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Controlled formation of nanostructurated $CaCO_3$-PEI microparticles with high biofunctionalizing capacity

Adaris Lopéz_Marzo, [a,b] *Josefina Pons*, [b] and *Arben Merkoçi**[a,c]

[a] Nanobioelectronics and Biosensors Group,

Catalan Institute of Nanotechnology,

Campus de la UAB, 08193 Bellaterra, Barcelona, Spain

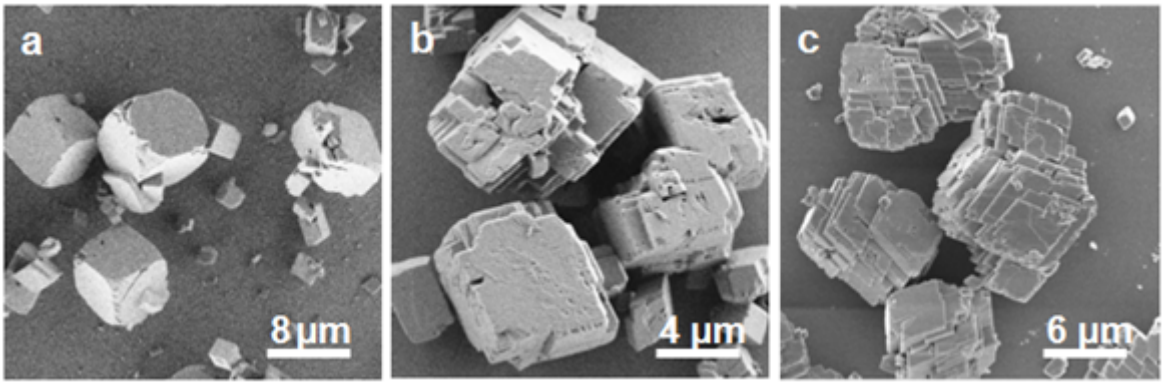
[b] Department of Chemistry,

Universitat Autònoma de Barcelona,

Bellaterra 08193, Barcelona, Spain.

[c] ICREA, Barcelona, Spain

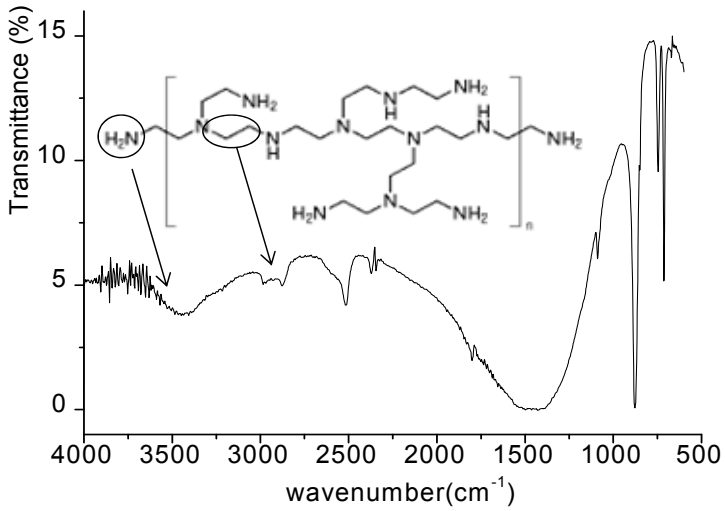
*Corresponding author: E-mail:arben.merkoci@icn.cat



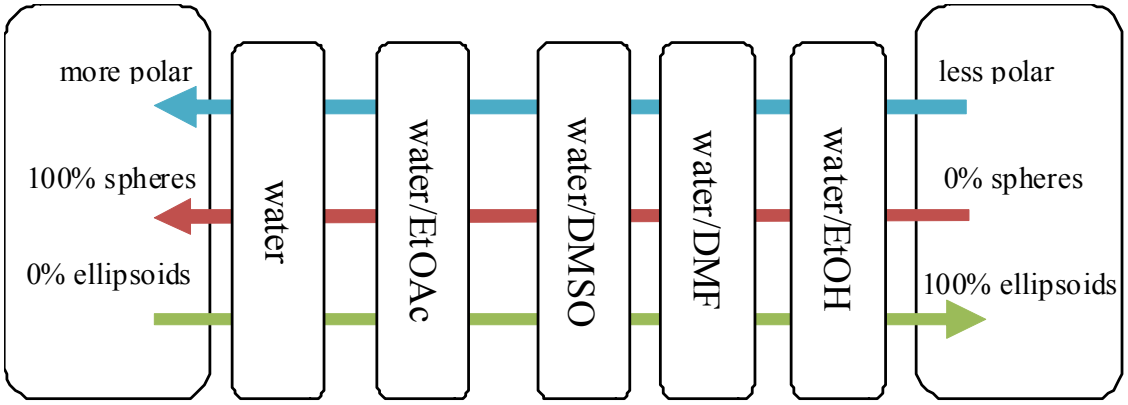
Figure_S1. SEM images of three different shape $CaCO_3$ in rhombohedra crystal phase recorded in all groups of assays: (a) standard rhombohedra, (b) intergrown rhombohedra and (c) layered rhombohedra. Other experimental conditions as described in the main text.

Tabla_S1. Variation of microspheres size and vaterite fraction by changing the PEI concentration in the initial $CaCl_2$ dissolution while using 5 mL of the reagents ($CaCl_2$ and Na_2CO_3) volume and 45 min of the sonication time. [a] Reaction with 4 mg/mL of PEI divided in 2 mg/mL in each $CaCl_2$ and Na_2CO_3 initial dissolutions. [b] 4 mg/mL of PEI divided in 2 mg/mL for each initial $CaCl_2$ and Na_2CO_3 dissolutions and including the reduction of volume to 2 mL.

PEI [mg/mL]	0	0.44	2	4	4 [a]	4[b]
microspheres size [μm]	2.0±0.3	1.8±0.25	1.3±0.13	1.32±0.16	1.13±0.11	0.83±0.16
vaterite fraction [%]	36	55	64	72	75	86



Figure_S2. IR-FTIR spectrum of $CaCO_3$ product using 4mg/mL of PEI, 5mL of reagents volume and 45min of ultrasonic agitation. Other experimental conditions as described in the main text.

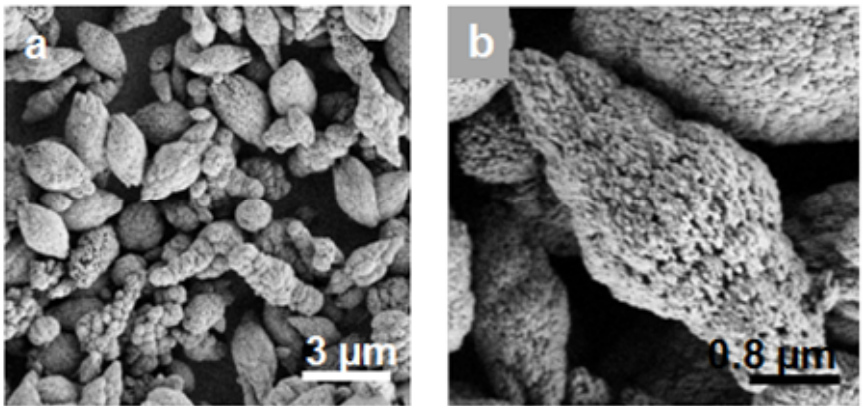


Figure_S3. Effect of the polarity of the mixture water/organic solvent on the particle shape when 8mg/mL of PEI is used.

Table_S2. Summary of the results achieved using water/organic solvents with or without PEI, 5mL of reagents volume and 45min sonication.

	Shape of particle	vaterite fraction [%]	calcite fraction [%]	microparticles size [μm]
water/EtOAc	r	0	100	-
water/DMSO	r	0	100	-
water/DMF	r	0	100	-
water/EtOH	r	0	100	-
water/EtOAc+4PEI	s >> e and few r	84	16	1.08±0.22
water/DMSO+4PEI	e > s and few r	85	15	1.57±0.21
water/DMF+4PEI	e > s and few r	85	15	1.98±0.28
water/EtOH+4PEI	e >> s and few r	88	12	1.28±0.18
water/EtOAc+8PEI	s >>> e	100	0	1.10±0.13
water/DMSO+8PEI	s>e	96	4	0.75±0.12
water/DMF+8PEI	e > s	99	1	1.18±0.13
water/EtOH+8PEI	e >> s	96	4	1.31±0.12

r: rhombohedra; e: microellipsoids; s: microspheres.



Figure_S4. $CaCO_3$ of different shapes obtained with the reduction of the reagent volume in the water/organic solvent +PEI system. Other experimental conditions as described in the main text.

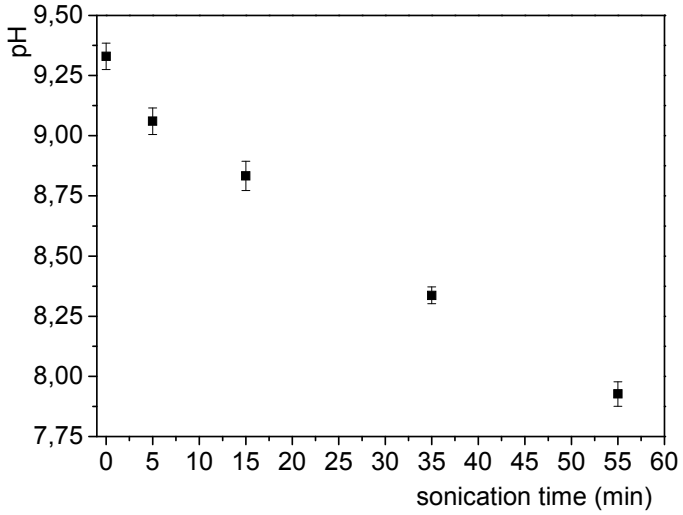


Figure _S5. pH decrease of water dissolutions of $CaCl_2$ (0.33M,15 mL) during the ultrasonic process. Other experimental conditions as described in the main text.

Tabla _S3. Estimation of the quantity of (bio)molecules (µg of immobilized biomolecule per mg of $CaCO_3$) deposited onto microparticles surface.

bio(molecule)	BSA-FITC	HIgG-FITC	HIgG-Per	Tyr	BG	MO	F	R	MR	MB
µg/mg	24	13	9	252	12.2	45	8.7	0.31	-	-
Charge at pH 6-7	-	+	+	-	0	0	0	+	+	+

Tyr (tyrosinase), BG (bromocresol green), MO (methyl orange), F (fluorescein), R (rhodamine B), MR (methyl red), MB (methylene blue).