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Composites of carbon and insights into the properties of the carbon-liquid interface: an account of the research involved in the AtomDeC project

V4-JP ATOMDEC

Visegrad Group–Japan Joint Research Program on Advanced Materials

Tamás Szabó, principal investigator

COLLOID LAYERS LAB University of Szeged

Colloid Layers Lab
Department of Physical Chemistry and Materials Science
University of Szeged
Hungary

2. Work plan for WP3: ANALYTICS

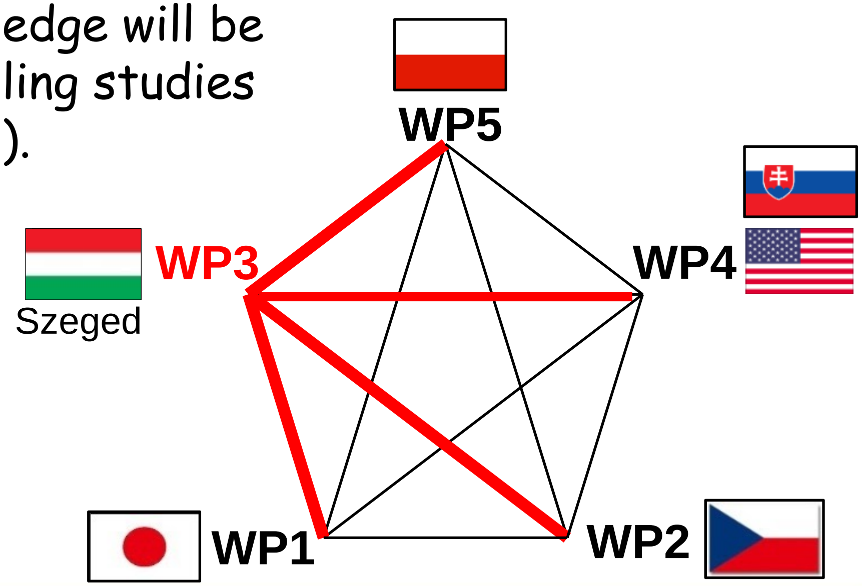
Coordinator: Dr. Tamás Szabó, University of Szeged, HU
Comprehensive characterisation at the atomic/molecular/colloidal scale

WP3 targets detailed structural characterisation of Carbon Based Materials of WP1 and WP2.

Research activities will converge to understanding materials properties both on the atomic level and on the nanoscale. The obtained knowledge will be the basis for the atomic-scale Modelling studies (WP4) and Device construction (WP5).

In Szeged, we focused on Colloidal characterization:

- composite formulation
- dispersion stability
- interfacial properties



V4-Japan project: – The Hungarian team

Kadosa Sajdik PhD student

Tatsiana Petrasheuskaya postdoc

Viktória Hornok senior researcher

Péter Nagy PhD student

Szeged

Máté Sütő MSc student

Publications related to AtomDeC

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A) Research articles with corresponding author T. Szabo:

1) E. González-Aguiñaga et al.:
Amino Acid Complexes of Zirconium in a Carbon Composite for the Efficient Removal of Fluoride Ions from Water
Int. J. Environ. Res. Public Health **2022**, *19*(6), 3640.

2) P.B. Nagy et al.: **Aqueous heterocoagulation-driven assembly of graphene oxide and polycation-coated sulfur particles for nanocomposite Li-S battery cathodes**
J. Coll. Interface Sci. **2024**, 655, 931.

3) I. Ayyubov et al.:
Composites of Titanium–Molybdenum Mixed Oxides and Non-Traditional Carbon Materials: Innovative Supports for Platinum Electrocatalysts for Polymer Electrolyte Membrane Fuel Cells
Nanomaterials **2024**, 14, 1053.

B) Review article with corresponding author T. Szabo:

1) R. Ikram et al.:
Recycling waste sources into nanocomposites of graphene materials: Overview from an energy-focused perspective
Nanotechnology Rev. **2023**, 12, 20220512.

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Publications related to AtomDeC

C) Research articles with consortial members:

1) P. Pietrzyk-Thel et al.:
Flexible, tough and high-performing ionogels for supercapacitor application
J. Materiomics, **2024**, in press.

2) M. Michalska et al.: **Comparative study of photocatalysis with bulk and nanosheet graphitic carbon nitrides enhanced with silver**
Sci. Rep. **2024**, 14, 11512.

D) In manuscript preparation phase:

1) P.B. Nagy et al. (with Nishihara group):
Variable ultrasound-assisted fragmentation of carbon materials: from activated carbons to mesosponge structures

2) T. Petrasheuskaya et al. (with Michalska group):
Interfacial acid-base reactions of graphitic carbon nitrides dispersed in aqueous electrolyte solutions

3) K. Sajdik et al.
Adsorption and intercalation of caine drugs into graphite oxide

Other activities related to AtomDeC

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Organization of scientific workshops:

1) 1st AtomDeC regional mini-symposium
Budapest Research Centre for Natural Sciences

March 16, 2022
Hybrid event
Budapest. Hungary

3 AtomDeC members in-person + online H. Nishihara (JPN)
7 scientific oral presentations

2) 2nd AtomDeC regional mini-symposium „Carbon Friday"
University of Szeged – Institute of Chemistry

September 22, 2023
Szeged, Hungary

3 AtomDeC members in person + T. Bandosz (USA)
8 scientific oral presentations

Other activities related to AtomDeC

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Hosting members of partner labs:

1) Amrita Jain + Monika Michalska (2022 March)
IPPT PAN + VSB

2) Takeharu Yoshii (2022 October)
Tohoku Univ.

3) Hirotomo Nishihara (2023 August)
Tohoku Univ.

4) E. Scholtzova + M. Michalska (2023 Sept.)
SAS + VSB

5) Robert Szilagyi (2023 December)
Univ. British Columbia

6) Jiri Pavlovsky + M. Michalska (2024 May)

Other activities related to AtomDeC

nanomaterials

IMPACT FACTOR 4.4 | Indexed in: PubMed | CITESCORE 8.5

an Open Access Journal by MDPI

Synthesis & Devices of Graphene-Based 2D Nanomaterials for Energy Storage and Conversion

Guest Editors:

Dr. Tamás Szabó
Department of Physical Chemistry and Materials Science, University of Szeged, Szeged, Hungary

Dr. Amrita Jain
Institute of Fundamental Technological Research, Polish Academy of Sciences, Pawińskiego 5B, 02-106 Warsaw, Poland

Special aspect of Special Issue: fabrication of graphene-based material devices.

This feature demonstrates the versatility of 2D nanostructures which are carbon based but may be doped with non-metallic elements for a range of innovative energetic applications such as supercapacitors or batteries.

- graphene (oxide)
- fluorographene (and graphite fluoride)
- layer-structured nitrides (hexagonal boron nitride, graphitic carbon nitride, borocarbonitrides)

Tidbits of findings in our laboratory

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Collaboration with Univ. Guadalajara, Mexico

Health problem: dental fluorosis

Origin: water supply – ground water up to 50 ppm (limit: 1-2 ppm)

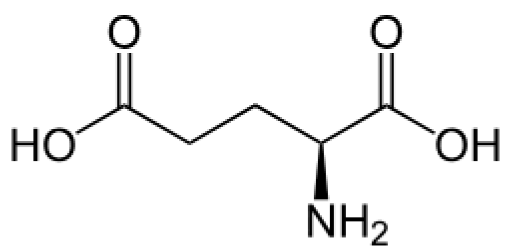
Adsorbed amount greatly increases with GO loading – adsorption capacity is not high but this is due to large particle size of commercial zirconia

	C_0 (mg L^{-1})	q_{max} (mg g^{-1})	Pseudo-second order kinetic fitting		
			q_{max} (mg g^{-1})	K_2 (g mg^{-1} min^{-1})	R^2
ZrO_2	9.0	0.775	0.78	3.73	0.9989
ZrO_2-GO (20% GO content)	9.0	1.3	**1.31**	1.56	0.9986

Amino Acid Complexes of Zirconium in a Carbon Composite for the Efficient Removal of Fluoride Ions from Water

International Journal of Environmental Research and Public Health, 2022

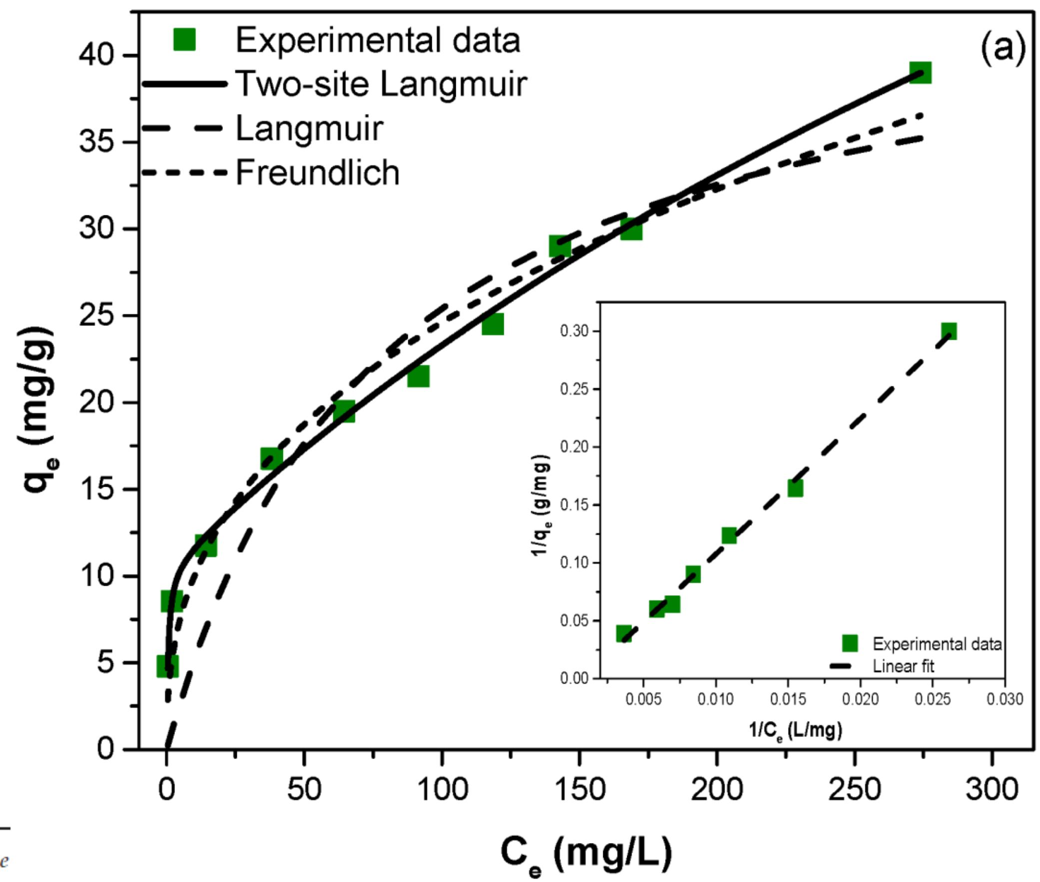
Adsorbent:
Solid Complex compound of Zr with glutamic acid:



$$\text{Langmuir isotherm}: \ q_e = \frac{Q^0_{max} K_L C_e}{1 + K_L C_e}$$

$$\text{Freundlich isotherm}: \ q_e = K_F C_e^n$$

$$\text{Two-site Langmuir isotherm}: \ q_e = \frac{q_1 b_1 C_e}{1 + b_1 C_e} + \frac{q_2 b_2 C_e}{1 + b_2 C_e}$$



Calculated parameters for fluoride-adsorption isotherm models of ZGluGO

Material	Isotherm Model	Parameters				R^2
	Langmuir	Q^0_{max} (mg/g)	K_L (L/mg)			
ZGluGO	Nonlinear	45.28	0.013			0.8492
	Linear	38.76	0.025			0.9070
	Freundlich	K_F (mg/g)	n			
ZGluGO	Nonlinear	4.044	0.392			0.9653
	Linear	6.112	0.299			0.9728
	Two-site Langmuir	q_1 (mg/g)	b_1 (L/mg)	q_2 (mg/g)	b_2 (L/mg)	
ZGluGO	Nonlinear	97.32	0.0015	10.64	1.8547	0.9937

Physisorption up to 100 mg/g

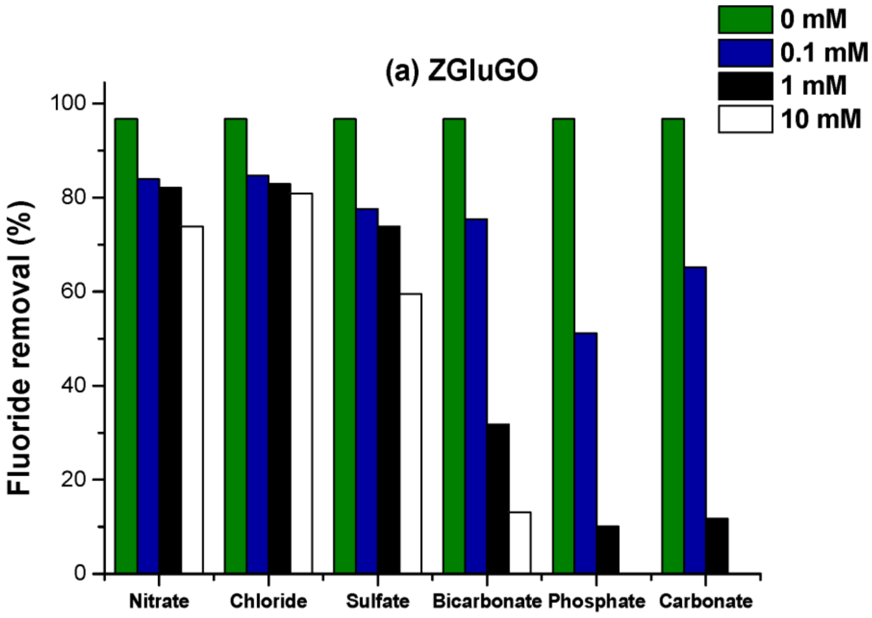
Chemisorption up to 10 mg/g

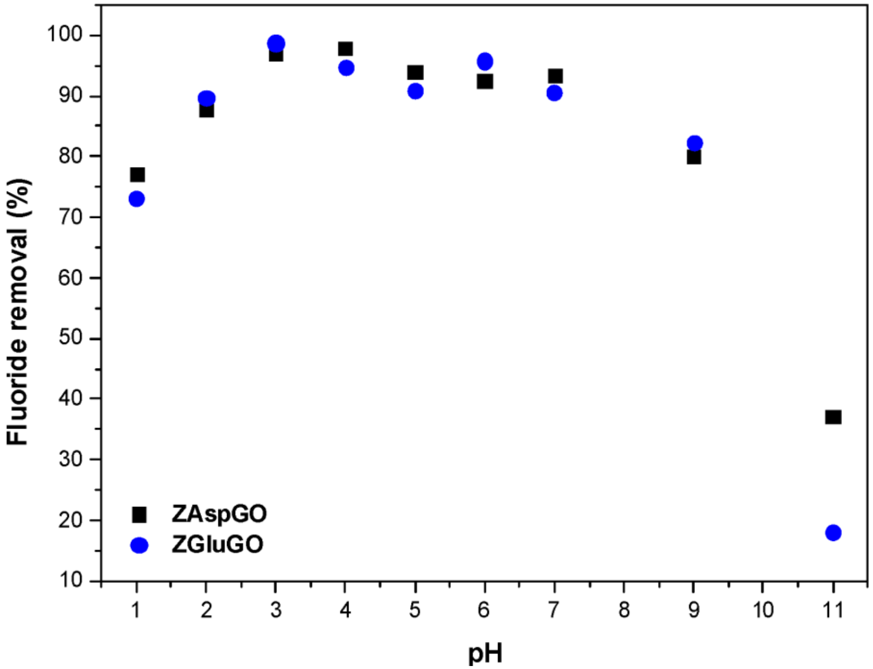
Origin of adsorption capability for F^-:

Zr:

1) **coordination to Ti-surface sites**
2) **Anion excange?**

GO: nucleophilic substitution?





Effect of pH on the adsorption of fluoride ion by the AA-GOs at 10 mg/L initial concentration.

phosphate, bicarbonate and carbonate ions presented a decrease of more than 50% at a concentration greater than 1 mM

pH-dependence strongly suggests that at least a part of the adsorption process is related to anion exchange

these ions can interact with zirconium and form a stable complex with the Zr^{4+} which occupies active sites

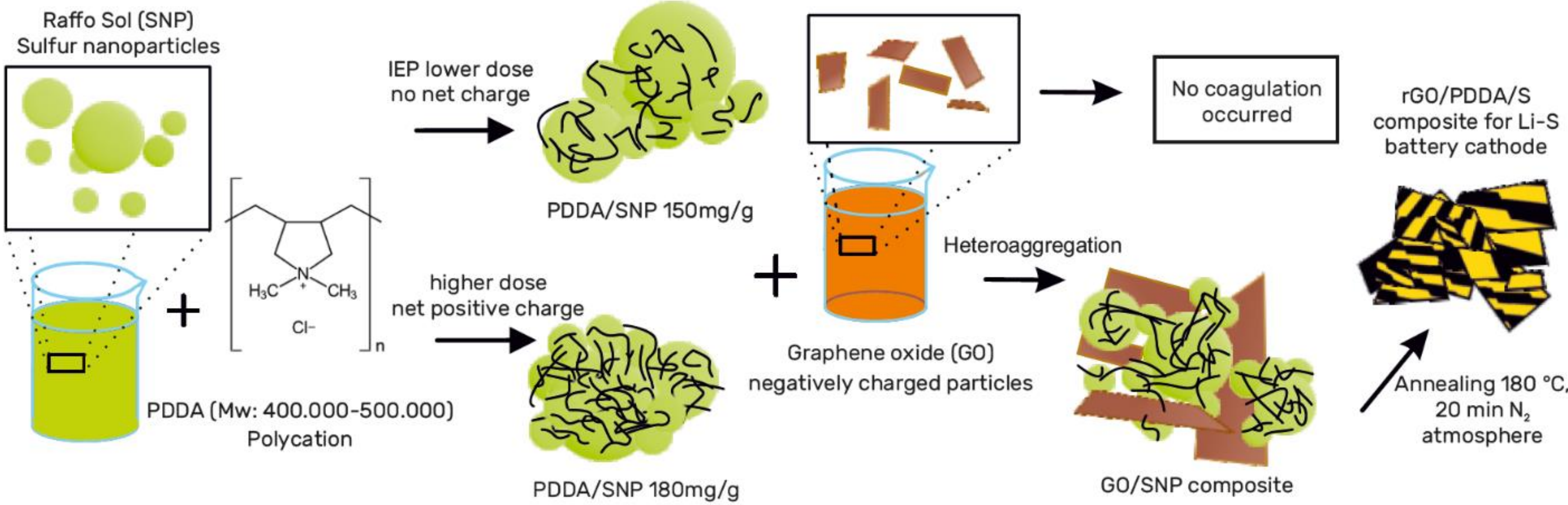
dicarboxylate-type amino acids can preferably coordinate to the zirconium ions by monodentate and bridge-type modes, leaving the amino groups available for interfacial protolytic reactions

Tidbits of findings in our laboratory – composite materials

Collaboration with the battery lab @ Budapest Res. Center

Aqueous heterocoagulation-driven assembly of graphene oxide and polycation-coated sulfur particles for nanocomposite Li-S battery cathodes
Journal of Colloid and Interface Science, 2024

Péter Nagy
PhD student



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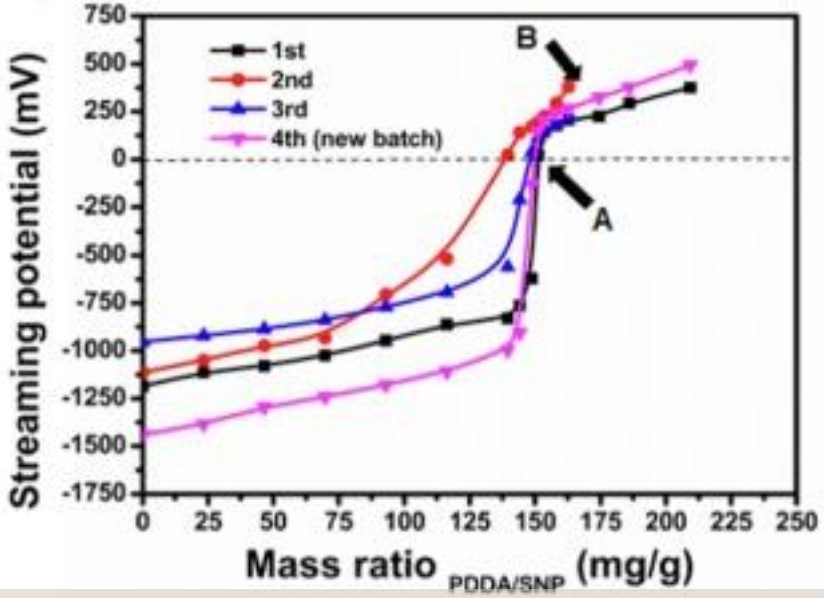
Li-S batteries suffer from serious setbacks such as low electrical conductivity of sulfur (5×10^{-30} S cm^{-1} at 25 °C) and solubility of lithium polysulfide (LiPS) intermediates in organic electrolytes resulting in shuttle effect.

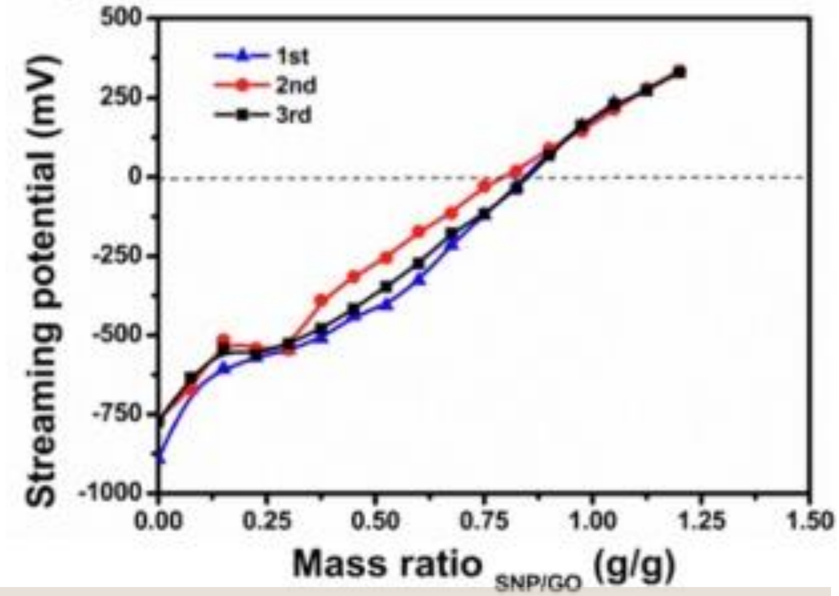
Use of advanced carbon materials:

- Providing a matrix of good electrical conductivity
- Providing hierarchical pore size distribution

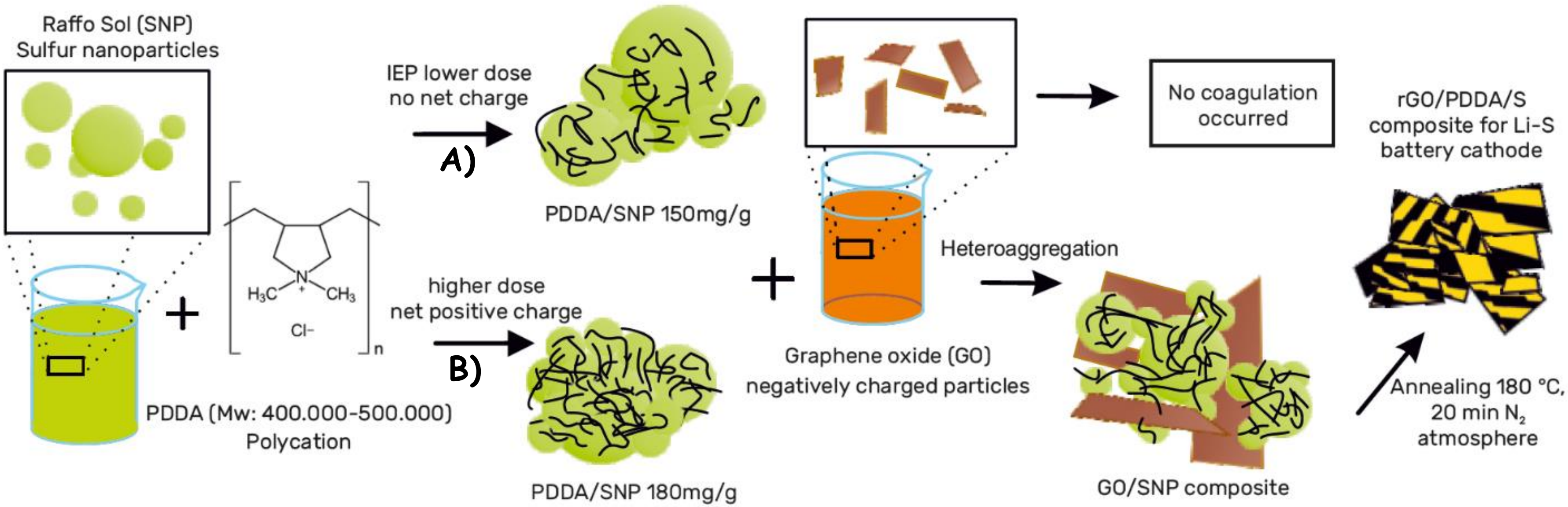
1) Their porous structure enables the **storage and immobilization** of the active materials.
2) The mesopores and macropores are capable to **improve the Li-ion and electrolyte transport** as well as raising the tolerance towards high sulfur loading.
3) The porous structure serves to **buffer** the continuous **volume changes** occurring during the cell operation, thereby maintaining the structural integrity and stability of the composite cathodes

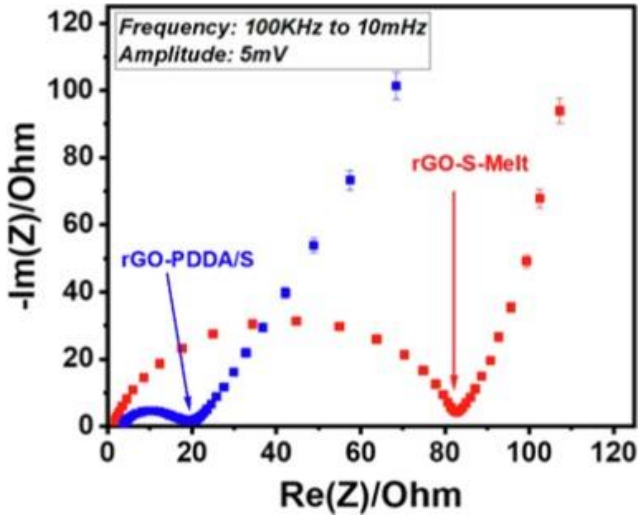


1) Coating sulfur particles with polycation

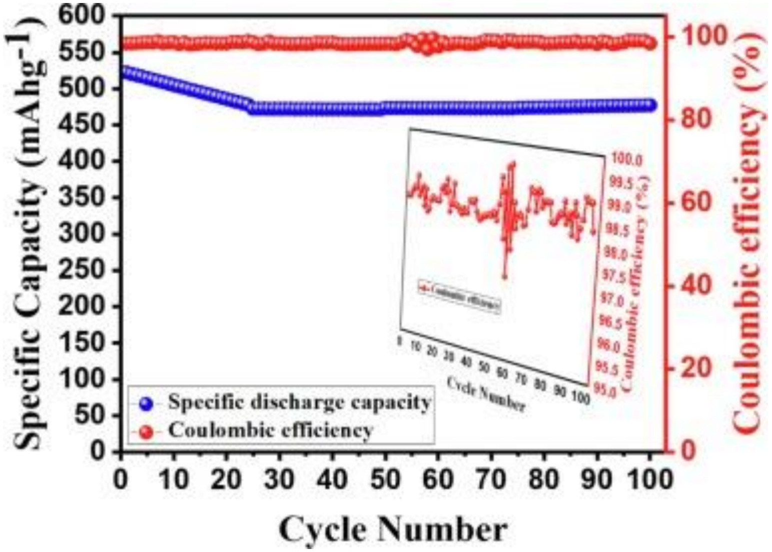


2) Assemble GO sheets with PDDA/SNP





The composite prepared via heterocoagulation route shows much lower total impedance then melt-inserted S, owing to the sulfur nanoparticles homogenously distributed onto the conductive rGO matrix.



The composite cathode showed an initial discharge capacity of 522 $mAhg^{-1}$ at 0.2C rate with an excellent capacity retention of 91.4 % and coulombic efficiency of 98.5% after 100 charge–discharge cycles.

The proposed methodology of **polyelectrolyte-assisted heteroaggregation** can be easily performed under ambient conditions and **entirely relies on water as a dispersion medium**, in contrast to previously reported procedures that utilize organic solvents, conductive polymers, polymer mixtures or elevated temperatures.

Summary

- The Hungarian side of the consortial project started with delay in starting date and funding, so there is still plenty of time to finish up things.

- Declared deliverables: Only one paper in Q1 SciMago ranking OR 4 papers individually or consortially

(currently 6 papers in Qi-D1 ranking and 3 in ms. Preparation)

- We finish the project in 2025 November

Thank you for project partners and advisory team…