Cyclodextrin-based Hybrid Materials

Sachin P. Patil, Haneen Omar, Basem Moosa, Dalaver Anjum, Georges Mouchaham and Niveen M. Khashab*

Smart Hybrid Materials (SHMs), Advanced Membranes and Porous Materials Center (AMPMC)

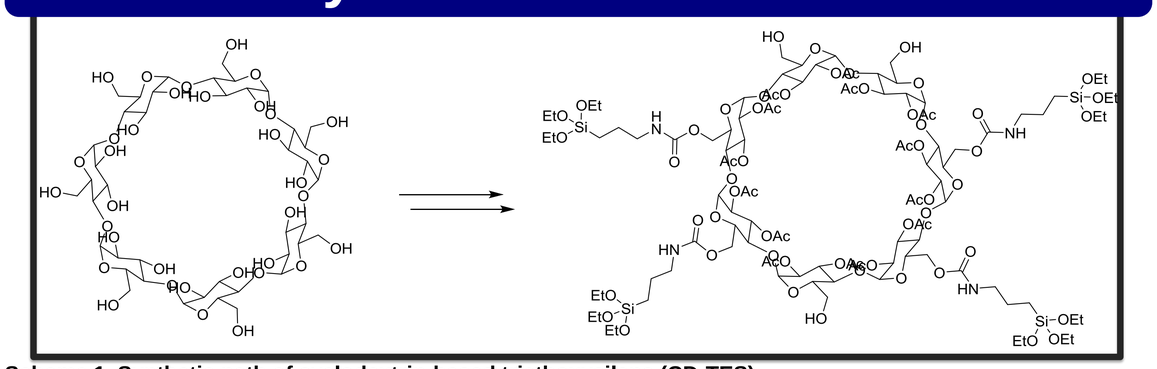
Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology (KAUST)

Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides consisting of six or more linked D-glucopyranose units. Because of their toroidal shape, these macromolecules contain geometrically well-defined angstrom-scale cavities which are known to form inclusion compounds with organic molecules of suitable geometry and function. A potentially important application for cyclodextrins is the removal of toxic organic contaminants in water.[1-5] Moreover, the chiral nature of the cavity in these molecules makes them promising candidates for enantiomeric separation applications.[2] Recently several methods of producing CD-functionalized materials have been reported.[1-5] These involved the cross-linking of CDs into polymers using C-OH linkers such as epichlorohydrin and diisocyanato compounds.[3-5] The another approach utilizes the coating or grafting of CD moieties onto a stationary phase such as organic polymers or silica gel.[2] Although CD-containing polymers have proven to be useful for the separation of organic pollutants from water, these materials often have somewhat of a low binding affinity with organic molecules.[3-5] A notable exception to this is the recently reported preparation of a new "nanoporous" CD polymer, which proved to be very effective in the removal of small organic molecules from water.[1 and 4] Although this material can be considered "nanoporous" in the sense that it contains cavities resulting from the CD molecules, the polymer had a very low surface area[2] and is thus completely lacking in framework nanoporosity.

Periodic mesoporous organosilicas nanoparticles (PMOs-NPs) materials are fundamentally unique thanks to the combination of all the advantages of a robust porous organic/inorganic framework, along with the intrinsic properties of the organic fragments. Our strategy is to introduce cyclodextrin into the PMOs-NPs to combine the numerous assets of mesoporous silica and unlimited applications of cyclodextrins.

Synthesis Of CD-TES



Scheme 1. Synthetic path of cyclodextrin-based triethoxysilane (CD-TES)

Characterization Of CD-TES

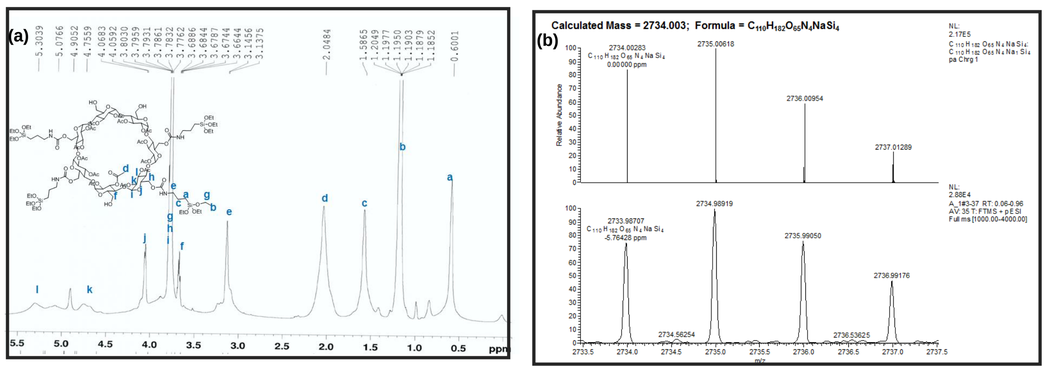
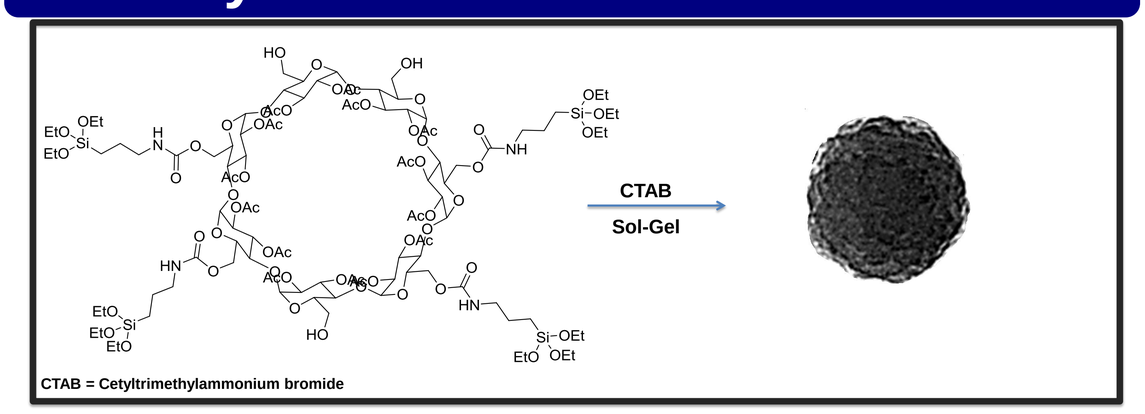


Figure 1.(a)[1]H NMR and (b)[13]HR-Mass spectra of CD-Silane

Synthesis Of CD-PMOs-NPs



Scheme 2. Synthetic path of cyclodextrin-based Periodic Mesoporous Organosilicas Nanoparticles (CD-PMOs-NPs)

FTIR Of CD-silane & CD-PMOs-NPs

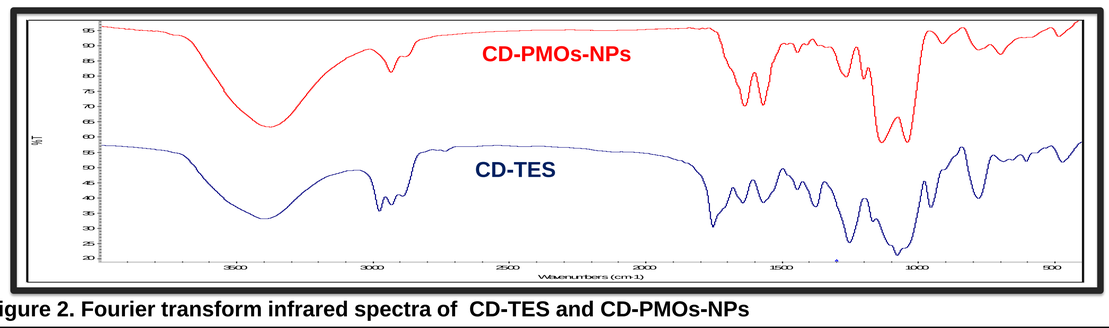


Figure 2. Fourier transform infrared spectra of CD-TES and CD-PMOs-NPs

Characterization Of CD-PMOs-NPs

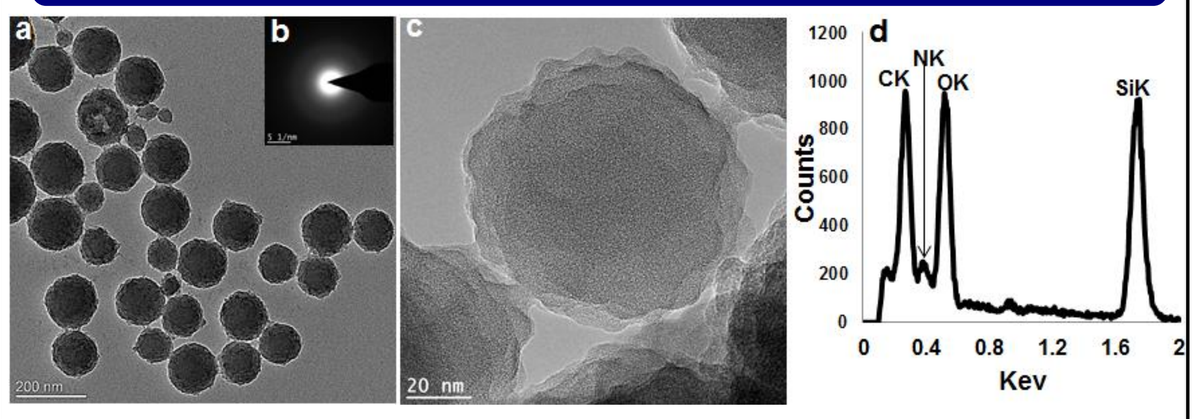


Figure 3. (a & c) TEM images (b) SAED image; (d) EDS of CD-PMOs-NPs.

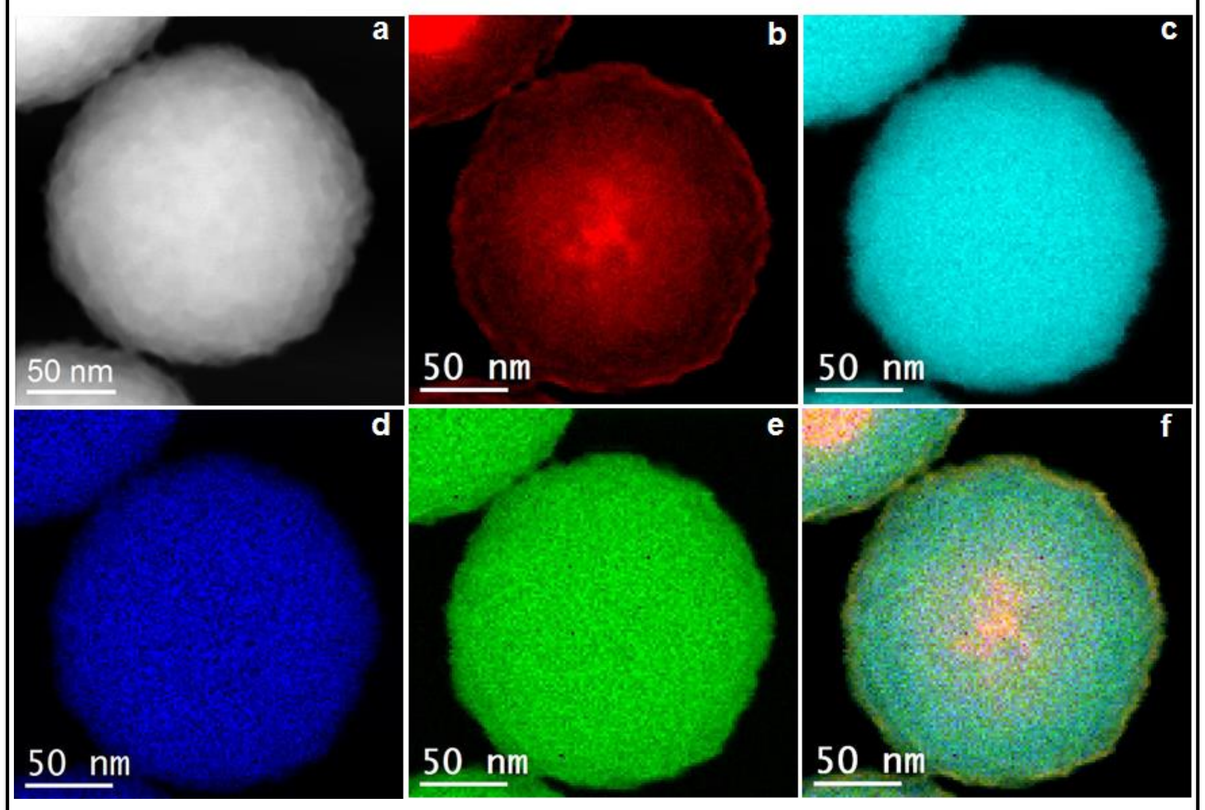


Figure 4. STEM-EELS elemental mapping (a) STEM; (b) silicon; (c) Carbon (d) Nitrogen; (e) Oxygeno of representative CD-PMOs-NPs. (f) The merged image consists of silicon, nitrogen, and oxygen.

BET of CD-PMOs-NPs

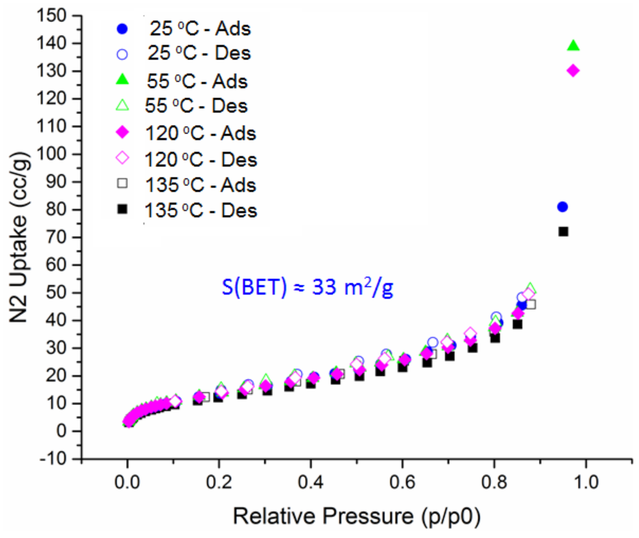


Figure 5. Nitrogen adsorption–desorption isotherms of CD-PMOs-NPs.

Conclusions

We have successfully synthesized cyclodextrin–based PMOs-NPs hybrid materials. Our results show that the produced materials have 33 m^2/g surface area, which is comparatively better than β-CD polymer crosslinked with epichlorohydrin (EPI-CDP, SBET = 23 $m^2\ g^{-1}$), which is the most extensively studied β-CD polymer for water purification and has been commercialized.[4] We will synthesize mixed cyclodextrin–based PMOs-NPs with commercially available TES derivatives (Phenylene or ethylene) to improve surface area.

References

1. Alsbaiee, A.; Smith, B. J.; Xiao, L.; Ling, Y.; Helbling, D. E. and Dichtel, W. R. Rapid removal of organic micropollutants from water by a porous β-cyclodextrin polymer. *Nature* **2016**, *529*,190.

2. Wang, L.; Donga, S.; Hana, F.; Zhaoa, Y.; Zhanga, X.; Zhanga, X,; Qiua, H.; Zhaoa, L. Spherical -cyclodextrin-silica hybrid materials for multifunctionalchiral stationary phases. *J. Chromatogr. A* **2015**, *1383*, 70.

3. Morin-Crini, N. and Crini, G. Environmental applications of water-insoluble β-cyclodextrin–epichlorohydrin polymers. *Prog. Polym. Sci.* **2013**, *38*, 344.

4. Lo Meo, P., Lazzara, G., Liotta, L., Riela, S. and Noto, R. Cyclodextrin–calixarene co-polymers as a new class of nanosponges. *Polym. Chem*. **2014**, *5*, 4499.

5. Crini, G. and Morcellet, M. Synthesis and applications of adsorbents containing cyclodextrins. *J. Sep. Sci.* **2002**, *25*, 789.

Acknowledgements: We acknowledge financial support from KAUST and technical assistance from the Core Laboratories at KAUST.