

Supporting Information

Self-Assembly of Metal-Phenolic-Mesocrystals and Morphosynthetic Transformation towards Hierarchically Porous Carbons

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Materials and Methods

Reagents and chemicals

Zinc acetate dihydrate (ZAD; $\geq 99.5\%$, Carl Roth), ellagic acid (EA; 97%, Acros), and *N*-Methyl-2-pyrrolidone (*NMP*; 99%, Alfa Aesar) were used without further purification.

Synthesis of mesocrystals

In a typical experiment (EAZn2), 0.52 mmol of ZAD and 0.26 mmol of EA were dissolved in 25 ml of *NMP* solvent in a vial under ambient condition. After desired time at room temperature, the precipitate was filtered, washed with *NMP* and ethanol, and then dried at 40 °C under vacuum.

Direct carbonization of mesocrystals

The prepared mesocrystals were transferred to a box furnace and heat-treated at a target temperature (900 °C) under nitrogen atmosphere with a heating 10 °C min⁻¹ to carbonized the mesocrystal. After reaching the target temperature, the furnace was maintained for 1hr and then cooled to room temperature.

For the synthesis of the *reference carbon* (*Micro_C*, composition: C 64.45 wt%, N 11.77 wt%, H 2.3 wt%), 1 g of carbon precursor obtained from reference [R1: compound 1], was thoroughly mixed with the respective 3 g of eutectic salt mixture (1 g of LiCl and 10.76 g of ZnCl₂) prior to the calcination process. The resulting mixtures were placed in a ceramic crucible and heated to 800 °C under nitrogen atmosphere with a heating rate of 2.5 K min⁻¹ in a box-type oven. After holding this temperature for 1 h the samples were allowed to cool to room temperature. In order to remove the residual salt porogen, the materials were grinded and washed in water for several hours and finally filtrated and dried in vacuum.

Characterizations

Powder X-ray diffraction patterns were taken on a Bruker D8 Advance instrument using Cu K α -radiation. TEM micrographs were obtained on a Zeiss EM 912 Ω instrument. SEM micrographs were obtained on a LEO 1550-Gemini instrument after sputtering with platinum. Optical microscopy images were taken with OMCL-AC160TS (Olympus). FT-IR spectroscopy was performed with a Varian 600 FT-IR spectrometer. ICP-OES was examined using Optima 2100 DV (Perkin-Elmer). Elemental analysis was accomplished as combustion analysis using a Vario Micro device. UV-visible spectra were recorded on a Lambda 2 UV/Vis spectral photometer (Perkin-Elmer). Nitrogen isotherms were measured at 77 K after degassing the samples at 150 °C under vacuum for 20 hours. CO₂ sorption was conducted at 273 K up to 1 bar. The nitrogen adsorption data in the relative pressure range $P/P_0 < 0.3$ in the linear region permitted calculation of the apparent surface area based on the BET equation. The pore size distributions were determined using the quenched solid density functional theory (QSDFT); the QSDFT software is an integral part of the QuadraWin Version 5.05. A Rhodamine B (RhB) solution with a concentration of 20 mg L⁻¹ was prepared by dissolving the dye in distilled water. 10 mg of the samples was then dispersed into the RhB solution (5 mL). To measure the maximum capacity in 10 min, 10 times denser RhB solution (200 mg L⁻¹) was used. The resultant mixture was stirred under the dark for a desired time and, then, the adsorption capacity was evaluated based on the time-dependent absorption at 554 nm in the UV-VIS spectra.

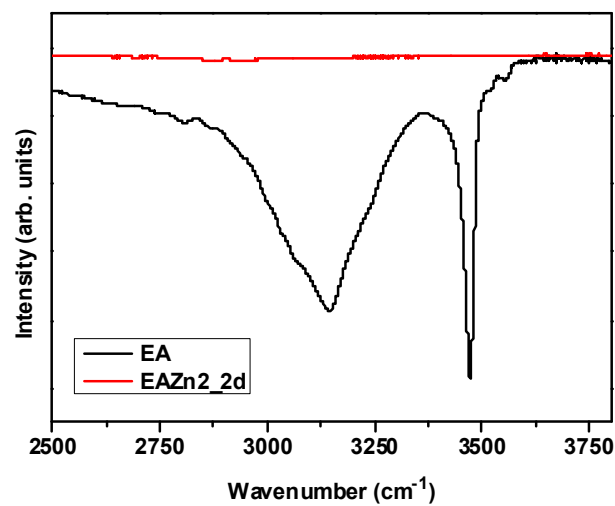


Figure S1. FT-IR spectrum of EA and EAZn2 mesocrystal.

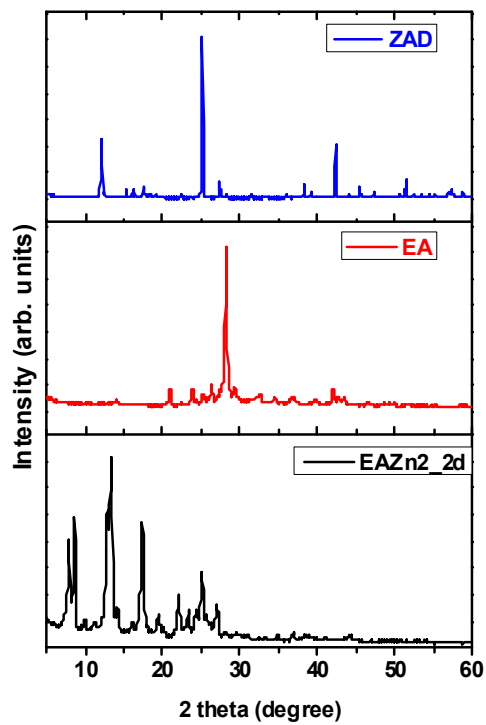


Figure S2. XRD patterns of ellagic acid, zinc acetate dehydrate, and EAZn2_2d mesocrystal.

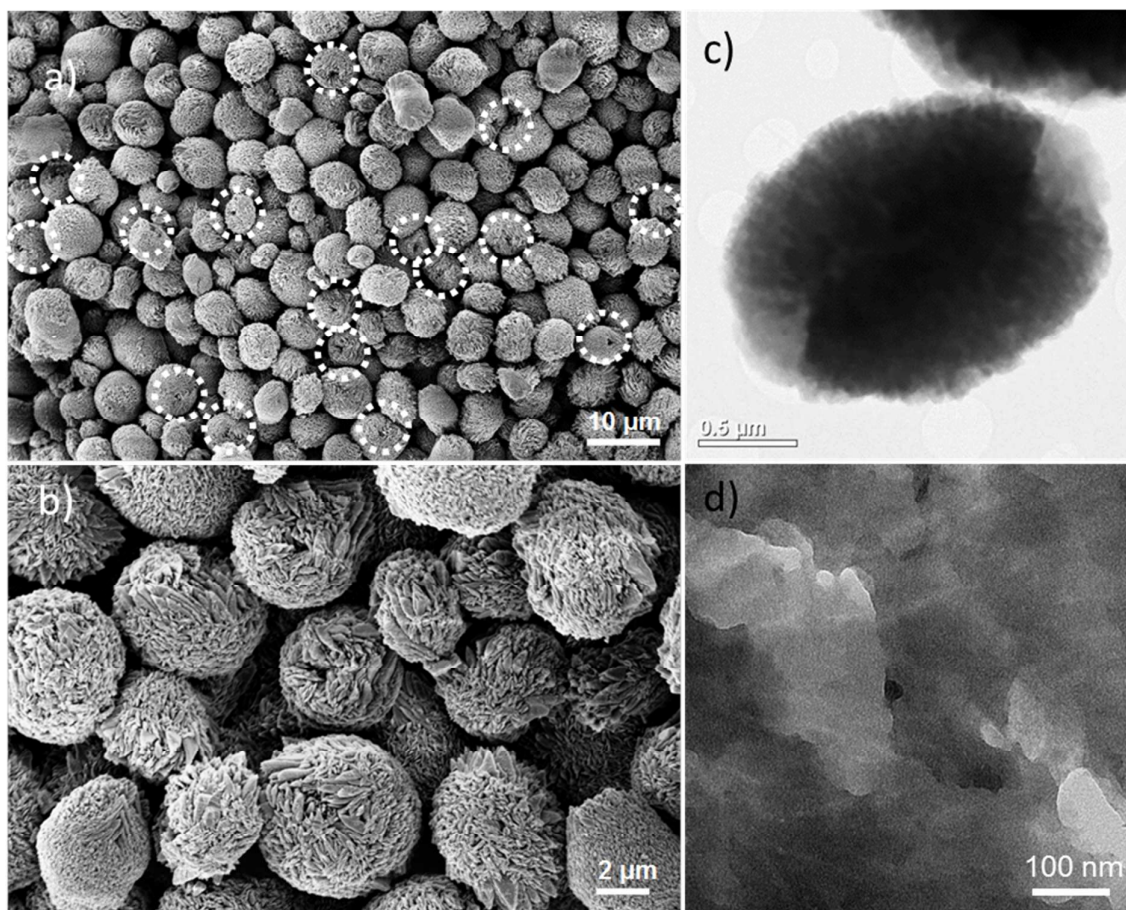


Figure S3. a, b) SEM c) TEM and d) ultramicrotome TEM micrographs of EAZn₂_2d mesocrystals. White circles indicate the holes in the mesocrystals.

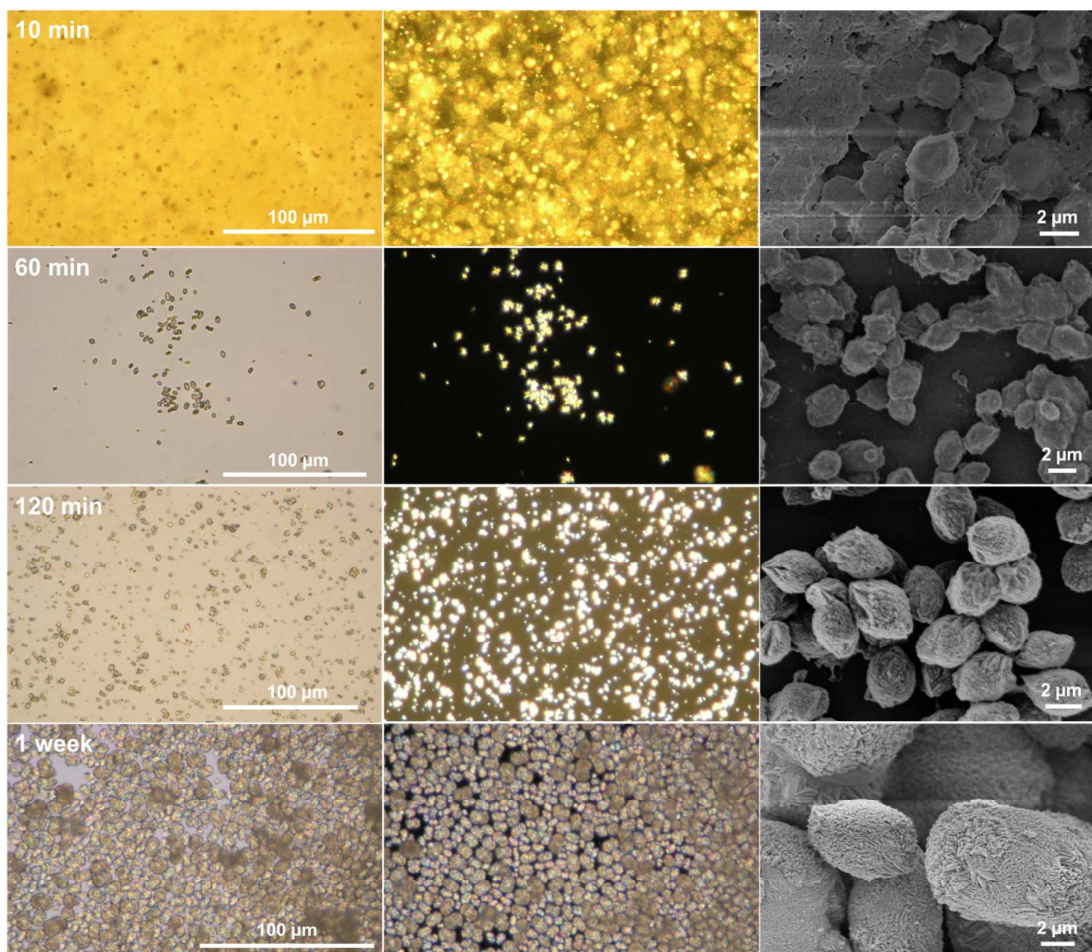


Figure S4. OM images (left), corresponding polarized images (middle) as well as SEM pictures (right) of EAZn₂ mesocrystals in dependence of reaction time.

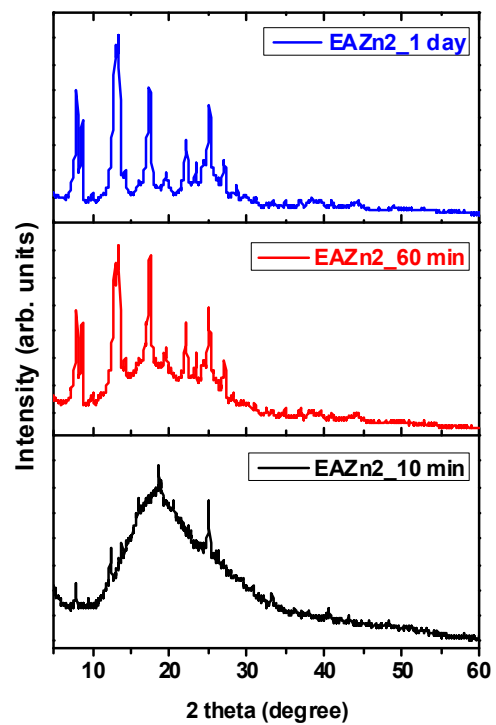


Figure S5. XRD patterns of EAZn₂ mesocrystals in dependence of reaction time.

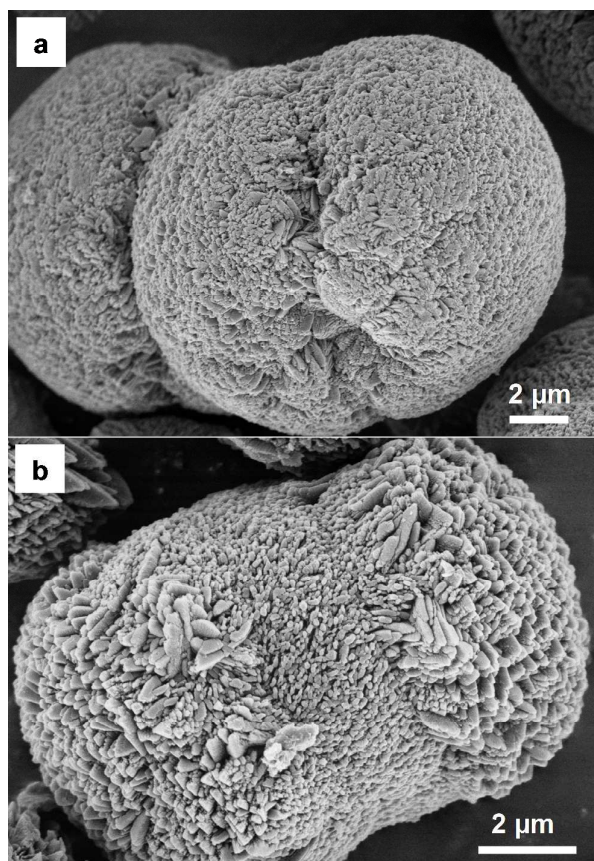


Figure S6. SEM micrographs of EAZn2_7d mesocrystal.

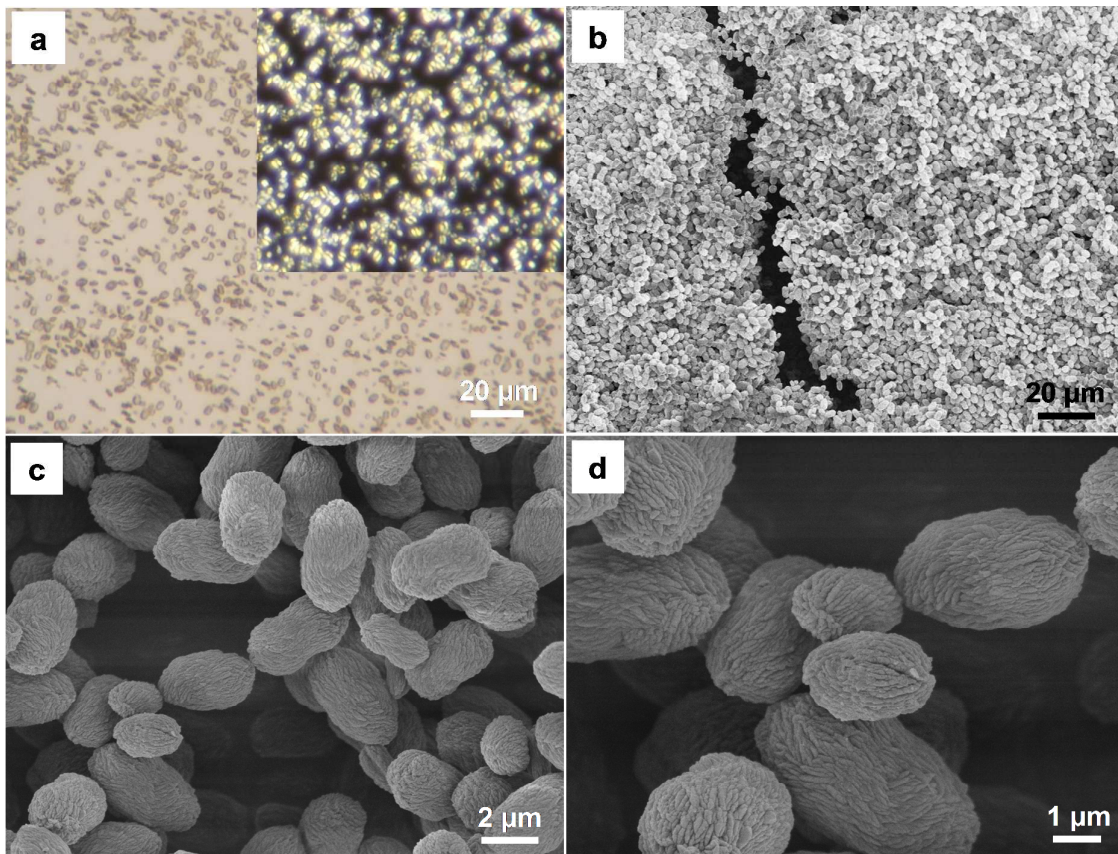


Figure S7. a) OM image (inset: polarized OM image) and b–d) SEM micrographs of EZn1_2d mesocrystal.

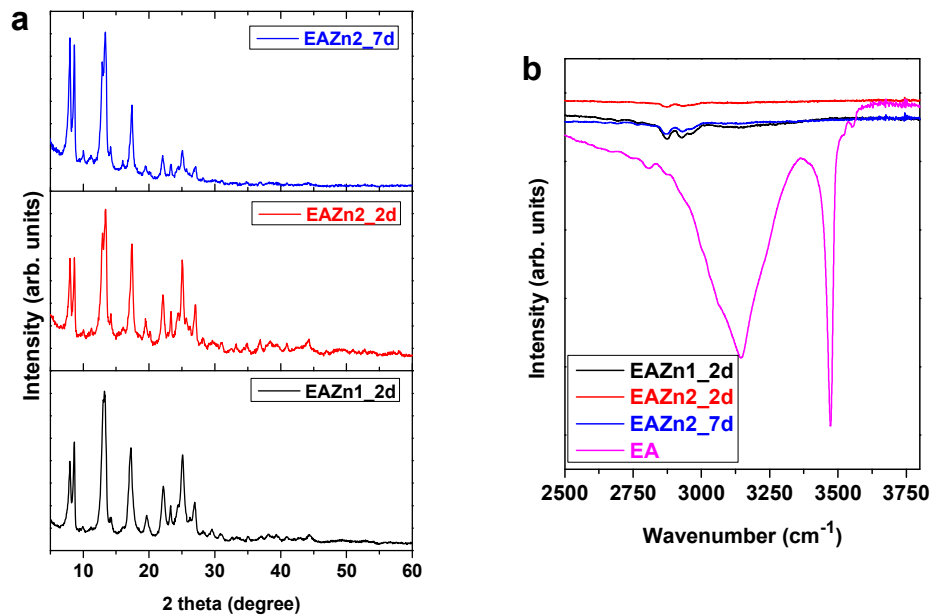


Figure S8. a) XRD patterns b) FT-IR spectra of mesocrystals prepared from different molar ratios of EA and zinc.

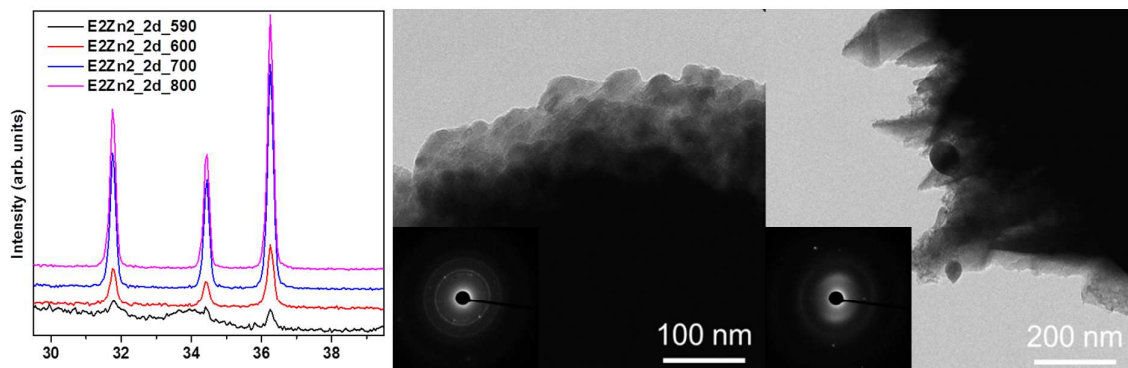


Figure S9. a) XRD patterns (left) of the products synthesized below the Zn vaporization at varying temperatures. TEM pictures of carbons prepared at 590 °C (middle) and 800 °C (right).

Oxide particles become visible in XRD at 590 °C synthesis temperature, i.e. from this point on there exists a crystalline zinc oxide species (left). According to the Scherrer equation, the crystallite size growth from 17-50 nm upon a synthesis temperature increase from 590 to 800 °C.

These particles are too big to be the origin of porosity, thus they likely result from resublimation on the outside of the carbon particles. TEM pictures from the sample prepared at 590 °C do not reveal any oxide particles in as they are probably too small for clear detection (middle). However, EAZn2_2d prepared at 800 °C (right) reveals bigger oxide particles with a size of about 30-50 nm supporting the XRD results.

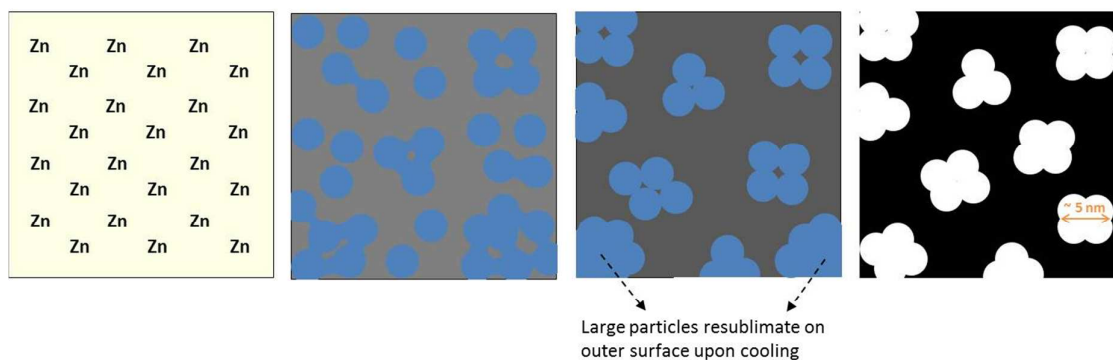
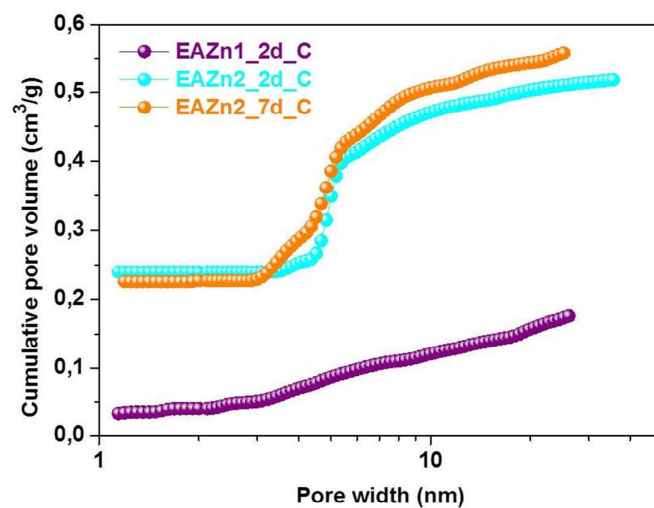


Figure S10. Cumulative pore size volume of the mesocarbon products (top). Scheme for pore formation (bottom): First, zinc and EA form a mesocrystalline material based on coordination of the two components (bottom, left). Upon heat treatment, nanocrystalline zinc oxide particles start to grow (bottom, second left) while at the same time carbothermal reduction of the surrounding organic matrix occurs. Eventually, the thinnest carbon walls are oxidized first which then leads to local fusion events of the zinc oxide nanocrystals (bottom, second, right). Here, the activation occurs very uniform due to the previous coordination within the zinc-EA mesocrystals (bottom, right). Larger zinc oxide particles (30-50 nm) resublimate on the outer surface upon cooling (see also figure S9).

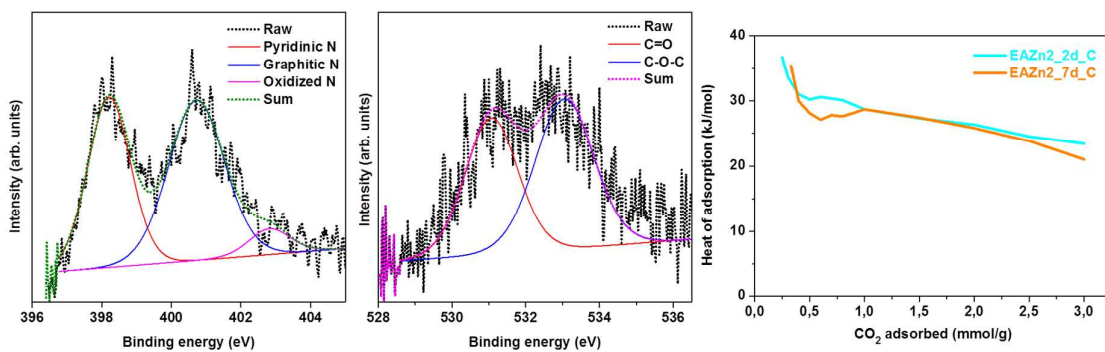


Figure S11. XPS of the carbon EAZn2_2d_C, high resolution N1s (left) and O1s (middle). Heat of adsorption (right) calculated from CO₂ measurements performed at 0 °C and room temperature (25 °C), EAZn2_2d_C (light blue) and EAZn2_7d_C (orange).

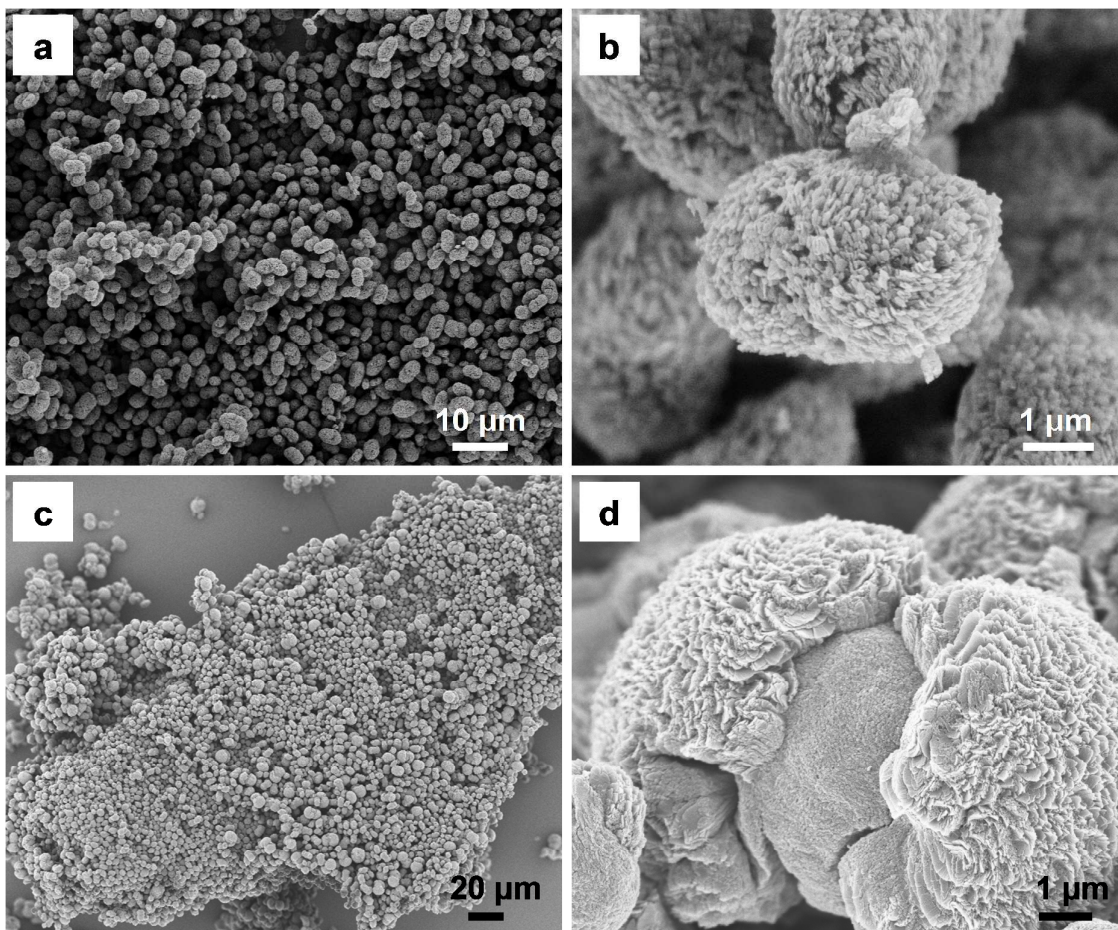


Figure S12. SEM micrographs of a–b) EAZn1_2d_C and c–d) EAZn2_7d_C mesocarbons.

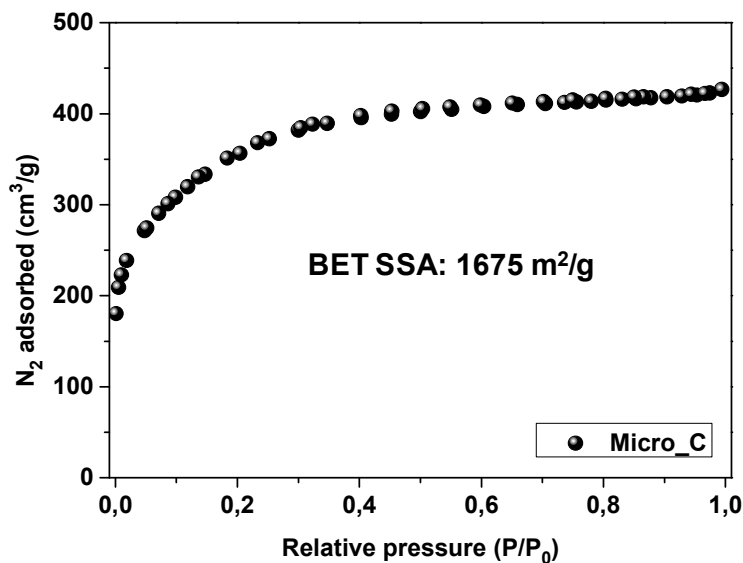


Figure S13. Nitrogen isotherm at 77 K of Micro_C. In a typical synthesis of the Micro_C, the 1 g of carbon precursor obtained from reference [R1: compound 1], was thoroughly mixed with the respective 3 g of eutectic salt mixture (1 g of LiCl and 10.76 g of ZnCl₂) prior to the calcination process. The resulting mixtures were placed in a ceramic crucible and heated to 800 °C under nitrogen atmosphere with a heating rate of 2.5 K min⁻¹ in a box-type oven. After holding this temperature for 1 h the samples were allowed to cool to room temperature. In order to remove the residual salt porogen, the materials were grinded and washed in water for several hours and finally filtrated and dried in vacuum.

[R1] D. Esposito, S. Kirchhecker, M. Antonietti, *Chem. Eur. J.* **2013**, *19*, 15097.

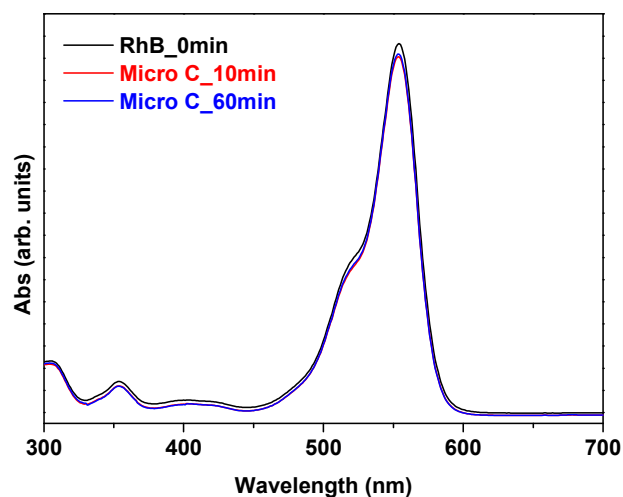


Figure S14. UV-VIS absorption of RhB solutions with Micro C material after 10 and 60 min mixing under dark condition.