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A tunable single-monochromator Raman system based on the supercontinuum laser and tunable filters for resonant Raman profile measurements

X.-L. Liu,[1,2] H.-N. Liu,[1] and P.-H. Tan[1,2]
[1]*State Key Laboratory of Superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China*
[2]*College of Materials Science and Opto-Electronic Technology, University of Chinese Academy of Sciences, Beijing 100049, China*

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Resonant Raman spectroscopy requires that the wavelength of the laser used is close to that of an electronic transition. A tunable laser source and a triple spectrometer are usually necessary for resonant Raman profile measurements. However, such a system is complex with low signal throughput, which limits its wide application by scientific community. Here, a tunable micro-Raman spectroscopy system based on the supercontinuum laser, transmission grating, tunable filters, and single-stage spectrometer is introduced to measure the resonant Raman profile. The supercontinuum laser in combination with transmission grating makes a tunable excitation source with a bandwidth of sub-nanometer. Such a system exhibits continuous excitation tunability and high signal throughput. Its good performance and flexible tunability are verified by resonant Raman profile measurement of twisted bilayer graphene, which demonstrates its potential application prospect for resonant Raman spectroscopy. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4999451]

I. INTRODUCTION

Raman spectroscopy is an effective and non-destructive technique to probe electronic properties and lattice vibrations and has been widely used in the research on two-dimensional materials (2DMs).[1] It is also one of the most popular tools for structural characterization of carbon materials.[2,3] When the excitation energy is chosen to match or be close to an optical transition bandgap of the material, the Raman intensity can be enhanced by orders of 2–6, which is the so-called resonant Raman spectroscopy. Resonant Raman profile measurement exhibits the evolution of the Raman intensity as a function of the excitation energy, which can provide information on transition energies, exciton-phonon coupling, spin orbit coupling, and lifetime of the excitonic states.[4–7]

Resonant Raman profile measurement was usually performed by a triple-stage Raman spectrometer. By using the double subtractive technique, it is possible to realize Raman measurements without any Raman filters. Therefore, any continuous-tunable excitation lasers, such as Ti:sapphire and dye lasers, can be utilized by the triple-stage Raman spectrometer for the resonant Raman profile measurement.[8] However, such a system is complicated with low signal throughput, which limits its wide application by scientific community. The signal throughput of the modern single-stage Raman system is fairly high by using Raman filters to block the Rayleigh line. The supercontinuum laser has been developed to be broad as a lamp and bright as a laser. They can deliver high brightness and diffraction limited light with small beam divergence, which can be served as the excitation source for Raman spectroscopy if its output linewidth can be filtered narrowly down to sub-nanometer. It is an essential issue whether and how one can introduce a tunable Raman system based on the above two components for the resonant Raman profile measurement.

To satisfy the requirements for the Raman measurement, the supercontinuum laser must be filtered as monochromatic as possible to prevent stray lights overlaying Raman signals. In this work, we introduce a tunable micro-Raman system to perform resonant Raman profile measurements. Transmission grating and tunable bandpass filters are used to filter out the tunable monochromatic light from the supercontinuum laser. The excitation source and tunable longpass (TLP) filter are coupled into a single-stage spectrometer to form a tunable Raman system with efficient stray light filtering down to 200 cm^{-1}. It can offer continuously tunable excitation with experimental full width at half maximum (FWHM) as narrow as sub-nanometer. The TPL can provide a broad transmission band covering Raman signal up to 2000 cm^{-1} with high signal transmission of above 90%. The system performance is evaluated on a twisted bilayer graphene to obtain its G mode resonant Raman profile under tunable excitation wavelength between 550 nm and 700 nm. A good agreement is achieved between the present and pervious results,[5] which suggests its promising applications in resonance Raman researches.

II. INSTRUMENTATION AND PERFORMANCE

A Raman system mainly consists of excitation lasers, signal collection optics, and a spectrometer. In a commercial filter-based Raman system, filters are utilized to reflect the laser beam into the microscope objective and to block the Rayleigh line and transmit the scattered Raman signal to the spectrometer for the measurement. The longpass edge filters are most used Raman filters to probe the Stokes components of Raman signal because of their ultra-steep cut-off edge in transmission and long lifetime. The edge wavelength would blue shift with

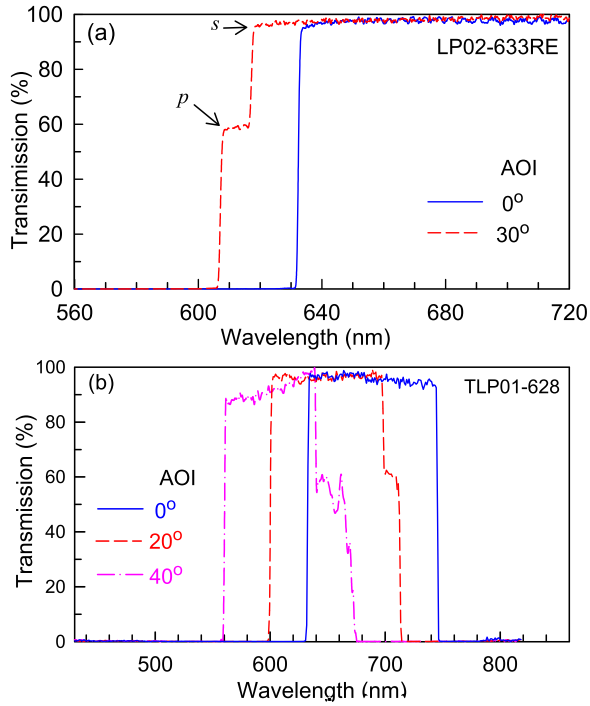

FIG. 1. (a) Transmission spectra of a longpass edge filter (LP02-633RE, Semrock) using an un-polarized light source when AOI = 0° and 30°. (b) Transmission spectra of a tunable longpass filter (TLP01-628, Semrock) using an un-polarized light source when AOI = 0°, 20° and 40°.

increasing the angle between the incident light and the normal of filters, which is often referred as the angle of incidence (AOI). In principle, one can tune the cut-off edge wavelength by changing AOI. However, as AOI increases from normal incidence, the filter edge shifts toward to shorter wavelengths and the edges associated with *s*- and *p*-polarized light shift by different amounts, which makes it inappropriate for the resonant Raman profile measurement. For example, Fig. 1(a) shows the transmission spectra of a ultrasteep longpass edge filter (LP02-633RE, Semrock) with two AOI, where AOI = 0° indicates the normal incidence. A tungsten halogen lamp is used to measure the transmission spectra of all the optical filters in this work. When AOI = 30°, its cut-off wavelength blue shifts about 20 nm, however, *s*- and *p*-polarized components exhibit a splitting of 7.0 nm, which corresponds to 180 cm^{-1} at 620 nm. The cut-off edge shift of the *p*-polarized component is larger than the *s*-polarized one. This indicates that such types of edge filters are not suitable for tunable excitation in the Raman measurement.

Recently, Semrock has developed a kind of TLP filter. By using advanced proprietary design techniques, this type of filters is insensitive to polarization from 0° to 60° AOI, allowing angle-tuning over a wide range without degrading edge steepness or high transmission. It offers excellent out-of-band blocking and a tuning range of at least 12% of the cut-off edge wavelength at normal incidence over the full range of AOI from 0° to 60°. Figure 1(b) presents the transmission spectra of such a filter (VersaChrome, TLP01-628, Semrock) at various AOI. The measurement shows that it can provide deep out-of-band blocking (OD > 6) and high transmission of above 90% over the full range of 0°–60° AOI, and the tunable edge wavelength is as wide as 60-70 nm. With only several pieces of those filters, the tunable edge wavelength can cover from 400 nm to 1100 nm, which is enough for most measurements of the resonant Raman profile.

Gratings are widely used to remove stray lines of lasers and Raman signals. Because transmission gratings have the output separated from the input, they are much easier to be aligned in the optical path. In this work, we try to isolate monochromatic light from the supercontinuum lasers using transmission gratings.

By combining the above transmission gratings and TLP filters with the supercontinuum laser and single-stage spectrometer, it is possible to realize resonant Raman profile measurements. Figure 2(a) shows the configuration of the tunable Raman system for such purpose. The system consists of the following components: a broadband excitation source, a super cold filter, a broadband bandpass filter, a transmission grating, a beam splitter, a microscope, a TLP filter, a single-stage spectrometer, and alignment optics, such as mirrors (M1, M2, M3, and M4). The broadband excitation source is provided by a supercontinuum laser (NKT EXW-12). This laser has a broadband and un-polarized output covering 400-2400 nm region, which guarantees a continuously tunable excitation range.

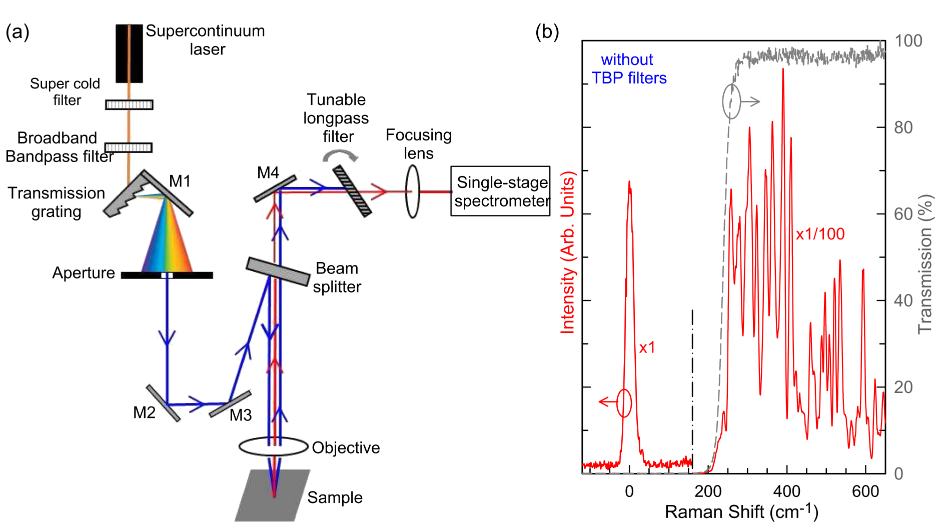

FIG. 2. (a) Schematic diagram of a tunable Raman system without using tunable bandpass filters. M1, M2, M3, and M4 are the mirrors to align the optical path. (b) Raman spectrum (red solid line) of a Si wafer excited at 620 nm filtered by transmission grating from a supercontinuum laser (NKT EXW-12). The stray lines are weaken by 100 times for clarity. Transmission spectrum (gray dashed line) of a tunable longpass filter (TLP01-628, Semrock) at a cut-off wavenumber of 200 cm^{-1} relative to 620 nm.

The pulse repetition rate of the supercontinuum laser is 78 MHz, with a pulse width of about 50 ps in the visible region. This pulse width corresponds to a spectral linewidth of 0.03 nm or 2.0 cm^{-1} at 400 nm. If the bandpass filter is as good as enough, the supercontinuum laser can be used as a laser excitation for Raman spectroscopy. The near-infrared light source of the laser above 1100 nm is filtered by a super cold filter (YSC1100, Asahi Spectra) placed at the fiber export of the laser. A broadband bandpass filter is inserted in the laser path to allow 90-200 nm of transmission bandwidth depending on its center wavelength and to provide extended out-of-band blocking between 300 and 1200 nm. We select VIS-1379-911 (Ibsen Photonics) as the transmission grating, which covers a wavelength range of 400-800 nm with grating resolution of 1379 lines/mm. A mirror (M1) is mounted on the same manually rotatable stage of transmission grating. By changing the AOI of transmission grating and M1, the dispersed monochromatic light is selected by the aperture after the transmission grating and is further used to excite the Raman signal of a Si wafer. A beam splitter (50% transmission and 50% reflection) is used to reflect the monochromatic laser to a 100× objective lens (numerical aperture = 0.90) of the microscope to excite the Raman signal from the sample and to transmit the Rayleigh and Raman signals to one or two TLP filters. The TLP filters provide the blocking of the Rayleigh signal and transmission of the Rayleigh signal, which are mounted on a manually rotatable stage and placed in the scattering light path after the beam splitter. In the visible region, the average laser power of the monochromatic light from the supercontinuum laser after the aperture is around 1.0 mW, depending on specific wavelength. The average laser power reaching the sample in our system is around 100–200 μW, which is sufficiently enough for the characterization of low-dimensional materials. The Raman signal after the TLP filters are focused by a lens into the single-stage spectrometer for the measurement. The spectrometer is equipped with a 600 lines/mm grating and a CCD detector. The focal length of the spectrometer is 800 mm.

We demonstrate the performance of rejection efficiency of Rayleigh and stray lines of this system by measuring Raman spectrum from a Si wafer, which exhibits a characteristic peak at 520.7 cm^{-1}. The TLP01-628 filters are used to block the Rayleigh line and transmit Raman signal to the spectrometer for the Raman measurement. As shown in Fig. 2(b), its Rayleigh line can be narrowed down to 15 cm^{-1}, suggesting the good dispersion of a broad laser source from the supercontinuum laser by the transmission grating. It is possible to further improve the line width by smaller aperture and higher density grating. Although the Rayleigh line can be narrowed down to 15 cm^{-1}, there are intense stray lines in the spectral region, whose intensity is 100 times stronger than the leaked Rayleigh line. This intense stray lines overlap the Si mode at 520.7 cm^{-1}. The stray lines are absolutely from the excitation source, and further purification of monochromatic excitation is necessary.

A bandpass filter is widely used to purify the laser excitation with a specific wavelength from plasma lines. Such a traditional bandpass filter is defined by its two edges, and by the blocking range that provides out of band. Each edge is a transition from deep blocking to high transmission—a long-wave pass (LWP) edge and a short-wave pass (SWP) edge. The wavelengths at which these two edges define the passband, which is then matched with the laser wavelength of interest. Such standard bandpass filters would exhibit distortion and polarization splitting as the AOI increases, similar to the case of standard edge filters. Therefore, it is not applicable to a tunable excitation source. Recently, Semrock has also developed a kind of tunable bandpass (TBP) filters. Such TBP filters are designed to maintain high transmission, steep edges and polarization insensitivity from 0° to 60°, allowing the user to angularly tune the filter according to specific needs. By combining the LWP edge of one TBP filter with the SWP edge of another TBP filter, one can create the bandpass shape at any wavelength of interest within the tunable range. Figure 3(a) shows the transmission spectra of two pieces of TBP01-628/14 (VersaChrome, Semrock) with different AOI. Two TBP01-628/14 positioned in the excitation beam with different AOI can generate different monochromatic excitation sources from the supercontinuum laser. Indeed, Fig. 3(b) shows the intersected transmission spectrum of two TBP01-628/14 with different but finely adjusted AOI, indicating that the line width filtered by the two TBP sets can reach down to as narrow as 1 nm. Thus, it is one of the best choices to purify the tunable excitation source by changing the AOI of two TBP filters.

As demonstrated in Fig. 4(a), two TBP filters are placed in tandem after the transmission grating in the tunable Raman

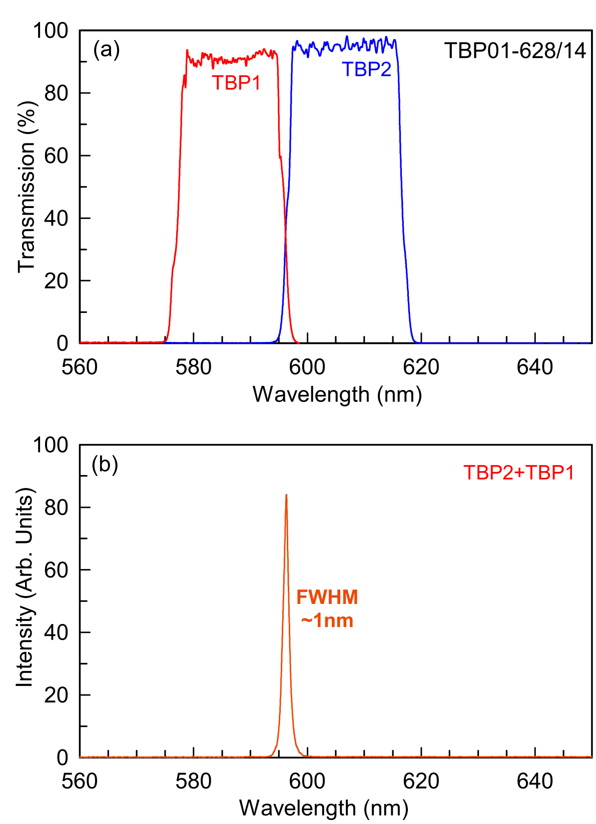

FIG. 3. (a) Transmission spectrum of two tunable bandpass filters TBP01-628/14 (VersaChrome, Semrock) with different AOI. (b) Intersected transmission spectrum of two TBP01-628/14 with different but finely adjusted AOI, generating a passed band with FWHM of ~1 nm.

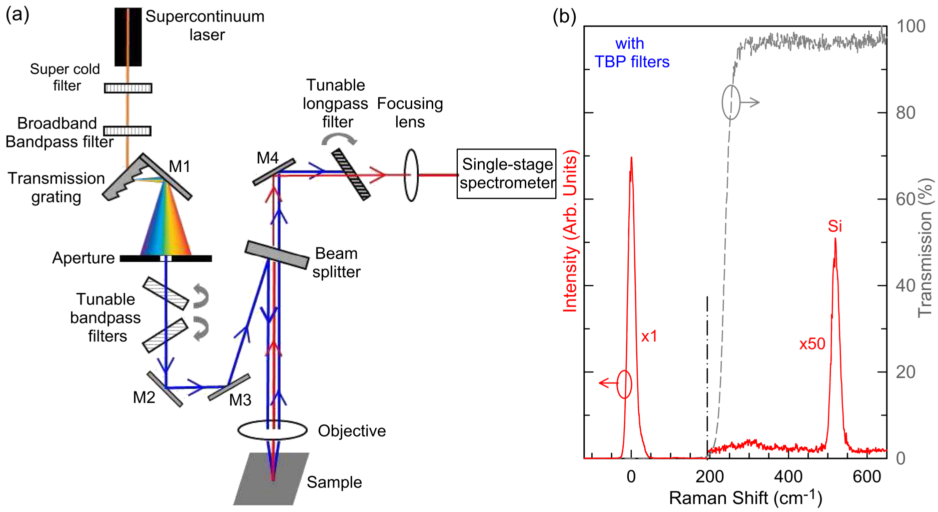

FIG. 4. (a) Schematic diagram of a tunable Raman system including tunable bandpass filters. M1, M2, M3, and M4 are the mirrors to align the optical path. (b) Raman spectrum (red solid line) of a Si wafer excited at 620 nm. Transmission spectrum (gray dashed line) of a tunable longpass filter (TLP01-628, Semrock) at cut-off wavenumber of 200 cm^{-1} relative to 620 nm.

system to purify the monochromatic excitation source from the supercontinuum laser. When the monochromatic laser is tuned to 620 nm by the transmission grating, the monochromatic laser goes through the two TBP filters mounted on respective manually rotatable stage to obtain purified monochromatic light. As shown in Fig. 4(b), after using two TBP filters, the stray lines can be well suppressed so that one can obtain clean background down to 200 cm^{-1}. The Raman signal from a Si wafer can be well resolved in this tunable Raman system, whose intensity is only 50 times weaker than the leaked Rayleigh signal. The measured Si signal can be used as a standard for frequency calibration and intensity normalization, as the resonant Raman profile of Si is already known.[9]

As discussed above, the tunability of TBP and TLP filters makes the tunable Raman system compact and easy for operation. By changing the AOI of both the transmission grating and two TBP filters, the monochromatic laser can be tuned in wavelength and purified. By changing the AOI of the TLP filters, the Raman spectra excited by the purified monochromatic laser can be measured accordingly. The tuning wavelength range of the tunable Raman system demonstrated in Fig. 4(a) is determined by the working wavelengths of the broadband bandpass filter, transmission grating, TBP filters and TLP filters. The broadband bandpass filter of FF01-632/148 offers a tunable laser source within 550-700 nm. In this range, two sets of Semrock TBP filters (TBP01-620 and TBP01-628, covering 550 nm–625 nm; TBP01-700 and TBP01-704, covering 625 nm–700 nm) can be used to purify the monochromatic source filtered by the transmission grating of VIS-1379-911. Two Semrock TLP filters of TLP01-628 (covering 550 nm–628 nm) and TLP01-704 (covering 628 nm–704 nm) can be used to block the Rayleigh signal corresponding to the tunable monochromatic laser. With these TBP and TLP filters, the resonant Raman profile can be measured in the range of 550-700 nm.

To evaluate the performance and tunability of the tunable Raman system, twisted bilayer graphene (t2LG) is used as a testing sample. t2LG has been well studied by Raman spectroscopy[5,10,11] and its resonant profile of the G mode had been measured by several discrete laser wavelengths.[5] Figure 5(a) exhibits the Rayleigh line at 620 nm with a FWHM of ~15 cm^{-1} (about 0.6 nm at 620 nm). The G mode of t2LG exhibits significantly resonant behaviors,[5] and its intensity I(G) is 45 times stronger than that of 1LG, as shown in Fig. 5(b). By tuning the excitation source to other wavelengths, the resonant Raman profile of the G mode can be obtained for t2LG in the range of 550-700 nm. I(G) of 1LG is used as a reference to normalize that of t2LG. This normalization can eliminate the discrepancy in efficiency of diffraction grating and CCD at different wavelengths. Figure 5(c) shows the normalized

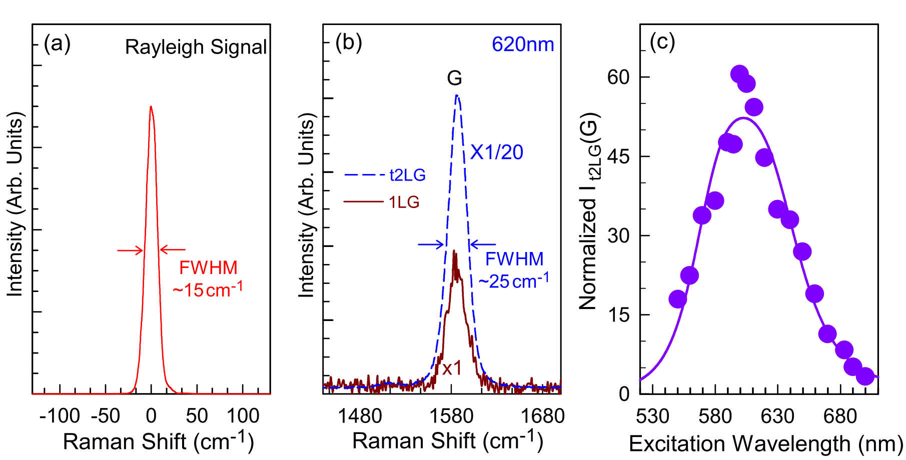

FIG. 5. (a) Rayleigh signal from a Si wafer excited by 620 nm. (b) Raman signal of 1LG (solid) and t2LG (dashed) excited by 620 nm. (c) Resonant Raman profile of the G mode (solid circles) of t2LG and the corresponding fitting result (solid line).

resonant profile (solid circles) of I(G) for t2LG. It can be well fitted by the theoretical one in which only one van Hove singularity of joint density of states is considered, as indicated by the previous work.[5] The typical FWHM of the G mode, FWHM(G), in 1LG and t2LG is about 12 cm^{-1}. The broad FWHM(G) of ~25 cm^{-1} measured here originates from the broadening of the excitation line. However, such broadening has little influence on the measured resonance profile of t2LG.

It should be noted that there is a working wavelength range for any continuous-tunable laser. Therefore, to extend the measurement wavelength range of resonance Raman profile by a triple-stage Raman spectrometer, one must purchase the corresponding continuous-tunable laser. It is a challenge to cover the excitation range from 400 nm to 1000 nm by several continuous-tunable lasers. In this work, we demonstrate an operation region of 550-700 nm as addressed above because the G mode intensity of this twisted bilayer graphene sample is resonantly enhanced in this excitation range. However, it is easy to extend the excitation laser to other wavelength ranges only by purchasing additional transmission grating, TBP filters and TLP filters. For example, if one needs a monochromatic light above 780 nm, one can use transmission grating of SNIR-966-901 from Ibsen Photonics to disperse the supercontinuum laser, which can work well in the range of 500 nm-1000 nm. Two TBP01-900 filters (covering 780 nm–910 nm) can be used to purify the monochromatic light filtered by the transmission grating for the Raman measurement. From this point of view, the supercontinuum laser can surely serve as an economic and flexible alternative of several tunable lasers for the resonance Raman profile measurement in the range of 400 nm-1000 nm. When the tunable Raman and bandpass filters are available above 1000 nm, the excitation range can be further extended to near-infrared range above 1000 nm.

III. CONCLUSIONS

In conclusion, we demonstrated a tunable micro-Raman single-stage spectrometer combined with the supercontinuum laser, transmission grating, and tunable filters. The combination of a broad bandpass filter and transmission grating can achieve tunable excitation light with a bandwidth of subnanometer. The tunable bandpass filter can efficiently remove the stray light down to 200 cm^{-1} relative to the excitation wavelength of interest. The system performance is verified by the resonant Raman profile measurement on a twisted bilayer graphene, which is in accordance with the previous result. It suggests that the supercontinuum laser can surely serve as economic and flexible tunable excitation lasers for the resonance Raman profile measurement in the range of 400 nm-1000 nm.

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[1] X. Zhang, X.-F. Qiao, W. Shi, J.-B. Wu, D.-S. Jiang, and P.-H. Tan, "Phonon and Raman scattering of two-dimensional transition metal dichalcogenides from monolayer, multilayer to bulk material," Chem. Soc. Rev. **44**, 2757–2785 (2015).
[2] M. Dresselhaus, A. Jorio, and R. Saito, "Characterizing graphene, graphite, and carbon nanotubes by Raman spectroscopy," Annu. Rev. Condens. Matter Phys. **1**, 89–108 (2010).
[3] A. C. Ferrari and D. M. Basko, "Raman spectroscopy as a versatile tool for studying the properties of graphene," Nat. Nanotechnol. **8**, 235–246 (2013).
[4] A. B. Myers, "Resonance Raman intensity analysis of excited-state dynamics," Acc. Chem. Res. **30**, 519–527 (1997).
[5] J.-B. Wu, X. Zhang, M. Ijäs, W.-P. Han, X.-F. Qiao, X.-L. Li, D.-S. Jiang, A. C. Ferrari, and P.-H. Tan, "Resonant Raman spectroscopy of twisted multilayer graphene," Nat. Commun. **5**, 5309 (2014).
[6] L. Sun, J. Yan, D. Zhan, L. Liu, H. Hu, H. Li, B. K. Tay, J.-L. Kuo, C.-C. Huang, D. W. Hewak, P. S. Lee, and Z. X. Shen, "Spin-orbit splitting in single-layer MoS_2 revealed by triply resonant Raman scattering," Phys. Rev. Lett. **111**, 126801 (2013).
[7] B. R. Carvalho, L. M. Malard, J. M. Alves, C. Fantini, and M. A. Pimenta, "Symmetry-dependent exciton-phonon coupling in 2D and bulk MoS_2 observed by resonance Raman scattering," Phys. Rev. Lett. **114**, 136403 (2015).
[8] C. Fantini, A. Jorio, M. Souza, M. S. Strano, M. S. Dresselhaus, and M. A. Pimenta, "Optical transition energies for carbon nanotubes from resonant Raman spectroscopy: Environment and temperature effects," Phys. Rev. Lett. **93**, 147406 (2004).
[9] A. Compaan and H. Trodahl, "Resonance Raman scattering in Si at elevated temperatures," Phys. Rev. B **29**, 793 (1984).
[10] R. W. Havener, H. Zhuang, L. Brown, R. G. Hennig, and J. Park, "Angle-resolved Raman imaging of interlayer rotations and interactions in twisted bilayer graphene," Nano Lett. **12**, 3162–3167 (2012).
[11] J.-B. Wu, Z.-X. Hu, X. Zhang, W.-P. Han, Y. Lu, W. Shi, X.-F. Qiao, M. Ijiaes, S. Milana, W. Ji, A. C. Ferrari, and P.-H. Tan, "Interface coupling in twisted multilayer graphene by resonant Raman spectroscopy of layer breathing modes," ACS Nano **9**, 7440–7449 (2015).