

In Situ and Nonvolatile Tuning of sp^2/sp^3 Fraction in Graphene Oxide For All-Solid-State Multifunctional Devices

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Abstract

In situ and nonvolatile tuning of the sp^2/sp^3 fraction in graphene oxide (GO) based on electrochemical reduction and oxidation (redox) reaction caused by ion migration in a solid-state electrolyte has been developed. It uses an all-solid-state ionics device with a multilayer GO and proton-conducting oxide thin films. This method provides in situ tuning of the sp^2/sp^3 fraction by application of DC bias. In addition to the useful tuning function on the transport property, the nonvolatile variation of the GO sp^2/sp^3 fraction was further applied to achieve photoluminescence (PL) tuning for nano-optoelectronic devices including non-volatile PL memory devices and on-demand rewritable biosensors.

1. Introduction

Graphene oxide (GO) has become a promising 2D material for exploring a variety of physical properties, including variable bandgap and transport properties, wide energy range of photoluminescence (PL), and room-temperature ferromagnetism. Recent investigations of the functions of GO revealed that the unique physical properties of GO strongly depend on the sp^2 domain to sp^3 domain (sp^2/sp^3) fraction, or the corresponding carbon/oxygen fraction (C/O). While the fraction is usually controlled using a chemical method, we recently reported in situ tuning through redox reaction using a solid electrolyte thin film.^{1,2} With this technique, the fraction can be tuned by simply applying DC voltage.

Among the various functions of GO, PL in particular is receiving much attention in the distinct aspect: the various potential applications. Although the origin of PL in GO is still open for further discussion, it is nevertheless promising for optoelectronic application for several reasons. Particularly, the stability of GO against photodegradation compared to conventional organic fluorophores is attractive for nano medicine applications. For instance, biosensors that can selectively detect various biomolecules including pathogens and neurotransmitters have been achieved by using the PL in GO. From the application viewpoint, the sp^2/sp^3 fraction tuning in GO is crucially important. The PL wavelength greatly varies with the fraction; this variance is related to the oxygen atoms in the GO functional groups. The extent of oxidation of the GO functional groups affects the charge transfer behavior in the biomolecule detection process by tuning of the relative potential energies in GO.

Accordingly, application of this technique to PL should lead to a new class of optoelectronic device. Here, we report the development and testing of an all-solid-state variable wavelength PL device based on solid state ionics.³ The technique is applicable to a wide range of nano-optoelectronic devices including non-volatile PL memory devices and on-demand rewritable biosensors which are transparent, ultrathin, flexible and low cost.

2. Experimental

Device fabrication and characterization.

The all-solid-state PL source we used is schematically shown in Fig. 1. It was fabricated of GO and mesoporous SiO_2 thin film by using spin coating, sol-gel method with template organics,³ electron beam deposition, and so on. A high-resolution transmission electron microscope (HR-TEM) image of the GO/mesoporous SiO_2 thin film interface is shown in Fig. 1 inset. The internal pore diameter and wall thickness were determined to be 3.3 and 1.0 nm, respectively on the basis of the FE-SEM, XRD, and HR-TEM observations. About ten layers of graphene sheets were observed in the GO layer and the average interlayer distance was 3.84 Å (d_{002}).

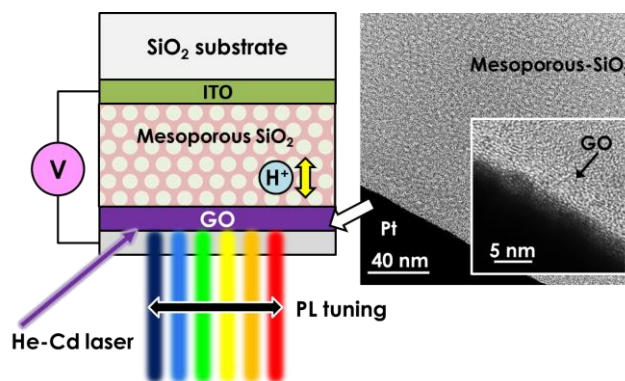


Fig. 1 Schematic illustration of all-solid-state PL source made of GO and mesoporous SiO_2 thin film. Inset shows HR-TEM image of mesoporous SiO_2 (mp- SiO_2)/GO/Pt interface, and magnification of GO layers.

PL measurement.

PL measurement was performed using the PL device and detection system schematically shown in Fig. 1. The 325-nm line of the He-Cd laser was used as the excitation source. The light emitted from the device was collected using achromatic lenses and then analyzed using a spec-

trograph equipped with a liquid-nitrogen-cooled charge-coupled device (CCD) detector.

3. Results and discussion

PL tuning behavior in the all-solid-state ionics device.

Figure 2 shows the variation in PL spectra of the device tuned by DC bias voltage application ($V=-2.5$ V) for 2000 s. The polarity of V is defined as positive when GO is oxidized. The initial spectrum has a broad peak around 700 nm and average wave length is 684 nm. The spectra showed a gradual variation in both the shape and intensity while the DC voltage was applied. Figure 2(b) shows the variation in the integrated PL intensity (left axis) and average wavelength (right axis) calculated from the PL spectra. Please note that the integrated intensity is shown by the value normalized by the initial value. Upon DC bias voltage application, the integrated PL intensity immediately started to decrease and the behavior saturated after around 1000 s. On the other hand, the average wavelength showed no considerable variation spectra in around 50 s just after DC bias voltage application, followed by a significant blue shift to average wavelength of 530 nm.

DC voltage dependence of the PL wavelength and intensity.

We further investigated the effect of a DC bias voltage on the PL spectra and the peak wavelength. Figures 2(c) shows the DC bias dependence of peak wavelength (left axis, indicated by black circles) and relative intensity (right axis, indicated by green circles, indicated as value relative to intensity (with $V=2.5$ V) tuned by various DC bias voltage applications for 1200 s. The peak wavelength in the reduction process was widely modulated, from 544 nm ($V=-2.5$ V) to 393 nm ($V=-3.5$ V). This behavior is qualitatively consistent with the considerable voltage dependence of the optical bandgap in the reduction process, which was previously investigated using UV-Vis-NIR reflectance measurement.¹ Note that the GO bandgap can be a measure of the extent of reduction, while the bandgap does not correspond to the PL emission energy. The peak wavelength of 393 nm with $V=-3.5$ V agrees well with 390 nm for extensively reduced GO.⁴ The peak wavelength in the oxidation process was not significantly altered even though the bias voltage was varied from 1.5 V to 2.5 V. The longest peak wavelength of 712 nm (with $V=2.5$ V) is 38 nm shorter than reported peak wavelength of 750 nm.⁵

4. Conclusions

An all-solid-state PL device using GO and mesoporous SiO_2 enabling *in situ* and nonvolatile tuning of the PL wavelength was achieved on the basis of the solid state ionics principle. The PL tuning range covers that for chemically tuned GO except for near the long wavelength extreme (750 nm). The present technique should lead to a new class of nano-optoelectronic devices for display, lighting, and biosensing featuring *in situ* and nonvolatile operation.

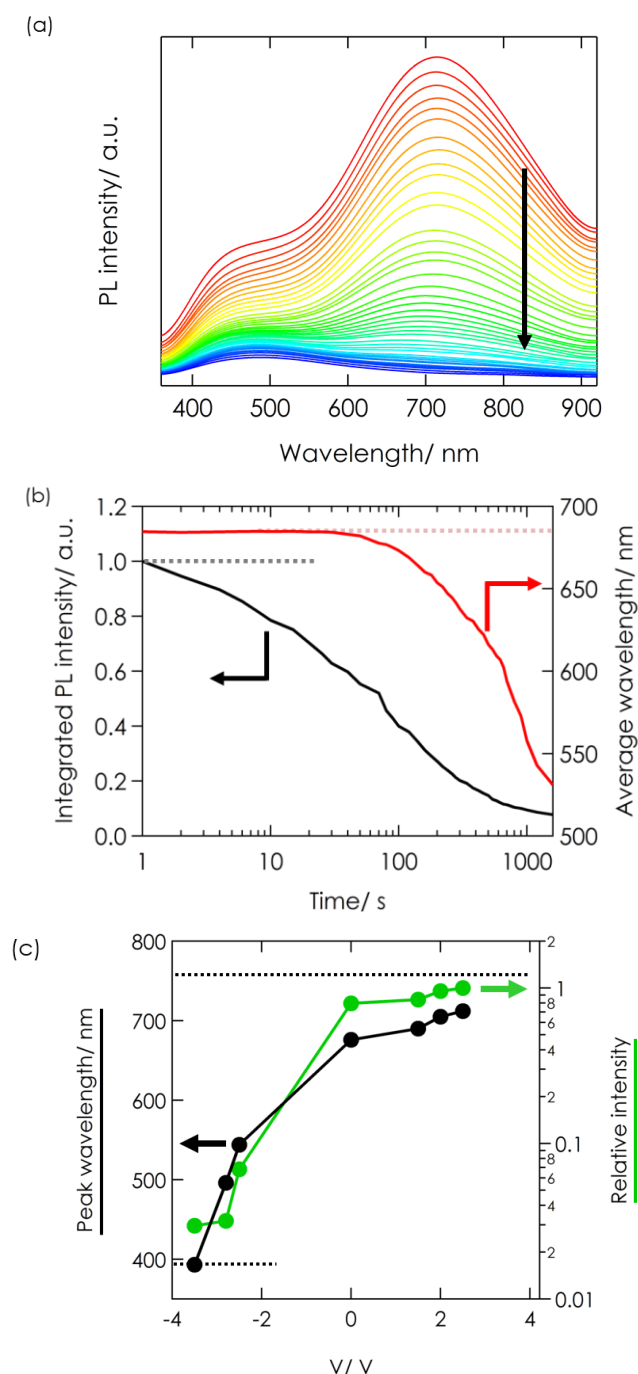


Figure 2. (a) Variation in normalized PL spectra tuned by DC bias voltage application. (b) variation in the integrated PL intensity and average wavelength. (c) DC bias dependence of peak wavelength and relative intensity.

References

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