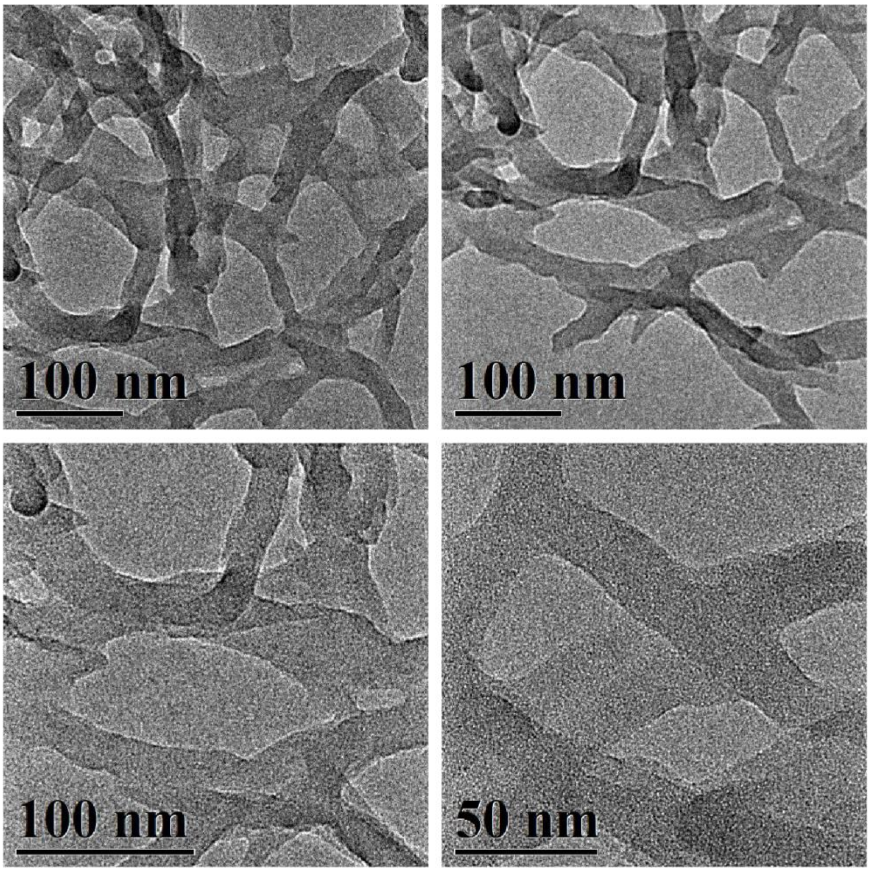

Figure S5. TEM images of s-HPANi.

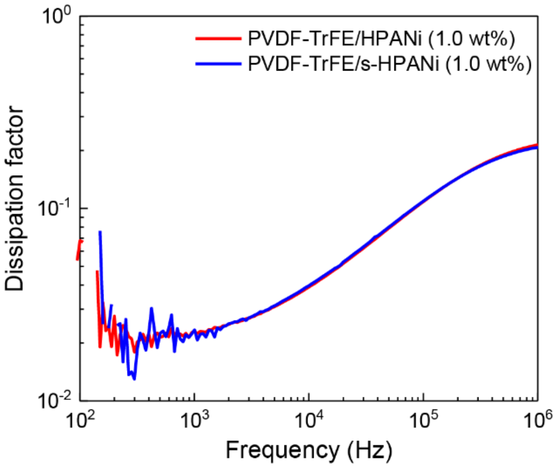

Figure S6. The dissipation factor of PVDF-TrFE/HPANi and PVDF-TrFE/s-HPANi with a concentration of 1.0 wt% of HPANi and s-HPANi, respectively.

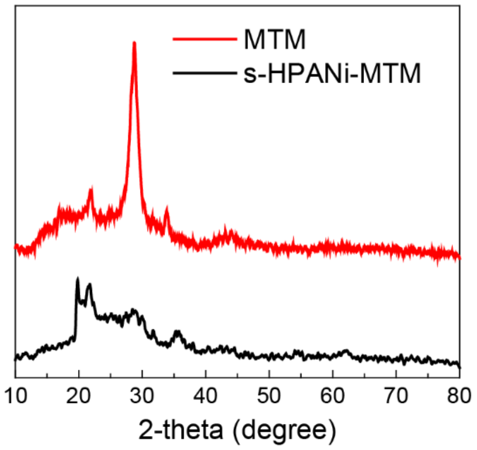

Figure S7. XRD patterns of MTM nanosheets and s-HPANi-MTM heterostructures.

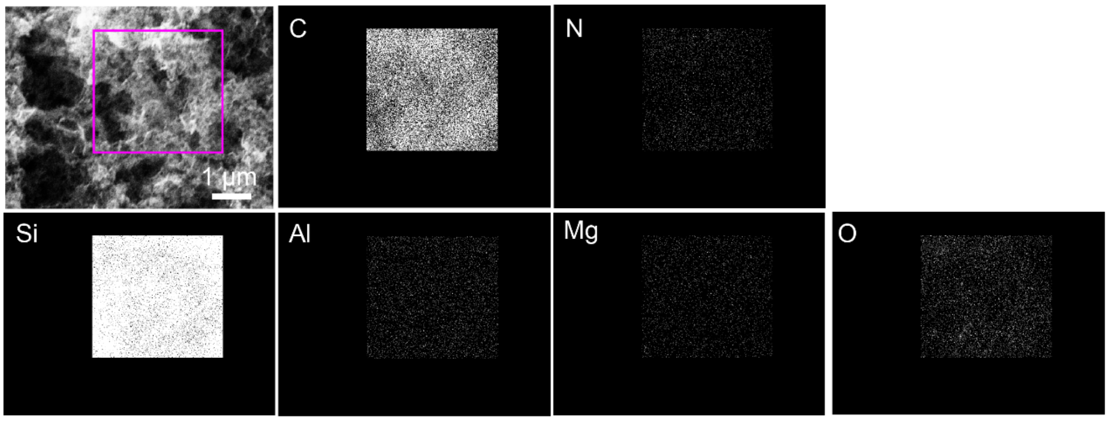

Figure S8. SEM image and EDS mapping of s-HPANi-MTM.

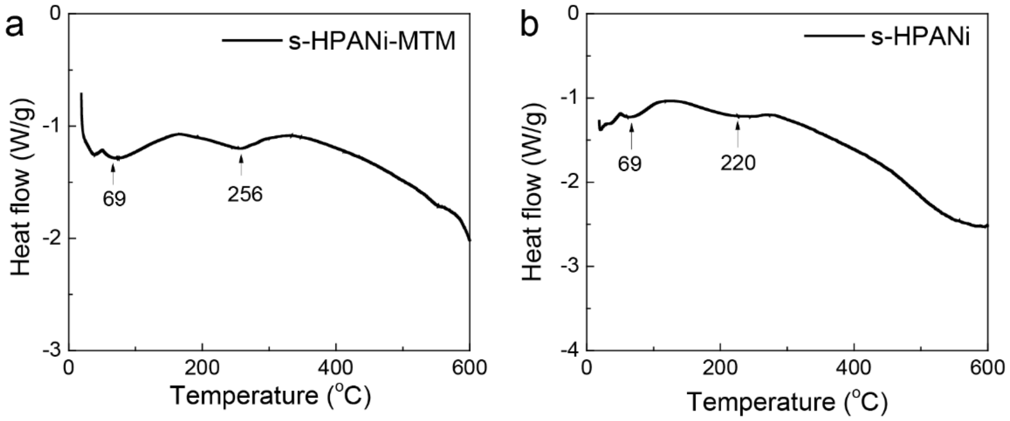

Figure S9. DSC curves of s-HPANi-MTM and s-HPANi.

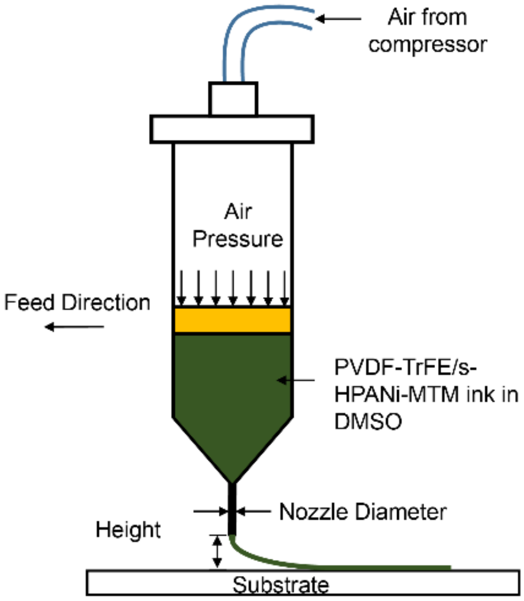

Figure S10. Schematic figure of direct writing.