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Optical imaging and spectroscopy of atomically precise armchair graphene nanoribbons

Sihan Zhao¹, Gabriela Borin Barin², Ting Cao^{1,3}, Jan Overbeck², Rimah Darawish², Tairu Lyu¹, Steve Drapcho¹, Sheng Wang^{1,4}, Tim Dumsclaff⁵, Akimitsu Narita⁵, Michel Calame², Klaus Müllen^{5,6}, Steven G. Louie^{1,4}, Pascal Ruffieux², Roman Fasel^{2,7} and Feng Wang^{1,4,8*}

¹ Department of Physics, University of California at Berkeley, Berkeley, California 94720, United States

² Empa, Swiss Federal Laboratories for Materials Science and Technology, 8600 Dübendorf, Switzerland

³ Department of Materials Science and Engineering, University of Washington, Seattle, WA, USA

⁴ Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

⁵ Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany

⁶ Johannes Gutenberg-Universität Mainz, Institute of Physical Chemistry, 5128 Mainz, Germany

⁷ Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, CH-3012 Bern, Switzerland

⁸ Kavli Energy NanoSciences Institute at the University of California, Berkeley and the Lawrence Berkeley National Laboratory

Corresponding author: fengwang76@berkeley.edu

Abstract: We report the optical imaging and absorption spectroscopy on atomically precise armchair graphene nanoribbons (GNRs) on insulating fused silica substrates. This is achieved by controlling light polarization on macroscopically aligned GNRs, which greatly enhances the sub-monolayer GNR optical contrast on the insulating substrates. We measured the linear absorption spectra of 7-armchair and 9-armchair GNRs in this study, and the experimental data agree qualitatively with *ab initio* calculation results. The polarization spectroscopy technique enables an unambiguous optical identification of GNR samples and provides a rapid tool to characterize the transferred film over large area.

Key words: graphene nanoribbons, armchair graphene nanoribbons, optical imaging, optical properties, absorption spectroscopy, polarization spectroscopy

Recent advances in bottom-up synthesis of graphene nanoribbons (GNRs) have led to realization of atomically precise GNRs with well-defined edge structures.¹⁻¹⁶ The unprecedented structural control with atomic precision opens new opportunities to engineer GNR bandstructures, making GNRs a promising material platform for nanodevices.¹⁵⁻²⁰ Armchair GNRs (AGNRs) are the most extensively studied atomically precise GNRs. AGNRs with different widths (N-AGNRs, where N represents the number of carbon dimer lines across the GNR width) were synthesized and they are structurally stable in ambient conditions.^{1,5,10,18,19,21,22} Theoretically, the one-particle bandgap in AGNRs varies with the nanoribbon width following distinct family patterns: the bandgap in N-AGNRs does not decrease monotonically with the GNR width, but oscillates periodically with the family index $i = N \bmod 3$.²³⁻²⁶

Most of the sample characterizations so far are carried out by scanning tunneling microscopy (STM) *in situ* on gold and Raman spectroscopy *ex situ*.^{1,5,10,27-29} However, the linear optical absorption which characterizes the fundamental light-matter interactions of transferred AGNRs on insulating substrates have remained challenging.^{22,30-33} Limited absorption studies were previously reported for monolayer AGNRs on gold surfaces and for stacked multilayer AGNRs on insulating substrates, which, however, involved complicated metal screening effect and coupling effect among AGNR stacks.^{22,30-33} Absorption

spectroscopy study of the intrinsic one-dimensional (1D) AGNRs is hindered by a combination of impurities/residues introduced in the transfer process (e.g. fig. 1c) and the intrinsic weak optical absorption of the sub-monolayer 1D objects.

Here we report the first optical imaging and absorption spectroscopy for sub-monolayer atomically precise AGNRs with different widths on insulating substrates. These are achieved by applying a light polarization spectroscopy technique on macroscopically aligned AGNR samples, where the weak optical contrast of GNRs is greatly enhanced with the suppressed background signal from substrate and from impurities/residues. We experimentally obtain absorption spectra from 7-AGNRs and 9-AGNRs transferred on fused silica substrates whose results qualitatively agree with our theoretical GW-BSE calculations.^{1,13} We experimentally observe optical bandgaps of ~ 2.3 eV for 7-AGNRs and ~ 1.3 eV for 9-AGNRs.

Results and discussion

Figure 1. Microscopy and spectroscopy characterizations of aligned 7-AGNRs before and after transfer. (a) STM topology image for the as-grown aligned 7-AGNRs on Au (11,12,12). (b) Polarization-resolved Raman of G- and RBLM-modes for as-grown aligned 7-AGNRs. The data (e.g. G-mode) nicely follow a $\sin^4 \theta$ fit, with an extracted polarization anisotropy of 0.90. (c) AFM topology image for the transferred aligned 7-AGNRs on insulating substrate. It shows GNR film non-uniformity and residues/impurities incurred during the transfer process. (d) Polarization-resolved Raman of G- and RBLM-modes for the transferred aligned 7-AGNRs. The polarization anisotropy after transfer is 0.82 indicating that the macroscopic alignment of GNRs is largely preserved after transfer process. 532 nm laser excitation is used in (b) and (d).

The aligned AGNRs samples are directly grown on Au (11,12,12) and/or Au (7,8,8) (**Methods section 1**). Figure 1a shows a representative STM topology image of the as-grown 7-AGNRs, where the individual

GNRs exhibit a unidirectional alignment direction on along the Au (11,12,12) terraces. The width of each 7-AGNRs is ~ 1 nm and their average length is ~ 30 nm. Figure 1b shows the polarization-resolved Raman intensity of the G-mode (~ 1600 cm^{-1}) and RBLM-mode (~ 400 cm^{-1}) for the as-grown 7-AGNRs. The data nicely follow $\sin^4 \theta$, where θ denotes the relative angle between light polarization and AGNR aligned axis and thus confirm that the as-grown 7-AGNRs are macroscopically aligned.²⁸ To probe the intrinsic optical properties, we transfer AGNRs onto transparent and insulating substrate (i.e. fused silica which is amorphous) by using an electrochemical delamination process (also known as “bubble transfer”) (**Methods section 2**).²⁸ We characterize the morphology of the as-transferred GNRs by atomic force microscopy (AFM). Figure 1c shows the typical GNR film after transfer. We note that there exists GNR film non-uniformity and residues/impurities induced in the transfer process (fig. 1c). Figure 1d presents the polarization-resolved Raman intensity of G- and RBLM-modes for the transferred 7-AGNRs. For a quantitative description of the alignment, we calculate the Raman polarization anisotropy P for the G-mode as $P = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp})$. This yields $P = 1$ for GNRs that are perfectly aligned with the step edges and $P = 0$ for randomly oriented GNRs.²⁸ For the as-grown 7-AGNRs on Au (11,12,12) we find an anisotropy of $P = 0.90$ (fig. 1b), which slightly decreases to $P = 0.82$ (fig. 1d) after transfer, indicating that the macroscopic alignment is largely preserved upon transfer.

A combination of the weak optical absorption of the sub-monolayer GNRs and the background from unavoidable impurities/residues introduced in transfer process makes the absorption spectroscopy of transferred GNRs on an insulating substrate very challenging. To overcome this difficulty, we exploit a polarization spectroscopy technique on these 1D aligned AGNRs. Figures 2a and 2b illustrate our optical setup and measurement scheme of the polarization spectroscopy technique. From an interferometric point of view, the optical contrast of GNRs on a substrate in a reflection configuration results from interference between the GNR-reflected electric field E_{GNR} and the substrate-reflected electric field E_{sub} at the detector site:

$$dR/R = \frac{|E_{GNR} + E_{sub}|^2 - |E_{sub}|^2}{|E_{sub}|^2} \approx \frac{2\text{Re}[E_{sub}^* E_{GNR}]}{|E_{sub}|^2} = \frac{2|E_{GNR}|}{|E_{sub}|} \cos \theta \quad (1).$$

Here R is the reflected optical signal from the substrate, dR is the reflected optical signal difference with the presence of GNRs, and θ represents the relative phase difference between E_{GNR} and E_{sub} . We treat E_{GNR} as a perturbation of E_{sub} because it is usually much smaller comparing with E_{sub} . Therefore, in principle, the GNR optical contrast can be significantly enhanced by reducing the reflected electric field from substrate while maintaining the electric field from GNRs. This is achieved by polarization manipulation, as shown in fig. 2a and 2b. The horizontally polarized incident light after the first polarizer P1 illuminates the macroscopically-aligned GNR samples on fused silica substrate. To maximize the GNR optical contrast, the incident laser polarization is at about 45° relative to the GNR axis (fig. 2b). The GNR-reflected electric field at sample site E_{GNR}^0 is mostly polarized along the GNR axis direction due to the strong depolarization effect in the direction perpendicular to GNR axis.^{34,35} On the other hand, the electric field reflected from the isotropic insulating substrate at the substrate site E_{sub}^0 remains the horizontal polarization direction. The second polarizer P2 is set nearly orthogonal to P1 (with a small deviation angle δ shown in fig. 2b) in the outgoing beam path. The substrate-reflected field (as well as those from impurities/residues incurred during sample transfer) is thus significantly reduced by $\sin \delta * E_{sub}^0$. In contrast, the GNR-reflected electric field after P2 is still largely kept (reduced by $1/\sqrt{2} E_{GNR}^0$). Therefore, the GNR optical contrast is greatly enhanced by $1/(\sqrt{2}\sin \delta)$ against signals from substrate and impurities/residues.

The substrate used in this study is insulating and transparent fused silica substrate with semi-infinite thickness (~ 500 μm). In this case, the measured GNR optical contrast in eq 1 is proportional to $\text{Im}(\chi)/\sin \delta$ when δ is small, where χ is the optical susceptibility of GNRs. This yields a direct

measurement of GNR optical absorption. The sign of optical contrast depends on the angle δ . The GNRs can appear brighter or darker than the environment (i.e. substrate) depending on the sign of the deviation angle from vertical direction (fig. 2b illustrates a small positive δ). By gradually decreasing the magnitude of δ , GNR optical contrast will show a monotonic increase (**Methods section 3**).³⁶

Figure 2. Application of the polarization spectroscopy technique in aligned AGNRs. (a-b) Schematic illustration of our optical setup and measurement scheme. To maximize the GNR optical contrast, GNR axis is at about 45° to the first polarizer P1. The second polarizer P2 is nearly orthogonal to P1 with a deviation angle defined as δ . The optical signals from substrates and impurities/residues are significantly reduced when δ is set small, whereas, on the other hand, signals from GNRs are largely kept. (c) Optical imaging of transferred GNR samples on fused silica substrate with the polarization spectroscopy technique as schematically illustrated in (a) and (b). The left and right are two microscope images corresponding to imaging conditions with δ at $\sim 2^\circ$ and at $\sim -2^\circ$, respectively. The dashed lines are boundary contours separating the bare substrate on the left and GNRs on the right. GNRs appear either brighter (left image) or darker (right image) comparing with the substrate when δ is changed from positive values to negative ones. The measuring spots where the spectroscopy data are obtained in fig. 3a are shown by dot markers. Scale bar is about 10 μm . The ring-like fringes in the images are imaging artifacts due to the small opening of the iris used to block the stray light.

Our polarization spectroscopy technique enables a direct optical imaging of GNRs on fused silica substrate. Figure 2c shows the typical imaging results for the aligned 7-AGNR samples that were transferred. The image on the left is obtained when δ is set at $\sim 2^\circ$ whereas the one on the right is obtained when δ is set at $\sim -2^\circ$. The ring-like fringes in two images are imaging artifacts due to the small opening of the iris used to block the stray light. We clearly see that the optical contrast in two images changes sign when δ

crosses zero: the brighter (darker) region becomes darker (brighter) when δ is changed from $\sim 2^\circ$ to $\sim -2^\circ$. In addition, the optical contrast becomes higher with decreasing the magnitude of δ for both positive and negative values. These unique behaviors are assigned to the GNRs' optical response arising from its unique 1D nature. The contours separating two distinct contrast regions are indicated by dashed lines. The GNR optical contrast on substrate is significantly enhanced with this polarization manipulation, and can achieve to more than 10% depending on the local densities of transferred GNR films. We detected GNR Raman signals over the brighter (darker) contrast region on the left (right) images and that no GNR Raman features were observed in the corresponding darker (brighter) contrast region (**Figure S1**), which further confirms the successful optical imaging and identification of GNRs on substrates with the polarization spectroscopy technique. Note that we always observe contrast variations within the transferred film area by this polarization spectroscopy technique, whereas, on the other hand, the film usually appears optically invisible and featureless under conventional optical microscope. The enhanced GNR optical contrast against the substrate thus enables an unambiguous optical identification of GNR samples and provides a rapid tool to characterize the transferred film over large area.

In the following, we will focus on the reflection contrast spectroscopy of aligned 7-AGNRs and 9-AGNRs, which are representative AGNRs belonging to $3p + 1$ and $3p$ family respectively. The optical spectra in this study are taken from ~ 0.7 eV to ~ 2.8 eV, limited by the spectral range of our supercontinuum laser. Figure 3a representatively presents reflection contrast spectra (dR/R) for 7-AGNRs. The measuring spots for dR/R in fig. 3a are indicated by the dot markers in fig. 2c. Spectra measured with different deviation angles δ are plotted with different colors. Consistent spectra are observed at different sample locations (**Figure S2**). As shown in fig. 3a, a systematic evolution of dR/R spectra with varying the deviation angles is observed: i) the measured dR/R is positive (negative) when δ is positive (negative) and they exhibit a sign change when δ crosses zero; ii) by gradually decreasing the magnitude of deviation angles, we observe a monotonic increase in the magnitude of dR/R . These systematic behaviors unambiguously demonstrate the measured dR/R arise from the GNR optical contrast and correspond to its optical absorption.

Figure 3. Experimental results and theoretical calculations on the optical absorption of 7-AGNRs. (a) Reflection contrast spectra (dR/R) as a function of deviation angle δ . E^{11} transition arising from the first bright exciton is indicated by the dashed line. (b) Theoretically calculated absorption spectra for 7-AGNRs with e-h interactions (solid red) and without e-h interactions (dashed black). The experimentally observed optical bandgap for 7-AGNRs on fused silica substrate is ~ 2.3 eV.

We focus on dR/R spectra at deviation angles of $\sim 2^\circ$ and $\sim -2^\circ$ because the GNR optical contrasts at these angles are mostly enhanced against signals from substrates and from residues/impurities. The strong

optical resonance observed at ~ 2.3 eV (dashed line) is attributed to the bright exciton from first inter-subband (E^{11}) transition in 7-AGNRs. The strongly asymmetric spectral shape of E^{11} is likely due to higher energy bright exciton transition (E^{22}) in 7-AGNRs. However, the very broad optical transition in the experimental spectrum prevents us to fully resolve multiple exciton resonances that may be present. The experimental interpretation on the observed spectra is supported by our theoretical GW-BSE calculation. Figure 3b shows the calculated absorption spectra for 7-AGNRs with electron-hole (e-h) interactions (solid red) and without e-h interactions (dashed black). The calculated GW bandstructure for 7-AGNR is shown in **Figure S3**. Theoretically, the strong e-h coulomb interactions largely modify the optical absorption spectrum of 7-AGNRs, which causes a significant energy redshift for E^{11} from ~ 3.7 eV to ~ 2.1 eV as shown in fig. 3b.^{37,38} Our calculation predicts that 7-AGNRs have two bright exciton transitions E^{11} and E^{22} that are close in energy. Our experimentally observed absorption spectra and interpretation (fig. 3a) thus shows a qualitative agreement with the GW-BSE calculated spectra. The optical bandgap (i.e. the energy of E^{11}) for 7-AGNRs on fused silica is experimentally determined to be ~ 2.3 eV.

Figure 4. Experimental results and theoretical calculations on the optical absorption of 9-AGNRs. (a) Reflection contrast spectra (dR/R) as a function of deviation angle δ . The transition associated with the first bright exciton (E^{11}) and an X peak are indicated by dashed lines. (b) Theoretically calculated absorption spectra for 9-AGNRs with e-h interactions (solid red) and without e-h interactions (dashed). The experimentally observed optical bandgap for 9-AGNRs on fused silica substrate is ~ 1.3 eV.

9-AGNRs are predicted to have a smaller bandgap compared to the 7-AGNRs. The representative dR/R spectra for aligned 9-AGNRs with systematically varying deviation angles are presented in fig. 4a (more absorption data in **Figure S4**). The calculated absorption spectra with and without e-h interactions for 9-AGNRs are shown in fig. 4b. The calculated GW bandstructure is shown in **Figure S5**. Similar to the spectra of 7-AGNRs in fig. 3a, a systematic evolution of dR/R on deviation angles is observed for 9-AGNRs over the whole spectral range. We observe a very strong optical resonance at ~ 1.3 eV. Consistent optical absorption spectra around ~ 1.3 eV resonant peak are confirmed with extending spectral range to lower energy by using an InGaAs detector (**Figure S6**). We attribute this strong optical resonance at ~ 1.3 eV to the bright E^{11} transition in 9-AGNRs. This assignment agrees with the GW-BSE calculated E^{11} transition with taking into account of e-h interactions (solid red in fig. 4b). The optical bandgap for 9-AGNRs on fused silica is thus experimentally determined to be ~ 1.3 eV. We also observe a weaker absorption peak (X peak in fig. 4a) at ~ 2.2 eV for 9-AGNR samples. This absorption peak locates at a much lower energy than the theoretically predicted E^{22} bright exciton transition (see fig. 4b). We do not

know the origin of this absorption peak yet, and further theoretical and experimental studies will be required for its understanding.

In summary, by using the polarization spectroscopy technique, we successfully performed the optical imaging and absorption spectroscopy on two representative atomically precise AGNRs (i.e. 7-AGNRs and 9-AGNRs) with sub-monolayer thickness on insulating substrates. The unambiguous optical identification of GNRs and the systematic spectral evolution upon varying the polarization conditions consolidate that our observed spectroscopy results correspond to the 1D GNRs absorption. The experimentally observed absorption spectra and interpretation qualitatively agree with the GW-BSE calculations. The experimentally observed optical bandgaps for 7-AGNRs and 9-AGNRs on fused silica substrate are at ~ 2.3 eV and at ~ 1.3 eV.

Methods

1. Growth and STM characterization of aligned AGNRs

On surface synthesis of AGNRs

9-AGNRs were synthesized from 3',6'-diiodo-1,1':2',1''-terphenyl (DITP) as the precursor monomer and 7-AGNR from 10,10'-dibromo-9,9'-bianthryl (DBBA).³⁹ In this study, 7-AGNRs and 9-AGNRs were grown on Au (11,12,12) and Au (788), respectively. First, Au (11,12,12) or Au (788) substrate was cleaned in ultra-high vacuum by two sputtering/annealing cycles: 1 kV Ar⁺ for 10 minutes followed by annealing at 420 °C for 10 minutes. Next, the monomer was sublimed onto the Au surface from a quartz crucible heated to 70 °C (DITP) and 200 °C (DBBA) respectively, with the substrate held at room temperature. After 1 monolayer coverage deposition, for both 7-, and 9-AGNRs the substrate was heated (0.5 °C/s) up to 200 °C with a 10 minute holding time to activate the polymerization reaction, followed by annealing at 400 °C (0.5 °C/s with a 10 minute holding time) in order to form the GNRs via cyclodehydrogenation.

Scanning tunneling microscopy (STM)

Topographic scanning tunneling microscopy images of as-grown AGNRs on Au (11,12,12) and Au (788) were taken with a Scienta Omicron VT-STM operated at room temperature. Constant-current STM images were recorded with 1.5 V sample bias and 0.03 nA setpoint current.

2. GNR transfer and ex-situ characterization

AGNRs were transferred from their growth gold substrate onto fused silica by electrochemical delamination method. First, PMMA was spin-coated (2500 rpm for 90 seconds) on GNR/Au to act as a support layer during the transfer. In a second step the PMMA/GNR/Au was heated at 80 °C for 10 minutes. In order to decrease the delamination time the PMMA on the edges of the Au substrate was etched by UVO exposure (80 minutes) followed by 3 minutes development in water: IPA.

The electrochemical delamination transfer was carried using 1 M NaOH aqueous solution as electrolyte. The electrochemical cell was mounted using a carbon rod as anode and the PMMA/GNRs/Au as the cathode. A DC current of 0.2 A (5 V) was applied between anode and cathode during 1 minute. Hydrogen bubbles were formed in the cathode as a results of water reduction reaction. These bubbles permeates into the PMMA/GNRs and Au interface resulting in the detachment of the PMMA layer. The PMMA/GNR layer was cleaned for 5 minutes in ultrapure water before the transfer to the target substrate. After transfer onto fused silica PMMA/GNRs was baked for 10 minutes at 80 °C followed by 20 minutes at 110 °C in order to increase the adhesion between the target substrate and the PMMA/GNR layer. Finally, PMMA was dissolved by soaking it in acetone (15 minutes).

Polarized Raman spectroscopy

Polarized Raman spectra were performed with Witec Alpha 300 R Confocal Raman microscope, using 532 nm (2.33eV) as excitation wavelength. The incident light was focused on the sample using a 50x long working distance objective with a numerical aperture NA = 0.55, resulting in a spot size of about 600 nm FWHM. A motorized half wave plate was used to change the polarization direction of the incident laser beam from -90 to +90 degree, and a manual analyzing polarizer was kept parallel in the detection path. In order to improve signal to noise ratio Raman maps (10x10um) were obtained for GNRs on Au and on fused silica under vacuum (1×10^{-2} mbar).⁴⁰

Atomic Force Microscopy

The topography of transferred graphene nanoribbon samples was characterized using tapping mode AFM (Bioscope, Bruker) with silicon probes from OPUS (model 160AC-SG Ultrasharp Cantilever) with tip radius < 1 nm (force constant $\sim 26 \text{ N m}^{-1}$, resonance frequency in the range of 300 kHz). Height diagrams were recorded with scan sizes of 1.5 μm and scan speeds of 1 Hz (512×512 points). The WSxM software was used for AFM analysis.⁴¹

3. Polarization spectroscopy technique

Optical imaging and absorption spectroscopy measurements were carried out using a supercontinuum laser (YSL SC-PRO). Light polarization was controlled by a paired calcite polarizers (Glan-Thompson) and high polarization purity was achieved and retained in the imaging and spectroscopy (extinction ratio > 20,000). Sample contrast was imaged by a standard Si CCD camera. Reflection contrast spectra dR/R were obtained by measuring the reflectance at two close-by spots with and without GNRs with a piezoelectric motor. The light was collected into a grating spectrometer (Princeton Instruments) and InGaAs CCD (iDus 1.7 μm InGaAs) with grating to obtain spectra in the visible and near-IR spectral range.

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Author contributions

F.W. and R.F. supervised this project. S.Z. proposed and performed the imaging and spectroscopy measurements. G.B.B., J.O., R.D., M.C. and P.R. prepared and characterized the AGNR samples prior to imaging and spectroscopy. T.L., S.D. and S.W. helped in the optical measurements. T.C. and S.G.L. carried out the theoretical calculations. T.D., A.N. and K.M. prepared the precursors for GNR growth. All authors discussed the results and wrote the paper.

Competing interests. The authors declare no competing financial interests.

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