Abstract

The research and development of the novel composite materials for electrodes used in supercapacitor applications are indeed in the great demand due to the need of the improving electrodes that can largely enhanced capacitance. Supercapacitors are generally governed by the same fundamental equations as the typical capacitors. The notable differences are that supercapacitors have utilized their electrodes with higher surface area materials and dielectrics with smaller gap between electrode and insulator to achieve several orders of magnitude greater than conventional capacitors. These lead them to have higher energies than those of typical capacitors and greater power than battery.

In order to realize the supercapacitors, the key strategy is to improve the electrode with larger surface area and also enhanced ability to attract more electrolyte ions. Therefore, the main focus in this dissertation aims to rectify and seek for electrode materials that would improve the ability to attract more ions with the supported larger surface of graphene-based electrodes. The desired materials for the extra-attached layer should also be easy to realize the charge transfer within the material inducing double layer and more stable stacking for better lifetime of device. The promising candidate is proposed with the transition metal phthalocyanines (TMPcs). The available electrons between these interlayers would form a π-π interaction, and the central metallic ion of TMPcs can also be adsorbed as an anchor for attaching a molecule on graphene sheet. Thus, the central target of this research is to investigate the molecular and electronic structures of each selected TMPcs (MnPc, FePc, CoPc, NiPc, and CuPc) that are used as model to formulate stability in microscopic perspective. *Ab initio* calculation is possible by using density functional theory (DFT) for evaluating binding energies and geometry optimization.

In this dissertation, the exchange-correlation (XC) functionals of LDA, PBE, and B3LYP were used to describe and predict the energies and formations of TMPcs and graphene interlayers, and also the individual geometries of TMPcs and graphene. The computational results expect the binding energies of TMPcs on a graphene surface, and the bond length and angle of each TMPc molecular structures whereas experiment and calculation results are in good agreement. Their binding energies show large stabilities for the TMPc/G interlayers, and for comparison under the same XC functional, CoPc/G possesses the lowest one, except the B3LYP results of MnPc/G. The results indicate that, among these formations, CoPc has the most stable structure of stacking TMPc on a basal graphene layer, compared with other candidates within the same calculation parameters. However, it is also pointed out the prediction depends on the choice of selected XC functionals, where the results obtained from PBE and B3LYP share similar trend while those from LDA show several fluctuated ones.

Furthermore, HOMO orbital distribution of completely isolated CoPc molecule has one of the $a_{1g}(d_z^2)$ electron is available, and the empty b_{1g} orbital, which is largely composed of $d_{x^2-y^2}$. The CoPc states e_g are mixed due to hybridization, the interaction between the CoPc and graphene, one electron from the $a_{1g}(d_z^2)$ would transferred from graphene. This suggestion comes from the charge transfer between the d^7 Co configuration and graphene through the d_z^2 orbital. This may lead to one of the possible reason for intermediate formation between CoPc and graphene with strong interaction. However, the computational HOMO-LUMO results from LDA has noticeably failed to represent the $a_{1g}(d_z^2)$ of CoPc, but PBE and B3LYP achieved to reproduce this state so LDA may not be a preferable XC choice for calculation of both energy and orbital distribution.

In addition to the geometry optimization results, most of the TMPc molecules are settled and immobilized at one of the center of benzene ring, hexagonal site (H-site), except for the cases of CuPc and MnPc that are slightly of the central grid. For the case of NiPc/G, the edges of graphene sheet are bent toward the NiPc monomer from the PBE and B3LYP results while there is no such noticeably change in

NiPc structures from all other obtained results. This might be possibility to have strong artifact on the distortion estimations due to too small size of graphene fragment with only 25 benzene rings. However in contrast, there are also several cases that the graphene sheets are still in flat shape, but TMPcs structures are distorted after the geometry have been optimized, such as FePc and MnPc. The deformation of graphene fragment in the model would lead deformation of TMPc layers in reality because the basal graphene substrate would be infinity spread firmly. On the other hand, when the deformation occurred as spatially non-uniform force to graphene substrate, this particular case would lead to substrate damaging where graphene would be eventually peeled off by TMPc layer, and then shortened in electrode lifetime.

Therefore from the computational prediction of CoPc for the strongest anchoring on basal graphene sheet, the production of CoPc/G electrode process in the laboratory scale is feasible that would lead to the possible construction of these tunable hybrid electrodes used for supercapacitor applications.

Keywords: DFT, Electrode, Graphene, Supercapacitor, TMPc.