Stacking Configuration Dependent Chemical Reactivity of Graphene

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Introduction

Background

- Graphene is a two-dimensional (2D) material composed of sp^2 hybridized carbon.
- Twisted bilayer graphene (tBLG) Moiré superlattice which can be realized by vertically stacking two monolayer (1L) graphene and rotating one of the them to a finite angle, has been studied extensively[1][2][3] for its excep -tional optical and electrical properties.
- Works focusing on the chemical properties of graphene Moiré superlattice are still limited.

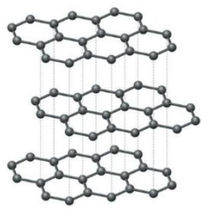

Figure 1. Lattice structure of graphene.

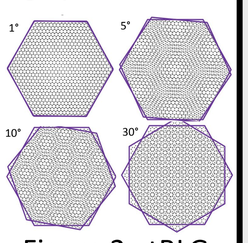

Figure 2. tBLG at various twist angles.

Objective: This study aims to study the chemical properties of tBLG in the regime of Moiré superlattice. We expect open a door and build the foundation of "Moiré Chemistry" and emerge the development of 2D materials in chemistry area.

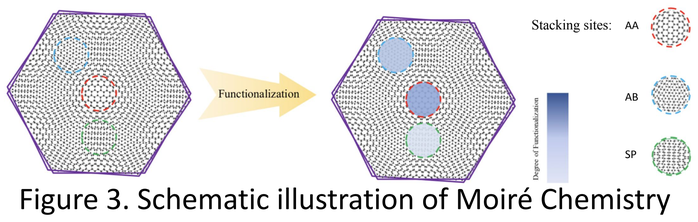

Figure 3. Schematic illustration of Moiré Chemistry in twisted bilayer graphene.

Methods

Sample Preparation

- Graphene were mechanically exfoliated using the scotch tape method and deposited on a SiO_2/Si substrate.
- tBLG was fabricated through a dry transfer process using Poly(Bisphenol A carbonate) (PC).
- Graphene was functionalized with three different diazoniumosalts (4-Nitrobenzene -diazonium tetrafluoroborate (4-NBD), 4-Bromobenzene diazonium tetrafluoroborate (4-BBD)and 4-Methoxybenzene diazonium tetrafluoroborate (4-MBD)) aqueous solutions at 50°C. Electrons transfer from the graphene to the diazonium salt, forming phenyl radicals, which attack surface C atoms and form chemical bonds. This reaction changes the hybridization of the C atom from sp^2 to sp^3.

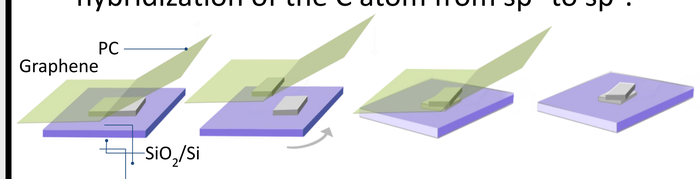

Figure 4. Schematic illustration of twisted bilayer graphene fabrication through dry transfer.

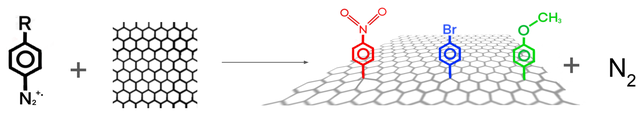

Figure 5. Schematic images of the functionalization reaction on 1L graphene.

Raman Spectroscopy

- Raman measurements are performed to provide detailed information about the chemical structures of the samples. A 532nm laser is used in this work.

Nano-FTIR

- Nanoscale Fourier Transform Infrared Spectroscopy (nano-FTIR) measurements are performed to monitor the distribution of the bonded molecules on graphene surface .

Results

Thickness Dependence Reactivity of Graphene Functionalization

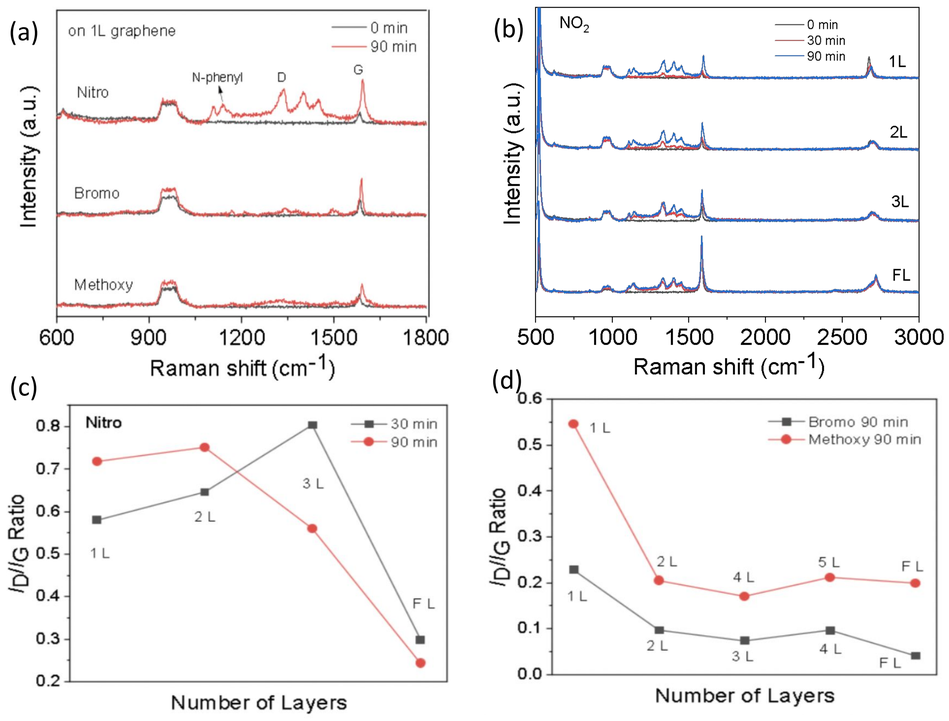

Figure 5. (a) Raman spectra of 1L graphene functionalized with three different diazonium salts. (b) Raman spectrum of 4-NBD functionalized graphene with different number of layers. (c-d) *I*D/IG ratio of functionalized graphene with different number of layers.

Nano-FTIR of 4-NBD Functionalized Graphene

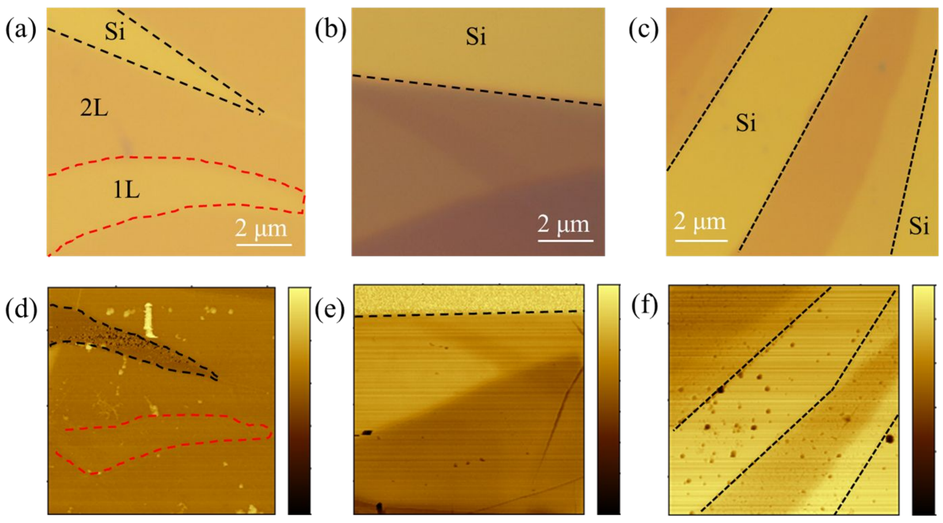

Figure 6. Optical images (a-c) and corresponding nano-FTIR images (d-f) of 4-NBD functionalized graphene and unfunctionalized graphene with using N-phenyl stretch at 1136 cm^{-1}. Distinctions between graphene and Si are shown with a black dotted line. 1L and 2L graphene are separated with a red dotted line.

Twist Angle Dependence of Graphene Functionalization

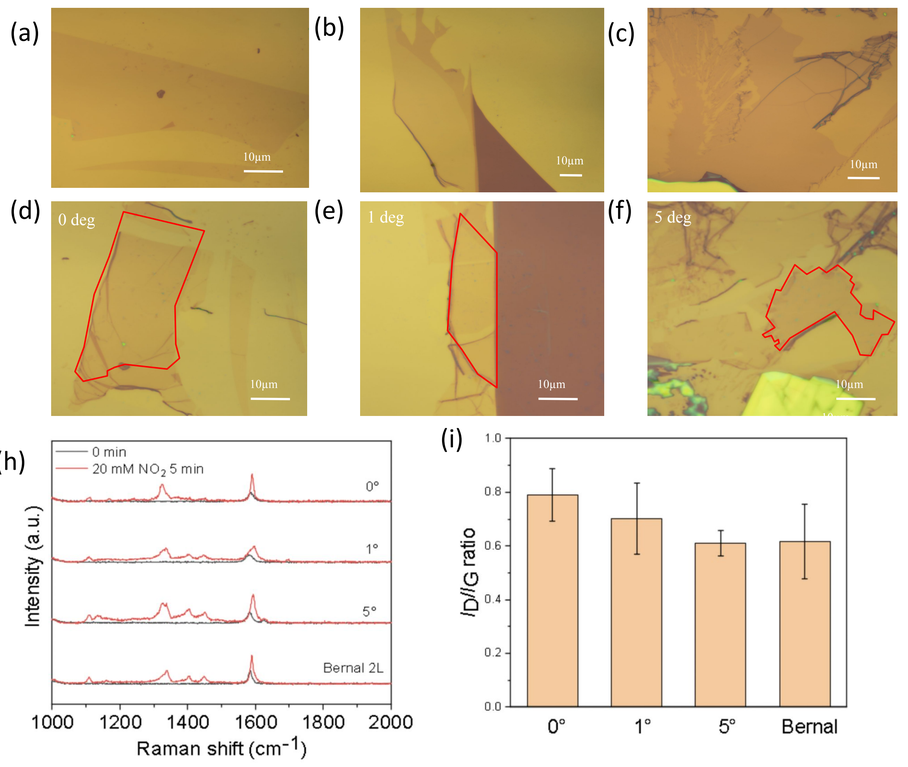

Figure 7. (a-c) Optical images of (a-c) 1L graphene and (d-f) tBLG with different twist angles fabricated from their 1L counterpart. Twisted bilayer regions are outlined in red. (h) Raman spectra comparison of tBLG before and after the functionalization. (i) I_D/I_G ratio of functionalized graphene with different twist angles.

Discussion

Summary

- Functionalization reaction on graphene is realized using three different diazonium salts, indicated by the emerging D-band and blue shifted G-band of graphene through Raman spectra.
- Thickness dependent chemical reactivity of graphene is observed. Graphene with less number of layers exhibit higher degree of functionalization, as suggested by the I_D/I_G ratio and nano-FTIR.
- Twist angle dependent chemical reactivity of graphene is observed on tBLG at 0°, 1° and 5°. This indicates the functionalization reaction is a good model system and provide us a promising platform to study "Moiré chemistry".

Future plans

- Conducting more systematic studies by controlling the concentration of diazonium salt solution, reaction time on tBLG with more twist angles.
- Perform nano-FTIR characterizations on tBLG.

References

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[3] Li, G., Luican, A., Lopes dos Santos, J. et al. Observation of Van Hove singularities in twisted graphene layers. *Nature* Phys *6*, 109–113 (**2010**).

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