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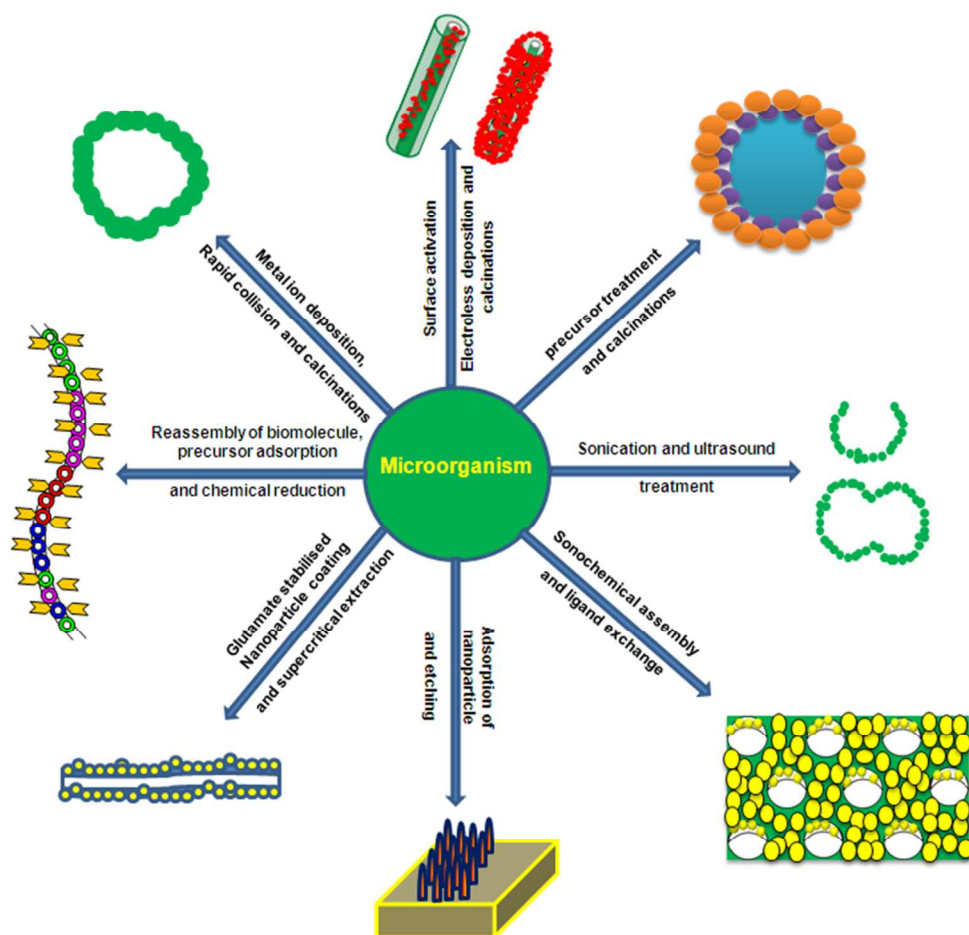
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Graphical Abstract



Microbial biotemplates for synthesizing inorganic nanostructures of defined morphology and size

ARTICLE

Recent advances in synthesis of inorganic nano/microstructures using microbial biotemplates and their applications

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Biotemplates from microbial origin has been a new source of inspiration for designing and fabrication of intricate, high surface area structures that possess potent application in nanotechnology. Microbial biotemplates are useful for synthesizing nano/micro structural materials based on bottom up approach. Being from nature, microbial biotemplates with their extraordinarily molecular machinery have been reported to be much superior and cost effective for fabricating complex and heterogeneous structures when compared to the conventional and advanced lithographic techniques. The advantage of speedy growth and multiplication along with controlled shape, structure and size, make microorganisms a viable template for making nanomaterials of defined size and shape. In this review, we have consolidated the recent advances in synthesis of nano/micro structures using biotemplate obtained from various types of microorganisms like bacteria, fungi, algae and virus and have highlighted its possible application. This review excludes biomolecules like DNA, protein and lipid based biotemplates extracted from various microorganisms.

1. Introduction

Synthesis of nanomaterials having controlled and defined geometries have been considered as a most challenging part of nanotechnology. Realization of such controlled geometries mainly depends on the method by which the nanomaterials have been synthesized. Synthesizing such nanomaterials with controlled geometries favor easy material assembly at nanoscale and in turn increases the overall performance of the material. These assemblies ultimately can be used to form unique patterns essential for device fabrication.¹ Various top down and bottom up approaches have been developed by many scientists to achieve such geometries that can be used in various applications. Recent techniques used for obtaining such unique geometries in nanomaterials using top down approach are photolithography, electron, ion beam lithography, dip pen lithography, microcontact printing, electrochemical synthesis and nanoimprint lithography. The bottom up approach includes patterned self-assembly process using topographically /chemically patterned surfaces and biotemplates. Amidst various advantage and disadvantage of the top down and bottom approach, biotemplating always remain a cost effective alternative for the synthesis of size/shape controlled patterned nanostructures. (For further details on the advantages and disadvantages of top down and bottom up approach for size and shape dependent nanomaterial formation, please read the review written by Sotiropoulou et al.¹). Template assisted synthesis is a low cost, easy and versatile method to fabricate nanomaterials with defined structures. This method uses templates having micro/nano sized known patterns/pores or shapes of metal/biological/polymeric or of chemical origin. A material of choice can be deposited onto such templates and grown to form

respective nanomaterials having the shape of the template. Once the material is grown over the template, the templates are removed either partially or completely by suitable methods to produce free standing nanostructures.² Integrating biosystems into the nanotechnology has been taken up as an important and novel task by many researchers in the recent years. Being from nature, the molecular machinery of biosystem always outperform extraordinarily when compared to all the above mentioned man made manufacturing technologies.³ The natural molecular self-assembly process and the resultant precise and unique biological structures have inspired material scientist to look at them as a possible biotemplate for nanotechnology. The biotemplates used for biomorphic mineralization process impart nanoscale constraint for synthesis of nanoscale materials resembling the biotemplate. Biotemplates also act as stabilizers and make them monodisperse in nature.⁴ The nanostructures formed using these types of biotemplate from living system have many advantages. These biotemplates are natural, ecofriendly, inexpensive, having metal ion binding capacity, stability and high production yield. They can be used to synthesize nanomaterials at room temperature using soft chemical processes which are mostly ecofriendly in nature. Biological system has been reported to exhibit multiple levels of hierarchical structures from microscopic to macroscopic length scale.⁵ Despite the presence of micro and macroscale structures in biological systems, their building blocks are mostly in nanoscale. Examples of such naturally available nanostructures include bone formation,⁶ nanostructures in lotus leaf,⁷ nanostructure reported in butterfly wings,⁸⁻¹⁰ nanostructure in various living organism. Microorganism and its nano and microstructures are always the most preferable biotemplate due to the its low generation time, easy growth condition, possibility of

mass multiplication and scalability and its inherent resistant properties towards various environmental condition. The microbial cell wall functional groups like carboxyl, phosphate and amide groups favor an atmosphere for metal binding and nucleation which in turn leads to formation of nanoparticles/structures on its surface.¹¹ The exopolysaccharides produced by these microbes especially bacteria impart negative charge through carboxyl and phosphate groups which also allow nucleation of positive charged metals like silver and leads to formation of nanostructures in solution.¹²

Considering these facts and advantages of biotemplating, many researchers have started looking into microbes with unique structural and functional properties as a possible biotemplate for synthesis of nanostructures of different size, shape and morphology. In this review, we have consolidated the recent updates on use of microorganism as biotemplate for nanostructure formation. We have excluded extracellular and intracellular synthesis of nanoparticle by microorganism since many reviews are available on it. Bacterial, viral, fungal and algae including diatoms based biotemplates have been taken into consideration. We have also tried to highlight the application of the nanostructures derived through these microorganism based biotemplates.

2. Microorganism based biotemplate

2.1 Bacteria based biotemplates

2.1.1 Whole cell template

Various living microorganisms and their features are closely related to the recent nanostructures developed using chemical and physical methods. Hence these living microbes and their special structures can be used as biotemplate. Bacterial surface structures and morphology is one such feature looked into as a biotemplate. Different strains of bacteria such as *B. subtilis*, *E. coli*, *S. thermophilus*, *S. typhimurium* have been used as templates for the micro/nanostructure formation. Some of the bacteria possess self-assembled nanostructures on its cell wall which is made up of surface layer proteins (S layer).¹³ These S-layer proteins have multiple functions like maintenance of cell shape and structure, template for fine grain mineralization, pathogenicity and cell adhesion, surface recognition, as a protective coat and for attachment to surface which makes them survive in adverse environmental conditions.^{14,15} These protein nanostructures are either found embedded into the cell wall surface or attached to the cell wall superficially through secondary cell wall polymers.¹⁶ The assembly of S-layer protein can be of different symmetries like P1, P2, P3, P4 and P6 and differs from one organism to the other. Such symmetries give different structural arrangement and shape to cell wall surface which can in turn be used as biotemplate. The P1 and P2 symmetry give oblique template structure where as P3 and P6 give hexagonal structure to the cell wall surface. P4 gives square shaped structure (fig. 1). These S-layers can be reassembled into defined symmetries even onto various matrices like mica, silicon, lipid interfaces, liposomes, nanocapsules, polyelectrolyte layers and even on solution there by acting as a suitable biotemplate for further synthesis of different nanostructure having precise shape and size.¹⁷ Mark et al.^{18,19} used 2D microbial S-layer protein biotemplate for preparing dendrimer-encapsulated nanoparticle arrays and metallic and semiconductor nanoparticle arrays. Mark et al.²⁰ tried using S-layer protein based biotemplated assembly of colloidal gold etch mask for the fabrication of silicon nanopillar arrays. These nanopillars were of 60-90 nm tall, 8–13 nm wide at the tip, 15–20 nm wide at half height and 20-30 nm at base (fig. 2). Silica enhanced S-layer protein cages were prepared by Schuster et al.²¹ using

liposomal assembly. S-layers were reassembled onto liposomes and subjected to silicification. After silicification, the lipid components were dissolved using suitable detergent. The organism without S-layer and with S-layer can as such be used as biotemplate to synthesis defined nano/microstructures. Bacteria use their efflux system/oxidation/reduction mechanisms/cell wall functional groups to detoxify the metal contaminants that they encounter in the surrounding media and escapes from the environmental stress. Bacteria like *Shewanella* sp. strain HN-41 have been reported to produce arsenic-sulphide nanotubes of 20–100 nm in diameter by 30 μm in length via reduction of As(V) and $\text{S}_2\text{O}_3^{2-}$ using dissimilatory metal reducing process. These nanotubes behaved as metal and semiconductor nanomaterial with electrical and photocatalytic property which can find application in nano and optoelectric properties.²² This potential of bacteria to accumulate metals/minerals intra or extracellularly has made them to be an ideal candidate for biotemplate leading to nanostructure formation.^{4,23} Nickel nanostructure was synthesized using *Bacillus subtilis* as biotemplate by exploiting the redox reactions of their surface amino acids. Microscopic studies revealed the formation of nanostructure according to the morphology of the bacteria used.²⁴ ZnO, ZnS and TiO_2 nanostructures were made using *Streptococcus thermophilus* and *Lactobacillus bulgaricus* as biotemplate (fig. 3). ZnO hollow spheres were prepared using *Streptococcus thermophilus* as biotemplate through simple hydrothermal process followed TiO_2 micro/nanostructures using these bacterial templates through surface sol-gel process. The hollow sphere and tube structures of TiO_2 nanostructures were formed through series of hydrolysis process and calcinations (at 700°C) and tested for photocatalytic activity. These structures were found to show high photocatalytic activity under UV-Visible radiation (fig. 3, method 3). Recently, Zhang et al.²⁹ have prepared Co_3O_4 decorated ZnO hollow spheres with porous shell at low temperature using *Microzyme* cells as biotemplate and have tested it for sensing gases like CO, H_2 , H_2S , and vapors of ethanol and acetone. These Co_3O_4 -decorated ZnO hollow spheres were effective in sensing acetone followed by ethanol; whereas the same structures were ineffective in sensing CO, H_2 and H_2S at 50 ppm of initial concentration. Bacteria/ZnO core shell spheres have been prepared by hydrothermal method. The formation of such structures mainly depends on the pH of medium. At acidic pH, metal ions bind to the carboxyl and phosphate groups of the bio template. The metal ions form complex with amine group when pH is above 8 and leads to core shell like structure.²⁶ Hollow zirconia particles were synthesized using *E. coli* cells as bio template. It has been observed that the presence of water in templates causes hydrolysis of zirconium butoxide leading to the formation of zirconia hollow particles.³⁰ Yang et al.³¹ developed hierarchically branched Au-nanowire/*E. coli* nanocomposites using CTAB directed bacterial template (*E. coli*). These Au-nanowires showed increased adsorption at near IR region (1900 nm). Kaehr and Brinker³² reported that segregation of catalytic region on a biotemplate is possible by exploiting the polar segregation process of dividing *E. coli* cells. They also suggested that formation of more complex materials and architectures are possible by using chemical, genetical and confinement induced modification in bacterial morphology and bacterial surface properties. Various nanostructures obtained using whole bacterial cell as biotemplate has been consolidated in fig. 4.

2.1.2 Bacterial flagella

Other than the whole cell, bacterial structures like flagella and pili have been used as biotemplate for synthesis of nanostructures. These flagella and pili are used for mobilization and communication between one bacterium to

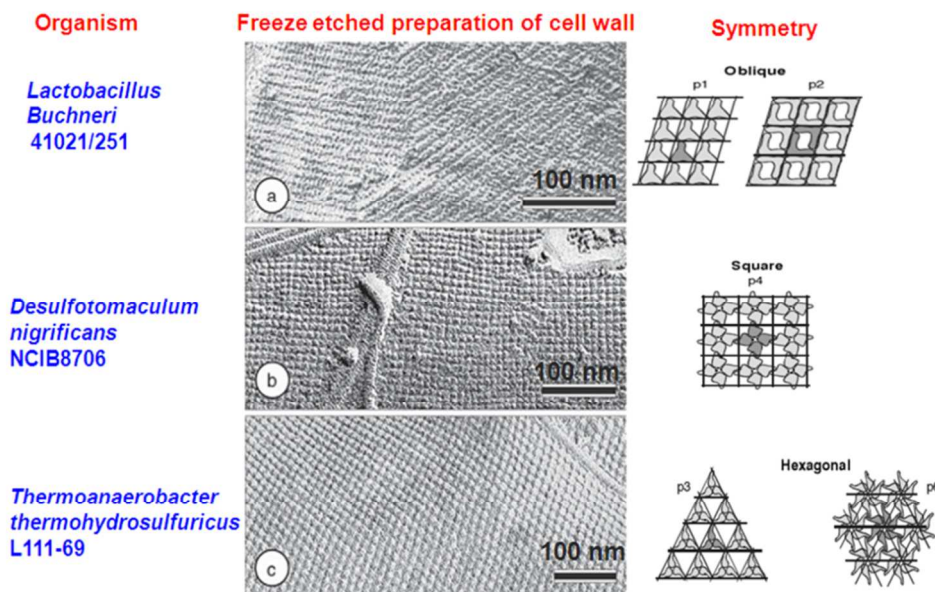


Fig. 1. Bacteria with different types S-layer symmetries and structures. Adopted from ref 16 with permission.

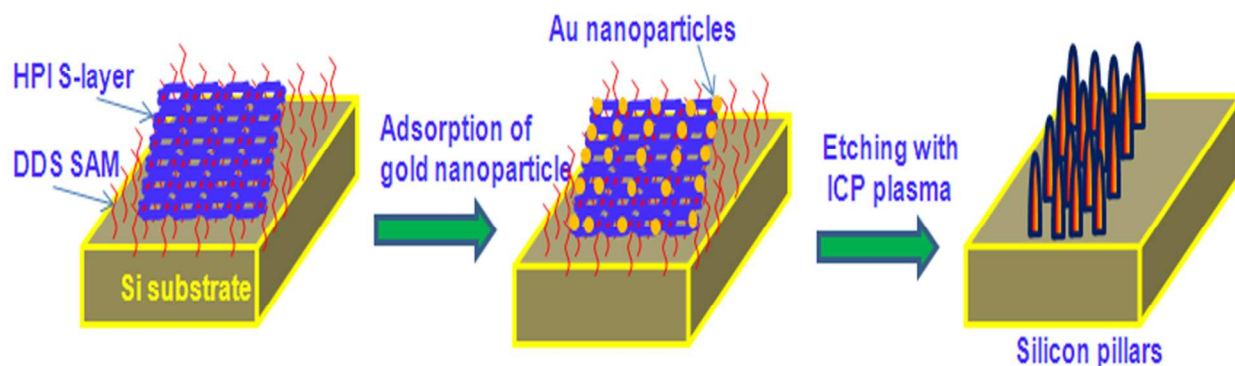


Fig. 2. Bionanofabrication of vertically aligned silicon based nanostructures using bacterial S-layers. Modified from ref 20 with permission.

the other. Natural and genetically engineered flagella have been studied as templates/scaffolds for the formation of metal nanostructures.^{33,34} Hesse et al.³⁴ used mineralization process for the formation of nanotubes from bacterial flagella. They depolymerised the flagella into flagellin monomers and repolymerized it using Na_2SO_4 to make flagellin seeds. These seeds were further used to develop lengthy flagella. The repolymerised lengthy flagella were deposited with titanium by ceramic thin film deposition technique and further mineralization at 50 °C to achieve flagella coated with TiO_2 nanoparticles of anatase phase having a particle size of 5-10 nm. On annealing these flagella coated with TiO_2 nanoparticles at 200 °C, they achieved nanotubes of 200-300 nm diameter in size. Our group used similar approach to develop one dimensional silver nanoparticle coated nano/micro structure

using *Salmonella typhimurium* flagella.³⁵ In this work, we have demonstrated two different approaches to prepare flagella based silver nanoparticle coated bionanomaterial (fig. 5) having increased conductivity. We have also proved that deposition of such bionanomaterials onto graphite electrode can enhance the conductivity of the electrode surface that can be used in microbial fuel cells.³⁶ Similar nanoparticle impregnated flagella was prepared by Deplanche et al.³³ They immobilized stable gold and palladium nanoparticle onto normal and genetically engineered flagella isolated from *Desulfovibrio desulfuricans* to form nano-microstructures that can be useful for catalyst formulations. Mudalige et al.³⁷ synthesized various nanoparticle arrays using engineered bacterial flagellar FliC proteins obtained from mesophilic bacteria. The FliC protein was further

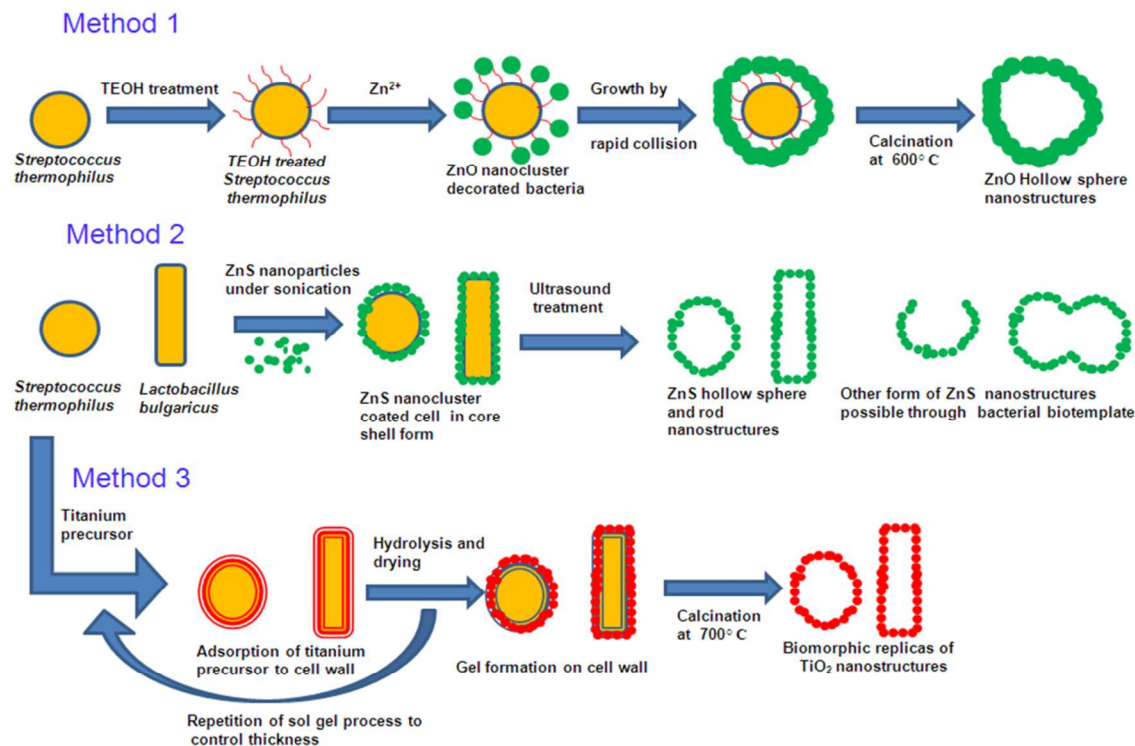


Fig.3. Synthesis of various forms of ZnO, ZnS and TiO_2 nano/microstructure using bacterial morphology.^{25,26,28}

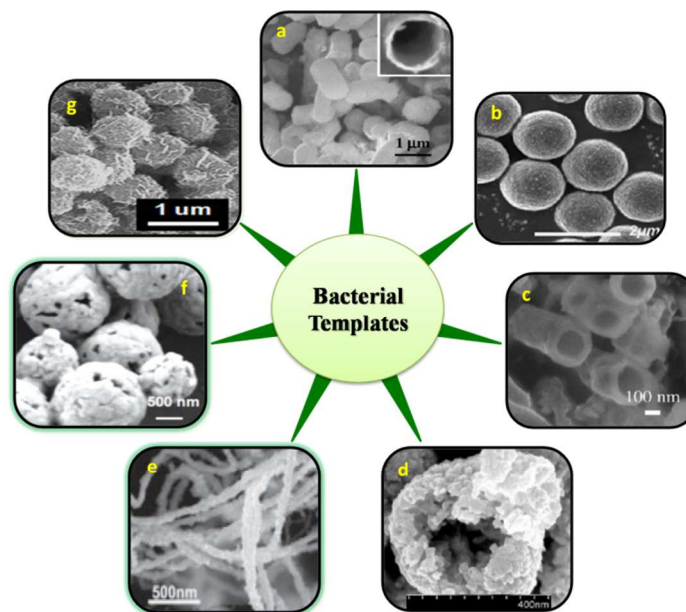


Fig. 4. Various nanostructures derived using whole cell of bacteria. FESEM images of *E. coli* templated hollow silica microparticles(a),⁸⁴ *B. sthermophilus*/ZnO core shell spheres (b),²⁵ SEM images of Crushed calcined zirconia particles using *E. coli* template (c),³⁰ Co_3O_4 -decorated ZnO hollow spheres (d),²⁹ Au nanostructures synthesized through the reduction of aqueous $HAuCl_4$ (e),³¹ SEM image of H_2O_2 etched Ag microspheres at higher magnification using *S. thermophilus* template (f),²⁷ FE-SEM image of uniform, bacteria-supported, hierarchical Co_3O_4 superstructures produced without changing the spherical shape of the original micrococcus template(g)⁸⁵ [All images were obtained with permission].

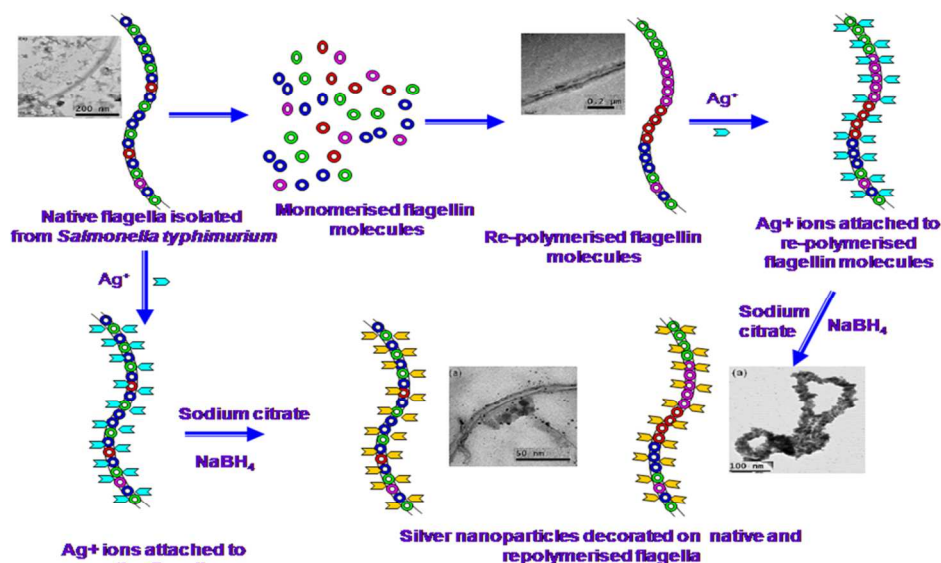


Fig. 5. Possible mechanism for silver nanoparticle impregnation onto bacterial flagella³⁵ (Reproduced with permission).

modified at peptide loops such as histidine and cysteine loops and various nanoparticles like Au, Ag, and Cd were allowed to bind to the histidine loops. Such binding resulted in an ordered array of nanoparticles on flagella nanotubes. They also prepared other organic and inorganic nanoparticle arrays and nanotubes made of hydroxyapatite, silica and titania using similar approach.³⁸ Ovalbumin coated flagellin nanoparticle were prepared from *Salmonella enteritidis* derived flagellin and studied for its immune adjuvant capacity for development of oral vaccine.³⁹ They reported that the vaccine conjugated with flagellin in the form of nanoparticle along with ovalbumin were found to exhibit strong, long lasting systemic and mucosal immune responses than the respective non-conjugated vectors. Wang et al.⁴⁰ synthesized periodic nanohole arrays along with silica fibers using high temperature calcinations of silica nanotubes synthesized using flagella obtained from *Salmonella* sp. They also demonstrated the application of these double-layered silica-flagella nanotubes for selective CdTe quantum dot uptake into the inner channels or selective Au nanoparticle coating on the outer wall of the nanotubes through the difference in chemistry between inner flagellum core protein and outer silica wall of the nanotubes. Jo et al.⁴¹ prepared silica nanotubes using bacterial flagella as template and coated them with various types of nanoparticle made up of gold, palladium and iron oxide using reductive metallization nor oxidative hydrolysis. Similar to Jo et al.,⁴¹ and Li et al.⁴² prepared morphologically controlled silica nanotubes using bacterial flagella as biotemplate. They manipulated the morphology by changing the pH and by using a peptide display to prepare silica nanotubes. They were also successful in preparation of sol-gel mediated hollow double

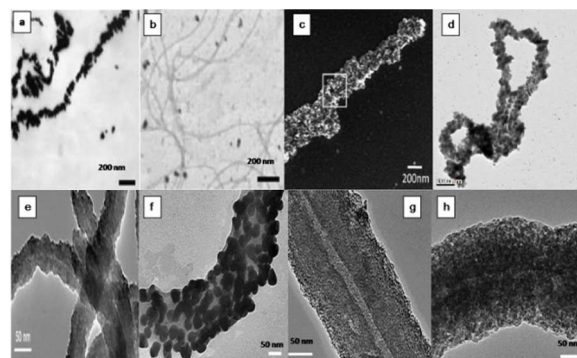


Fig. 6. Microscopic images of materials prepared using bacterial flagella as biotemplate. TEM images of Pd(II) (a) and Au(III) treated flagella (b). SEM micrographs of annealed TiO₂ thin film covered flagella filament (c). Polymerised flagella with silver nanoparticle impregnation (d). TEM micrographs of silica-mineralized flagella nanotubes (SMFNs) (e), gold NPs-metallized SMFNs (f), Palladium NPs-metallized SMFNs (g), iron oxide NPs-metallized SMFNs (h)⁴¹ (All images reproduced with permission)

layered core shell titania/silica nanotubes under ambient conditions using bacterial flagella as template.⁴³ Various materials synthesized using bacterial flagella are presented in fig. 6.

2.1.3 Bacterial pili

Recently, bacterial pili have also been studied as biotemplate for making bionanomaterials of various morphologies. Pili from various bacteria like *Geobacter sulfurreducens* and *Geobacter metallireducens* behave as conductive protein filaments which are produced under physiologically relevant conditions. Because of their metal like conductive nature, these pili are often called as 'microbial nanowires'. They are responsible for electronic interaction between bacteria with inorganic electron acceptor and also for inter species electron exchange. Such conductive pili nanowires can be used in the field of microbial electrode synthesis and bioelectronics.⁴⁴ Many types of nanostructures have been reported using pili as biotemplate. Zhu et al.⁴⁵ reported atomic layer deposition of various oxides like Al_2O_3 , TiO_2 and ZnO onto bacterial pili isolated from *E.coli*. Using this technique, they obtained 20-25 nm Al_2O_3 coating onto the pili surface which appeared like a nanofiber. These oxide coated pili based nanofiber may be used for functional nanoelectronic materials. Cao et al.⁴⁶ synthesized multichannel, nanorhombuses, and nanoflowers like silica pili hybrid nano- architectures using pili bundles, double layer lattices and multilayer lattices of pili respectively using tetraethyl ortho silicate (TEOS).

2.2 Fungal biotemplate

Fungi are eukaryotic microorganisms which include yeasts and molds. These organisms are mostly filamentous in nature with few exceptions (like yeast). Owing to the greater metal bioaccumulation and tolerance, fungi have been looked in as a potential candidate for biotemplate.⁴⁷ Fungi and yeasts have the ability to produce metal nanoparticles/ meso and nanostructure through intracellular or extracellular reducing enzymes and by biomimetic mineralization process.^{4,48} Fungal hyphae have been used as biotemplate for synthesis of these structures. Fungal microwires were prepared from *Aspergillus nidulans*, *Aspergillus niger* and *Neurospora crassa* exploiting the self-assembly property of gold ions onto surface of fungal

hyphae. Monosodium glutamate was used as a external reducing agent for the synthesis and growth of gold nanoparticles onto the surface of fungal hyphae. The gold nanoparticle coated fungal hyphae grew along with fungal hyphae. Further these gold microwires were converted into free standing gold microtubules after subjecting them to super critical carbon-di-oxide extraction process.⁴⁹ Bigall et al.⁵⁰ developed three dimensional macroscopic and microscopic structures from hybrid fungus-platinum structure by dehydrating the organic part using critical point dryer. It was observed that such structures had the property to catalyse redox reaction and possessed optical properties similar to that of nanoparticles. Similar to Sugunan et al.⁴⁹, Rehman et al.⁵¹ prepared wire like structure by coating gold nanoparticles onto *Aspergillus niger* hyphae. Growth of gold nanoparticle coated hyphal wire was achieved by growing the fungus in a nutrient medium. However heat treatment was used instead of carbon di oxide extraction process for extracting fungal organic template to produce porous wire like structure. Gold nanowires were prepared by allowing self-organization of colloidal gold nanoparticles onto *Aspergillus niger* hyphae using positive phototropic fungal response. Increase of hyphal growth through visible light stimulation was exploited to achieve unidirectional growth of gold nanowires.⁵² Sharma and Srivastava⁵³ fabricated gold microwires using self organized amino acid functionalized gold nanoparticle on fungal mycelium of *Rhizopus oryzae*, *Penicillium funiculosum*, and *Aspergillus parasiticus*. These gold nanowires were tested for their potential application in biosensors as functional electrodes. The gold microwires were found to have good electrochemical response, high stability, sensitivity and biocompatibility that can be potentially applied in the field of biosensors and catalysis. Yu et al.⁵⁴ synthesized lithium manganese oxide microtubes using Mn oxidizing fungus *Paraconiothyrium sp WL-2* as biotemplate and biooxidiser. These microtubes were found to have varying level of lithium adsorption when calcined at different temperature ranging from 300 to 700 °C. Other than metal based nano/micro structures, scientist have also reported

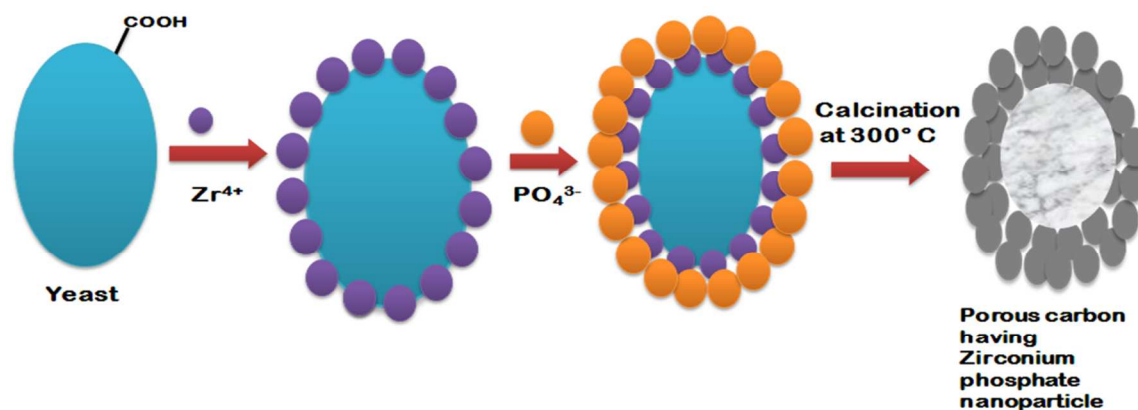


Fig. 7. Synthesis of porous carbon containing ordered hierarchical zirconium phosphate nanoparticles using yeast as biotemplate. Adopted from ref 57 with permission.

the synthesis of organic nanoparticle with potential application in medicine. A novel naturally synthesized organic nanoparticle made of glycosaminoglycan and protein has been isolated from *Arthrobotrys oligospora* fungus. These organic nanoparticles were of 360-370 nm size and had immune stimulatory and antitumor activity that can be used for immunochemotherapy.⁵⁵ Similar to fungal mycelium; many researchers have considered yeast cells as a potential biotemplate for micro and nanostructure synthesis. Bio-templated hierarchical anatase phase TiO₂ mesoporous structure with ordered pore was prepared using yeast cells via biomimetic mineralization process. These highly porous TiO₂ mesoporous structure showed high electrocatalytic activity and excellent oxygen reduction reaction.⁵⁶ Tian et al.⁵⁷ synthesized yeast templated zirconium phosphate mesoporous structure having high electrocatalytic property for oxygen reduction reaction (fig. 7). These mesoporous zirconium phosphate structures showed better electrocatalytic property when compared to commercially available manganese dioxide air electrode and hence can be widely used in fuel cell technology. Wang et al.⁵⁸ exploited *Pastoris* (PPCs) cells as biotemplate to prepare closely packed, size controllable gold nanohorns (AuNHs) and AuNHs/PPCs nanocomposite by chemical method. These AuNHs/PPCs nanocomposite exhibited high Raman enhancement effect when tested with Rhodamine 6G.

2.3 Algal biotemplates

Algae are aquatic organisms with photosynthetic ability. They appear as either single cellular or multicellular organisms. Similar to bacteria, the different morphological forms of algae like unicellular, filamentous and as colonies can be used as a biotemplate for synthesis of nanostructures. Various structured and patterned skeletal morphology of algae that can be used for biomimetic fabrication of nanostructures are presented in figure 8.

Some algae like diatoms take part in the process of mineralization, which is more fascinating to form the different nanostructures. Diatoms are unicellular, eukaryotic microalgae that can be seen in fresh- and saltwater ecosystems. Diatoms have a very interesting model system with high potential in the nano-structured production as there are almost 100000 different species with unique frustule morphologies.⁵⁹ Diatoms have rigid cell wall structure called frustules which are made of silica. These structures are created naturally in a controlled manner which provides them a unique morphology. These frustules have two halves called thecae. The top and bottom part of these thecae are called as valves which are made of nanostructures granular silica.^{60,61} The new theca are created in a vesicle called as silica deposition vesicle which have silaffins and long-chain polyamines, that are involved in precipitation of silicic acid into silica. These silica shells

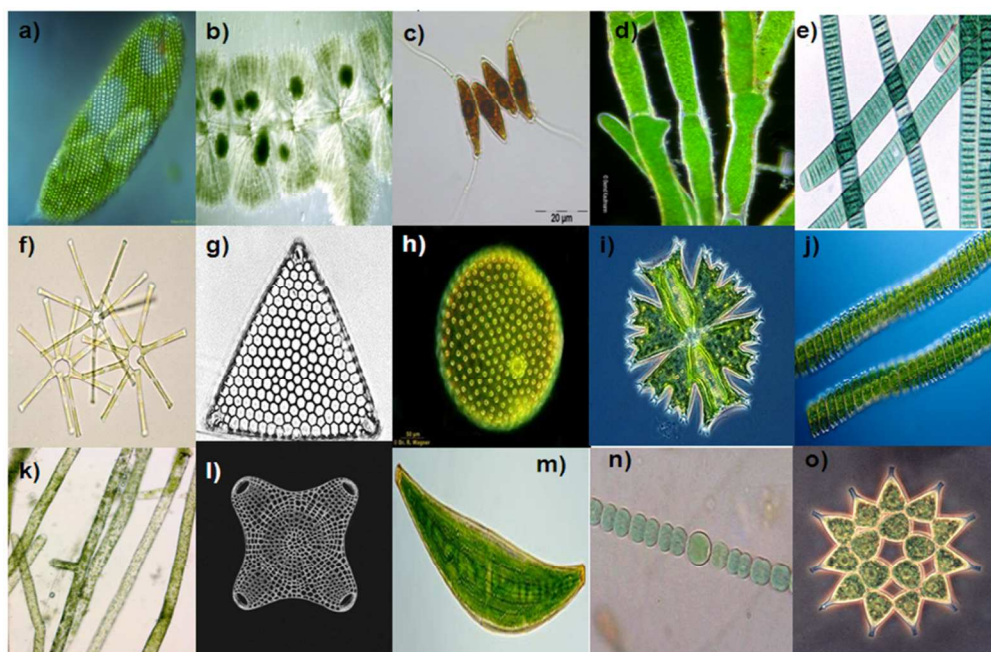


Fig. 8. Various structural and patterned skeletal morphology of algae that can be used for biomimetic fabrication of nano/microstructures (a) *Euglena spirogyra* (b) *Batrachospermum sp* (c) *Desmodes musopoliensis* (d) (*with multiseriate morphology*), *Oscillatoria sp* (e) *Asterionella sp* (f) *Triceratium favus* (g) *Volvox sp* (h) *Micrasterias crux melitensis* (i) *Desmidium swartzii* (j) *Vaucheria sp* (k) *Biddulphia antediluvian* (l) *Closterium costatum* (m) *Anaebena sp* (n) *Pediatrum sp* (o) (Courtesy: Google images on algae and diatoms, microscopy.uk.org)⁸⁶.

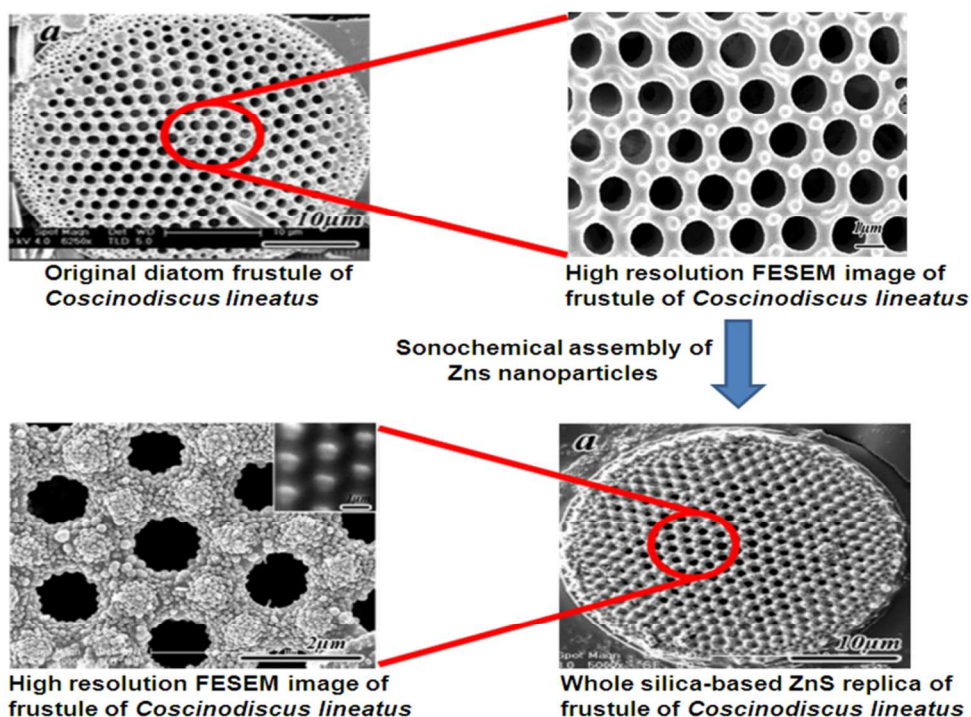


Fig. 9. Synthesis of diatom-templated ordered porous ZnS meso/nanostructures.⁶⁸ (Reproduced with permission)

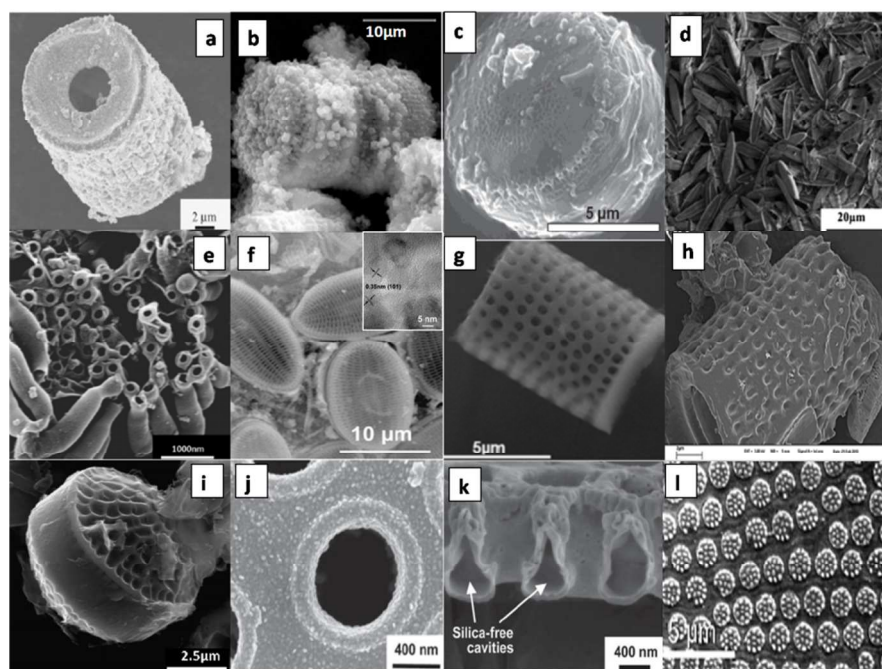


Fig. 10. Microscopic images of materials prepared using various diatom as biotemplate, Palladium frustule replica synthesized via electroless deposition(a),⁸⁷ Diatomite with faujasitic crystals(b),⁸⁸ Polymer-silica composite made using *T. weissflogii* frustules(c),⁸⁹ Navicula frustules after annealing at 1000°C for 2 h(d),¹²³ Macroporous carbon/aluminium composite obtained from *Thalassiosira pseudonana*(e),⁶⁷ Diatom-TiO₂/SiO₂ composite of *Cocconeis placentula* frustules (insert: high resolution image of TiO₂/SiO₂(f),⁹⁰ SEM images of an *Aulacoseira sp.* frustule after the magnesiothermic conversion process (g),⁹¹ Carbon nitride coated onto single frustules of Celatom FW-14 diatomite(h),⁸² Carbon/Al-*Thalassiosira pseudonana* (C/Al-Tp) composites (i),⁶⁷ Gold-coated *Coscinodiscus asteromphalus* frustule valve(j),⁹³ Free standing silica free cavities after ion milling gold coated *Coscinodiscus asteromphalus*(k),⁹³ Gold structures replicated from the frustules of *Coscinodiscus* species(l)⁹⁴. (All images reproduced with permission)

are synthesized by polymerization of silicic acid. This individual silica frustule consists of two valves which are held together by bands like structures called girdle bands. There are three types frustules based on its structure viz., rod, flake and three dimensional (3D) shaped frustules. Rod shaped frustules show higher assembling property with larger area coverage when compared to other shapes which can be used in monolayer formation. Flake shaped frustules act as possible biocarriers and are used for biodetection. 3D frustules have very good porosity that can be used in drug delivery applications.^{62,63} The frustules valves are separated by plates which appears like chambers. These plates contain pores varying in diameter either increasing or decreasing from outside to inside. Size and positioning of these pores are genetically determined. The smallest pore (40 nm) has been observed in *Coscinodiscus* species and *Thalassiosira eccentrica*.^{64,65} These unique structure and its skeletons have been considered as potential biotemplate for synthesis of various nanostructures that cannot be easily prepared by conventional and advanced techniques available. Although the silica structures in diatoms are brittle in nature, its nanoporous structure provides good toughness to the frustules which can withstand considerable environmental stress. The brittle nature of these frustules can be changed into ductile through structural arrangements at the nanoscale level.⁶⁶ Al/Tp ordered macroporous-mesoporous carbonaceous materials were prepared using *Thalassiosira pseudonana* as a bio template.⁶⁷ Zhou et al.⁶⁸ synthesized ordered porous ZnS nanostructures using *Coscinodiscus lineatus* as biotemplate via sonochemical method (fig. 9). Using such biotemplate and biomineralisation process various materials have been developed for multiple applications. Few of the recently reported diatom based materials are given table 1. The nano and microstructures produced using diatoms as biotemplates are presented in fig. 10.

2.4 Viral templates

Viruses are infectious agents composed of proteinaceous shell surrounding their genetic material that can live only in living cells. They lack their innate metabolic activity and remains as virions. (For more introductions on viruses, its classification and structure, the readers are advised to refer basic microbiology books). This property makes viruses as suitable and safe building block for preparing composite materials.⁶⁹ The protein shell of virions facilitates mineralization/ metallization process via amino acids present on their surface. For example, aspartic acid, glutamic acid, lysine, arginine and cysteine amino acids present in viral cell wall have more affinity towards the metal ions due to the presence of carboxylate, amino and thiol groups. Such affinity of viruses and virus like particles towards metals and ions has found immense application as scaffolds and templates for nanostructure formation. Molecules of interest are liganded via bioconjugation process. The possibilities of viral manipulation and engineering through molecular biology techniques to impart specific display peptide have been a major boon for preparing customized nanomaterials through mineralization/metallization process.⁶⁹ The viral surfaces can also be chemically engineered to attain desirable properties. Few of

the chemical and molecular biology approaches used to modify viral surfaces are bioconjugation, covalent modification, introduction of specific surface display genes through genetic engineering and membrane anchoring. These virus based materials can be two dimensionally arranged in large scale by integrating with conventional patterning techniques like microcontact printing, dip pen nanolithography, Langmuir–Blodgett lithography, molecular combing, etc.⁷⁰⁻⁷². Please refer Fischlechner and Donath,⁶⁹ for knowing more on basics of using viruses as building blocks for preparing materials and devices. Most of the viruses used by scientists are plant viruses and have been selected based on their nonpathogenicity to human beings and animals. The frequently studied viruses for biotemplating are non enveloped plant viruses like tobacco mosaic virus (TMV), cowpea mosaic virus (CPMV), or cowpea chlorotic mottle virus (CCMV). They are also selected based on the shape and size requirement. For example, viruses like M13 phage and TMV are rod shaped and CCMV and CPMV are spherical shaped viruses. The length, inner and outer diameter of TMV is 300, 4 and 18 nm respectively.⁷³ This inner diameter has a great significance in forming nanostructures. Various metal nanowires, nanorods and nanotubes have been made exploiting central channel and out coat proteins of virus as template and as metal binding sites (fig. 11). Apart from these methods few recent studies have also reported the synthesis of new nanomaterials using TMV for various applications (fig. 12). Since, Love et al.⁷⁴ and Li and Wang,⁷⁵ have made a detailed review on TMV, we have excluded those details cited in those articles in order to avoid duplication. More focus is given to M13 viruses.

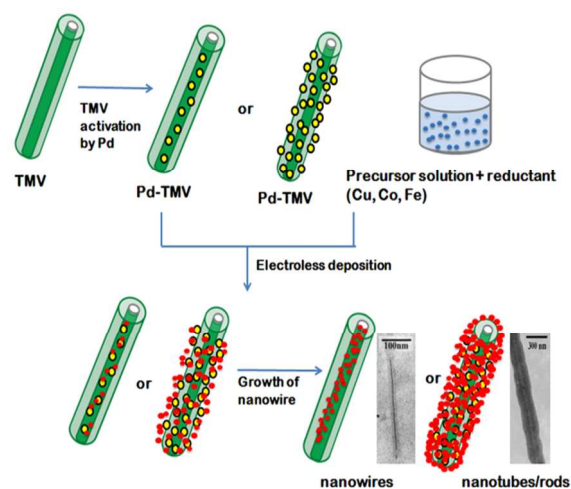


Fig. 11. Schematic diagram of synthesis of nanowires and nanotubes/rods using inner channel and out coat protein of TMV respectively^{95-97,110}. (All images reproduced with permission)

2.4.1 M13 Viruses

M13 is a rod shape filamentous virus having different types of outer coat proteins (pIII, pVI, pVII, pVIII and pIX) which can be modified genetically. The property of these outer proteins of M13 phages have been used in nanomaterial synthesis. Among these proteins, pVIII is a major coat protein that has been extensively studied. Nurajeet al.⁷⁶ produced perovskite nanomaterials using genetically engineered M13 virus that expresses pVIII coat protein. Strontium titanate and bismuth ferrite nanomaterials were prepared using genetically engineered therapeutics and imaging⁷⁷ and nanowires for lithium ion battery electrodes.⁷⁸ Ghosh et al.⁷⁷ used M13 phages as scaffold to carry more iron oxide nanoparticle and SPARC-binding peptide ligand that can bind with cancer cell surface more efficiently than iron oxide nanoparticle carrier. Recently Dong et al.⁷⁹ achieved high discharge capacity in lithium batteries using sulfur bound M13 phage particles as negative cathode. They have used the innate binding affinity of phage towards sulfur. It was found that the binding of sulfur occurs on the sides of p8 coat protein of the phage rather than the ends (p3). M13 phage was used to develop an electrode for battery applications. Manganese oxide was coated on the integrated phage particles; these composites showed good discharge capacity

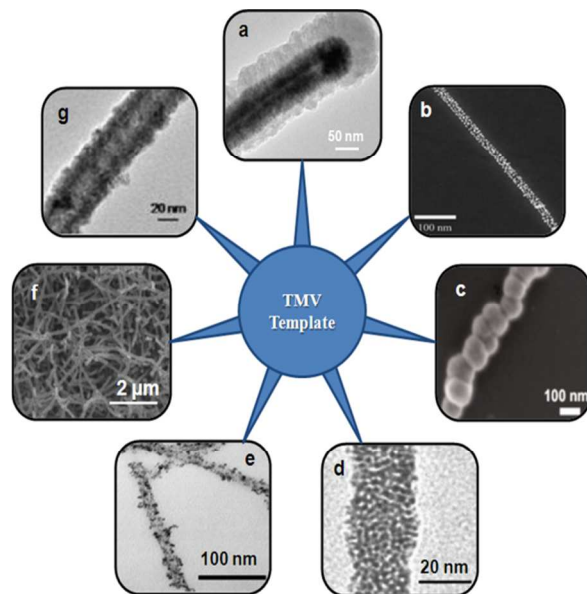


Fig. 12. Various nanostructures prepared using TMV as biotemplate. TEM image of a nonvertical TMV1cys/Ni/Sinanostructure after 45 min of silicon PVD(a)⁹⁸, SEM image of TMV rods decorated with citrate-coated AuNPs(b)⁹⁹, SEM micrograph of the growth of nickel on TMV during ELD(c)¹⁰⁰, TEM image of Pt-TMV nanotube (d)¹⁰¹, TEM image of palladium-deposited TMV1Cys at 25 °C with different molar ratio of palladium-ion to TMV1Cys(e)¹⁰², SEM image of TMV after tin electrodeposition (f)¹⁰³, TEM image of Cu-TMV (g)¹¹⁴.

upto 60 cycles.⁸⁰ M13 phage particles were modified or functionalized with gold binding peptide to express on their surface. These functionalized phages showed controlled mineralization of gold nanoparticles compared to non-modified M13 phages. Binding strength of gold nanoparticles was depending on the expression of gold binding peptides on the phages.⁸¹ Liu et al.⁸² have worked on genetically modified M13 phages which express positively charged peptide to form nanocomposite films. Films were formed layer by layer (LBL) assembly of positively charged peptides on M13 templates. Gold nanoparticles have also been assembled through LBL assembly and these biotemplated architectures were used for surface plasmon resonance based applications. Filamentous M13 phage mutated by site directed mutagenesis has been used as a photo responsive organic nanowire. The virus was engineered genetically for tyrosine to react with azo dye. Due to this chemical reaction, the M13 and azo complex showed reversible photo responsive property. This is one of the examples that organic M13 phage can be used for the chemical reaction through site directed mutagenesis. These modified viral nanowires have major applications in optics and data storage.⁸³ Table 1 gives a consolidated review on nano/ microstructures synthesized using bacteria, fungi, algae and viruses and their applications studied.

3. Conclusion

The need of nano/microstructures with different and defined size, shape and morphology for various applications in the field of electronics, environment, biotechnology, healthcare etc is always in rise. Such diverse nanoparticle morphology is achievable using microorganisms as biotemplates. These microbial templates have many advantages which can be potentially utilized to produce/synthesis nano/ micron sized structures/particles of varying morphology that are not possible in recent advanced manufacturing/synthesis techniques like lithography. The major advantages of using microbes as biotemplates are easy mass production, defined shape, tunable size, metal binding capacity, reproducibility of results, possibility for surface functionalization and its green and ecofriendly process. From this review, it is evident that many of the nano/microstructures prepared using microbial biotemplates has required properties that are needed for specific applications. Although this review indicates the possibility of using various microbes as biotemplates, the research is still in early stage and yet to realized at the product level. The microbial biotemplates, in future may be applicable to new concepts like non toxic high conductivity organic based electronic materials like transistors and supercapacitors. Hence these nanomaterials derived from microbial template may be studied for its effect on real time application for sustained use in product manufacturing.

Table 1: Nano and micro structure prepared using various microorganisms as biotemplate

Name of the species	Template	Nano/micro structure formed	Application	Reference
Bacteria				
<i>Bacillus subtilis</i> 1A772	Bacterial cell	Rod shape (Ni nanostructure)	-	24
<i>Streptococcus thermophilus</i> and <i>Lactobacillus bulgaricus</i>	„	TiO ₂ Hollow spheres and tubes	Photocatalytic	28
„	„	ZnS hollow nanospheres and tubes	-	26
<i>S.thermophilus</i>	„	ZnO hollow sphere	-	25
„	„	Hollow Ag microspheres	SERS substrate	27
<i>Escherichia coli</i>	„	Zirconia hollow particles	-	30
„	„	Au nanowire/ composite	-	31
<i>Microzyme sp</i>	„	ZnO hollow spheres	Acetone sensor	29
<i>S.typhrimurium</i>	Flagella	Si nanotubes	Electronic devices	119
„	„	Ag nanoparticles impregnated flagella	-	35
„	„	TiO ₂ nanotubes	-	34
<i>Deinococcu sradiodurans</i>	S layer proteins	Ge Nanowires	-	13
<i>D.desulfuricans</i>	„	Pd& Au nanoparticles	Catalytic	33
<i>Sulfolobu sacidocaldarius</i> and <i>D.radiodurans</i>	„	Pt nanoparticle array	-	18
<i>D.radiodurans</i>	„	Array of Au nanoparticles	-	104
<i>Shinorhizobium meliloti</i> 1021	Oligosaccharides	Se nanowires	-	120
<i>E. coli</i>	Flagella	Silica nanotube	Electronics	121
Fungi and Yeast				
<i>Aspergillus niger</i>	hyphae	Au microwires	-	51
Yeast (genus not specified)	Yeast cell	Zirconium phosphate mesoporous structure	Fuel cell	57
<i>Pichia pastoris</i>	„	Au nanohorns	SERS application	58

ARTICLE			Journal Name	
Yeast (genus not specified)	„	TiO ₂ mesoporous structure	Photocatalytic	56
Yeast (genus not specified)	„	CdO hollow microspheres	-	105
Yeast (genus not specified)	„	ZrO ₂ hollow porous microspheres	-	106
Algae and Diatoms				
<i>Coscinodiscus lineatus</i>	Whole cell	Porous nanospheres	Photonic	68
<i>Aulacoseirasp</i>	Frustules	Zirconia, MgO/TiO ₂ replica, BaTiO ₃ coated MgO replica	3-D GEMS	122
„	„	silicon frustule replicas	catalysis, filtration, sensor, electrical, and thermal applications	87
„	„	free-standing porous 3-D microscale assemblies of silver, gold and palladium NPs	„	87
„	„	Gold bearing diatom frustules replicas	Immobilization of functional enzymes for energy harvesting, fluid purification	107
„	„	Gold microstructures with complex 3-D morphology	-	108
<i>Thalassiosira weiflogii</i>	Frustules	TiO ₂ integrated frustules	-	109
„	Frustules	polymer-silica composite	Microscale particle assembly	89
<i>Thalassiosira pseudonana</i>	Whole cell	macroporous carbon/aluminium composite	-	67
<i>Coscinodiscus asteromphalus</i>	Whole cell	freestanding gold structures with frustule-derived 3-D morphologies	-	93
<i>Navicula sp</i>	Whole cell	Patterned nanostructures of silicate-based red phosphors	white LED lighting applications	123
<i>Coccone s placentula</i>	Frustules	Diatom-TiO ₂ /SiO ₂ composite	Photocatalytic	90
<i>Aulacoseira sp.</i>	Frustules	magnesiothermic conversion of silica to silicon diatom frustules	-	91

<i>Cyclotella maneghiniana</i>	Outer valve	PDMS replica of outer valve	-	92
Virus				
Tobacco mosaic virus (TMV)	Virus	ZnO coat	-	110
„	„	Ni nanostructure (rods)	Microbattery	111
„	„	Si shell	-	112
„	„	PbS, Silica, CdS and Iron oxide nanotubecomposites	-	113
„	Central channel of virus	CoPt & FePt ₃ nanowires	-	97
„	„	Cu nanowire	-	96
„	„	Ni & Co nanowires	-	95
TMV, fd & M13 viruses	Virus	Cu nanorods & wires	-	114
M13 virus	„	STO nanowire	Photocatalytic	76
„	„	Co ₃ O ₄ nanowire	Li ion battery	78
fd phage	Phage	Layered HAP nanostructure	-	116
„	„	Silica rods, wires & bundles	-	115
Chilo iridescent virus (CIV)	„	Au nanoshell	-	117
Z1 peptide	Viral peptide	ZnO platelets & nanorods	Solar cell	118

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