

Supporting Information

***β* Phase PVDF-*hfp* Induced by Mesoporous SiO₂ Nanorods: Synthesis and Formation Mechanism**

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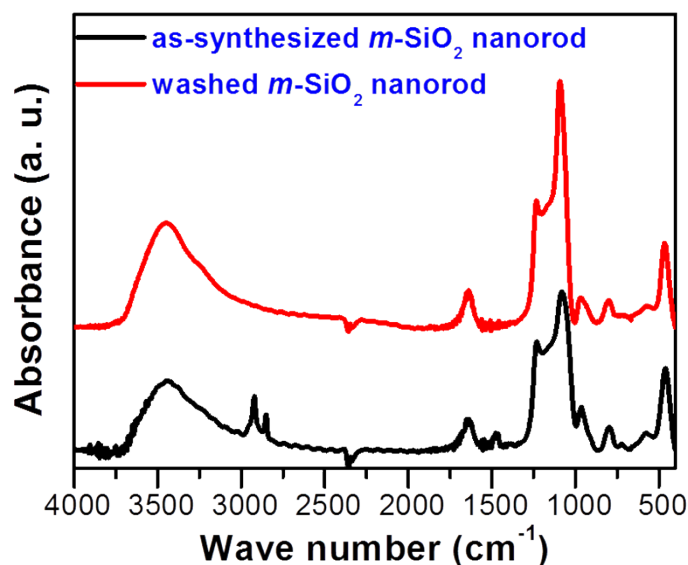


Fig. S1 FTIR spectra of the *m*-SiO₂ nanorods before and after washing by hot ethanolic solution: the disappearance of peaks at 1475 cm⁻¹ (N⁺-CH₃ deformation and -CH bending), 2850 and 2920 cm⁻¹ (-OH stretching of ethoxy group) clearly indicates the removal of template molecules.[1,2]

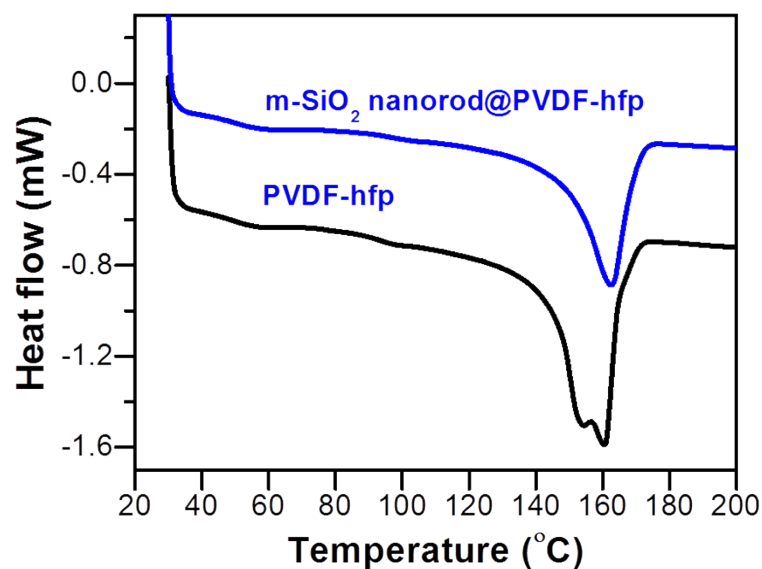


Fig. S2 DSC study comparing the PVDF-*hfp* reference and *m*-SiO₂ nanorod@PVDF-*hfp*. For the PVDF-*hfp* reference, bimodal endothermic peaks at 154.3 and 160.5 °C were assigned to α and β phase, correspondingly. For the *m*-SiO₂ nanorod@PVDF-*hfp*, only single endothermic peak was found for β phase at 162.5 °C.

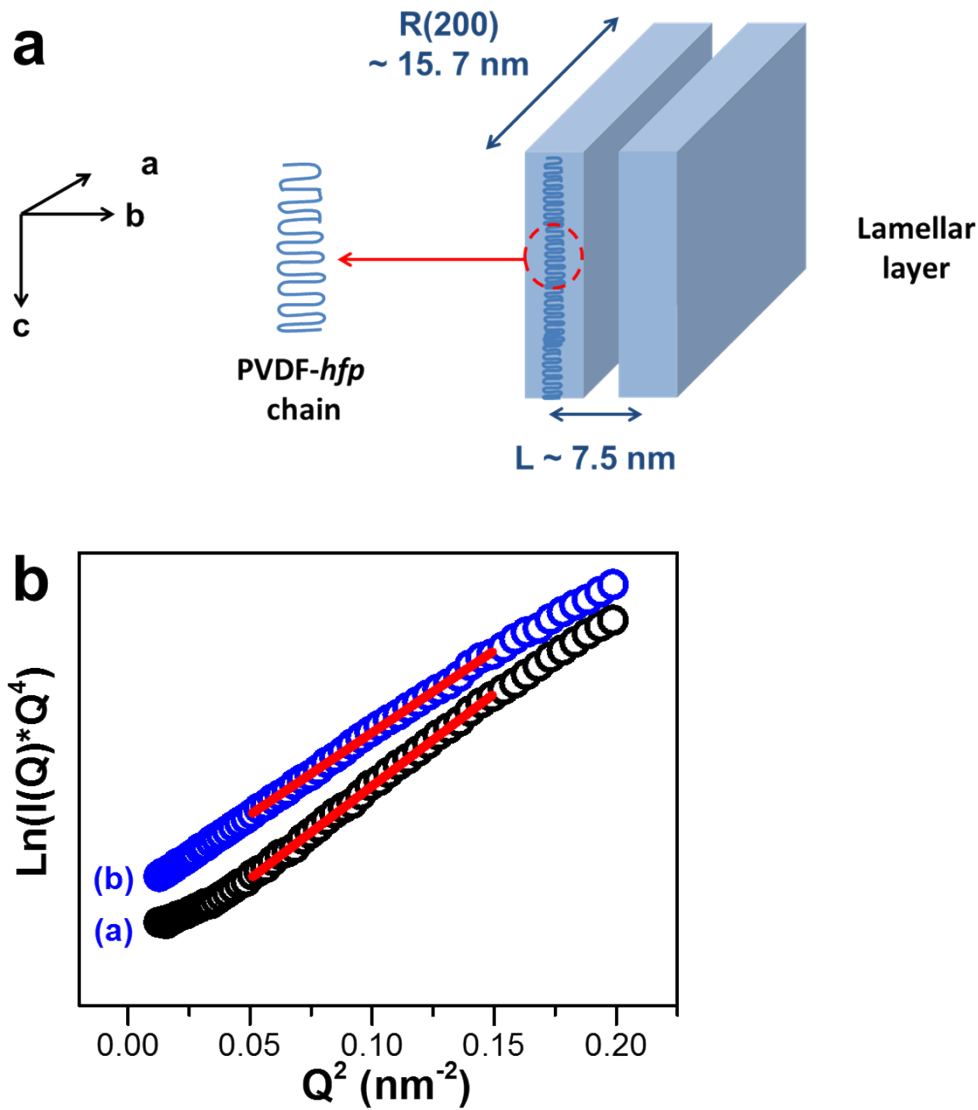


Fig. S3 (a) Schemes for the lamellar structure of *m*-SiO₂ nanorod@PVDF-*hfp*, where the crystallographic axes for PVDF-*hfp* are labeled and the physical dimensions are based on SAXS/WAXS study; (b) Porod analysis for (a) PVDF-*hfp* and (b) *m*-SiO₂ nanorod@PVDF-*hfp*, where the positive slopes (15.3 and 15.6, respectively) were obtained via extrapolation. This positive deviation from Porod's law indicates statistical electron density fluctuation. [3-6]

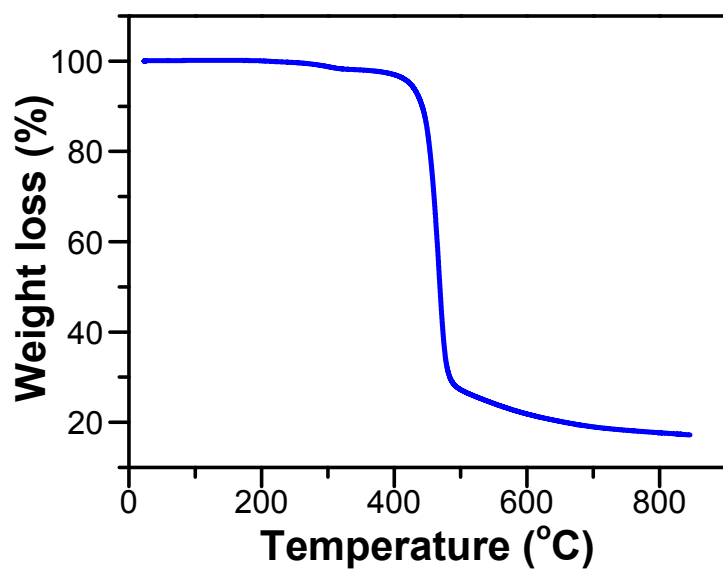


Fig. S4 TGA of the *m*-SiO₂ nanorod@PVDF-*hfp* revealing a 17.2 wt% content of nanorods.

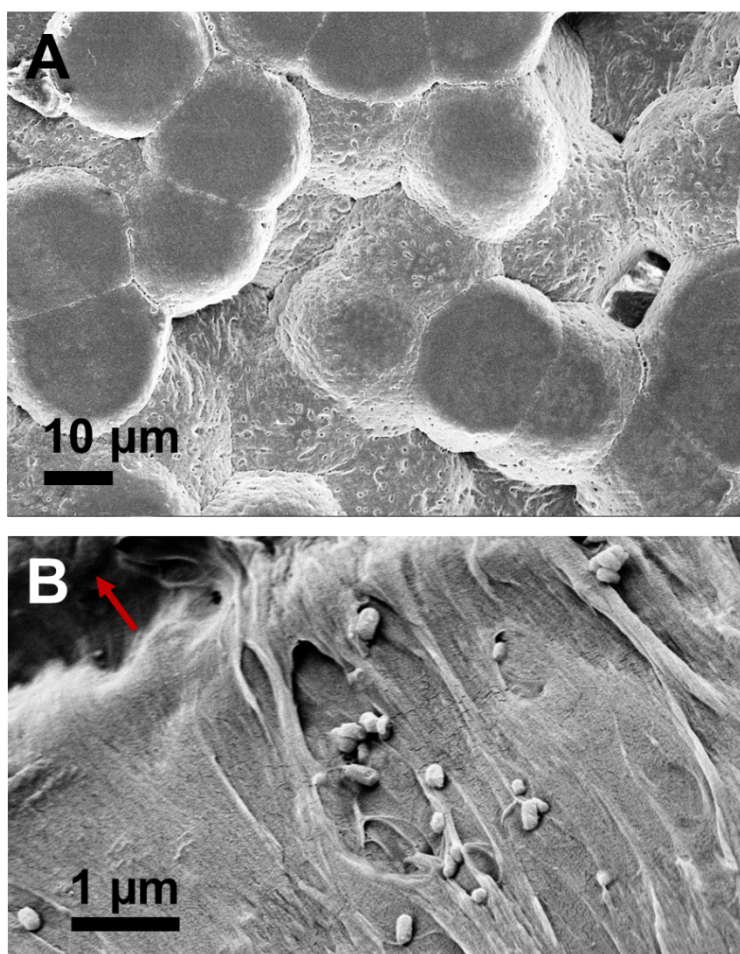


Fig. S5 FESEM image for (a) PVDF-*hfp* film with columnar morphology and (b) cross section of *m*-SiO₂ nanorod@PVDF-*hfp*.

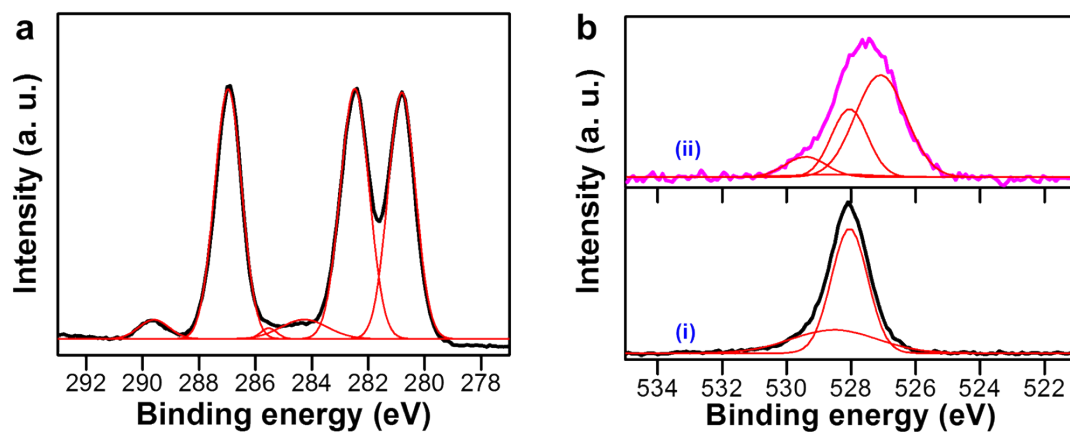


Fig. S6 Gaussian fitting for (a) C1s spectrum for the PVDF-*hfp* reference and (b) O1s spectra for the PVDF-*hfp* with (i) 0 wt% and (ii) 34.4 wt% *m*-SiO₂ nanorods, where the red lines represent the fitted peaks.

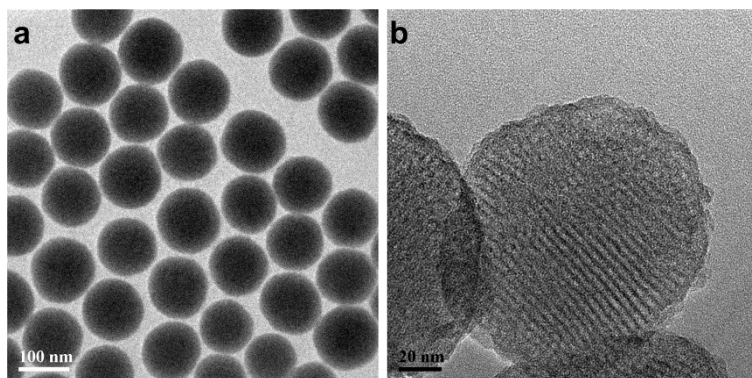


Fig. S7 TEM images for (a) SiO₂ nanospheres and (b) *m*-SiO₂ nanospheres.

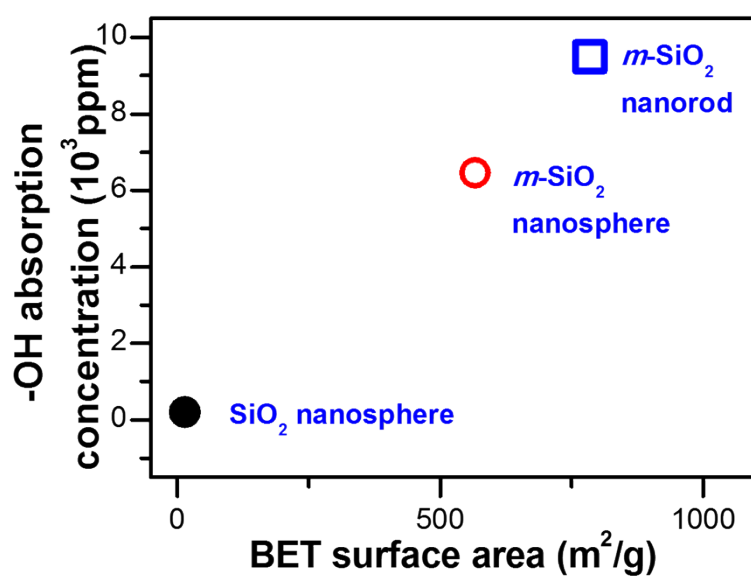


Fig. S8 Estimated -OH absorption concentrations for SiO₂, *m*-SiO₂ nanosphere, and

m-SiO₂ nanorod with their corresponding BET surface areas of 15, 566, and 786 m²/g, where an approximate linear proportionality can be visualized.

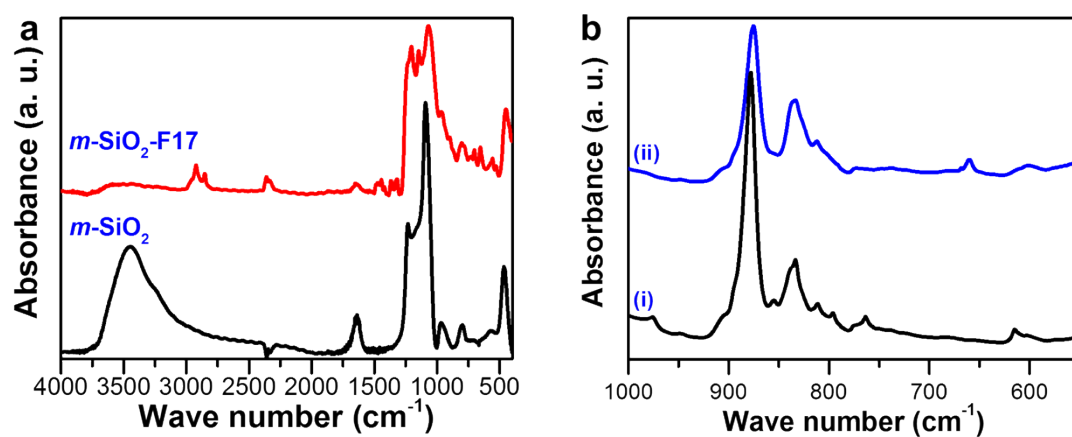


Fig. S9 FTIR spectra for (a) *m*-SiO₂ nanorods modified with fluoroalkyl groups (*m*-SiO₂-F17) by hydrolysis of 1H, 1H, 2H, 2H, -perfluorodecyl triethoxysilane; (b) FTIR-ATR spectra for the PVDF-*hfp* nanocomposites with *m*-SiO₂-F17 (i) nanospheres and (ii) nanorods.

Table S1. Peak positions of the *C1s* species through Gaussian fitting on the XPS spectra for the PVDF-*hfp*, 17.2 wt% *m*-SiO₂ nanorod@PVDF-*hfp*, and 34.4 wt% *m*-SiO₂ nanorod@PVDF-*hfp*.

	PVDF-<i>hfp</i>	17.2 wt% nanorod	34.4 wt% nanorod
-CF ₃ (eV)	289.60	289.75	289.82
-CF ₂ (eV)	286.97	287.15	287.20
-CF (eV)	285.53	285.69	285.69
-CO (eV)	284.27	284.27	284.27
-CH ₂ (eV)	282.48	282.67	282.72
C-H/C-C (eV)	280.81	280.99	281.08

Table S2. Peak positions of the *O1s* species on the XPS spectra for the PVDF-*hfp*, 17.2 wt% *m*-SiO₂ nanorod@PVDF-*hfp*, and 34.4 wt% *m*-SiO₂ nanorod@PVDF-*hfp*.

	PVDF-<i>hfp</i>	17.2 wt% nanorod	34.4 wt% nanorod
-OH* (eV)	-	527.21	527.01
-OH (eV)	528.05	528.05	528.05
-CO (eV)	528.53	528.53	528.53
-SiO (eV)	-	529.57	529.41

A brief discussion on the polarization loop of m -SiO₂ nanorod@PVDF-*hfp*

The nominal polarization in Fig. 4b may not be due to intrinsic ferroelectric polarization. The possible source can be the dielectric loss under large field. It is worth noting that the measurement range for dielectric loss is in the order of mV, which is much lower than the voltage applied for hysteresis loop measurement (some volts). Thus, dielectric constant and loss measurement may not be supporting for investigating the effects of m -SiO₂ on the polarization of PVDF-*hfp*. The large remanent polarization for both PVDF-*hfp* and m -SiO₂@PVDF-*hfp* has not been reported for this material. Such large value might be due to space charge relaxation/leakage. This is also why we concluded it to be attributed to “space charge-induced polarization” at the first place. Note that space charge relaxation/leakage is one kind of dielectric loss mechanism. A detailed analysis in dielectric loss mechanism is beyond our scope in this study though we did demonstrate the ferro-/piezo-electric properties via PFM.

In our study, the polarization loops for both PVDF-*hfp* and m -SiO₂ nanorod@PVDF-*hfp* can be reproduced among different sample batches under a certain applied voltage. However, for the same sample, multiple measurements at the same applied voltage yielded different results, which was due to the injected space charge as discussed previously. Therefore, the PUND measurement, where five sequential pulses are applied, may not be appropriate for our samples because the space charge injected by pulses "P" and "N" will strongly affect the results measured by pulses "U" and "D".

References:

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