## MESOPOROUS UIO-66-NH2 THIN FILM GROWTH ON TIO2 COATED FABRICS USING ATOMIC LAYER DEPOSITION (ALD) FOR ENHANCED ORGANOPHOSPHATE DEGRADATION

<u>Mai O. Abdelmigeed</u>,<sup>a</sup> Gregory W. Peterson,<sup>b</sup> John J. Mahle,<sup>b</sup> Gregory N. Parsons<sup>a</sup> <sup>a</sup> Chemical and Biomolecular Engineering, North Carolina State University, 911 Partners Way, Raleigh, NC, 27695 (United States) <sup>b</sup> U.S. Army Combat Capabilities Development Command Chemical Biological Center.

0.5. Army Compatible Capabilities Development Command Chemical Biological Center

8198 Blackhawk Road, Aberdeen Proving Ground, MD, 21010 (United States)

E-mail: moabdelm@ncsu.edu

Keywords: Mesoporous UiO-66-NH<sub>2</sub>, thin films, ALD, Organophosphate Degradation.

Nowadays, most of the UiO-66-NH<sub>2</sub> research focuses on the capabilities of the microporous UiO-66-NH<sub>2</sub>-fabric composites for organophosphate degradation via hydrolysis. Unfortunately, microporous UiO-66-NH<sub>2</sub> suffers from diffusion limitation of the bulky organophosphates accessing the active sites. As a novel solution, we are introducing the aqueous phase synthesized mesoporous UiO-66-NH<sub>2</sub> thin film on fabric coated with ≈20 nm TiO<sub>2</sub> using ALD. The mesoporous version of UiO-66-NH<sub>2</sub> overcomes the mass transfer limitation issues while the TiO<sub>2</sub> layer works as nucleation centers to form a dense, robust, and homogeneous MOF thin films. The mesoporosity of the solvothermally synthesized UiO-66-NH<sub>2</sub>-fabric composites is mainly due to the utilization of an amphoteric surfactant, CAPB, as a template to construct these mesochannels.<sup>[1]</sup> Fig.(1,a) shows the benign MOF synthesis process avoiding the common toxic solvents and highly acidic medium at elevated temperatures. Importantly, Fig.(1,b) shows the pore size distribution of mesoporous UiO-66-NH<sub>2</sub> has both characteristic pore width peaks corresponding to the microporous range and a new peak at ≈28 Å corresponding to the mesoporous range. The benign synthesis approach allows mesoporous UiO-66-NH<sub>2</sub> growth on a range of fabrics. Fig.(1,c) shows a MOF thin film on PP coated with TiO<sub>2</sub> using atomic layer deposition that achieves BET SA up to  $\approx 360 \text{ m}^2/q_{\text{comp}}$ , Fig.(1.d) shows that these mesoporous UiO-66-NH<sub>2</sub> composite enhanced the paraoxon methyl (DMNP) degradation with a half-life time of less than a minute compared to a half-life time of 2.5 minutes for microporous UiO-66-NH<sub>2</sub>. Similar trends were found for live nerve agent degradation. To conclude, the benign synthesis process of the mesoporous UiO-66-NH<sub>2</sub> thin film improves the growth of this MOF on a large range of fabrics and enhances the organophosphates degradation, respectively. These thin film MOF-fabric composites have great potential in filtration, protection, and catalysis applications.



Figure (1): a) Chemical Reaction of Uniform Mesochannels of Crystalline Microporous UiO-66-NH<sub>2</sub>, b) Pore Size Distribution of Mesoporous vs Microporous UiO-66-NH<sub>2</sub>, c) SEM of Mesoporous UiO-66-NH<sub>2</sub> on Treated PP, d) DMNP Hydrolysis Results.

[1] K. Li, S. Lin, Y. Li, Q. Zhuaang, J. Gu, Angewandte Chemie - Int. Ed. 57 (2018) 3439-3443.