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学 位 論 文 題 名

Liquid-Phase Photo-induced Covalent Modification (PICM) of Single-Layer Graphene
(単層グラフェンの液相光誘起共有結合修飾 (PICM))

Tailoring the electronic structure (bandgap engineering) of graphene is crucial for multi-purpose applications, especially in semiconductor devices. To this end, various efforts have been made to contribute to this modulation. Among them, chemical modification of graphene is a potential method, which can introduce sp^3 defects to graphene, accompanied by forming the covalent bond. By using chemical modification, the electronic nature, chemical and optical property of graphene can be well tailored. Recent years, the electrochemical and photo-induced chemical modification (PICM) at solid-phase has been most studied because of designable, high efficiency and reversible. Nonetheless, to spatially tailor the surface property of graphene, mask is required to prevent the reaction of graphene at the undesired area for the electrochemical method. In the case of solid-phase PICM, the reaction molecule is pre-deposited on graphene surface (forming solid film) followed by laser-irradiation generating the covalent grafting. However, the modified graphene is difficult for further application because of hard to keep clean and slightly low efficiency. In addition, both these two methods are involving complex organic molecules, which is difficult to understand and investigate the reaction mechanism of this covalent modification.

To response, liquid-phase PICM is attracted to develop mask-free, clean, and simplified chemical modification of graphene. Our research group previously investigated the PICM of graphene in pure water, demonstrating the liquid-phase PICM is available and reliable. Without any chemicals, the specific pattern can be achieved by irradiating tightly focused laser at the liquid phase. Furthermore, the sp^2 hybridized carbon of graphene can be restored by high density of laser power or direct heating at high temperature, indicating the liquid-phase PICM induced defects is reversible. However, although the successful modification of graphene is obtained, low efficiency and low degree of functionalization extremely limits the further investigation and applications. Thus, this thesis aims to develop high efficiency, a facile preparation process and controllable design of liquid-phase PICM of graphene. Also, by using this liquid-phase PICM, the reaction mechanism is deeply explored. After that, we aim to extend the application of PICM modified graphene investigating the electronic property.

In the first section (chapter 2), a high-efficiency liquid-phase PICM of graphene is established. In this study, we proposed a simple method to induce highly efficient modification of graphene in short-chain fatty acids (SCFAs) aqueous solutions. In-situ Raman is employed to monitor the efficiency of the liquid-phase PICM. By carefully analyzing, we found that SCFAs with alkyl chain present much higher PICM efficiency than those in pure water and formic acid, indicating the high-efficiency liquid-phase PICM reaction depends on alkyl chains. Furthermore, solid evidences (infrared and theoretical calculation) were conducted to analyze the attached groups on graphene. These results suggest radicals

from the aqueous solution, such as alkyl, ester, and ether, can be stabilized to the graphene surface under laser irradiation and form the sp^3 hybridized bond. A greater downshift of the G-band in Raman spectra is observed upon the PICM with longer alkyl chains, suggesting alkyl chain is covalently attached and the charge doping effect can be controlled by the alkyl chain length of the SCFAs. Finally, we proposed a two stage radicals' reaction mechanism contributes to the high-efficiency liquid-phase PICM in the presence of SCFAs with alkyl chain.

In the second section (chapter 3), we further investigate the electronic property of photo-induced covalently modified graphene (PICM-G) by graphene-enhanced Raman scattering (GERS), thanks to that the liquid-phase PICM modified graphene is easily to be washed and spatially controllable. The PICM-G is fabricated following our study in chapter 2. The covalent patterning area can be easily obtained by this liquid-phase PICM method. We found that the GERS effect from the covalently patterned graphene substrate yields a significantly higher Raman enhancement of the absorbed fluorescent molecules compared to the pristine graphene. The signal enhancement from the PICM region can be attributed to the modulation of electronic structure of graphene. Furthermore, the Langmuir-Blodgett (LB) technique is employed to deposit the mono and multilayer film of the probed 3,3'-Diocadecyloxacarbocyanine Perchlorate (DiO) dye molecule on the PICM-G substrate. The Raman signal enhancement with respect to the layer thickness of probed molecule, excitation wavelength at the PICM region is discussed. To further estimate the GERS effect of the PICM graphene substrate, a most commonly used molecule (Rh6G) is employed. The GERS effect is estimated by calculating the ratio of peak intensity of from PCIM area to that of PG area, which shows highest than any reports (25), indicating the Fermi level of PICM graphene with acetic is more appropriate than pristine graphene for GERS. Finally, we investigate the role of covalent grafting types on GERS enhancement factor (EF) by comparing the graphene substrates prepared in pure water and acetic acid solution. Our findings provide evidence that the functional groups within the chemically patterned region plays a critical role in determining the EF of GERS.