SYNTHESIS AND CHARACTERIZATION OF GRAPHENE OXIDE DERIVATIVES VIA FUNCTIONALIZATION REACTION WITH HEXAMETHYLENE DIISOCYANATE

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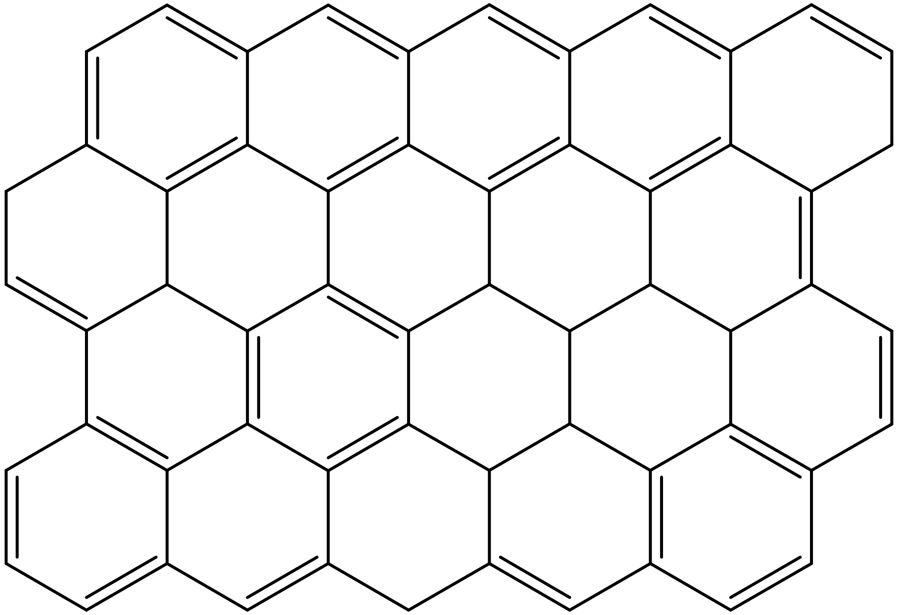
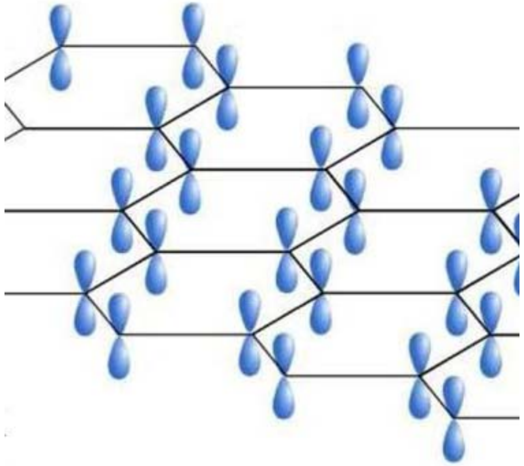
1. INTRODUCTION

1.1 Graphene and properties

- Graphene (G) is an allotrope of carbon like diamond:

2D atomically thick single layer of sp^2 carbon atoms





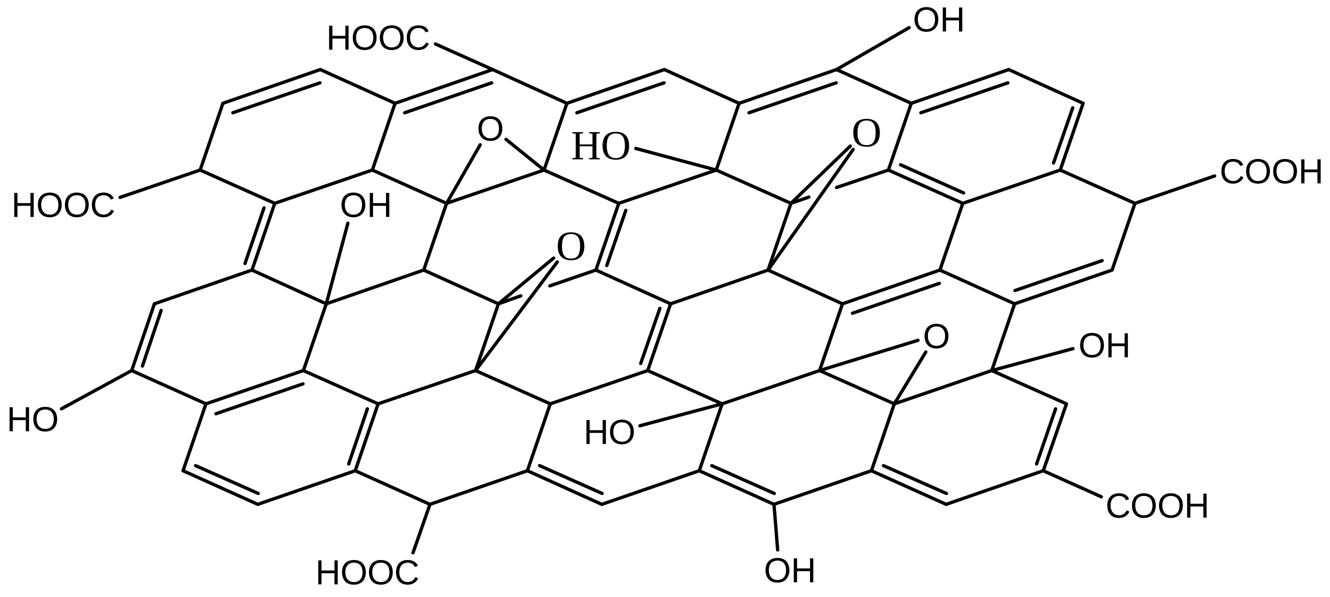
1.1 Graphene and properties

- Properties of G:
  - 2D atomically thick single layer of sp^2 carbon atoms.
  - Outstanding electrical conductivity (higher than Cu) and high electron mobility.
  - Great thermal conductivity (higher than Cu).
  - One of the strongest materials on Earth.
  - Low light absorption (aprox. 2,3%).
  - Insoluble in water.
  - No fluorescence.

1.2 Graphene Oxide and properties

- Graphene Oxide (GO) is the oxidated form of G:

Functional groups are arbitrarily located and randomly aggregated



1.2 Graphene Oxide and properties

- Properties of GO (I):
  - Contains epoxy, hydroxyl and carbonyl groups on the basal plane, and carboxylic groups on the edges.
  - Higher interlayer spacing than G, due to sp^3 carbons.
  - Higher ability to retain compounds.
  - Lower electron mobility.
  - Soluble in water.
  - Amphiphilicity.
  - Surface-functionalization capability and versatility.

1.2 Graphene Oxide and properties

- Properties of GO (II):
  - Biocompatibility and able to interact with biological cells and tissues.
  - Highly hydrophilic, forming stable aqueous colloids.
  - Substrate-deposition capability.
  - Convertible into a conductor.

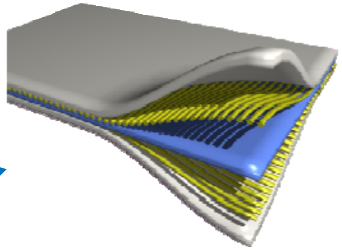
Important on large-scale processing

Great potential for electronic application

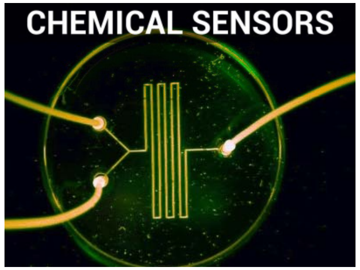
1.3 G and GO applications

G AND GO POSSIBLE APPLICATIONS

MEDICINE



HIGH PERFORMANCE COMPOSITES



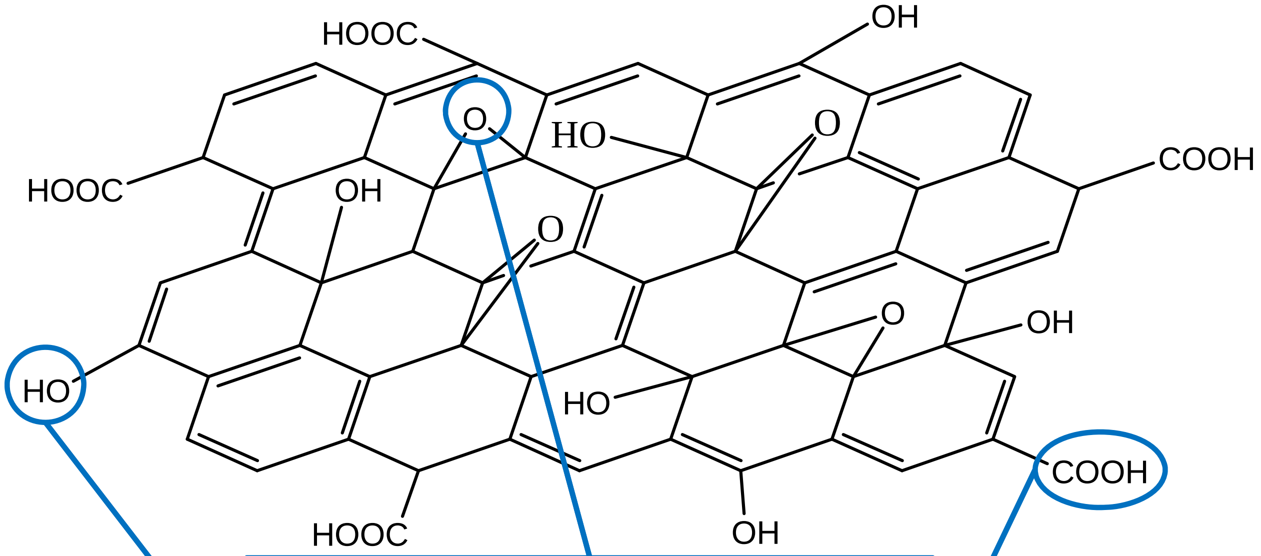
CHEMICAL SENSORS

SOLAR CELLS

2. FUNCTIONALIZATION REACTION

2. Functionalization reaction

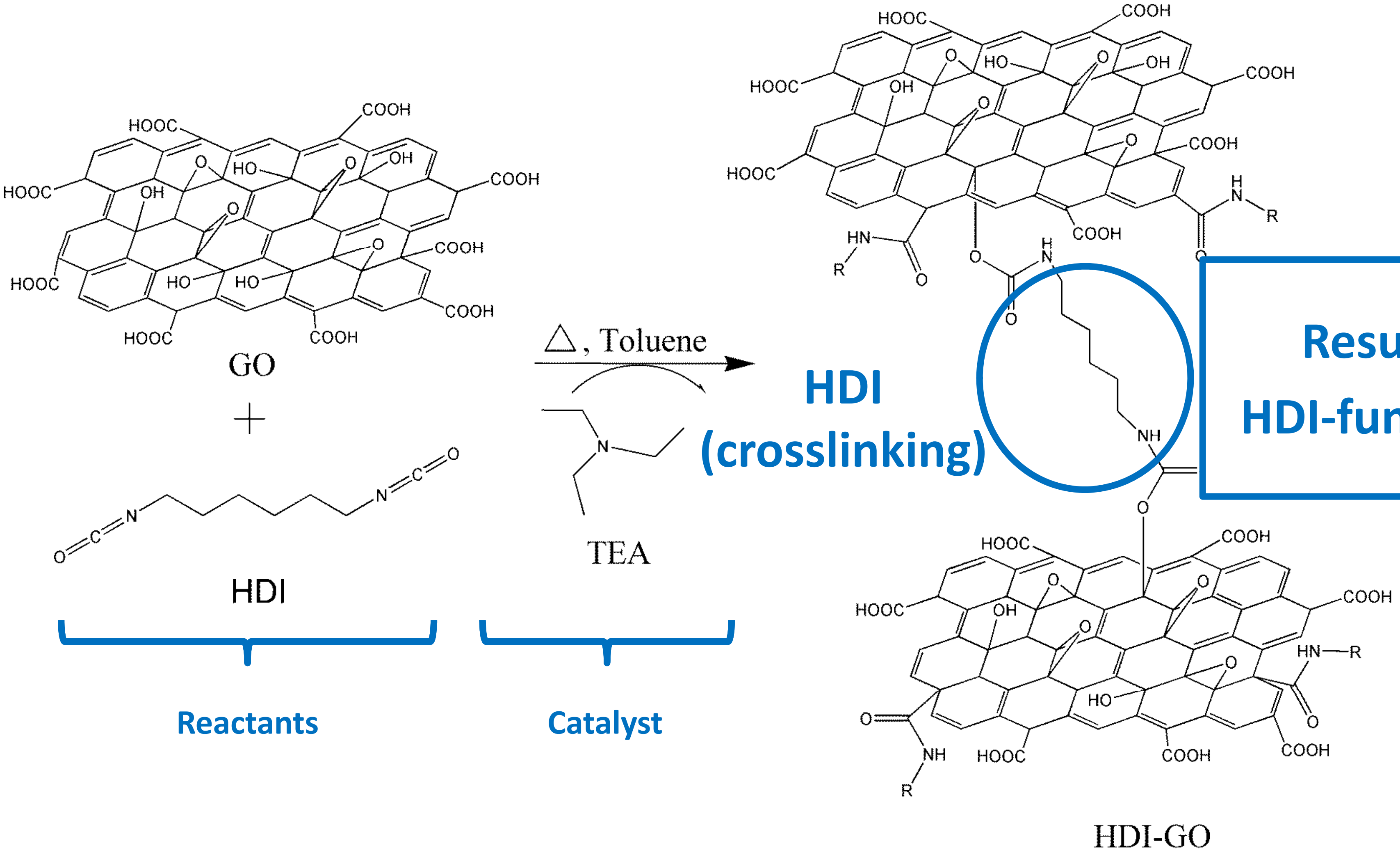
- Reason to use GO inside pristine G:



Possible functionalization points:

- Hidroxyl group
- Epoxy group
- Carboxylic group

2. Functionalization reaction



HDI (crosslinking)

Result:

HDI-func GO

Reactants

Catalyst

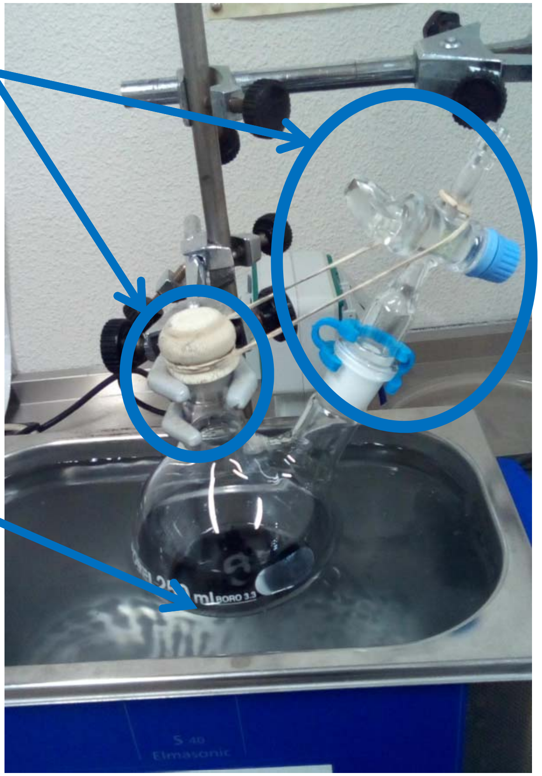
3. EXPERIMENTAL PROCEDURE

3.1 Synthesis of GO

- Hummer's method:
  1. Heating of G powder during 5h at 80ºC (with H_2SO_4, $K_2S_2O_8$ and P_2O_5).
  2. Stirring of previous mixture overnight (with deionized H_2O).
  3. Filtration and drying of mixture.
  4. Oxidation with strong acids (H_2SO_4, $KMnO_4$) and water in ice-water bath.
  5. Decomposing of excess $KMnO_4$ with H_2O_2 and HCl.
  6. Recovery of GO (1. centrifugation and removal of the liquid; 2. addition of aqueous solution of H_2SO_4/H_2O_2; 3. bath ultra-sonication 30min; 4. washing with deionized water; and 5. vacuum freeze-dried).

3.2 Functionalization of GO

1. Adding Toluene to GO:
    - ✓ Use of spherical bottom flask with two mouths
2. Ultrasonication:
    - ✓ 2h in ultrasonication bath



3.2 Functionalization of GO

3. Adding triehylamine (TEA).
4. Adding hexamethylene diisocyanate (HDI).

☐ Instrument employed:

- ✓ Dropping funnel
- ✓ Dropwisely

3.2 Functionalization of GO

5. Reaction:
   - ✓ 60 ^{o}C overnight.
   - ✓ Stirred under an inert atmosphere of argon.

6. Recover the product:
   - ✓ Coagulate with dichloromethane (CH_2Cl_2).
   - ✓ Filtration and washing with CH_2Cl_2.

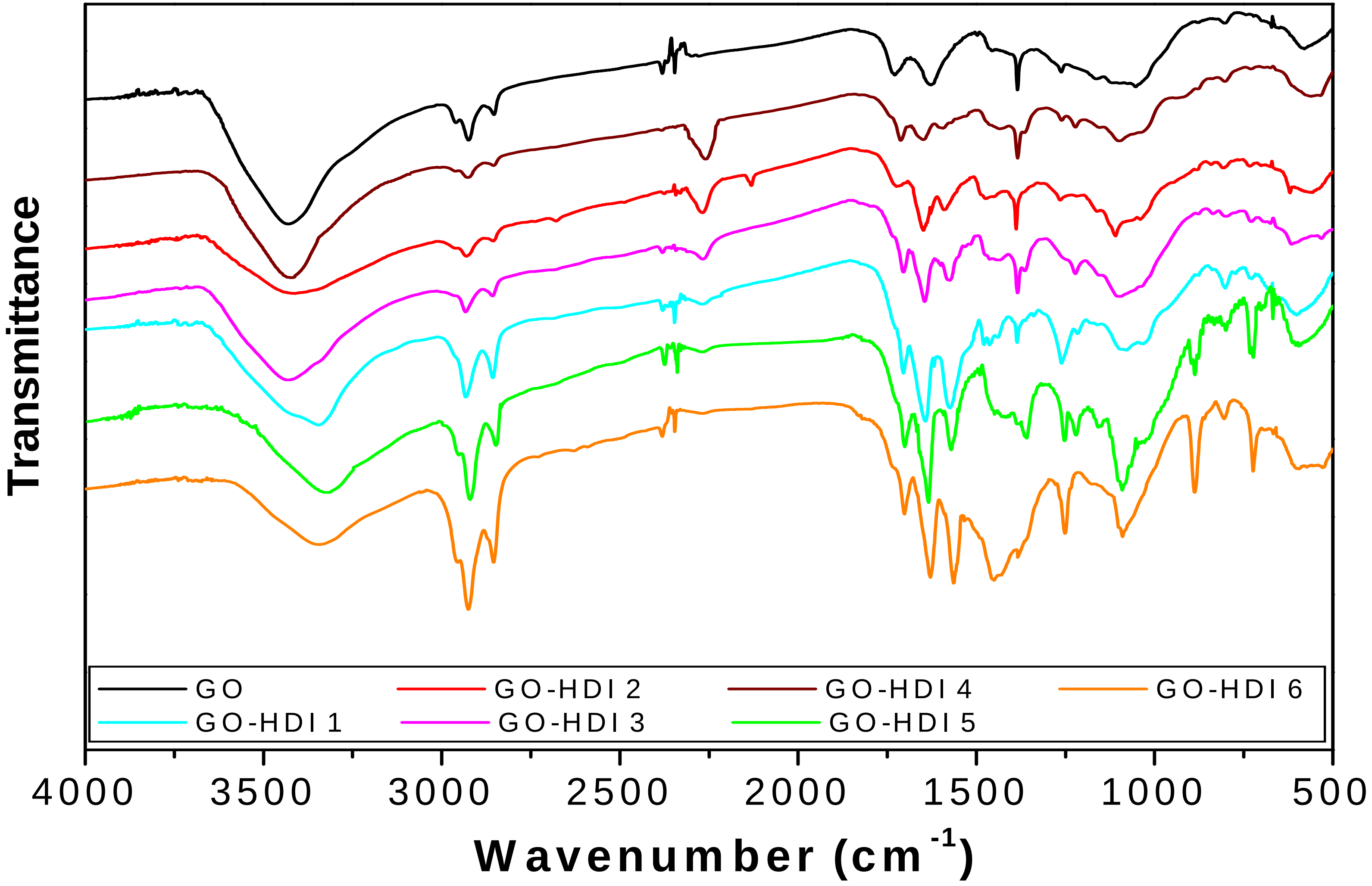
4. RESULTS AND DISCUSSION

4. Results and Discussion

GO/HDI/TEA ratio	REACTION TIME	REACTION TEMPERATURE	G/HDI/TEA ratio	%C	O%	%H	%N	%S	FD*	Sonication time	Solvent volume (ml)
GO	-	-	-	41.93	51.96	3.44	0	2.67	0	-	-
GO-HDI 1	12	60	1/1/1	53.08	35.70	4.22	6.02	0.98	12.28	2 h	25
GO-HDI 2	12	60	0,5/1/1	47.38	44.75	3.83	2.49	1.55	5.08	2 h	25
GO-HDI 3	48	60	1/1/1	50.36	40.16	4.01	4.46	1.01	9.10	2 h	25
GO-HDI 4	12	90	1/1/1	45.98	46.97	3.67	1.53	1.85	3.12	2 h	25
GO-HDI 5	12	60	1/1/1	55.49	31.07	4.50	8.43	0.51	17.20	5 min + 2 h	50
GO-HDI 6	12	60	1/1/1	56.04	30.09	4.55	8.88	0.44	18.13	5+5+5 min + 2 h	50

*Assuming that the formation of carbamate esters through reaction of HDI with the OH or epoxide groups of GO is the hydroxyls or epoxies is the unique reaction pathway, the nitrogen-to-carbon atomic ratio can be used to roughly estimate the functionalization degree (FD), expressed as moles of carbamate ester unit incorporated per mol of carbon atoms of GO.

4. Results and Discussion



5. CONCLUSIONS

5. Conclusions

- Hexamethylene diisocyante-functionalized graphene oxide (HDI-GO) samples with different functionalization degree have been prepared following a simple two-step approach.
- The FT-IR spectra corroborate the successful synthesis of the HDI-GO samples and that the functionalization route via carbamate ester formation predominated.
- Further characterization of HDI-GO by Transmission electron microscopy (TEM), Raman spectroscopy, water contact angle and thermogravimetric analysis (TGA) will be carried out.
- The HDI-GO could further react with other organic molecules or polymers via the remaining oxygen groups, which makes them ideal candidates as nanofillers for high-performance GO-based polymer nanocomposites

THANK YOU FOR YOUR ATTENTION