Micro- and Nanostructure of Diatom Silica–Titania Frustule Synthesized at Different Hydraulic Retention Times (HRT) in a Membrane Bioreactor

Yan Li [1], Zhiqiang Hu [1].

1 Department of Civil & Environmental Engineering, University of Missouri, Columbia, MO 65211, USA

The diatom cell wall known as frustule is composed of biosilica, where highly ordered nano-silica structures are produced. Because of its unique nanostructure, there is growing research in exploring the use of diatom as nanomaterials [1] or use diatom as a template to explore new nanomaterials [2]. Demand for well-defined silica materials continues to grow because of wide applications of silica-based materials in different industrial processes, consumer market, and the environment.

The objective of this study is to evaluate the effect of HRT on the nanostructure of diatom cell frustule and biologically incorporated titanium into diatom cell wall at different hydraulic retention times (HRTs) to synthesize nanomaterials with photocatalytic activity for water treatment and air purification. The nanostructures of diatom were first evaluated in a membrane bioreactor at a fixed SRT by decreasing HRT from 24h, 12h, to 3h.

Average diameter of foramen, number of sieve-pores on the cribrum layer, and the specific surface area increased with HRT. After the MBR were operated for a sufficiently long period of time (>3 SRTs) until the steady-state conditions were achieved at different HRTs, diatom was sampling for FIB-SEM analysis. FIB-SEM images of nanostructure and pore organization of diatom *Stephanodiscus hantzschii* at different HRTs shown in Fig. 1.

A comparative SEM images (Fig. 1) showed similar pore organization of diatom frustule at different HRTs. Diatom maintains the cylinder cell morphology and the circular valve face with the average diameter of 4.4 ± 0.3 µm at different HRTs. A more detailed SEM images of nanostructure of diatom valve face was presented in Fig. 1 B, D, F. The foramen on aerola layer are still radially arranged in lines of 7–11 holes from the center of the cell to the frustule edge, which are separated by slightly raised ridges from uniseriate at the central area to biseriate near the edge at different SRTs. However, the average diameter of foramen significantly increased from 130 ± 15 nm to 165 ± 10 nm and a pore to pore distance decreased from 220 ± 15 nm to 160 ± 13 nm as HRT increased from 3h to 24h ($P < 0.05$). Within each foramen, the number of sieve-pores on cribrum layer increased from 12 ± 5 to 20 ± 3 with HRT, while the diameter of sieve-pores maintains the same of 20 ± 3 nm.

Diatom frustules consist of architecture hydrated silicon with micro- to nanostructure. One attractive characteristic of diatom is their ability to incorporate titanium into their porous 3D silica frustule. It is hypothesized that improved mixing in hierarchical structures of diatoms associated with the increased flow rate (or short HRTs) could result in more titanium uptake, thus resulting in higher photocatalytic activities.

Cultivation of diatom by feeding titanium sources in a continuous membrane bioreactor at different HRTs, which led to the integration of titanium dioxide into their hierarchical silicon frustules. The photocatalytic activity of the produced silica - titania frustule cultivated with N-TiO_2 increased as HRT decreased, as evidenced by the degradation test of three selected pharmaceutical and personal care products (PPCPs). Compared with frustules cultivated at 24 h HRT, frustules cultivated at 3 h HRT resulted in almost doubled the pseudo first order rate constants of degradation of triclosan, DEET and bisphenol A.

References:

[1] Garcia, A.P. and Buehler, M.J. (2010) Bioinspired nanoporous silicon provides great toughness at great deformability. Computational Materials Science 48(2), 303-309.

[2] Losic, D., Mitchell, J.G. and Voelcker, N.H. (2009) Diatomaceous lessons in nanotechnology and advanced materials. Advanced Materials 21(29), 2947-2958.

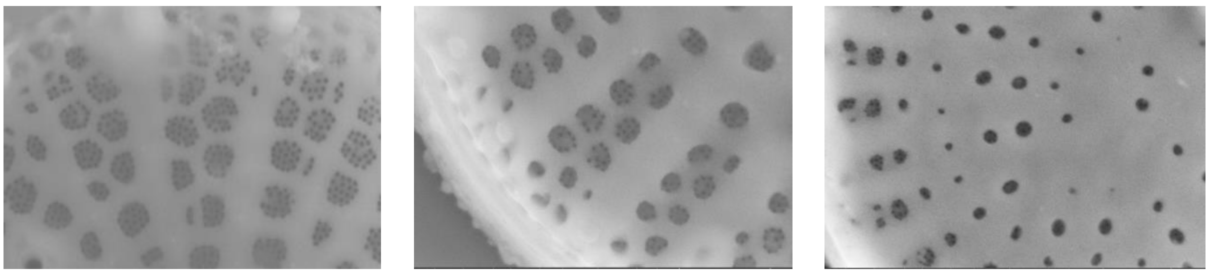

Fig. 1. Pairs of SEMs showing nanostructure of *Stephanodiscus hantzschii* at different HRTs. (A) Top view of *Stephanodiscus hantzschii* frustule at 24 h HRT. (B) Top view of *Stephanodiscus hantzschii* frustule at 12 h HRT. (C) Top view of the valve surface of *Stephanodiscus hantzschii* at 3 h HRT.

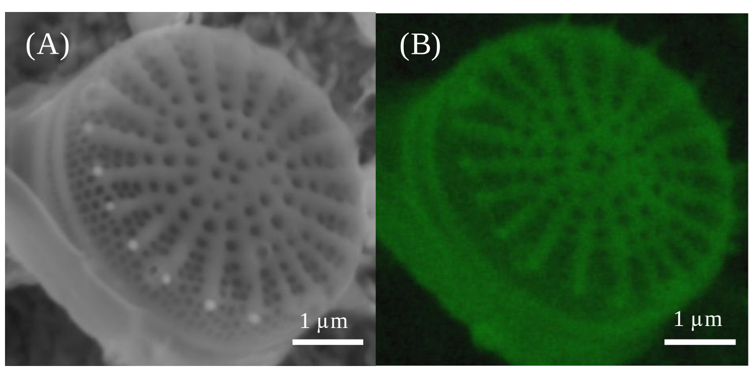

Fig. 2. (A) ESEM images of the silica–titania diatom frustules cultivated with N-TiO_2. (B) EDX Si map of the diatom frustule.