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Japan Advanced Institute of Science and Technology

氏　　　　　　　名	APICHAI JOMPHOAK	
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論　　文　　題　　目	First-Principle Calculations of Transition Metal Phthalocyanines for Graphene-based Supercapacitor （グラフェン系スーパーキャパシタ用遷移金属フタロシアニンの第一原理計算）	
論 文 審 査 委 員	主査　前園　　涼　　　　北陸先端科学技術大学院大学　　准教授	
	飯田　弘之　　　　　　　同　　　　　　　　　　教授	
	下田　達也　　　　　　　同　　　　　　　　　　教授	
	水田　　博　　　　　　　同　　　　　　　　　　教授	
	小口　多美夫　　　　　大阪大学　　　　　　　　教授	

論文の内容の要旨

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.

論文審査の結果の要旨

　従前の誘電体から充放電特性が改善された「スーパーキャパシタ」素子の実現に向けて、電気二重層形成を通じて誘電効率を増強する方策に関する実験的理論的研究が精力的になされている。電極上に吸着して電荷移動を促進する金属フタロシアニン分子の添加が、この目的での有力な技術手段となっているが、どのような金属種のフタロシアニンが最も安定な電極上積層を実現するかどうかについて、その微視的機構を含めて解明が待たれている。本論文では「安定積層に向けた望ましい特性」を、「より深い表面吸着エネルギー(耐剥離性)」と「より平面を保つ少ない分子変形」と特徴づけた上で、対象となる電極系を「グラフェン層上に配置された金属フタロシアニン単分子」として現実的規模で計算可能なモデルに落とし込み、大規模計算機を活用した第一原理電子状態シミュレーションが適用できる問題として構成した。広範な文献調査を行い、可能な調査候補物質として 5 種の遷移金属元素種に対象を絞り、第一原理構造最適化計算(電子論的エネルギー値を最小にするように原子核位置を緩和させ安定構造を得る手法)を適用した。この結果、コバルトフタロシアニン分子が最も深い表面吸着エネルギーと少ない分子変形を与える事を明らかにした。本論文で適用した手法においては、交換相関汎関数の選定が予見信頼性を大きく左右することが知られているが、本論文では、その影響を検証するために 3 種の異なる典型的な汎関数を用いて予見を注意深く比較検証し、いずれの汎関数を用いてもコバルト系が最良の特性を実現するという予見結果は変わらないという確証を得た。さらに、電子状態計算から得られる電子準位の大小関係や、結合に与する最高占有軌道や最低非占有軌道の空間分布可視化から、コバルト系がどのような理由により最安定特性を実現しているのかについて一定の考察を展開した。本論文に関わる研究成果の一部は既に、申請者を主著者とする査読付原著論文成果 [Surf. Coat Tech. 306, 236-239 (2016). (IF = 2.199)]に発表されており、当該コミュニティにおいて一定の評価を獲得している。

　以上、本論文は、次世代電子デバイスにおける革新的な性能向上実現に向けてのキーとなる基礎的な課題の 1 つを洗い出し、大規模シミュレーションを駆使した系統的な研究調査により新たな知見を提供した業績として、学術的に貢献するところを認め、よって博士(情報科学)の学位論文として十分価値あるものと判断した。