Research article

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Optical characterizations of two-dimensional materials using nonlinear optical microscopies of CARS, TPEF, and SHG

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Abstract: In this paper, we employ the nonlinear optical microscopies of coherent anti-Stokes Raman scattering spectroscopy, two-photon excitation fluorescence, and second harmonic generation to characterize the properties of two-dimensional (2D) materials. With these nonlinear optical microscopy methods, we can not only clearly observe the surface topography of 2D materials but also reveal the quality of 2D materials. These nonlinear optical microscopies offer great potential for characterization of the properties of 2D materials.

Keywords: nonlinear microscopy; multiphoton processes; coherent anti-Stokes Raman scattering; TPEF; SHG.

1 Introduction

Two-dimensional (2D) materials are ultrathin intrinsically layered nanostructure materials. The characterization methods for 2D materials include atomic force microscopy [1], X-ray powder diffraction [2], Raman spectroscopy [3], ultrafast transient absorption spectroscopy [4], scanning tunneling spectroscopy and microscopy [5, 6], angular resolved photoemission [7], low energy

electron diffraction [8], infrared spectroscopy [9, 10], tip enchantment Raman spectrum [11, 12], X-ray photoelectron spectroscopy [13, 14], transmission electron microscopy (TEM) [15], and scanning electron microscopy (SEM) [16]. Although these methods can well characterize the surface topography as well as the quality of 2D materials, SEM and TEM may damage the surface of 2D materials via interaction with electron beams having high kinetic energy. Because of the deposition of carbonaceous material on the sample surface, contamination can be induced by the electron beam in SEM imaging. This contamination always occurs after TEM and SEM characterization and is strongly dependent on the electron beam exposure and accelerating voltage.

Coherent anti-Stokes Raman scattering spectroscopy (CARS) is a form of spectral technology that is used primarily in physics, chemistry, and other related fields [17–19]. CARS is a very sensitive form of molecular Raman spectroscopy. The image resolution of CARS is significantly better than that of traditional molecular Raman microscopy; furthermore, the distribution of molecular bonds can be very clearly measured using Raman analysis.

Two-photon excitation fluorescence (TPEF) microscopy is an important technique of fluorescence imaging that allows imaging of a sample to approximately 1 mm in depth direction [20–24]. TPEF is distinguished from traditional fluorescence microscopy (where the emission wavelength is larger than the excitation wavelength) because the wavelength of the resulting emitted light is shorter than the wavelengths of two exciting photons; as a result, the background signals are significantly suppressed because of the multiphoton absorption.

Second harmonic generation (SHG) is a second-order nonlinear optical process in which photons with the same energy interact with a nonlinear material; every two incident photons can be effectively “combined” to generate a new photon with twice the photon energy (and therefore half the wavelength) of the initial photons [25–29]. The SHG is only allowed in materials without inversion symmetry because of the even-order nonlinear optical effect.

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Based on the nonlinear optical SHG, second-harmonic imaging microscopy is widely used in spectral analysis.

In this paper, we provide new invasive nonlinear optical microscopies of CARS, TPEF, and SHG to optically characterize graphene with very high nonlinear optical resolution. Using these nonlinear optical microscopies, not only can the surface topography be clearly observed but also the quality of 2D material can be well characterized. The CARS technique demonstrates the unique advantages in the application of the characterization of 2D materials.

2 Experimental section

(a) The experimental setup and its schematic illustrations are shown in Figure 1A,B, respectively. A femtosecond mode-locked Ti:Sapphire laser (80 fs, wavelength 800 nm, pulse width at 80 MHz repetition rate) is employed in this CARS system (Mai Tai DeepSee, Spetra-Physics, Santa Clara, USA). The femtosecond beam is separated into two beams by a beam splitter. One beam functions as the pump and probe beam,

which passes through the time-delay device, and the other beam is used to pump a photonic crystal fiber to produce white light as the Stokes light beam. The two beams are combined at the dichroic mirror, and then the combined beam is focused onto the sample using a multiphoton laser-scan microscope (FV1200, Olympus, Tokyo, Japan) equipped with an objective (UplanSApo 40×, NA0.95, Olympus, Tokyo, Japan). The average power of 75 mW is used for the pump and the probe beam, and an average power of 23 mW is used for the Stokes at the sample. The forward CARS, bright field, SHG, and epi CARS signals are collected by photomultipliers with the appropriate bandpass filters.

(b) Graphene was synthesized on 20- μm -thick unpolished Cu foils (Alfa Co.). The Cu foils were immersed in acetone, ethanol, and deionized water for 15 min in each solvent at room temperature. Each Cu foil was then placed into a chemical vapor deposition (CVD) quartz tube with gases flowing (100 sccm H_2 and Ar 900 sccm), and the temperature of the CVD chamber was raised from room temperature to 400°C in 40 min to remove the oxide layer of the Cu foils. Next, the Cu foil sample was exposed to gas flows of 5 sccm H_2 and

Figure 1: Home-made instrument of nonlinear optical microscopy. (A) The experiment setup. (B) Schematic illustration.

20 sccm CH_4 at a temperature of 1040°C for 5 min to grow graphene on the Cu foil. At the end of the process, the sample was cooled down to room temperature in the Ar and H_2 environment. After cooling, the sample was removed from the CVD chamber and then immersed in FeCl (0.1 M) to remove the Cu foil. Next,

the graphene was transferred to other substrate in deionized water and then dried at room temperature.

- (c) The monolayer graphene was purchased from the Six Carbon Tech. (Shenzhen, P.R. China). The graphene on the polished copper film was transferred onto quartz in FeCl solution with polymethyl methacrylate (PMMA).

Figure 2: (A) The Raman spectrum of graphene grown on unpolished Cu foils. (B) Raman spectrum of monolayer graphene.

Figure 3: (A) The CARS. (B) The TPEF+SHG. (C) SHG image of graphene at 1360 cm^{-1} .

Figure 4: (A) Bright field of graphene. (B) CARS image of graphene. (C) TPEF+SHG image of graphene, at Raman mode 1560 cm^{-1} .

3 Results and discussion

Figure 2A shows the Raman spectroscopy results of graphene grown on an unpolished copper film; the results

demonstrate that the graphene is in the form of multiple single layers because $I_{2D}/I_G \approx 1$ in Figure 2A. A strong Raman peak at 1331 cm^{-1} is observed, indicating a defect of graphene. In addition, we measured the Raman spectrum of

Figure 5: (A) Bright field image of graphene. (B) CARS image of graphene. (C) TPEF image of graphene. (D) SHG image of graphene. (E) The merged image of CARS + TPEF + SHG at Raman mode 1560 cm^{-1} .

graphene grown on a polished copper film – see Figure 2B; the results revealed that it is a single layer by comparing the Raman intensity of G and 2D peaks, where $I_{2D}/I_G \approx 2.5$.

Figure 3 shows the CARS, TPEF, and SHG images of multilayer graphene (see Raman spectrum in Figure 2) grown on an unpolished copper film that has a Raman peak at 1331 cm^{-1} ; the graphene was directly transferred into FeCl solution without PMMA. The figure reveals that not only is the surface topography clearly observed, but the quality of graphene grown on the unpolished copper film is also revealed – see CARS image in Figure 3A. The wrinkles and stripes are well observed, reflecting the characteristics of graphene grown on an unpolished copper film. Even after the graphene is transferred to a mica substrate, the characteristics of the unpolished copper

film can still be clearly seen in the stretched-out sample. Figure 3B shows the TPEF image, revealing strong fluorescence caused by the defects of graphene. Note that the measured region of TPEF ranges from 400 to 480 nm; as a result, the SHG signal may also be in the TPEF. To check this possibility, we measured the SHG image. Figure 3C is the SHG image of graphene grown on the unpolished copper film, which also exhibits the wrinkled surface topography *in situ*; obviously, the CARS image is better than that of the SHG. Although both images are nonlinear optical technologies, the vibration resolution in CARS is one of its unique advantages.

Moreover, we obtained the CARS at 1584 cm^{-1} along with TPEF + SHG images. Figure 4A shows the bright field image of graphene grown on the unpolished copper film,

Figure 6: (A) Bright field of monolayer graphene. (B) CARS image of graphene. (C) TPEF + SHG image of graphene. (D) The merged image of bright field + CARS + TPEF + SHG at Raman mode 1560 cm^{-1} .

and Figure 4B shows the *in situ* CARS image of graphene at 1584 cm^{-1} , which clearly demonstrates the surface topography of graphene, including the wrinkles and strips as well as the layers. Figure 4C shows the TPEF + SHG image measured in the region from 400 to 480 nm, which reveals the surface topography of graphene; however, the wrinkles and strips of graphene are not as clear as those in the CARS image shown in Figure 4B.

To obtain the TPEF image without SHG, we also obtained TPEF images in the region from 495 to 540 nm. Figure 5A shows a bright field image of multilayer graphene, and Figure 5B shows the CARS image, from which we can clearly observe both the topography and the quality of graphene. The TPEF image in the region from 495 to 540 nm is seen in Figure 5C, where the SHG signal is excluded. The SHG image seen in Figure 5D, reveals that

the TPEF and SHG images are almost of the same signal quality. The merged image of CARS, TPEF, and SHG is seen in Figure 5E, which can clearly show the relationship between them.

In centrosymmetric graphene, SHG is allowed when the photon momentum can be efficiently transferred to the electron system [30]. The perturbation of the Dirac cone occurs when a multilayer is grown epitaxially, resulting in the opening of the band gap. In the electronic spectrum of graphene, the gap indicates broken inversion symmetry, which promises to provide an enhanced second-order response. In multilayer graphene, the fluorescence can be clearly observed; this result provides direct evidence that photon momentum transfer to the electron system occurs. In the multilayer graphene, the SHG is also observed [31]. The large defect of graphene (D peak of Raman mode at

Figure 7: (A) Bright field of monolayer graphene. (B) CARS image of graphene. (C) TPEF + SHG image of graphene. (D) The merged image of bright field + CARS + TPEF + SHG at Raman mode 1560 cm^{-1} .

1331 cm^{-1} in Figure 2) and the zigzag edge of graphene can further increase the fluorescence intensity of graphene, thereby enhancing the signal of SHG.

We also measured the CARS of single-layer graphene (see Raman spectrum in Figure 2B) grown on polished copper film and then transferred onto quartz in FeCl solution with PMMA. In Figure 2, the G peaks of graphene are clearly observed; thus, we first study the CARS and TPEF at this Raman mode. Figure 6A shows the bright field image of single-layer graphene; Figure 6B shows the CARS image of monolayer graphene, which clearly demonstrates the surface topography. On comparing Figure 6B with Figures 3A and 4B, the quality of the single-layer graphene is found to be much better, with the wrinkles and strips in Figures 3A and 4B which are not observed in Figure 6B. Furthermore, we also studied the TPEF + SHG image – see

Figure 6C – where both the TPEF signal and the SHG signal are included because the detection range is from 400 to 480 nm. We can see that the TPEF + SHG image of single-layer graphene is significantly weaker than the CARS image. The weak TPEF + SHG signal also reveals the high quality of single-layer graphene, where the centrosymmetry of single-layer graphene can hardly be broken down. The merged image of bright field, CARS, TPEF + SHG is seen in Figure 6D. Because the TPEF of graphene reveals the defect of graphene, the weaker the TPEF, the smaller the defect of graphene. Because of the high centrosymmetry, inversion symmetry is hardly broken down; thus, the TPEF + SHG signal is very weak (see Figure 6D).

For a better observation of the CARS and TPEF + SHG, we study the images with smaller size – see Figure 7. Figure 7A shows the bright field of single-layer graphene.

Figure 8: (A) Bright field of monolayer graphene. (B) CARS image of graphene. (C) TPEF + SHG image of graphene. (D) The merged image of bright field + CARS + TPEF + SHG at Raman mode 1360 cm^{-1} .

Figure 9: (A) Bright field of monolayer graphene. (B) CARS image of graphene. (C) TPEF + SHG image of graphene. (D) Merged image of bright field + CARS + TPEF + SHG at Raman mode 1360 cm^{-1} .

It is found that the signal of the CARS image in Figure 7B is significantly stronger than the signal of the TPEF + SHG image in Figure 7C, where the detection range is from 400 to 480 nm. By direct comparison between these figures in Figure 7D, we see that the TPEF + SHG signal is vanishingly small and can be almost ignored, which strongly supports the above conclusions.

In Figure 2, the D peak of graphene is too weak to be observed for single-layer graphene when using normal Raman spectroscopy, i.e. the defect of single-layer graphene is very small. To explore the advantages of CARS in the characterization of 2D materials, we also measured the CARS image of monolayer graphene at 1331 cm^{-1} . Figure 8A shows the bright field image of the single-layer graphene. In Figure 8B, it clearly demonstrates that the CARS image is also of high quality and with very weak

TPEF + SHG measured in the range from 400 to 480 nm in Figure 8C. Thus, the CARS resolution is much better than that of the traditional Raman spectroscopy in Figure 2. Figure 8D is the merged image of bright field, CARS and TPEF + SHG, which directly reveals the ratio of signals of the CARS and TPEF images. To provide better resolution of the CARS image, the CARS image and the TPEF + SHG image with smaller scale bar ($10\text{ }\mu\text{m}$) are also shown (see Figure 9).

4 Conclusion

We performed nonlinear optical microscopies of CARS, TPEF, and SHG to characterize the properties of 2D

materials. With these methods of nonlinear optical technology, not only can the surface topography be clearly seen but also the quality of 2D material can be well characterized.

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