Preparation of photoluminescence carbon dots from renewable liquid sources by hydrothermal synthesis

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- Seed germination of mung bean using GO/CDs

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Introduction

Bio-based carbon materials

Algal biomass – Source does not have competition with food crops in land issues – Can be efficiently and productively cultivated in less space.

Bio-oil – Obtained by thermal conversion processes such as fast pyrolysis or hydrothermal liquefaction of all kind of biomass (including algal sources). Unique physical properties (high viscosity, high acidity) and chemical composition (high carbon content along with considerable amounts of nitrogen, oxygen and sulphur contents) can make **bio-oil as a effective source for the preparation of carbon materials.**

Introduction

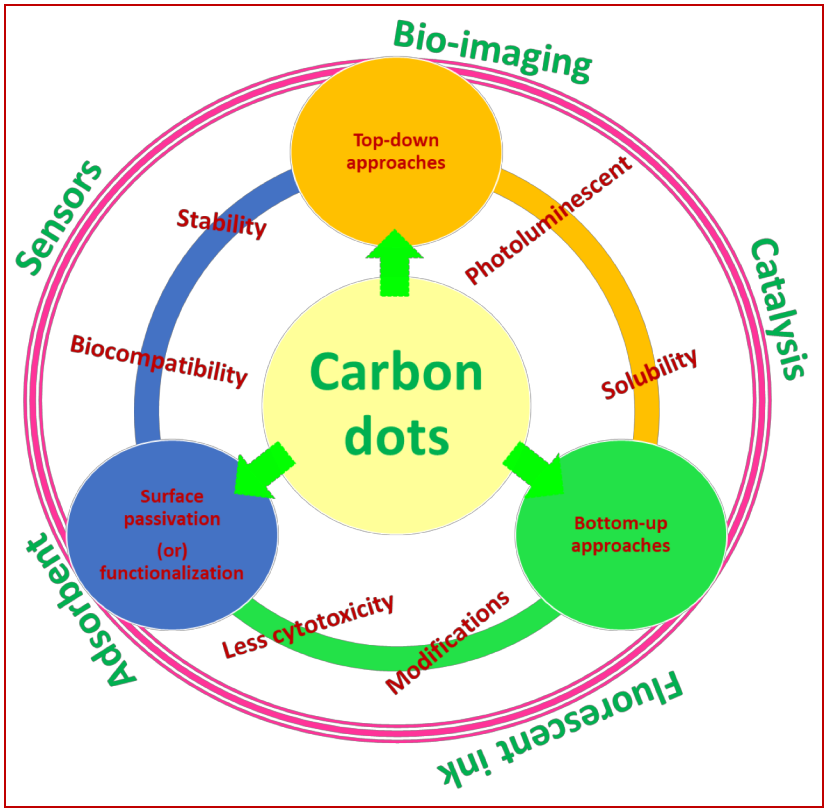
Carbon dots

Carbon dots (CDs) – Unique carbon materials that are fluorescent in nature and have sizes below 10 nm

CDs – show excellent electronic, physicochemical, optical and fluorescence emission properties and also flexible for further modifications.

Due to their **tunable properties** CDs find application in numerous fields

Use of renewable sources for the preparation of CDs - high interest at this stage.



Experimental

Carbon dots from bio-oil by hydrothermal process

- **Preparation of carbon dots**
  - **Top-down approach**
    - Lasar ablation
    - Arc discharge
    - Electrochemical process
    - Plasma treatment
  - **Bottom-up approach**
    - Pyrolytic process
    - Template method
    - **Hydrothermal process**
    - Microwave-assisted method
    - Chemical oxidation
    - Template method
    - Sol-gel method
    - Reverse micelle method
    - Ultrasonic treatment
    - Supported synthetic method
    - Combustion process
    - Hot-injection process

- Brown macroalgae
- Produced in large scale in 2010 (1.7 million tonnes)

Macrocystis pyrifera

Pyrolysis

Algal bio-oil

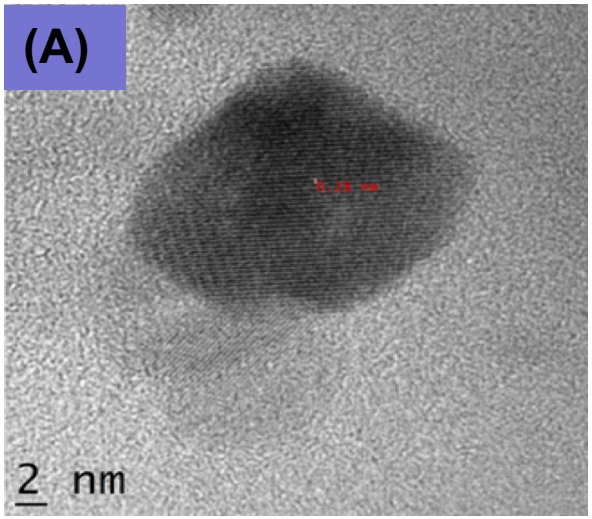
Water medium, Hydrothermal process

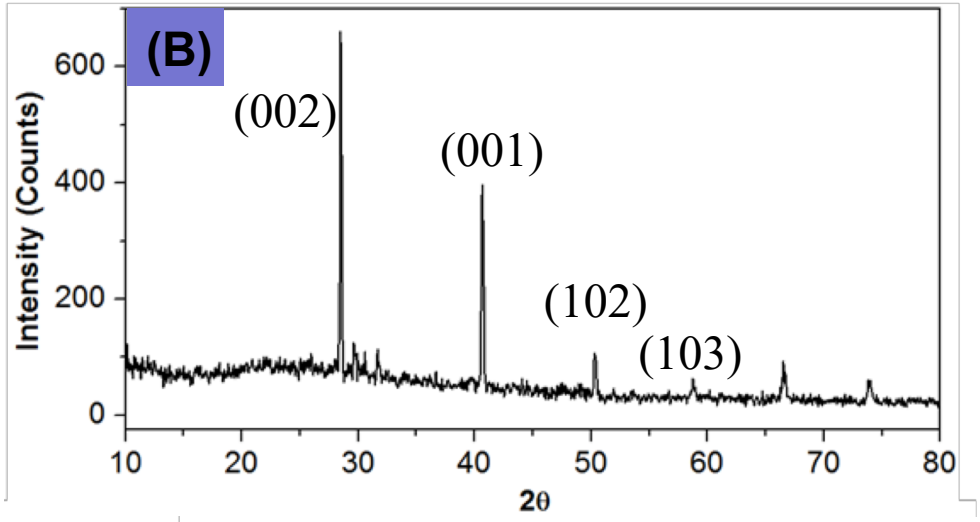
Carbon dots

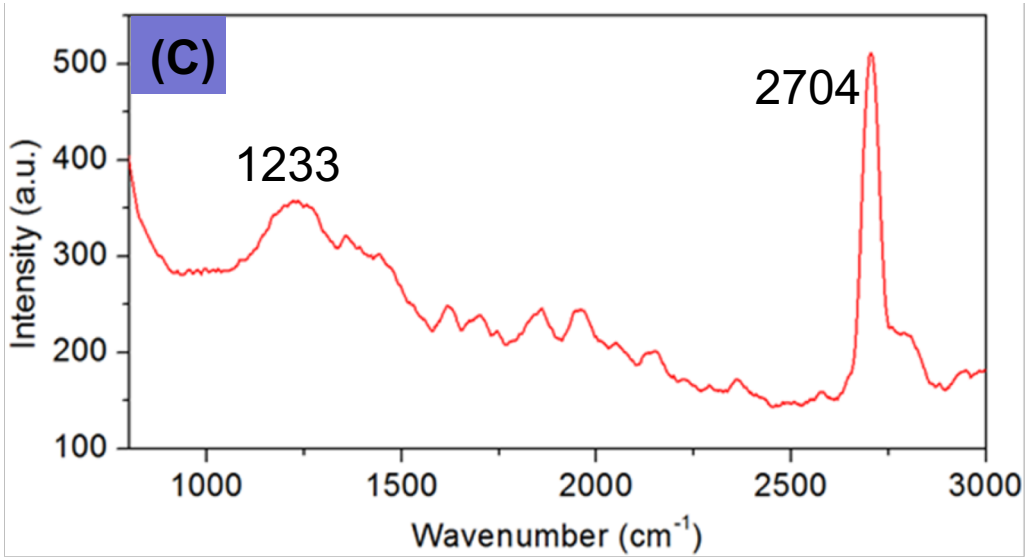
Ultraviolet (UV) exposure

Results

Characterization of GO/CDs composite



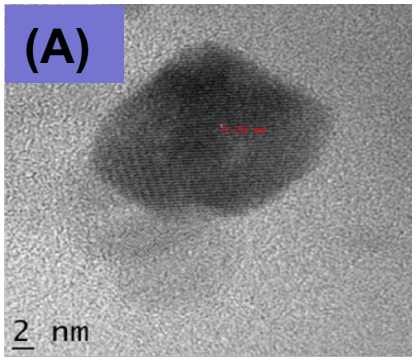


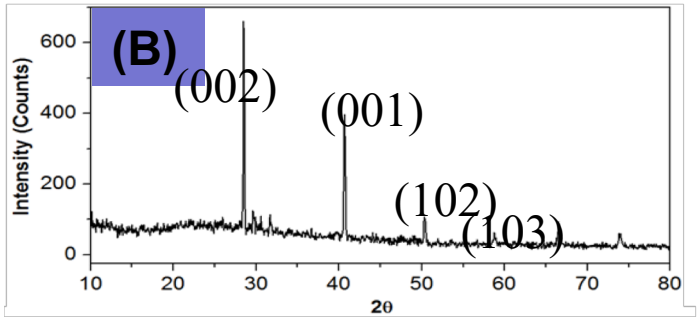


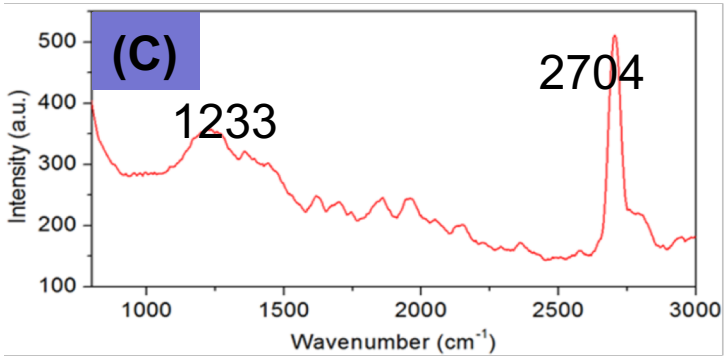
(A) High-resolution transmission electron microscope (HR-TEM) image
(B) X-ray diffraction (XRD)
(C) Raman analyses of prepared graphene oxide-carbon dots (GO/CDs) composite

Results

Characterization of GO/CDs composite



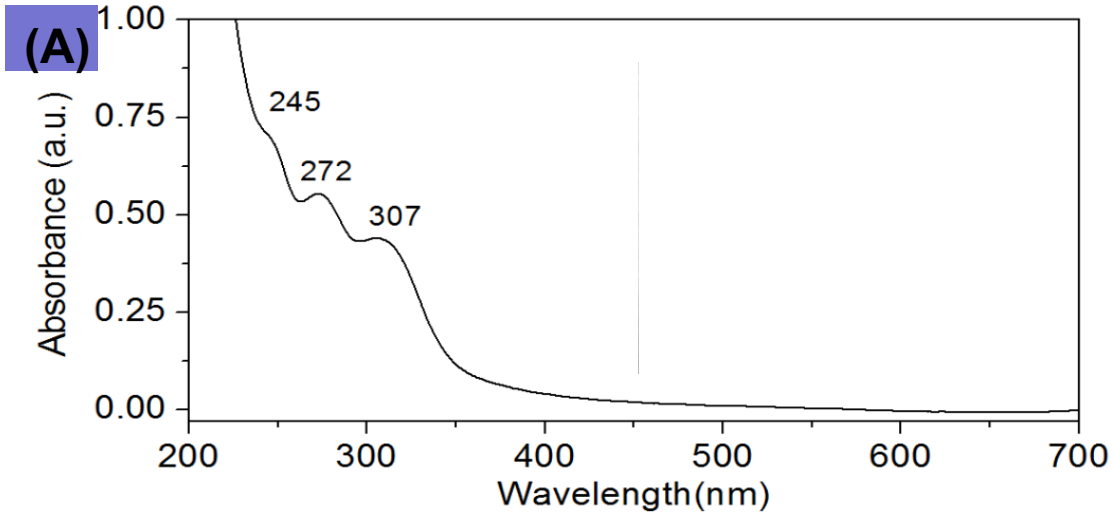


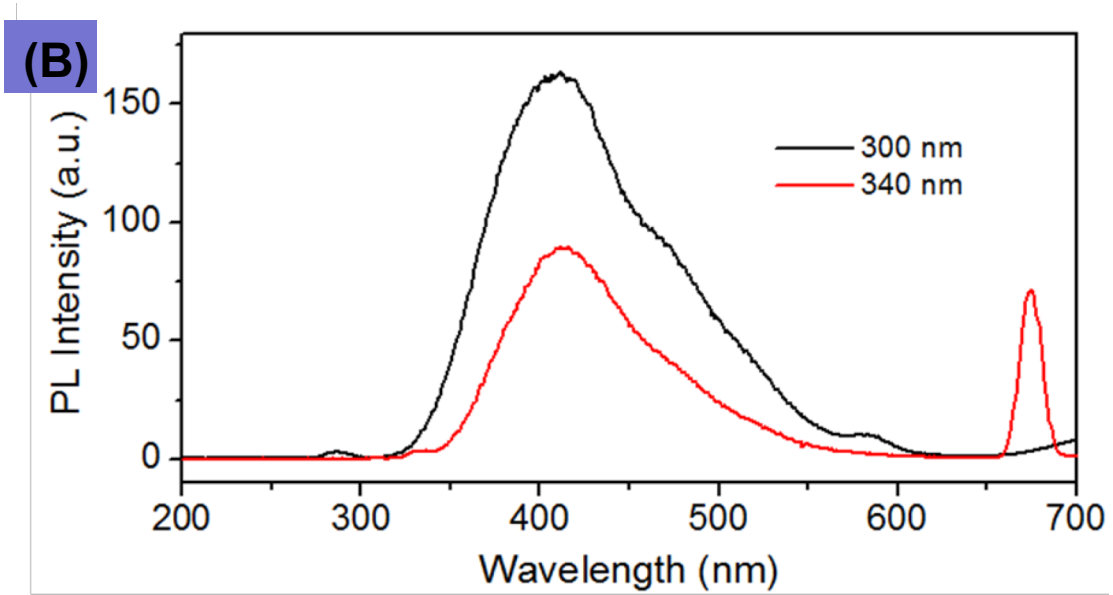


- HR-TEM micrograph - shows the formation of well dispersed spherical sized carbon dots on graphene oxide multi layer sheets that supports the presence of composite structure. Also indicates the presence of ordered lattice fringes with the d-spacing value of 0.2-0.3 nm (graphitic carbon).
- XRD analysis - further revealed the presence of graphitic carbon in the composite structure.
- Raman analysis - shows the broad peaks respectively at 1233, 1408 and 2704 cm^{-1}, corresponding to the characteristic D and G bands of disordered and graphitic carbon archi-structures and E_{g2} of graphene oxide.

Results

Characterization of GO/CDs composite



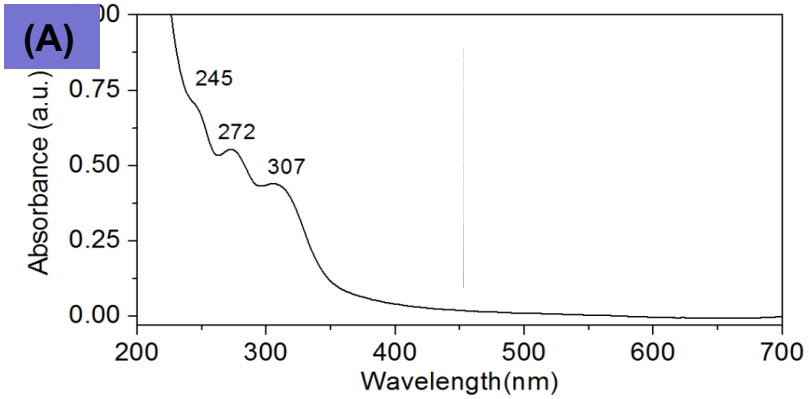


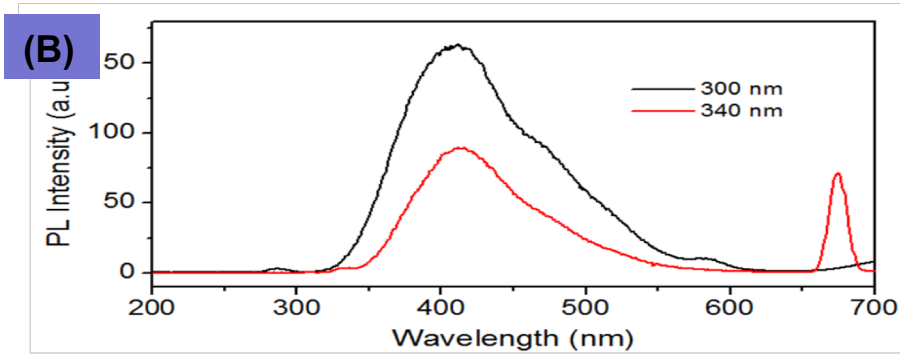
(A) UV-visible (UV-vis) absorption

(B) Photoluminescence (PL) spectra analyses of prepared GO/CDs composite

Results

Characterization of GO/CDs composite





- UV-vis spectra - peaks at 245 and 272 nm, attributed to the π-π* electron transition of the C=C bonds. Also, absorption band with peak maxima of 307 nm may correspond to the n- π* transition of C=O bonds.
- PL spectra - increase in the excitation wavelength resulted in the decrease in the fluorescence intensity at ~430 nm, indicating that CDs were excitation-independent with more uniform size and less surface defects. Emission peak around ~670 nm may be due to the larger size of the particles and presence of nitrogen content in the CDs.

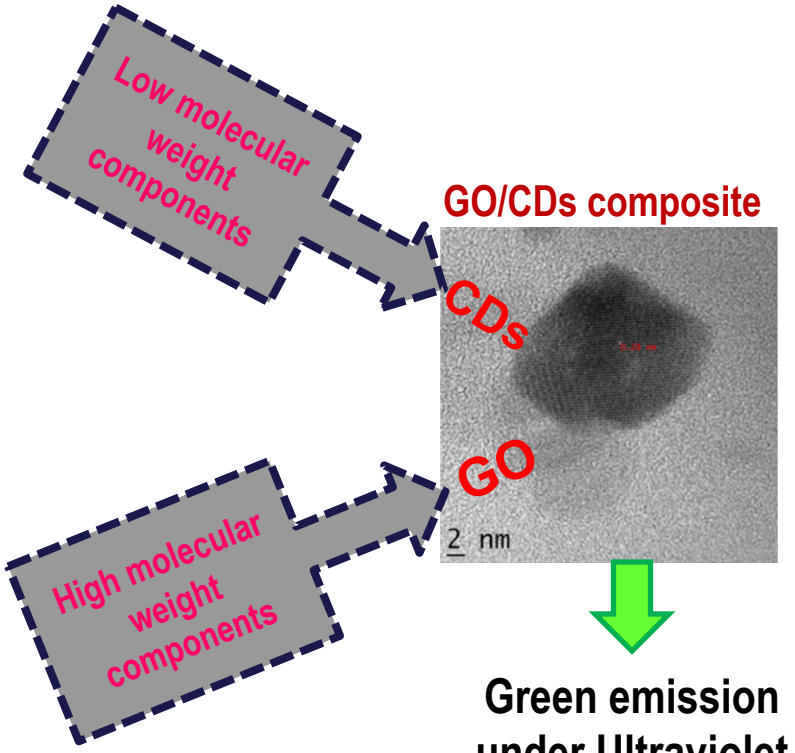
Results

Possible mechanism on GO/CDs formation

Compounds identified in bio-oil

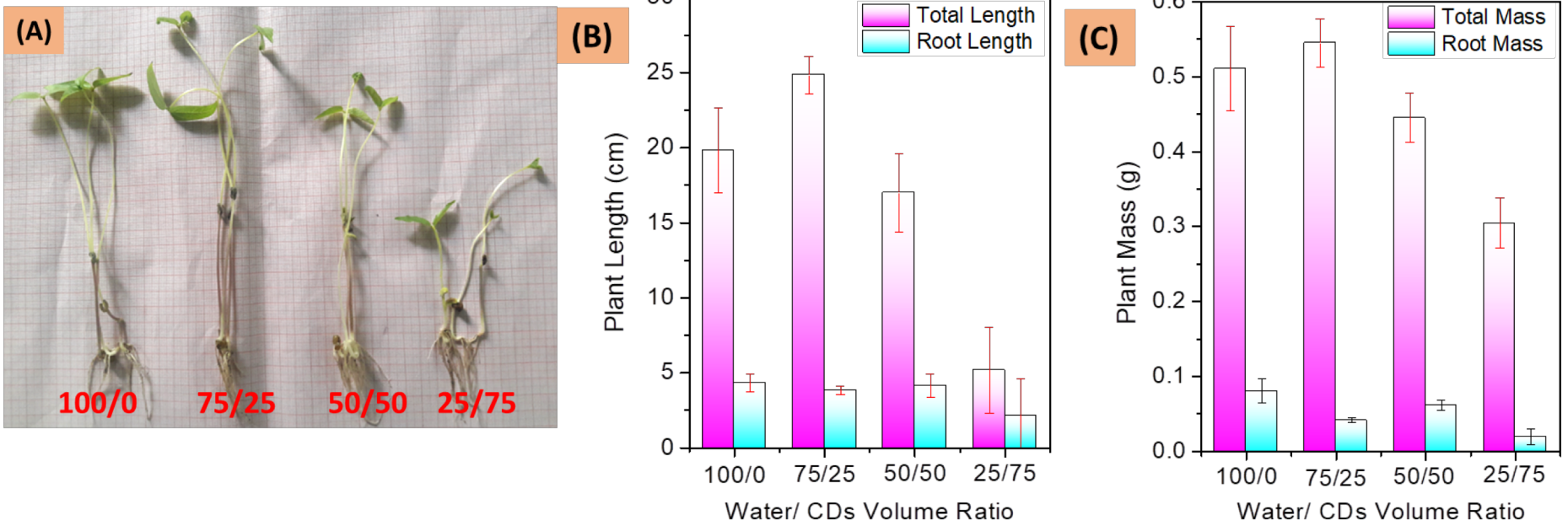
Compound	Formula	Area (%)[a]
Protein derived compounds		
Acetamide	C_2H_5NO	0.6
N,N-dimethyl acetamide	C_4H_9NO	0.1
1,2,2,3,3 Pentamethyl aziridine	$C_7H_{15}N$	1.7
Propanamide	C_3H_7NO	0.1
5-Deoxypyridoxal	$C_8H_9NO_2$	0.1
2-propen-1-amine	C_3H_7N	0.1
Triacetonamine	$C_9H_{15}NO_3$	1.7
2-Pyrrolidinone	C_4H_7NO	0.1
1-methyl 2,5-Pyrrolidinedione	$C_5H_7NO_2$	0.1
Pyridone	C_5H_5NO	0.1
Carbohydrate/Cellulose/Hemicellulose derived compounds		
Dianhydromannitol	$C_6H_{10}O_4$	3.0
Methyl 3,6 anhydrohexopyranoside	$C_7H_{12}O_5$	0.2
Isosorbide	$C_6H_{10}O_4$	0.3
1,5 anhydro-d-mannitol	$C_6H_{12}O_5$	0.3

[a]Based on peak area of GC-MS chromatogram



Results

Seed germination of mung bean using GO/CDs

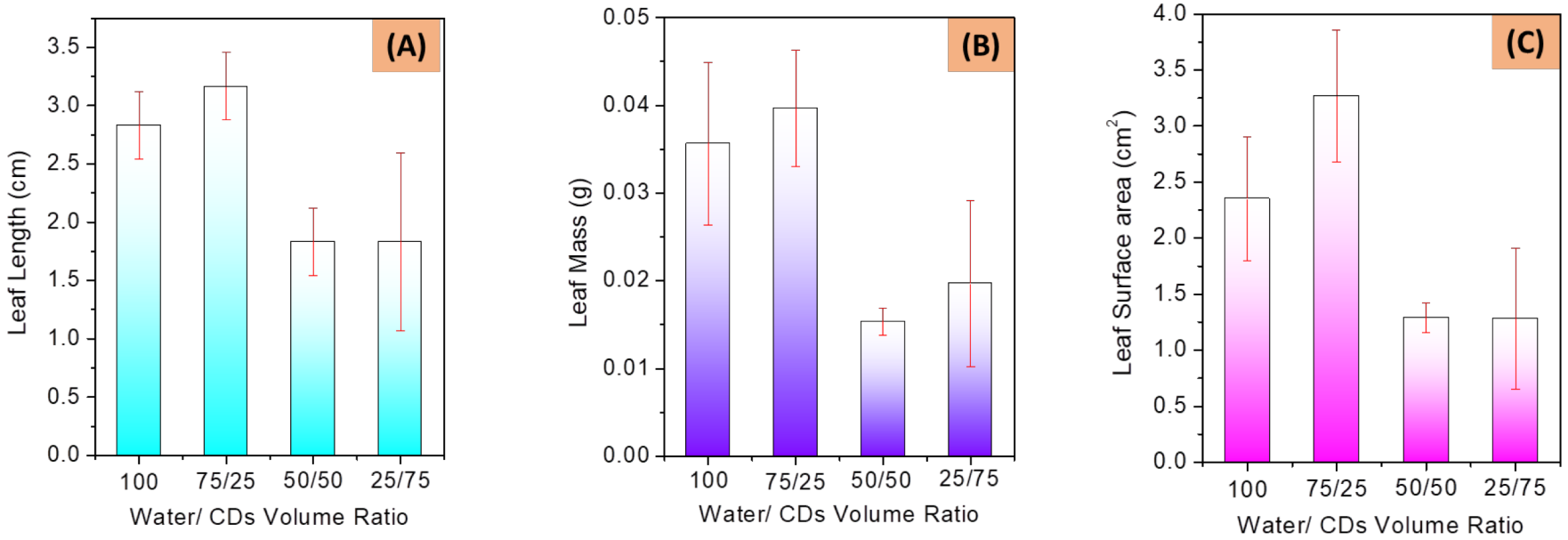


(A) Photographs of mung bean plant growth, comparison of **(B)** Total/root length and **(C)** Total/root mass under different concentration of water/CDs volume ratio

- 75/25 volume% of water/CDs ratio showed better seed germination (total/root length: ~25/5 cm) compared to control (100/0) condition (total/root length: ~20/5 cm). Increase in the CDs ratio (>25) resulted a drop in the growth - may be the higher concentration CDs ended with the filling of active pores in the seed.
- Plant mass also follows the same trend like plant length. 75/25 volume % of water/CDs ratio showed better result (total/root mass: ~0.5/0.1 g) than other concentrations.

Results

Seed germination of mung bean using GO/CDs



(A) Leaf length, **(B)** Leaf mass and **(C)** Leaf surface area of grown mung bean plant under different concentration of water/CDs volume ratio

- 75/25 volume % of water/CDs ratio showed better grown leaf (leaf length & mass : 3.2 cm & 0.04 g) compare to control (100/0) condition (leaf length & mass : 2.8 cm & 0.035 g).
- Leaf length and surface area beyond 75/25 volume % of water/CDs ratio showed almost same values with huge change in the error bar values.
- 75/25 volume % of water/CDs ratio is the better condition for the seed germination of mung bean.

Conclusions

- ✓ Graphene oxide-carbon dots (GO/CDs) composite was successfully prepared from macroalgal biomass (*marocystis pyrifera*) derived bio-oil by simple hydrothermal process using water medium
- ✓ The characterization techniques such as HR-TEM, XRD and Raman analyses and UV-vis absorption spectra supported the formation of green emitting GO/CDs composite
- ✓ Presence of different molecular weight components in the bio-oil source may promote the formation of composite materials rather than simple CDs.
- ✓ 75/25 volume % of water/CDs ratio showed enhanced growth of mung bean plant compared to control condition. Higher concentration of CDs beyond optimum resulted in a drop of plant growth
- ✓ Further studies are ongoing regarding the use different synthetic organic molecules to produce GO/CDs

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