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Chapter 7

Summary, Conclusions and Outlook

7.1 Summary and conclusions

Advanced sensing techniques require graphene with high quality and well-controlled surface chemistry. The intrinsic high mobility, low electrical noises and uniform graphitic crystallinity are the prerequisites for high-performance graphene electronics. More importantly, chemical functionalization contributes to unlock the sensing potential of the graphene basal plane. This thesis focuses on manipulating the surface chemistry of a graphene monolayer and explores the impacts on the electrical and electrochemical properties for sensing applications. Heteroatoms like hydrogen, nitrogen and oxygen were systematically introduced into the graphene lattice as defect sites to modify the surface chemistry, and consequently the electronic properties. In particular, the interplay between the in-plane electron transport and the electrochemical activity of the graphene basal plane was investigated by modulating the density of H-sp^3 defects (Chapter 2). Moreover, the electronic structure of graphene was found to also determine the electrochemical activity and catalytic properties of the surface. Therefore the electrocatalysis of oxygen reduction reaction on nitrogen doped monolayer graphene was conducted to pinpoint the catalytic active sites (Chapter 3). Meanwhile, the delicate surface of graphene is very sensitive to any surface contaminations, which are found to impair its intrinsic active electrochemistry by covering the crystalline lattice. Hydrogenation treatment was also able to improve and maintain the cleanliness of graphene surface by forming a protective layer of adsorbed water (Chapter 4). Furthermore, the interaction at the supportive interfaces of graphene can also impact its intrinsic properties. The mechanics of a centimeter-scale graphene floating on water was characterized by biaxial compression, and was found to be significantly influenced by lattice defects (Chapter 5). Especially, the introduced H-sp^3 defect sites locally interact with the underlying water molecules to stabilize the corresponding carbon atoms, leading to an enhanced in-plane stiffness. Finally, gas sensors based on hydrogenated and nitrogenated graphene were tested to understand the impacts of chemical functionalization on the sensing performance.

Chapter 2 shows how the electronic nature interplays with the electrochemical activity of a monolayer graphene upon hydrogenation. Through a hydrogen radical plasma, hydrogen atoms were systematically introduced onto the lattice as defects to modulate the chemical and electrical properties of graphene. Raman spectroscopy characterized the density growth and sp^3 nature of the hydrogenated defects. In contrast to the typical decrease of mobility and minimum conductance of graphene induced by hydrogenation, improved conductance and electrochemical activity was obtained after the first second treatment of hydrogen radical plasma. The increase is ascribed to the intrinsically active graphene lattice exposed by removing the

hydrocarbons coverage at the surface. Moreover, the quantum capacitance effect in graphene, originating from the low density of states (DOS) at the Dirac point, was studied to understand the interaction between the electrical and electrochemical properties. By correlating the DOS with the electrochemical activity, the electrochemical kinetics of graphene is conclude to be highly dependent on the DOS upon the addition of hydrogenated defects even in a low density.

In Chapter 3, nitrogen doping in monolayer graphene is investigated for the electrocatalysis of oxygen reduction reaction (ORR). Pyridinic and graphitic nitrogen atoms as the two main doping configurations were confirmed to introduce a n-doping effect in graphene. At high levels of nitrogenation, nitrogen dopants tended to cluster and to form domain-like defect sites, which increased the accompanying surface oxidation. Both sides of the chemical vapor deposition (CVD) graphene, referred to as pure graphene (the side facing the growth substrate) and RRDE graphene (the side facing the air), were adopted for ORR study. For pure graphene containing minimized surface oxidation, decreased ORR currents were observed upon the increase of nitrogen doping levels. In contrast, RRDE graphene accommodating more surface oxidation due to air exposure and ageing showed improved ORR activity with increased nitrogenation. As a consequence, nitrogen dopants are not the essential sites for improved ORR currents. Instead, the content of single-bonded oxygen-containing groups is positively correlated to the enhanced ORR activity in nitrogenated graphene.

As aforementioned, the surface of graphene is sensitive to airborne contaminations, which can significantly alter the surface-related properties including electrochemistry and wettability. Chapter 4 demonstrates an effective and non-invasive cleaning protocol to improve and maintain the cleanliness of the graphene surface. In comparison to pristine graphene and argon treated graphene, hydrogenated graphene presented a quantitatively cleaner surface with less coverage of amorphous patterns arising from airborne hydrocarbons. Moreover, hydrogenated graphene revealed a higher affinity towards water adsorption as compared to pristine graphene, which is closely related to the observed cleaning effect.

Chapter 5 explores the mechanics of a centimeter-scale graphene remaining in its natural form by using water as the supporting substrate. Upon a biaxial compression by a surrounding lipid monolayer in a Langmuir-Blodgett trough, graphene was subjected to deformation (both elastic and plastic) due to the strain in the lattice induced by stress. Characterized by the Young's modulus ($\bar{E}_{2D}$), the stiffness of graphene is two orders of magnitude smaller than flat graphene, featuring an anharmonic approximation for the total elastic energy. In the anharmonic framework

coupling the stretching and flexural mode in 2D materials, the Young's modulus in hydrogenated graphene was found to be improved by 1.5 times. The improved stiffness is attributed to the localization of the long wavelength flexural modes by H-sp^3 defects in the lattice. In contrast, the inclusion of vacancy defects dramatically lowered the critical stress of graphene, leading to a collapsed graphene upon even a negligible surface pressure.

Chapter 6 shows the field effect gas sensing on hydrogenated and nitrogenated graphene. The introduced chemical functionalization contributed to improve the sensitivity by changing the doping effect and adsorption affinity to gas molecules. Positive doping was found to be positively related to improved electrical responses while negative doping showed decreased responses. Upon dynamic gas detection, the graphene sensors produced saturated and then decreased responses with increased gas concentrations. The consumption of the limited active sites in graphene by the trapped gas molecules can be the explanation. In comparison, hydrogenated graphene exhibited higher sensitivity with less saturation effect than nitrogenated graphene. On the other hand, the limited selectivity for both graphene sensors can be ascribed to the deficiency of specific interaction between the chemical functionalization with the target gas molecules.

7.2 Outlook

A graphene surface is a robust and flexible platform for electrical and electrochemical sensing applications. The work in this thesis provides important insights into the manipulation of the surface chemistry and understanding the corresponding impacts on the intrinsic electrical, electrochemical and mechanical properties of a monolayer of graphene. Chemical defects in the lattice hold the great promise to modulate the electrochemical activity, charge doping and surface adsorption behaviors, to name a few, which are closely involved in the sensing process. Especially, surface contaminations and oxidation of graphene during the handling and ageing process can exert significant impacts on the electrical and electrocatalytic properties. The cleaning approach introduced in the thesis provides not only practical strategy for the electron microscopy study of graphene, but also fundamental insights into the physical chemistry of the graphene surface.

For hydrogenated graphene, it is worthwhile to further investigate its potential as an ideal platform for surface/interface related study. The proposed clean, hydrophilic, mechanically robust and well-preserved graphitic lattice is appealing to (cryo-) electron microscopy study and biointerface involved research. In the viewpoint of GFETs sensing applications, high mobility of graphene after medium hydrogenation is

reasonably preserved while the electrochemical leakage current as a potential leakage signal is minimized. Moreover, the electrochemically active graphene surface after mild hydrogenation functions as an excellent two-dimensional electrode with a low capacitive background current and a large potential window. Furthermore, unpaired electrons or highly reactive free radical trapped at graphene surface can be probed by electron paramagnetic resonance (EPR) or spin-sensitive scanning tunneling microscopy (STM) to reveal mechanisms of certain reactions and gain deep understanding of graphene chemistry.

In particular, the electrocatalytic study on nitrogenated graphene promise monolayer graphene films as a robust and functional surface to monitor *in-situ* reactions using *operando* techniques. For example, surface characterization techniques like Raman and infrared spectroscopy can be employed to monitor systematically how subtle changes of graphene surface chemistry correlate with the mechanism of electrocatalytic reactions, i.e. ORR or hydrogen evolution reactions.

A major problem of polycrystalline CVD graphene is the inevitable oxidation and atmospheric contaminations accompanied with the loss of electrical quality, referred to as "ageing" process. Domain sizes and the amounts of grain boundary in CVD graphene are suspected to be closely related to the ageing effect. According to the recent experimental findings in Leiden, CVD graphene with smaller crystalline domain size is more prone to air oxidization and electrical degradation. For sensitive and stable graphene-based sensing applications, monocrystalline graphene is recommended.

The surface of graphene even after chemical functionalization has limited sensitivity and low selectivity towards the sensing of gas molecules as revealed in Chapter 6. To reach ultra-high sensitivity and selectivity in sensing, specific recognitions like antigen-antibody interactions or biomarkers functionalization should be introduced. Diazonium chemistry can open up a wide range of options for the selective and controlled surface modification of graphene. In spite of the loss of mobility to certain levels, diazonium functionalized graphene can be functioning as sensitive and selective GFET sensing platforms.