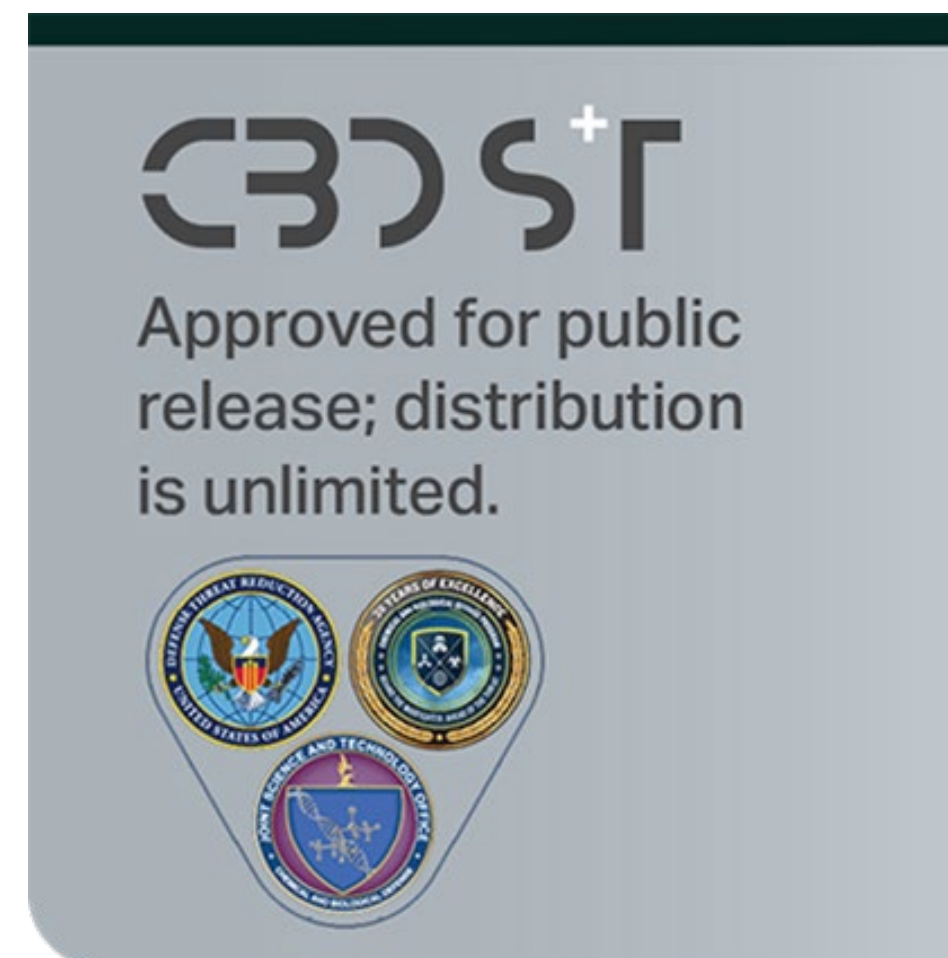


Formulation of chitosan-MOF-808 core-shell fibers for organophosphate hydrolysis under non-buffered conditions

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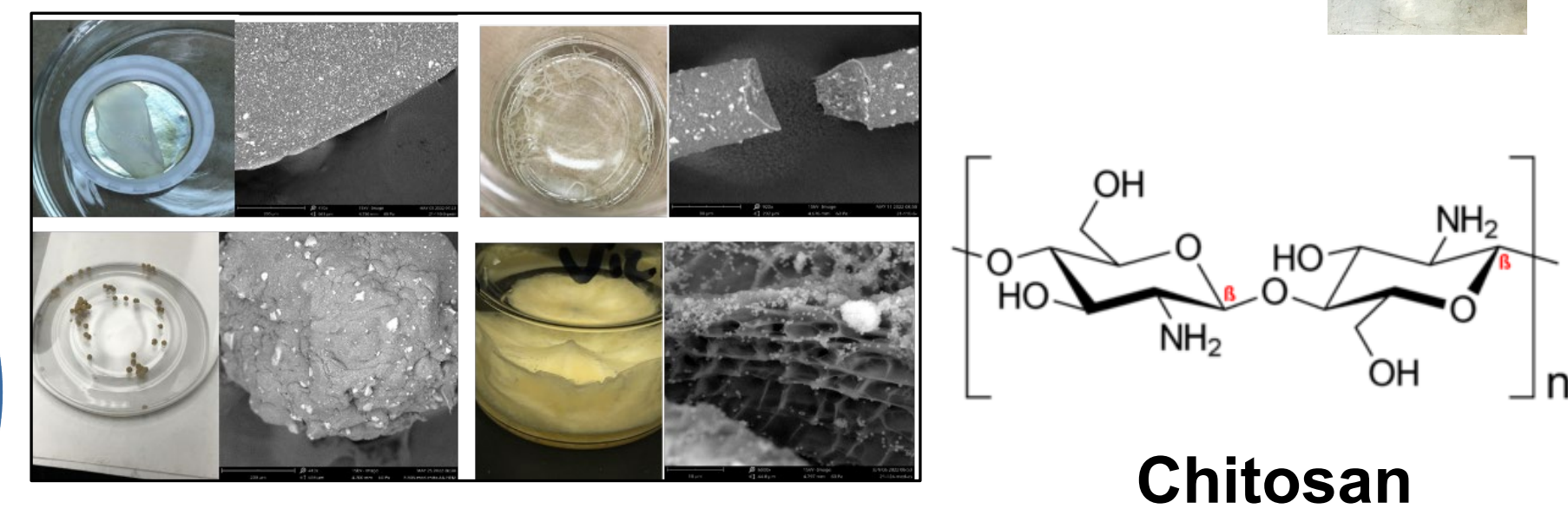
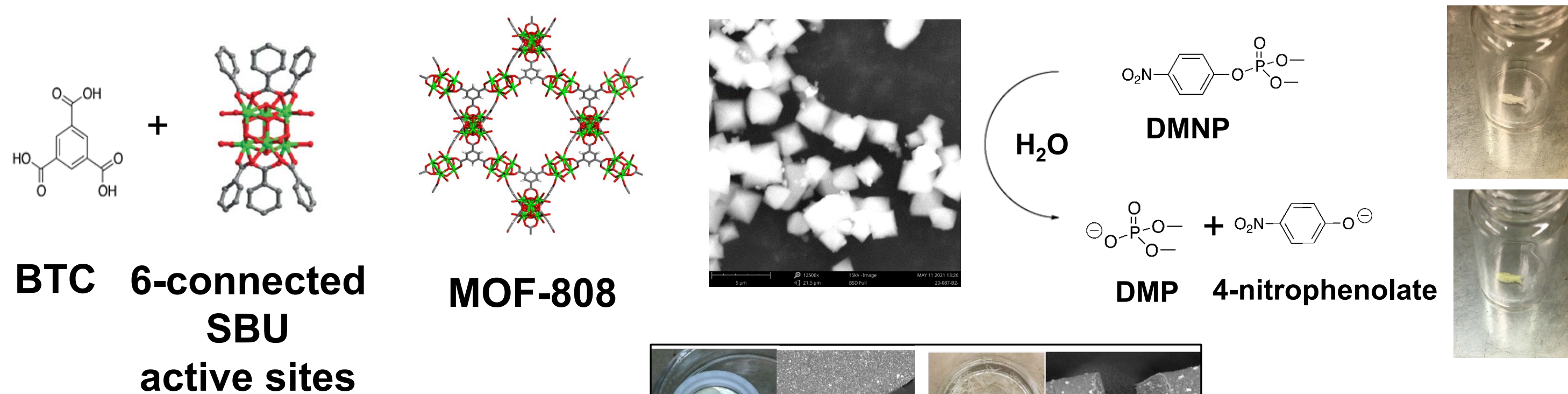
Relevance

- Toxic organophosphates pose a threat to health and life
- Organophosphates covalently bind to the acetylcholinesterase enzyme causing a build up of acetylcholine, which prevents contraction of respiratory muscles which eventually leads to death by asphyxiation or cardiac arrest
- Stable materials capable of fast organophosphate hydrolysis within a gas mask or protective suits are greatly needed
- Certain enzymes that can render organophosphates inactive are only effective under certain conditions, however, susceptible to degradation¹

Metal-Organic Frameworks (MOFs)

- Metal-organic frameworks (MOFs) are porous materials comprised of organic struts which are connected to metal-containing nodes named secondary building units (SBUs)
- Zirconium based MOFs are comprised SBUs that can be connected with a maximum of 12 bridging carboxylate organic linkers, however, 10, 8, 6 and 4-connected SBUs can be obtained.² SBUs with < 12 connectivity have missing-linkers Zr(OH)(H₂O) sites
- While missing-linker sites can facilitate organophosphate hydrolysis under buffered reaction conditions, they are relatively inactive under non-buffered conditions³

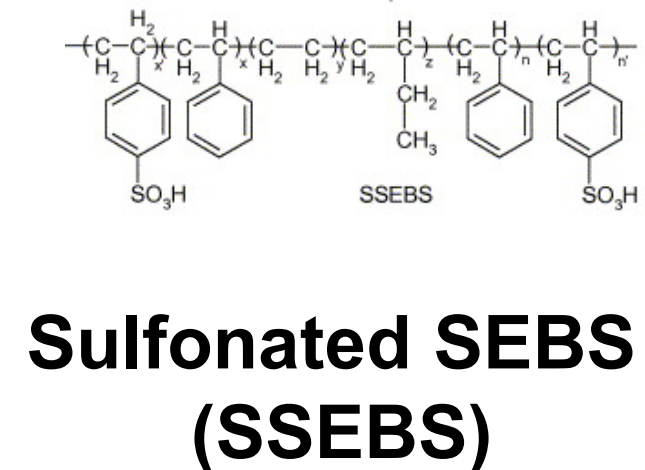
Chitosan (CS)/MOF-808 composites



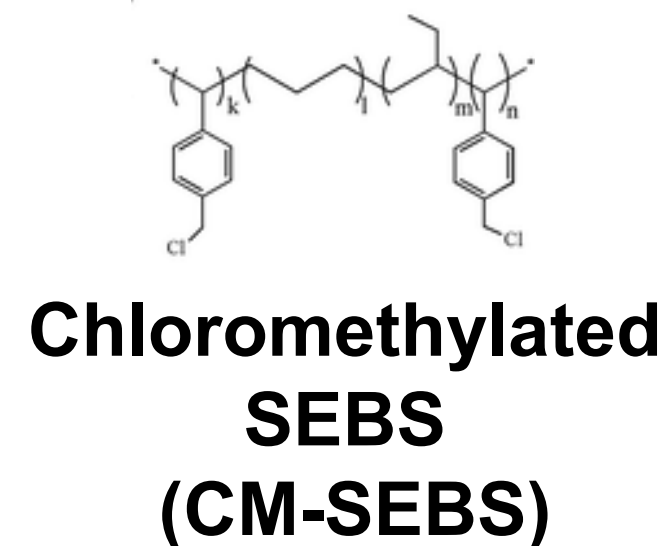
Chitosan MOF composites

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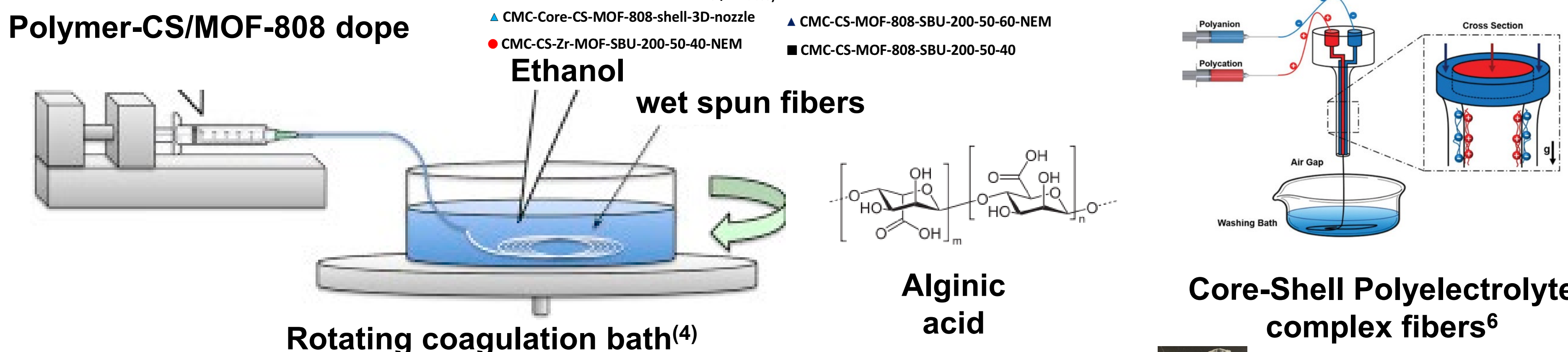
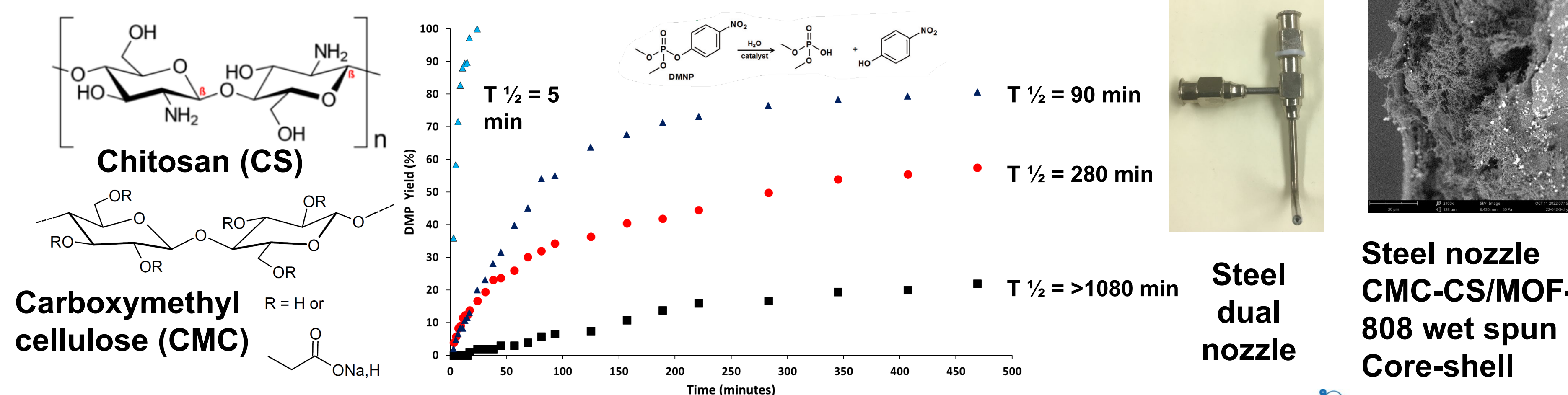


Sulfonated SEBS (SSEBS)

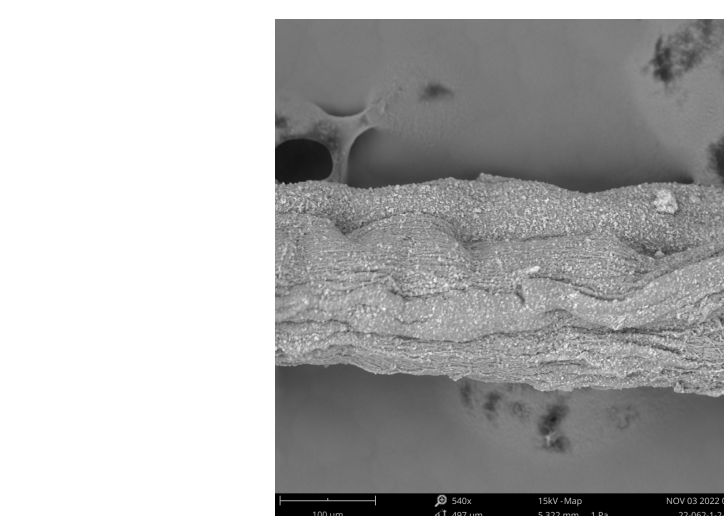


Chloromethylated SEBS (CM-SEBS)

Pre-mixed vs. core-shell polymer-CS/MOF-808 wet spun fibers



Increasing dope concentration
Fiber quality



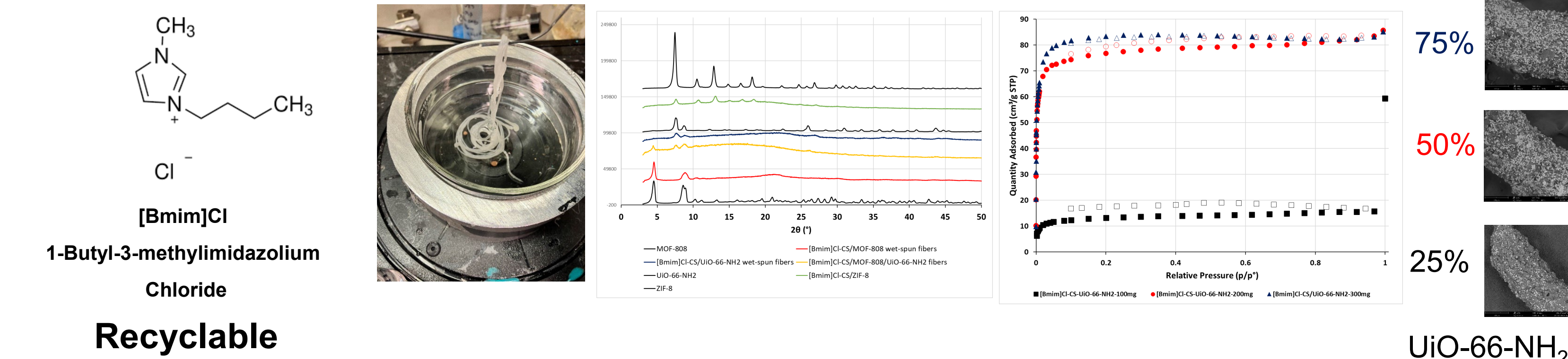
CaCl₂-Alginate-CS/MOF-808 wet spun Core-shell fiber



3D printed dual nozzle
CMC-CS/MOF-808 wet spun Core-shell fiber

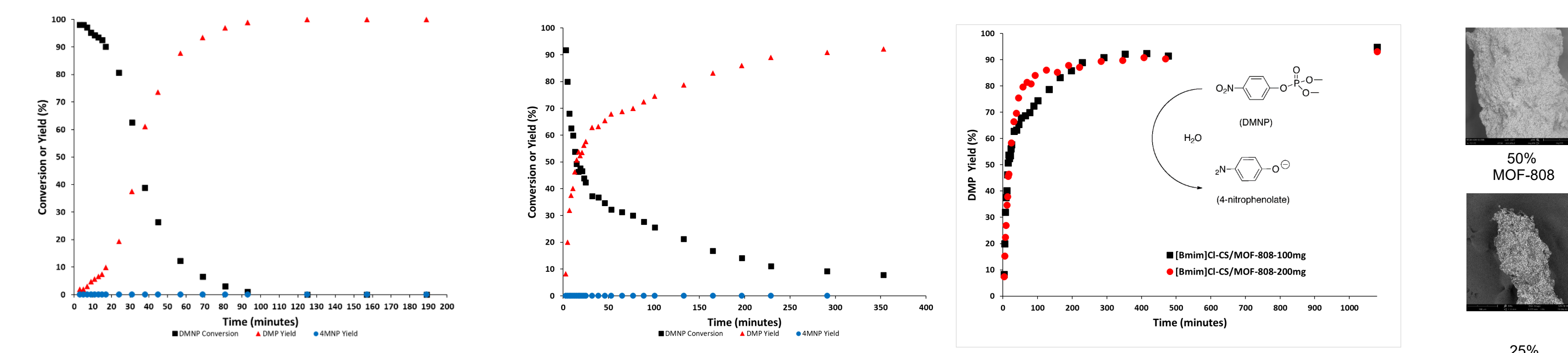
- Incorporation of CMC to CS/MOF-808 dope generates wet spun fibers that are less brittle than CS/MOF-808 fibers, however, a limited 80% DMNP total conversion observed
- Hypothesis: surface reactivity and elastic functionality of fibers should be enhanced through core-shell formulation
- Utilization of acrylic 3D printed dual nozzle facilitates better core-shell fibers than steel nozzle on account of better polyelectrolyte complexation of ionic core polymers with cationic CS/MOF-808 sheath, however, acrylic nozzle unstable to SEBS THF dopes which results in loss of fiber quality

Utilization of ionic liquid for CS-MOF fibers



Recyclable

- Utilization of ionic liquid [Bmim]Cl facilitates recyclable fabrication of wet-spun chitosan-MOF robust fibers without the need for basic activation



- Residual ionic liquid within [Bmim]Cl-CS/MOF-808 fibers significantly affects porosity and DMNP hydrolysis under non-buffered conditions, [Bmim]Cl alone does not enhance hydrolysis

Conclusions

- Chitosan was utilized as a polymeric matrix that facilitated the fabrication of MOF fiber, beads, films, and sponge composites, however, they suffer from brittleness
- Incorporation of pre-mixed co-polymers increases fiber strength, however, inhomogeneity of MOF/CS on the surface of the fibers inhibits full DMNP conversion
- CS/MOF-808 sheath coverage on core polymers and consequently DMNP reactivity where enhanced through polyelectrolyte complexation with the use of an acrylic 3D printed dual nozzle
- The use of ionic liquids facilitates recyclable fabrication of chitosan-MOF composites without the need for basic activation, however, it affects porosity and hydrolysis reactivity of the MOF
- Surface of chitosan-MOF composites dictates porosity and hydrolysis reactivity
- Our newly synthesized core-shell fibers offer advancements for the practical and recyclable utilization of MOFs as organophosphate hydrolysis catalyst within fibers for organophosphate protection

References

- (1) Li, P. et al., Chen Q. *Chem.* **2018**, 4, 1022-1034
- (2) Chen, Z. et al., *Coordin. Chem. Rev.*, **2019**, 386, 32-49
- (3) Mondloch, J. E. et al., *Nat. Mater.*, **2015**, 14, 51
- (4) Araki, J. et al., *Polymer*, **2020**, 188, 122116

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