

COMMENT OPEN



Organic nanotubes for smart anticorrosion and antibiofouling coatings

Viswanathan S. Saji ¹✉

The easy and scalable synthesis, biocompatibility, one-dimensionality, high aspect ratio, viability for surface modifications, and the ability for cargo-loading and release make organic nanotubes ideal candidates for smart coatings with slow and controlled release corrosion inhibitors and anti-biofouling agents. The wide-ranging applicability of organic nanotubes as controlled release nanocarriers for smart anti-corrosion and anti-biofouling coatings is foreseen.

npj Materials Degradation (2022)6:30; <https://doi.org/10.1038/s41529-022-00243-3>

MAIN BODY

Organic nanotubes, also called soft-matter nanotubes, have been in the research limelight in recent years for their potential applications in drug delivery, sensors, catalysts, hydro/organogels, optical devices, ferro/piezoelectrics, energy storage devices, biomarkers, micron-size engines, superhydrophobic surfaces, templates, and reinforcing materials. Compared to the one-dimensional inorganic peers, the flexibility of organic synthesis permits fine-tuning of their properties via specific chemical modifications. Their mechanical properties can be improved by different approaches such as covalent cross-linking and metal-ligand coordination^{1–6}. Metal-organic nanotubes are a related group made through careful selection of metal ions and ligands^{7–9}.

Self-assembled supramolecular assemblies^{10–12} are primarily investigated to develop organic nanotubes. The earlier reports on self-assembled lipid-based organic nanotubes from amphiphilic molecules date back to the 1980's^{13–15}. In liquid media, the formation kinetics can be controlled by tuning the molecular structure of the precursor chemicals and the solution parameters (concentration, solvents used, temperature, and pH)^{16,17}. Plethora of information is available in the literature where nanotubes were reported from various organic compounds, including lipids, peptides, proteins, amino acids, nucleic acids, dyes, heterocycles, synthetic polymers, and other π -conjugated molecules^{1,18}. Other than the spontaneous self-assembly, they can be made by different approaches such as template-based and pulsed electric field-assisted methods¹⁹.

Organic nanotubes are shown to be highly efficient for drug delivery^{20–22}. They could efficiently exploit the tunable internal and external surfaces and the nanotube wall¹. The most investigated organic nanotubes for drug delivery include lipids/bolaamphiphiles-based²³, peptides²⁴, and DNA²⁵. Several other nanotubes based on macrocycles²⁶, polyethylene glycol²⁷, naphthalimide²⁸, polydopamine²⁹, and polyelectrolyte³⁰ were also reported. Drug loading is typically achieved by simple physical encapsulation or chemical conjugation. The loading can be carried out by impregnating the nanotubes in a suitable cargo solution, or the nanotube assembly could be performed in an optimized solution containing the cargo material. The loading and release meticulously vary with the aspect ratio of the nanotubes. The aspect ratio of the nanotubes could be regulated by precise selection and optimization of the assembling organic components.

On the other side, corrosion and biofouling are the two critical problems causing material destruction and economic loss. Protective coatings and corrosion inhibitors/anti-biofouling agents are the most economical and practical approaches to control these destructive events. Recent years have witnessed significant developments in on-demand slow-release smart coatings. Compared to the conventional active corrosion protection (by the embedded inhibitors in the coating matrix) offered by the protective barrier coatings, a smart coating normally employs inhibitors/anti-biofouling agents loaded onto nanocarriers, facilitating the on-demand release of the encapsulants, providing self-healing effect. A smart coating typically relies on supramolecular chemistry-based extrinsic/intrinsic self-healing. The intrinsic self-healing depends on the inherent covalent/non-covalent interactions within the polymer coating matrix, whereas the extrinsic self-healing utilizes external added nano/microcarriers loaded with corrosion inhibitors/anti-biofouling agents. The release is typically triggered by changes in the environment such as pH variation due to localized corrosion events, releasing the encapsulants and self-healing the damages. Due to the dynamics of non-covalent interactions, supramolecules and assemblies can undergo reversible switching of structure, morphology and function in response to external stimuli³¹.

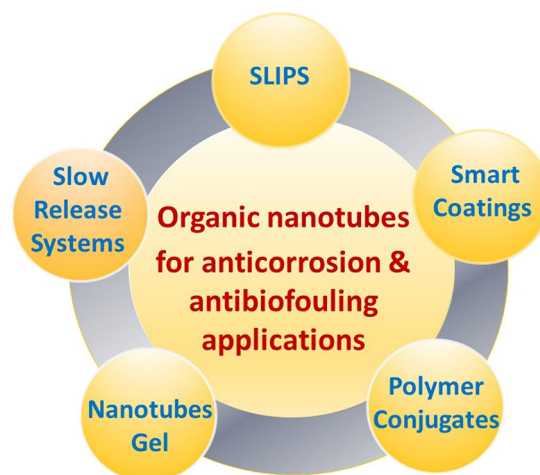


Fig. 1 A scheme showing the application potentials.

¹Interdisciplinary Research Center for Advanced Materials, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia. ✉email: saji.viswanathan@kfupm.edu.sa



Fig. 2 A potential list of components for loading/conjugation with organic nanotubes.

The organic nanocarriers have high significance as the current greener resolutions are demanding more and more strictest measures. Proper synthesis methods and functionalization could optimize the hydrophilicity/hydrophobicity of the organic nanotubes. Hydrophilic organic nanotubes could be utilized in delivering relatively hydrophobic corrosion inhibitors. Polymer-organic nanotubes conjugates^{32,33}, could combine the slow-release property of the nanotubes and the superior protective effect of polymeric inhibitors/anti-biofouling agents. Covalent/non-covalent conjugation of water-soluble polymers to organic nanotubes is beneficial to regulate the nanotubes' size and functionality and reduce the aggregation tendency^{34–36}. They have several application potentials related to corrosion and biofouling R&D (Fig. 1).

Nanotubes could be fabricated directly from amphiphilic heterocyclic compounds having corrosion inhibition/anti-biofouling effect. They could be further used to load synergistic co-inhibitors for controlled release. Here, both the nanotubes and the encapsulants provide the protective effect. A bioactive coating with incorporated lipid or peptide nanotubes carrying biocompatible corrosion inhibitors can be an attractive approach to extend the life of a biodegradable implant to the desired extent.

Hydrogels of organic nanotubes are an essential topic to be explored. Here, the individual organic nanotubes and the gel system can participate in the cargo-loading and release. Nanotube's reinforcement is also beneficial to enhance the mechanical properties of the hydrogels³⁷. They are particularly attractive for applications in anti-biofouling surfaces and slippery liquid infused porous surfaces.

Organic nanotubes based on dynamic covalent chemistry can provide a more robust platform. Organic nanotubes fabricated via hard templates such as anodized aluminium oxide²⁷, or other non-self-assembled strategies can provide several advantages over their inorganic and carbon nanostructures-based one-dimensional counterparts. Figure 2 shows a potential list of components for loading/conjugation with the nanotubes for smart anti-corrosion/anti-biofouling coatings applications.

Promising successes of using organic nanotubes in diverse applications have shown that these biocompatible materials could be widely explored in the domain of corrosion and biofouling, despite these assemblies facing many real engineering challenges that need to be solved.

METHODS

The information presented was accessed from authentic scientific sources, analyzed, and discussed.

DATA AVAILABILITY

All data generated or analyzed during this study are included in this published article.

CODE AVAILABILITY

No custom code or mathematical algorithms were associated with this work.

Received: 19 January 2022; Accepted: 21 March 2022;
Published online: 19 April 2022

REFERENCES

- Shimizu, T., Ding, W. & Kameta, N. Soft-matter nanotubes: a platform for diverse functions and applications. *Chem. Rev.* **120**, 2347–2407 (2020).
- Jin, H. et al. Designable and dynamic single-walled stiff nanotubes assembled from sequence-defined peptoids. *Nat. Commun.* **9**, 270 (2018).
- Agarwal, S., Melissa, A. K., Passa, E. P. & Elisa, F. Dynamic self-assembly of compartmentalized DNA nanotubes. *Nat. Commun.* **12**, 3557 (2021).
- Darnall, S. M. et al. Organic nanotube with subnanometer, pH-responsive lumen. *J. Am. Chem. Soc.* **141**, 10953–10957 (2019).
- Fan, H. et al. Switchable circularly polarized luminescence from a photoacid co-assembled organic nanotube. *Nanoscale* **11**, 10504–10510 (2019).
- Larnaudie, S. C. et al. Cyclic peptide-polymer nanotubes as efficient and highly potent drug delivery systems for organometallic anticancer complexes. *Biomacromolecules* **19**, 239–247 (2018).
- Jia, J. G. & Zheng, L. M. Metal-organic nanotubes: designs, structures and functions. *Coord. Chem. Rev.* **403**, 213083 (2020).
- Rani, D., Bhasin, K. K. & Singh, M. Visible-light-assisted gasochromic sensing of nicotine from cigarette smoke by metal-organic nanotube. *ACS Mater. Lett.* **2**, 9–14 (2020).
- Vailonis, K. M., Gnanasekaran, K., Powers, X. B., Gianneschi, N. C. & Jenkins, D. M. Elucidating the growth of metal-organic nanotubes combining isoreticular synthesis with liquid-cell transmission electron microscopy. *J. Am. Chem. Soc.* **141**, 10177–10182 (2019).
- Lehn, J. M. *Supramolecular Chemistry: Concepts and Perspectives*, 1st edn. (Wiley, 1995).
- Lehn, J. M. Towards complex matter: supramolecular chemistry and self-organization. *Proc. Natl Acad. Sci. USA* **99**, 4763–4768 (2002).
- Atwood, J. L. & Steed, J. W. *Encyclopedia of Supramolecular Chemistry*, 1st edn. (CRC Press, 2004).
- Yager, P. & Schoen, P. E. Formation of tubules by a polymerizable surfactant. *Mol. Cryst. Liq. Cryst.* **106**, 371–381 (1983).
- Yamada, K., Ihara, H., Ide, T., Fukumiti, T. & Hirayama, C. Formation of helical super structure from single-walled bilayers by amphiphiles with oligo-L-glutamic acid-head group. *Chem. Lett.* **10**, 1713–1716 (1984).
- Georger, J. H. et al. Helical and tubular microstructures formed by polymerizable phosphatidylcholines. *J. Am. Chem. Soc.* **109**, 6169–6175 (1987).
- Schnur, J. M. Lipid tubules—a paradigm for molecularly engineered structures. *Science* **262**, 1669–1676 (1993).
- Spector, M. S., Price, R. R. & Schnur, J. M. Chiral lipid tubules. *Adv. Mater.* **11**, 337–340 (1999).

18. Ariga, K. et al. Self-assembly as a key player for materials nanoarchitectonics. *Sci. Technol. Adv. Mater.* **20**, 51–95 (2019).
19. Katouzian, I. & Jafari, S. M. Protein nanotubes as state-of-the-art nanocarriers: synthesis methods, simulation and applications. *J. Control. Release* **303**, 302–318 (2019).
20. Shimizu, T., Masuda, M. & Minamikawa, H. Supramolecular nanotube architectures based on amphiphilic molecules. *Chem. Rev.* **105**, 1401–1443 (2005).
21. Liu, X. et al. Biomimetic DNA nanotubes: nanoscale channel design and applications. *Angew. Chem. Int. Ed.* **58**, 8996–9011 (2019).
22. Saji, V. S. Supramolecular organic nanotubes for drug delivery. *Mater. Today Adv.* **14**, 100239 (2022).
23. Kameta, N., Minamikawa, H., Masuda, H., Mizuno, G. & Shimizu, T. Controllable biomolecule release from self-assembled organic nanotubes with asymmetric surfaces: pH and temperature dependence. *Soft Matter* **4**, 1681–1687 (2008).
24. Porter, S. L., Coulter, S. M., Pentlavalli, S. & Laverty, G. Pharmaceutical formulation and characterization of dipeptide nanotubes for drug delivery applications. *Macromol. Biosci.* **20**, 2000115 (2020).
25. Pearce, T. R. & Kokkoli, E. DNA nanotubes and helical nanotapes via self-assembly of ssDNA-amphiphiles. *Soft Matter* **11**, 109–117 (2015).
26. Mamad-Hemouch, H. et al. Versatile cyclodextrin nanotube synthesis with functional anchors for efficient ion channel formation: design, characterization and ion conductance. *Nanoscale* **10**, 15303–15316 (2018).
27. Alghamdi, M. et al. Poly(ethylene glycol) based nanotubes for tunable drug delivery to glioblastoma multiforme. *Nanoscale Adv.* **2**, 4498–4509 (2020).
28. Pantoş, G. D., Pengo, P. & Sanders, J. K. M. Hydrogen-bonded helical organic nanotubes. *Angew. Chem. Int. Ed.* **46**, 194–197 (2007).
29. Sun, Y. & Davis, E. W. Facile fabrication of polydopamine nanotubes for combined chemo-photothermal therapy. *J. Mater. Chem. B* **7**, 6828–6839 (2019).
30. Enomoto, Y., Akiyama, M., Morita, Y. & Komatsu, T. Polyelectrolyte/gold nanoparticle nanotubes incorporating doxorubicin-loaded liposomes. *Chem. Asian J.* **16**, 4057–4061 (2021).
31. Saji, V. S. *Supramolecular Chemistry in Corrosion and Biofouling Protection*, CRC Press, Taylor and Francis (CRC Press, 2021). <https://doi.org/10.1201/9781003169130>.
32. Catrouillet, S. et al. Tunable length of cyclic peptide-polymer conjugate self-assemblies in water. *ACS Macro Lett.* **5**, 1119–1123 (2016).
33. Duncan, R. Polymer conjugates as anticancer nanomedicines. *Nat. Rev. Cancer* **6**, 688–701 (2006).
34. Xu, T. et al. Subnanometer porous thin films by the co-assembly of nanotube subunits and block copolymers. *ACS Nano* **5**, 1376–1384 (2011).
35. Chapman, R., Warr, G. G., Perrier, S. & Jolliffe, K. A. A water-soluble and pH-responsive polymeric nanotubes from cyclic peptide templates. *Chem. Eur. J.* **19**, 1955–1961 (2013).
36. Chapman, R., Danial, M., Koh, M. L., Jolliffe, K. A. & Perrier, S. Design and properties of functional nanotubes from the self-assembly of cyclic peptide templates. *Chem. Soc. Rev.* **41**, 6023–6041 (2012).
37. Wu, D., Ding, W. & Kameta, N. Functionalized organic nanotubes with highly tunable crosslinking site density for mechanical enhancement and pH-controlled drug release of nanocomposite hydrogels. *Polym. J.* **54**, 67–78 (2022).

ACKNOWLEDGEMENTS

The support and fund provided by the King Fahd University of Petroleum & Minerals (KFUPM), Saudi Arabia, is greatly acknowledged.

AUTHOR CONTRIBUTIONS

V.S.: Manuscript writing and editing.

COMPETING INTERESTS

The author declares no competing interests.

ADDITIONAL INFORMATION

Correspondence and requests for materials should be addressed to Viswanathan S. Saji.

Reprints and permission information is available at <http://www.nature.com/reprints>

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>.

© The Author(s) 2022