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Chemical Modification of Graphene Controlled by Substrate Surface Treatment with Self-Assembled Monolayers

Graphene is a two-dimensional sheet in which carbon atoms are arranged in a honeycomb lattice form. Its ultimate thinness is one of the most prominent features in its structure. Owing to the thinness, it is possible to change its characteristics by chemical adsorption of foreign atoms or molecules. In addition, the ultimate thinness enables us to modulate an electron density in graphene by field-effect gating in a field-effect-transistor configuration. Therefore, it is expected that the surface chemical modification of graphene can be controlled by such gating method. We have demonstrated that the degree of surface chemical modification of graphene is indeed controllable by electron density modulation of graphene [1, 2]. In this study, we investigate on another methodology of field-effect gating, *i.e.*, molecular gating by means of modification of the supporting substrate surface with a self-assembled monolayer (SAM). The local electric field generated by the electric dipoles of the constituent molecules of the SAM [3] is found to control various chemical modification reactions of graphene.

We used two types of triethoxysilane molecules shown in Figure 1, which have antiparallel dipole moments. A SAM of these molecules was formed on a SiO₂ substrate (hereinafter, referred to as (a) F SAM and (b) CH₃ SAM). Graphene flakes were exfoliated on the SAM-treated substrate with adhesive tape. The degree of chemical modification was determined by the *D* band (~1350 cm⁻¹) in a Raman scattering spectrum.

We have performed molecular gate control on various chemical modifications of graphene. Among them, here we show results of photochemical reactions based on benzoyl peroxide (BPO) [4] deposited on graphene. Figure 2 displays Raman scattering spectra after ultraviolet irradiation to the BPO-covered graphene on (a) F SAM and (b) CH₃ SAM treated substrates. Even after the UV irradiation to induce the photochemical reaction, the *D* band is not seen from graphene on F SAM. On the other hand, it is clearly discernible in the spectrum of graphene on CH₃ SAM. The results indicate that the reactivity of graphene towards the photochemical reaction with BPO is higher on the CH₃-SAM treated substrate than on F-SAM treated one. Graphene on the CH₃ SAM should be more electron rich owing to the electrostatic effect (molecular gating effect) from the adjacent positive charge. Thus, graphene becomes more instable than the hole-rich one on the F SAM, leading to the higher reactivity. In the presentation, we will discuss other chemical modifications such as gas-phase photo-oxidation by atmospheric oxygen and liquid-phase modification by aryl diazonium salt.

References

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Figures

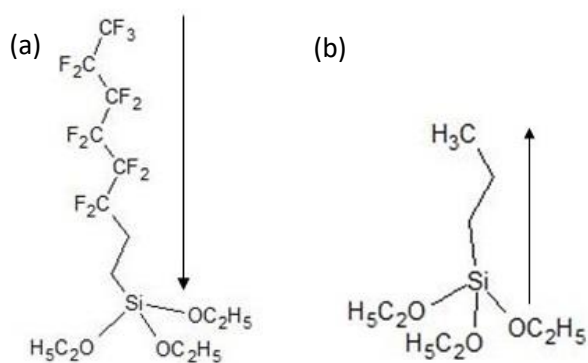


Figure 1: Chemical structure of triethoxysilane molecules used for (a) F-SAM and (b) CH_3 -SAM treatments of the substrate surface. The arrows indicate the direction of the electric dipole moment.

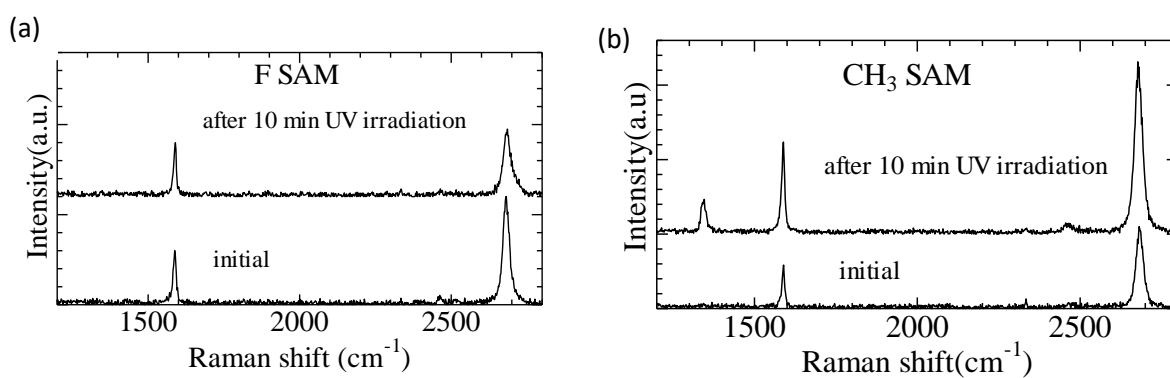


Figure 2: Raman scattering spectra after photo-oxidation of BPO-covered graphene on (a) F-SAM and (b) CH_3 -SAM treated substrates.