Supplementary Information

EXPERIMENTAL SECTION

In-situ Synthesis of PVDF-g-HEMA/$BaTiO_3$: PVDF (M=420,000) powder was purchased from Solvay Solexis Inc. 2- Hydroxyethylmethacrylate (HEMA) was obtained from Sigma Adrich Chemie Gmbh, Germany.

PVDF powder samples were dried in an oven before irradiation at room temperature under N_2. Samples were placed in plastic bags and purged with nitrogen for 10 minutes to remove oxygen and the bags were then filled with nitrogen and sealed. The irradiation process was performed in vacuum using the Electron Beam Accelerator from Energy Sciences Inc at room temperature (25 ^{o}C). The maximum accelerating voltage used was 175 kV, with the radiation dose ranging from 0.2 to 2.0 Mrad by means of a conveyer, whose speed was fixed at 18 MPM in order to have maximum exposure of radiation to the polymer. The beam current was 0.1 mA. The dose per pass was set as 0.1 Mrad. After irradiation, unless otherwise stated, the samples were immediately used for grafting with HEMA.

Irradiated PVDF (250 mg) was suspended in a 1M NaOH solution in the flask. A definite amount of the HEMA monomer was added. Subsequently, nitrogen was purged through the solution for 30 minutes to remove oxygen. After that, the graft polymerization was performed at a particular temperature for a definite time period under stirring in a heating mantle fitted with a reflux condenser which was sealed. After the completion of grafting reaction, the $BaTiO_3$ solution was added into the HEMA-g-PVDF solution and the reaction was carried out at 100 ^{o}C/2h with a reflux condenser. The $BaTiO_3$ solution was prepared as follows. Titanium acylate precursor was prepared by reacting titanium (IV) isopropoxide with excess glacial acetic acid at 25 ^{o}C for an hour. Deionized water was slowly added into the titanium acylated precursor with moderate agitation. The initial hazy solution turned into clear solution with the hydrolyzation of titanium isopropoxide to titanium acylated solution. Barium acetate was dissolved in deionized water and added to the titanium acylate solution. Ti-Ba mixed solution was added into 10 M NaOH solution.

After the reaction, the product (HEMA-g-PVDF/$BaTiO_3$) was centrifuged at 8000 rpm and washed with deionized water and methanol for several times to remove residual HEMA monomer and possible homopolymer that was formed. Finally, the HEMA-g-PVDF/$BaTiO_3$ powder was dried to obtain constant weight in vacuum oven at 100 ^{o}C.

Preparation of Nanocomposite Dielectric Films: In-situ synthesized nano-powders were dissolved in Dimethylformamide (DMF) at room temperature. The solution was stirred overnight. The thin film was drop-coated onto a clean glass slide and dried at 60 °C. The film thickness of ~20 μm was used in this investigation. Platinum electrodes were sputtered on both sides of the samples for testing the electrical properties.

Materials Characterizations: Fourier Transform Infrared (FTIR) Spectroscopy was done using a Perkin-Elmer system 2000 FTIR to verify changes in the structure of PVDF before and after in-situ surface functionalization. The crystallinity of the as-synthesized powders was identified by XRD Shimadzu with Cu Kα, radiation (λ =1.5418 Å) at 30 kV and 20 mA and at the scan rate of 2° min^{-1} from 10 to 80° (2θ). Field emission scanning electron microscopy (FE-SEM, JEOL 7600F), operating at 5 kV was employed to determine the particle morphology and size. Detailed microstructural analyses were performed using transmission electron microscopy (TEM, JEOL2010) operating at 200 kV. The chemical compositions were analyzed using energy dispersive spectroscopy (EDS). For TEM and EDS analyses, the products were dispersed in ethanol by ultrasonication for 5min, and then the solutions were dropped onto a copper grid coated with holey carbon film. Frequency-dependent capacitance and loss tangent were measured using Agilent E4980A.

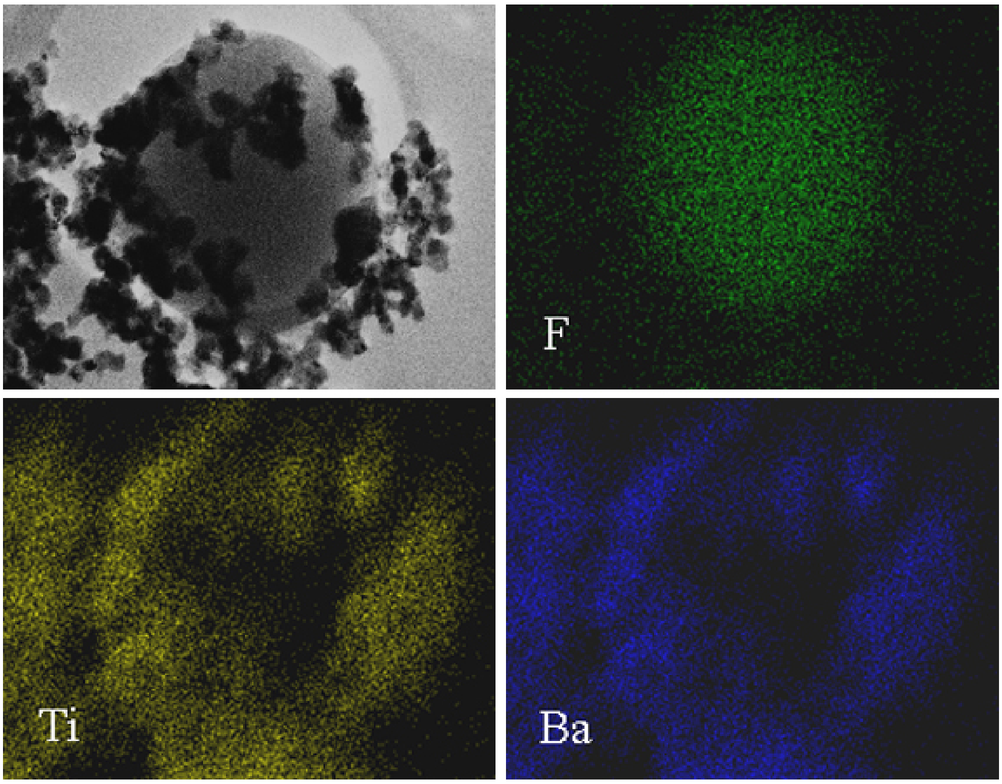

Figure S1. The TEM mapping image of 30 wt% PVDF-g-HEMA/$BaTiO_3$ in-situ powder