Self-Assembled Dendron-Cyclodextrin Nanotubes for Biosensory Platform

Chulhee Kim, Jeonghun Lee
Polymer Science and Engineering, Inha University, Incheon, Korea
chk@inha.ac.kr

Abstract

Nanotubes have been a subject of great interests due to their innovative properties and potential applications in a variety of areas of nanoscience. In particular, for organic nanotubes, the precise functionalization and interconnection of the building blocks provided a vision that they could exhibit not only unprecedented architectures but also valuable functions for applications such as electronics and biomedicine.

Even though various self-assembling building blocks for nanotubes have been developed, a molecular recognition motif has not been employed for controlling the self-organization of building blocks into organic nanotubes. Recently, we have reported that the cyclodextrin (CD)-covered dendron nanotubes (Den-CD-NTs) were obtained by a hierarchical self-assembly process derived from a host-guest complexation between the amide dendrons with the focal pyrene moiety and cyclodextrins.[1,2] The smaller rim of CD is exposed to the surface of the nanotube upon inclusion of the focal pyrene groups into the cavity of CD. We reasoned that this type of hierarchical self-assembly approach would provide a facile methodology for the construction of diverse nanotube architectures via the host-guest interaction between the dendron and the C-6 modified CDs. The tunability in the surface functionalization would enable us to construct the hybrid of the nanotubes with metal nanoparticles. Furthermore, we also reasoned that the fluorescence characteristics of the nanotube in response to the change of the surface environment for the application of the nanotube as a biosensory vehicle. In the primary building block, amide dendron, the focal pyrene group was introduced not only as the guest moiety for a CD host but also as a fluorescent probe. Dendron self-organizes into vesicles in aqueous solution. Upon addition of CDs into the vesicular solution, the CD-pyrene complexation occurs through the inclusion of the hydrophobic focal pyrene unit into the cavity of CD. This supramolecular recognition transforms the self-assembled structures from the vesicle to the CD-covered nanotubes. The fluorescent nature of Den-CD-NTs with the tunable surface functionality described in this work provides an opportunity for utilizing the nanotubes as a biosensing platform when the surface functional groups of the nanotubes are designed to interact specifically with the analytes. The sensitive emission property of the pyrene unit in the cavity of CDs of the nanotube toward the change in local environment would allow such binding of the biomolecules on the nanotube to trigger the change in the fluorescence emission of the nanotubes. For that purpose, we prepared the biotin-covered nanotubes (Den-biotin-CD-NT and Den-biotin-C4-CD-NT) as a biosensing platform for utilizing the specific binding of biotin with receptor proteins such as streptavidin and avidin. When streptavidin-AuNP conjugate (SA-AuNP) was added to the Den-biotin-C4-CD-NT solution, the fluorescence was quenched due to proximity of the pyrene moiety to the AuNP of SA-AuNP which binds to the biotin unit on the tube surface. These fluorescence characteristics of Den-CD-NTs along with well-defined surface architecture suggest that Den-CD-NTs can be utilized as a biosensor. The functional tunability of Den-CD-NTs demonstrated the substantial advantages of our supramolecular approach for development of unique nanotubes as a sensory vehicle.

References

[1] J. Lee, C. R. Lohani, K.-H. Lee, C. Kim**,** *New J. Chem.,* 2013, 37 (11), 3598.

[2] J. Lee, S. Park, C. R. Lohani, K.-H. Lee, C. Kim**,** *Chem. Eur.* ***J.,*** 2012, 18 (24), 7351.
[3] C. Park, J. Lee, C. Kim , *Chem. Commun**.,*** 2011, 47 (44), 12042.
[4] C. Park, M. S. Im, S. Lee, J. Lim, C. Kim, *Angew. Chem.Int. Ed.* 2008, 47 (51), 9922.
[5] C. Park, I. H. Lee, S. Lee, Y. Song, M. Rhue, C. Kim**,** *Proc. Natl. Acad. Sci. U. S. A.,* 2006, 103, 1199.