METABOLIC INSERTION OF ORGANOALKOXYSILANES INTO THE FRUSTULE OF THE DIATOM *THALASSIOSIRA WEISSFLOGII*

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Functionalization of cleaned non-living diatoms with silanes *via* reaction with the free hydroxyl groups on the frustule surface has been employed to successfully introduce amino-[1,2,3,4], mercapto-[5,6] and vinyl-[6] groups. These moieties serve as an anchor for further reactions or attachment of biomolecules to the diatom. Modification of the living diatom *via* metabolic insertion of silanes and organo-alkoxysilanes remains under explored. It was hypothesised that a solution of tetramethylorthosilicate (TMOS) and 3-mercaptopropyltrimethoxysilane (MPTMS) will provide an alternative source of silica for the growth of the diatom *T. weissflogii* enabling metabolic insertion of an organo-alkoxysilane into the diatom frustule.

Synchronised *T. weissflogii* cultures were inoculated in enriched artificial seawater. Hydrolysed TMOS/MPTMS was added to the culture at the time of inoculation and at 48 hour intervals. Cultures were harvested at 192 hours post inoculation. Control cultures were prepared using sodium metasilicate ($NaSiO_3$). Diatoms were cleaned by successive washes in hydrochloric acid, de-ionised water and methanol. The chemical composition of the cleaned diatom was determined using ^{29}Si-NMR and energy dispersive X-ray analysis (EDX). The architecture of the diatom was characterised and quantified using transmission electron microscopy (TEM), scanning electron microscopy (SEM) and atomic force microscopy (AFM).

EDX analysis confirmed the presence of sulphur in the TMOS/MPTMS modified diatom. ^{29}Si-NMR analysis confirmed the presence of an organic moiety extending from the Si backbone of the TMOS/MPTMS modified diatom skeleton. The gross morphology of the TMOS/MPTMS modified diatom is unaltered. AFM analysis revealed that the distance between ribs in both a radial and a rotational direction is decreased in the TMOS/MPTMS modified diatom compared to $NaSiO_3$ diatom. There is significant reduction in the pore dimensions of width, length, perimeter and area in TMOS/MPTMS modified diatoms compared to $NaSiO_3$.

This is the first study to demonstrate that organo-alkoxysilanes can be used as a source of silica for the growth of the diatom *T. weissflogii*. The possibility to use the living diatom following modification of the chemistry of the frustule is an exciting area of research and requires further investigation.

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References:
1. N. L. Rosi, C. S. Thaxton, C. A. Mirkin, *Angew. Chem. Int. Ed.* 2004, 43, 5500
2. L. De Stefano, A. Lamberti, L. Rotiroti, M. De Stefano, *Acta Biomater.* 2008, 4, 126
3. H. Townley et al., *Nanotech.* 2007, 18, 295101
4. D. K. Gale, T. Gutu, J. Jiao, C.-H. Chang, G. L. Rorrer, *Adv. Funct. Mater.* 2009, 19, 926
5. Y. Yang, A.-M. Jonas, L. Dusan, *Sci. Technol. Adv. Mater.* 2012, 13, 015008.
6. C. E. Fowler et al., *Appl.Surf. Sci.* 2007, 253, 5485