Visible Light Induced Ferroelectric to Paraelectric Reversible Phase Transition in Polyvinylidene fluoride Based Nanocomposites

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The control of ferroelectric properties of a material has received great interest in recent years due to its varied application in ferroelectric devices. The spontaneous polarization of a ferroelectric is largely controlled using an external electric field for dipole switching. But the ferroelectric and paraelectric nature of any non-centrosymmetric material is predominantly determined by its Curie temperature. Hence it is a challenging task to switch between the ferroelectric and paraelectric phases of a non-centrosymmetric material in lower timescales. Very recently the optical control of the ferroelectric polarization and the domain walls in single crystalline materials with evidenced charged multi-domains has become a great deal of interest among the researchers[1,2].

Polyvinylidene fluoride (PVDF) has received great attention as a semi-crystalline polymer with good mechanical flexibility and functionality. PVDF based nanocomposite materials have been used for various applications in ferroelectrics, dielectrics, energy harvesting, etc. In this work, we have observed a visible light-induced reversible ferroelectric β-phase transformation to paraelectric α phase in PVDF-multiwalled carbon nanotubes (PVDF-CNTs) nanocomposites.

PVDF-CNTs nanocomposite was prepared by dispersing required amounts PVDF and unfunctionalized CNTs (Sigma Aldrich) in Dimethylformamide separately by ultrasonication. Both the solution were then mixed and ultrasonicated to achieve a homogenous solution. The solution was spin coated on Au coated Si substrates. The thickness of the thin film ranged from 50-100 nm. CNTs induce the crystallization of the ferroelectric β phase in PVDF. Crystalline structure and surface morphology was examined by micro-Raman spectroscopy and atomic force microscopy (AFM).

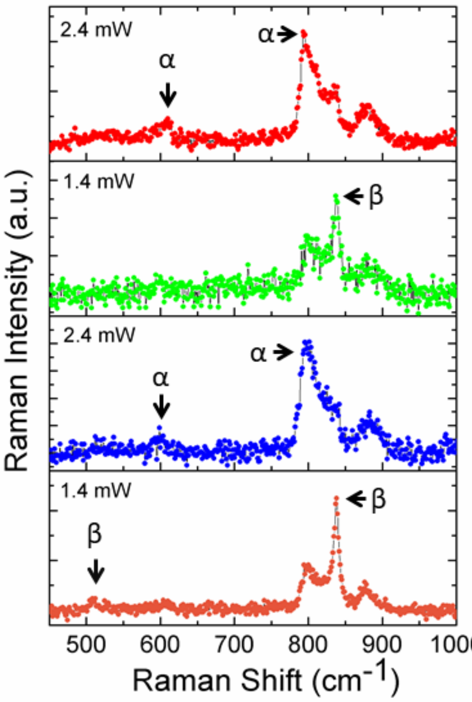

Figure 1:Switching between the Ferroelectric and Paraelectric Phases of PVDF for Different laser powers (λ = 632 nm)

The phase transformation was investigated using laser power dependent Micro-Raman Spectroscopy (533 nm and 632 nm lasers) to observe the structural changes (laser spot area of 12~15 μm^2). Figure 1 shows wavelength independent reversible transition between the β phase and the α phase due to laser power alteration at the same spot under investigation. This kind of switching behavior between the β phase and the α phase is very less obvious and unusual. For pristine PVDF, no such phase transformations were observed. The alteration of the ferroelectric phase to the paraelectric phase can be due to the enhanced pyroelectric currents that occur due to the laser heating. Also, the photoexcitation of carbon nanotubes sets the π electrons responsible for the ferroelectric β-phase to motion thereby generating a photocurrent combined with the pyroelectric currents[3]. The phase change also implies changes in the crystal structure and thereby, the dimensions of the domain (photostrictive nature) which is very vital in ferroelectric devices. This kind of dynamic optical control of ferroelectricity is highly desirable for Micro/Nanoelectromechanical systems and ferroelectric memories. More detailed nanoscale characterizations are being performed to explain the observed effect.

1. Rubio-Marcos, F. *et al*, Nature Photonics, 12, 29–32 (2018).
2. Rubio-Marcos, F. *et al*, Nature Communications, 6, 6594 (2015).
3. Zhao, H. *et al*, Macromolecules, 41, 8566-8574 (2008).