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Molecular modeling of ZnO nanoclusters interacting with various dopant and PVDF

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Zinc oxide (ZnO) is a versatile material, which has unique optical, semiconducting and most important piezoelectric properties [1]. Alternatively, poly(vinylidene fluoride) (PVDF) and PVDF-trifluoroethylene (TrFE) (i.e., its copolymer) are piezoelectric polymers, has been used for dynamic strain sensing and energy harvesting [2]. Ideally, piezoelectric materials should possess high piezoelectricity, while remaining conformable and flexible like piezo-polymers. One of the method for simultaneously achieving improved piezoelectric and mechanical performance is by embedding piezoelectric ZnO nanomaterials into PVDF polymer matrices for enhancing piezoelectricity of such composite architectures [3]. Similarly is possible to enhance piezoelectric property in ZnO structures by doping it's crystals by various atomic dopants [4].The goal of this study is to perform the estimation of the ZnO crystal cluster models, "ZnO+PVDF" and "ZnO+A" composite structures and properties using molecular modeling and computational physical properties calculations. We take out the initial unit cell crystal structure of ZnO crystal in the hexagonal P63m group [6-8] from CCDC data base (lattice constant a = 3.249 Å and c = 5.204 Å) [6] and reconstruct it to the HyperChem [9] workspace, where built first a minimal ZnO cluster (from 18 atoms) and second a nanorod ZnO model cluster (from 72 atoms). Then we construct here the "ZnO+PVDF" and "ZnO+A" models with various atoms. Computational molecular models of ZnO cluter, PVDF chain and composite of "ZnO+PVDF" were considered and performed in this study using HyperChem software by various semi-empirical methdos PM3, MNDO/d in restricted/unrestricted Hartree-Fock (RHF/UHF) approximation [9, 10]. For "ZnO+A" the a*b initio* methods was used with various basis set (3-21G with 675-735 primitive Gaussians, and 6-31G* with ~1200 Gaussians) [9], depending of the atom "A". Distance between "A" and cluster's centre of mass ~ 3.5 Å. Initial pure ZnO model were calculated using both approaches. Models are presented on Figure 1, results in Table 1.

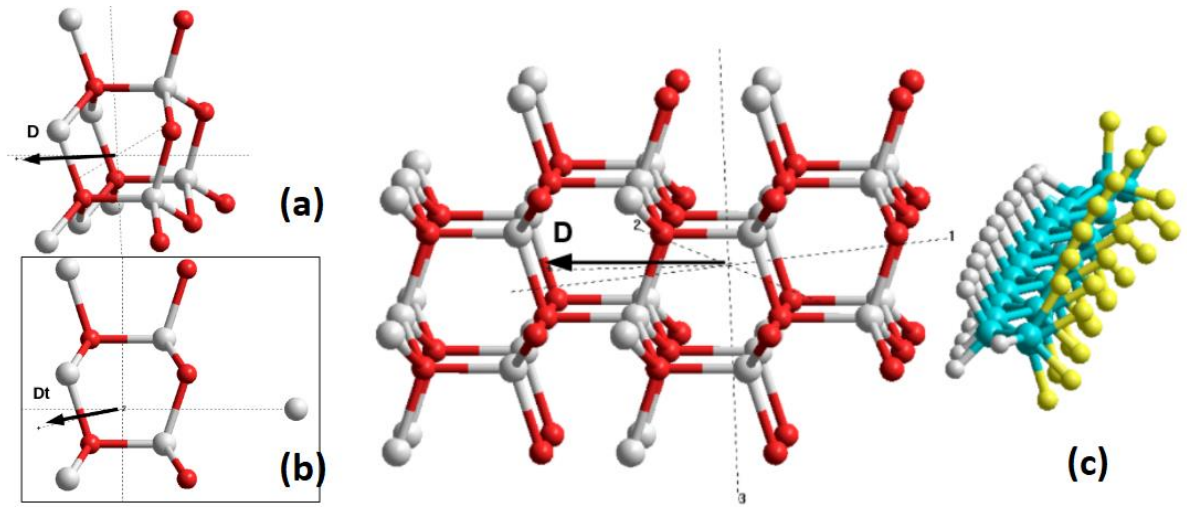

Figure 1. ZnO cluster model: (a) ZnO initial minimal cluster, (b) ZnO nanoparticle interacting with atom "A", (c) ZnO nanorod interacting with PVDF chain in composite structure model.

Table 1. Polarization characteristics of "ZnO+PVDF" composite cluster, obtained by various methods.

Model	Parameters	Methods (in RHF/UHF)			Other data		
		PM3	MINDO-d	Ab initio 3-21G	Calculat. P, C/m^2 [7,8]	Experimental [1,5]	
						P, C/m^2	d*, pm/V
ZnO-18	Dipole, Debye	17.728	15.123	16.1815			
	Polarization, C/m^2	0.1032	0.0885	0.0947	0.07-0.08		9.9-12.4
ZnO-72	Dipole, Debye	13.441	11.739				
	Polarization, C/m^2	0.0944	0.0825		0.07-0.08		9.9-12.4
ZnO-18 + Cr	Dipole, Debye			11.8837			
	Polarization, C/m^2			0.0669		0.0618	120
ZnO-18 + V	Dipole, Debye			4.627			
	Polarization, C/m^2			0.0258		0.02	110
ZnO-18 + Mg	Dipole, Debye			15.245			
	Polarization, C/m^2			0.08535		0.002	54
ZnO-18 + Y	Dipole, Debye			6.0831			
	Polarization, C/m^2			0.0339			420
PVDF12	Dipole, Debye	25.12	29.971				
	Polarization, C/m^2	0.167	0.199		0.1	0.1	20-40
PVDF12 + ZnO-72	Dipole/ at distance between, Debye / Å	45.082/10.0 45.338/10.5	51.927/10.0 47.844/11.5				
	Polarization, C/m^2	0.154 0.155	0.1775 0.1634				

Data obtained show good agreements with experimental data. However, it is only first step of our calculations and work will be continued further, similarly as in our previous calculations of the piezoelectric coefficients in PVDF and Graphene-based polymer ferroelectrics [9-11]. Authors wish to acknowledge the Russian Foundation for Basic Researches (RFBR) grant # 19-01-00519 A.

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