
Ryo Nouchi^{1,2}

Kei-ichiro Ikeda¹

¹Department of Physics and Electronics, Osaka Prefecture University, Sakai 599-8570, Japan

²PRESTO, Japan Science and Technology Agency, Kawaguchi 332-0012, Japan

r-nouchi@pe.osakafu-u.ac.jp

Chemical Modification of Graphene Controlled by Polar Self-Assembled Monolayers

Ultimate thinness of graphene is one of the most prominent features in its structure. The thinness enables us to change its characteristics by chemisorption of foreign atoms/molecules and to modulate an electron density in graphene by field-effect gating. 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). A local electric field generated by electric dipoles of the constituent molecules of SAMs [3] is found to control a chemical modification reaction of graphene.

We used two types of triethoxysilane molecules possessing antiparallel dipole moments. Single layer graphene was mechanically exfoliated on a SiO₂ substrate modified with SAMs of these molecules. As shown in Figure 1a, graphene on the CH₃ (F) SAM should be more electron rich (poor) owing to the electrostatic effect (molecular gating effect) from the adjacent positive (negative) charge. Figure 1b shows results of molecular gate control of a photochemical reaction based on benzoyl peroxide (BPO) deposited on graphene [4]. In the Raman scattering spectra acquired after UV irradiation, the D band, which is an indicator of the degree of chemical modification, is discernible in the spectrum of graphene on the CH₃-SAM-modified substrate. It has been proposed that phenyl radical formation triggered by electron transfer from photo-excited graphene to BPO is the rate-limiting step of the whole reaction [4]. This step is more efficient with more electron-rich graphene, *i.e.*, graphene on CH₃ SAM, than the hole-rich one on the F SAM (Figure 1c).

In the presentation, we will also discuss a data correction procedure in which a carrier-concentration dependence of the shape of Raman scattering spectra is taken into consideration.

References

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Figures

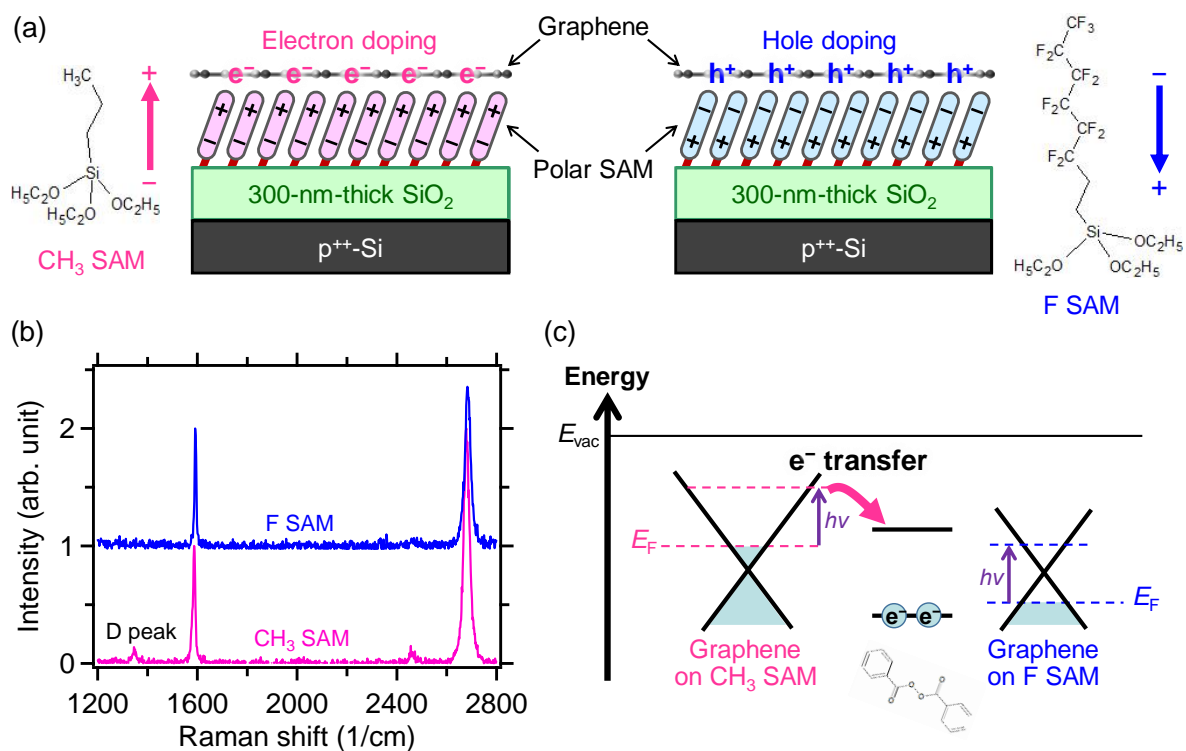


Figure 1: Molecular-gate-controlled solid-phase photochemical reaction of graphene with BPO. (a) Carrier concentration control of graphene by polar SAMs. (b) Raman scattering spectra taken after the reaction. (c) Schematic energy diagram for the rate-limiting step of the reaction.