

## SUPPORTING INFORMATION

# Reactivity of Perfluorophenyl Azide with Graphene Supported on Cu: Effect of Substrate Crystallinity

Jia Tu, Mingdi Yan\*

University of Massachusetts Lowell, 1 University Ave., Lowell, MA 01854

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# 1. Reactions of Graphene with Azides – Summary of Literature Examples

**Table S1. Functionalization of graphene with azides: literature summary**

Year	Types of graphene	Azide	Reaction conditions	Results	Refs
2009	Epitaxial graphene on SiC	SiMe <sub>3</sub> N <sub>3</sub>	100 °C	N/C ≈ 1:53	1
2009	Graphene sheets mechanically exfoliated from HOPG	Perfluorophenyl azide (PFPA)	140 °C, 40 min	Graphene covalently immobilized on PFPA-functionalized silicon wafer	2
2010	Exfoliated graphene	Boc-Phe(4-N <sub>3</sub> )-OH	Reflux	<i>I<sub>D</sub>/I<sub>G</sub></i> increased from 0.66 to 0.78; ~1 addend per 10 graphene C atoms	3
2010	CTAB-exfoliated graphene	N <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> COOH	160 °C, 45 min	D peak intensity increased	4
2010	Solution-exfoliated graphene flakes	PFPA	UV ( $\lambda > 280$ nm)	Formed patterned, covalently bound graphene films	5
2010	Few-layer graphene obtained by liquid exfoliation of graphite in <i>o</i> -dichlorobenzene	PFPA derivatized with alkyl, ethylene oxide, or perfluoroalkyl groups	90 °C, 72 h or UV ( $\lambda > 280$ nm)	Solubility of graphene changed after functionalization	6
2015	Solvent exfoliated few-layer graphene, mechanically exfoliated graphene from HOPG, CVD-grown monolayer graphene	PFPAs derivatized with silane or disulfide	UV ( $\lambda > 280$ nm)	Covalent immobilization of PFPA-functionalized nanoparticles (SiO <sub>2</sub> , gold, TiO <sub>2</sub> ) on graphene	7
2016	Three-dimensional graphene (3DG) grown on Ni foam by CVD	PFPAs derivatized with carboxyl group	150 °C for 3 h	Formation of covalent 3DG-TiO <sub>2</sub> nanocomposite; Enhanced catalytic performance of 3DG-TiO <sub>2</sub> compared to TiO <sub>2</sub>	8
2019	Few-layer graphene obtained by liquid exfoliation of graphite	<i>N</i> -Succinimidyl 4-azidotetrafluorobenzoate	Microwave radiation (150 °C, 0.5 h) vs. Conventional heating (150 °C, 1.5 h)	Covalent functionalization of graphene with carbohydrates; Higher PFPA grafting density by microwave radiation (5.3 ± 0.6 wt%) than by conventional heating (4.0 ± 1.0 wt%)	9
2020	Few-layer graphene flakes prepared by liquid exfoliation	PFPA derivatized with aniline	Microwave radiation (150 °C, 1 h)	Fabrication of graphene–polyaniline nanocomposite by graft polymerization of aniline on aniline-functionalized graphene	10
2021	CVD graphene on Ni, Cu, or silicon wafer (SiO <sub>2</sub> /Si)	Methyl-4-azidotetrafluorobenzoate	UV ( $\lambda > 280$ nm)	Higher reactivity of graphene supported on Ni than on Cu or wafer	11
2021	CVD graphene transferred onto patterned substrates (SiO <sub>2</sub> /Si with OTS background, or PFPA-filled)	<i>N</i> -(3-Trimethoxysilylpropyl)-4-azido-2,3,5,6-tetrafluorobenzamide	140 °C, 40 min	Reaction of graphene with PFPA inhibits out-of-plane graphene lattice deformation, reducing AFM friction by 30–50%	12
2025	CVD Graphene transferred to SiO <sub>2</sub> /Si	Methyl-4-azidotetrafluorobenzoate	Laser (532 nm)	Local <i>I<sub>D</sub>/I<sub>G</sub></i> up to 1.0–1.2 in laser written zones	13
2025	CVD Graphene on Cu(111), polycrystalline Cu (pCu)	Methyl-4-azidotetrafluorobenzoate	UV ( $\lambda > 280$ nm)	Higher reactivity for graphene on Cu(111) than on pCu	This work

## 2. Additional Raman Spectra

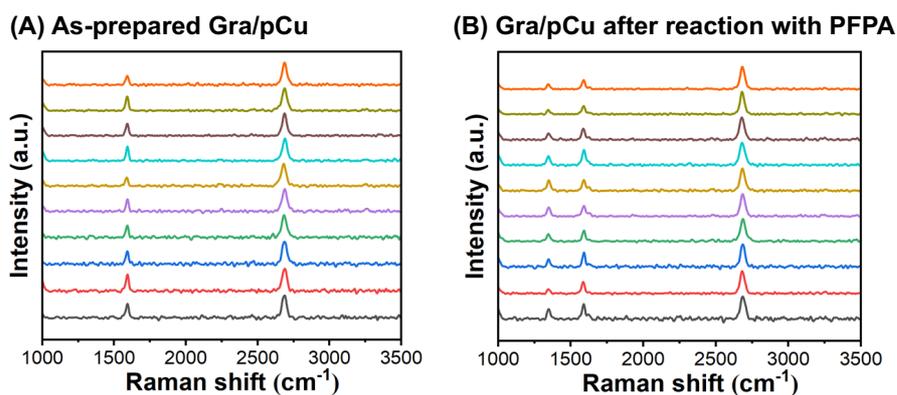


Figure S1. Representative Raman spectra of Gra/pCu (A) before, and (B) after functionalization with PFPA **1**. Samples were transferred to silicon wafer before collecting the spectra.

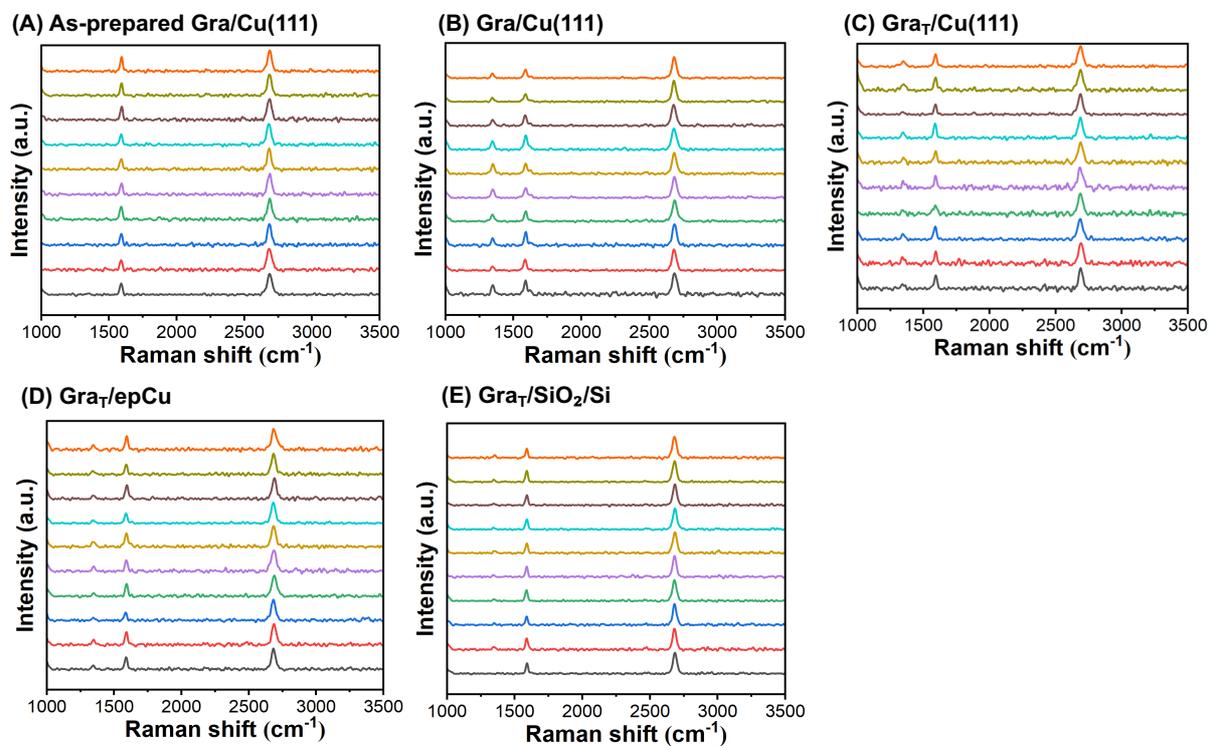


Figure S2. (A) Representative Raman spectra of as-prepared Gra/Cu(111). Representative Raman spectra after functionalization with PFPA **1** for (B) Gra/Cu(111), (C) Gra<sub>7</sub>/Cu(111), (D) Gra<sub>7</sub>/epCu, (E) Gra<sub>7</sub>/SiO<sub>2</sub>/Si. Except for Gra<sub>7</sub>/SiO<sub>2</sub>/Si, samples were transferred to silicon wafer before collecting the spectra.

### 3. Additional Optical and AFM Images

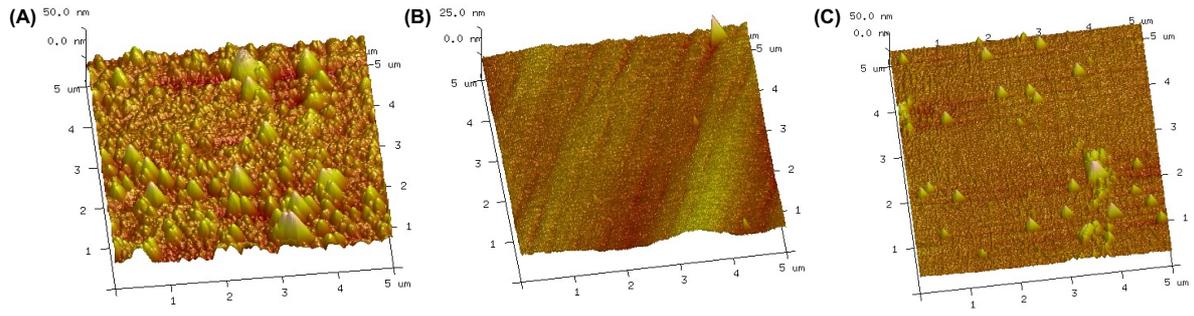


Figure S3. Additional AFM images of (A) Gra/pCu, (B) Gra/Cu(111), and (C) Gra<sub>T</sub>/SiO<sub>2</sub>/Si.

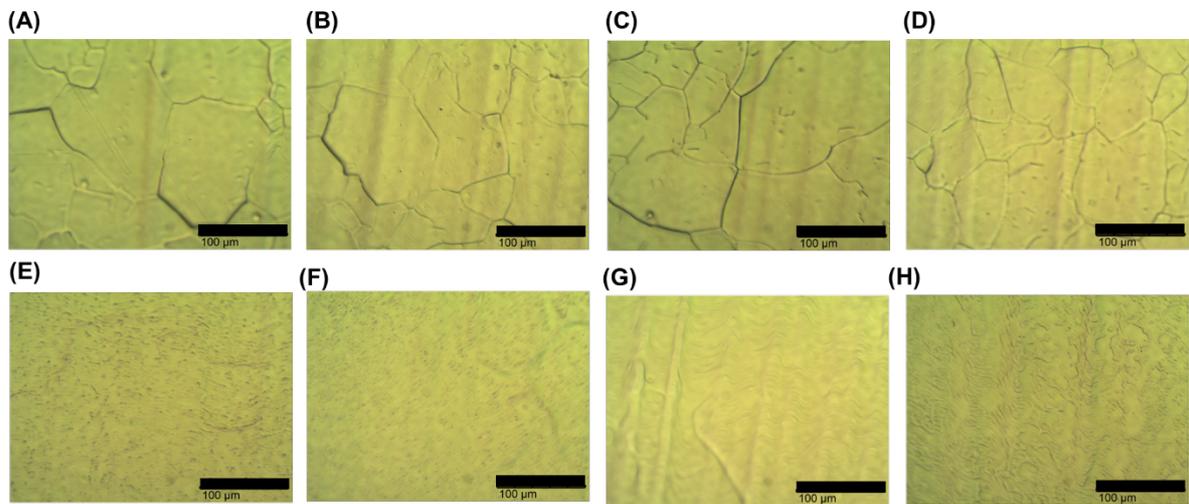


Figure S4. Additional optical microscopy images of (A-D) Gra/pCu, and (E-H) Gra/Cu(111).

### 4. Calculation of $L_D$ and $n_D$

$L_D$  and  $n_D$  are calculated following the method proposed by Cançado et al. for Ar<sup>+</sup>-treated graphene in the low-defect-density region ( $L_D > 10$  nm).<sup>14</sup>

$$L_D^2 = (1.8 \pm 0.5) \times 10^{-9} \lambda^4 (I_D/I_G)^{-1} \quad (\text{Eq. 1})$$

where  $\lambda$  (in nm) is the laser excitation wavelength, which was 532 nm in this work.

$$n_D = 10^{14} / (\pi L_D^2) \quad (\text{Eq. 2})$$

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