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Objectives

- Preparation of functionalized graphene layers, introducing oxygen containing functional groups, without substantially affecting the sp^2 hybridization of carbon atoms. [1,2]
- Preparation of confined reactors as a technological platforms to carry out organic reactions in more environmentally friendly and cost-effective conditions. [3]

High surface area graphite (HSAG) was selected as carbon allotrope.

HSAG

	Surface area (m ² /g)	number of layers	D / D _⊥
HSAG	330	35	3.1

HSAG has high shape anisotropy $D_{||} / D_{\perp}$ defined as the ratio between the size of the crystallites in directions parallel and orthogonal to the layers.

SP: Janus molecule

SP: two hydroxyl groups promote the compatibility with water.

The pyrrole ring favours the interaction with the aromatic rings of carbon allotropes

HSAG-SP

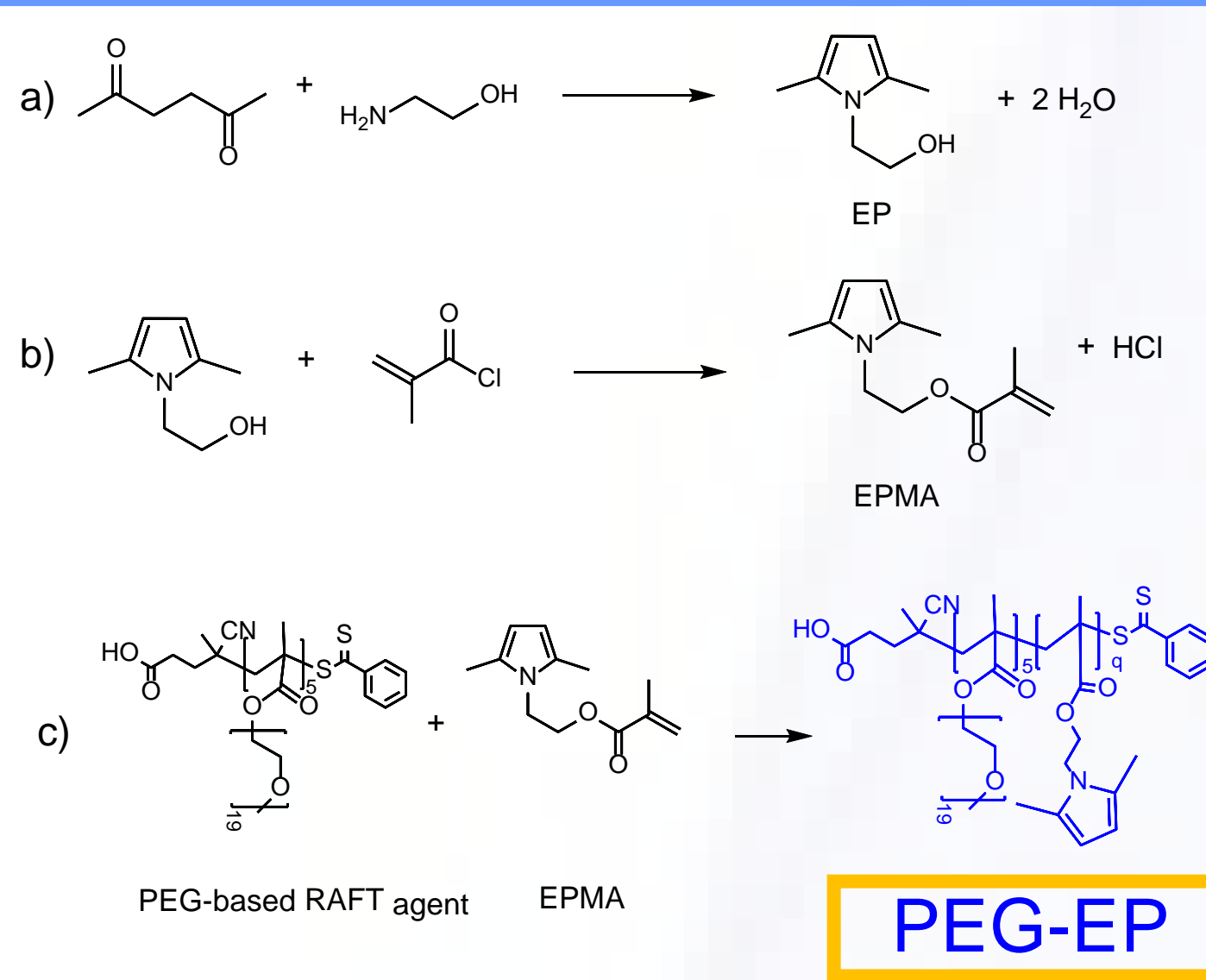
HSAG-SP/PEG-EP

Nanoencapsulated graphene layers

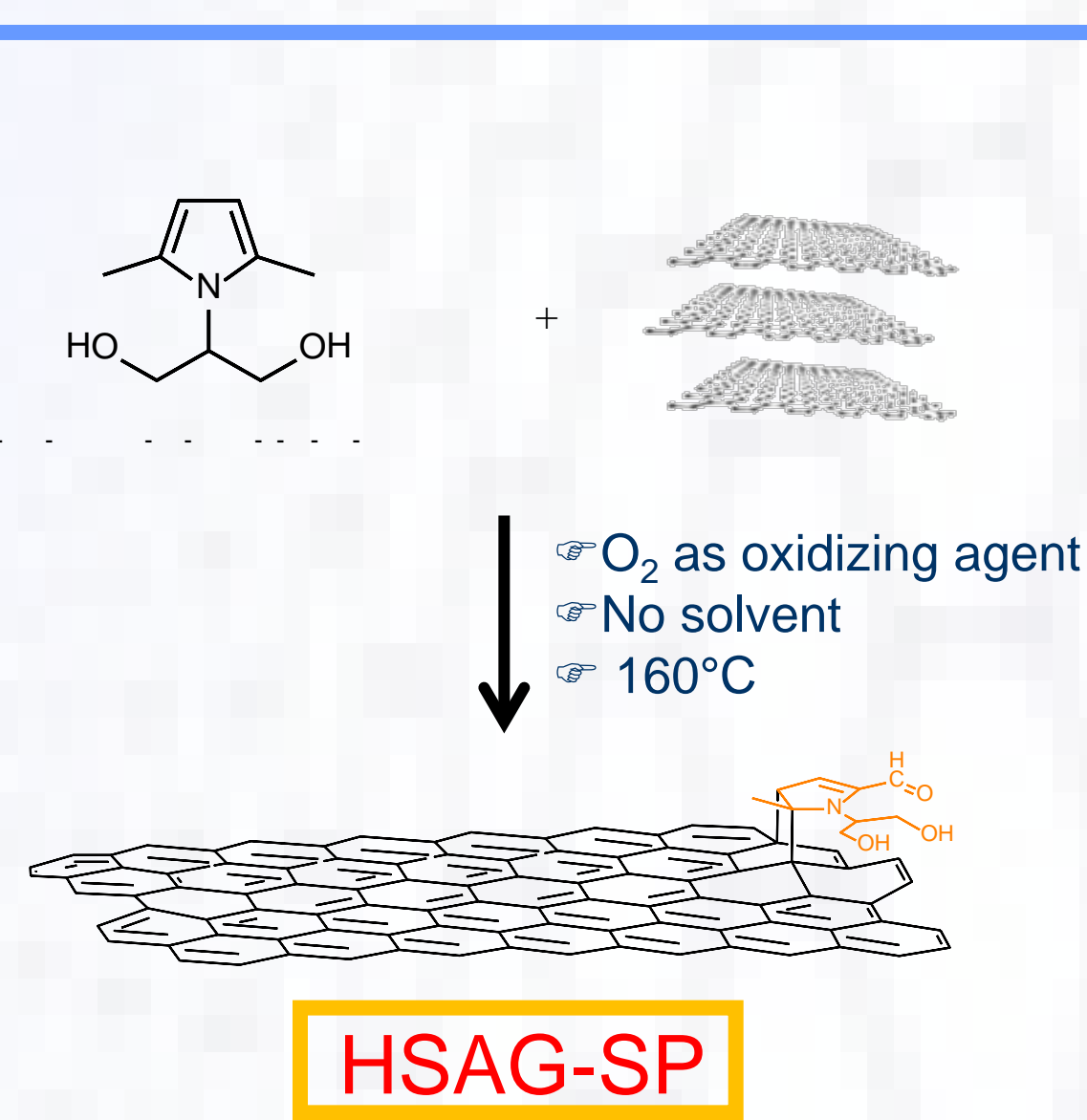
Preparation of the reactor

Synthesis of imines

Synthesis of the pyrrole-based amphiphilic block-copolymers

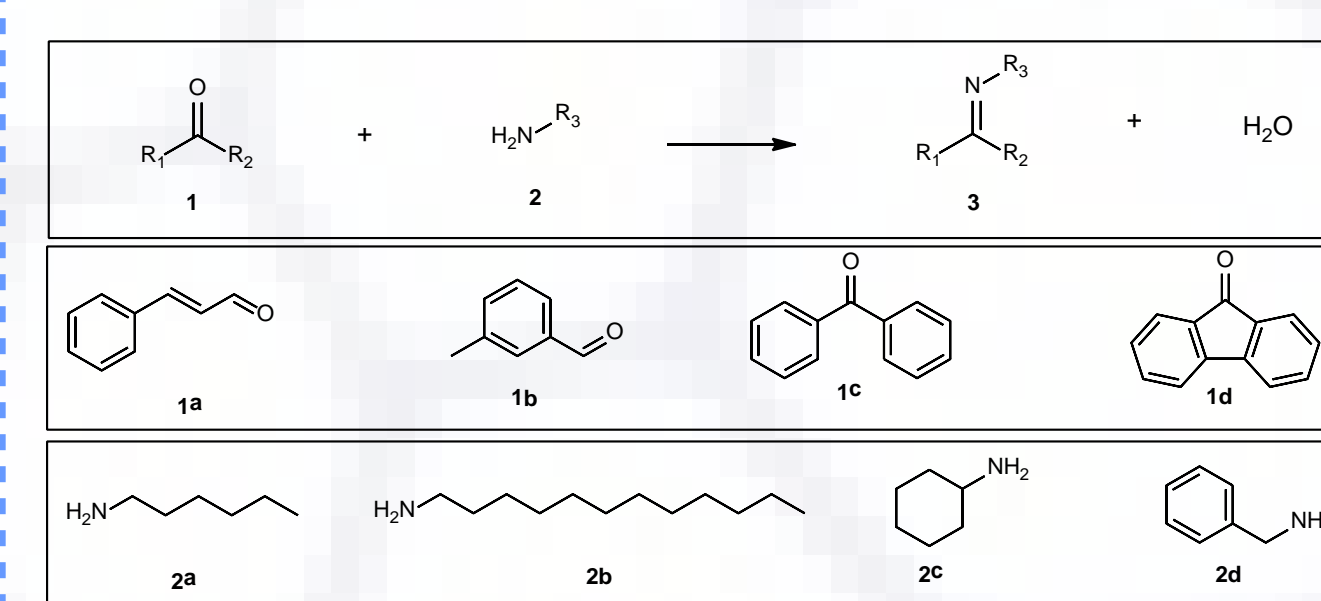


Functionalization of HSAG with SP



HSAG-SP/PEG-EP

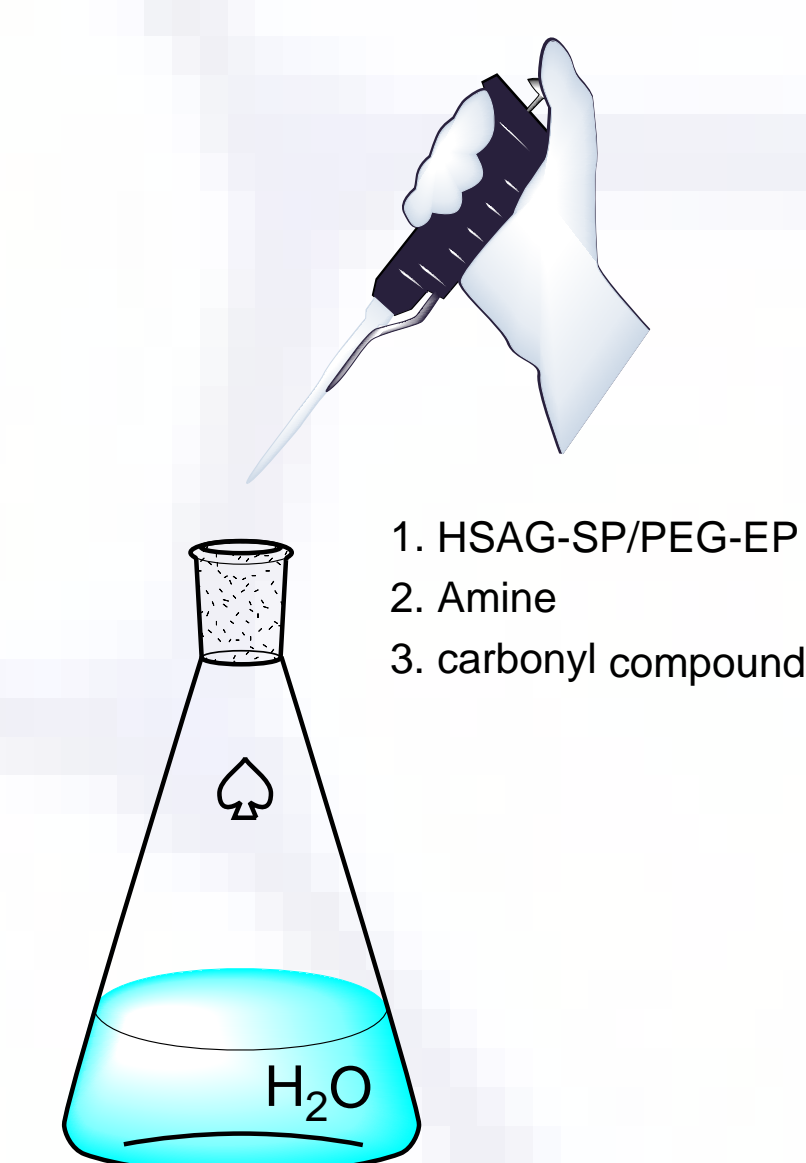
High-resolution transmission electron microscopy (HR-TEM)



Performed reactions and reagents

entry	reag. ^a	time (min)	catalyst/stabilizer	T (°C)	yield (%)
1	1a + 2a	240	-	180	60
2	1a + 2a	120	HSAG-SP/PEG-EP5	25	91
3	1a + 2a	120	HSAG-SP/PEG-EP10	25	91
4	1a + 2a	120	HSAG-SP/PEG-EP20	25	91
5 ^b	1a + 2a	120	HSAG-SP/PEG-EP10	25	61
6	1a + 2a	120	-	25	0
7	1a + 2a	120	HSAG-SP	25	0
8	1a + 2a	120	PEG-EP10	25	0
9	1a + 2a	120	HSAG/PEG-EP10	25	0
10	1a + 2a	120	HSAG-SP/SDS	25	0
11 ^c	1a + 2a	120	HSAG-SP/PEG-EP10	25	0
12	1a + 2b	120	HSAG-SP/PEG-EP10	25	80
13	1a + 2c	120	HSAG-SP/PEG-EP10	25	81
14	1a + 2d	120	HSAG-SP/PEG-EP10	25	72
15	1b + 2a	120	HSAG-SP/PEG-EP10	25	82
16	1c + 2a	120	HSAG-SP/PEG-EP10	25	10
17	1d + 2a	120	HSAG-SP/PEG-EP10	25	10

Only by stirring 5 minutes!



^aThe molar ratio is 1:1; ^bReaction without mechanical stirring; ^cReagents were mixed in THF without precipitation in water

Conclusions

A hybrid supramolecular reactor composed of an amphiphilic block copolymer and a functionalized graphene has been developed and tested in the synthesis of imines directly in water. Although these reactions are thermodynamically unfavored in aqueous media, they occur instantaneously at room temperature with high yield in the developed reactor (Y = 90% after 5 minutes). Moreover, a strategy to recycle the catalyst has been developed without losing efficacy after each cycle (Y > 80%), making this technology more appealing for industrial applications.



References:

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- V. Barbera, L. Brambilla, A. Milani, A. Palazzolo, C. Castiglioni, A. Vitale, R. Bongiovanni, M. Galimberti, (2019). Nanomaterials, 9(1), 44.
- V. Barbera, D. Moscatelli, U. Capasso, M. Galimberti. Submitted for publication