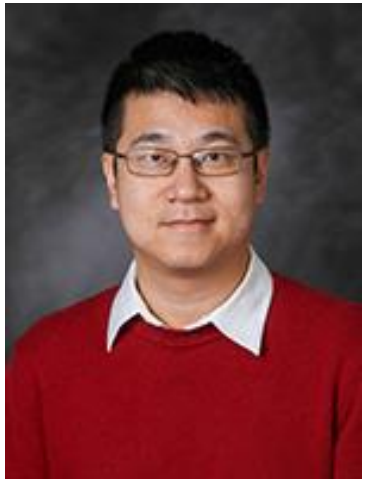


Dr. Tao Yu

A Friend, Mentor, and Supervisor

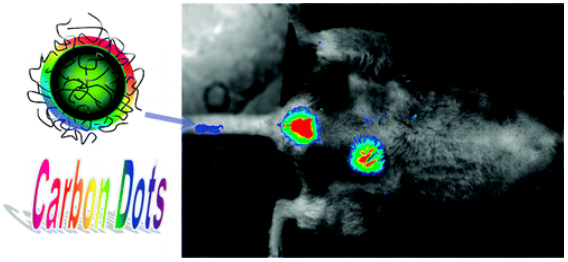
April 18, 1982 - June 13, 2021

Understanding the Optoelectronic Properties of N-doped Graphene QDs

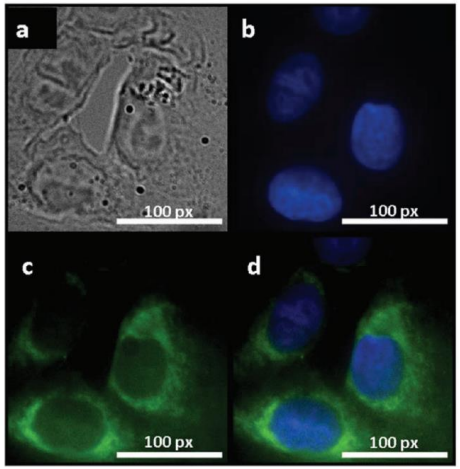
Mohammed A. Jabed
Postdoctoral Researcher
Department of Chemistry
University of North Dakota

Graphene Quantum Dots (GQD)

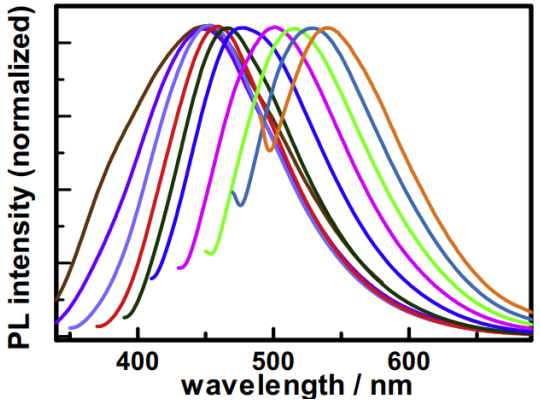
→ GQD and its derivatives are water soluble.[1]



Graphene/Carbon quantum dots are relatively non-toxic or low cytotoxic.[2]



Fluorescent image of human breast cancer cell after incubation with green GQDs.[3]



Easy and efficient tunability.[4]

1. Zhu et al., *RSC Adv*., 2012, 2, 2717–2720
2. Yang et al., J. *Am. Chem. Soc.* 2009, 131, 32, 11308–11309
3. Peng et al., *Nano Lett.* 2012, 12, 2, 844–849
4. Dong et al., *Carbon*, 50 (2012) 4738-4743

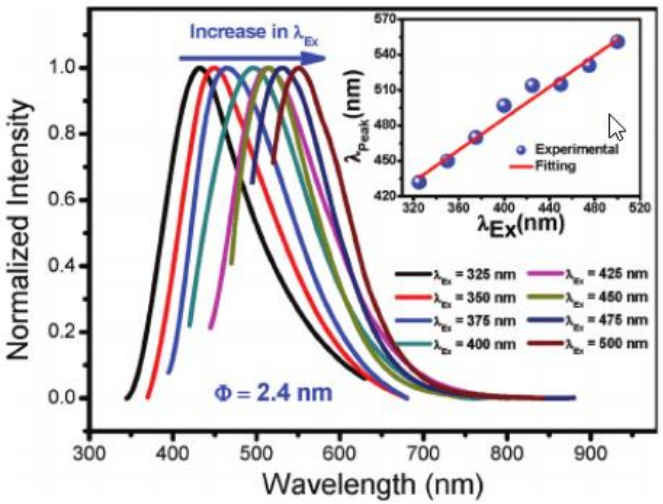
Photoluminescence Mechanism of G QDs and its Derivatives

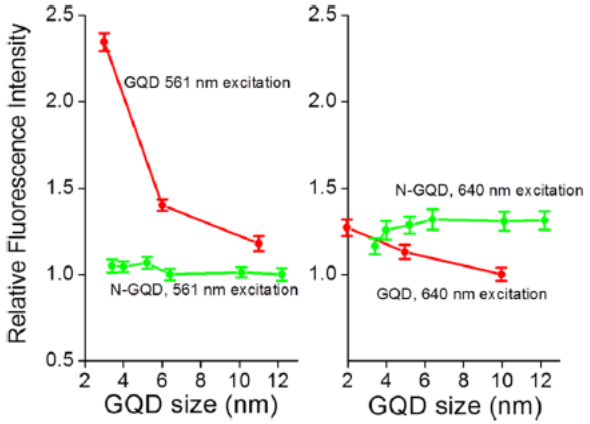
Challenges:

☹ Edge Effects

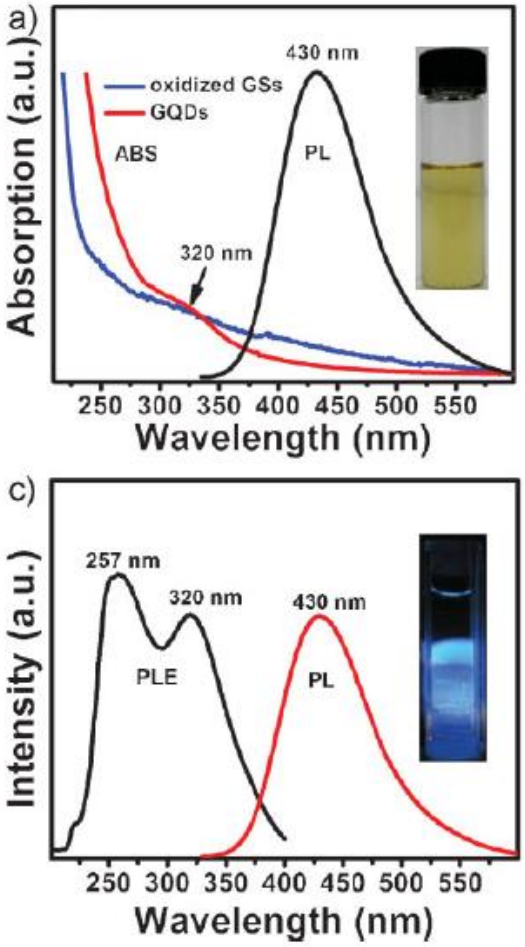
☹ Low quantum yield

☹ Lack of control on PL mechanism





The average fluorescence intensity of non-doped (red line) and N-doped (green line) GQDs.

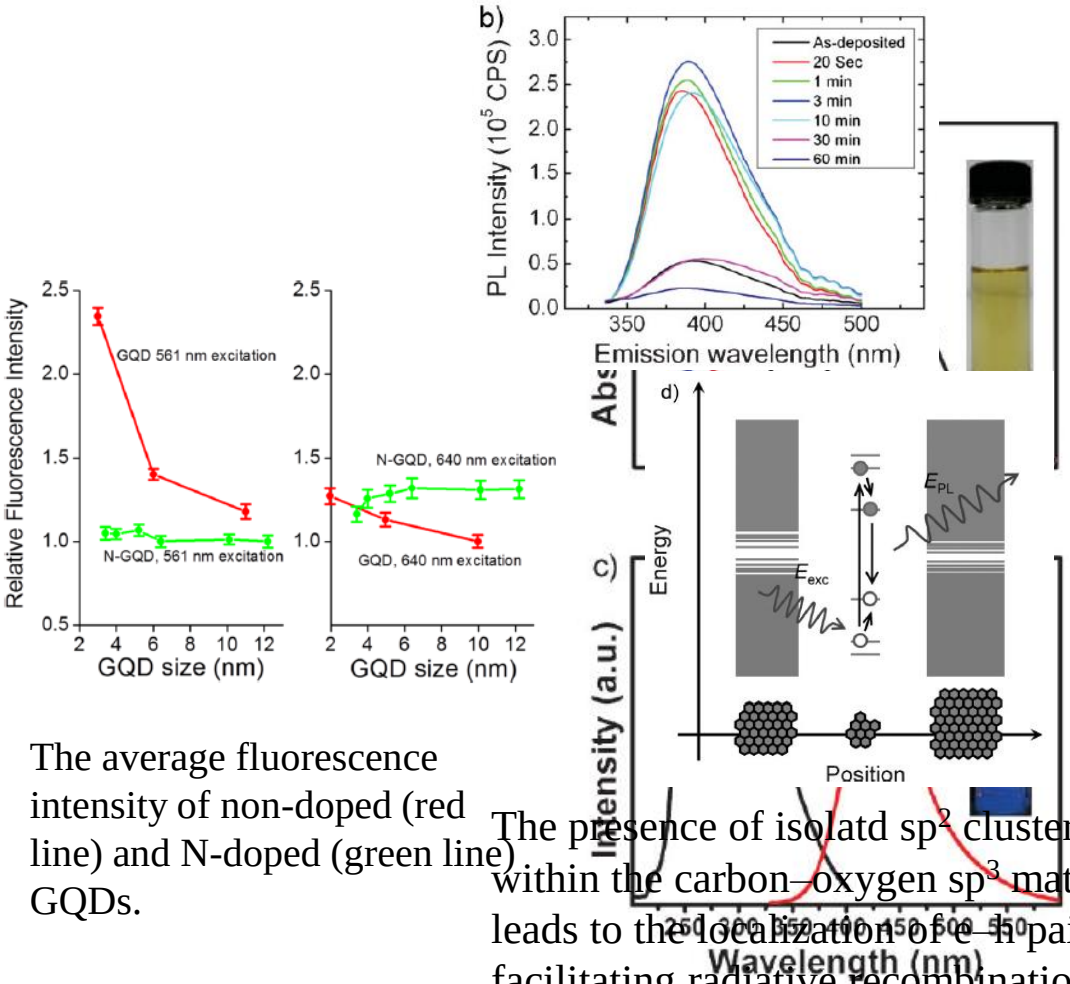


Tang et al., *Part. Part. Syst. Charact.* **2013,** *30* (6), 523-531

Das et al., *Phys. Chem. C* **2015,** *119* (31), 17988-17994

Pan et al., *Adv. Mater.* **2010,** *22* (6), 734-738

Photoluminescence Mechanism of G QDs and its Derivatives



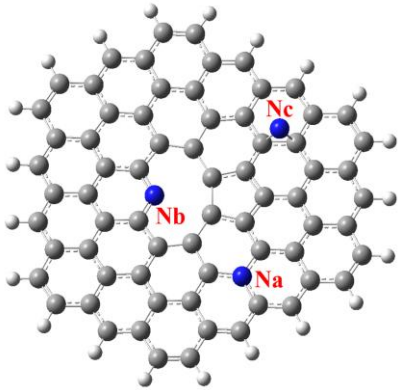
The average fluorescence intensity of non-doped (red line) and N-doped (green line) GQDs.

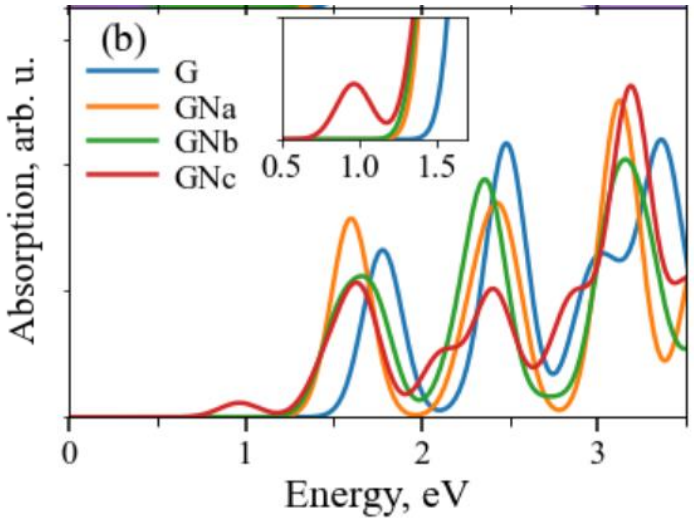
Das et al., *Phys. Chem. C* **2015,** *119* (31), 17988-17994

The presence of isolatd sp^2 clusters within the carbon–oxygen sp^3 matrix leads to the localization of e–h pairs, facilitating radiative recombination

Pan et al., *Adv. Mater.* **2010,** *22* (6), 734-738
Eda et al, Adv. Mater. 2010, 22, 505–509

Photophysical Properties of the N-doped Graphene

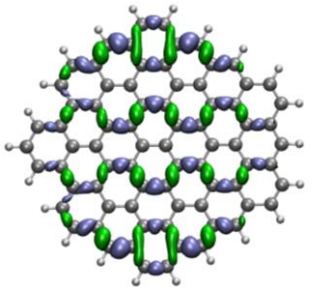




Methodology:
- DFT & TDDFT
- PBE0 functional
- Water solvent

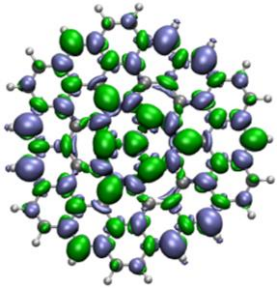
S_1

G



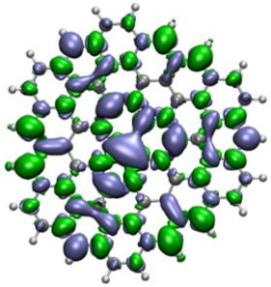
f=0.752
Δ*r* =1.78

GNa



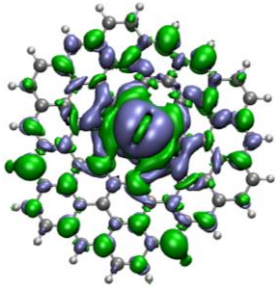
f= 0.00
Δr =0.756

GNb



f= 0.00
Δr =0.65

GNc



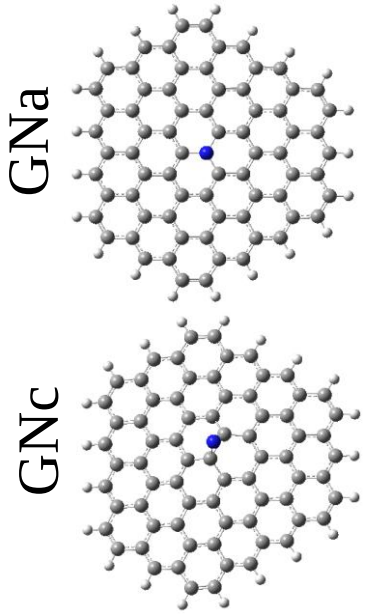
f= 0.00
Δr =0.49

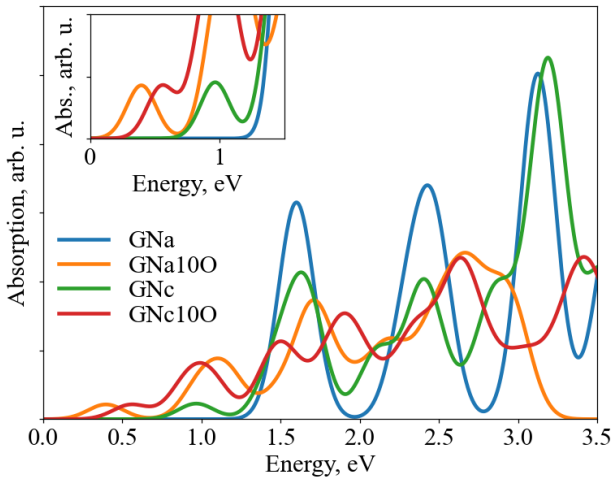
Charge Transfer Length:

$$\Delta r = \frac{\sum_{mn} K_{mn}^2 \, | \langle \varphi_n | r | \varphi_n \rangle - \langle \varphi_m | r | \varphi_m \rangle |}{\sum_{mn} K_{mn}^2}$$

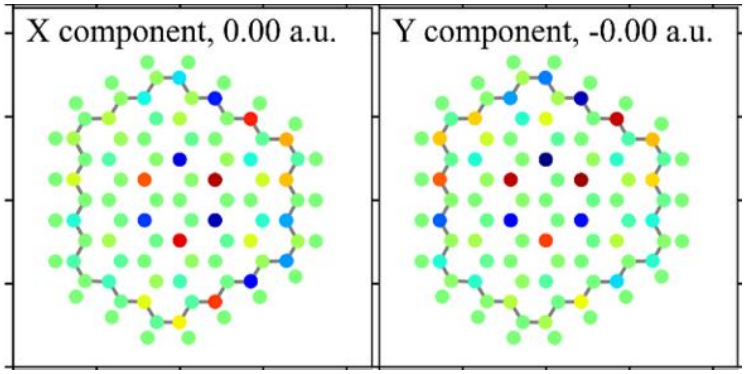
- N-doping and edge oxidation red-shift the lowest energy absorption band.

Photophysical Properties of the N-doped Graphene Oxide

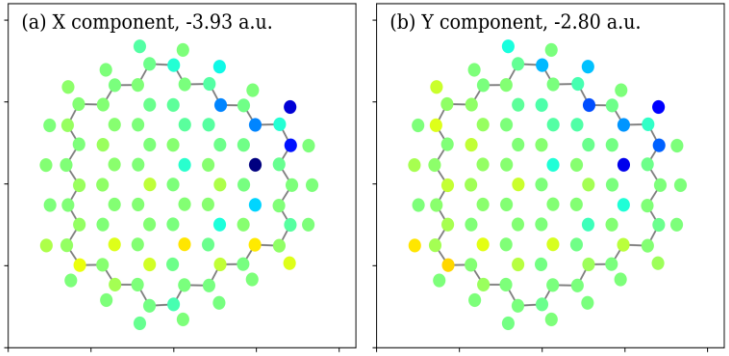




GNa



GNa10O



- The lowest energy transition in N-doping GQD and edge oxidized GQD are dark.
- The redistribution of transition dipole moment in oxidized N-dope graphene would increase the total transition dipole.

Mohammed A. Jabed, Julia Zhao, Dmitri Kilina, Tao Yu, A Comprehensive Understanding of Light Absorption Properties of the N-Doped Graphene Oxide Quantum Dots with TD-DFT, ***J. Phys. Chem. C 2021, 125, 27, 14979–1499***

Simulation of PL Spectra

Oscillator Strength between ***i*** and ***j***

$$f_{ij} = \frac{4\pi m_e \omega_{ij}}{3he^2} \left|\vec{D}_{ij}\right|^2$$

Excites state lifetime and Spontaneous emission -

$$\tau = \frac{4\pi^2 c^3 \epsilon_0 m_e}{f_{ij}\omega_{ij}^2 e^2}$$

Transition of an electron from orbital *a* to orbital *b*

$$\dot{\rho}_{jk} = -\frac{i}{\hbar}\sum_l \left(F_{jl}\rho_{lk} - \rho_{jl}F_{lk}\right) + \left(\frac{\mathrm{d}\rho_{jk}}{\mathrm{d}t}\right)_{\mathrm{diss}}$$

Nonadiabatic couplings

$$V_{ij}(t) = \frac{1}{\Delta t}\int d\vec{r}\ \varphi_i^{KS^*}\left(\left\{\vec{R}_I(t)\right\},\vec{r}\right)\varphi_j^{KS}\left(\left\{\vec{R}_I(t+\Delta t)\right\},\vec{r}\right)$$

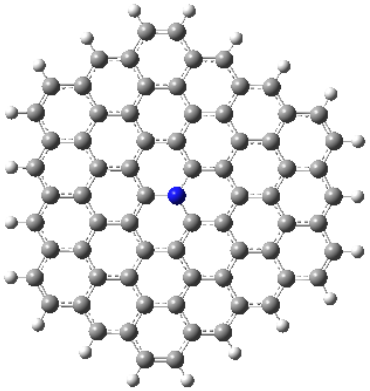
ACF → FFT → Redfield Tensor

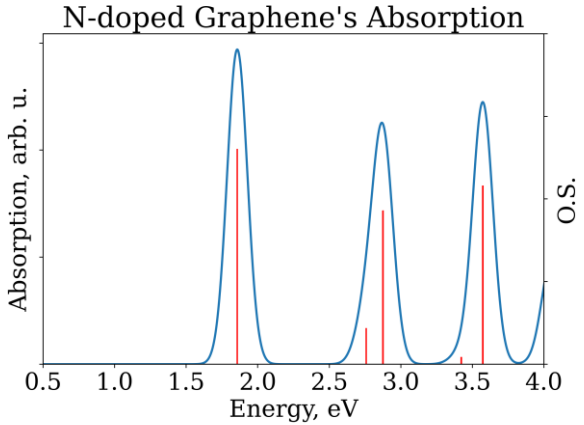
$$\mathrm{R}_{ijkl} = \Gamma^{+}_{ljik} + \Gamma^{-}_{ljik} - \delta_{jl}\sum_m \Gamma^{+}_{immk} - \delta_{ik}\sum_m \Gamma^{-}_{jmml},$$

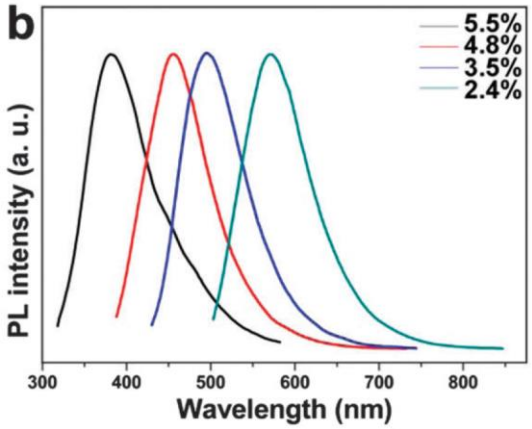
$$\left(\frac{d\rho_{jk}}{dt}\right)_{diss} = \sum_{lm} R_{jklm}\rho_{lm}$$

J. Phys. Chem. Lett. 2013, 4, 2906−2913
J. Phys. Chem. Lett. 2010, 1, 1073–1077

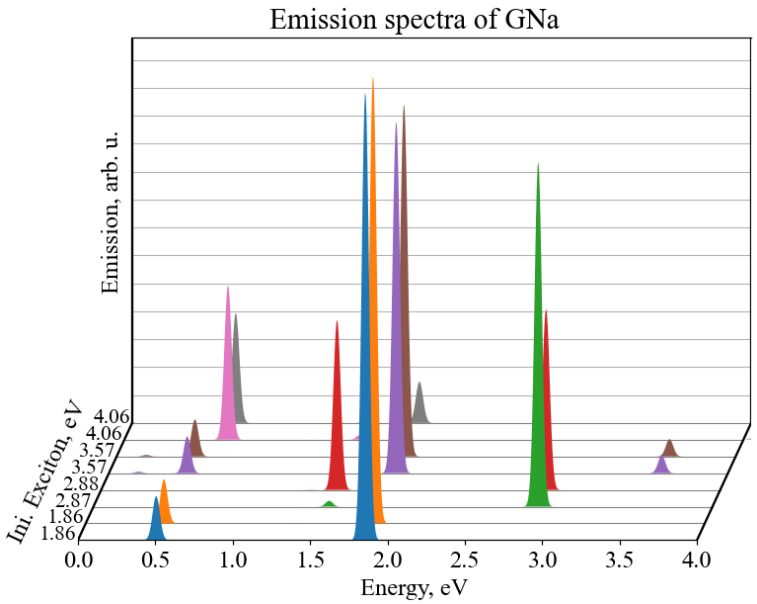
PL of N-dope Graphene

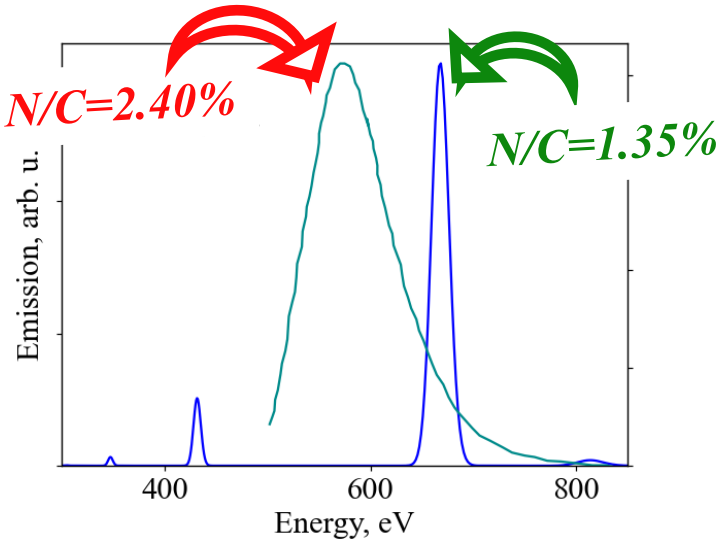






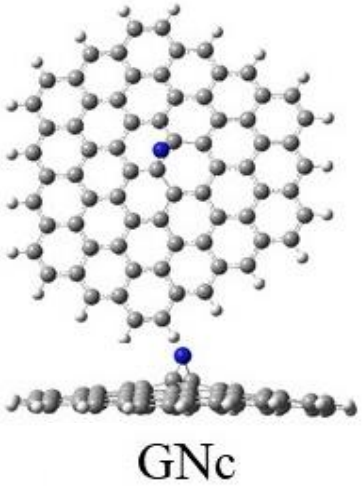
N concentration in N-doped Graphene and PL spectra[1]

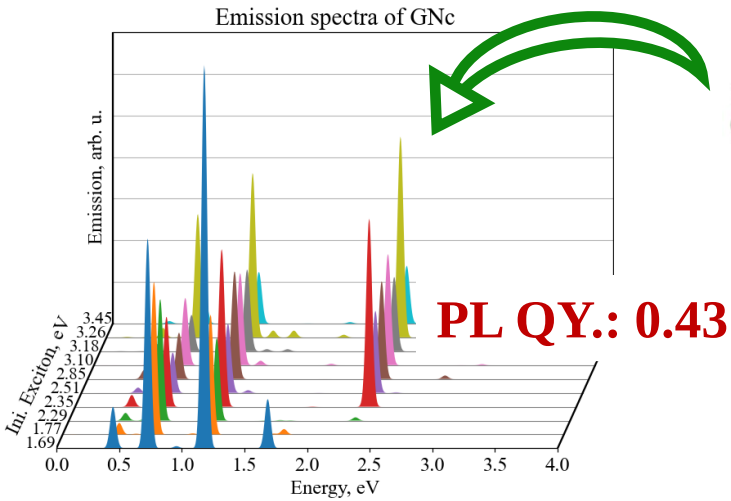


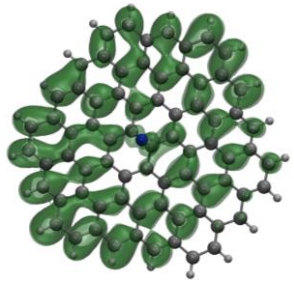


1. *J. Mater. Chem. C*, 2015, 3, 8810-8816

N Chemisorption on Graphene QDs

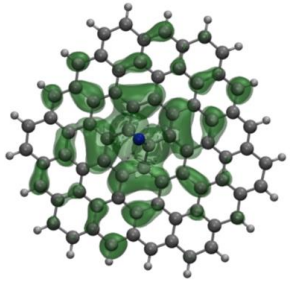




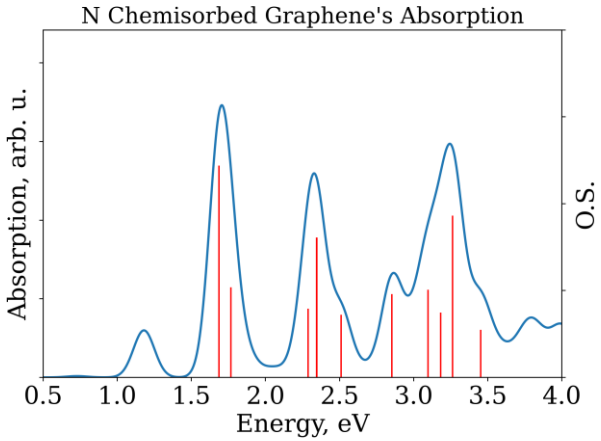


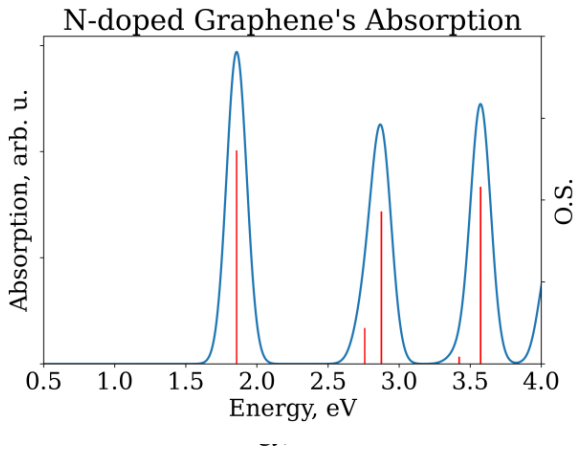
LU+1

PL QY.: 0.43



HO-1

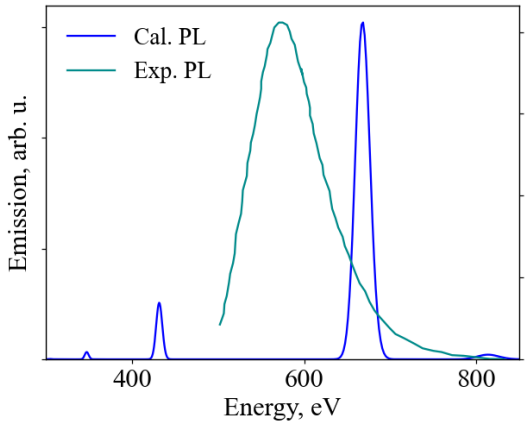


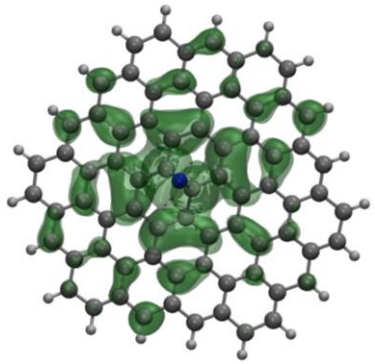


$$\tau = \frac{4\pi^2 c^3 \epsilon_0 m_e}{f_{ij}\omega_{ij}^2 e^2}$$

Conclusion

- Depending on doping concentration, Graphitic N-doping redshift the absorption and emission energy.
- Edge oxidation increases the structural deformation, hence thermal relaxation.
- N Chemisorption creates localized but emissive hole states





HO-1

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- Late Dr. Tao Yu, UND
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THANK YOU