Extraordinary photoluminescence in UV/ozone treated graphene flakes

Haihua Tao¹, Ziyu Zhang¹, Hao Li¹, Guqiao Ding², Zhenhua Ni³, Xianfeng Chen¹

¹Department of Physics and Astronomy, Shanghai Jiao Tong University, Shanghai 200240, China
²State Key Laboratory of Functional Materials for Informatics, Shanghai Institute of Microsystem and
Information Technology, Chinese Academy of Sciences, Shanghai 200050, China
³Department 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
MoS₂/WS₂ [1-3]. In 2013, H. R. Gutiérrez et. al. observed extraordinary PL from edges of the chemically
grown triangular WS₂ and MoS₂ monolayer flakes [2]. They proposed that the edge structure and
chemistry of as-grown monolayer WS₂/MoS₂ 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/SiO₂ (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 SiO₂ 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
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) C1s and (b) O1s XPS spectra of the freshly cleaved and ozonized Kish graphite; (c) Fitting C1s spectrum of the ozonized Kish graphite with six mixed Gaussian-Lorentzian curves.