Hydrophilic-Lipophilic Balance Engineering for Controllable Self-Assembly of Hierarchical Macroporous UiO-66 (Ce) Films

Chanhwi Lee[1], Sung Hyun Park[1], Joonseok Lee[1]
[1]*Department of Chemistry, Hanyang University, Seoul 04763, Republic of Korea*
calllucky@hanyang.ac.kr

Metal–organic framework (MOF) films have attracted significant interest in various fields due to their diverse chemical functionalities, intrinsic microporosity, and three-dimensional (3D) nanostructures. However, the precise control of macroporous MOF films with both high structural integrity and tunable porosity remains a great challenge [1]. In this study, we present a hydrophilic-lipophilic balance (HLB)-guided self-assembly strategy to synthesize hierarchical macroporous UiO-66 (Ce) films with a well-defined micro– macroporous structure. By systematically tuning the overall hydrophilic-lipophilic balance (HLB_{total}) of micelles and interfacial tension properties, uniform hierarchical macroporous UiO-66 (Ce) films were successfully fabricated at an HLB_{total} of 11, with P123/P105 serving as a soft template. Dissipative particle dynamics (DPD) simulations revealed that HLB disparities between surfactants govern miscibility and interfacial stability, directly influencing micelle organization and structural evolution. The resulting hierarchical macroporous UiO-66 (Ce) films exhibited enhanced catalytic performance in glycerol acetalization, attributed to improved mass transport and an increased number of active sites. This strategy provides fundamental insights into self-assembly mechanisms and interfacial dynamics of hierarchical macroporous MOF films, contributing to the rational design of advanced porous materials [2].

References

[1] Jiang, Z., Xu, X., Ma, Y., Cho, H.S., Ding, D., Wang, C., Wu, J., Oleynikov, P., Jia, M., Cheng, J., Zhou, Y., Terasaki, O., Peng, T., Zan, L., Deng, H., Nature, 586 (2020) 549-554.
[2] Jeon, E., Koo, B., Kim, S., Kim, J., Yu, Y., Jang, H., Lee, M., Kim, S.-H., Kang, T., Kim, S.K., Kwak, R., Shin, Y., Lee, J., Nature communications, 15 (2024) 1366.

Figures

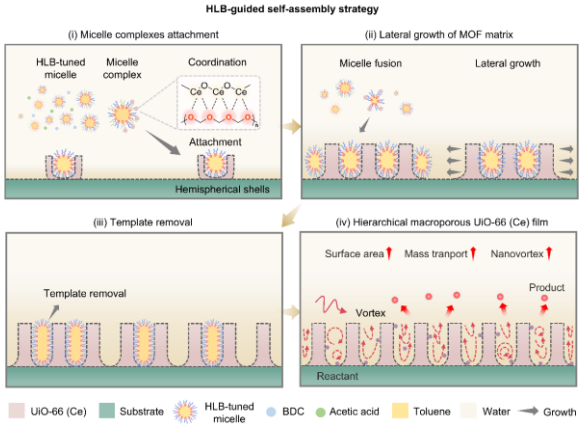

Figure 1: Schematic illustration of the HLB-guided self-assembly mechanism for synthesizing hierarchical macroporous UiO-66 (Ce) films. HLB-tuned micelles coordinate with Ce oxo-clusters, forming micelle-Ce complexes. These complexes adhere to the PVP-coated substrate and self-assemble into hemispherical shells. Subsequent micelle fusion and lateral growth connect these structures, resulting in uniform hierarchical macroporous UiO-66 (Ce) films. The final architecture induces vortices within the macropores, enhancing mass transport and significantly improving catalytic performance in glycerol acetalization.

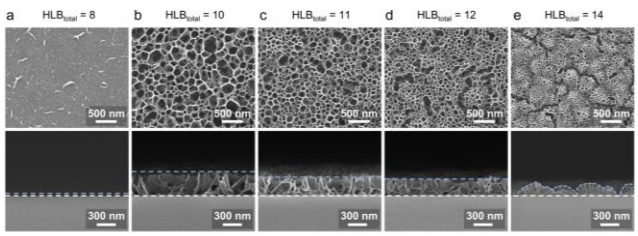

Figure 2: Top-view (top) and cross-sectional (bottom) SEM images of hierarchical macroporous UiO-66 (Ce) films prepared with P123/P105 at various HLB_{total} values: (a) 8, (b) 10, (c) 11, (d) 12, and (e) 15.