Supplementary Information for

Precision Graphene Nanoribbons: Chemical Strategies for Tailored Edge, Backbone, and Electronic Structure

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Before discussing the charge carrier mobility of GNRs, we first provide a detailed introduction to the core principles, mobility extraction methods, and sample preparation of ultrafast optical pump-terahertz probe spectroscopy, so that readers can better understand the data discussion related to charge carrier mobility in this review.

Basic principle and mobility extraction process

Ultrafast optical-pump terahertz-probe spectroscopy is a time-resolved terahertz technique, and its basic principle is as follows.[1–5] It should be noted that the charge carrier concentration of intrinsic GNRs is extremely low (intrinsic semiconductor). Without pump light excitation, the terahertz probe exhibits almost no absorption, making it impossible to directly measure the conductivity. Therefore, it is necessary to generate non-equilibrium carriers in GNRs through optical pumping, and then monitor their dynamic processes using a terahertz probe. It is precisely this time-resolved mode of optical-pump terahertz-probe spectroscopy that enables the acquisition of intrinsic carrier transport behavior in GNRs in a non-contact, electrode-free manner.[6–10]

The specific procedure is as follows: First, a femtosecond laser pulse (pump light) is irradiated onto the GNR sample to excite photogenerated carriers (electron-hole pairs). Subsequently, a broadband terahertz pulse (probe) with a time delay is transmitted through the sample. By measuring the changes in terahertz electric field transmission (or reflection) through the sample, the complex optical conductivity at different delay times after photoexcitation is obtained. By comparing the terahertz signal after photoexcitation with the original terahertz signal without excitation (or with a reference signal without the sample), the photoconductivity σ contributed by the photogenerated carriers can be extracted. On this basis, if the carrier concentration n is known (which can be estimated from the pump light intensity, absorption coefficient, and quantum efficiency), the carrier mobility μ can be calculated using the relation $\mu = \sigma/(n\cdot e)$. A more rigorous approach is to fit the frequency-domain spectrum (real and imaginary parts) of the complex optical conductivity using the Drude-Smith model, with the formula as follows:

$$\Delta\sigma = \frac{\varepsilon_0 \omega_P^2 \tau}{1 - i\omega\tau}\left(1 + \frac{c}{1 - i\omega\tau}\right)$$

Here, ε_0 is the vacuum permittivity, ω_p is the plasma frequency ($\omega_p = \sqrt{ne^2/(\varepsilon_0 m^*)}$, determined by the charge carriers concentration (n) and effective mass (m^*)), and τ is the average carrier momentum scattering time. Fitting the frequency-domain spectrum of the complex optical conductivity using the Drude-Smith model allows simultaneous extraction of τ and the backscattering parameter c (where c reflects the contributions from boundary scattering, edge scattering, and defect scattering). From these, the intrinsic mobility $\mu = e\tau/m^*$ and the DC mobility $\mu_{DC} = \mu(1 + c)$ can be further calculated.

Sample preparation

Depending on the measurement requirements, GNR samples can be prepared in two forms. For solution-phase measurements, GNRs need to be well dispersed in a suitable solvent (such as toluene, 1,2,4-trichlorobenzene, etc.) to form a dilute solution, which is then placed in a quartz cuvette for measurement. In this case, the GNRs are isolated from each other without π-π stacking, and the obtained mobility fully reflects the intra-band transport within individual GNRs, i.e., the intrinsic mobility. For thin-film measurements, the GNR solution can be deposited onto a quartz or high-resistivity silicon substrate by spin coating or drop casting to form a film of a certain thickness. In the film, GNRs may partially stack with each other, so the measured mobility includes contributions from both intra-band and inter-band π-π transport, with the latter increasing as the packing density of the film increases.

Summary

In summary, ultrafast optical-pump terahertz-probe spectroscopy generates carriers through photoexcitation, uses terahertz pulses to probe their photoconductive response, and extracts carrier mobility through model fitting. It is an ideal tool for studying the intrinsic transport properties of GNRs and can be applied to samples in either solution or thin-film form.

Reference

1 R. Ulbricht, E. Hendry, J. Shan, T. F. Heinz and M. Bonn, *Rev. Mod. Phys.*, 2011, **83**, 543–586.

2 E. Hendry, J. M. Schins, L. P. Candeias, L. D. A. Siebbeles and M. Bonn, *Phys. Rev. Lett.*, 2004, **92**, 196601.

3 E. Hendry, M. Koeberg, J. M. Schins, H. K. Nienhuys, V. Sundström, L. D. A. Siebbeles and M. Bonn, *Phys. Rev. B*, 2005, **71**, 125201.

4 F. Wang, J. Shan, M. A. Islam, I. P. Herman, M. Bonn and T. F. Heinz, *Nat. Mater.*, 2006, **5**, 861–864.

5 S. A. Jensen, R. Ulbricht, A. Narita, X. Feng, K. Müllen, T. Hertel, D. Turchinovich and M. Bonn, *Nano Lett.*, 2013, **13**, 5925–5930.

6 A. Narita, X. Feng, Y. Hernandez, S. A. Jensen, M. Bonn, H. Yang, I. A. Verzhbitskiy, C. Casiraghi, M. R. Hansen, A. H. R. Koch, G. Fytas, O. Ivasenko, B. Li, K. S. Mali, T. Balandina, S. Mahesh, S. De Feyter and K. Müllen, *Nature Chem*, 2014, **6**, 126–132.

7 X. Wang, J. Ma, W. Zheng, S. Osella, N. Arisnabarreta, J. Droste, G. Serra, O. Ivasenko, A. Lucotti, D. Beljonne, M. Bonn, X. Liu, M. R. Hansen, M. Tommasini, S. De Feyter, J. Liu, H. I. Wang and X. Feng, *J. Am. Chem. Soc.*, 2022, **144**, 228–235.

8 Q. Chen, A. Lodi, H. Zhang, A. Gee, H. I. Wang, F. Kong, M. Clarke, M. Edmondson, J. Hart, J. N. O'Shea, W. Stawski, J. Baugh, A. Narita, A. Saywell, M. Bonn, K. Müllen, L. Bogani and H. L. Anderson, *Nat. Chem.*, 2024, **16**, 1133–1140.

9 R. K. Dubey, M. Marongiu, S. Fu, G. Wen, M. Bonn, H. I. Wang, M. Melle-Franco and A. Mateo-Alonso, *Chem*, 2023, **9**, 2983–2996.

10 I. Ivanov, Y. Hu, S. Osella, U. Beser, H. I. Wang, D. Beljonne, A. Narita, K. Müllen, D. Turchinovich and M. Bonn, *J. Am. Chem. Soc.*, 2017, **139**, 7982–7988.

Abbreviations

1. Abbreviations for Different GNRs

Abbreviation	Full Name
GNR	Graphene Nanoribbon
AGNR	Armchair-edged Graphene Nanoribbon
ZGNR	Zigzag-edged Graphene Nanoribbon
chGNR	Chiral-edged Graphene Nanoribbon
CGNR	Cove-edged Graphene Nanoribbon
cGNR	Curved Graphene Nanoribbon
cMGNR	Curved Multi-edged Graphene Nanoribbon
CcGNR	Cove-edged Chiral Graphene Nanoribbon
CZGNR	Cove-Zigzag Hybrid-edged Graphene Nanoribbon
FGNR	Fjord-edged Graphene Nanoribbon
JGNR	Janus-type Graphene Nanoribbon
PyGNR	Pyrene-based Curved Graphene Nanoribbon
Por-ZGNR	Porphyrin-extended Zigzag Graphene Nanoribbon
PGNR	Porphyrin-embedded Graphene Nanoribbon
wGNR	Wave-shaped Graphene Nanoribbon
ANR	Azulene-based Non-benzenoid Graphene Nanoribbon
pGNR	Porous Graphene Nanoribbon
npGNR	Non-porous Graphene Nanoribbon
NPG	Nanoporous Graphene

BN-GNR	Boron-Nitrogen co-doped Graphene Nanoribbon
S-GNR	Sulfur-doped Graphene Nanoribbon
N-AGNR	Nitrogen-doped Armchair Graphene Nanoribbon
N-ZGNR	Nitrogen-doped Zigzag Graphene Nanoribbon
N_2-cGNR	Nitrogen-pair doped Cove-edged Graphene Nanoribbon
NBN-ZGNR	Nitrogen-Boron-Nitrogen doped Zigzag Graphene Nanoribbon
OBO-GNR	Oxygen-Boron-Oxygen doped Graphene Nanoribbon
GNR-H	Hydrogen-terminated Gulf-edged Graphene Nanoribbon
GNR-OMe	Methoxy-functionalized Gulf-edged Graphene Nanoribbon
GNR-COOH	Carboxyl-functionalized Graphene Nanoribbon
GNR-PEO	Poly(ethylene oxide)-grafted Graphene Nanoribbon
GNR-AHM	Anthracene-Hexadecylmaleimide-grafted Graphene Nanoribbon
GNR-Por	Porphyrin-edge-functionalized Graphene Nanoribbon
GNR-NMI	Naphthalene Monoimide-functionalized Graphene Nanoribbon
GNR-PMI	Perylene Monoimide-functionalized Graphene Nanoribbon
***p*T-GNR**	*para*-Thiophene-edged Graphene Nanoribbon
***o*T-GNR**	*ortho*-Thiophene-edged Graphene Nanoribbon
K-chGNR	Ketone-functionalized Chiral Graphene Nanoribbon
P-chGNR	Pristine Chiral Graphene Nanoribbon
CNS	Chiral Nanocarbon Structure
N-CNS	Nitrogen-doped Chiral Nanocarbon Structure

L-PyGNR	Linear Pyrene-based Graphene Nanoribbon
H-PyGNR	Helical Pyrene-based Graphene Nanoribbon
CGNRH	Cove-edged Graphene Nanoribbon Heterojunction
MGNR	Molecular Graphene Nanoribbon

2. Abbreviations for characterization and computational methods

Abbreviation	**Full name**
STM	Scanning Tunneling Microscopy
nc-AFM	non-contact Atomic Force Microscopy
BR-STM	Bond-Resolved Scanning Tunneling Microscopy
STS	Scanning Tunneling Spectroscopy
DFT	Density Functional Theory
ARPES	Angle-Resolved Photoemission Spectroscopy
iDPC-STEM	integrated Differential Phase Contrast Scanning Transmission Electron Microscopy
SPM	Scanning Probe Microscopy
XPS	X-ray Photoelectron Spectroscopy
FT-IR	Fourier Transform Infrared Spectroscopy
PL	Photoluminescence
UV-Vis	Ultraviolet-Visible Spectroscopy
UV-Vis-NIR	Ultraviolet-Visible-Near Infrared Spectroscopy
NMR	Nuclear Magnetic Resonance
DQ-SQ NMR	Double-Quantum Single-Quantum Nuclear Magnetic Resonance

Abbreviation	Full name
GPC	Gel Permeation Chromatography
Raman	Raman Spectroscopy
GW	GW approximation
QM/MM	Quantum Mechanics/Molecular Mechanics
FET	Field-Effect Transistor

3. Abbreviations for synthetic strategies and reactions

Abbreviation	Full name
SCTP	Suzuki-Miyaura Catalyst-Transfer Polymerization
PAIS	Protecting-group-assisted Iterative Synthesis
SMC	Suzuki-Miyaura Coupling
MAD	Matrix-Assisted Direct Transfer
CDHC	Cyclodehydrochlorination

4. Abbreviations for electronic structure and physical parameters

Abbreviation	Full name
CBM	Conduction Band Minimum
VBM	Valence Band Maximum
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
CBO	Conduction Band Offset

Abbreviation	Full name
VBE	Valence Band Edge
CBE	Conduction Band Edge
DC	Direct Current
LDOS	Local Density of States
PDOS	Projected Density of States
DOS	Density of States

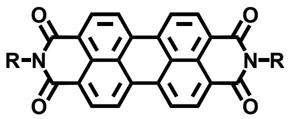
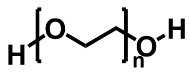
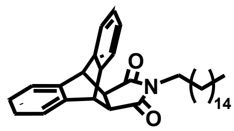
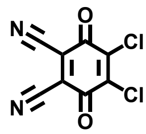
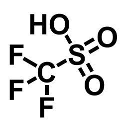
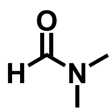
5. Abbreviations for materials and compounds

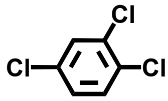
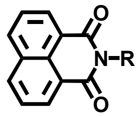
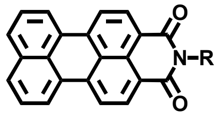
Abbreviation	Full name
PDI	Perylene Diimide
PEO	Poly(ethylene oxide)
AHM	Anthracene-Hexadecylmaleimide
DDQ	2,3-Dichloro-5,6-dicyano-1,4-benzoquinone
TfOH	Trifluoromethanesulfonic Acid
THF	Tetrahydrofuran
NMP	N-Methylpyrrolidone
TCB	1,2,4-Trichlorobenzene
NMI	Naphthalene Monoimide
PMI	Perylene Monoimide
IF	Indenofluorene

6. Others

Abbreviation	Full name
UHV	Ultra-High Vacuum
THz	Terahertz
SSH	Su-Schrieffer-Heeger

Chemical structures

Abbreviation	Full name	Structure
PDI	Perylene Diimide	
PEO	Poly(ethylene oxide)	
AHM	Anthracene-Hexadecylmaleimide	
DDQ	2,3-Dichloro-5,6-dicyano-1,4-benzoquinone	
TfOH	Trifluoromethanesulfonic Acid	
NMP	N-Methylpyrrolidone	

Abbreviation	Full name	Structure
TCB	1,2,4-Trichlorobenzene	
NMI	Naphthalene Monoimide	
PMI	Perylene Monoimide	
IF	Indenofluorene