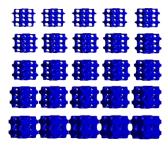
Kinetically Trapped Micelles: Cavitation Induced Exchange for Persistent Micelle Templates

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Kinetically trapped micelles are beneficial for a range of developing applications such as drug delivery, nanoreactors, and templates for porous materials. Kinetic control allows for decoupling of micelle size from subsequent application. However, homogenization and size tuning are innately challenging due to the high- χ N barrier toward chain exchange. Sonication was recently discovered to enable switchable chain exchange where cavitation induces exchange and cessation returns micelles to kinetic entrapment.¹ SANS measurements were done to quantify mixing during cavitation induced exchange (CIE). The extent of exchange increases linearly with time, where the rate was directly proportional to polymer concentration. The CIE mechanism allows for switchable chain exchange where cessation is particularly useful for micelle templates. Persistent Micelle Templates (PMT) were developed to enable independent tunability over pore and wall dimensions.^{2,3} Typical PMT recipes involve water-reactive material precursors that lower the barrier to exchange upon addition through hydrolysis. A new *ex situ* hydrolysis approach was developed, significantly decoupling micelle kinetic control from materials chemistry to expand the PMT window.⁴ SAXS and SEM data confirmed high-resolution control over the nanomaterial

series. Electrochemical experiments revealed two TiO_2 polymorphs (anatase and bronze) that exhibited monotonic trends attributed to confinement effects. Here, increasing wall-thickness led to larger crystallites and greater extent of lithiation, reaching $Li_{0.66}TiO_2$. These works support the homogenization of kinetically controlled micelles via CIE and subsequent processing methods to support robust deployment of these micelles as templates for functional materials.

- (1) Lantz, K. A.; Sarkar, A.; Littrell, K. C.; Li, T.; Hong, K.; Stefik, M. *Macromolecules* **2018**, *51* (17), 6967–6975.
- (2) Lokupitiya, H. N.; Jones, A.; Reid, B.; Guldin, S.; Stefik, M. Chem. Mater. 2016, 28 (6), 1653–1667.
- (3) Sarkar, A.; Stefik, M. J. Mater. Chem. A 2017, 5 (23), 11840–11853.
- (4) Lantz, K.; Clamp, N. B.; van den Bergh, W.; Sarkar, A.; Stefik, M. Small 2019, Accpeted.