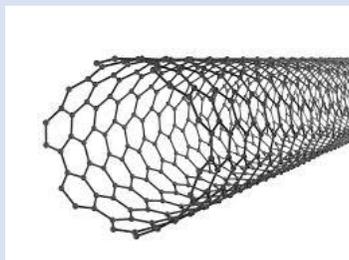


UNIVERSITÀ  
DI PARMA

# *OTHERS CARBON NANOSTRUCTURES*

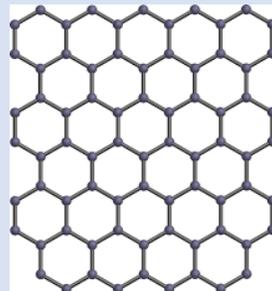
*Giada Battaglioni*

# CNs timeline



**CARBON NANOTUBES**

1991

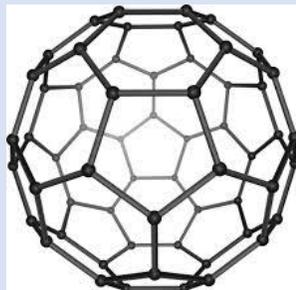


**SINGLE LAYER  
GRAPHENE**

2004

1993

**FULLERENES**



2010s

**GROWTH OF CARBON-BASED  
NANOMATERIALS APPLICATION**

# Overview

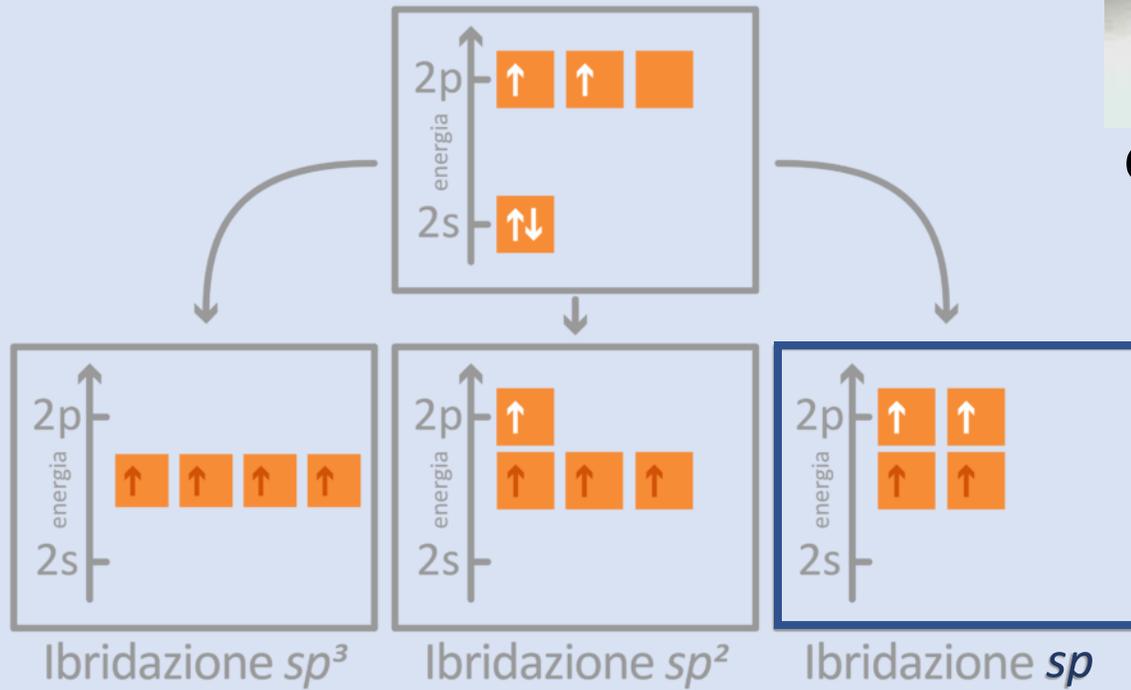
## CARBYNES

- Carbynoids;
- Synthesis of carbynes with Supersonic Cluster Beam Deposition (SCBD);
- Study about the stability of carbynes.

## CARBON DOTS

- Classification:
  - Graphene quantum dots
  - Carbon quantum dots
  - Carbon nanodots
  - Carbonized polymer dots
- Quantum confinement
- Optical properties
- Synthesis
- Applications

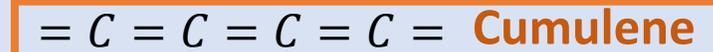
# Carbynes



Chaoite

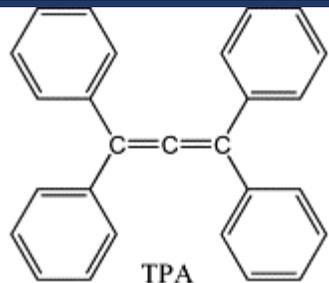


Bavaria crater

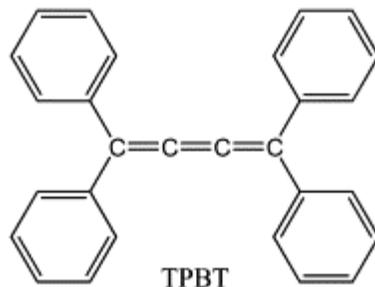


# Carbynoids

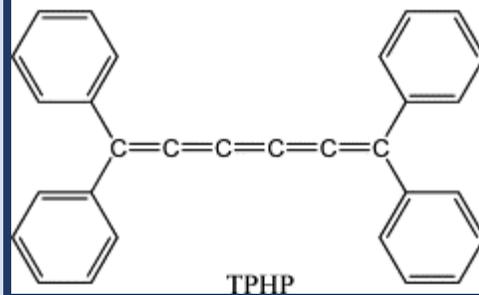
Tetraphenylallene  
(TPA)



Tetraphenylbutatriene  
(TPBT)



Hexapentaene  
(TPHP)

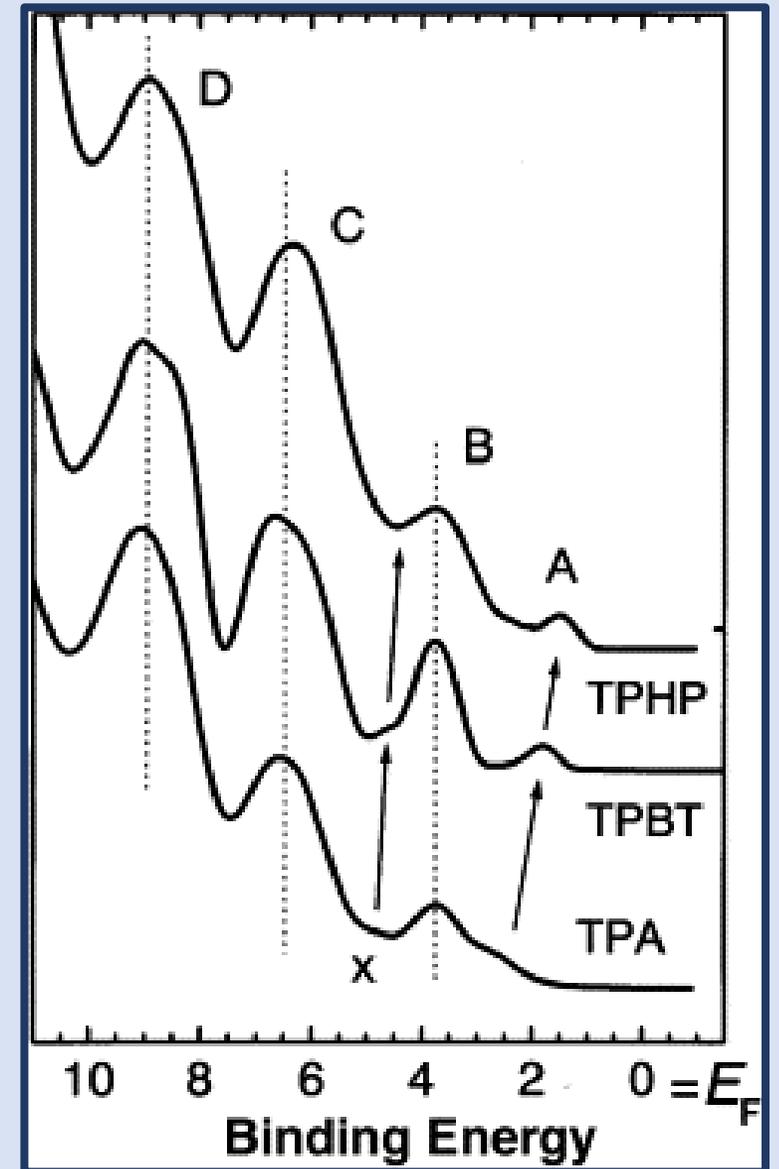
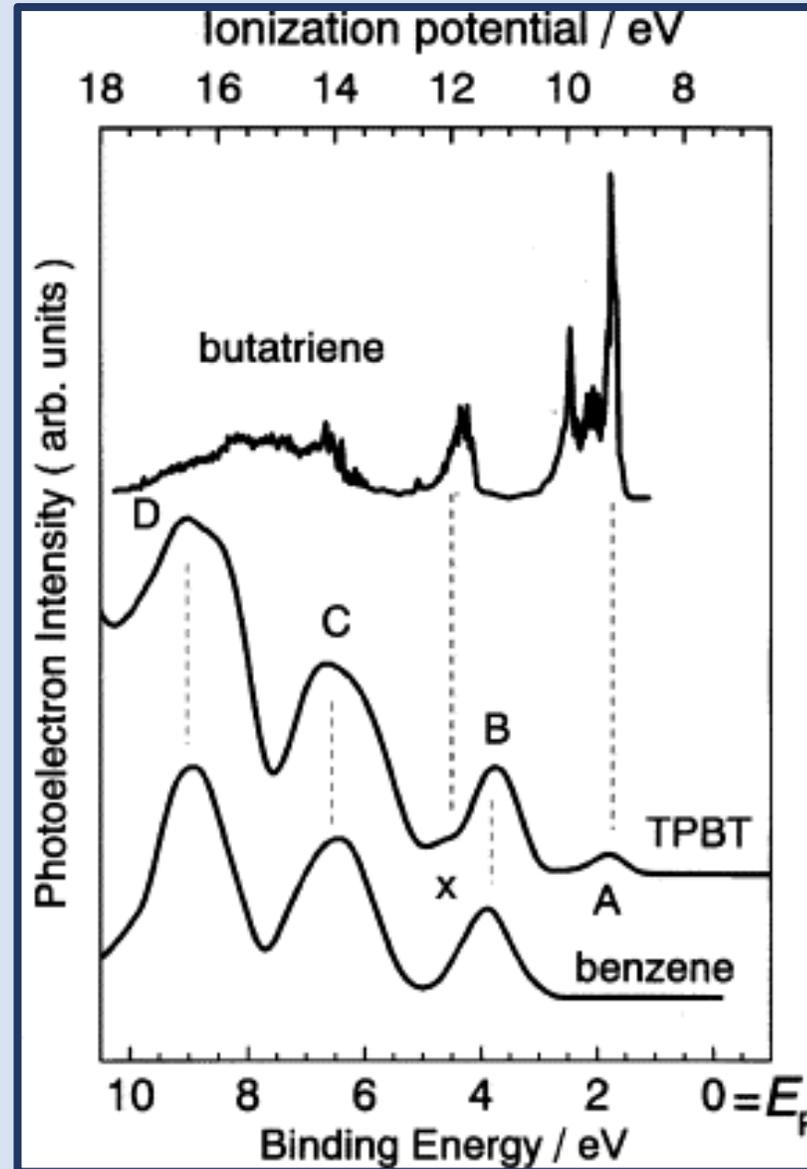


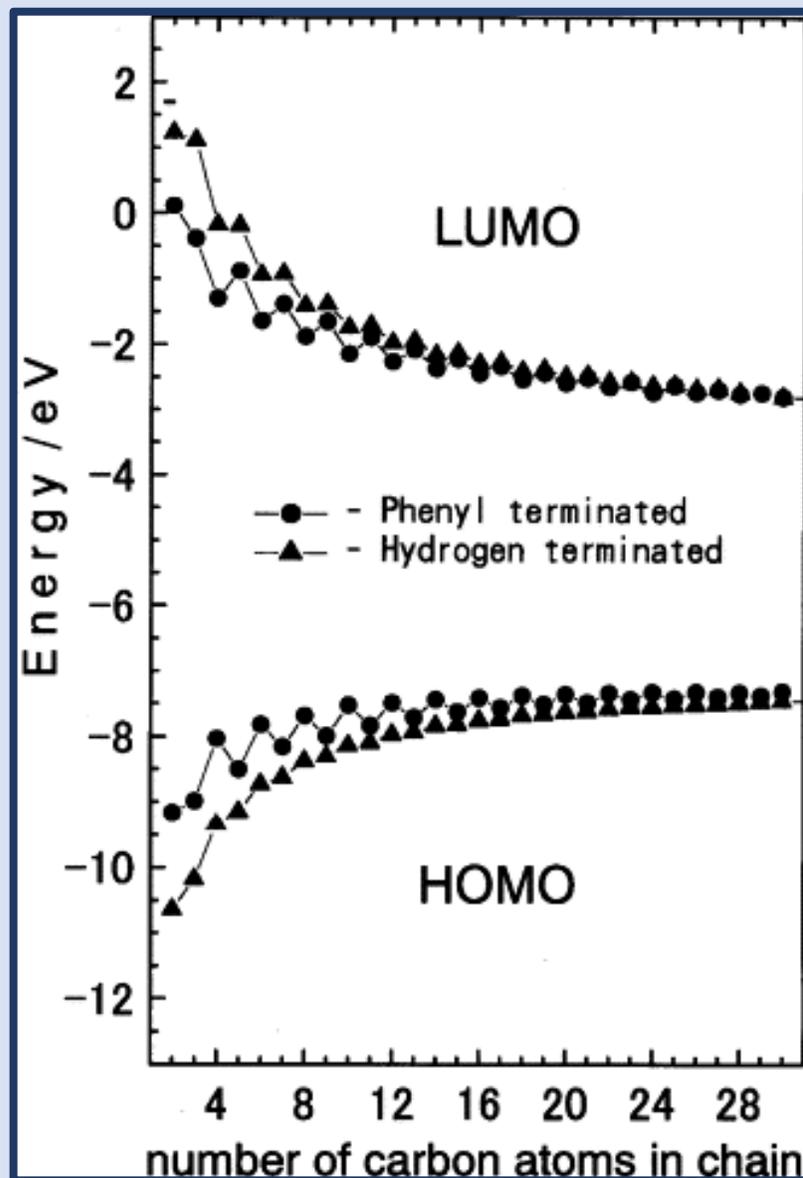
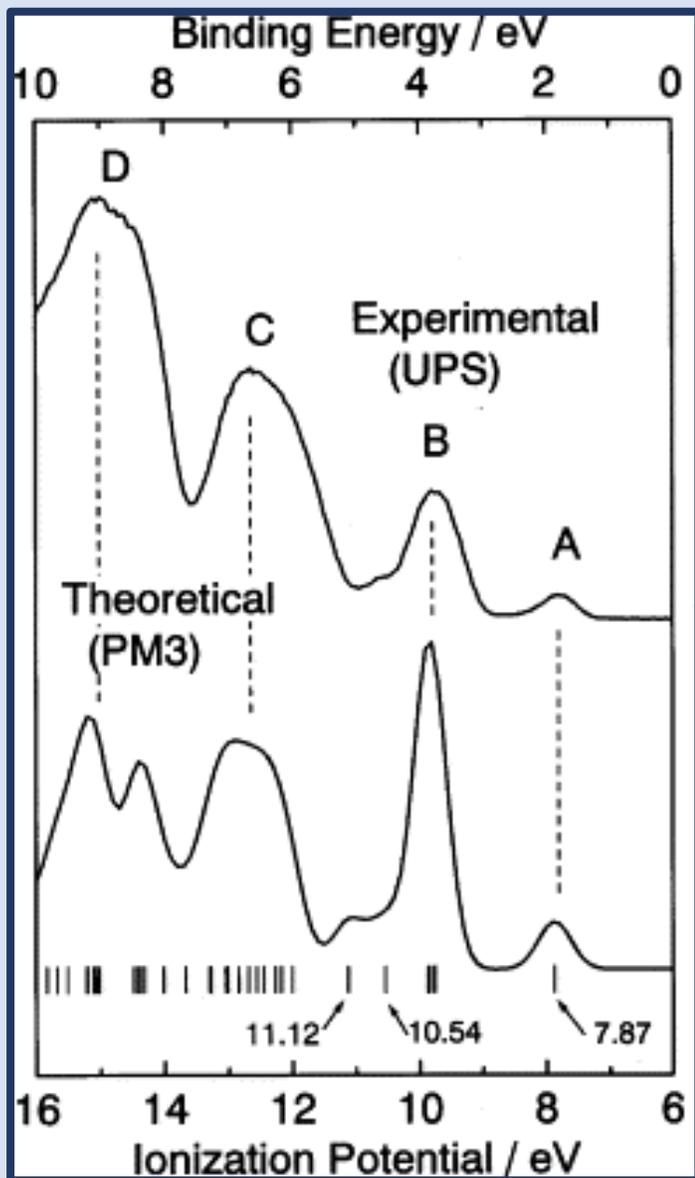
## Experimental

- **Photoelectron spectra** were measured with a Kratos XSAM-800 photoelectron spectrometer;
- **TPA, TPBT, TPHP films have been prepared** by vacuum deposition onto a gold disk;
- The **Molecular Orbital calculation** was carried out.

**Comments:**

- semi-conductive nature
- Structures A and x are attributed to the chain part;
- structures B–D are attributed to phenyl groups;
- Structure A moves toward lower binding energy side in accordance with extension of the chain length.

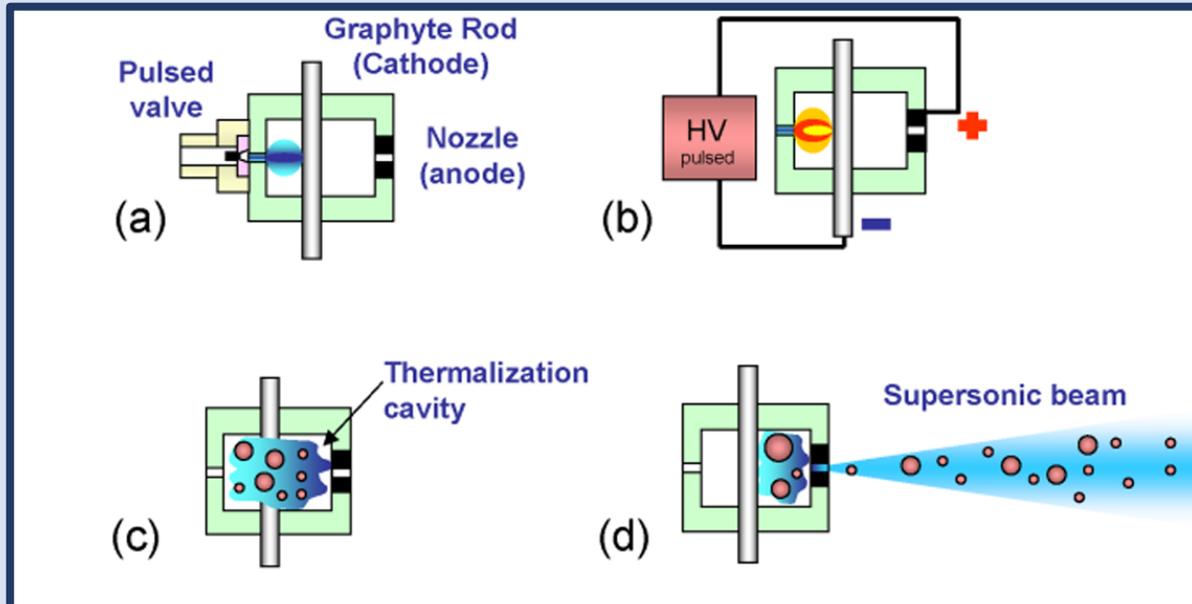




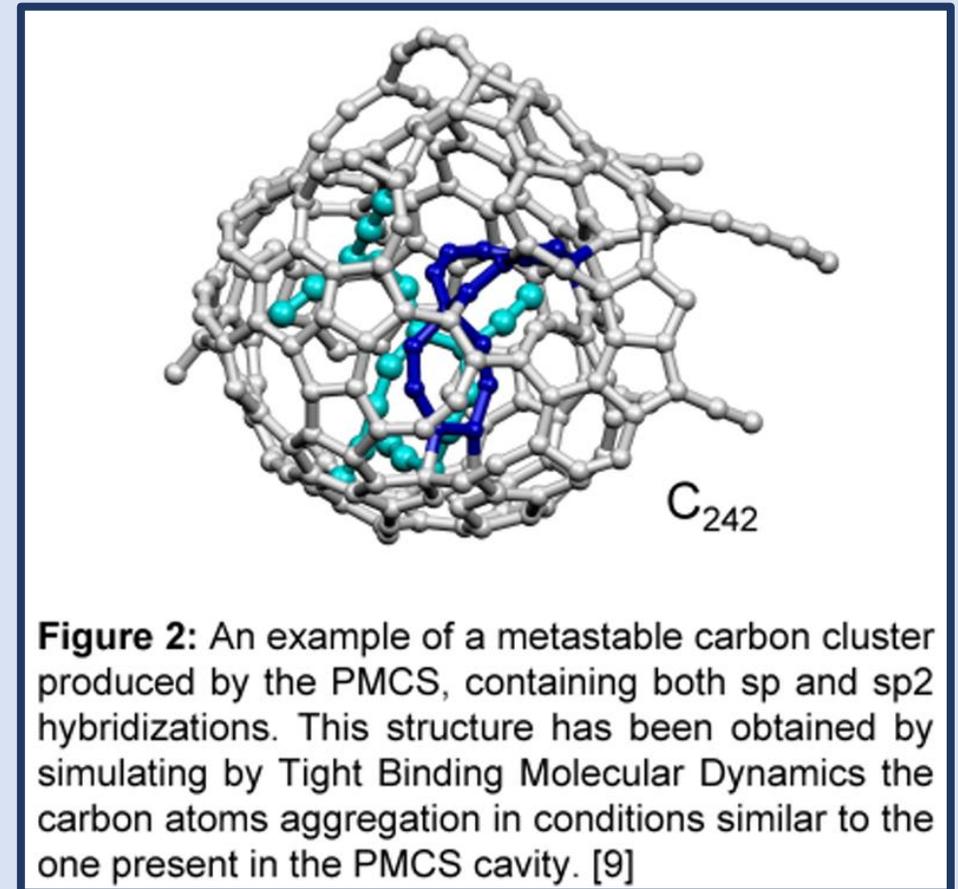
### Conclusions:

- Theoretical spectrum reproduces experimental one very well;
- HOMO levels becomes shallower in accordance with increase of chain length;
- Quantum well.

# Supersonic Cluster Beam Deposition

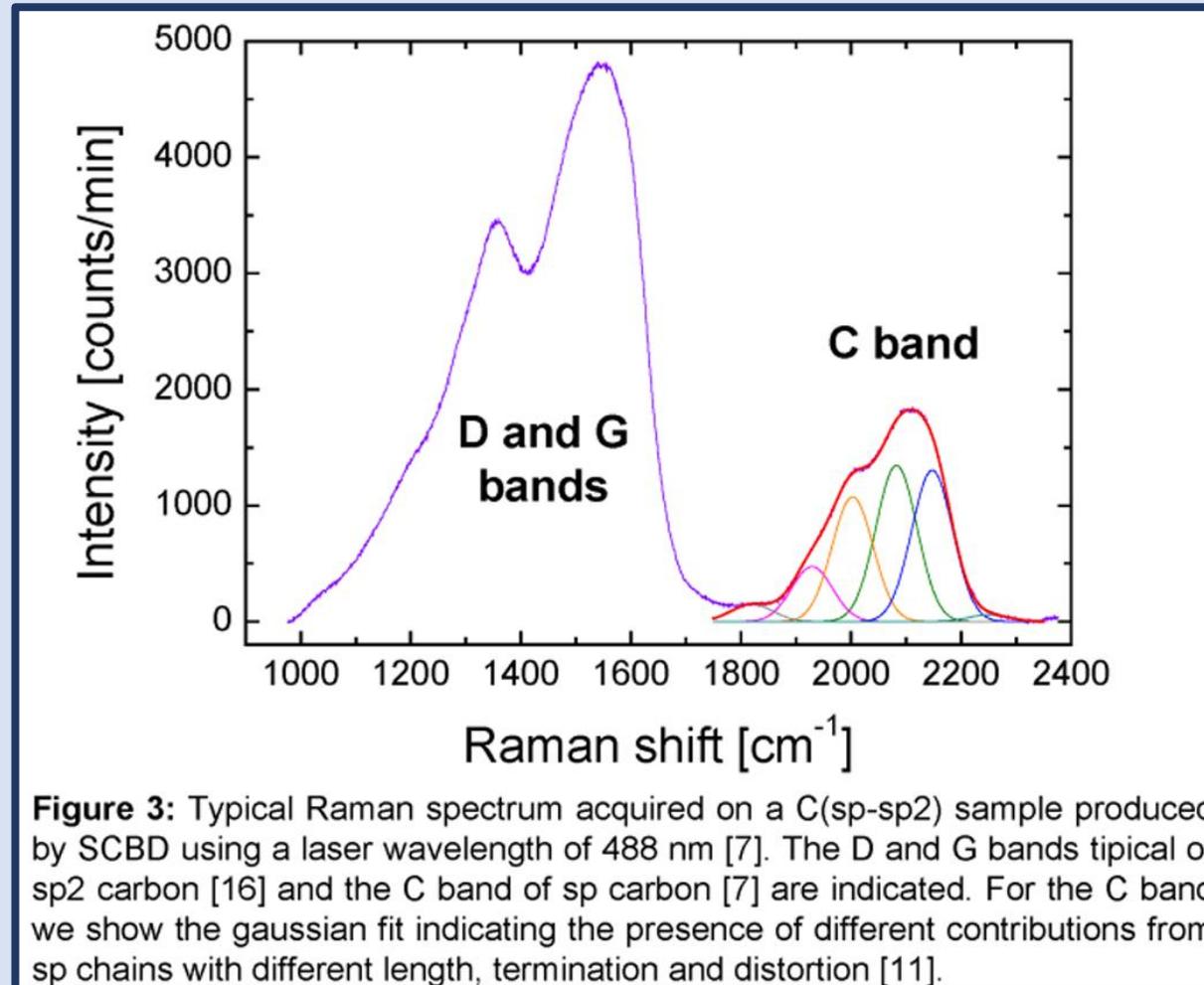


**Figure 1:** Schematic representation of the PMCS principle of operation. At every source pulse: (a) He at high pressure (50 Torr) is injected in the source cavity; (b) High voltage is applied to the graphite cathode igniting an intense discharge between the electrodes. The micro-plasma of ionized helium sputters a small area of cathode surface; (c) The carbon atoms and He thermalize and cluster aggregation occurs; (d) The mixture of He and carbon clusters expand through the nozzle in the supersonic beam. [8]



**Figure 2:** An example of a metastable carbon cluster produced by the PMCS, containing both sp and sp<sup>2</sup> hybridizations. This structure has been obtained by simulating by Tight Binding Molecular Dynamics the carbon atoms aggregation in conditions similar to the one present in the PMCS cavity. [9]

# Raman Spectroscopy



# Conclusions about carbynes

- Free energy carbynes  $\gg$  free energy of graphite and diamond.
- Carbynes needs to contain additional components to become stable
- if the films are exposed to oxygen, a complete decay of the chains is observed

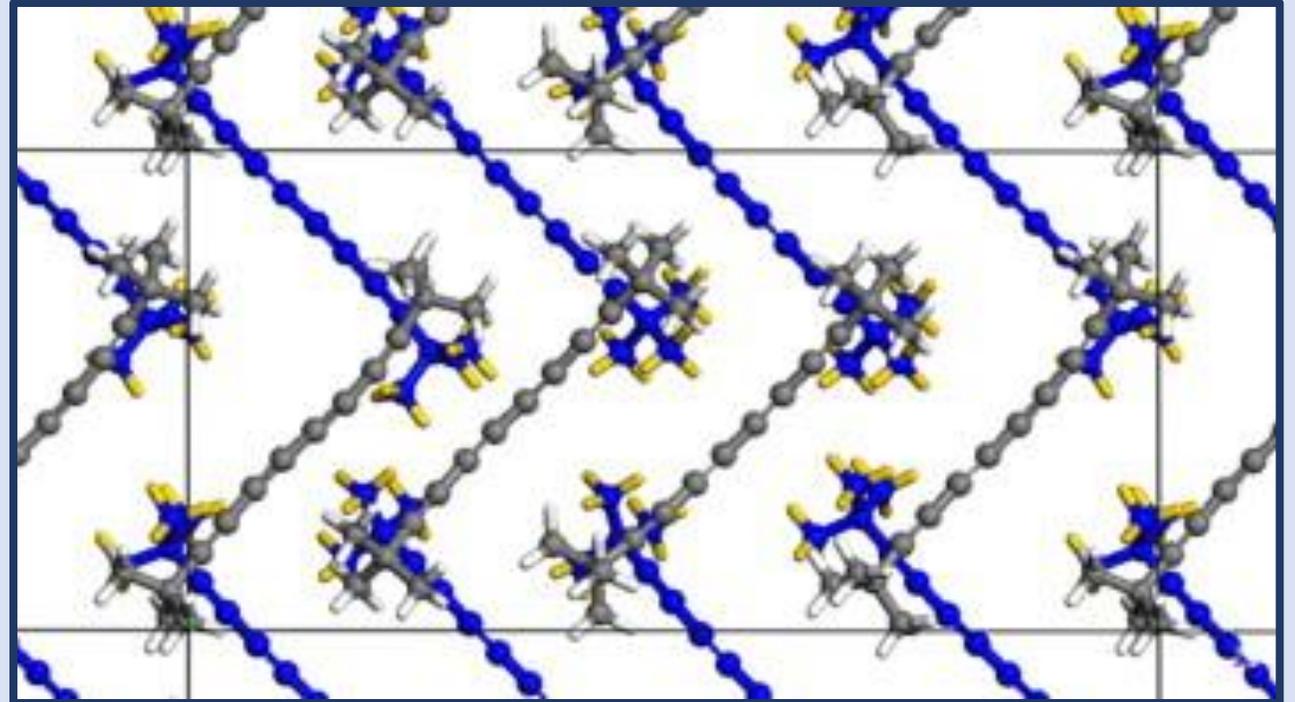
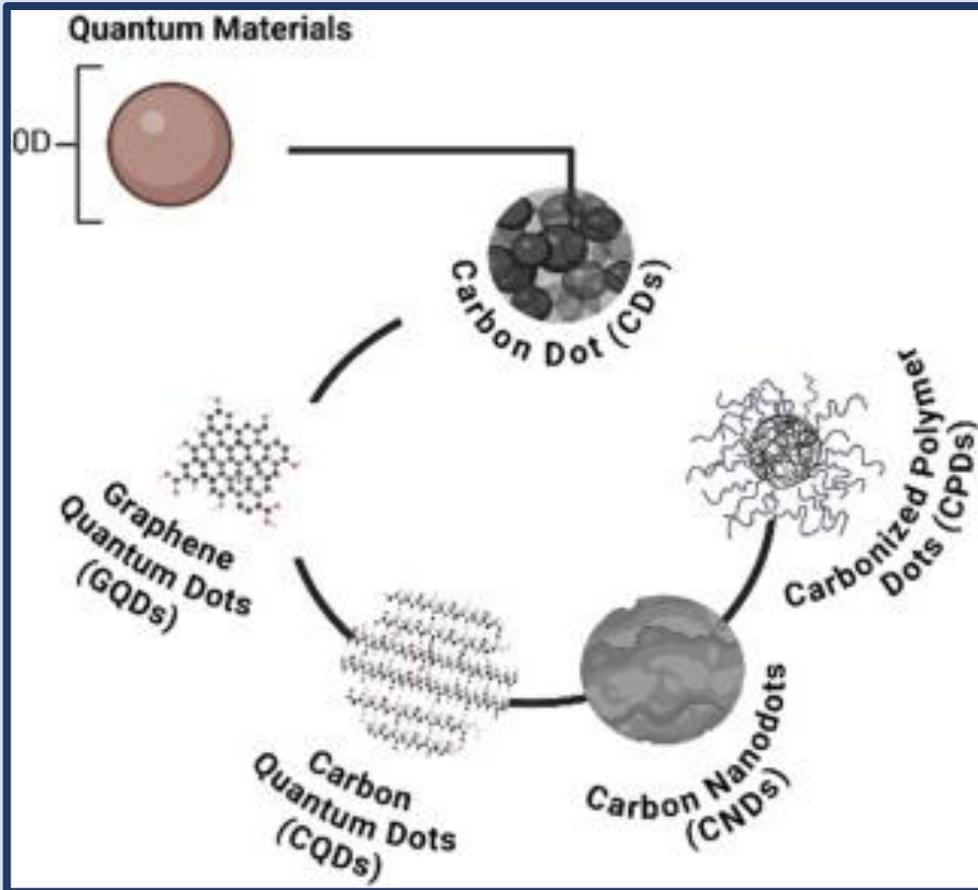


Fig. 18. (0 0 1) Projection of the computationally optimized crystal structure of the solid (tert-butyl) $C_8$ (tert-butyl) carbynoids. The structure consists of alternating layers of molecules with different orientation, indicated by medium dark (grey) C and white H atoms; and dark (blue) C and light (yellow) H atoms, respectively.

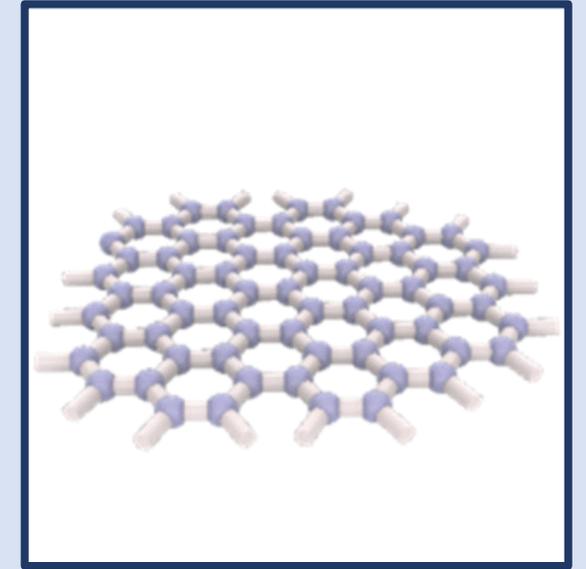
# Carbon dots



- 0-dimensional nanoparticles
- Optical and electrical properties comparable to traditional quantum dots;
- Non-toxic because they are carbon based;
- Suitable for a broader range of applications.

## GRAPHENE QUANTUM DOTS (GQDs)

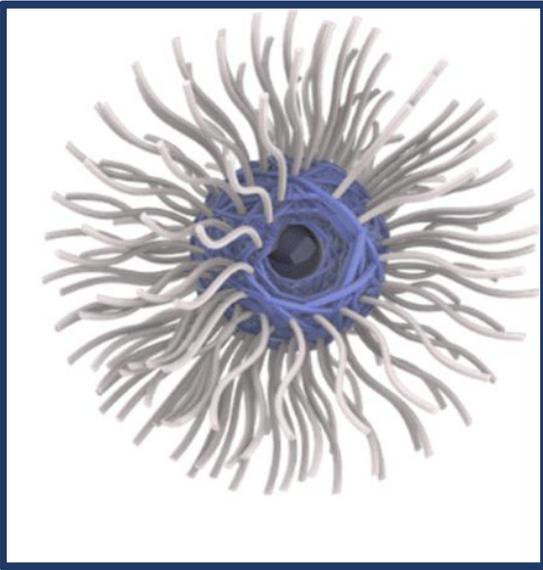
- Graphene lattice structure;
- Diameter is similar to 100nm and layer's thick is less than 10nm;
- Behave as semiconductors or insulators.



## CARBON NANODOTS (CNDs)

- Amorphous core;
- Despite their lack of crystalline structure carbon nanodots exhibit fluorescent properties;
- Comparison with CQDs



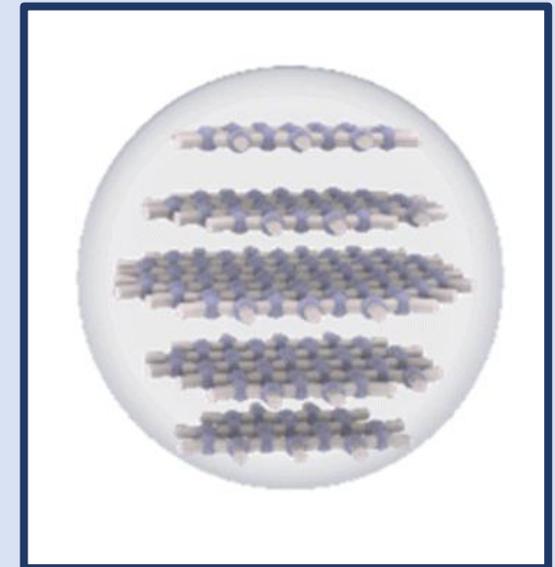


### CARBONIZED POLYMER DOTS (CPDs)

- Hydrophilic polymeric chains wrap a hydrophobic core
- Presence of abundant functional groups and short polymer chains on the exterior
- Highly crosslinked core

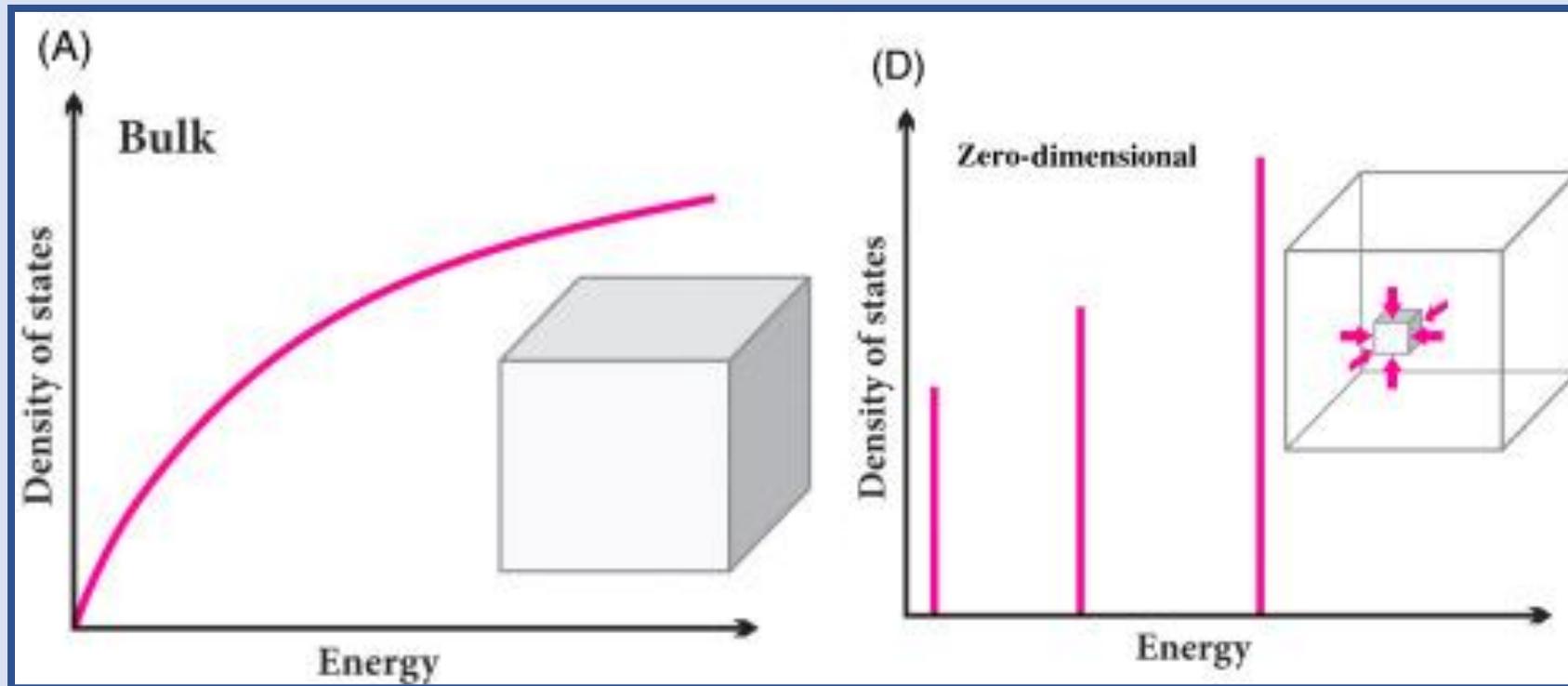
### CARBON QUANTUM DOTS (CQDs)

- These nanoparticles are composed of graphitic or turbostratic carbon with an  $sp^2$  configuration;
- The cores are remarkably small, ranging in size from 2 to 3 nm;
- Abundance of functional groups that providing active sites for functionalizing the original carbon quantum dot with various materials.



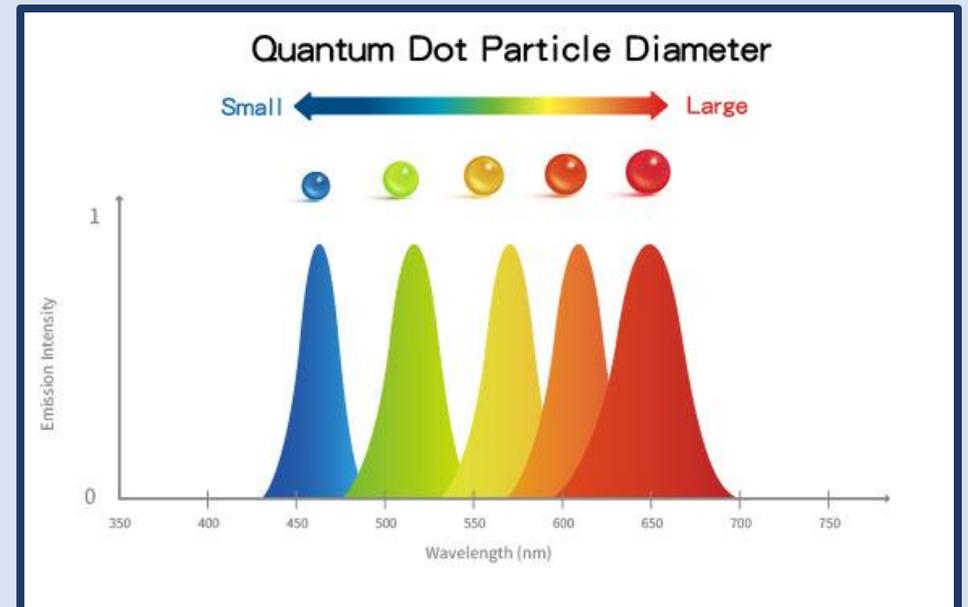
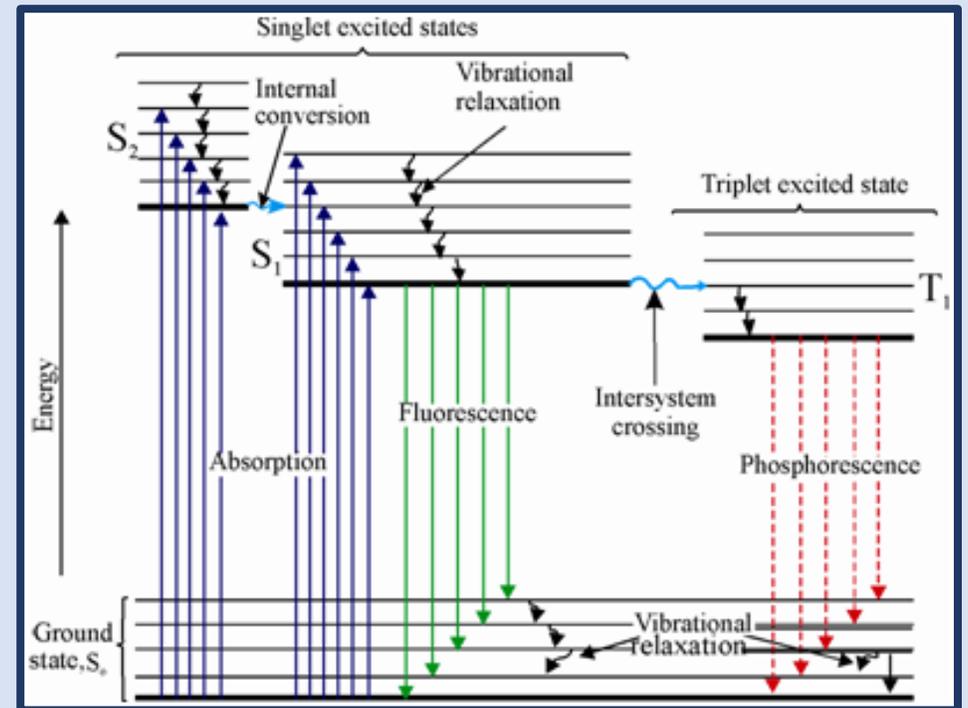
# Quantum confinement

- Concept of « particle in a box»;
- The electronic energy levels become quantized into discrete states;
- Bandgap energy became higher with the decrease of CQDs size.



# Optical properties

- Distinct absorption bands, photoluminescence, fluorescence, and phosphorescence
- Radiative transitions
- Tunable emissions
- Difference between fluorescence and phosphorescence



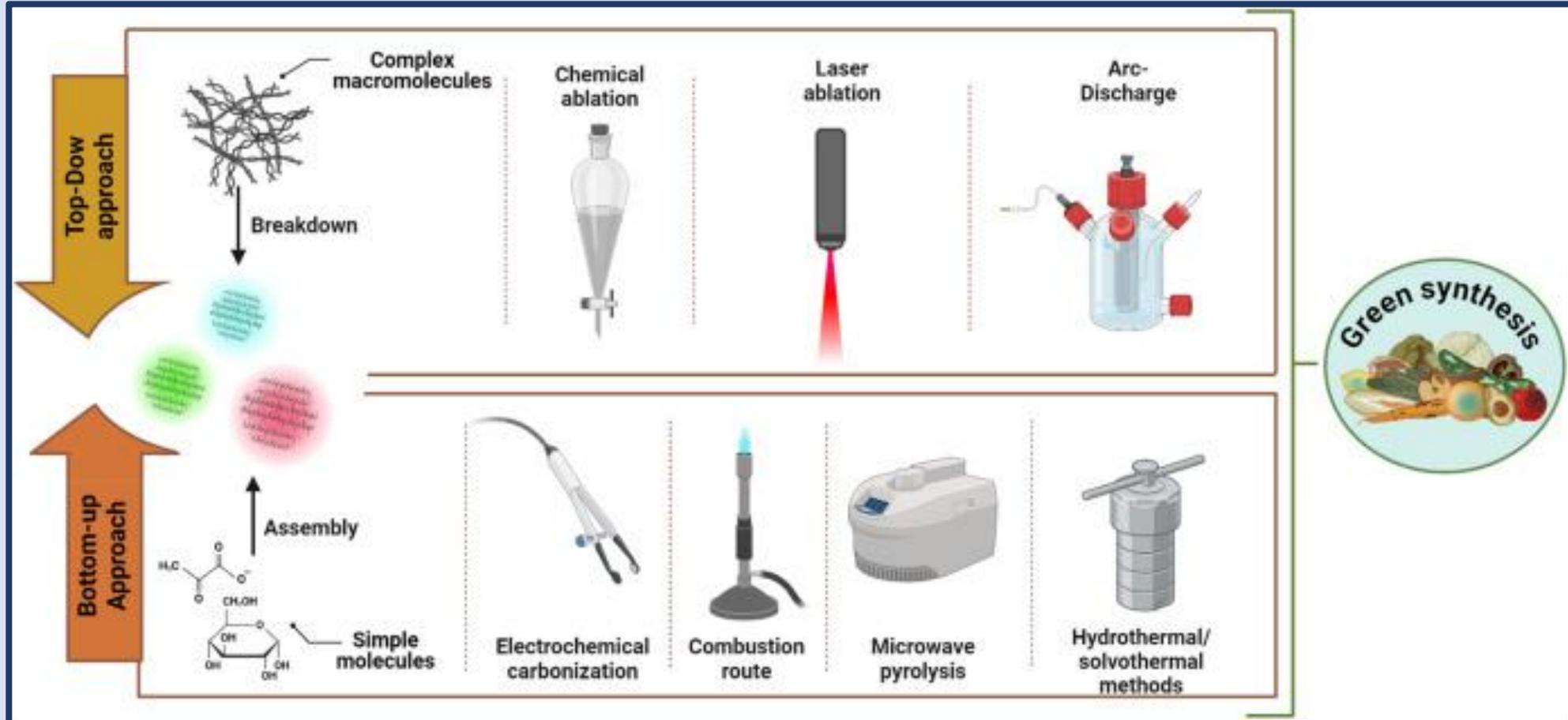
# How to enhance fluorescence?

- **Surface passivation** involves some materials that create a protective layer on the CQD surface

Quantum Yield       $QY = \frac{\text{Number of photons emitted}}{\text{Number of photons absorbed}}$

- **Heteroatom doping** improving properties such as photoreversibility, stability, low toxicity, and biocompatibility;
- **functional group** doping modifies the  $\pi$ - $\pi^*$  energy level which changes the bandgap

# Synthesis

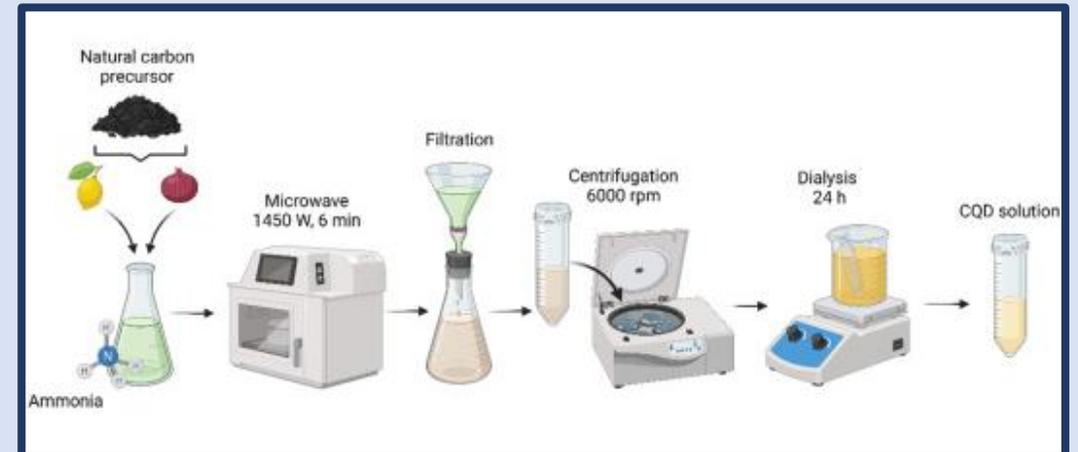
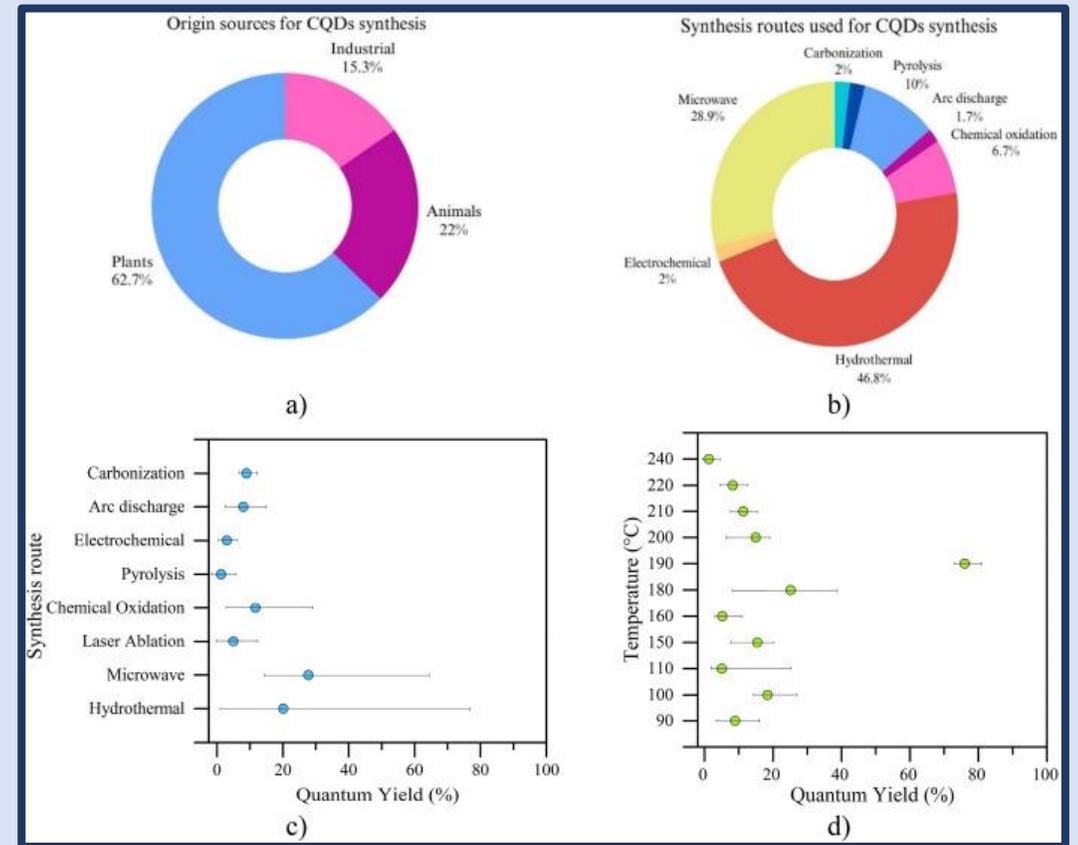


# Microwave pyrolysis

- Using microwave irradiation to induce controlled pyrolytic processes;
- The technique involves **mixing poly(ethylene glycol) (PEG200)** with a **saccharide** (such as glucose, fructose, etc.) in water to create a transparent solution, which is then heated in a microwave oven.

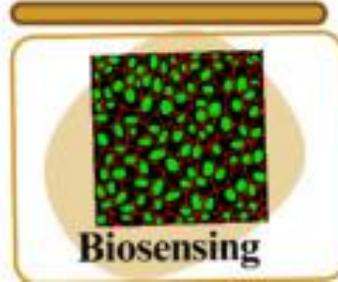
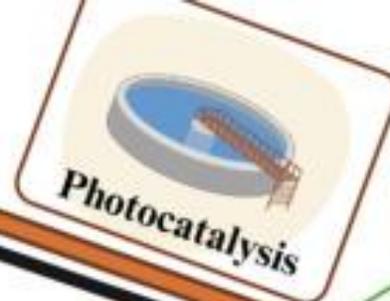
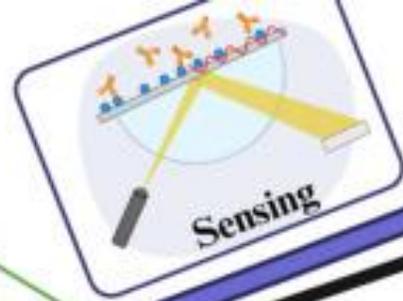
# Green synthesis

- One of the latest approaches to synthesizing CQDs;
- Traditional synthesis protocols are applied with organic waste as the precursors.

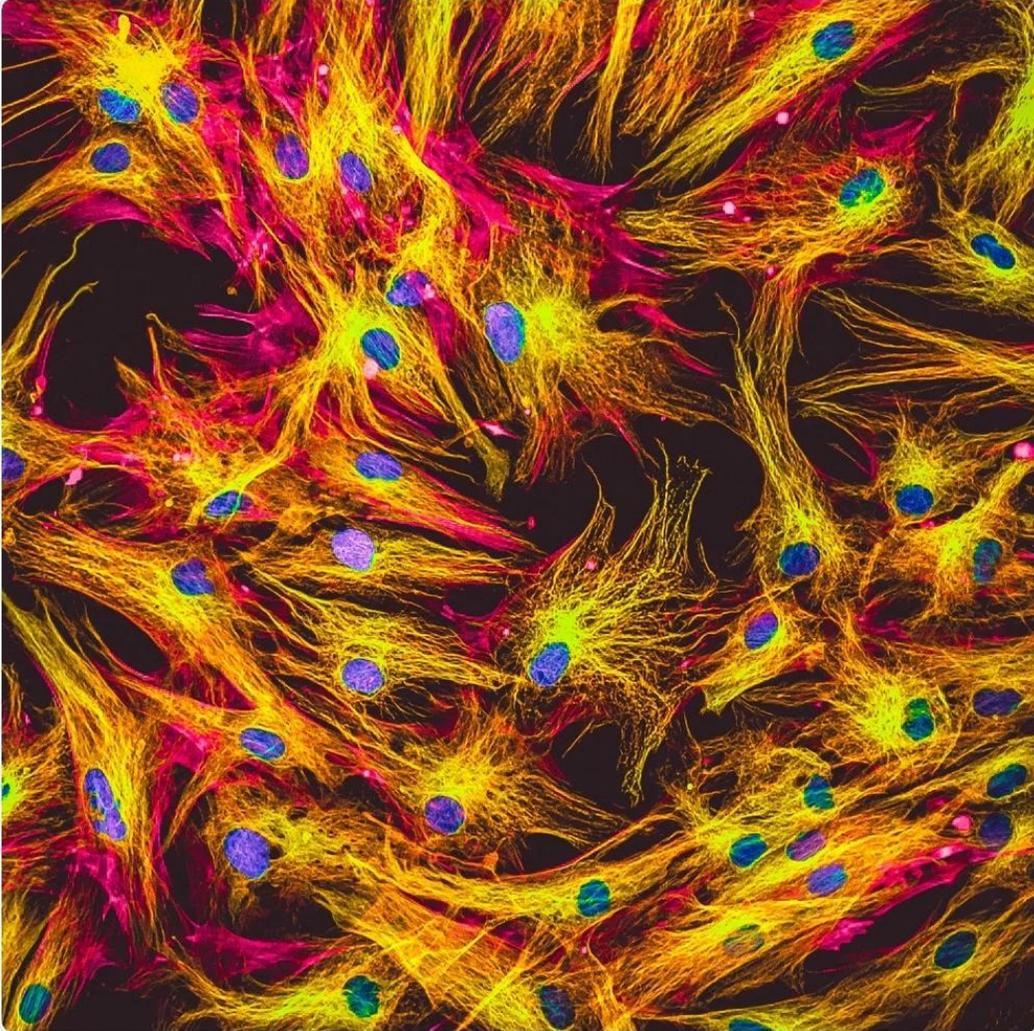


# Carbon Quantum Dots

## Applications



# Bioimaging and biosensing



- High solubility in water, excitation and emission lengths in the visible range, high QYs and photostability make them promising candidates for various applications involving in vivo assays;
- They allow obtaining a luminous contrast background;
- They manage to penetrate cellular structures for detailed observation.
- When the target biomolecule is introduced there is a change in fluorescence, current, or potential, which indicates a successful target detection.

# Photocatalysis

- Important for environmental remediation and water splitting using sunlight
- CQDs could absorb light at long wavelengths
- They can also exchange energy through quenching mechanisms with other species in solution
- Applications in this direction focused on improving the efficiency of titanium oxide by using CQDs.

