

## Photoluminescence comparison of CNTs-SRO and GO-SRO films deposited on silicon substrates

### Comparación de la fotoluminiscencia de películas CNT-SRO y GO-SRO depositadas sobre sustratos de silicio

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#### Abstract

In this work, we make a comparative study of the photoluminescence (PL) obtained from the structures formed by carbon nanotubes (CNTs) and graphene oxide (GO) deposited by Spin Coating on silicon rich oxide (SRO) thin films which were obtained by hot filament chemical vapor deposition (HFCVD) technique. The objective of building these hybrid structures is to increase the photoluminescence response. The PL measurements show that the CNTs-SRO heterostructures exhibit a stronger photoluminescence when compared to that obtained from the GO-SRO heterostructure, similar behaviour exhibit the GO-CNTs/SRO ones when compared to the CNTs-GO/SRO ones. It is worthy to note that the CNTs-SRO structures PL displays blue light emission, while green light emission is present in the CNT-GO ones. By deconvolution of the PL spectra, we identify the emission mechanisms present in graphene oxide, carbon nanotubes layers and the silicon rich oxide films. Due to the good properties of PL exhibited by the CNTs-SRO and GO-CNTs/SRO structures, they are excellent candidates to be applied in the field of photonic and electroluminescent devices.

**SRO, HFCVD, Photoluminescence**

#### Resumen

En este trabajo, se realizó un estudio comparativo de la fotoluminiscencia (FL) de nanotubos de carbono (CNTs) y óxido de grafeno (GO) depositados por Spin Coating y películas de óxido de silicio rico en silicio (SRO) depositadas mediante la técnica de depósito químico en fase vapor asistido por filamento caliente (HFCVD). Para mejorar la respuesta de la fotoluminiscencia, se combinaron los CNTs y el GO para formar un híbrido de estos dos materiales. Los espectros muestran que la heteroestructura CNTs-SRO muestra una fotoluminiscencia más alta en comparación con la GO-SRO, mientras que la estructura GO-CNTs/SRO muestra una respuesta fotoluminiscente más alta que la estructura CNTs-GO/SRO. Los espectros muestran que los CNTs emiten luz azul, mientras que la luz verde domina en el híbrido CNTs-GO. A través de la deconvolución de los espectros de PL, se obtuvieron los mecanismos de emisión presentes en las capas de GO, CNTs y la película de SRO. Por lo tanto, debido a estos resultados, las heteroestructuras con CNTs (CNTs-SRO and GO-CNTs/SRO) presentan un gran potencial de aplicación en el campo de los dispositivos fotónicos y electroluminescentes.

**SRO, HFCVD, Fotoluminiscenc**

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## Introduction

One of the most technologically interesting materials is silicon-rich oxide (SRO), which is considered to be a material with great potential for the fabrication of optoelectronic devices because it is a material compatible with CMOS technology. In addition to various methods can be used to obtain the SRO, such as LPCVD, PEVCD, HFCVD, implantation of silicon in SiO<sub>2</sub>, sputtering, etc. [1].

A relevant characteristic of the SRO is that it facilitates the formation of silicon nanocrystals embedded in a SiO<sub>2</sub> matrix [2], which generate low dimensional effects and therefore, an efficient emission of light [1]. The SRO possesses interesting structural, optical, and electrical properties which can be tailored by the silicon excess and defects contained in the films [3]. The incorporation of silicon into SiO<sub>x</sub> modifies its bandgap as well as its optical properties such as photoluminescence, absorption and emission of light. The latter is attributed to quantum effects present in silicon nanocrystals and localized defects at the interface between nanocrystals and silicon matrix [4].

On the other hand, carbon nanostructures such as fullerenes, carbon nanotubes (CNTs), nanodiamond (ND) films, and graphene oxide (GO) are very attractive functional groups in the fabrication of important optoelectronic devices such as sensors, field emitters, and light-emitting applications [5]. Luminescent carbon nanostructures are also expected to achieve high-efficiency photoluminescence in light-emitting devices and low toxicity in biological and biomedical applications [6].

There are two types of CNTs; single-wall carbon nanotubes (SWCNTs) and multi-wall carbon nanotubes (MWCNTs). MWCNT is a CNT structure consisting of several coaxially concentric shells of graphene sheets rolled up. In both cases, their one-dimensional structure, interlayer interaction and curvature effects lead to many extraordinary mechanical, electrical, optical, thermal and chemical properties. All of this makes them suitable for enhancing the functionalization of existing materials and even creating other heterostructures. Furthermore, CNTs thin films are electrically conductive and transparent, and have recently been used as ohmic contacts in GaN and organic materials [7].

In this context, the SRO may be used to realize novel heterostructures using CNTs to improve its optical properties. On the other hand, Graphene oxide is a bidimensional carbon-based material that can be used in graphene-based optoelectronic devices, especially for biomedical applications, due to its unique electronic properties and large specific surface area [8, 9]. Since graphene has no band gap as an intrinsic material, it is not expected to exhibit photoluminescence due to relaxation of excited carriers; however, when, it is functionalized, such as graphene oxide, it has a band gap and exhibits photoluminescence [10]. Therefore, the GO may be used to form new structures in order to enrich their optical properties.

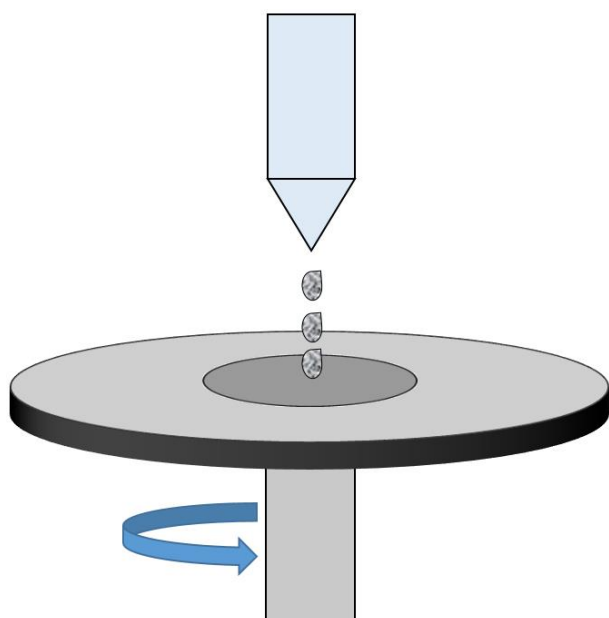
Thus, by using CNTs and GO along with the SRO it is possible to make up nanostructured materials which may be of great interest because of their outstanding photoluminescent properties based on the quantum effects due to low dimensions and energy band structures. Thus, these photoluminescent properties may be focused on forming new light-emitting devices in the field of optoelectronics.

## Development and methodology

CNTs and GO thin films were deposited on n-type crystalline silicon substrates with 100 orientation and <0.005 Ω-cm resistivity by the spin-coating method shown in Figure 1. The substrate is subjected to a MOS cleaning process (RCA standard) [11]. Si/CNTs, Si/GO, Si/CNTs-GO and Si/GO-CNTs structures were obtained. All structures to be deposited (CNTs and GO) are dissolved in an alcoholic solvent, in this case methanol, due to the low molarity, to avoid aggregation of the particles to be deposited, in the case of GO and CNTs, according to the report [12], because ideal solvents for dispersing graphene are those that minimize the interfacial tension between graphene and the solvent.

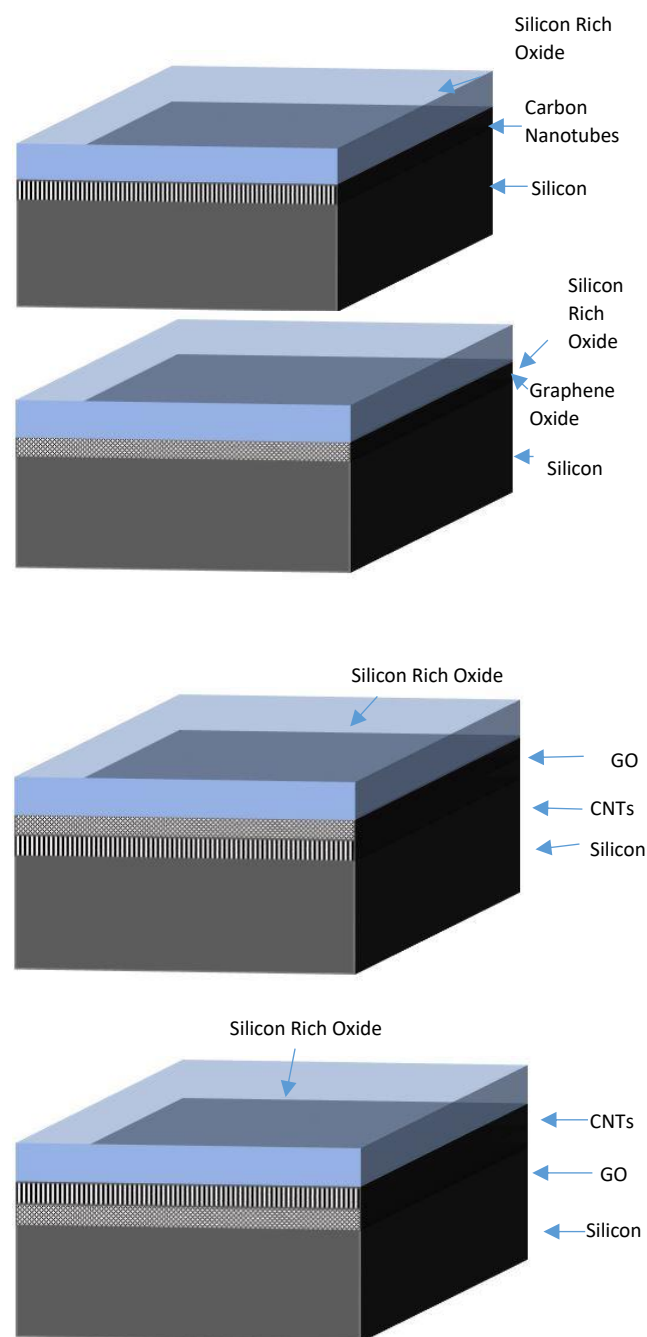
For the deposition of each layer of solvent and solute, it was attached to a Si substrate on a rotating plate, and then solution droplets were deposited on the substrate and rotated at a certain speed with a motor mounted on the plate. A certain angular velocity in order to create a thin film of solution by centrifugal force.

The parameters used for thin film deposition are as follows: the first speed is 700 rpm for a deposition time of 10 s, and the second speed is 3000 rpm for 15 s to deposit 3 drops of the solution, using methanol as the solvent and repeat the process three times. The concentrations of CNTs and GO solutions were 1.8 g/L and 1.3 g/L, respectively.



**Figure 1** Spin coating process

The SRO films were deposited on the Si/CNTs, Si/GO, Si/CNTs-GO and Si/GO-CNTs structures using a HFCVD (Hot Filament Chemical Vapor Deposition) reactor. These depositions were carried out with a constant flow of molecular hydrogen ( $H_2$ ) at 100 sccm level, the source-to-substrate distance (ssd) was kept at 7 mm. Some parameters were fixed during the deposition process, such as the filament-to-source distance (fsd), which was kept constant at 8 mm, the deposition time (td) was 1 min, the voltage applied to the filaments was 84 V and the system pressure at one atmosphere.

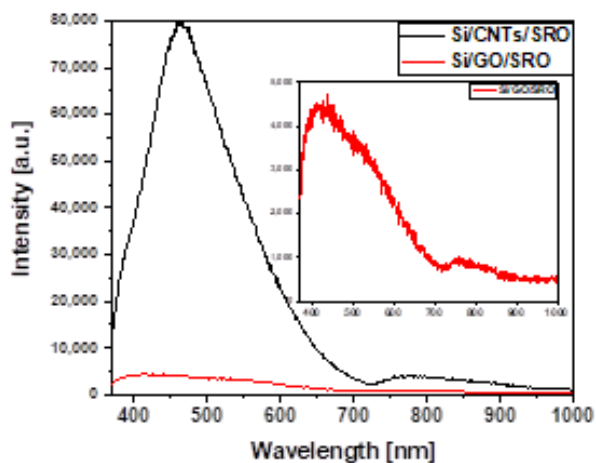


**Figure 2** Scheme of the 4 manufactured structures

Using photoluminescence (PL) spectroscopy, emission spectra were obtained and emission-related defects were identified. Spectra were acquired on a Horiba Jobin Yvon FluoroMax 3 fluorescence spectrophotometer equipped with a 150 W xenon excitation lamp, 0.3 nm resolution, 370-1000 nm range, and high sensitivity emission detector. Measurements were performed under excitation at 330 nm.

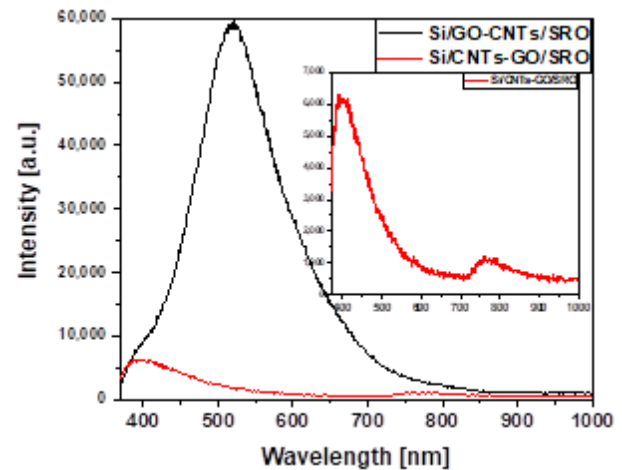
## Results and analysis

Graph 1 shows the photoluminescence spectrum of the Si/CNTs/SRO structure, and the inset shows the photoluminescence spectrum of the Si/GO/SRO structure. The PL intensity of the Si/CNTs/SRO structure shows a strong and well-defined peak in blue (450 nm), which is attributed to the CNTs, in addition, a lower intensity peak can be seen in the red band around 750 nm. For Si/GO/SRO structure two peaks appeared, a more defined peak around 420 nm was attributed to GO, just like in the structure with CNT, a smaller peak appeared around 750 nm, and this is a characteristic of SRO films.



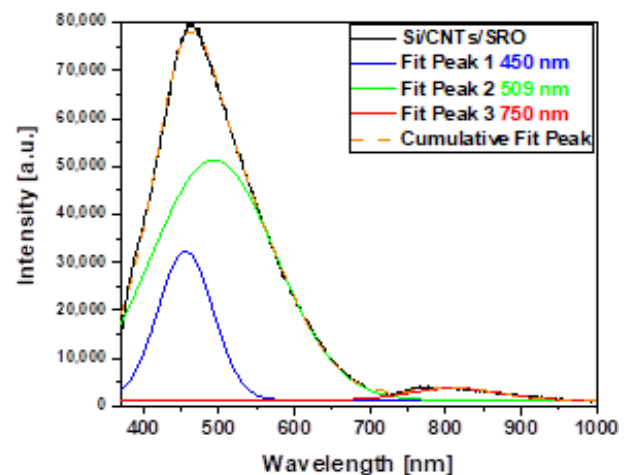
**Graphic 1** PL spectra of the Si/CNTs/SRO and Si/GO/SRO structures

Graphic 2 shows the photoluminescence spectrum of the Si/GO-CNTs/SRO structure, and the inset shows the photoluminescence spectrum of the Si/CNTs-GO/SRO structure. The PL intensity of the Si/GO-CNTs/SRO structure shows a strong and clear green peak (519 nm), which is attributed to the existence of the GO-CNTs composite [13]. For the Si/CNTs-GO/SRO structure, two peaks are shown, a more defined peak around 400 nm is attributed to GO, and another weaker peak around 750 nm and as mentioned above, is characteristic of SRO films. As can be seen from the inset figure, the photoluminescence emission decreases when the carbon nanotubes layer is covered with graphene oxide particles. The latter produces a quenching effect.



**Graphic 2** PL spectra of the Si/GO-CNTs/SRO and Si/CNTs-GO/SRO structures.

As shown in Graphics 1 and 2, the photoluminescence spectrum is very broad, suggesting that multiple emission mechanisms may be involved. To find all possible contributions to the photoluminescence process in the structure, the deconvolution of each spectrum is shown in Graph 3. The different peaks defined by the deconvolution are associated with different types of defects, as shown below, with their respective positions in energy, see Table 1.



**Graphic 3** Deconvoluted spectra of the Si/CNTs/SRO structure

CNTs/SRO photoluminescence emission mechanisms.	
Luminescent centers associated with diamond films	450 nm [13]
Defects due to Nitrogen	509 nm [14]
Nonbridging oxygen hole centers	750 nm [15]
GO/SRO photoluminescence emission mechanisms.	
It is attributed to the excimer present in the GO	405 nm [16]
Interactions between graphene planes and OD (Oxidative debris)	495 nm [16]
Nonbridging oxygen hole centers	750 nm [15]

**Table 1** Types of defects linked to the position of the PL peaks of the structures

Table 1 shows the emission mechanisms associated with CNTs, GO and SRO, two mechanisms have been identified for carbon nanotubes, one in the blue region at 450 nm and the other in the green region, likewise, graphene oxide exhibits two emission mechanisms, the first in the purple region (405 nm) and the other in the green region (495 nm). Finally, a peak associated to nonbridging oxygen hole centers (NBOHC) was identified for silicon rich oxide. In the structures with CNTs and GO, both a photoluminescence shift and a stronger emission is observed for the case of CNTs contribution because in these structures both curvature effects and inter-walls interaction as well as the edge effects and chiral indexes (n,m) modify significantly their electronic structure which favors the electronic transitions and therefore the radiative emission [17]. Blue-green photoluminescence has been previously observed in diamond films [14]. The blue luminescence is thought to be due to nitrogen contamination, as N-bonded carbons have been reported to act as luminescent centers in CNTs, similar to N-defects in CVD-derived nanodiamonds, as well as in natural diamond [14]. In general, CVD-derived carbon nanotubes and diamond are known to contain nitrogen and nitrogen-related defects [14], so the spectra suggest that the photoluminescence of the samples may have a similar origin based on nitrogen-bonded carbon, although the predominant phase in the samples is sp<sup>2</sup>-bonded carbon [14]. The C=O functional groups present on the surface of carbon nanotubes are responsible for the green emission. [13].

Graphene oxide exhibits two emission bands at 405 nm and 495 nm, respectively. These bands are similar to those reported in literature. [16]. Graphene oxide contains highly oxidized polycyclic aromatic hydrocarbon fragments, called oxidative debris (OD), which are present in graphene oxide, and they are attached to graphene oxide in a graphene-like plane [16]. OD has oxygen-containing groups like GO, so oxygen-containing groups should not be a direct source of the 495 nm band. Therefore, it is reasonable to attribute the 495 nm band to the interaction between the graphic plane and OD. The emission mechanism at 405 nm is due to the formation of excimer molecules, which can occur between polyaromatic molecules and conjugated polymers. Similarly, excimers can form GO sheets through  $\pi$ - $\pi$  overlap [16].

Oxygen-containing groups in GO, such as carboxyl or epoxy groups, always induce non radiative electron-hole pair recombination, making the emission intensity of GO very weak. [17]. The deposited SRO films show weak emission. However, the observed photoluminescence emission has a peak around 750 nm, which proves that the PL emission does not occur via interband recombination.

Therefore, emission through localized states present in nonbridging oxygen hole centers is the most likely mechanism [15]. As shown in Figure 4, when CNT was combined with GO, as described above, a shift of photoluminescence emission towards 500 nm was observed in the structure of CNTs in the upper part, which was due to the functional group C=O, except that the addition of GO did not increase the emission. On the other hand, in the structure with CNT and GO on top, the emission is similar to that of graphene oxide and is not affected by the interaction with carbon nanotubes. While for both heterostructures, the 750 nm peak associated with the SRO thin film still exists.

## Conclusions

The photoluminescence properties of CNTs, GO, and SRO thin film layers and heterostructures formed from these materials were investigated and compared. The photoluminescence spectra show the emission of CNTs in the blue-green region, which is thought to be caused by contamination caused by nitrogen binding to carbon in the blue region, and the characteristic green-emitting functional groups of CNTs due to C=O. GO emission was observed in two bands, 405 and 495 nm, caused by oxidative debris and excimers, respectively. Whereas for the SRO film, a contribution of 750 nm due to nonbridging oxygen hole centers is present. In the structure of mixed CNT and GO, the emission shift and its shielding are observed, which is due to the presence of nitrogen defects in the CNTs, whereas for the structure with GO on top, the emission is the same as that of GO without carbon nanotubes. Structures with CNTs have great potential in light-emitting device applications due to their good emission behavior.

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## References

- [1] Martínez, H., Luna, J., Morales, R., Casco, J., Hernández, J., & Luna, A. et al. (2021). Blue Electroluminescence in SRO-HFCVD Films. *Nanomaterials*, 11(4), 943. <https://doi.org/10.3390/nano11040943>
- [2] Simón, Z., López, J., de la Luz, Á., Salgado, G., Leyva, K., & López, J. et al. (2021). SiO<sub>x</sub> films deposited by HFCVD: Their conduction response to light and intrinsic photovoltaic effect. *Surfaces And Interfaces*, 26, 101411. <https://doi.org/10.1016/j.surfin.2021.101411>
- [3] Hernández Simón, Z., Luna López, J., de la Luz, A., Pérez García, S., Benítez Lara, A., & García Salgado, G. et al. (2020). Spectroscopic Properties of Si-nc in SiO<sub>x</sub> Films Using HFCVD. *Nanomaterials*, 10(7), 1415. <https://doi.org/10.3390/nano10071415>
- [4] Martínez Hernández, H., Luna López, J., Hernández de la Luz, J., Luna Flores, A., Monfil Leyva, K., & García Salgado, G. et al. (2020). Spectroscopic and Microscopic Correlation of SRO-HFCVD Films on Quartz and Silicon. *Crystals*, 10(2), 127. <https://doi.org/10.3390/cryst10020127>
- [5] Avouris, P., Freitag, M., & Perebeinos, V. (2008). Carbon-nanotube photonics and optoelectronics. *Nature Photonics*, 2(6), 341-350. <https://doi.org/10.1038/nphoton.2008.94>
- [6] Cayuela, A., Soriano, M., & Valcárcel, M. (2015). Photoluminescent carbon dot sensor for carboxylated multiwalled carbon nanotube detection in river water. *Sensors And Actuators B: Chemical*, 207, 596-601. <https://doi.org/10.1016/j.snb.2014.10.102>
- [7] Lee, K., Wu, Z., Chen, Z., Ren, F., Pearton, S., & Rinzler, A. (2004). Single Wall Carbon Nanotubes for p-Type Ohmic Contacts to GaN Light-Emitting Diodes. *Nano Letters*, 4(5), 911-914. <https://doi.org/10.1021/nl0496522>
- [8] Montes-Navajas, P., Asenjo, N., Santamaría, R., Menéndez, R., Corma, A., & García, H. (2013). Surface Area Measurement of Graphene Oxide in Aqueous Solutions. *Langmuir*, 29(44), 13443-13448. <https://doi.org/10.1021/la4029904>
- [9] Han, J., Kim, J., Jo, S., Kim, S., Kim, J., & Kang, B. et al. (2012). Graphene oxide as a multi-functional p-dopant of transparent single-walled carbon nanotube films for optoelectronic devices. *Nanoscale*, 4(24), 7735. <https://doi.org/10.1039/c2nr31923c>
- [10] Jin, Y., Zheng, Y., Podkolzin, S., & Lee, W. (2020). Band gap of reduced graphene oxide tuned by controlling functional groups. *Journal Of Materials Chemistry C*, 8(14), 4885-4894. <https://doi.org/10.1039/c9tc07063j>
- [11] Ruzyllo, J. (2004). *Cleaning technology in semiconductor device manufacturing VIII*. Pennington, New Jersey: Electrochemical Society.
- [12] Wang, W., Ruderer, M., Metwalli, E., Guo, S., Herzig, E., Perlich, J., & Müller-Buschbaum, P. (2015). Effect of Methanol Addition on the Resistivity and Morphology of PEDOT:PSS Layers on Top of Carbon Nanotubes for Use as Flexible Electrodes. *ACS Applied Materials & Interfaces*, 7(16), 8789-8797. <https://doi.org/10.1021/acsami.5b01327>
- [13] Fedoseeva, Y., Bulusheva, L., Okotrub, A., Kanygin, M., Gorodetskiy, D., & Asanov, I. et al. (2015). Field emission luminescence of nanodiamonds deposited on the aligned carbon nanotube array. *Scientific Reports*, 5(1). <https://doi.org/10.1038/srep09379>
- [14] Zhou, J., Zhou, X., Li, R., Sun, X., Ding, Z., Cutler, J., & Sham, T. (2009). Electronic structure and luminescence center of blue luminescent carbon nanocrystals. *Chemical Physics Letters*, 474(4-6), 320-324. <https://doi.org/10.1016/j.cplett.2009.04.075>

- [15] Vaccaro, L., Cannas, M., & Radzig, V. (2009). Luminescence properties of nonbridging oxygen hole centers at the silica surface. *Journal Of Non-Crystalline Solids*, 355(18-21), 1020-1023. <https://doi.org/10.1016/j.jnoncrysol.2008.11.028>
- [16] Du, D., Song, H., Nie, Y., Sun, X., Chen, L., & Ouyang, J. (2015). Photoluminescence of Graphene Oxide in Visible Range Arising from Excimer Formation. *The Journal Of Physical Chemistry C*, 119(34), 20085-20090. <https://doi.org/10.1021/acs.jpcc.5b04529>
- [17] Liu, F., Cao, Y., Yi, M., Xie, L., Huang, W., & Tang, N. et al. (2013). Thermostability, Photoluminescence, and Electrical Properties of Reduced Graphene Oxide–Carbon Nanotube Hybrid Materials. *Crystals*, 3(1), 28-37. <https://doi.org/10.3390/cryst3010028>.