

## Biogenic Formation of Photoactivity Arsenic-Sulfide Nanotubes by *Shewanella* Strains

Shenghua Jiang and Hor-Gil Hur\*

*Department of Environmental Science and Engineering, Gwangju Institute of Science and Technology,  
1 Oryong-Dong, Buk-Gu, Gwangju 500-712*

Microorganisms facilitate the formation of a wide range of minerals that have unique physical and chemical properties as well as morphologies that are not produced by abiotic processes(1). An extensive extracellular network of filamentous, arsenic-sulfide (As-S) nanotubes (20–100 nm in diameter by ~30  $\mu\text{m}$  in length) was produced by the dissimilatory metal-reducing bacterium *Shewanella* sp. HN-41(1, 2). The As-S nanotubes, formed via the reduction of As(V) and  $\text{S}_2\text{O}_3^{2-}$ , were initially amorphous  $\text{As}_2\text{S}_3$  but evolved with increasing incubation time toward polycrystalline phases of the chalcogenide minerals realgar (AsS) and duranusite ( $\text{As}_4\text{S}$ ). Upon maturation, the As-S nanotubes behaved as metals and semiconductors in terms of their electrical and photoconductive properties, respectively.

Subsequently, ten different *Shewanella* strains including *Shewanella* sp. HN-41, *Shewanella* sp. PV-4, *S. alga* BrY, *S. amazonensis* SB2B, *S. denitrificans* OS217, *S. oneidensis* MR-1, *S. putrefaciens* CN32, *S. putrefaciens* IR-1, *S. putrefaciens* SP200 and *S. putrefaciens* W3-6-1, were tested to produce As-S nanotubes in the same conditions as did strain *S. sp.* HN-41. The results indicated that strain *S. putrefaciens* CN-32 formed As-S materials in 7 days like strain HN-41 did, and strains *S. alga* BrY and *S. oneidensis* MR-1 formed As-S after 30 days. The rest of strains did not precipitate As-S materials in the incubations. Electron microscopy, EDX and EXAFS analyses showed the morphological and chemical properties of As-S formed by strains *S. putrefaciens* CN-32, *S. alga* BrY, and *S. oneidensis* MR-1 were similar to the As-S nanotubes formed by strain *S. sp.* HN-41. Among the ten strains tested, strain *S. putrefaciens* CN-32 contained both As(V) respiratory reductase gene *arrA* and detoxificational reductase gene *arsC*(4, 5), and strain *S. sp.*HN-41 has only *ars* genes. Neither *arrA* nor *arsC* gene had been detected from the other strains by PCR reaction with the primers which were designed based on the sequence of an *arr-ars* operon from *Shewanella* sp. strain ANA-3(6). Consequently, strain *S. sp.* HN-41 and *S. putrefaciens* CN-32 rapidly reduce As(V) to As(III) in the incubation with thiosulfate existing. However, strain *S. alga* BrY and *S. oneidensis* MR-1 could also reduce both As(V) and thiosulfate and form the yellow-colored materials but not as fast as *S. sp.* HN-41 and *S. putrefaciens* CN-32 did under the same conditions. This indicates that in addition to the necessary arsenate reducing reactions, there appears to be other unclear factors governing the rapid formation of the photoactive As-S nanotubes by strains *S. sp.* HN-41 and *S. putrefaciens* CN-32.

The As–S-filamentous nanotubes produced by *Shewanella* strains behaved as metals and semiconductors in terms of their electrical properties and were photoconductive. We suggest that the biogenic As–S nanotubes may be useful as building blocks for the construction of the next generation of nanoscale optoelectronic materials(3).

## References

- [1] Lee, J. H., M. G. Kim, B. Yoo, N. V. Myung, J. Maeng, T. Lee, A. C. Dohnalkova, J. K. Fredrickson, M. J. Sadowsky, and H. G. Hur. 2007. Biogenic formation of photoactive arsenic-sulfide nanotubes by *Shewanella* sp. strain HN-41. Proc. Natl. Acad. Sci. U S A 104:20410-5.
- [2] **Lee, J. H., Y. Roh, K. W. Kim, and H. G. Hur.** 2007. Organic acid-dependent iron mineral formation by a newly isolated iron-reducing bacterium, *Shewanella* sp. HN-41. Geomicrobiol. J. **24**:31-41.
- [3] Mao, C., D. J. Solis, B. D. Reiss, S. T. Kottmann, R. Y. Sweeney, A. Hayhurst, G. Georgiou, B. Iverson, and A. M. Belcher. 2004. Virus-based toolkit for the directed synthesis of magnetic and semiconducting nanowires. Science 303:213-217.
- [4] **Saltikov, C. W., A. Cifuentes, K. Venkateswaran, and D. K. Newman.** 2003. The *ars* detoxification system is advantageous but not required for As(V) respiration by the genetically tractable *Shewanella* species strain ANA-3. Appl. Environ. Microbiol. **69**:2800-2809.
- [5] **Saltikov, C. W., and D. K. Newman.** 2003. Genetic identification of a respiratory arsenate reductase. Proc. Natl. Acad. Sci. USA **100**:10983-10988.
- [6] **Saltikov, C. W., R. J. Wildman, and D. K. Newman.** 2005. Expression dynamics of arsenic respiration and detoxification in *Shewanella* sp. strain ANA-3. J. Bacteriol. **187**:7390-7396.