Phonon Energy Transfer in Graphene-Photoacid Hybrids

Xiaoyong Pan,[†] Hao Li,[†] Kim Truc Nguyen,[†] George Grüner,[§] and Yanli Zhao[†,‡]*

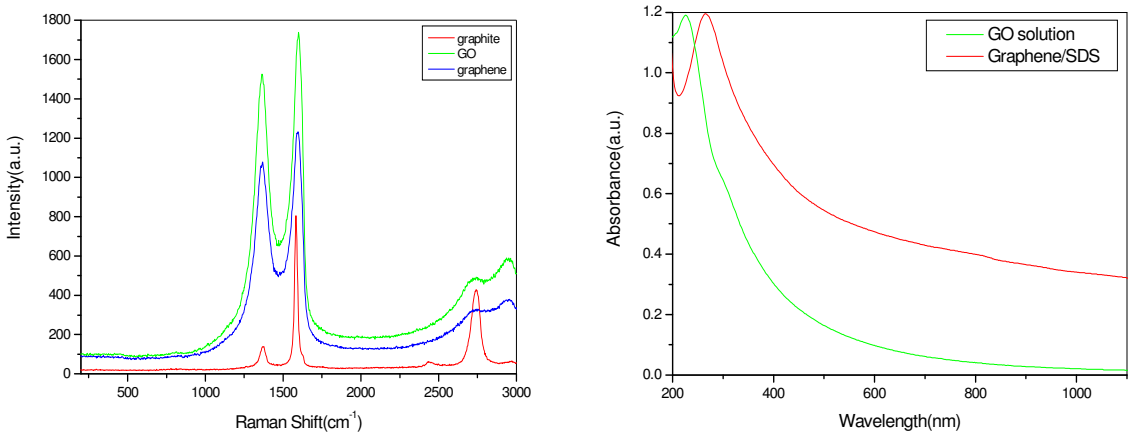
[†]Division of Chemistry and Biological Chemistry, School of Physical & Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, Singapore 637371

[‡]School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798

[§]Department of Physics and Astronomy, University of California, Los Angeles, 405 Hilgard Avenue, Los Angeles, California, 90095; Visiting Professor, Chemistry Department, Faculty of Science, King Abdul-Aziz University Jeddah, Saudi Arabia, 21589

E-mail: zhaoyanli@ntu.edu.sg; Phone: +65-6316-8792

Supproting Information



(a) (b)

Figure S1. Raman Scattering and UV-Vis absorbance spectra of graphite, GO, and graphene. (a) Raman spectra of graphite, GO, and graphene powders using a 457 nm laser. (b) UV-Vis absorbance spectra of GO solution in DI water and graphene solution in 1% sodium dodecyl sulphate (SDS) solution.

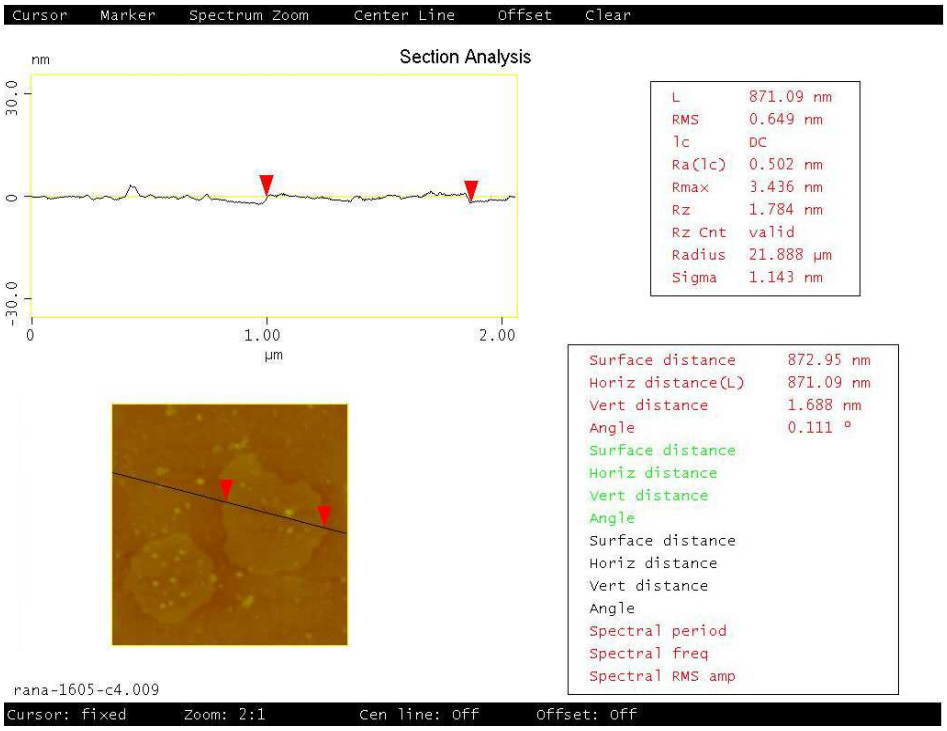


Figure S2. AFM image of the graphene flakes on the glass substrate. AFM image indicates that the dimension of the graphene flakes is on the order of 1 µm.

Effect of Graphene on the Optical Absorbance of PAS.

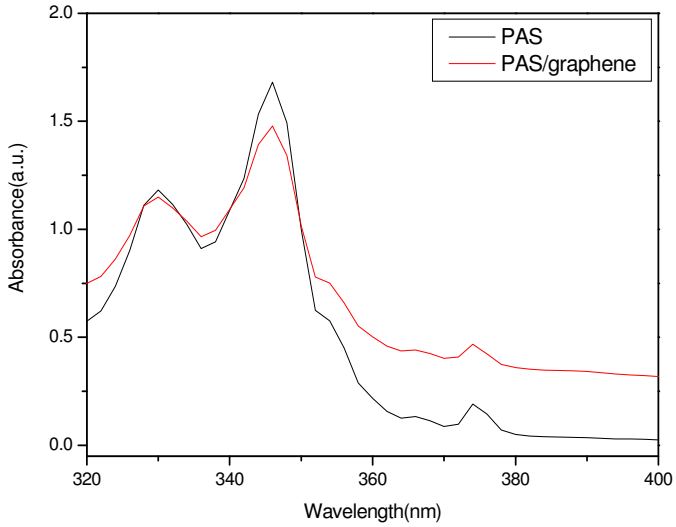


Figure S3. Absorbance spectra of PAS in the absence/presence of graphene. The spectra of PAS in the absence/presence of graphene indicate that there is no evident effect of graphene on the absorption spectrum of PAS, except for slight modification of the relative intensities of distinct peaks upon interaction with graphene.

Observation of Vibration Energy Transfer with Reversed Direction. The obtained results indicate the transfer of phonon energy from graphene to photoacids. One concern about this conclusion is whether the phonon energy transfer from photoacids to graphene is possible or not. Fine tune of the pH value for DHPDS demonstrates that the phonon energy transfer from DHPDS to graphene is possible under specific pH condition. The UV-Vis spectra and photoluminescence spectra at other two pH values are shown in Figure S4. The pH value of DHPDS in the absence of graphene in Figure 3b is determined to be 7.1. It can be seen from Figure S4a,c that the vibration energy transfer can be switched off at pH 7.28. The direction of the vibration energy transfer can even be reversed at pH 7.49 (Figure S4b,d). The observation is theoretically

understandable since there is no criterion which will limit the vibration energy transfer from graphene to photoacids rather than from photoacids to graphene.

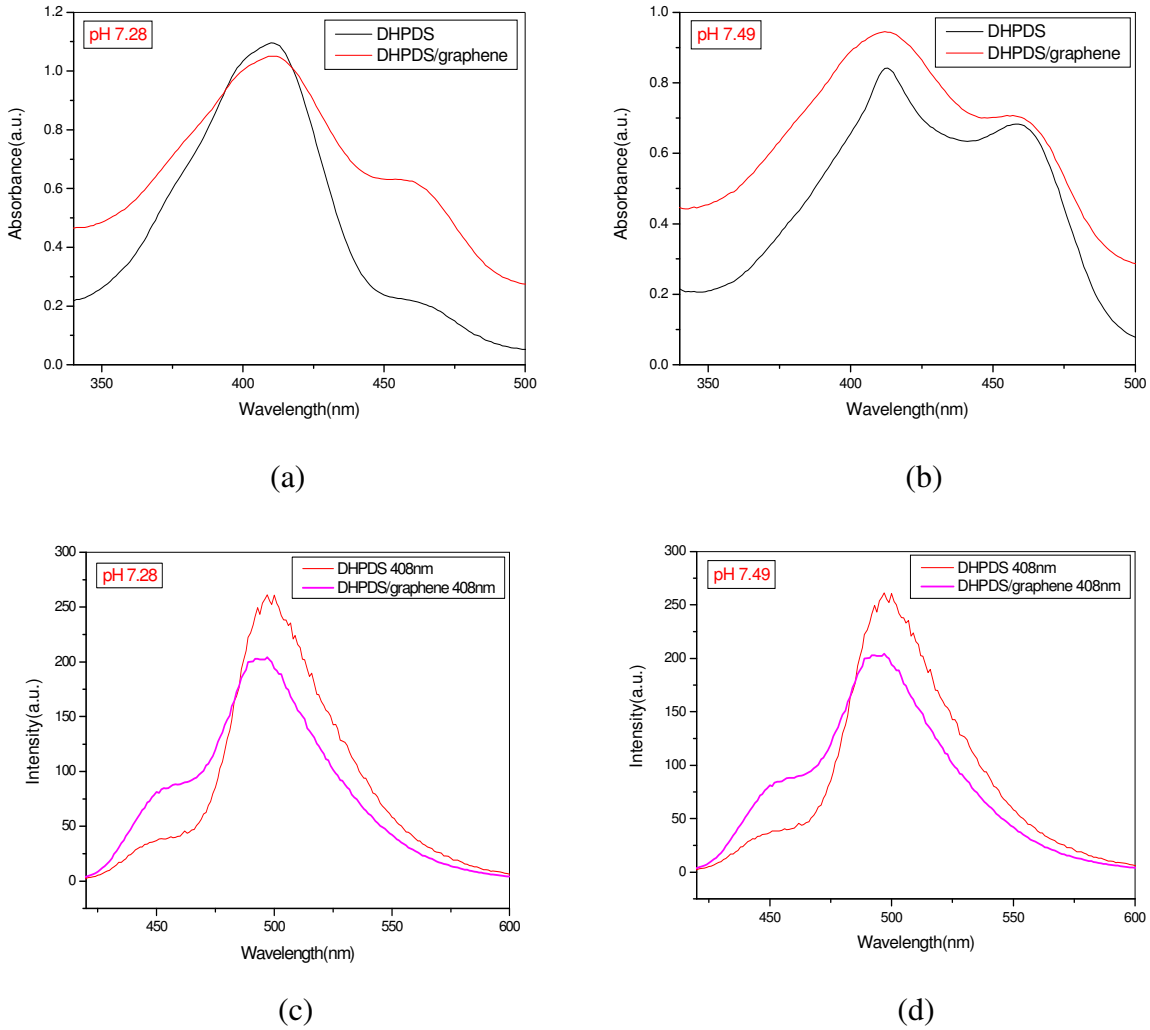


Figure S4. Optical behaviour of DHPDS at different pH values. (a) UV-Vis spectra of DHPDS at pH 7.28 in the absence and presence of graphene. (b) UV-Vis spectra of DHPDS at pH 7.49 in the absence and presence of graphene. (c) Photoluminescence spectra of DHPDS at pH 7.28 in the absence and presence of graphene, with an excitation wavelength of 408 nm. (d) Photoluminescence spectra of DHPDS at pH 7.49 in the absence and presence of graphene, with an excitation wavelength of 408 nm.

Temperature Influence on the Absorbance Spectrum of HPTS. Figure S5 shows the influence of temperature on the absorbance spectrum of HPTS in the absence of graphene. It can be seen that temperature effect on the absorbance spectrum was substantially suppressed without the phonon coupling interaction.

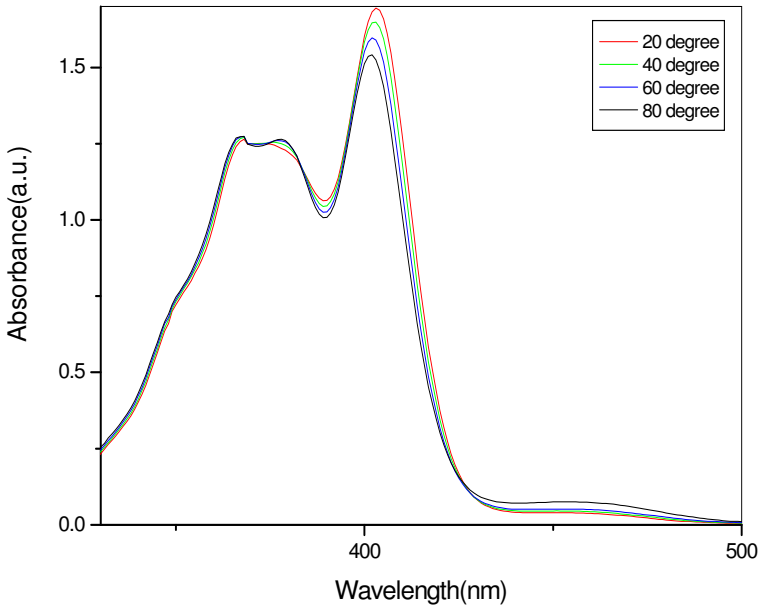
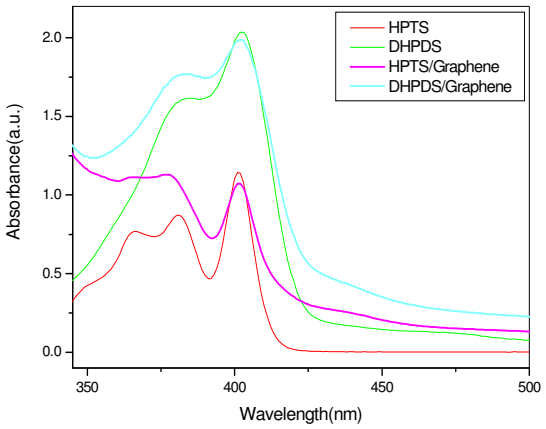
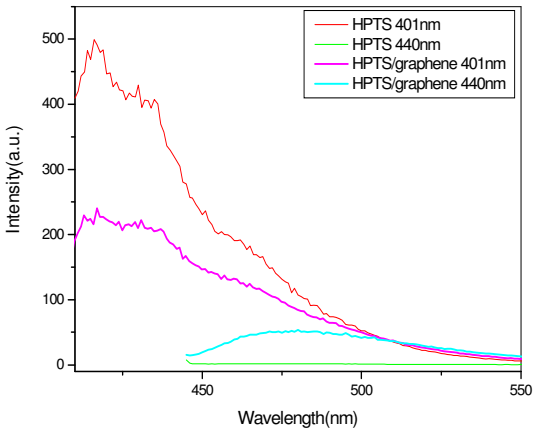


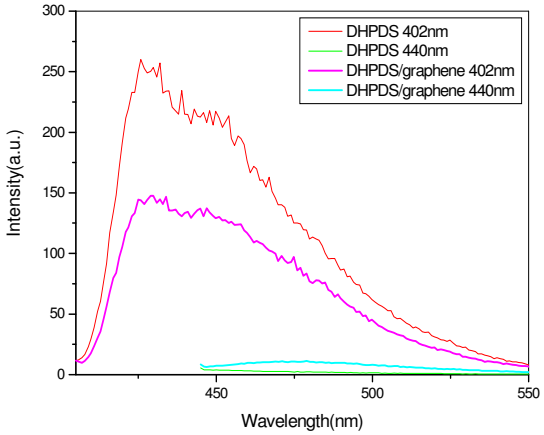
Figure S5. Temperature effect on the absorbance spectrum of HPTS in the absence of graphene.

Solvent Effects. Figure S6 shows the optical behavior of HPTS and DHPDS in DMSO. The existence of the phonon coupling interaction between the photoacids and graphene is confirmed by both UV-Vis spectra (appearance of absorption peak around 440nm) and substantial photoluminescence increase with an excitation wavelength of 440 nm.



(a)



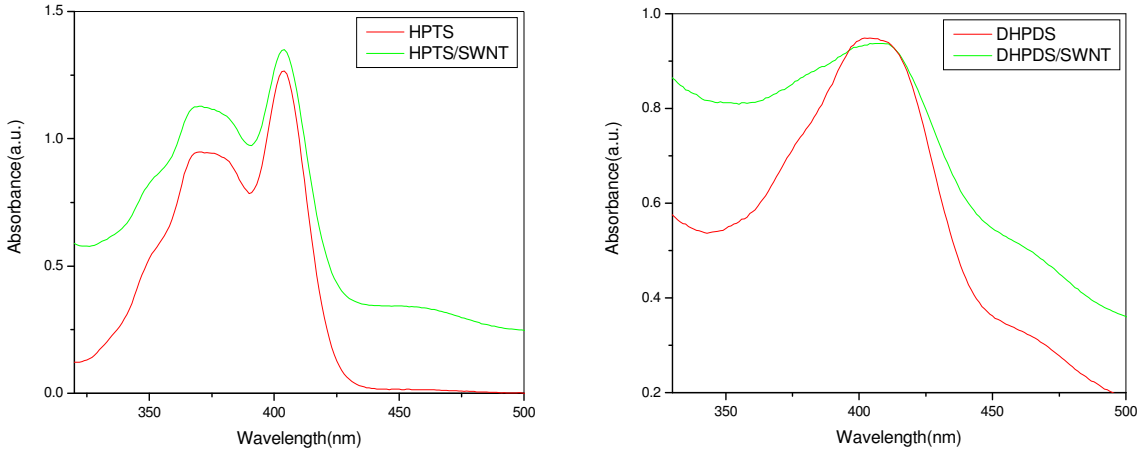


(b) (c)

Figure S6. Optical behavior of HPTS and DHPDS in DMSO. (a) UV-Vis spectra of HPTS and DHPDS in DMSO. (b) Photoluminescence spectra of HPTS in DMSO, with excitation wavelengths of 401 and 440 nm. (c) Photoluminescence spectra of DHPDS in DMSO, with excitation wavelengths of 402 and 440 nm.

Phonon Coupling Interaction between Photoacids and SWNTs. Figure S7 shows the absorbance spectra of HPTS and DHPDS in the absence and presence of SWNTs. The existence of the phonon coupling interaction between the photoacids and SWNTs is substantially weaker

than that between the photoacids and graphene. This observation indicates that the 2D framework of graphene is a critical factor for the attachment of aromatic molecules onto graphene, which serves as the prerequisite for the phonon coupling between the aromatic molecules and graphene.



(a) (b)

Figure S7. Optical behavior of HPTS and DHPDS in the presence of SWNTs. (a) UV-Vis spectra of HPTS in the absence and presence of SWNTs. (b) UV-Vis spectra of DHPDS in the absence and presence of SWNTs.