Full Length Article

Broadband optical properties of graphene and HOPG investigated by spectroscopic Mueller matrix ellipsometry

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A B S T R A C T

Optical properties of mono-graphene fabricated by chemical vapor deposition (CVD) and highly oriented pyrolytic graphite (HOPG) are comparatively studied by Mueller matrix ellipsometry (MME) over an ultra-wide energy range of 0.73–6.42 eV. A multilayer stacking model is constructed to describe the CVD mono-graphene, in which the roughness of the glass substrate and the water adsorption on the graphene are considered. We introduce a uniaxial anisotropic dielectric model to parameterize the optical constants of both the graphene and the HOPG. With the established models, broadband optical constants of the graphene and the HOPG are determined from the Mueller matrix spectra based on a point-by-point method and a non-linear regression method, respectively. Two significant absorption peaks at 4.75 eV and 6.31 eV are observed in the extinction coefficient spectra of the graphene, which can be attributed to the von-Hove singularity (i.e., the \( p\)-to-\( p\) \( \pi \)-exciton transition) near the M point and the \( \sigma\)-to-\( \sigma\) \( \pi \)-exciton transition near the \( \Gamma \) point of the Brillouin zone, respectively. Comparatively, only a major absorption peak at 4.96 eV appears in the ordinary extinction coefficient spectra of the HOPG, which is mainly formed by the \( p\)-to-\( p\) \( \pi \)-interband transition.

1. Introduction

Since the successful exfoliation of the graphene in 2004 by A. K. Geim and his associates [1], a variety of 2D materials, such as graphene family, transition metal dichalcogenides (TMDs) [2,3], 2D-perovskites [4], black phosphorus [5], borophene [6] and heterogeneous structures based on these 2D materials [7,8], have been prepared in laboratories. These 2D materials are considered to be promising substitutes of those traditional optoelectronic materials (e.g. oxides of indium, tin, zinc, their alloys etc.), and have been the subject of considerable interest of many scientists [9–14]. The updates of some optoelectronic devices, such as light-emitting diodes, organic light emitting diodes, and solar cells, have been implemented by introducing 2D materials. It is worth noting that the performances of optoelectronic devices highly depend on the materials’ optical properties, which are closely relating to the basic optical constants, such as the refractive index and the extinction coefficient. Unfortunately, the optical constants of 2D materials are more changeable than those of their bulk counterparts, and they are sensitive to the preparation processes, the number of layers [15] and the types of substrates [16]. Therefore, accurate determination of the basic optical constants of these 2D materials is extremely challenging but of great importance for the optimal design of the next-generation optoelectronic devices.

Among various 2D materials, large area polycrystalline graphene prepared by mature CVD process [15,17] is regarded as one of the most promising candidates that can be firstly applied in industrial products. Thus, the investigation of the optical properties of the graphene recently becomes one of the research focuses [18–23]. Among various techniques, the reflection (or absorption) spectra methods [19] and the ellipsometry [24,25] are two widely accepted methods to determine the optical constants or optical conductivity of graphene. The method based on the reflection (or absorption) spectra needs an additional function named the Kramers-Kronig (K-K) relation to solve the refractive index as well as the extinction coefficient [26]. However, the K-K relation describes the relationship between the real part and the imaginary part of an ideal linear passive system, and the optical constants

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solved by this method for a practical material under finite experimental conditions may contain significant errors. Moreover, the measurement accuracy and reliability of this method directly depend on the detected light intensity signal which is easily affected by the experimental environment. In comparison, the ellipsometry detects the polarization state change of polarized light before and after reaction (reflection or transmission) with the samples, and the optical constants of the graphene can be extracted from the ellipsometric spectra without any additional functions [24,25,27–35]. Thus, ellipsometry is a more competitive method for investigating the optical properties of materials by providing more measurement information. Besides the two mentioned experimental approaches, some methods based on theoretical calculations have also been put forward to deduce the optical properties of the graphene [22,23].

Recently, the optical properties of the graphene prepared by the CVD [24,25,27–30], micromechanical exfoliation [31–33], and molecular beam epitaxy [34,35] were investigated quite intensively by spectroscopic ellipsometry (SE). With a variable angle ellipsometer, Geim’s group extracted the in-plane optical constants of the graphene, and they asserted the graphene has the same out-of-plane optical constants as the highly oriented pyrolytic graphite (HOPG) [25]. Weber et al. determined the optical constants and the thickness of a graphene flake by fitting the ellipsometric spectra with the dielectric function parameterized by B-splines [31]. Goran Isci et al. introduced an island-film model to fit the ellipsometric spectra of the exfoliated few-layer graphene film [32], but their results are significantly different from other papers due to some unclarified features [25,31,34]. However, most of the existing studies on the optical properties of the graphene employ the conventional SE, which is not competent to characterize those 2D materials with emerging features in structures and optical properties, such as heterogeneous structures, puckered structures, optical anisotropy, and optical depolarization. Compared with the conventional ellipsometry that can only provide two ellipsometric angles, Mueller matrix ellipsometry (MME) can offer much more useful sample information by measuring the full $4 \times 4$ Mueller matrix in each measurement. Therefore, the MME will be a promising and powerful tool for the characterization of nanomaterials [36], especially those features mentioned above, including optical anisotropy, optical depolarization, and nanostructures.

In this paper, we investigate the optical properties of the CVD graphene and the HOPG over an ultra-wide energy range of 0.73–6.42 eV by a spectroscopic MME. The investigated samples include a large-area polycrystalline mono-graphene film on quartz glass prepared by mature CVD process and a purchased A-level HOPG. These samples are meticulously prepared and processed, and their qualities are comprehensively checked by the means of optical microscope (OM), micro-Raman spectrometer, and atomic force microscope (AFM). To perform the ellipsometric analysis, a uniaxial anisotropic dielectric model is introduced to embody optical properties of the HOPG and the graphene. To more accurately describe the optical structure of the CVD graphene sample, a multilayer stacking model is established, in which the roughness of the glass substrate and the water adsorption on the top of the graphene are considered. Furthermore, both a point-by-point mathematical calculation method and a nonlinear least-square fitting method are proposed to extract the optical constants of the graphene and the HOPG, including the refractive index and the extinction coefficient, from the measured Mueller matrix spectra. Some intrinsic characteristics are observed on the optical constant spectra and their corresponding physical mechanisms are revealed. The results are consistent with the published literatures and the theoretical calculations but with a wider spectral range and more physical and reasonable explanation by considering the optical anisotropy.

2. Graphene and HOPG

Large area polycrystalline mono-graphene films on the quartz glass substrate used in our experiments were prepared by a standard CVD process [17]. Firstly, the copper (Cu) foils were annealed at 1000 °C under hydrogen and argon flow before the growth of the graphene, for the purpose of improving the uniformity of the graphene film by enlarging the crystalline grains of the Cu foils. Then, the graphene was synthesized on the Cu foils by using the methane as the carbon source in a cold walled CVD reactor at 1000 °C. After that, a polymer material named polymethyl methacrylate (PMMA) was spin coated onto the graphene as the support layer in the following transfer process, and then the Cu foils were dissolved in a ferric chloride containing solution. Finally, the graphene was transferred onto the quartz glass substrate with the support of PMMA, which was removed by acetone at last. The graphene sample prepared by this method is polycrystalline monolayer graphene with a large area of $10 \text{mm} \times 10 \text{mm}$.

For a comprehensive understanding of the optical characteristics of the graphene, an A-level HOPG (with the dimensions of $10 \text{mm}$ in length, $10 \text{mm}$ in width, and $2 \text{mm}$ in height) purchased from the Institute of Metal Research, Chinese Academy of Sciences, was used to perform a comparative study. The mosaic angle of the HOPG measured by XRD is 0.5° $\pm$ 0.1°, meaning that the HOPG can be approximately regarded as single-crystal graphite. For the sake of convenience, in this paper, the plane of the HOPG sample, from which the graphene can be exfoliated, is defined as c-plane (i.e., the cleavage plane), and the plane perpendicular to the c-plane is called s-plane (i.e., the side plane). Before measurement, the oxidation layer covering the surface of the c-plane has been exfoliated with a Scotch 810 tape. And the s-plane was also polished by an abrasive paper to decrease the surface roughness as much as possible.

As show in Fig. 1, several means, including OM, AFM, and micro-Raman spectrometer, were applied to comprehensively check the qualities of samples, such as the uniformity, the crystal quality, and the surface morphology. It can be seen from Fig. 1(a) that the uniform brightness of the OM picture indicates a well uniformity of the CVD mono-graphene, which can be also confirmed from the ratio (2D/G) $\sim$ 2, the typical ratio of the mono-graphene is 2–3) of the Raman peaks as shown in Fig. 1(f) [37,38]. There are only two intrinsic Raman peaks, i.e., 2D peak and G peak, and no obvious disorder-induced D peak corresponding to zone-edge mode exists in the Raman spectra, meaning that the CVD graphene has a good crystal quality [39]. As illustrated in Fig. 1(b) and (f), it can be observed from the OM picture and the Raman spectra that the c-plane of the HOPG shows a comparable surface uniformity and a higher crystal quality compared with the CVD mono-graphene. However, the s-plane of the HOPG has a much poorer surface condition as shown in Fig. 1(c) than the c-plane. What’s more, a significant D peak ($\sim$1335 cm$^{-1}$) appears in the Raman spectra of the s-plane, which implies that there are more disorders and defects in the s-plane of the HOPG. As further shown in Fig. 1(d, e) by the AFM test, the graphene and the c-plane of the HOPG exhibit the root-mean-square (RMS) roughness $R_q$ of 1.904 nm and 0.658 nm, respectively. Note that the measured $R_q$ of the graphene is larger than that of the HOPG, which is due to the significant surface roughness of the glass substrate and some PMMA residuals (i.e., the white spots in Fig. 1(d) on the graphene. Moreover, the graphene shows many wrinkles, formed due to the different thermal coefficients between the graphene and the Cu foil, which is another important reason for the larger surface roughness. As for the HOPG, the value of $R_q$ implies that the surface conditions of the c-plane of HOPG are acceptable. Although the c-plane has been processed, some local fluctuations on this plane
are inevitable as shown in the AFM picture due to imperfect peeling. Because of the significant waviness of the s-plane of the HOPG, it is difficult to perform AFM probing on the s-plane HOPG. From the above results and analysis, it is better to select the c-plane rather than the s-plane to perform the ellipsometric investigation on the HOPG.

3. Mueller matrix ellipsometry

3.1. Experimental setup

Ellipsometry is a technique to investigate the optical properties and the structure parameters of samples by detecting and analyzing the change in the polarization state of polarized light. Since the MME has advantages compared with the conventional SE, a commercial spectroscopic MME (ME-L ellipsometer, Wuhan Eoptics Technology Co., Wuhan, China) is employed to investigate the optical properties of the mono-graphene and the HOPG in this paper. Further information on the basic principles and instrumentation of the MME can be found in references [36,40]. The MME can measure the full Mueller matrix of the samples covering the energy range of 0.73–6.42 eV in a single measurement. Two measurement modes, named the transmission mode and the reflection mode, can be selected by rotating the two arms of the MME, and the incident angle can be set among the range of $45^\circ$–$90^\circ$. For anisotropic samples, the azimuths can be adjusted within the range of $0^\circ$–$360^\circ$ by rotating the sample stage of the MME. And the diameter of light spot on the sample can be as small as 200 $\mu$m by using a pair of focusing probes.

In this paper, the CVD mono-graphene and the HOPG were measured by the MME at the reflection measurement mode. And the incident angle was set at $65^\circ$ for the graphene and the c-plane of the HOPG, while an incident angle of $55^\circ$ was optimally selected when measuring the Mueller matrix of the s-plane of the HOPG to maximally present the optical anisotropy. In order to maximally reduce the influences of the surface fluctuations of the sample on the measurement results, the focusing probes are used in the experiments.

3.2. Ellipsometric analysis for graphene and HOPG

Since the ellipsometry is a model-based method, proper models must be constructed to describe the optical structures of the graphene and the HOPG before performing the ellipsometric analysis. Fig. 2(a) shows the optical model of the mono-graphene, which is a stack of four-layer films surrounded by the ambient air. The top layer of the stack is a water film with a nominal thickness of 0.7 nm to take consideration of the water adsorption on the surface of the graphene [25,28]. The primary layer of the sample is mono-graphene with a nominal thickness of 0.335 nm [41], which is the major object to be studied. Considering the surface roughness of the quartz glass, a Bruggeman EMA layer, containing 50% H$_2$O and 50% quartz glass, is inserted between the quartz glass and the graphene to describe the interfacial transition layer. As for the HOPG, it is simply regarded as bulk graphite with a surface roughness layer.

Graphene with honeycomb-like lattice structure belongs to the hexagonal crystal system. The symmetry elements of the graphene are six-fold rotation axis and six mirror planes, denoting that the graphene is an in-plane isotropic 2D material. The HOPG can be regarded as an orderly stack of countless layers of mono-graphene along the direction of the c-axis (i.e., the optical axis of the HOPG). Thus, both graphene and HOPG are uniaxial crystals, and their dielectric tensors can be written in a unified form.

Fig. 1. (a–c): OM pictures for the mono-graphene, the c-plane and the s-plane of the HOPG, respectively; (d, e) AFM pictures of the mono-graphene and the c-plane of the HOPG; (f) Raman spectra of the mono-graphene and the HOPG.
where, $e = e_0 + 1$, $N = n + ik$, $e_0$, $N_0$, $N_2$, $e_1$, $e_2$, $Q$ are the real part and imaginary part of the dielectric function, $n$ and $k$ are the refractive index and extinction coefficient, and the subscripts “$o$” and “$e$” refer to the ordinary parameters and the extraordinary parameters, respectively. The diagrams shown in Fig. 2(b) and (d) describe the relations between the instrument coordinate system and the dielectric functions of the sample under the measurement conditions as shown in Fig. 2(a) and (c). For the measurement of the c-plane of the HOPG, it is the same as the s-plane as shown in Fig. 2(a), the direction of $e_x$ is parallel to the z-axis of the instrument coordinate system as shown in Fig. 2(b). For measurement of the s-plane of the HOPG, it is the same conditions as the graphene plane. While measuring the s-plane, the optical axis lies in the x-o-y plane with an azimuth with respect to the z-axis.

In the ellipsometric analysis, the dielectric functions shown in Eq. (1) can be parameterized by S-poline or generalized oscillators. In the former method, the dielectric functions are described by splicing a number of B-spline curves, and it is a mathematical technique without any sense of physics. While the generalized oscillators can reflect some intrinsic characteristics of the band structure and reveal the physical mechanisms of the electron transitions to some extent. In this paper, the dielectric functions are firstly described by S-plines to fit the measured Mueller matrix spectra, and then modeled by combining several classical oscillators, including the Lorentz model, the Drude model, the Cauchy-Urbach model, and the Gaussian model. The ordinary dielectric function of the graphene and the HOPG is represented by the Lorentz and the Drude models, which are suitable to describe van Hove singularity in the ultraviolet band and energy absorption in infrared band of the graphene and the HOPG, respectively. The extraordinary dielectric function conforms to the Cauchy-Urbach model, which is suitable to approximate most of the dielectric responds of s electrons [42]. In addition, Gaussian models are selected to compensate the lack of strength of above oscillators in the visible region. Thus, the ordinary dielectric function is given by

$$
\varepsilon = \begin{bmatrix}
\varepsilon_0 & 0 & 0 \\
0 & \varepsilon_0 & 0 \\
0 & 0 & \varepsilon_e
\end{bmatrix} = \begin{bmatrix}
N_0^2 & 0 & 0 \\
0 & N_0^2 & 0 \\
0 & 0 & N_e^2
\end{bmatrix},
$$

where, $e = e_0 + 1$, $N = n + ik$, $e_0$, $N_0$, $N_2$, $e_1$, $e_2$, $Q$ are the real part and imaginary part of the dielectric function, $n$ and $k$ are the refractive index and extinction coefficient, and the subscripts “$o$” and “$e$” refer to the ordinary parameters and the extraordinary parameters, respectively. The diagrams shown in Fig. 2(b) and (d) describe the relations between the instrument coordinate system and the dielectric functions of the sample under the measurement conditions as shown in Fig. 2(a) and (c). For the measurement of the c-plane of the HOPG, it is the same as the s-plane as shown in Fig. 2(a), the direction of $e_x$ is parallel to the z-axis of the instrument coordinate system as shown in Fig. 2(b). For measurement of the s-plane of the HOPG, it is the same conditions as the graphene plane. While measuring the s-plane, the optical axis lies in the x-o-y plane with an azimuth with respect to the z-axis.

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$$
\varepsilon = \varepsilon_0 + \sum_{i=1}^{n} \varepsilon_{\text{Lorentz}}(f_i, E_{0i}, \Gamma_i, E) + \varepsilon_{\text{Drude}}(\rho, \tau; E),
$$

where, $\varepsilon_{\text{Lorentz}}$ and $\varepsilon_{\text{Drude}}$ are the Lorentz model and the Drude model. They can be written as

$$
\varepsilon_{\text{Lorentz}}(E) = \frac{f_i E_{0i}}{(E_{0i}^2 - E^2) + (\Gamma_i E)^2},
$$

$$
\varepsilon_{\text{Drude}}(E) = \frac{\rho^2}{\rho(\tau^2 E^4 + h^2 E^2)}(1 - \tau E^2 + ihE),
$$

where, $f$, $\Gamma$, $E_{0i}$, $\rho$ and $\tau$ represent oscillator strength, full width at half-maximum, center energy, resistivity, and scattering time, respectively. The complex refractive index can be solved from the dielectric functions according to the following equations

$$
n = \left\{ \frac{\varepsilon_1 + (\varepsilon_1^2 + e_2^2)^{1/2}}{2} \right\}^{1/2},
$$

$$
k = \left\{ \frac{-\varepsilon_1 + (\varepsilon_1^2 + e_2^2)^{1/2}}{2} \right\}^{1/2}.
$$

The refractive index and the extinction coefficient for the extraordinary direction are defined by the Cauchy-Urbach dispersion equations

$$
n_e(E) = A + BE^2 + CE^4,
$$

$$
k_e(E) = k_{\text{amp}} \exp [s(E - E_g)],
$$

where, $A$, $B$, and $C$ represent the analytical parameters of the Cauchy-Urbach dispersion equations, $E_g$ is the bandgap of materials, and $s$ is an amplification coefficient.

With the above established optical models and dielectric functions, the theoretical Mueller matrix spectrum of the graphene and the HOPG can be calculated by the transfer matrix method [43]. Then the dielectric functions can be determined by fitting the measured Mueller matrix spectra with the theoretical ones by a regressive iteration method. The fitting procedure is evaluated by the root mean square error (RMSE), which is defined by

$$
\text{RMSE} = \sqrt{\frac{1}{15Q - P} \sum_{q=1}^{Q} \sum_{i=1}^{4} \left( M_{ij}^M - M_{ij}^T \right)^2 \times 1000.}
$$

where, $Q$ is the total number of energy dispersion points, $P$ is the total number of fitting parameters in the optical model, $q$ is the q-th energy dispersion point from the total number $Q$, indices $i$ and $j$ show all the Mueller matrix elements except $M_{11}$ (normalized to $m_{11}$), $M_{ij}^M$ and $M_{ij}^T$ are the measured and theoretical Mueller matrix elements at the q-th energy point, respectively.

4. Results and discussions

The full Mueller matrix contains 16 elements, which provide abundant information about the optical properties and the geometric structures of samples. In ellipsometry, the properties of samples along the directions parallel to and perpendicular to the measured plane are usually defined as the in-plane and the out-of-plane properties, respectively. The in-plane anisotropy can be roughly evaluated from the two off-diagonal $2 \times 2$ blocks of the Mueller matrix, while the out-of-plane anisotropy is more sensitive to the two diagonal $2 \times 2$ blocks. Thus, the MME can comprehensively characterize the optical anisotropy of samples. In this work, the optical properties of the graphene, and those of the c-plane and the s-plane of the HOPG are investigated by the MME, and the results are shown in Figs. 3–7 and Table 1.
Since the optical axis lies in the s-plane as illustrated in Fig. 2(c, d), the Mueller matrix of the s-plane of the HOPG will mainly exhibit in-plane anisotropy, while that of the c-plane will mainly exhibit out-of-plane anisotropy. Figs. 3 and 4 illustrate the measured and the best fitting Mueller matrix spectra of the c-plane and the s-plane of the HOPG, respectively. It can be seen from Fig. 3 that the two off-diagonal $2 \times 2$ blocks in the Mueller matrix of the s-plane obviously deviate from zero, which indicates significant in-plane anisotropy in the s-plane. Although an ideal c-plane of the HOPG should not exhibit in-plane anisotropy, the off-diagonal elements in the measured Mueller matrix of the c-plane slightly deviate from zero as shown in Fig. 4. The in-plane anisotropy in the measured Mueller matrix of the c-plane may be introduced by a slight tilt between the optical axis of the HOPG and the z-axis of the instrument coordinate system due to imperfect sample alignment in the measurement. As shown in Fig. 4, when a tilt angle of about $2.6^\circ$ is taken into account, the theoretical Mueller matrix can perfectly fit the measured ones. The good agreement between the measured Mueller matrix spectra and the theoretically calculated ones demonstrates the validity of the proposed models for the HOPG and confirms the above theoretical predictions about the in-plane and the out-of-plane anisotropy. What’s more, by comparing the
results shown in Figs. 3 and 4, it can be observed that the fitness between the measured Mueller matrix spectra and the theoretical ones of the c-plane is much better than that of the s-plane, which can also be confirmed from the RMSEs shown in Table 1. This can be attributed to the better surface conditions of the c-plane, which will bring lesser errors in the measured Mueller matrix.

The optical constants corresponding to the best fitting Mueller matrix spectra of the HOPG are presented in Fig. 5. It can be seen that the ordinary optical constants are obviously larger than the extraordinary optical constants over most of the spectra. In addition, the optical constants of c-plane of the HOPG are higher than those of the s-plane especially in the visible and near-infrared regions. The poorer crystal quality and surface conditions as presented in Fig. 1 (c, f) make the Braggman EMA theory insufficient to describe the large-sized surface roughness (>λ/10) layer of the s-plane, which further results in underestimating the fraction of the air in the surface composite layer and pulls down the measured optical constants of the s-plane. As illustrated in Fig. 5 (b), the major absorption peak at about 4.96 eV in the extinction coefficient spectra of the HOPG corresponds to the interband transitions.

The ultra-thin thickness of the mono-graphene induces neglected variations in the ellipsometric information in the direction of the optical axis, which makes the ellipsometry is not sensitive enough to determine the extraordinary optical constants of the mono-graphene. Since the HOPG can be regarded as an orderly stack of the mono-graphene, the optical properties of the graphene are similar to those of the c-plane of the HOPG. Thus, in this paper, the extraordinary optical constants of the graphene adopt the measured results of the c-plane of the HOPG shown in Fig. 5. With the above assumptions, the measured and the best fitting Mueller matrix spectra of the CVD mono-graphene are presented in Fig. 6. It can be observed that the off-diagonal 2 x 2 blocks of Mueller matrix spectra slightly deviate from the measured ones especially in the high energy region, which can be attributed to the complex many-body effect and the depolarization effect in the graphene.

![Fig. 5. Optical constants of the HOPG: (a) refractive index n; (b) extinction coefficient k.](image-url)

![Fig. 6. Measured (blue circle) and best fitting (red line) Mueller matrix spectra of the mono-graphene.](image-url)
decrease the forming energy of excitons [44, 45]. In other words, reduced compared with its bulk counterpart HOPG, which further attraction between the electron and hole in mono-graphene is of the HOPG. This is because that the screening of the Coulomb

Table 1

<table>
<thead>
<tr>
<th>Oscillator</th>
<th>Parameter</th>
<th>CVD mono-graphene</th>
<th>c-plane of HOPG</th>
<th>s-plane of HOPG</th>
</tr>
</thead>
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<tr>
<td>Lorentz</td>
<td>$f$ (eV)</td>
<td>7.71 ± 0.645</td>
<td>11.63 ± 0.559</td>
<td>12.26 ± 0.918</td>
</tr>
<tr>
<td></td>
<td>$E_0$ (eV)</td>
<td>0.85 ± 0.043</td>
<td>1.07 ± 0.011</td>
<td>1.06 ± 0.072</td>
</tr>
<tr>
<td>Drude</td>
<td>$\mu$ ((\Omega) cm)</td>
<td>4.28 ± 10^{-4} ± 1.780 × 10^{-5}</td>
<td>6.09 × 10^{-4} ± 4.002 × 10^{-6}</td>
<td>1.17 × 10^{-3} ± 4.540 × 10^{-3}</td>
</tr>
<tr>
<td></td>
<td>$\tau$ (fs)</td>
<td>0.73 ± 0.038</td>
<td>0.37 ± 0.009</td>
<td>0.14 ± 0.157</td>
</tr>
<tr>
<td>Cauchy</td>
<td>$E_0$ (eV)</td>
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<td>0.00</td>
</tr>
<tr>
<td></td>
<td>$A$</td>
<td>1.42 ± 0.027</td>
<td>1.35 ± 0.040</td>
<td>6.56 × 10^{-1}</td>
</tr>
<tr>
<td></td>
<td>$B$</td>
<td>2.90 × 10^{-3}</td>
<td>6.56 × 10^{-3}</td>
<td>18.10</td>
</tr>
<tr>
<td></td>
<td>$C$</td>
<td>3.19 × 10^{-4}</td>
<td>3.19 × 10^{-4}</td>
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<tr>
<td>RMSE</td>
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<td>1.13</td>
<td>2.28</td>
<td>8.52</td>
</tr>
<tr>
<td>Roughness (nm)</td>
<td></td>
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</table>

Fig. 7. Ordinary optical constants of the mono-graphene: (a) refractive index $n_o$; (b) extinction coefficient $k_o$. The inset in (b) shows the band structure of the mono-graphene calculated by first principles.

The vital analytical parameters of dielectric functions as well as RMSEs corresponding to the best fitting results of the CVD mono-graphene and the HOPG as shown in Figs. 3–7 are summarized in Table 1. For the CVD mono-graphene, the positions of the absorption peaks are mainly determined by the center energy of the two Lorentz oscillators (i.e., $E_{01} = 4.60$ eV and $E_{02} = 6.25$ eV). Since the Mueller matrix measurement precision of the MME used in this paper is about 0.001, the RMSE of an ideal fitting procedure should be about 1 [40]. The RMSE will be influenced by many factors, such as the complexity of the Mueller matrix spectral curves, the surface conditions of samples, and the signal-to-noise ratio of the measurement. In general, the fitting results are acceptable if the RMSE is less than 10 for the analysis of most cases. It can be seen from Table 1 that the RMSE of the CVD mono-graphene is about 1, which indicates that the established models are effective to describe the mono-graphene and the fitting results are reliable. As for the HOPG, the RMSE are much larger due to the poor surface conditions and the more complex Mueller matrix caused by the in-plane

\footnote{For interpretation of color in Fig. 7, the reader is referred to the web version of this article.}
5. Conclusions

In summary, the optical properties of the CVD mono-graphene and the HOPG over a broad energy region from 0.73 eV to 6.42 eV were investigated by spectroscopic MME. Large-area polycrystalline CVD mono-graphene on quartz glass substrate and a purchased A-level HOPG were prepared and processed, and their qualities were comprehensively checked by OM, micro-Raman spectrometer, and AFM. In the ellipsometric analysis, a multilayer stacking model was constructed to more accurately describe the optical structure of the CVD mono-graphene, in which the roughness of the glass substrate and the water adsorption on the top of the graphene were considered. Moreover, a uniaxial anisotropic dielectric model was introduced to embody optical properties of the mono-graphene and the HOPG. With the established models, the basic optical constants including the refractive index and the extinction coefficient of the mono-graphene and the HOPG were extracted from the measured Mueller matrix spectra by a point-by-point method and a nonlinear least-square fitting procedure, respectively. Benefiting from the powerful capability of the broad-band MME and the proper models, some intrinsic characteristics rarely reported before were observed in the optical constant spectra of the HOPG and the graphene and their corresponding physical mechanisms were revealed. Two significant absorption peaks at 4.75 eV and 6.31 eV were observed in the extinction coefficient spectra of the mono-graphene, and a major absorption peak at 4.96 eV was observed in the ordinary extinction coefficient spectra of the HOPG. The peaks at 4.75 eV and 6.31 eV correspond to the von-Hove singularity (i.e., the $\pi$-to-$\pi^*$ exciton transition) near the M point and the $\sigma$-to-$\sigma^*$ exciton transition near the $\Gamma$ point of the Brillouin zone, while the peak at 4.96 eV is mainly formed by the $\pi$-to-$\pi^*$ interband transition. The high agreement with the published literatures and the theoretical calculations demonstrates the reliability of our results. It can be expected that the MME-based method proposed in this paper will provide an effective and powerful approach to investigate the optical properties of not only the graphene but also other 2D materials especially those with emerging features, such as optical anisotropy, puckered structures, and heterogeneous structures.

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