Extraordinary photoluminescence in UV/ozone treated graphene flakes

Haihua Tao[1], Ziyu Zhang[1], Hao Li[1], Guqiao Ding[2], Zhenhua Ni[3], Xianfeng Chen[1]

[1]Department of Physics and Astronomy, Shanghai Jiao Tong University, Shanghai 200240, China
[2]State Key Laboratory of Functional Materials for Informatics, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, Shanghai 200050, China
[3]Department of Physics, Southeast University, Nanjing 211189, China

tao.haihua@sjtu.edu.cn, xfchen@sjtu.edu.cn

Abstract

Photoluminescence (PL) originating from two dimensional materials is attracting intense attention due to emergence of graphene and other direct bandgap materials like phosphorene and monolayer MoS_2/WS_2 [1-3]. In 2013, H. R. Gutiérrez et. al. observed extraordinary PL from edges of the chemically grown triangular WS_2 and MoS_2 monolayer flakes [2]. They proposed that the edge structure and chemistry of as-grown monolayer WS_2/MoS_2 are crucial for localized PL enhancement even though the actual mechanism leading to the edge-enhanced PL is still to be determined. Different from direct-bandgap monolayer metal dichalcogenides, luminescent graphene-based nanostructures usually have two distinct characteristics, i.e., shrinking nanometer scale structures and adsorbed surface chemical functional groups [1,4]. Aside from regular chemical synthesis routes, realizing in-situ PL in high-quality graphene flakes is significant in the future photonic and optoelectronic applications [1].

As previously reported, UV/ozone photochemical oxidation has a unique capability of carving few layer graphene (FLG) into about one nanometer deep patterns [4,5]. In this talk, we present extraordinary PL imaged by a confocal laser scanning microscope (CLSM) in the suspended and edge area of UV/ozone treated FLG flakes [Fig. 1]. Atomic force microscopy (AFM) and confocal Raman spectroscopy analyses [Fig. 2] indicate that monolayer graphene, the most adequate for characterizing ozonation, turn into some isolated amorphous nano-dots with an average size of ~20 nm. In addition, no obvious topographic difference can be detected between the suspended and Si/SiO_2 (300 nm) supported FLG. X-ray photoelectron spectroscopy (XPS) results [Fig. 3] indicate a minute amount of luminescent-inducing surface chemical groups are created after the ozonation. We think the properly etched nanostructures and luminescent-inducing surface chemical groups contribute together to the PL in FLG. However, the subjacent intact carbon layers and charge impurities resided in SiO_2 substrate can cause severe PL quenching, and as a consequence result in non-detectable PL in the mono-/bilayer graphene and substrate supported FLG [6]. Our results deviate from report by Gokus et al. that they could detect PL only in monolayer graphene flakes instead of in FLG after oxygen plasma treatment [1]. We conclude the simultaneously ozonized graphene bottom layers, which are ascertained by high temperature vacuum annealing process, can efficiently decrease PL quenching and facilitate PL detection in the suspended and edge area of FLG. Our work may shed light on the understanding of luminescent two dimensional materials as well as contribute to building graphene-based nanophotonics and optoelectronics.

References

[1] T. Gokus, R. R. Nair, A. Bonetti, M. Böhmler, A. Lombardo, K. S. Novoselov, A. K. Geim, A. C. Ferrari, and A. Hartschuh, ACS Nano **3**, 3963 (2009).
[2] H. R. Gutiérrez, N. P.-López, A. L. Elías, A. Berkdemir, B. Wang, R. Lv, F. L.-Urías, V. H. Crespi, H. Terrones, and M. Terrones, Nano Lett. **13**, 3447 (2013).
[3] S. Zhang, J. Yang, R. Xu, F. Wang, W. Li, M. Ghufran, Y.-W. Zhang, Z. Yu, G. Zhang, Q. Qin, and Y. Lu, ACS Nano **8**, 9590 (2014).
[4] N. Leconte, J. Moser, P. Ordejón, H. Tao, A. Lherbier, A. Bachtold, F. Alsina, C. M. Sotomayor Torres, J.-C. Charlier, and S. Roche, ACS Nano **4**, 4033 (2010).
[5] H. Tao, J. Moser, F. Alzina, Q. Wang, C. M. Sotomayor-Torres, J. Phys. Chem. C **115**, 18257 (2011).
[6] X. T. Guo, Z. H. Ni, C. Y. Liao. H. Y. Nan, Y. Zhang, W. W. Zhao, and W. H. Wang, Appl. Phys. Lett. **103**, 201909 (2013).

Figures

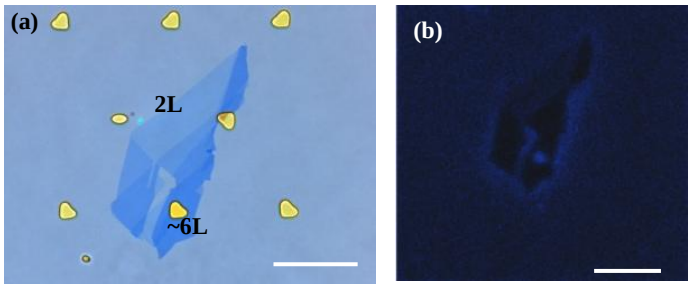

Fig. 1. (a) Optical image of a graphene flake composed of bilayer and FLG elements; (b) its CLSM picture excited at 364 nm after proper UV/ozone treatment with a low initial oxygen pressure. Each scale bar is 20 μm.

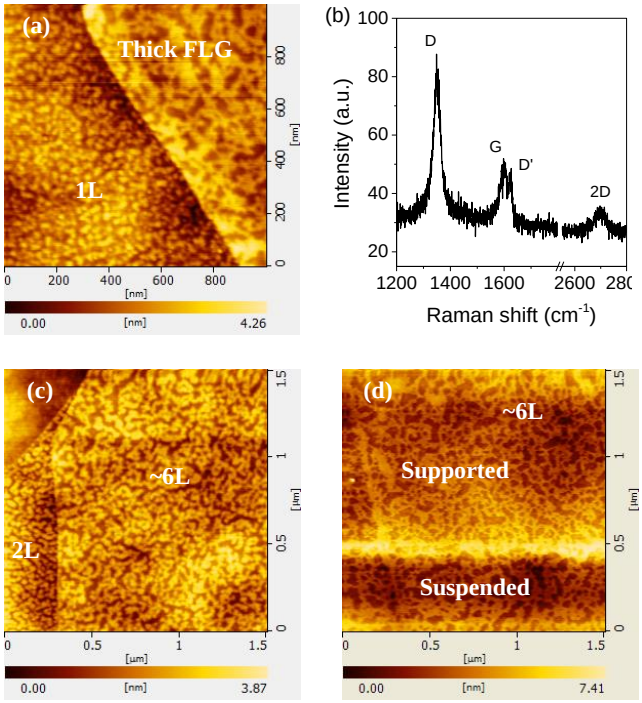

Fig. 2. (a) AFM image and (b) Raman spectrum of UV/ozone treated monolayer graphene; AFM image of (c) bi-/hexalayer FLG adjacent to the suspended region in Fig. 1; (d) AFM comparison of the supported (top) and suspended (bottom) regions of FLG (～6L thick). All samples are the same UV/ozone treated as photoluminescent FLG.

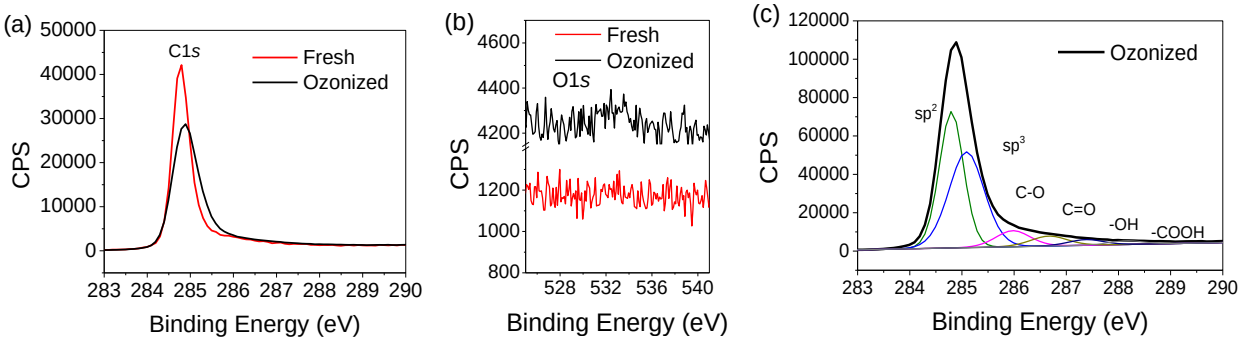

Fig. 3. Highly resolved narrow band (a) C1*s* and (b) O1*s* XPS spectra of the freshly cleaved and ozonized Kish graphite; (c) Fitting C1*s* spectrum of the ozonized Kish graphite with six mixed Gaussian-Lorentzian curves.