

Polarization switching and piezoresponse in PVDF/P(VDF-TrFE) ferroelectric films and multifunctional G/GO composites

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Experimental and computational studies of new multifunctional nanomaterials are presented. Molecular modeling of the polarization switching in the polyvinylidene fluoride (PVDF) and poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) films were investigated and analyzed in comparison with the experimental data at the nanoscale. The obtained values of the coercive field is within the $E_C \sim 0.5 - 2.5$ GV/m, corresponding to experimental data. The thickest samples having the polarization switching mostly correspond to the domain mechanism. The performed analysis of data shows that the critical size is $\sim 3-10$ nm, MD run show the 6-10 parallel polymer chains (3-5 nm) for the non-homogeneous layered switching and the formation of new layered domain structures are observed [1]. Then, usual domains are formed. Further, we perform the computational molecular modeling of the graphene/graphene oxide (G/GO) and PVDF ferroelectric polymer composite nanostructures, using the same semi-empirical quantum approximation PM3 in HyperChem [2, 3]. Piezo-properties of these nanostructures are analyzed in comparison with experimental data obtained for VDF-TrFE-GO thin film by PFM method [4]. Modeling shows qualitative agreement of properties of piezo-coefficient $d_{33\text{eff}}$ values under influence of G/GO layers with its various concentrations. Modeling of G layer with 54 carbon atoms shows decreasing of piezoelectric coefficient d_{33} up to $d_{33} = -9.8$ pm/V for one-side model PVDF/G and $d_{33} = -18.98$ pm/V for sandwich model G/PVDF/G in compare with pure PVDF $d_{33} = -42.2$ pm/V. Piezoelectric coefficient for GO models with 96 carbon atoms shows that d_{33} decreases up to $d_{33} = -14.6$ pm/V for the one-side PVDF/GO models and $d_{33} = -29.8$ pm/V for the sandwich GO/PVDF/GO model [2] as compared with pure PVDF $d_{33} = -38.5$ pm/V from previous work [3]. See details in Figs. 1, 2, 3, and 4.

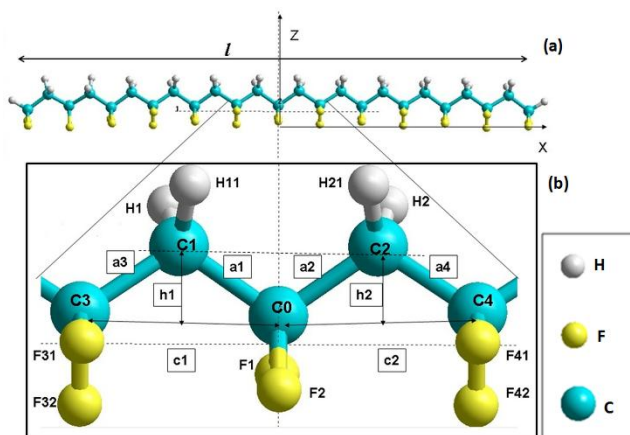


Figure 1. Scheme of PVDF chain from $12.5 \text{ F}_2\text{C}_2\text{H}_2$ elementary units (a), with central part (b).

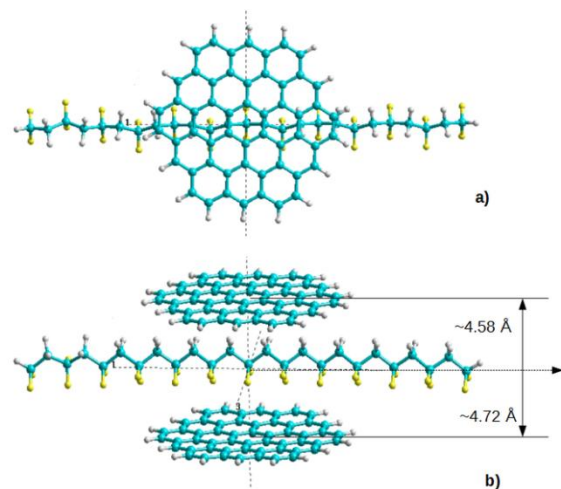


Figure 2. Model of Graphene-54 (54 carbons) and PVDF chain (a), model of 2 layers Gr-54 and 1 PVDF chain (b).

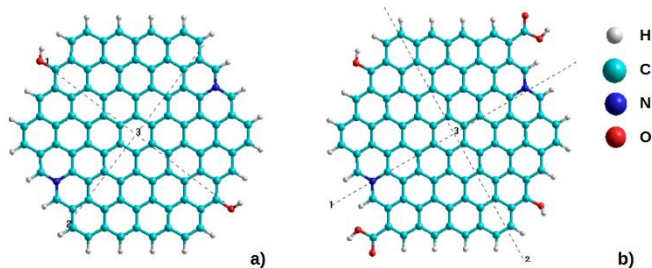


Figure 3. Models of Graphene-96 (96 carbons) with oxygen (O) and nitrogen (N) atoms as Models of Graphene Oxide (GO).

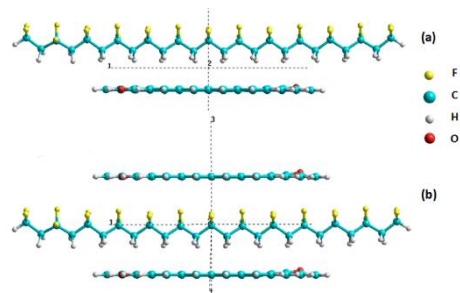


Figure 4. Models of GO-96 and PVDF chain: a) one layer of GO, b) two layers of GO.

Several new multilayered GO nanostructures with inserted PVDF chain and layer are developed for further investigations of the GO content and concentration dependence of these composites.

Some examples presented below in Figs. 5, 6.

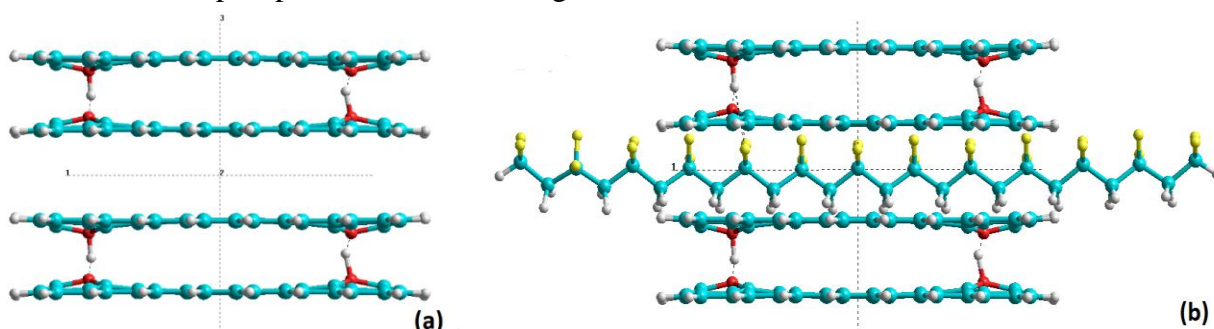


Figure 5. Model of 4-layered GO (a) and GO-PVDF (b) composite in initial state with inserted OH-bonds

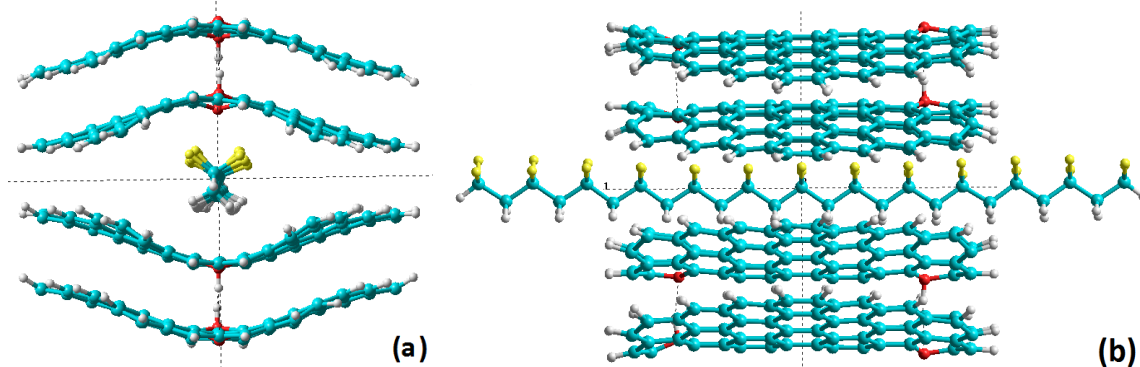


Figure 6. Model of 4-layered-GO-PVDF after structural optimization by BIO CHARM method: a) in X-plane projection, b) in Y-plane projection.

Such composites can serve as a multifunctional molecular unit. Further models are in progress. The work is supported by RFBR grants # 15-01-04924, # 16-51-53017 and RSF grant #16-19-10112.

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