Field-effect surface chemistry: chemical reactions on two-dimensional materials controlled by field-effect transistor configurations

Ryo Nouchi
Department of Physics and Electronics, Osaka Prefecture University and Osaka Metropolitan University, Sakai 599-8570, Japan
PRESTO, Japan Science and Technology Agency, Kawaguchi 332-0012, Japan
E-mail: r-nouchi@pe.osakafu-u.ac.jp and r-nouchi@omu.ac.jp

Abstract
Because chemical reactions are largely governed by the movement of electrons, it is possible to control chemical reactions using electronic devices that provide functionality by controlling the movement of electrons in a solid. In this perspective, we discuss the concept of ‘field-effect surface chemistry,’ which controls chemical reactions on two-dimensional materials using field-effect transistors (FETs), a representative electronic device. The electrical voltages to be applied for the FET operation are the gate voltage and drain voltage. The former is expected to control the Fermi level and exert the effect of the electric field directly on the reactants, while the latter is expected to provide local heating by Joule heat and energy transfer to the reactants. Further, we discuss a sample structure that does not require any voltage but has the same effect as the gate voltage.

1. Introduction
Chemical reactions are largely governed by the movement of electrons in a substance. According to the frontier orbital theory [1], the interaction between the highest occupied molecular orbital of an electron donor and the lowest unoccupied molecular orbital of an electron acceptor causes the delocalisation of electrons by transferring them from the donor to the bonding orbital newly formed via donor–acceptor interactions. Research in the field of electronics has long been focussed on such movement of electrons. With the development of semiconductor engineering technology, electronics have become a technological system that fundamentally supports advanced information processing. With the recent development of the Internet of Things, its importance is further increasing. Although there are various electronic devices, the basic operating principle can be summarised as providing functionality by controlling the movement of electrons in a substance [2]. Consequently, electronic devices that can control the movement of electrons can also control chemical reactions that are largely governed by the movement of electrons.

Electrochemistry involves harnessing electrical energy for chemical reactions; this branch of chemistry has been successfully implemented in industry toward battery engineering, plating, electrorefining, and electrolytic synthesis. However, electrochemical devices require a liquid-phase reaction system that uses electrolyte solutions. In contrast, the method proposed in this article is based on a solid-state device, making it possible to control the reactions without involving a liquid phase. While conventional electrochemical cells are limited to liquid-phase reactions, the proposed method is expected to be applicable to gas-phase reactions.

In this article, chemical reaction control using field-effect transistors (FETs), the most representative electronic devices, is outlined. In FETs, as shown in figure 1(a), the active layer (a semiconductor in most cases), which is the layer through which charge carriers (i.e. electrons or holes) propagate, is placed across an insulator facing an electrode called a gate, which has the same structure as a parallel-plate capacitor. Therefore, when the voltage applied between the two parallel plates (the active layer and the gate electrode) is the $V_G$ and the electrical capacitance of this capacitor structure is $C$, the amount of charge $Q$ in the active layer can be controlled...
according to the representative equation for a capacitor, \( Q = CV\). Because this is identical to controlling the electron concentration, it is highly expected to lead to the control of chemical reactions. However, the surface of the active layer should be bare because the reactants must meet for a chemical reaction to occur. Therefore, a gate stack consisting of an insulator and electrode, which is necessary for the application of the gate voltage, should be formed on the opposite side of the bare surface. The problem here is the screening of the gate electric field. When a sufficient amount of mobile charge exists in the active layer, the charge moves to screen the gate electric field, and the effect of the gate electric field usually does not extend to the bare surface side, which is the reaction field. To avoid this problem, the thickness of the active layer should be lower than the screening length of the gate electric field. Ideally, the thickness should be at the atomic level to maximise the gate electric field effect on the surface (figure 1(b)). In recent years, many two-dimensional (2D) atomic layer materials obtained by the exfoliation of layered materials, such as graphene (monolayer graphite) \[3\], have been identified \[4\]. Further, various ultrathin materials with activities for various chemical reactions have been reported \[5–10\]. In this perspective, the control of chemical reactions on the surface of 2D atomic layer materials using FET configurations is outlined with results mainly for graphene surface reactions and with prospects.

2. Effects of the gate voltage \( V_G \)

The primary effect of \( V_G \) application is the Fermi-level modulation effect due to the parallel-plate capacitor structure of the FET (figure 2(a)), which causes the Fermi level \( E_F \) of the active layer to change because of potential modulation due to \( V_G \) application. This is the origin of the controllability of the charge amount, as mentioned in the introduction. In most cases, it takes a finite \( V_G \) to start accumulating charge; thus, this voltage is defined as the threshold voltage \( V_T \) and is written as \( Q = CV_G - V_T \) \[2\]. The change in \( E_F \) implies that the rate of electron transfer to and from the reactants is modulated, which leads to the control of chemical reactivity. However, it should be noted that even if \( Q \) is controlled, \( E_F \) is hardly moved by the application of \( V_G \) when the density of states (DOS) in the vicinity of \( E_F \) is large, as in common metals. Therefore, the \( E_F \) modulation effect of \( V_G \) is limited to semiconductors and materials with a metallic electronic structure but a small DOS near the \( E_F \), such as graphene \[11\]. As a typical example, the gate control of the attachment of phenyl groups to the graphene surface has been reported \[12\]: benzoyl peroxide (BPO) was deposited on graphene FET structures, and the degree of attachment of phenyl radicals formed by the heat-induced dissociation of the inter-oxygen bonds in BPO was investigated by Raman scattering spectroscopy (figure 2(b)). The intensity of the D band, which is frequently used as a measure of the degree of reaction, correlates with the value of \( V_G \) during the reaction.

Specifically, since the D-peak intensity increased as \( V_G \) increased in the positive direction, it can be understood that the electron transfer from graphene to phenyl radical dominates the reactivity. A similar \( V_G \) dependence has been observed in hydrogen evolution reactions on MoS\(_2\) \[13\], one of liquid-phase electrochemical reactions. The controllability by \( V_G \) was explained by an increase in the electron concentration in the Mo centres adjacent to the S defects, which led to an enhancement of the H abstraction ability. In the case of photo-thermal oxidation of graphene by a green laser, the application of \( V_G \) was found to enhance the reaction regardless of the voltage polarity \[14\]. This polarity independence can be understood by the fact that the bond order of graphene decreases with either electron or hole doping upon the application of positive or negative gate voltages.

The gate-induced \( E_F \) shift can control various redox reactions, including gas-phase reactions, in addition to conventional liquid-phase electrochemical reactions. In addition, solid electrolytes are preferable to solid-state gate dielectrics used in conventional electronics because the extent of \( E_F \) shift is determined by parallel-plate
capacitance. For example, ionic gels containing ionic liquids can be used as the solid electrolyte insulator between plates. However, in reality, the size of the plates is adsorbates. Therefore, it is possible to induce various redox reactions in this energy range.

Considering the electrochemical potential window, the upper limit of $V_G$ is approximately 3 V in several cases. Therefore, it is possible to induce various redox reactions in this energy range.

Another effect of $V_G$, besides the $E_F$ modulation effect, is the direct interaction of the gate electric field on the adsorbates (figure 2(c)). In an ideal infinite-plane parallel-plate capacitor, the gate electric field exists only in the insulator between plates. However, in reality, the size of the plates is finite, and there is a fringing field around the edges of the plates to the surface. In particular, nanomaterials, such as 2D atomic layer materials are often micrometre-scale in the lateral direction, and in such cases, the effect of the fringing field cannot be ignored [16]. Fringing field effects are exerted on the surface side and are not limited by gate electric field screening within the active layer (figure 1(b)). Therefore, it is expected that the limitation of the active-layer thickness will be overcome to some extent. When applied to (liquid-phase) reactions involving ions, the field-induced movement of the ions should be considered. Notably, the Fermi level of the active layer shifts owing to the gating effect of the electric double layer formed by the ions, accumulated on the active layer surface. If the reactant adsorbed on the surface is a molecule with a permanent dipole, it will also be significantly affected by the electric field around the surface side [17]. In the photo-oxidation reaction of graphene by (UV) light irradiation in air, the reactivity increases when a negative $V_G$ is applied [18]. The reactivity of the oxidation reactions should be enhanced by the application of positive $V_G$, which accumulates more electrons (higher $E_F$) than that of negative $V_G$; however, the result is contrary to the expectation. This peculiar $V_G$ dependence is caused by the control of the orientation of the adsorbed water molecules by the electric field around the surface side, where the oriented water molecules are considered to suppress the UV-light-induced photo-desorption of adsorbed oxygen molecules and enable the subsequent generation of reactive oxygen species upon UV light irradiation [19].

The fringing field effect is significant for molecules with ionic bonds because of the strong Coulomb coupling of electric dipoles with an external electric field. Coulomb coupling is known to reduce the bond energy and lead to enhanced dissociation of ionic bonds [17]. In addition, the Diels–Alder addition reaction has recently been reported as an example of a reaction catalysed by an electric field [20]. Density functional theory calculations show that the reaction barriers of the Diels–Alder reaction can be altered by applying an electric field whose strength is as low as the sub-1 V nm$^{-1}$ order [20]. The finite element analysis of the fringing field strength was performed, as shown in figure 2(d) (EStat 6.0, Field Precision LLC). The simulation results show that the field strength at the centre of the surface becomes as high as 3/2 of that inside the gate dielectric, when the width of the active layer reduces to $< 1$ μm. Considering the breakdown voltage of a typical gate dielectric (1.36 V nm$^{-1}$ for SiO$_2$ [21]), a field strength of the sub-1 V nm$^{-1}$ order is expected to be obtained by the fringing field.
3. Effects of the drain voltage \(V_D\)

The first thing that comes to mind is that the effect of applying \(V_D\) is the generation of Joule heat (figure 3(a)). In the photo-oxidation reaction of graphene in air, the reaction proceeds more easily when large Joule heat is generated at high \(V_D\), and the reaction does not proceed easily near the source and drain electrodes, where heat dissipation to the electrodes is likely to occur [18]. Additionally, when the shape of graphene is non-uniform and there is a bottleneck in the electrical current path, position-selective oxidation proceeds because of the high current density and the increase in the local temperature at the bottleneck (figure 3(b)) [19]. This result indicates that the location of the reaction can be controlled by pre-processing the shape of the active layer.

In addition to Joule heat generation, another \(V_D\) effect is phonon excitation via the kinetic energy of the conduction charge carriers (electrons and holes) (figure 3(c)). As \(V_D\) increased, the drain electric field accelerates the carriers and increases their kinetic energy. Regarding the electrical properties of the FET, the excitation of the optical phonon of the gate dielectric causes the saturation of the carrier velocity [22]. Optical phonon scattering has been detected in graphene deposited on hexagonal boron nitride, which has an optical phonon energy of approximately 200 meV, based on the measurements of the electronic transport properties [23]. If adsorbates are present on the surface, the adsorbate vibration can be similarly excited via energy transfer from the kinetic energy of the conduction carriers. When carriers are injected into the adsorbed molecules on a surface through quantum tunnelling from the tip of a scanning tunnelling microscope, the inelastic scattering of the carriers causes the vibrational excitation of the adsorbed molecules, which, in some cases, leads to surface chemical reactions [24–28]. The inelastic scattering of conduction carriers by adsorbates in FETs is expected to create a similar situation. However, to eliminate the energy dissipation path due to the optical phonon excitation of the underlying gate dielectric, it is necessary to employ a suspended active layer [29].

Similarly, the \(V_D\) application can activate the active layer. In the case of the oxidative coupling of methane over cerium tungsten oxide catalysts, the reaction temperature was found to decrease when an electrical current flowed through the catalyst bed [30]. The proposed mechanism involves the activation of lattice oxygen through the oxidation of Ce cations, which enhances the ability of H abstraction from methane. This catalyst is not a 2D material; however, the \(V_D\) effect can be applied to non-2D materials if the current path is not limited to a small area, such as near the gate dielectric in FETs. Considering the existence of various 2D catalysts [31], the active layer would also get activated in 2D catalytic FETs.

Unlike the \(V_G\) effect, the \(V_D\) effect can be applied to (liquid-phase) reactions involving ions, without the influence of ion movement. The movement of ions is generally slow, and it is impossible to follow rapidly varying electric fields. Therefore, the application of a high-frequency AC \(V_D\) can create a scenario with no ionic motion. In contrast, because the polarity of \(V_G\) affects the species of the accumulated charge carriers in the active layer (electrons or holes), and the modulation direction of the carrier concentration/Fermi level can increase or decrease, the application of AC voltage is not suitable for reaction control by \(V_G\).

4. Sample structure to mimic the \(V_G\) effect

In the above, reaction control using the FET structure is outlined. However, those who are not familiar with electrical measurements may find the method requiring an understanding of FET operation to be challenging. In this section, we discuss the ‘molecular gating’ effect using the self-assembled monolayers (SAMs) of polar...
molecules, as they have the same effect as applying the gate voltage but without the requirement of applying the actual voltage (figure 4). This concept can be extended to polar surfaces, including 2D materials with out-of-plane ferroelectricity [32] and intrinsic polarity [33]. The advantage of using polar molecules is the flexibility of molecular design enabled by organic synthetic chemistry. The constituent molecules of polar SAMs generally consist of three building blocks: the binding group to the underlying surface; polar terminal group; and spacer connecting these two blocks. When the active layer is deposited on the polar SAM, the electric field formed by the electric dipole formed by the polar terminal group electrostatically induces a charge opposite to that of the adjacent pole of the dipole. In other words, holes are induced from the electron-withdrawing terminal group (negative pole), and electrons are induced from the electron-donating terminal group (positive pole), and they have the same effect as applying negative or positive \( V_G \) respectively.

The effect of the polar SAMs on the active layer has been used to control the threshold voltage \( V_T \) of FETs [34, 35] and later to control the carrier concentration of 2D materials, such as graphene [36–39] and transition metal dichalcogenides [40]. The reactivity of phenyl radicals formed from BPO with graphene formed on the polar SAMs with different dipole orientations has been examined. It has been confirmed that the reactivity is enhanced on SAMs with dipoles oriented to increase the concentration of the electrons in graphene [41]. This result is consistent with the \( E_F \) modulation effect of the \( V_G \) as described in the \( V_G \) section.

5. Conclusions

In this perspective, we have discussed the possibility of controlling chemical reactions, which are largely governed by the movement of electrons, using electronic devices that are functionalised by controlling the movement of electrons. In particular, the concept of chemical reaction control using FETs, a typical electronic engineering device, was outlined with prospects. Graphene, monolayer graphite, was mainly used as an example. However, it should be noted that the effects of the voltages (\( V_G \) and \( V_D \)) required for the operation of FETs on surface chemical reactions apply not only to graphene but also to all 2D atomic layer materials, although some effects are mainly limited to semiconductors or can be applied to non-2D materials. Further, by extracting the essence of the effect of the voltage application, it is possible to construct a system that does not depend on the voltage application.

A possible outcome of chemical reaction control in electronics is the surface modification of the active layer toward the development of high-performance sensors. The affinity of the surface to analytes can be increased by the chemical attachment of surface functional groups that possess high affinity to the analytes. 2D materials, the main target of this study, are highly sensitive to surface phenomena owing to their structural features (extreme thinness), and surface modification for sensor applications is a major application target. Among the reactions described in this article, the photo-oxidation of graphene proceeds from the edges, thereby reducing the width of the graphene layer, which may lead to the development of patterning techniques for the active layer. Thus, this methodology can be significant for the chemical modification of electronic materials.

The concept of 'field-effect surface chemistry' discussed in this article will help electronics researchers to deal with chemical reactions as well as chemists to control reactions using electronic devices, leading to the further development of the fusion discipline of electronics and chemistry. Although the size of individual FETs is small, wafer-scale integration using semiconductor engineering technologies enables the upscaling of FET-controlled reactions. Nevertheless, there are challenges to be addressed toward practical applications, such as the uniformity of operation of individual FETs; however, this methodology still retains ample potential for the development of next-generation systems.

Acknowledgments

This work was supported by JST, PRESTO Grant Number JPMJPR17S6; and JSPS KAKENHI Grant Number JP19H02561.
Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

ORCID iDs

Ryo Nouchi @ https://orcid.org/0000-0002-7232-4827

References

[1] Fukui K and Fujimoto H 1997 Frontier Orbitals and Reaction Paths: Selected Papers of Kenichi Fukui (Singapore: World Scientific)
[2] See S and Ng K K 2006 Physics of Semiconductor Devices (New York, NY: Wiley)
[3] Geim A K and Novoselov K S 2007 The rise of graphene Nature Mater 6 183–91
[4] Ashton M, Paul J, Simnett S B and Hennig R G 2017 Topology–Scaling Identification of Layered Solids and Stable Exfoliated 2D Materials Phys. Rev. Lett. 118 106101
[5] Li H, Jia X, Zhang Q and Wang X 2018 Metallic transition-metal dichalcogenide nanocatalysts for energy conversion Chem 4 1510–37
[6] Noh S H, Hwang I, Kang J, Seo M H, Choi D and Han B 2018 Tuning the catalytic activity of heterogeneous two-dimensional transition metal dichalcogenides for hydrogen evolution J. Mater. Chem. A 6 20005–14
[7] Lemes G, Sebastián D, Pastor E and Lázaro MJ 2019 N-doped graphene catalysts with high nitrogen concentration for the oxygen reduction reaction J. Power Sources 438 227036
[8] Ida S and Ishihara T 2014 Recent progress in two-dimensional oxide photocatalysts for water splitting J. Phys. Chem. Lett. 5 2533–42
[9] Zhaung, Li G, Yang Y, Li M, Jia Y, Yao X and Zhu Z 2017 Ultrathin iron-cobalt oxide nanosheets with abundant oxygen vacancies for the oxygen evolution reaction Adv. Mater. 29 1606793
[10] Yu Y, Huang S Y, Li Y, Steinhann SN, Yang W and Cao L 2014 Layer–dependent electrocatalysis of MoS2 for hydrogen evolution Nano Let. 14 553–8
[11] Castro Neto A H, Guinea F, Peres N M R, Novoselov K S and Geim A K 2009 The electronic properties of graphene Rev. Mod. Phys. 81 109–62
[12] Liu D, He M, Huang C, Sun X and Gao B 2017 Fermi-level dependence of the chemical functionalization of graphene with benzoyl peroxide J. Phys. Chem. C 121 10546–51
[13] Wang Y, Udyavara S, Neurock M and Frisbie C D 2019 Field effect modulation of electrocatalytic hydrogen evolution at back-gated two-dimensional MoS2 electrodes Nano Lett. 19 6118–23
[14] Kim M A, Qiu N, Li Z, Huang Q, Choi Z, Du S and Liu H 2020 Electric field effect on the reactivity of solid state materials: the case of single layer graphene Adv. Funct. Mater. 30 1909269
[15] Huang W, Chen J, Wang G, Yao Y, Zhaung X, Pankow RM, Cheng Y, Marks T J and Facchetti A 2021 Dielectric materials for electrolyte gated transistor applications J. Mater. Chem. C 9 39348–76
[16] Venugopal A, Chan J, Li X, Magnuson C W, Kirk W P, Colombo L, Ruoff R S and Vogel E M 2011 Effective mobility of single-layer graphene transistors as a function of channel dimensions J. Appl. Phys. 109 104511
[17] Shaik S, Danovich D, Joy J, Wang Z and Stuyver T 2020 Electric-field mediated chemistry: uncovering and exploiting the potential of (oriented) electric fields to exert chemical catalysis and reaction control J. Am. Chem. Soc. 142 12551–62
[18] Mitoma N and Nouchi R 2013 Gate-controlled ultraviolet photo-etching of graphene edges Appl. Phys. Lett. 103 201605
[19] Nouchi R, Matsumoto M and Mitoma N 2019 Gate-controlled photo-oxidation of graphene for electronic structure modification J. Mater. Chem. C 7 1904–12
[20] Huang X et al 2019 Electric field–induced selective catalysis of single-molecule reaction Sci. Adv. 5 eaaw3072
[21] McPherson JW, Kim J, Shanware A, Mogul H and Rodriguez J 2003 Trends in the ultimate breakdown strength of high dielectric-constant materials IEEE Trans. Electron Devices 50 1771–8
[22] Barreiro A, Lazzeri M, Moser J, Mauri F and Bachtold A 2009 Transport properties of graphene in the high-current limit Phys. Rev. Lett. 103 076601
[23] You Y G, Ahn J H, Park B H, Kwon Y, Campbell E E B and Jhang S H 2019 Role of remote interfacial phonons in the resistivity of graphene Appl. Phys. Lett. 115 043104
[24] Hla S-W, Bartels L, Meyer G and Rieder K-H 2000 Inducing all steps of a chemical reaction with the scanning tunneling microscope tip: towards single molecule engineering Phys. Rev. Lett. 85 2777–80
[25] Sloan P A and Palmer R E 2005 Two-electron dissociation of single molecules by atomic manipulation at room temperature Nature 434 367–71
[26] Lee H J and Ho W 1999 Single–bond formation and characterization with a scanning tunneling microscope Science 286 1719–22
[27] Dujardin G, Walkup R E and Avouris P 1992 Dissociation of individual molecules with electrons from the tip of a scanning tunneling microscope Science 255 1232–5
[28] Kim Y, Komeda T and Kawai M 2002 Single–molecule reaction and characterization by vibrational excitation Phys. Rev. Lett. 89 126104
[29] Bolotin K I, Sikes K J, Jiang Z, Klima M, Fudenberg G, Hone J, Kim P and Stormer H L 2008 Ultrahigh electron mobility in suspended graphene Solid State Commun. 146 351–5
[30] Ogo S, Nakatubo H, Ishiwaki K, Sato A, Murakami K, Yabe T, Ishikawa A, Nakai H and Sekine Y 2018 Electron-hopping brings lattice strain and high catalytic activity in the low-temperature oxidative coupling of methane in an electric field J. Phys. Chem. C 112 20809–96
[31] Deng D, Novoselov K S, Fu Q, Zheng N, Tian Z and Bao X 2016 Catalysis with two-dimensional materials and their heterostructures Nat. Nanotechnol. 11 218–20
[32] Fu C-F, Sun J, Luo Q, Li X, Hu W and Yang J 2018 Intrinsic electric fields in two-dimensional materials boost the solar-to-hydrogen efficiency for photocatalytic water splitting Nano Lett. 18 6312–7
[33] Wang F et al 2016 Nanometre–thick single-crystalline nanosheets grown at the water–air interface Nat. Commun. 7 10444
[34] Kobayashi S, Nishikawa T, Takenou T, Mori S, Shioda T, Mitani T, Shimotani H, Yoshimoto N, Ogawa S and Iwasa Y 2004 Control of carrier density by self-assembled monolayers in organic field–effect transistors Nat. Mater. 3 317–22
[35] Takeya J, Nishikawa T, Takenou T, Kobayashi S, Iwasa Y, Mitani T, Goldmann C, Krellner C and Batlogg B 2004 Effects of polarized organosilane self-assembled monolayers on organic single-crystal field-effect transistors Appl. Phys. Lett. 85 3078–80
[36] Yokota K, Takai K and Enoki T 2011 Carrier control of graphene driven by the proximity effect of functionalized self-assembled monolayers Nano Lett. 11 3669–75
[37] Sojoudi H, Baltazar J, Tolbert L M, Henderson C L and Graham S 2012 Creating graphene p–n junctions using self-assembled monolayers ACS Appl. Mater. Interfaces 4 4781–6
[38] Ku G M, Lee E, Kang B, Lee J H, Cho K and Lee W H 2017 Relationship between the dipole moment of self-assembled monolayers incorporated in graphene transistors and device electrical stabilities RSC Adv. 7 27100–4
[39] Nouchi R and Ikeda K 2019 Adsorbates as a charge-carrier reservoir for electrostatic carrier doping to graphene Appl. Phys. Express 13 015005
[40] Li Y, Xu C-Y, Hu P and Zhen L 2013 Carrier control of MoS$_2$ nanoflakes by functional self-assembled monolayers ACS Nano 7 7795–804
[41] Nouchi R and Ikeda K 2020 Photochemical reaction on graphene surfaces controlled by substrate-surface modification with polar self-assembled monolayers Phys. Chem. Chem. Phys. 22 1268–75