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Light intensity-induced phase transitions in graphene oxide doped polyvinylidene fluoride

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Abstract: The coupling of light with low-frequency functionalities of dielectrics and liquid crystals and an ability to turn "on" and "off" the pyro-, piezo-, or ferro- electric properties of materials on demand by optical means leads to fascinating science and device applications. Moreover, to achieve all-optical control in nano-circuits, the coupling of the light with mechanical degrees of freedom is highly desirable and has been elusive until recently. In this work, we report on the light intensity-induced structural phase transitions in graphene oxide doped piezoelectric polyvinylidene fluoride (PVDF) film observed by micro-Raman spectroscopy. Increasing the laser power results in a steady transformation of the Raman spectrum featured piezoelectric β phase to one of non-piezoelectric α structure. This effect is accompanied by volumetric change of a PVDF unit cell by a factor of two, useful for a photostriction materials application. Furthermore, we observed the reversible switching of α and β phases as a function of the light intensity (laser power between 5.7–31.3 mW). This opens up a new route for multi-functionality control where strain, piezoelectric constants and polarization can be modified by light.

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1. Introduction

A grand challenge in modern nanoscience and nanotechnology is an ability to control a material's functionalities (electrical, magnetic, thermal, mechanical) by optical means. Some examples of the optical control at the nanoscale include excitation of localized surface plasmons and surface plasmon polariton in metallic nanostructures [1] or by coupling of light with electrical or mechanical degrees of freedom of the smart electro-optical or photostrictive dielectrics [2,3].

Polyvinylidene fluoride (PVDF) is a well-known lightweight, flexible, and non-toxic piezoelectric polymer with relative large magnitude of spontaneous polarization (5 – 8 $\mu C/cm^2$) and Curie temperature near to 200°C [4,5]. These properties make PVDF suitable for a broad range of applications in electro-optics and electro-mechanical devices [6–8]. Since the discovery of piezoelectricity in PVDF in 1969 by Kawai [9], there were many studies on the structural, mechanical, and ferroelectric properties of the plain polymer and its nanocomposites [10–12]. It was found that PVDF functional properties are bound to its intrinsic crystalline polymorphism featuring four major crystalline phases: non-piezoelectric α, δ, γ and piezoelectric β phase, where α and β are common crystalline phases to be studied [9,12,13]. The α phase is the lowest energy conformation and is formed by $(CH_2 - CF_2)$ chains in TGTG conformation and crystallized in a monoclinic cell with lattice parameters a = 4.96 Å, b = 9.64 Å, c = 4.62 Å, $\beta = 90°$. The polar β phase is raised from trans planar zigzag structure (TTTT), which leads to an orthorhombic cell with lattice parameters a = 8.58 Å, b = 4.91 Å, c = 2.56 Å [14,15]. The difference of unit cell volumes of these phases is by a factor of two (V_α = 220.9 and V_β = 107.8 $Å^3$), which makes this material attractive for photostriction materials applications. There, mechanical degrees of freedom can be controlled by light via combination of photoconductivity and converse piezoelectric effect [3,16]. It needs to be mentioned that undoped PVDF is absolutely indifferent to light. Changes in its properties usually arise from environmental perturbations, such as temperature, pressure and electricity. To make it susceptible to high frequency electromagnetic radiation, one can embed the photosensitive nanofillers into PVDF matrix, which on the other hand can enhance β phase crystallization.

Among various dopants, such as cobalt ferrite, barium titanate, iron oxide, titanium oxide, silver films, and others [17–22], carbon based nanomaterials, particularly Graphene Oxide (GO), have gained much interest due to their chemical compatibility, high surface area, prominent mechanical properties and electron transport [23–26]. The presence of oxygen functional groups of GO such as carboxyl, carbonyl, epoxide and hydroxyl groups facilitates specific chemical interactions with polymer matrix and enables the synergy of components of composite system.

It has been demonstrated in the past, that a PVDF key feature, namely the phase transition from the non-polar α phase to the polar β phase, can be induced either by mechanical stretching and/or ordinary heating and has been investigated by different techniques, including X-ray diffraction, Differential Scanning Calorimetry, and vibrational spectroscopies, e.g. infrared absorption and Raman scattering [27–30].

In this work, we report on the puzzling experimental finding of light intensity induced phase transition in 0.3 wt. % GO doped PVDF drop casted film observed by micro-Raman spectroscopy. We found that the reversible $\alpha \leftrightarrow \beta$ phase transition can be activated and controlled by the variation of the light intensity, although, undoped PVDF is light insensitive. The result can be explained by considering both: (i) laser heating and (ii) underlying mechanism of photostriction: photoconductivity and converse piezoelectricity.

The finding is of great importance and directly linked to an ability to control the piezoelectric properties of materials on demand by optical means, which opens up a new route for multi-functionality control. It leads to fascinating device applications bridging low frequency material functionalities to high frequency operational domain.

2. Experimental

Polyvynilidene fluoride powder, Dimethylformamide (DMF) and Acetone (AC) were purchased from Sigma-Aldrich and used without further purification. Graphene oxide powder was purchased from Graphenea, Inc. (Spain).

The samples were prepared by the drop casting of undoped and 0.3 wt. % GO doped PVDF suspensions (12 wt. % PVDF in the mixture of 60 ml of DMF and 40 ml of AC) on the fused silica slide.

Raman measurements were taken using Horiba LabRam HR Evolution micro-Raman instrument. A diode laser with wavelength $\lambda = 532$ nm and tunable power in the range of P = $2 - 100$ mW was used as a light source. The objective lens of 10x magnification was utilized to spread out the laser light uniformly across the area of 20 μm^2. There were two major channels of the light energy attenuation: via the optical components of the Raman system and by an application of the neutral density filters.

3. Results and discussion

The vibrations of linear $(-CH_2-CF_2-)_n$ PVDF molecular chains crystallized in either α monoclinic or β orthorhombic arrangements raise the number of Raman active modes, which are documented and interpreted by researchers in the field, Table 1 [27,28].

Table 1. Vibrational mode wavenumbers (cm^{-1}) of undoped PVDF

Band (cm^{-1})	Phase	Group, vibrational mode
485	γ	
513	β	$CF_2\ \delta$
610	α	$CF_2\ \delta$
795	α	CH_2 r
812	γ	$CH_2\ \omega$
840	β	CH_2 r
881	α, β	$CC\ \nu_s$
		$CC\ \nu_s$
1076		$CC\ \nu_a$
1171		$CH_2\ \omega$
1265		$CC\ \nu_s\ CCC\ \delta$
1430		$CH_2\ \delta;\ CH_2\ \omega$
2440		CH_2 deform.
2980		$CH_2\ \nu_s$

ν_s symmetric stretching; ν_a asymmetric stretching; δ scissoring; ω wagging; r rocking

The structural difference between α and β phases is usually attributed to Raman lines associated with the rocking vibrations of CH_2 group at 795 cm^{-1} for α phase and 840 cm^{-1} for β phase, accompanying with the presence of $CF_2\ \delta$ – scissoring modes at 610 cm^{-1} and 510 cm^{-1} for α and β crystalline phases, correspondingly [27,28], as it is shown in the Fig. 1.
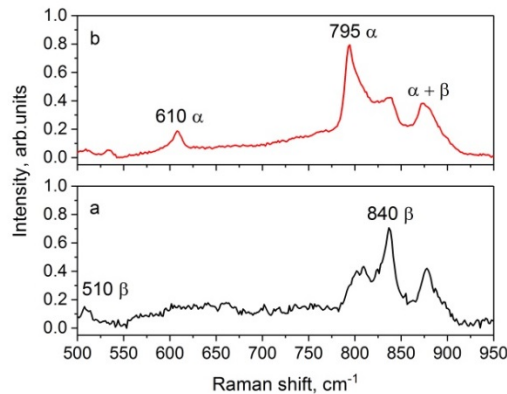

Fig. 1. Raman spectra of crystalline PVDF: (a) β and (b) α phases.

Figure 2 shows the Raman spectra taken with 532 nm laser excitation of 5.7 mW power at the sample surface (the lowest laser power used in our experiments) of undoped PVDF and 0.3% weight GO doped PVDF films drop casted on the glass slide.
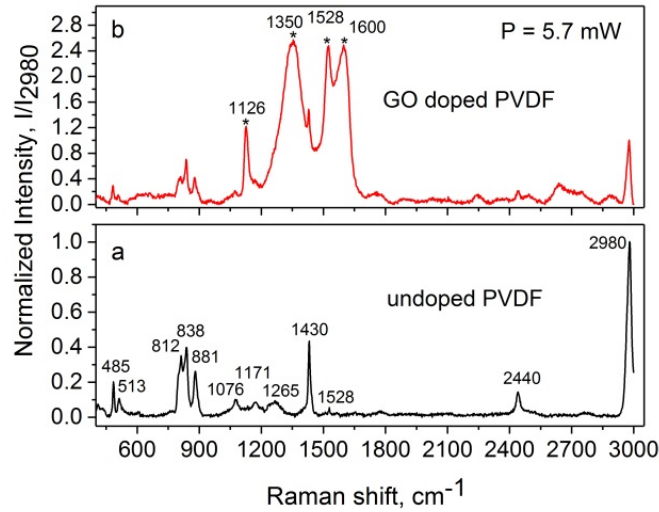
Fig. 2. Raman spectra of (a) undoped and (b) 0.3% wt. GO doped PVDF samples recorded with 5.7 mW laser power.

One can see that β piezoelectric phase is dominated in both samples with relatively larger fraction in GO doped PVDF (peak area of 838 cm^{-1}). Moreover, new extra features can be observed at 1126, 1528, 1350 and 1600 cm^{-1}. The first two peaks are associated with the presence of an oxygen functional group, such as COO$^-$ carboxylate and assigned to the C – O stretching and COO$^-$ carboxylate ν_a asymmetric stretching modes [31].The pair of the broad features are related to D (1350 cm^{-1}) and G (1600 cm^{-1}) characteristic GO bands, respectively [32]. To investigate the effect of illuminating light intensity on undoped and GO doped PVDF, we measured the set of Raman spectra as a function of the laser power in the range of 5.7 – 31.3 mW at the sample surface. Figure 3 presents the Raman spectra obtained from the same spot of undoped PVDF sample.
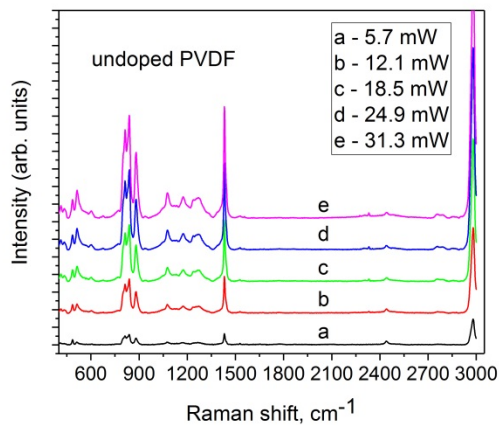

Fig. 3. Raman spectra of undoped PVDF recorded with the laser power between 5.7 - 31.3 mW.

It is clearly seen that the increase of the laser power results in the linear enhancement of the overall spectrum signal, negligible intensities interplay of Raman lines at 488, 510 and 610 cm^{-1}, suggesting no changes of the fraction of the crystalline phases.

However, the graphene oxide doping of PVDF significantly alters the sample's behavior under variation of the laser power, shown in Fig. 4.
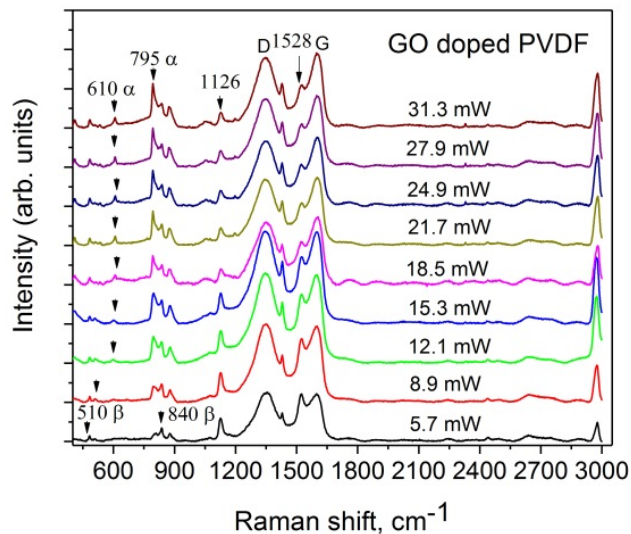

Fig. 4. Raman spectra of 0.3% wt. GO doped PVDF recorded with the laser power between 5.7 - 31.3 mW.

At the threshold power of 15.3 mW, several interrelated events evidently occurred. First, the increase of the light intensity results in the $\beta \rightarrow \alpha$ phase transition, which is conveyed by the constant rise of amplitude of the 795 cm^{-1} peak and the simultaneous reduction of the 840 cm^{-1}, that is accompanied by the rise of the 610 and reduction of the 510 cm^{-1} peaks. Second, this development is complemented with the sharp reduction of amplitudes of the peaks at 1126 and 1528 cm^{-1}. Third, the light intensity treatment leads to the evolution of GO D and G bands, namely the drop of their ratio of intensities from the magnitude slightly above one (1.03) for low laser power to slightly below one (0.92) for high laser power, which is indicated the partial reduction of GO. Moreover, the steady high light power leads to the narrowing of the 795 cm^{-1}, suggesting an improvement of the crystallinity of α phase. The simultaneous redistribution of 840 and 795 cm^{-1} peak weights, suppression of C-O and COO^{-} modes at 1126 and 1528 cm^{-1}, and changes of the ratio of D and G bands are manifested in the $\beta \rightarrow \alpha$ phase transition, where GO plays a crucial role and its changes shed a light on the possible mechanism of PVDF structural transformations.

There are two possible explanations of the observed effect. One could be related to the thermal heating, similar to the local laser heating effect causing, for example, the phase transition of ferroelectric copper indium thiophosphate $Cu_{1-x}In_{1\_x/3}P_2S_6$ reported in [33] and enhanced pyroelectricity reported for GO doped PVDF in [25]. Another explanation might be associated with the photoexcitation and charge transfer in GO [34]. In general, without any external disturbances, the spatial orientation and arrangement of $(CH_2 - CF_2)$ dipole molecules and crystalline phase domain formation is governed mainly by electrostatic interactions. The presence of oxygen contained functional groups of GO modifies the overall charge net and shifts energy balance towards β phase formation via spatial reorientation of polymer molecules. Under an external perturbation, such as high intensity light illumination

with threshold power of 15.3 mW, the generation of photoexcited charges in the photosensitizer GO sheet and partial reduced GO formation [34] results in the remapping of the surface energy landscape and is accounted for an arrangement of PVDF molecules in α crystalline phase. There is also a possibility that both aforementioned mechanisms are valid. The detailed discussion of this issue is beyond the scope of this paper, it will be addressed in subsequent studies.

Figure 5 shows the most striking finding of $\alpha \leftrightarrow \beta$ reversal phase changes under laser power switching. An intrigue is that sequential removing and inserting the neutral density filter causes the periodic alternation of piezo and non-piezo phases.
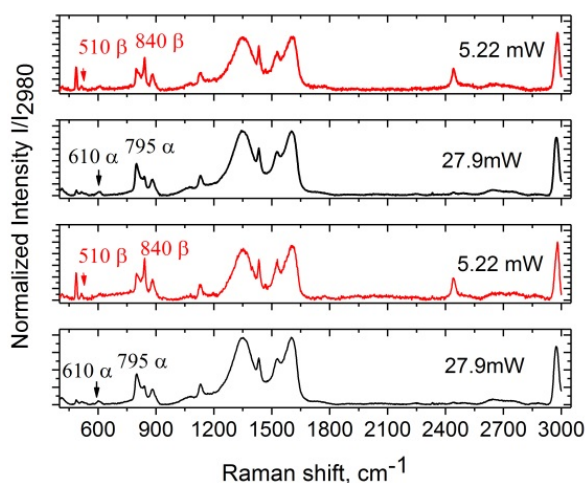

Fig. 5. The reversible $\alpha \leftrightarrow \beta$ phase transitions of 0.3% wt. GO doped PVDF under reversal laser power modulation.

As such, the 795 cm^{-1} peak of α phase observed in the initial Raman spectrum obtained with laser power of 27.9 mW at the sample surface in Fig. 5(a), is transformed into the 840 cm^{-1} peak of β phase in Fig. 5(b) once laser power reduces to 5.22 mW. Furthermore, the restoration of the laser power back to 27.9 mW by removing the filter results in the complete restoration of the spectrum characteristics of the α phase shown in Fig. 5(c), which follows by the re-appearance of the β phase spectrum under inserting the filter in the Fig. 5(d). Our measurements do not manifest any hysteresis, suggesting the process of the $\alpha \leftrightarrow \beta$ phase transition takes significantly shorter time.

4. Conclusion

In summary, we report an interesting observation of the light intensity induced, reversible $\alpha \leftrightarrow \beta$ phase transition in the 0.3% weight graphene oxide doped Polyvinylidene Fluoride observed by micro-Raman spectroscopy. Although, an exact origin of this phenomenon is unclear and it is a matter of further investigation, such reversible functional phase transformations with "on" – "off" behavior modulated by the intensity of light could be very attractive for the basic and applied science. The demonstrated easy-to-synthesize nanocomposite could be added to the toolbox of the smart photostrictive materials with volumetric changes of the unit cells.

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