

# STUDY OF THE FORMATION MECHANISMS OF SELF-ASSEMBLY MESOSTRUCTURED POLYMERS PRECURSOR FOR ORDERED MESOPOROUS CARBONS

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## Introduction

Ordered mesoporous carbons obtained by direct syntheses are exciting new materials with a wide range of application. Their preparations are based on the self-assembly of a polymer (e.g. resin obtained from phenol, resorcinol or phloroglucinol / formaldehyde systems) which acts as a carbon precursor and a pyrolysable surfactant (e.g. triblock copolymers) which is a pore structuring and porogene agent. The versatility of the process allows the preparation of numerous ordered structures as shown recently by Zhao's and Dai's groups, using different preparation routes via an aqueous media [1-3] or by a solvent evaporation induced self-assembly (EISA) process [4]. Despite these breakthroughs, mechanisms of formation of these materials are barely investigated with room for reproducibility improvement by the knowledge of the key experimental parameters. In this framework, we studied the formation mechanisms of FDU-14 (bicontinuous porous framework, space group: Ia-3d) and FDU-16 (interconnected cage-like pores, space group: Im-3m) phases obtained by solvent evaporation induced self-assembly and synthesis in aqueous media, respectively.

## Experimental

### *Aqueous route*

Mesoporous carbon material FDU-16 was prepared using a similar procedure to that described by Zhang et al.[3]. The influence of the mixing temperature of carbon precursors and surfactant solutions was particularly investigated. Both solutions were placed at 5, 20 or 40°C before being mixed at these temperatures; then the resulting solution was heated to 65°C for polymerization/precipitation. The obtained samples were calcined at 700°C during 3 hours in a nitrogen flow. The samples were characterized by X-ray diffraction, scanning electron microscopy (SEM) and nitrogen physisorption at 77K. The synthesis was followed by dynamic light scattering (DLS) and scanning electron microscopy (SEM).

### *EISA route*

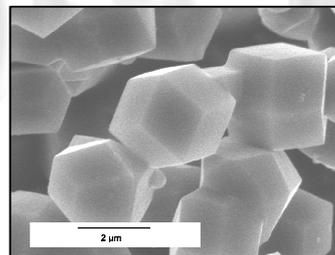
Mesoporous carbon material FDU-14 was prepared using an optimized procedure based on the process described by Meng et al. [4]. The final product, obtained after mixing the resin and the surfactant, was poured into Petri dishes in order to evaporate the solvent. After drying, these films were heated at

100 °C in an oven during 24 hours. The influence of the drying rate on the meso-organisation was investigated by modifying the liquid film thickness before drying (flash (one drop), 1 mm and 6 mm) and the evaporation temperature (14 or 21 °C). The samples were characterized by X-ray diffraction (XRD) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFT).

## Results and discussion

### *Aqueous route*

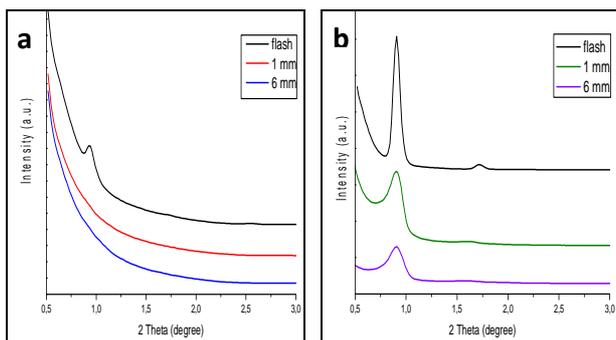
DLS measurements of particle size evolution for F127 surfactant solution, before and after the addition of carbon-precursor oligomers, at different temperatures ( $T= 5, 20, 40^{\circ}\text{C}$ ) show the strong interactions that take place between both components. Indeed, we observed, even below the critical micelle temperature ( $\sim 15^{\circ}\text{C}$ ), formation of micelles of about 20-30 nm. The color change of the solution during the heat-treatment at 65°C indicates an increase of the degree of polymerization of the carbon precursor oligomers within the composite micelles. At the precipitation time, the precipitate appears like a liquid since it can only be separated by centrifugation and its morphology is ill-defined (smooth film appearance). Longer treatments are necessary to complete the polymerization that leads to well-defined particles with rhombododecahedron shape (Fig. 1). The influence of the mixing temperature on the morphology, mesoscopic ordering and precipitation time is discussed in the light of the localization of carbon precursors in the composite micelles at the beginning of the synthesis.



**Fig. 1** SEM image of FDU-16 calcined at 700 °C with a rhombododecahedron morphology.

### *EISA route*

Concerning the FDU-14 carbon mesostructured phase, its structure organization and the polymer reticulation of the as-made sample were followed with X-ray diffraction, as shown in Fig. 2, and infra-red spectroscopy, respectively. By increasing the evaporation rate (low liquid film thickness and high temperature of evaporation), a better organisation is obtained.



**Fig. 2** XRD pattern of flash, thin and thick films thermopolymerized at 100 °C after being dried at 14 °C (a) and 21 °C (b).

## Conclusions

### *Aqueous route*

The temperature of the F127 surfactant and carbon-precursor polymer mixture affects the synthesis of mesoporous carbons even if identical experimental conditions are used latter. This parameter influences probably the carbon-precursor localization within the micelles and leads to different materials characteristics as regards organization and morphology.

### *EISA route*

Like for mesostructured oxide films, a clear correlation appears with the rate of evaporation, the degree of polymerisation of the carbon-precursors oligomers and the ordering of the mesostructure.

## Acknowledgements

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## References

- [1] Zhang, F. Q.; Meng, Y.; Gu, D.; Yan, Y.; Yu, C. Z.; Tu, B.; Zhao, D. Y., *Journal of the American Chemical Society* 2005,127 (39), 13508-13509.
- [2] Zhang, F. Q.; Meng, Y.; Gu, D.; Yan, Y.; Chen, Z. X.; Tu, B.; Zhao, D. Y., *Chemistry of Materials* 2006,18 (22), 5279-5288.
- [3] Zhang, F. Q.; Gu, D.; Yu, T.; Zhang, F.; Xie, S. H.; Zhang, L. J.; Deng, Y. H.; Wan, Y.; Tu, B.; Zhao, D. Y., *Journal of the American Chemical Society* 2007,129 (25), 7746-7747.
- [4] Meng, Y.; Gu, D.; Zhang, F. Q.; Shi, Y. F.; Cheng, L.; Feng, D.; Wu, Z. X.; Chen, Z. X.; Wan, Y.; Stein, A.; Zhao, D. Y., *Chemistry of Materials* 2006,18 (18), 4447-4464.