We are IntechOpen,
the world's leading publisher of
Open Access books
Built by scientists, for scientists

6,900
Open access books available

186,000
International authors and editors

200M
Downloads

154
Countries delivered to

Our authors are among the

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

CLARIVATE ANALYTICS
BOOK CITATION INDEX
INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Chapter

Applications of Graphene Modified by Self-Assembled Monolayers

Gulsum Ersu, Yenal Gokpek, Mustafa Can, Ceylan Zafer and Serafettin Demic

Abstract

Self-assembled monolayers (SAMs) are well-oriented molecular structures that are formed by the adsorption of an active site of a surfactant onto a substrate's surface. Aromatic SAMs were used to modify anode/hole transport layer interface in order to achieve preferable barrier alignment and charge carrier injection from anode to an organic-based thin film material. Other functions of SAMs include current blocking layers or moisture penetration blocking layers, dipolar surface layers for enhanced charge injection, and modification of work function of a material such as graphene acting as a spacer to physically separate and electrically decouple it from the substrate. Additionally, SAM modification of graphene leads to its electronic passivation at layers' edges, elimination of defects, and enhanced adhesion and stability. The surface modification with molecules capable of forming SAM is a fast, simple, low-cost, and effective technique for the development of novel materials especially for the production of electronic devices. The ability to modify its properties by SAM technique has opened up a wide range of applications in electronic and optoelectronic devices.

Keywords: self-assembled monolayer, graphene, surface modification, interface modification, optoelectronic devices

1. Introduction

The development of more efficient, multifunctional, and miniaturized electronic devices requires a continuous research in the area of suitable materials to meet the demand of the modern society. Self-assembled monolayers (SAMs), which are arranged spontaneously on surfaces of the substrate due to the chemical or physical interactions of molecules with a substrate, have gained considerable attention in the past decade. SAMs opened a way toward the miniaturization in microelectronics as well as tailoring the properties of surfaces such as graphene [1–6].

This review focuses on researches committed over the past decade about the modification of graphene via SAM technique. In Section 2, a brief overview of the modification methods of graphene with SAMs was given. In Section 3, the applications of graphene modified by SAMs are summarized and discussed.

## 2. Modification of graphene with self-assembled monolayers

Graphene is a good candidate material for many applications due to its unique optical, mechanical, and electronic properties [7–10]. Pristine graphene is a zero band gap material, chemically inert, and also insoluble in many organic and inorganic solvents [11–13]. Therefore, it cannot be used in many applications. In order to achieve commercial viability and provide to the specific needs of device applications, it is necessary to control the electrical properties of graphene without damaging its intrinsic properties. To fully utilize its potential, the surface and electronic structures of graphene have been modified via functionalization (post-synthesis) or doping (during in situ synthesis) methods [14–16]. Substitutional doping of graphene occurs during the synthesis by covalently bonding the chemical groups and thereby transforms carbon hybridization from sp^2 to sp^3 [17–19]. On the other hand, functionalization of graphene is a physical process involving the addition of functional species onto graphene sheets to manipulate van der Waals interactions occurring effectively among the graphene sheets. In the substitution process, electrons are exchanged between dopant molecules bonded onto the graphene surface and graphene. Surface charge transfer depends on the relative energy of the highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO) of the dopant with respect to the Fermi level of graphene [16, 20–23]. Many different chemical substances have been studied for the functionalization of graphene, and SAM technique is one of them. An ultrathin layer, SAM, can be uniformly formed on the surface by the attachment of the SAM-forming molecule through its functional group as a result of a covalent bond. This technique provides a suitable and flexible way to modify the surface properties of the substrate materials to some extent or completely depending on the molecular structure of acting as SAM-forming molecule. Recent reports have also shown that SAMs can significantly change the properties of graphene without sacrificing the intrinsic graphene performance. In order to modify the electronic properties of graphene by SAM technique, the usage of either electron donating or withdrawing terminal groups has been reported by Yan et al. [24]. As shown in **Figure 1**, the threshold voltage (V_{th}) which corresponds to the neutrality point in graphene field-effect transistor (FET) devices shifted to positive values after the decoration of SiO_2 substrates by using fluorinated molecules (F-SAMs), indicating p-type doping of the graphene layer. For the graphene FET device made by CH_3-SAMs and H_2N-SAMs, the negative V_{th} shift was observed, indicating p-type FET behaviors. This clearly indicates modification of the electronic properties of graphene which becomes available by suitably adapting the SAM techniques.

SAMs have been widely used to eliminate the Schottky barrier at the materials' interface by modifying the interface between graphene and its support substrate which is creating p-n junctions in graphene [25–27]. Sojoudi et al. used 3-aminopropyltriethoxysilane (APTES) and perfluorooctyltriethoxysilane (PFES) for the modification of the interface between transferred CVD-graphene films and its supporting dielectric [28]. Thus, n-type and p-type graphene was created by treating APTES and PFES, respectively. As shown in **Figure 2**, APTES and PFES are patterned on the same dielectric, thus creating a graphene p-n junction. They demonstrated that substrate functionalizing with these SAMs resulted in p-n junctions with controlled position and height.

Recent studies have shown that graphene functionalization has been enhanced significantly by electrochemical control [29–32]. Fermi level of graphene can be shifted and also increased its reactivity toward aggressive chemicals by application of electrochemical potential. The groups of Treossi and Palermo used electrochemical approach,
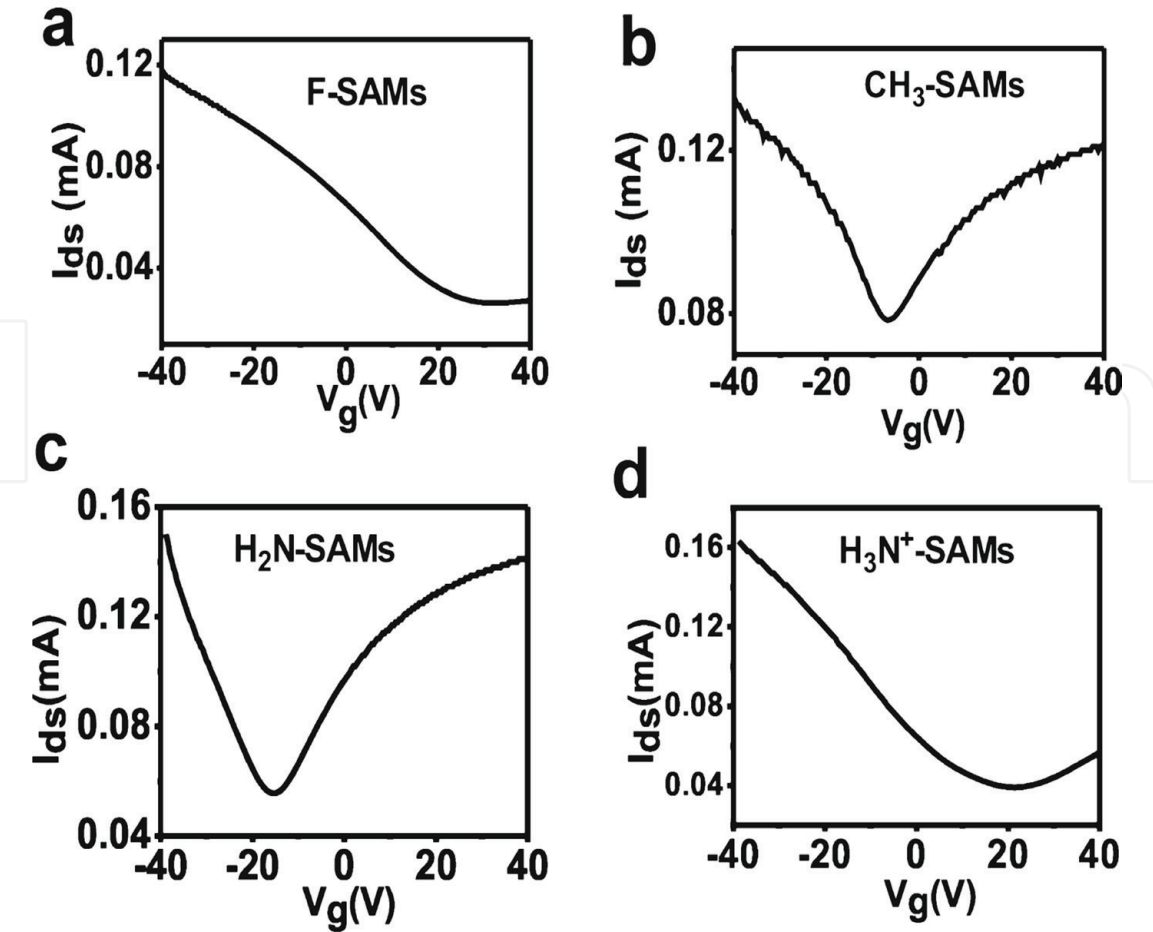
Figure 1.
I_{ds}/V_g characteristics of graphene-based FET devices fabricated on (a) 1H,1H,2H,2H-perfluorooctyltriethoxysilane (F-SAMs), (b) butyltriethoxysilane (CH$_3$-SAMs), (c) 3-aminopropyltriethoxysilane (H$_2$N-SAMs), and (d) protonated form produced from the H$_2$N (H$_3$N$^+$-SAMs) (this figure is reprinted from Ref. [24]).
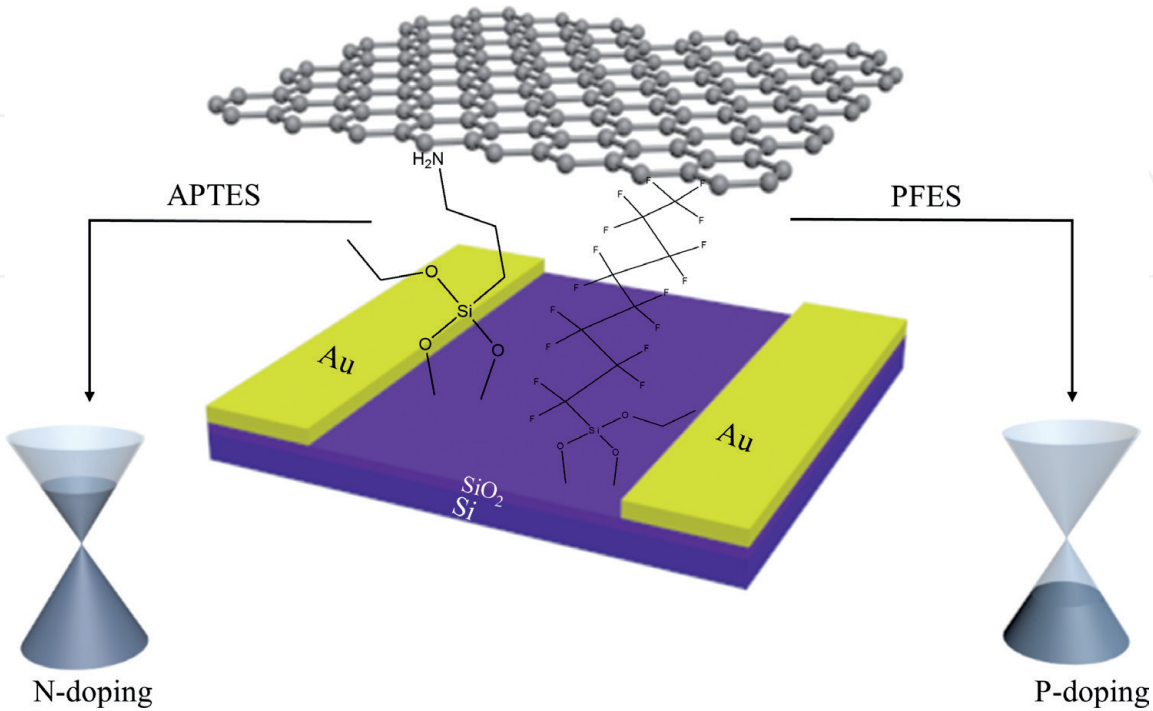
Figure 2.
Schematic representation of graphene p-n junction fabrication.

a fast and simple method, to functionalize graphene [33]. The electrochemical potential allowed good control over the morphology of the 4-docosyloxy-benzenediazonium tetrafluoroborate (DBT) suspended layer, which does not react randomly on the substrate, and also transformed the physisorption into a covalent chemisorption.

3. Applications of graphene/SAM structure

Graphene has well-known electrical properties, which may be utilized in various applications such as biosensors, environmental sensors, electronic and optical devices, etc. Modification with SAM can result in the change of properties at the interface, such as friction coefficient. The monolayer can also be utilized as a physical spacer, in order to enhance the sensing properties of the layer underneath. Apart from these applications, SAMs can be used in order to synthesize graphene, both by electrostatical assembly of graphene flakes onto the surface and by providing the carbon atoms that is required to assemble graphene from their own molecular structure.
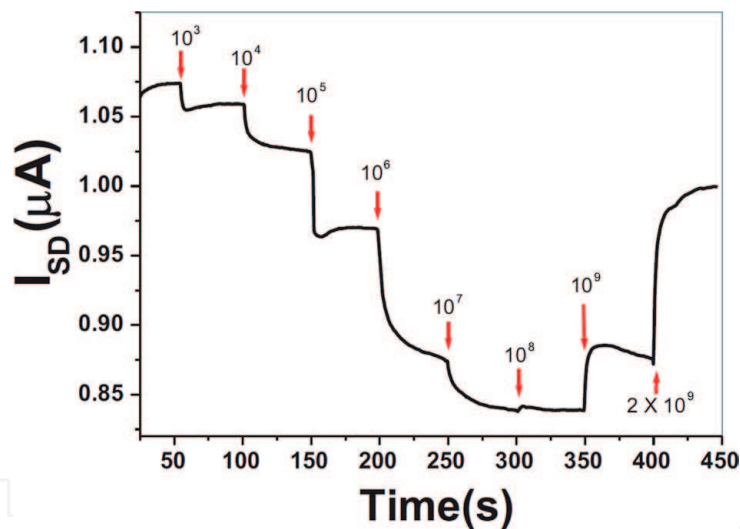
3.1 Biosensor

The enhancement effect of SAM is widely used in the field of biosensor and biomedical. Shi et al. formed a SAM from 4-aminothiophenol (4-ATP) solution on gold substrate and placed the prepared substrate in graphene oxide (GO) solution vertically. Coupling reagents ethylene dichloride and N-hydroxysuccinimide (EDC and NHS, respectively) were added to promote the reactions between $-NH_2$ groups of SAM molecules and $-COOH$ groups of GO. After the device fabrication, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were carried out, and ultrasensitive electrochemical Hg ion sensing properties were shown [34]. Sun et al. prepared GO and fluorescent SAMs with thrombin aptamer (TBA) fixed onto the outermost layer and used CdTe quantum dots as a fluorescence probe, which allow sensing biomolecules by interfacial energy transfer from CdTe in SAMs to GO. The measured fluorescence spectra showed that the increase of the intensity was related to the concentration of the target molecule (**Figure 3**) and the linear correlation was obtained by using GO which was necessary for defining the device as a sensor [35].

Thakur et al. prepared a graphene-based FET sensor using α-ethyl-tryptamine (AET) to add functionality to the electrodes. This approach enables the electrostatical adsorption of functional groups that are present in GO monolayers, such as carboxylic acid and epoxide, by the amine end of AET. The selectivity and response time showed great results, being able to detect a single *E. coli* cell from a vast amount of sample (**Figure 4**). With the incorporation of suitable probing molecules, this approach could be a useful tool to detect other bacteria as well [36]. For related bacteria sensing applications, Chang et al. reported that 2-aminoethanethiol molecules were self-assembled onto Au electrodes by immersion, and then thermally reduced monolayer of GO was deposited on the electrodes due to electrostatic interactions. After some treatments, the device was incubated in the PBS containing anti-*E. coli* O157 antibodies and introduced as a high-performance FET chemical sensor and biosensor [37].

As a selectivity study, Khan et al. suggested an ITO-based, APTES-modified sensor that contained electrochemically reduced GO. Positively charged amino groups (NH_3^+) within APTES have interacted with the negatively charged carboxyl and hydroxyl groups within GO. This electrostatic interaction has allowed deposit of GO onto ITO/APTES electrode. It was observed that the electronic transport is improved with the modification of the ITO surface with SAM, and the addition of
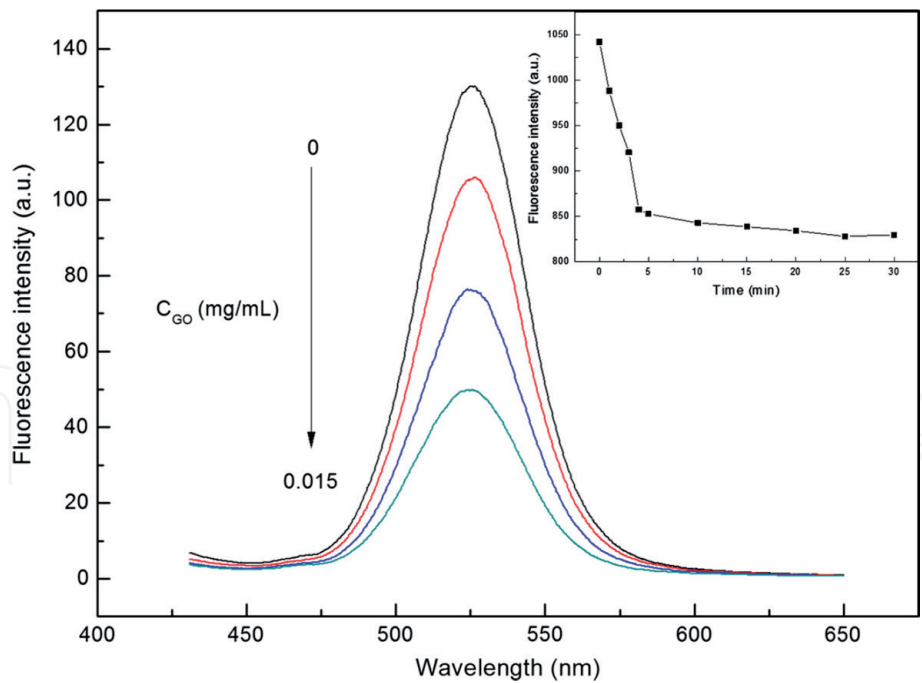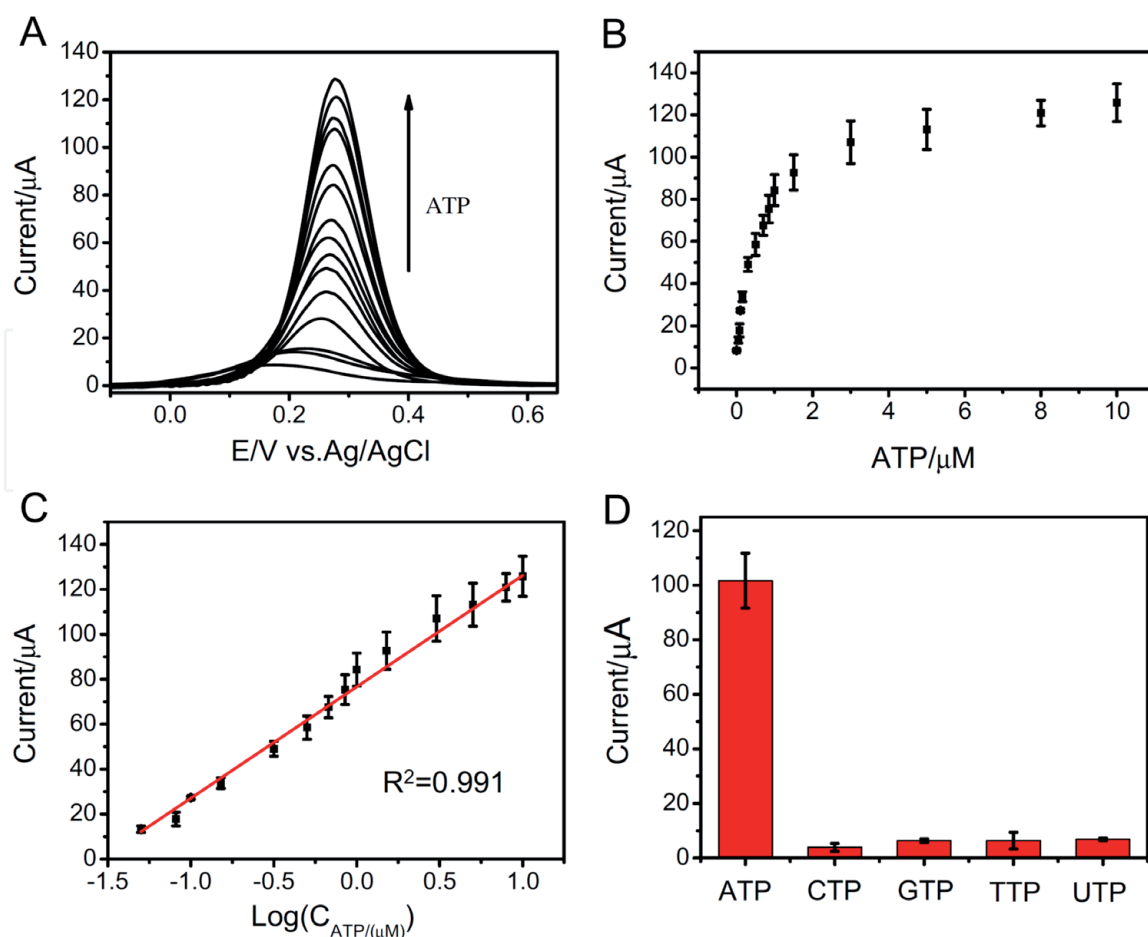
Figure 3.
Fluorescence spectra of sensor at different concentration of tDNA, inset: plot of fluorescence intensity ratio related to concentration with and without GO (figure image reprinted from Ref. [35]).

Figure 4.
Real-time detection (V_{ds} = 0.1 V) of E. coli (CFU/mL) in water with the anti-E. coli/AuNPs/Al$_2$O$_3$/rGO biosensor (figure image reprinted from Ref. [36]).

GO onto the ITO/SAM surface increased the conductivity. Therefore, the resulting device had the property of sensing the oxidation peak of tyramine due to selective behavior of electrode toward electrooxidation. The sensor had also stability and selectivity tests, which it stayed stable for 3 weeks (with the loss of <5% activity) and as selective for human urine, commercial milk, and beer sample. Final conclusions ended up with that the device had sensing capabilities for dopamine and ascorbic acid as well, and it is ready for commercial applications [38].

Feng et al. studied a new type of electrochemical aptasensor for highly sensitive detection of adenosine triphosphate (ATP) and adenosine deaminase (ADA) activity. For modification, 6-mercaptohexanol (MCH) was used. Fabricated sensor could sense different molecules with varying concentrations and had amplified electrochemical signals, due to the facilitation of electron transfer of the functionalized graphene (**Figure 5**) [39]. Yeh et al. demonstrated graphene field-effect transistors (G-FETs) for
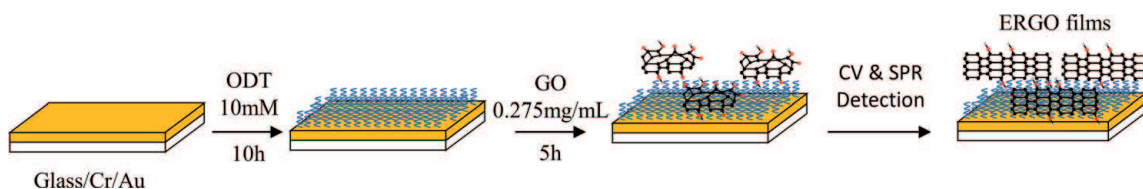
5

Figure 5.
(A) Differential pulse voltammetry (DPV) responses, (B) current intensities with different ADA active units, (C) a linear relationship between DPV peaks and ADA active units, and (D) specificity of the assay for ADA activity (figure image reprinted from Ref. [39]).
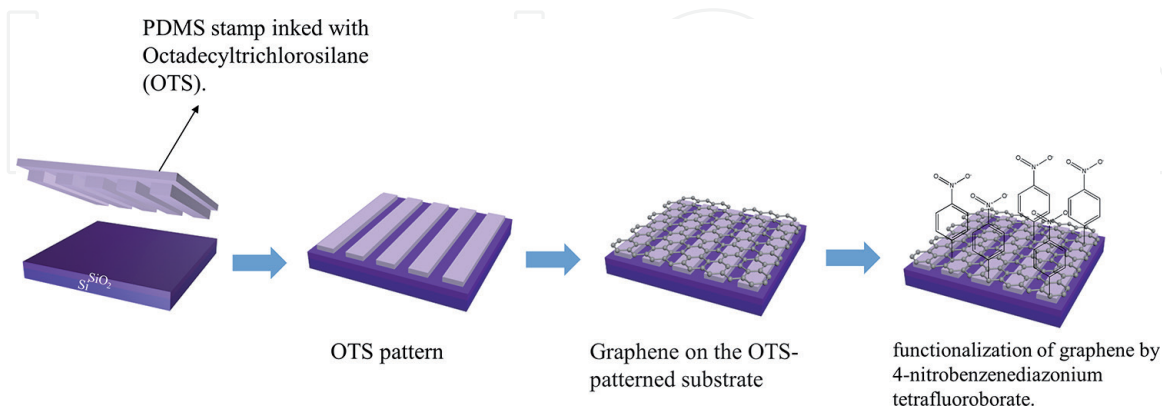
high-mobility applications that were both rigid and flexible. First, graphene was synthesized by CVD method and then transferred onto silicon substrates. The graphene-coated silicone samples were soaked into the solution of hexamethyldisilazane (HMDS) used as SAM-forming molecule for 17 h in a partially covered beaker. The samples were turned into G-FET devices using e-beam lithography and functionalized. As a result, they showed that modification of substrates for graphene electronic devices through patterned SAM arrays of HDMS can enhance the electrical properties of G-FETs by limiting and screening the interactions between graphene and hydrophilic polar groups attached. The HMDS-modified G-FET devices they built could detect cancer biomarker CSPG4 in serum samples at a concentration of as low as 0.01 fM, which is five orders of magnitude more sensitive than a conventional colorimetric assay [40].

Chiu et al. modified a gold electrode using 1-octadecanethiol (ODT) as SAM-forming molecule and then immersed it into GO aqueous solution. After the completion of the coating process, the GO film could be turned into electrochemically reduced GO (ERGO) films. The resulting film showed sensing properties, and the process variables can control the residual oxygen functionalities and conductivity in GO sheets in order to provide tools for sensitive immunoassay detection (**Figure 6**) [41]. Bhardwaj et al. prepared a biological sensor that contained covalently bonded GO array with a layer of SAM formed by 4-aminothiophenol on Au electrodes. After functionalizing the surface with lipase enzyme, the sensor could bind with tributyrin and found to be linearly correlated with concentration between certain limits [42].

In a study of binding mechanism, Wang et al. reported that included CVD-grown graphene, hexagonal boron nitride (hBN), and OTS as SAM-forming molecules. They also used a stamp-like micropatterning process in order to give SAM layer a

Figure 6.
Fabrication procedure of GO film.

PDMS stamp inked with
Octadecyltrichlorosilane
(OTS).

OTS pattern

Graphene on the OTS-
patterned substrate

functionalization of graphene by
4-nitrobenzenediazonium
tetrafluoroborate.

Figure 7.
Illustration of reactivity imprint lithography. PDMS stamp inked with OTS-SAM was used to pattern SiO₂
substrate. Graphene is transferred onto the patterned substrate and reacted with 4-nitrobenzenediazonium
tetrafluoroborate.

Si/SiO$_2$/Graphene

Si/SiO$_2$/TPA/Graphene

Si/SiO$_2$/CAR/Graphene
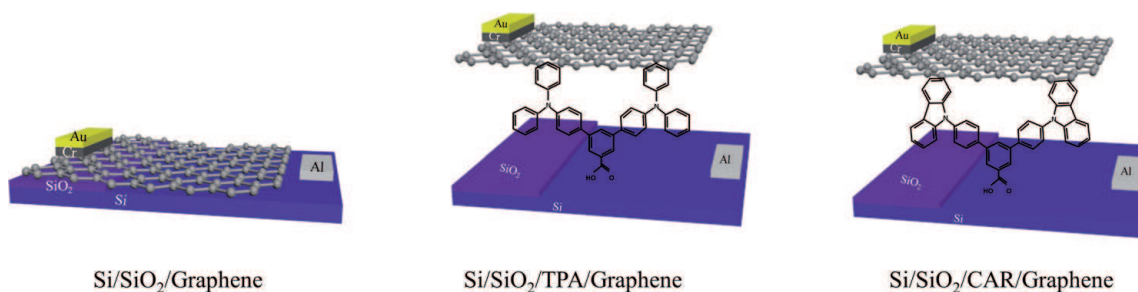
Figure 8.
The structure of devices.

pattern before the coating of the graphene, which affected the binding mechanism of target molecules (**Figure 7**) [43].
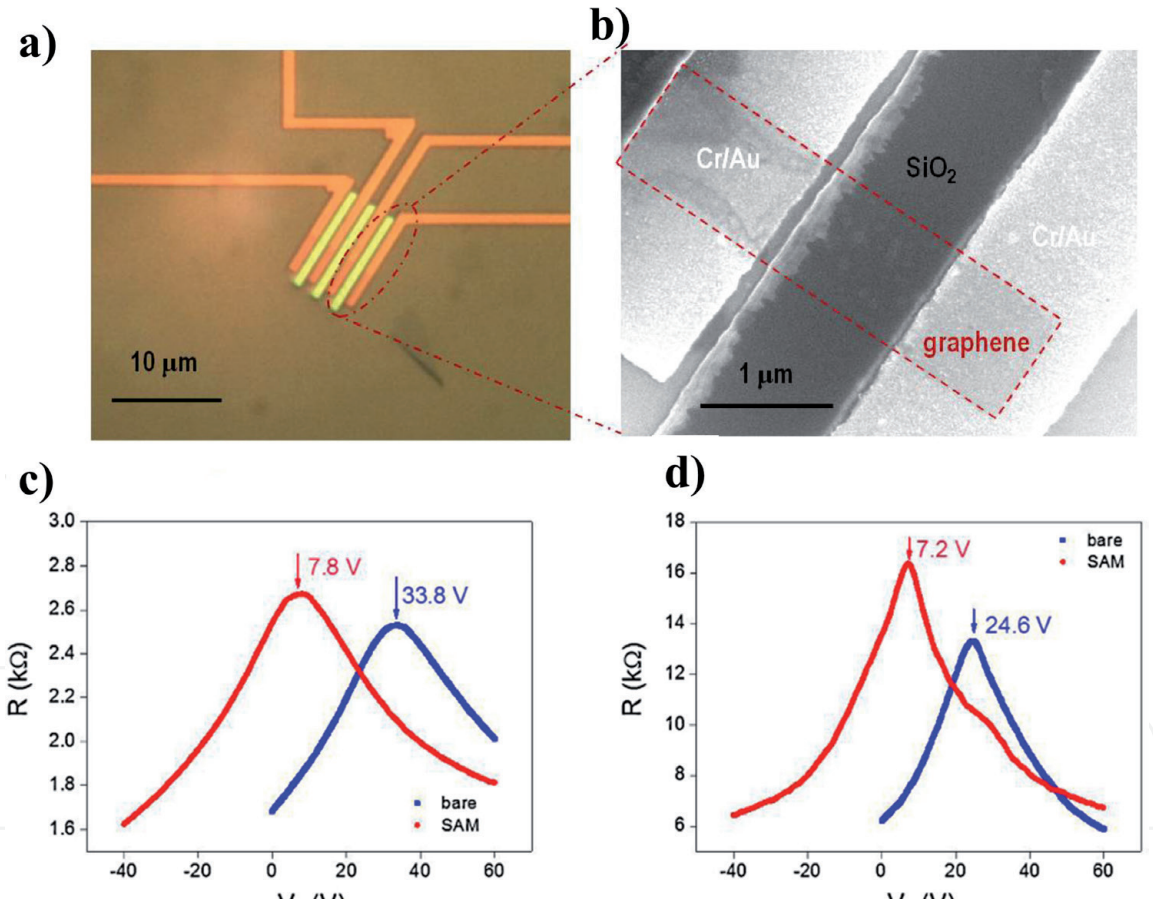
3.2 Device

One of the several properties of SAM layers is to alter the working conditions of the bare device. Aydin et al. investigated the properties of a diode that contained graphene, 4″bis(diphenylamino)-1, 1′:3″-terphenyl-5′carboxylic acids (TPA), and 4,4-di-9H-carbazol-9-yl-1,1′:3′1′-terphenyl-5′carboxylic acid (CAR) aromatic SAMs (**Figure 8**). The decrease in the Schottky barrier height and series resistance by forming a suitable interface between Si and graphene is also noted. The graphene forms π-π interaction with aromatic SAMs as well. The theoretical calculations of the study also confirmed that CAR molecules showed better results than TPA, due to the more compatible energy levels [44].

Kim et al. studied the electrical transport characteristics of graphene transistors functionalized with a SAM of cationic molecules. They used 1-aminoethanethiol as SAM molecule onto mechanically exfoliated graphene, and the device is completed after the electrical contact electrodes were fabricated by e-beam lithography (**Figure 9**).
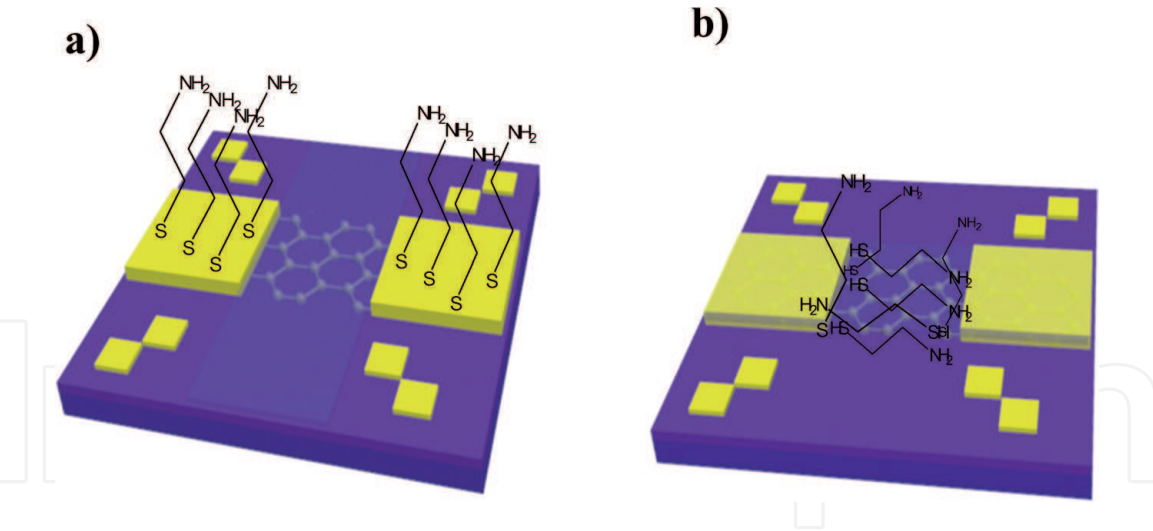
Figure 9.
*Schematic illustration of (a) the contact-opened and (b) the channel-opened device.*

Figure 10.
(a) Optical microscopy (b) SEM images of the contact-opened graphene device. The effects of SAM modification on (c) contact-opened and (d) channel-opened graphene transistor (figure image reprinted from Ref. [45]).

Finally they found that work-function engineering with SAMs results in a larger doping effect than the simple adsorption of amine-containing molecules onto the graphene channels (**Figure 10**) [45]. Jung et al. fabricated graphene hybrid film consisted of graphene/APTES/polyethylene terephthalate (PET) for enhancement of the conductivity. Basically, a CVD-grown graphene film is transferred onto an APTES layer on PET substrate. This process enhanced the conductivity of graphene effectively. As a result of the study, the carrier density of graphene was improved from 9.3×10^{12} to 1.16×10^{13}/cm^2 with transmittances of 82% and 86%, depending on the process parameters [46].

Gan et al. studied a new method for controlling H- and J-stacking in self-assembly. They used the property of GO and reduced graphene oxide (RGO) in order to control the self-assembly of perylene (Py). This new method suggested new materials for photosensitive applications in optoelectronics and liquid-junction solar cells [47]. Wieghold et al. demonstrated optoelectronic function in almost monolayer molecular architecture. The active layer consisted of a self-assembled terrylene diimide (TDI) derivative dye that formed a bicomponent supramolecular network with melamine. They found photocurrents of 0.5 nA and open-circuit voltages of 270 mV employing 19 mW/cm^2 irradiation intensities at 710 nm. They also estimated an incident photon to current efficiency of 0.6% at 710 nm with a contact area of 9.9×10^2 mm^2, meaning the opening up to the intriguing possibilities in bottom-up optoelectronic device fabrication with molecular resolution [48].

Kang et al. presented a new efficient and stable RGO doping method by employing two different types of alkylsilane compounds to produce p-type or n-type doping of RGO: (tridecafluoro-1,1,2,2,-tetrahydrooctyl) trichlorosilane (FTS) and APTES, respectively (**Figure 11**). The tunable electrical property of the SAM-functionalized RGO was utilized in developing source/drain (S/D) electrodes in bottom contact OFETs. The OFET device performance was improved significantly upon the use of FTS-RGO S/D electrodes [49]. Park et al. devised a method to optimize the performance of OFETs by controlling the work functions of graphene electrodes by functionalizing the surface of SiO$_2$ substrates with N,N′-ditridecyl-3,4,9,10-perylenetetracarboxylic
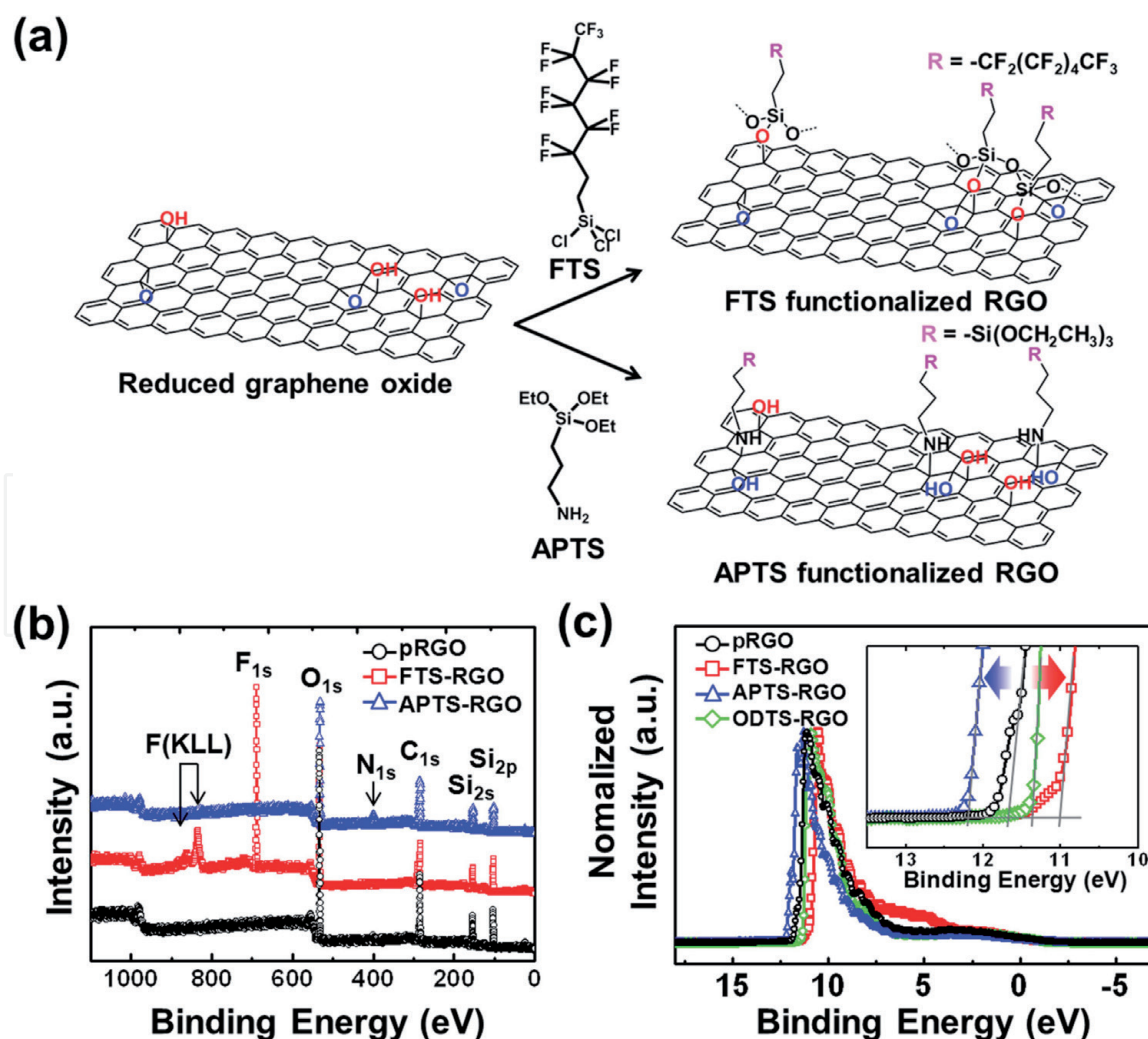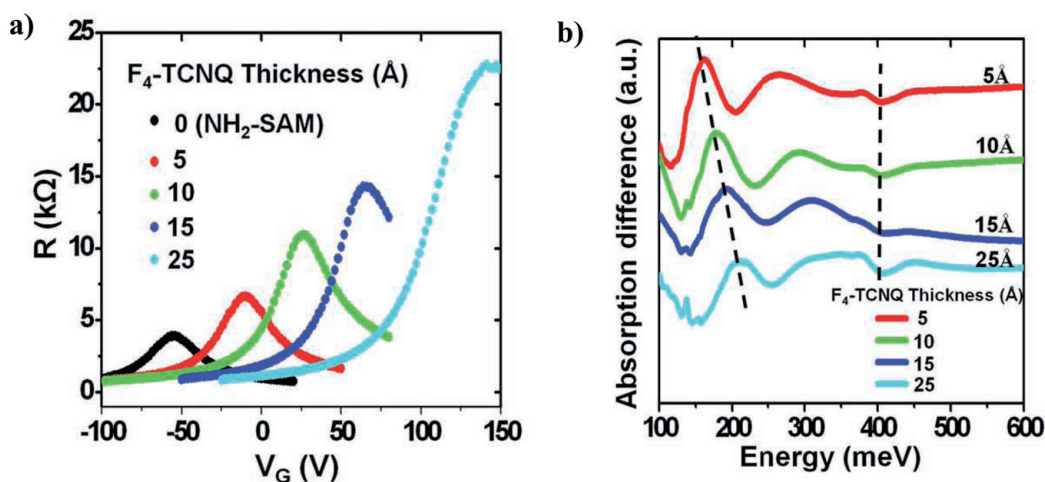

Figure 11.
(a) Representation of SAM functionalization of RGO with FTS and APTES, (b) XPS and (c) UPS spectra of SAM-functionalized RGOs. The inset figure in (c) shows the secondary electron emission region (figure image reprinted from Ref. [49]).
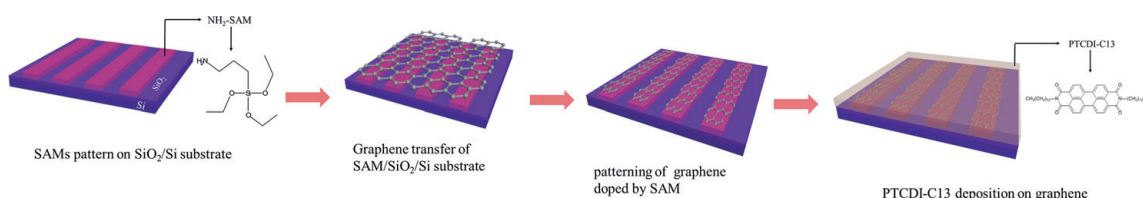
Figure 12.
Schematic illustration of PTCDI-C13 FET device process with patterned graphene onto SAM-modified SiO₂ substrate.
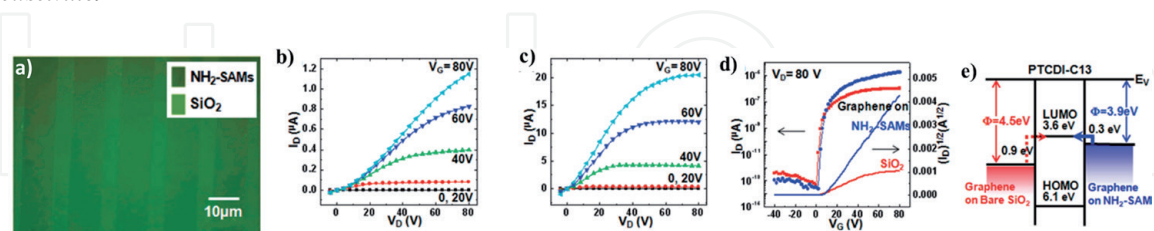
Figure 13.
(a) Optical microscopy images of samples. I-V measurements of (b) graphene S/D electrode containing n-type PTCDI-C13 FETs on pure SiO₂ and (c) on NH₂-SAMs, (d) transfer characteristics of electrodes on different SAM-modified SiO₂. (e) Band diagram structures of samples (figure image reprinted from Ref. [27]).
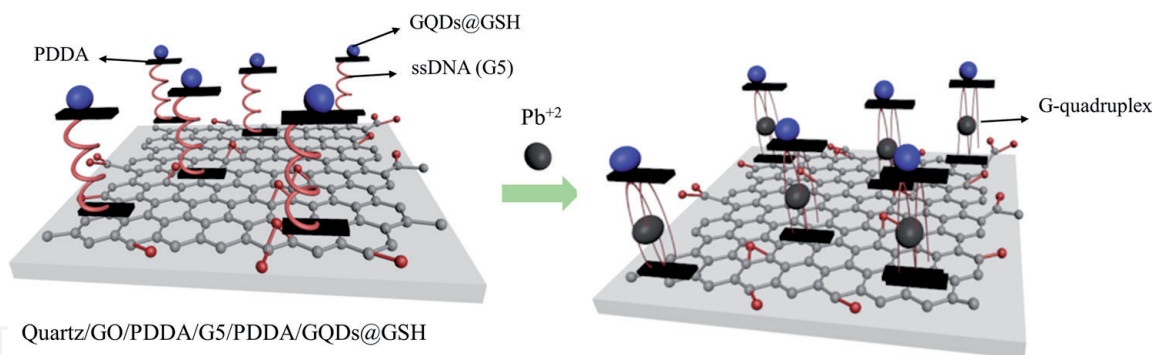

Figure 14.
(a) Current-voltage transfer characteristics of bilayer graphene FETs on a NH₂-SAM-modified SiO₂/Si substrates with various thicknesses of the F4-TCNQ layers, (b) absorption spectra of graphene on NH₂-SAM-modified SiO₂/Si substrates after applying different thickness of F4-TCNQ layers (figure image reprinted from Ref. [50]).

diimide (PTCDI-C13) as SAM molecules (**Figure 12**). In order to facilitate the electron injection, the work function of graphene is lowered to 3.9 eV in NH₂-SAM-modified SiO₂. The method of performance optimization of graphene-based OFETs which utilizes work-function engineering by functionalizing the substrate with SAMs is described and shows ~10 times enhancements in properties regarding the charge carrier mobility and the on-off ratio of OFETs (**Figure 13**) [27]. The same group also used APTES as SAM molecule and 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) as doping agent in order to modify the properties of graphene and examined the thickness of the F4-TCNQ related to the electrical properties of bilayer graphene FETs on NH₂-SAM-modified SiO₂/Si substrates. A single-gate bilayer graphene FET with high-current on/off current ratios is successfully fabricated, and tunable bandgap was demonstrated. (**Figure 14**) [50].

Gan et al. discovered a weak organic acid, 3,4,9,10-perylene tetracarboxylic acid (PTCA), and utilized to synthesize a supramolecular nanocomplex containing PTCA-graphene that showed wide voltage window and ultrahigh specific capacitance [51].
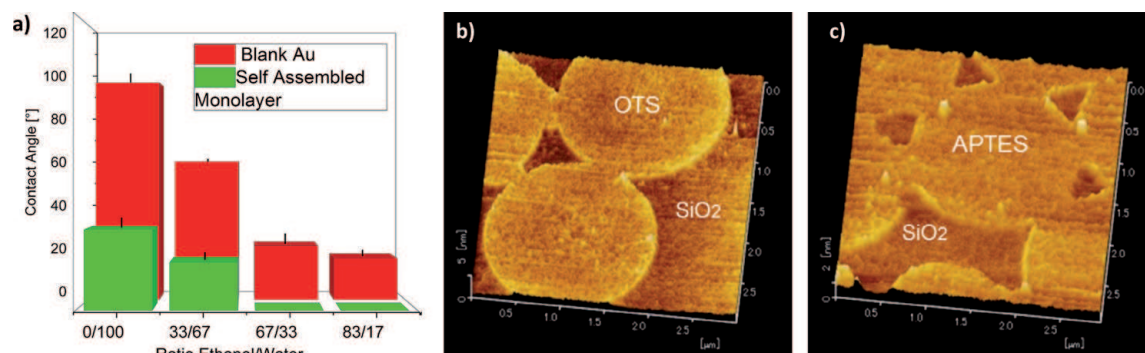
Figure 15.
Schematic diagram of the Pb²⁺ adding into quartz/GO/PDDA/G5/PDDA/GQDs@GSH SAMs.

In terms of environmental sensor, Sun et al. developed a sensor for the detection of Pb^{2+} ions by constructing quartz/GO/PDDA/G5/PDDA/GQDs@GSH system which included GO, glutathione-functionalized graphene quantum dots (GQDs@ GSH), poly(diallydimethylammonium) chloride (PDDA), and G5 (G-rich DNA) (**Figure 15**). The group showed that the detection concentration of the sensor for Pb^{2+} ions is as low as 2.2 nM [52].

3.3 Interface modifier

Pfaffeneder-Kmen et al. used 4-mercaptophenol as SAM molecule in order to produce homogeneous GO coatings. This process allowed the modification of the surface for contact angle to be low enough in order to achieve complete wetting that causes GO suspension to adhere onto the Au surface (**Figure 16a**) [53]. Larisika et al. used APTES as SAM-forming layer on SiO_2 substrates in order to enhance the adsorption of GO before the dip-coating process. The resulting sensor had potential as a high-performance and low-voltage operating graphene device [54]. Kamiya et al. investigated protein adsorption to graphene films which modificates the surface of substrates with two different SAMs in aqueous environment, octadecyltrichlorosilane (OTS) and APTES. They employed latex bead projection method for patterning SAMs and observed that the protein adsorption behavior on the graphene flakes is attached to partially SAM-modified SiO_2/Si substrates in aqueous environment (**Figure 16b–c**). It was also found that a high-density of agglomerated avidin molecule clusters was formed in the OTS-supported graphene areas, whereas a low-density of large clusters was formed in the SiO_2 and APTES-supported ones. For the high-performance graphene biosensors with small nonspecific adsorption of protein molecules, the suggested technique can control protein adsorption phenomena on graphene surfaces [55].

Figure 16.
(a) Contact angle vs. water/ethanol ratio with and without mercaptophenol SAM (figure image reprinted from Ref. [53]). AFM images of (b) an OTS-modified and (c) an APTES-modified SiO₂ substrate (figure image reprinted from Ref. [55]).

Ermakova et al. used the zinc complex of 5,10,15,20-tetra(4-pyridyl)-21H,23H-porphine (ZnTPyP) as an organic promoter for the interfacial adsorption of GO. The ZnTPyP/GO/ZnAc$_2$ bilayer was transferred as whole onto silicon slide by vertical LB method. As conclusion, they informed the stabilizing effect of GO which both anchored the assembled organic layer on the surface. By this result, the final multilayer structures showed large-area uniformity, especially for applications in catalysis, sensors, optoelectronics, etc. [56].

Hui et al. utilized a SAM molecule, 11-mercapto-1-undecanol (11-MU), for the blocking of Au surface, discovering the effect of the electrochemical kinetics of external-sphere redox mediators. For this purpose, metal electrodes were buried in the subsurface of continuous double-layer graphene electrodes. Modified Au tip exhibited a substantial decrease in its electron transfer kinetics [57].

In terms of mechanical modification, Bai et al. used APTES-SAM molecules between Si substrate and ceria/GO composite films in order to alter the mechanical properties of the final film. The friction coefficient was reduced drastically, and the anti-wear lifetime was longer than the GO films (**Figure 17**) [58]. Li et al. investigated and compared three different structures: titanium substrate, APTES-SAM, and GO-APTES nanolayer. The modifications changed the wettability, adhesion, and friction forces of the final structures (**Figure 18**) [59].

Li et al. used APTES as an intermediate coupling agent for chemisorption of RGO sheets on titanium alloy substrate. The results showed that the prepared films contain chemisorptive bonds on the substrate. Tribological results indicated that the prepared APTES-RGO film decreased the friction coefficient while improving antifriction properties of titanium alloy under dry friction (**Figure 19a**) [60]. Ou et al. utilized two different SAM layers including APTES and OTS in order to study lubrication coating properties. First, an APTES-SAM with amine (—NH$_2$) outer
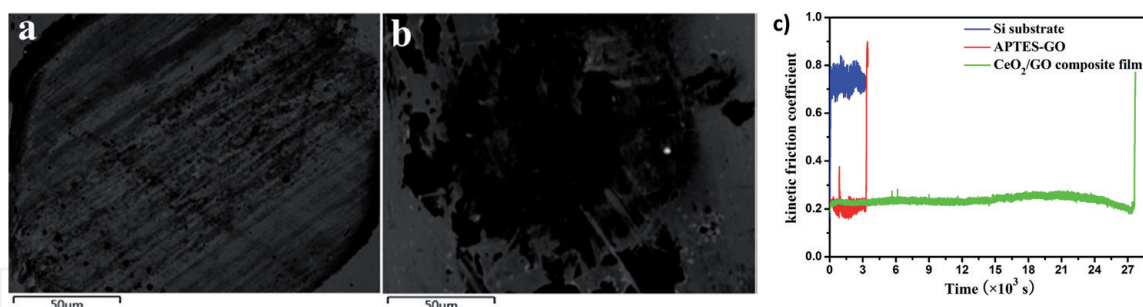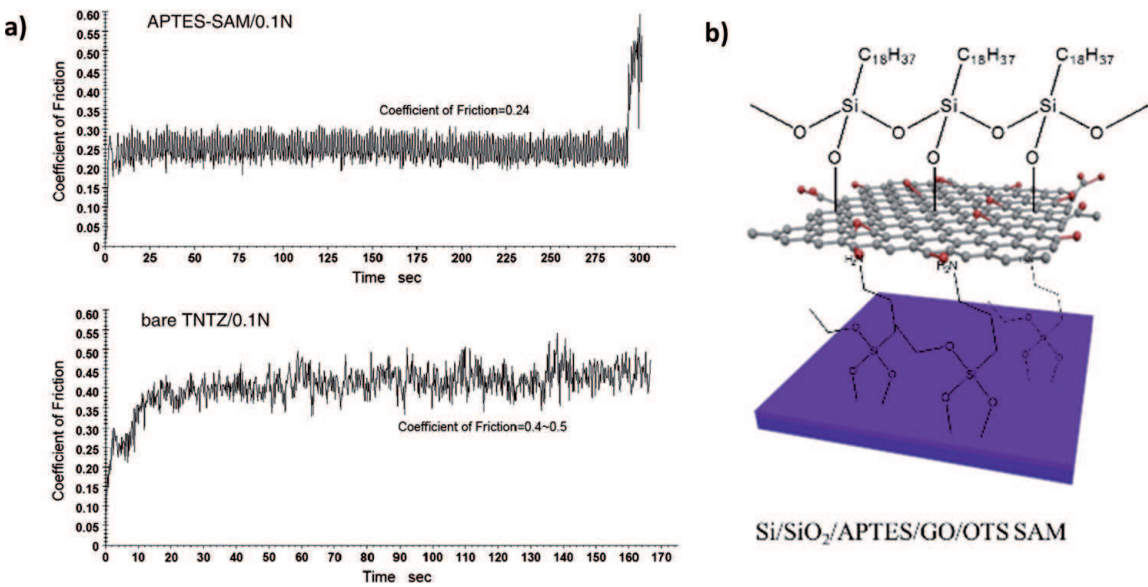

Figure 17.
SEM images of the wear scars on the steel balls sliding against (a) APTES-GO and (b) CeO$_2$/GO composite film. (c) Variation of kinetic friction coefficient with time for different samples under an applied load of 2 N and a constant speed of 10 mm/s (1 Hz) (figure image reprinted from Ref. [58]).
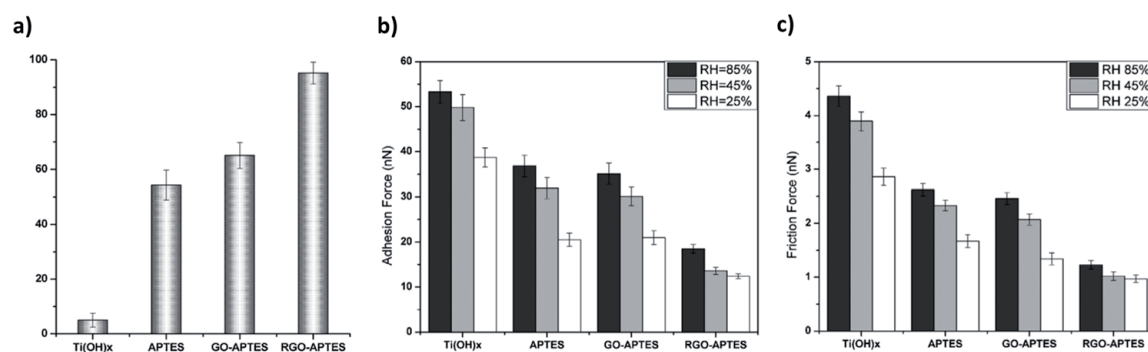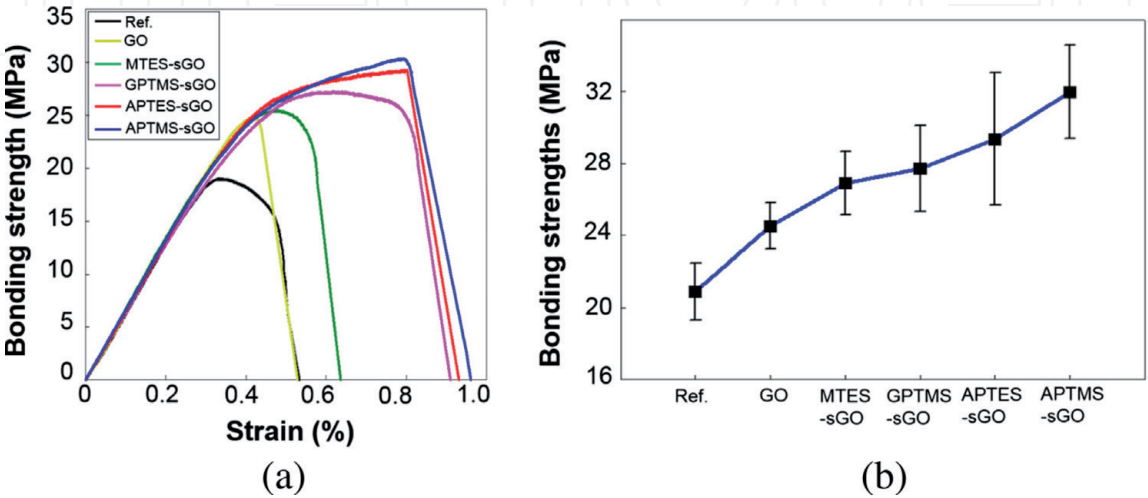

Figure 18.
(a) Water contact angle results of Ti substrate and prepared films; (b) adhesion force and (c) friction force with a normal load of 70 nN at ambient conditions at different relative humidity (figure image reprinted from Ref. [59]).

groups was covalently anchored onto the Si wafer. GO sheets were chemo-grafted onto the APTES-SAM surface. Finally, an OTS outer layer was assembled onto the GO surface (**Figure 19b**). In order to increase the hydrophobicity of the film, an outer layer of OTS-SAM is introduced, which reduced the friction and boosted the anti-wear life [61].

Lee et al. used four different SAMs, APTES, (3-aminopropyl)trimethoxysilane (APTMS), (3-glycidyloxypropyl)trimethoxysilane (GPTMS), and triethoxymethylsilane (MTES), in order to modify GO and silane-functionalized GO (sGO). The samples were prepared using epoxy and tested mechanically. The results showed that sGO, especially those containing amine functional groups, can strengthen the interfacial bonding between the carbon fibers and epoxy adhesive (**Figure 20**) [62]. Liu et al. used negatively charged poly(sodium 4-styrenesulfonate) (PSS)-mediated graphene sheets (PSS-GS) and the positively charged polyethyleneimine (PEI) repeatedly layer by layer, in order to obtain a multilayered film. Both the layer thickness and layer numbers were

Figure 19.
(a) Tribology results of varied materials on TNTZ surface in contact with Si_3N_4 balls under dry friction, (top) APTES-SAMs, 0.1 N applied load; (bottom) bare TNTZ, 0.1 N (figure image reprinted from Ref. [60]). (b) Schematic illustration of APTES-GO-OTS film structure on a Si wafer.
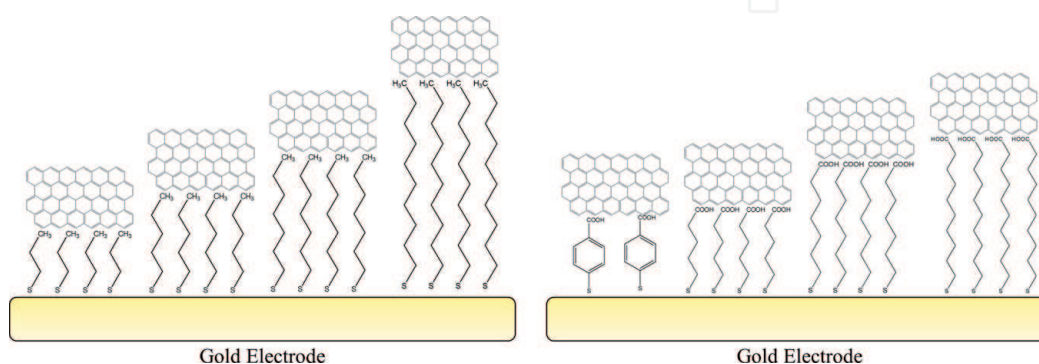

Figure 20.
(a) Bonding strength-strain relationships with the addition of GO or the sGOs in the carbon fiber/epoxy composite, (b) average bonding strength of the sample (figure image reprinted from Ref. [62]).
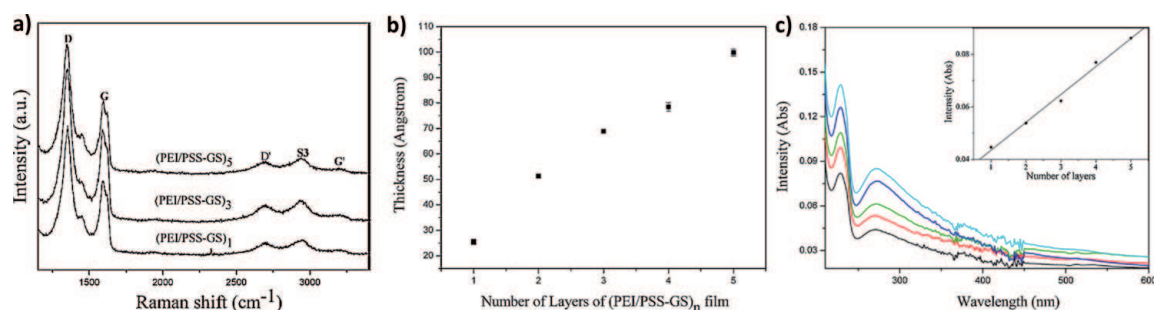
Figure 21.
(a) Raman spectra of sample films; (b) graph showing the correlation between the layer numbers of sample and ellipsometric thicknesses; (c) UV-vis spectroscopy results of samples that are assembled on a quartz slide via LBL method. Inset shows the correlation between the absorbance value at 270 nm and the layer number (n) (figure image reprinted from Ref. [63]).

Figure 22.
Schematic representation of CRGOs' self-assembly process on to the gold electrode.

changed in order to determine the relation. Their good tribological properties under the given testing conditions suggested that the use as a low-friction and anti-wear coating layer is possible (**Figure 21**) [63].

3.4 Spacer

Kong et al. reported the influence of chemically reduced graphene oxide sheets (CRGOs) on the electrochemical performance through methyl or carboxylic acid-terminated SAMs (**Figure 22**). Modified gold electrode and immobilization of the CRGOs on a SAM-treated surface showed effective enhancement of the heterogeneous electron transfer (ET) of the SAM due to the tunneling effect. They also reported that the kinetics of electron transfer activity between the CRGOs/SAM/ Au electrode and redox species in the solution was attributed to charge transfer being confined to CRGOs with different interactions with —CH_3 and —COOH terminated thiols, which can influence the electron transfer efficiency and the rate of charge transfer due to different electron transfer pathways [64].

Margapoti et al. reported the experimental studies of resonance oscillation in the current density of a SAM-graphene hybrid system. They used Au surface functionalized with a mixture of 4-(1-mercapto-6-hexyloxy) azobenzene as SAM treatment and 6-mercapto-1-hexanol as spacer molecules. A reversible change in conductivity was observed after transforming the molecular configuration from *trans* to *cis* (**Figure 23**) [65].

3.5 Graphene synthesis by SAM

It is also quite possible to synthesize high-quality graphene by using SAM technique as assembling surfaces. Xie et al. reported a simple and environmentally
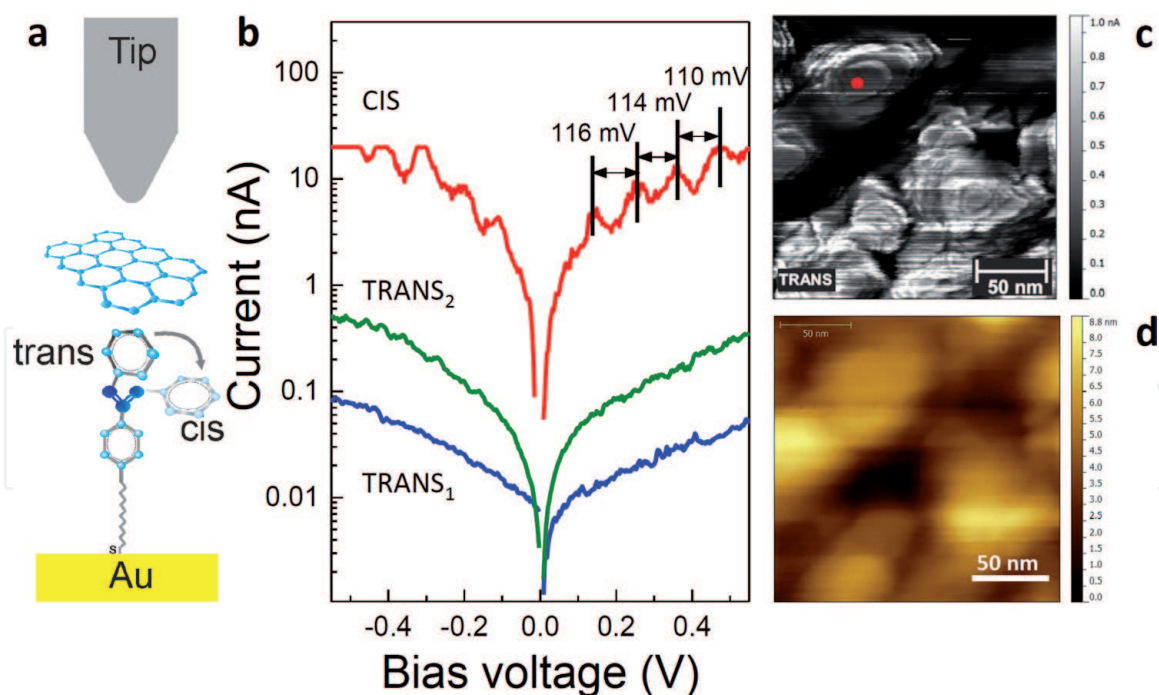
Figure 23.
(a) Measurement configurations and schematic representation of graphene/mSAM/Au hybrid with the azobenzene molecule in trans- and cis-configurations. (b) Typical I-V characteristics in trans-configuration before illumination (blue line) and in cis-configurations, which is controlled via UV-light (red line) and trans-configuration (green line) following white light exposure. (c) Topographical image and (d) current topography with the mSAM in the trans-configuration (figure image reprinted from Ref. [65]).
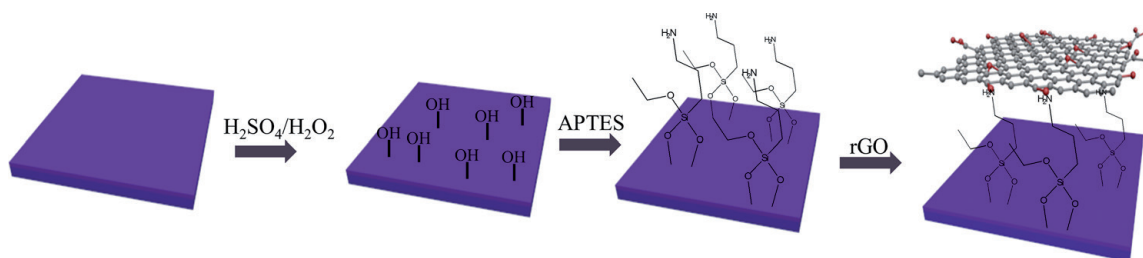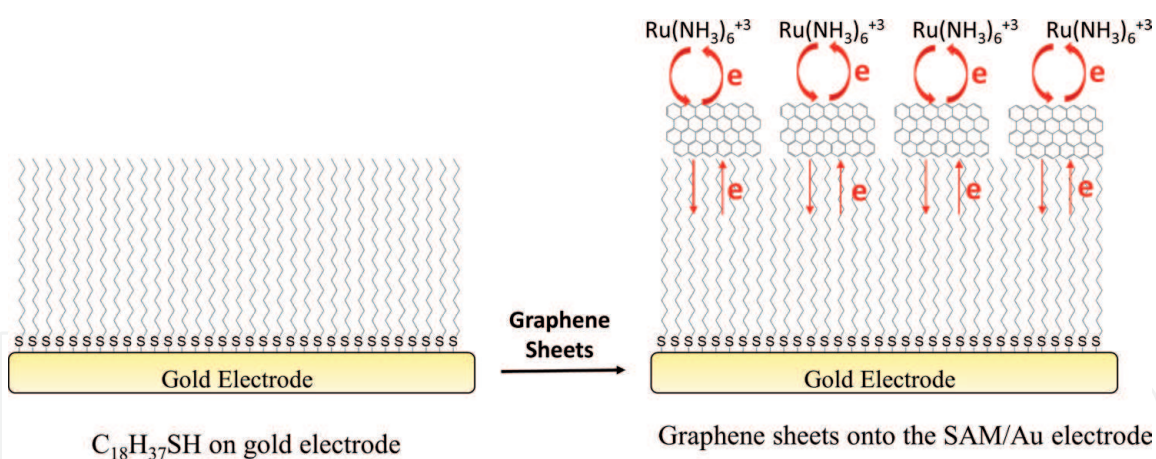

Figure 24.
Schematic representation for self-assembly of CRGO monolayer on APTES/Si/SiO$_2$ surface.

friendly approach for synthesizing a composite of graphene/gold nanoparticles (3DG/Au NPs) in one step. The selected molecule for SAM treatment is 4-amino-thiophenol. They immersed the SAM-coated glass substrate into the GO-HAuCL$_4$ solution, and the resulting sample showed catalytic reduction properties [66].

Yin et al. successfully bonded monolayer of CRGO nanosheets on Si sub-strates chemically and investigated their possible applications in Raman scatter-ing (**Figure 24**). The assembly of large-scale and uniform graphene sheet was performed by the electrostatic absorption between the —NH$_2$ groups of APTES that was coated onto the Si surface and residual groups on RGO. They also concluded that the mildly RGO substrate has the optimum graphene-enhanced Raman scattering (GERS) performance among all the CRGO substrates. The π-π stacking and the residual polarized oxygen groups on CRGO surface were mainly responsible for the excellent GERS effect of mildly RGO substrate [67].

Jing et al. reported a facile approach to the direct synthesis of graphene sheets based on the SAM technique. They used a thiophene-terminated silane molecule, triethoxy-(6-(thiophen-3-yloxy)-hexyl)silane (TEHS), as carbon source, and by heating the cross-linked polythiophene SAM up to 1000°C under high vacuum, single-layered or few-layered graphene sheets were successfully prepared on the

Figure 25.
Illustration of the fabrication of a graphene-/SAM-modified gold electrode and electron transfer of the mechanism on the graphene-modified electrode.

dielectric silicon oxide substrate [68]. Xie et al. investigated the electrochemical behaviors of graphene sheets attached to a SAM (n-octadecyl mercaptan) on a gold electrode (**Figure 25**). Their studies revealed that the heterogeneous electron transfer blocked by the SAM layer can be restored by graphene sheets, and the graphene-/SAM-modified Au electrode had a smaller interfacial capacitance, as compared with that of a bare one [69].

Three innovative methods are introduced by Nayak et al. for functionalizing bioinert ceramic. These methods include immobilizing rGO onto the surface using appropriate SAMs. Among these methods, activated —COOH groups of rGO and —NH$_2$ functionalized zirconia shows the most effective immobilization. They also concluded that further immobilization makes it possible to customize the surface properties for the desired application and could be easily performed on graphene-modified ceramics [70].

4. Conclusions

Following Geim and Novoselov study about graphene, it has been the most exciting and promising material discovered in the last few years. Due to its outstanding properties, it has enormous potential to develop many applications ranging from nanoelectronics to nanobiotechnology [71, 72]. However, tuning the physical and chemical properties of graphene, which possess high sheet resistance and zero bandgap, is crucial to the realization of graphene-based technologies. Furthermore, adsorption of graphene onto a solid surface is important for the device applications since it provides good charge transfer. Functionalization of the surface with SAMs is useful for controlling the electronic properties of the graphene layer and improving adsorption, paving the way to develop commercial applications.

In recent years, the interaction between SAMs with different chemical properties and graphene has been investigated by many research groups. For instance, SAMs with thiol group is most widely studied for electronic applications due to having delocalized π-electrons. These SAMs can also modify electrodes for electrochemical sensor applications. For example, SAM-decorated Au probes can electrostatically adsorb graphene derivatives, both functionalizing the sensor and improving the sensing ability. These researches demonstrate that SAMs are a utility for improving the performance of experimental devices. It is considered widely that overcoming the difficulties in the production of large-area graphene sheets may allow developing commercial applications.

In this chapter, we have demonstrated the functionalization, modification, and synthesis of graphene by SAMs and reviewed different applications. This chapter also demonstrates how to utilize the SAM-modified graphene and that SAM modification can improve the possibility of its usage in many applications.

Conflict of interest

The authors declare no conflict of interest for this publication.

Author details

Gulsum Ersu[1], Yenal Gokpek[1], Mustafa Can[2], Ceylan Zafer[3] and Serafettin Demic[1*]

1 Department of Material Science and Engineering, Faculty of Engineering and Architecture, Izmir Katip Celebi University, Izmir, Turkey

2 Department of Engineering Sciences, Faculty of Engineering and Architecture, Izmir Katip Celebi University, Izmir, Turkey

3 Ege University, Institute of Solar Energy, İzmir, Turkey

*Address all correspondence to: serafettin.demic@ikc.edu.tr

IntechOpen

References

[1] Heath JR. Molecular electronics. Annual Review of Materials Research. 2009;**39**(1):1-23. DOI: 10.1146/annurev-matsci-082908-145401

[2] Newton L, Slater T, Clark N, Vijayaraghavan A. Self assembled monolayers (SAMs) on metallic surfaces (gold and graphene) for electronic applications. Journal of Materials Chemistry C. 2013;**1**(3):376-393. DOI: 10.1039/C2TC00146B

[3] Devanarayanan VP, Manjuladevi V, Gupta RK. Interaction of graphene with self assembled monolayers. Macromolecular Symposia. 2015;**357**(1):23-29. DOI: 10.1002/masy.201400180

[4] Tu Q, Kim HS, Oweida TJ, Parlak Z, Yingling YG, Zauscher S. Interfacial mechanical properties of graphene on self-assembled monolayers: Experiments and simulations. ACS Applied Materials & Interfaces. 2017;**9**(11):10203-10213. DOI: 10.1021/acsami.6b16593

[5] Schwartz DK. Mechanisms and kinetics of self-assembled monolayer formation. Annual Review of Physical Chemistry. 2001;**52**(1):107-137. DOI: 10.1146/annurev.physchem.52.1.107

[6] Lee WH, Park J, Kim Y, Kim KS, Hong BH, Cho K. Control of graphene field-effect transistors by interfacial hydrophobic self-assembled monolayers. Advanced Materials. 2011;**23**(30):3460-3464. DOI: 10.1002/adma.201101340

[7] Geim AK, Novoselov KS. The rise of graphene. Nature Materials. 2007;**6**:183. DOI: 10.1038/nmat1849

[8] Bolotin KI, Sikes KJ, Jiang Z, Klima M, Fudenberg G, Hone J, et al. Ultrahigh electron mobility in suspended graphene. Solid State Communications. 2008;**146**(9):351-355. DOI: 10.1016/j.ssc.2008.02.024

[9] Choi W, Lahiri I, Seelaboyina R, Kang YS. Synthesis of graphene and its applications: A review. Critical Reviews in Solid State and Materials Sciences. 2010;**35**(1):52-71. DOI: 10.1080/10408430903505036

[10] Kim K, Choi J-Y, Kim T, Cho S-H, Chung H-J. A role for graphene in silicon-based semiconductor devices. Nature. 2011;**479**:338. DOI: 10.1038/nature10680

[11] Novoselov KS, Fal'ko VI, Colombo L, Gellert PR, Schwab MG, Kim K. A roadmap for graphene. Nature. 2012;**490**:192. DOI: 10.1038/nature11458

[12] Smerieri M, Celasco E, Carraro G, Lusuan A, Pal J, Bracco G, et al. Enhanced chemical reactivity of pristine graphene interacting strongly with a substrate: Chemisorbed carbon monoxide on graphene/nickel(111). ChemCatChem. 2015;**7**(15):2328-2331. DOI: 10.1002/cctc.201500279

[13] Wang X, Shi G. An introduction to the chemistry of graphene. Physical Chemistry Chemical Physics. 2015;**17**(43):28484-28504. DOI: 10.1039/C5CP05212B

[14] Liu H, Liu Y, Zhu D. Chemical doping of graphene. Journal of Materials Chemistry. 2011;**21**(10):3335-3345. DOI: 10.1039/C0JM02922J

[15] Wang X, Sun G, Routh P, Kim D-H, Huang W, Chen P. Heteroatom-doped graphene materials: Syntheses, properties and applications. Chemical Society Reviews. 2014;**43**(20):7067-7098. DOI: 10.1039/C4CS00141A

[16] Bong JH, Sul O, Yoon A, Choi S-Y, Cho BJ. Facile graphene n-doping

by wet chemical treatment for electronic applications. Nanoscale. 2014;**6**(15):8503-8508. DOI: 10.1039/C4NR01160K

[17] Georgakilas V, Otyepka M, Bourlinos AB, Chandra V, Kim N, Kemp KC, et al. Functionalization of graphene: Covalent and non-covalent approaches, derivatives and applications. Chemical Reviews. 2012;**112**(11):6156-6214. DOI: 10.1021/cr3000412

[18] Sarkar S, Bekyarova E, Haddon RC. Covalent chemistry in graphene electronics. Materials Today. 2012;**15**(6):276-285. DOI: 10.1016/S1369-7021(12)70118-9

[19] Johns JE, Hersam MC. Atomic covalent functionalization of graphene. Accounts of Chemical Research. 2013;**46**(1):77-86. DOI: 10.1021/ar300143e

[20] Kaur P, Shin M-S, Sharma N, Kaur N, Joshi A, Chae S-R, et al. Non-covalent functionalization of graphene with poly(diallyldimethylammonium) chloride: Effect of a non-ionic surfactant. International Journal of Hydrogen Energy. 2015;**40**(3):1541-1547. DOI: 10.1016/j.ijhydene.2014.11.068

[21] Wei P, Liu N, Lee HR, Adijanto E, Ci L, Naab BD, et al. Tuning the dirac point in CVD-grown graphene through solution processed n-type doping with 2-(2-methoxyphenyl)-1,3-dimethyl-2,3-dihydro-1H-benzoimidazole. Nano Letters. 2013;**13**(5):1890-1897. DOI: 10.1021/nl303410g

[22] Cai B, Zhang S, Yan Z, Zeng H. Noncovalent molecular doping of two-dimensional materials. ChemNanoMat. 2015;**1**(8):542-557. DOI: 10.1002/cnma.201500102

[23] Mao HY, Lu YH, Lin JD, Zhong S, Wee ATS, Chen W. Manipulating the electronic and chemical properties of graphene via molecular functionalization. Progress in Surface Science. 2013;**88**(2):132-159. DOI: 10.1016/j.progsurf.2013.02.001

[24] Yan Z, Sun Z, Lu W, Yao J, Zhu Y, Tour JM. Controlled modulation of electronic properties of graphene by self-assembled monolayers on SiO$_2$ substrates. ACS Nano. 2011;**5**(2):1535-1540. DOI: 10.1021/nn1034845

[25] Ito Y, Virkar AA, Mannsfeld S, Oh JH, Toney M, Locklin J, et al. Crystalline ultrasmooth self-assembled monolayers of alkylsilanes for organic field-effect transistors. Journal of the American Chemical Society. 2009;**131**(26):9396-9404. DOI: 10.1021/ja9029957

[26] Liu Z, Bol AA, Haensch W. Large-scale graphene transistors with enhanced performance and reliability based on interface engineering by phenylsilane self-assembled monolayers. Nano Letters. 2011;**11**(2):523-528. DOI: 10.1021/nl1033842

[27] Park J, Lee WH, Huh S, Sim SH, Kim SB, Cho K, et al. Work-function engineering of graphene electrodes by self-assembled monolayers for high-performance organic field-effect transistors. The Journal of Physical Chemistry Letters. 2011;**2**(8):841-845. DOI: 10.1021/jz200265w

[28] Sojoudi H, Baltazar J, Tolbert LM, Henderson CL, Graham S. Creating graphene p-n junctions using self-assembled monolayers. ACS Applied Materials & Interfaces. 2012;**4**(9):4781-4786. DOI: 10.1021/am301138v

[29] Xia ZY, Giambastiani G, Christodoulou C, Nardi MV, Koch N, Treossi E, et al. Synergic exfoliation of graphene with organic molecules and inorganic ions for the electrochemical production of flexible electrodes. ChemPlusChem. 2014;**79**(3):439-446. DOI: 10.1002/cplu.201300375

[30] Cooper AJ, Wilson NR, Kinloch IA, Dryfe RAW. Single stage electrochemical exfoliation method for the production of few-layer graphene via intercalation of tetraalkylammonium cations. Carbon. 2014;**66**:340-350. DOI: 10.1016/j.carbon.2013.09.009

[31] Chakrabarti MH, Low CTJ, Brandon NP, Yufit V, Hashim MA, Irfan MF, et al. Progress in the electrochemical modification of graphene-based materials and their applications. Electrochimica Acta. 2013;**107**:425-440. DOI: 10.1016/j.electacta.2013.06.030

[32] Sundaram RS, Gómez-Navarro C, Balasubramanian K, Burghard M, Kern K. Electrochemical modification of graphene. Advanced Materials. 2008;**20**(16):3050-3053. DOI: 10.1002/adma.200800198

[33] Xia Z, Leonardi F, Gobbi M, Liu Y, Bellani V, Liscio A, et al. Electrochemical functionalization of graphene at the nanoscale with self-assembling diazonium salts. ACS Nano. 2016;**10**(7):7125-7134. DOI: 10.1021/acsnano.6b03278

[34] Shi L, Wang Y, Ding S, Chu Z, Yin Y, Jiang D, et al. A facile and green strategy for preparing newly-designed 3D graphene/gold film and its application in highly efficient electrochemical mercury assay. Biosensors and Bioelectronics. 2017;**89**:871-879. DOI: 10.1016/j.bios.2016.09.104

[35] Sun X, Liu B, Yang C, Li C. An extremely sensitive aptasensor based on interfacial energy transfer between QDS SAMs and GO. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 2014;**131**:288-293. DOI: 10.1016/j.saa.2014.04.093

[36] Thakur B, Zhou G, Chang J, Pu H, Jin B, Sui X, et al. Rapid detection of single *E. coli* bacteria using a graphene-based field-effect transistor device. Biosensors and Bioelectronics. 2018;**110**:16-22. DOI: 10.1016/j.bios.2018.03.014

[37] Chang J, Mao S, Zhang Y, Cui S, Zhou G, Wu X, et al. Ultrasonic-assisted self-assembly of monolayer graphene oxide for rapid detection of *Escherichia coli* bacteria. Nanoscale. 2013;**5**(9):3620-3626. DOI: 10.1039/C3NR00141E

[38] Khan M, Liu X, Zhu J, Ma F, Hu W, Liu X. Electrochemical detection of tyramine with ITO/APTES/ErGO electrode and its application in real sample analysis. Biosensors and Bioelectronics. 2018;**108**:76-81. DOI: 10.1016/j.bios.2018.02.042

[39] Feng L, Zhang Z, Ren J, Qu X. Functionalized graphene as sensitive electrochemical label in target-dependent linkage of split aptasensor for dual detection. Biosensors and Bioelectronics. 2014;**62**:52-58. DOI: 10.1016/j.bios.2014.06.008

[40] Yeh C-H, Kumar V, Moyano DR, Wen S-H, Parashar V, Hsiao S-H, et al. High-performance and high-sensitivity applications of graphene transistors with self-assembled monolayers. Biosensors and Bioelectronics. 2016;**77**:1008-1015. DOI: 10.1016/j.bios.2015.10.078

[41] Chiu N-F, Yang C-D, Chen C-C, Kuo C-T. Stepwise control of reduction of graphene oxide and quantitative real-time evaluation of residual oxygen content using EC-SPR for a label-free electrochemical immunosensor. Sensors and Actuators B: Chemical. 2018;**258**:981-990. DOI: 10.1016/j.snb.2017.11.187

[42] Bhardwaj SK, Basu T. Study on binding phenomenon of lipase enzyme with tributyrin on the surface of graphene oxide array using surface plasmon resonance. Thin Solid Films. 2018;**645**:10-18. DOI: 10.1016/j.tsf.2017.10.021

[43] Wang QH, Jin Z, Kim KK, Hilmer AJ, Paulus GL, Shih C-J, et al. Understanding and controlling the substrate effect on graphene electron-transfer chemistry via reactivity imprint lithography. Nature Chemistry. 2012;**4**(9):724. DOI: 10.1038/nchem.1421

[44] Aydin H, Bacaksiz C, Yagmurcukardes N, Karakaya C, Mermer O, Can M, et al. Experimental and computational investigation of graphene/SAMs/n-Si Schottky diodes. Applied Surface Science. 2018;**428**:1010-1017. DOI: 10.1016/j.apsusc.2017.09.204

[45] Kim B-K, Jeon E-K, Lee J-O, Kim J-J. The effects of cationic molecules on graphene transistors. Synthetic Metals. 2013;**181**:52-55. DOI: 10.1016/j.synthmet.2013.08.013

[46] Jung D, Ko Y-H, Cho J, Adhikari PD, Lee SI, Kim Y, et al. Transparent and flexible conducting hybrid film combined with 3-aminopropyltriethoxysilane-coated polymer and graphene. Applied Surface Science. 2015;**357**:287-292. DOI: 10.1016/j.apsusc.2015.08.139

[47] Gan S, Zhong L, Engelbrekt C, Zhang J, Han D, Ulstrup J, et al. Graphene controlled H-and J-stacking of perylene dyes into highly stable supramolecular nanostructures for enhanced photocurrent generation. Nanoscale. 2014;**6**(18):10516-10523. DOI: 10.1039/C4NR02308K

[48] Wieghold S, Li J, Simon P, Krause M, Avlasevich Y, Li C, et al. Photoresponse of supramolecular self-assembled networks on graphene-diamond interfaces. Nature Communications. 2016;**7**:10700. DOI: 10.1038/ncomms10700

[49] Kang B, Lim S, Lee WH, Jo SB, Cho K. Work-function-tuned reduced graphene oxide via direct surface functionalization as source/drain electrodes in bottom-contact organic transistors. Advanced Materials. 2013;**25**(41):5856-5862. DOI: 10.1002/adma.201302358

[50] Park J, Jo SB, Yu YJ, Kim Y, Yang JW, Lee WH, et al. Single-gate bandgap opening of bilayer graphene by dual molecular doping. Advanced Materials. 2012;**24**(3):407-411. DOI: 10.1002/adma.201103411

[51] Gan S, Zhong L, Gao L, Han D, Niu L. Electrochemically driven surface-confined acid/base reaction for an ultrafast H^+ supercapacitor. Journal of the American Chemical Society. 2016;**138**(5):1490-1493. DOI: 10.1021/jacs.5b12272

[52] Sun X, Peng Y, Lin Y, Cai L, Li F, Li B. G-quadruplex formation enhancing energy transfer in self-assembled multilayers and fluorescence recognize for Pb^{2+} ions. Sensors and Actuators B: Chemical. 2018;**255**:2121-2125. DOI: 10.1016/j.snb.2017.09.004

[53] Pfaffeneder-Kmen M, Casas IF, Naghilou A, Trettenhahn G, Kautek W. A multivariate curve resolution evaluation of an in-situ ATR-FTIR spectroscopy investigation of the electrochemical reduction of graphene oxide. Electrochimica Acta. 2017;**255**:160-167. DOI: 10.1016/j.electacta.2017.09.124

[54] Larisika M, Huang J, Tok A, Knoll W, Nowak C. An improved synthesis route to graphene for molecular sensor applications. Materials Chemistry and Physics. 2012;**136**(2-3):304-308. DOI: 10.1016/j.matchemphys.2012.08.003

[55] Kamiya Y, Yamazaki K, Ogino T. Protein adsorption to graphene surfaces controlled by chemical modification of the substrate surfaces. Journal of Colloid and Interface Science. 2014;**431**:77-81. DOI: 10.1016/j.jcis.2014.06.023

[56] Ermakova EV, Ezhov AA, Baranchikov AE, Gorbunova YG, Kalinina MA, Arslanov VV. Interfacial self-assembly of functional bilayer templates comprising porphyrin arrays and graphene oxide. Journal of Colloid and Interface Science. 2018;**530**:521-531. DOI: 10.1016/j.jcis.2018.06.086

[57] Hui J, Zhou X, Bhargava R, Chinderle A, Zhang J, Rodríguez-López J. Kinetic modulation of outer-sphere electron transfer reactions on graphene electrode with a sub-surface metal substrate. Electrochimica Acta. 2016;**211**:1016-1023. DOI: 10.1016/j.electacta.2016.06.134

[58] Bai G, Wang J, Yang Z, Wang H, Wang Z, Yang S. Self-assembly of ceria/graphene oxide composite films with ultra-long antiwear lifetime under a high applied load. Carbon. 2015;**84**:197-206. DOI: 10.1016/j.carbon.2014.11.063

[59] Li PF, Zhou H, Cheng X-H. Nano/micro tribological behaviors of a self-assembled graphene oxide nanolayer on Ti/titanium alloy substrates. Applied Surface Science. 2013;**285**:937-944. DOI: 10.1016/j.apsusc.2013.09.019

[60] Li PF, Xu Y, Cheng X-H. Chemisorption of thermal reduced graphene oxide nano-layer film on TNTZ surface and its tribological behavior. Surface and Coating Technology. 2013;**232**:331-339. DOI: 10.1016/j.surfcoat.2013.05.030

[61] Ou J, Wang Y, Wang J, Liu S, Li Z, Yang S. Self-assembly of octadecyltrichlorosilane on graphene oxide and the tribological performances of the resultant film. The Journal of Physical Chemistry C. 2011;**115**(20):10080-10086. DOI: 10.1021/jp200597k

[62] Lee CY, Bae J-H, Kim T-Y, Chang S-H, Kim SY. Using silane-functionalized graphene oxides for enhancing the interfacial bonding strength of carbon/epoxy composites. Composites Part A: Applied Science and Manufacturing. 2015;**75**:11-17. DOI: 10.1016/j.compositesa.2015.04.013

[63] Liu S, Ou J, Li Z, Yang S, Wang J. Layer-by-layer assembly and tribological property of multilayer ultrathin films constructed by modified graphene sheets and polyethyleneimine. Applied Surface Science. 2012;**258**(7):2231-2236. DOI: 10.1016/j.apsusc.2011.09.011

[64] Kong N, Vaka M, Nam ND, Barrow CJ, Liu J, Conlan XA, et al. Controllable graphene oxide mediated efficient electron transfer pathways across self-assembly monolayers: A new class of graphene based electrodes. Electrochimica Acta. 2016;**210**:539-547. DOI: 10.1016/j.electacta.2016.05.143

[65] Margapoti E, Strobel P, Asmar MM, Seifert M, Li J, Sachsenhauser M, et al. Emergence of photoswitchable states in a graphene-azobenzene-Au platform. Nano Letters. 2014;**14**(12):6823-6827. DOI: 10.1021/nl503681z

[66] Xie J, Yang X, Xu X. Wet chemical method for synthesizing 3D graphene/gold nanocomposite: Catalytic reduction of methylene blue. Physica E: Low-dimensional Systems and Nanostructures. 2017;**88**:201-205. DOI: 10.1016/j.physe.2016.11.016

[67] Yin F, Wu S, Wang Y, Wu L, Yuan P, Wang X. Self-assembly of mildly reduced graphene oxide monolayer for enhanced Raman scattering. Journal of Solid State Chemistry. 2016;**237**:57-63. DOI: 10.1016/j.jssc.2016.01.015

[68] Jing H, Min M, Seo S, Lu B, Yoon Y, Lee SM, et al. Non-metal catalytic synthesis of graphene from a polythiophene monolayer on silicon dioxide. Carbon. 2015;**86**:272-278. DOI: 10.1016/j.carbon.2015.01.044

[69] Xie X, Zhao K, Xu X, Zhao W, Liu S, Zhu Z, et al. Study of heterogeneous

electron transfer on the graphene/
self-assembled monolayer modified
gold electrode by electrochemical
approaches. The Journal of Physical
Chemistry C. 2010;**114**(33):14243-14250.
DOI: 10.1021/jp102446w

[70] Nayak GS, Zybala R, Kozinski R,
Woluntarski M, Telle R, Schickle K.
Immobilization of reduced graphene
oxide nano-flakes on inert ceramic
surfaces using self-assembled
monolayer technique. Materials Letters.
2018;**225**:109-112. DOI: 10.1016/j.
matlet.2018.05.004

[71] Liu J, Tang J, Gooding JJ. Strategies
for chemical modification of graphene
and applications of chemically
modified graphene. Journal of Materials
Chemistry. 2012;**22**(25):12435-12452.
DOI: 10.1039/C2JM31218B

[72] Lonkar SP, Deshmukh YS,
Abdala AA. Recent advances in chemical
modifications of graphene. Nano
Research. 2015;**8**(4):1039-1074. DOI:
10.1007/s12274-014-0622-9