

photodesorption: photothermal reaction and hot electron injection. Photodesorption can occur even the power density is as low as 0.14 mW/cm^2 , which is, however, too low to raise the temperature of substrate and graphene. Hence the photodesorption of graphene is not a photothermal reaction. We suggest that the photodesorption is evoked by the photogenerated hot electrons in graphene (Fig. 5(a)) [17,18]. By tunneling, the hot electrons transit into the antibonding orbital of O_2 to form excited negative oxygen ions. The short-lived negative ions at the ground vibronic level relax into neutral molecules at the excited vibronic level by another electron tunneling (to graphene) via the Franck-Condon transition (Fig. 5(b)) [19]. The excited vibronic state of O_2 has the vibrational zero-point energy with harmonic frequency $\approx 1580 \text{ cm}^{-1}$ [20], which exceeds the binding energy of O_2 on graphene ($\sim 100 \text{ meV}$) [21] and causes the desorption of O_2 . Assume that $\sigma(E_{\text{ph}})$ is proportional to $\alpha_{\text{abs}}(E_{\text{ph}}) \cdot \eta_t(E_{\text{ph}}) \cdot \rho_{\text{oxy}}(E_{\text{ph}})$, where $\alpha_{\text{abs}}(E_{\text{ph}})$ is the optical absorbance of graphene, $\eta_t(E_{\text{ph}})$ the hot electron tunneling rate between graphene and O_2 , and $\rho_{\text{oxy}}(E_{\text{ph}})$ the density of antibonding states of O_2 . From $E_{\text{ph}} = 2.33 \text{ eV}$ to 3.82 eV , $\alpha_{\text{abs}}(E_{\text{ph}})$ increases by a factor of 2 [13] and $\eta_t(E_{\text{ph}})$ by a factor of 1.46 [estimated by the transmittance of tunneling, having the square potential barrier height = 5 eV (the work function of graphene), and width = 4 \AA (the size of O_2)]. Thus $\rho_{\text{oxy}}(E_{\text{ph}})$ is the remaining dominant term of the photodesorption of O_2 , responsible for a factor of 10^4 of the change in $\sigma(E_{\text{ph}})$, because $\rho_{\text{oxy}}(E_{\text{ph}})$ decreases rapidly as the electron energy is away from the band center of the antibonding orbital of O_2 .

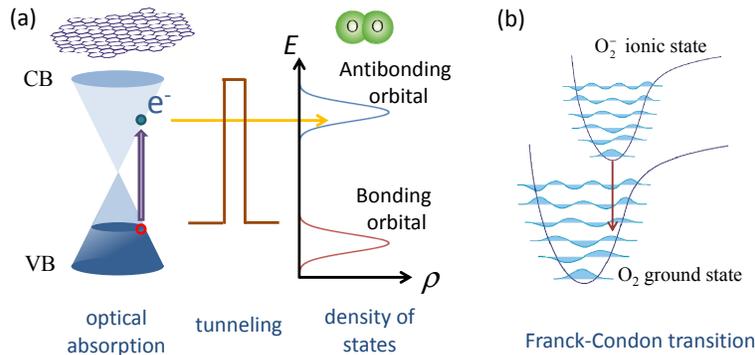


Fig. 5. (a) Photodesorption mechanism of graphene: (from left to right) excitation of electrons by the optical absorption of graphene, electron tunneling from graphene to the antibonding orbital of O_2 , and O_2 acquires kinetic energy to desorb via the Franck-Condon transition. (b) Schematic of the vibronic levels of O_2 and O_2^- to illustrate the Franck-Condon transition.

4. Conclusion

The UV-laser photodesorption of CVD graphene in air is studied by the current response. The analytical expressions of the power-dependent photodesorption kinetics are derived to describe the current response of graphene under illumination. The photodesorption quantities of current response (τ_d , I_s and ΔI) can be expressed as functions of τ_a , σ , and F . Additionally, the steady occupation rate of O_2 on graphene $N_s/N_{\text{max}} = \tau_d/\tau_a$ is derived. The photodesorption cross section σ of graphene increases by four orders of magnitude as E_{ph} increases from 2.33 eV to 3.82 eV . It is suggested that the photodesorption of adsorbed O_2 on graphene is induced by the photogenerated hot electrons and is restricted by the density of antibonding states of O_2 .

Acknowledgments

This work was supported by the Ministry of Science and Technology of Taiwan (Grant No. MOST 102-2112-M-029-005-MY3).