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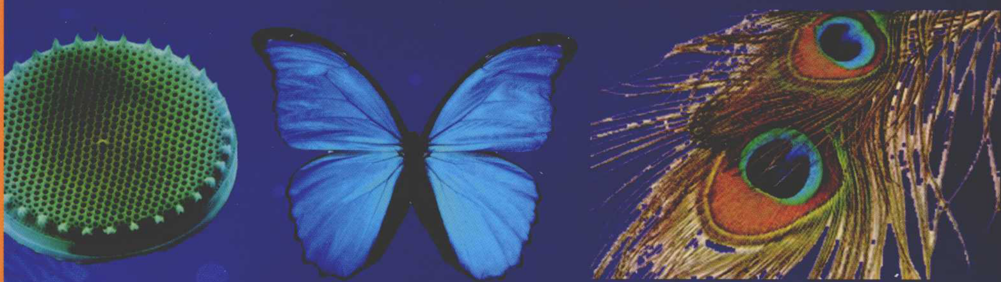
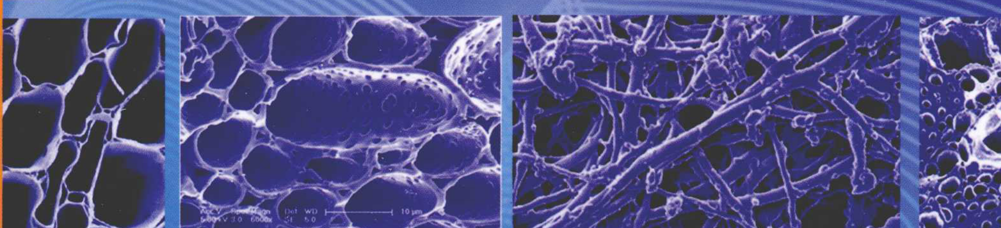


Di Zhang *Editor*

Morphology Genetic Materials Templated from Nature Species



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Preface

Supposing in a morning when we dress, use Velcro to fasten our jackets and bags, say goodbye to our pets, and leave for the office, we may not appreciate those burs or plant seeds with hooks which gave George de Mestral the idea of developing these hook-and-loop fasteners in 1941. We might yet not notice those road markers, which are equipped with reflectors inspired from the eye-shine reflection of kitty eyes. There are improving understandings in the natural species since Charles Darwin published his epochal book *On the Origin of Species* in late 1859. In his view, plants and animals on this planet have developed and have been developing complicated and precise structures, functions, and strategies, to survive themselves through a severe natural selection process. These solutions are usually much more effective than many other devices that have been developed by human beings. The secrets of their success keep on arousing great interest among curious researchers. To study and imitate the structures and behaviors of our natural-born neighbors started a promising area known as Bionics, or Biomimetics. Countless novel products have been successfully developed according to the blue prints of the natural species for the past decades, including the two examples we mentioned at the beginning of this preface.

However, simple imitation quickly met its bottle-neck. As we tried to design and fabricate similar structures or functions evolved from nature, we found we were very awkward when compared with those natural genetic engineers. This happened especially when we stepped into the microcosmic world with a rapid development in modern nanoscience. For example, people have already realized that some of the butterfly wing scales are natural photonic crystals, a term which has become very attractive since twenty years ago. That is, they are tiny optical devices that can control the propagation of a light beam. We knew that nature could spontaneously and easily generate millions of these micrometer size scales for one butterfly wing according to the animal's inner genes, with each composed of a complicated three dimensional (3D) nano to sub-micrometer structures. Such precise 3D structures are however unfortunately far beyond our present fabrication abilities to imitate either through a bottom-up self-organization method, or through a top-down photolithography process. This gave us a big push to find some new and efficient ways to effectively prepare these biomimetic microcosmic structures.

Again, we were inspired by nature herself almost ten years ago. Nature preserves her ancient species' remains and traces as fossils. These structured stones or minerals keep their original species' structures quite well, and convert the organism parts into inorganic materials. This fossilization or bio-templating process makes it possible for us to identify the extinct species' morphologies from the remote past. If we could find a way to directly keep the morphologies of some species, while transforming their original organism parts into our desired functional materials like oxides, we would then be able to fabricate our biomimetic materials in an operable, precise, and effective routine.

Now, the key point is how to explore such an approach. In contrast to a natural fossilization process that usually takes millions of years, an operable fossilization method should be finished in hours or days. We thus developed several quite fast methods to fabricate those functional fossils in the laboratory. Generally, we dip the original organism structures into solutions containing the ions that compose the final functional materials. This process is similar to the natural way, like burying the ancient plants or animal bodies to infiltrate the mineral contents inside. To speed up the fossilization process, we used heat or light during our synthesis. Through a careful adjustment of the fabrication parameters, we could control the final morphologies in a precise manner.

As to be effective, it not only means that something is easy to be fabricated, but also means an effective route from design to product. For example, we chose natural species with great diversities, which means once a fabrication route was developed, we could obtain bunches of various functional fossils using the same method. We also chose abundant and easy-to-raise species with functional structures for our bio-templates to avoid making them endangered or extinct. Materials like ZnO butterflies, Fe_2O_3 wood, TiO_2 plant leaves, SnO_2 cottons, etc., were then obtained.

Following these ideas and results, we name this family of novel materials as **Morphogenetic Materials**. The word "morphogenetic" here is a combination between "morphology" and "genetic", that is, the inheritance of the morphology. A morphogenetic material keeps its original bio-template's structures quite well, and replaces the organism parts by designed functional materials. On one hand, the original species' morphologies have been optimized by natural selection for millions of years and can offer special functions that are much more effective than solutions built up by human beings. On the other hand, the final designed materials like ZnO have some special functions that natural organisms cannot offer. The combination between the nature-born morphologies and the desired functional materials makes these novel materials competent for many applications.

I am happy to introduce this interesting new field to you in this book. We will report our works in the past ten years with several such examples. They include using wood tissues, cotton fibers, butterfly wings, bird feathers, plant leaves, etc., as bio-templates to fabricate morphogenetic materials. The prepared functional materials include carbon, ZnO, ZrO_2, Al_2O_3, TiO_2, Fe_2O_3, SnO_2, CdS, etc. The applications of morphogenetic materials will cover a wide range of fields including photonic crystals, solar cells, electromagnetic shielding, energy harvesting, gas sensitive devices, etc. We try to depict a general view of this exciting new-born area of study. Because of the length limit, a lot of content cannot be included.

Here, I wish to thank and acknowledge the following students for their valuable assistance: Dr. Xianqing Xie, Binghe Sun, Tianchi Wang, Qun Dong, Zhaoting Liu; Master Na Wang, Xufan Li, Na Yang, Bo Zhu; Ph.D Students: Jie Han, Fang Song, Yu Chen, Yongwen Tan.

We continually learn things and borrow ideas from nature, but we design devices beyond nature. What is more, since present genetic engineering is developing very quickly, we might be able to further adjust the original species' morphologies into our desires in the near future, giving rise to an even larger pool of bio-templates to be selected. Our ideas and methods of developing morphogenetic materials show an important step, bridging novel functional devices with natural concepts. It will not be such a great surprise to find that there will be micro devices with butterfly wing structures in our optical computers in the near future.

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Shanghai, China
June, 2011

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1

Functional Materials Templated from Natural Plants

1.1 Introduction

Nature provides a variety of plants with hierarchical structures for both fundamental and practical interests. Textural mesopores and intrinsic interconnected pore systems in hierarchical materials are able to transport guest species to framework binding sites efficiently. Typically, well-defined architecture porogens, such as emulsion colloidal crystals, virus liquid crystals, bacterial superstructures, polymer sponges, and wood cellular structures, have been used as templates to prepare functional materials. Similar to the wood tissues, agricultural waste materials, particularly those containing cellulose, show potential metal bio-sorption capacity. This kind of natural combination of multi-level, multi-dimensional, multi-component and multi-function agrees with the requirements for new material design, and provides new ideas for structural design and functional assembly of advanced materials.

The biomimetic method imitates structural characteristics of organisms and brings about the development of functional materials, but it is still very difficult to obtain artificial structures as complicated and delicate as organisms using present technologies. Therefore, the biotemplated method, using organisms more directly, has become an important researching means for advanced materials. The biotemplated method makes use of morph-genetic transformation technology, which is a material processing technology using biological macromolecules and their assembling structures as templates to fabricate inorganic materials and inherit organism's morphology and structure (Potyrailo et al., 2007).

The morph-genetic transformation technology is inspired by the mineralization of organisms. The mineralization is a normal natural phenomenon carried out by organisms, which can be divided into four stages (Calvo et al., 2008): (1) Pre-organize organic macromolecules to create an organized reactive environment before mineral deposition; (2) Interface molecular recognition: under control of organic macromolecules assembly, inorganic materials nucleate at the organic/inorganic interface in the solution; (3) Growth modulation: inorganic phases assemble to subunit through crystal growth, and the morphology, size, orientation and structure are controlled by organic molecules assembly; (4) Cellular processing: subunits assemble to a high-level structure participated by cells. The fourth stage is the main different source of natural mineralized materials and artificial materials. The above four stages have an important stimulation to inorganic composite materials: after formation of organic self-assembly, inorganic precursors occur, which cause chemical reactions at the self-assembly gathering/solution interface to form inorganic/organic composite under the guidance of self-assembly templates. The inorganic materials with a certain shape can be obtained after the removal of organic templates. The introduction of natural biological systems and the use of its self-assembled structure and function could break through the limits and avoid flaws of traditional materials design, and broaden the design ideas. This is done by using a multi-level and multi-dimensional biological structure as a template and by controlling the chemical reactions of synthesis to retain the morphologies and microstructures of the templates but to change their chemical composition. Then, a new type of materials, biotemplated materials, can be prepared with the fine natural structure with new properties and functions so as to provide the new materials with multi-dimension, multi-structure and multi-function.

Studies reveal that various natural waste plants such as rice husk, cotton, wood, vegetable residues, etc., have great potential in many applications. In this part, we will review the recent progress in the researches in our lab on morphogenetic materials fabricated from plants as well as the primary applications on adsorption, photocatalyst and gas sensors. Some research details are included in the following sections.

1.2 Morphogenetic Materials from Natural Plants

1.2.1 Synthesis of (Fe_2O_3), Nickel Oxide (NiO) and Zinc Oxide (ZnO) from Natural Plants

Researchers have successfully prepared wood-templated carbon ceramics, SiC ceramics, Si/SiC/C and SiOC/C composites, and metal/carbon composites for the preservation of wood's structures. Can we remove the carbon inside wood and reserve the wood structure intact to prepare wood-templated oxide ceramics? Until the beginning of this research, the researches over the world to address this question were still very rare, and the preparation technique of oxide ceramics was not mature and still at an exploratory stage.

Three kinds of oxides chosen as the target materials of morph-genetic transformation are iron oxide (Fe_2O_3), nickel oxide (NiO) and zinc oxide (ZnO), because of their low costs, simple production process, stable properties and diverse applications. Fe_2O_3 has good weatherability, lightfastness, magnetic property and absorption and shielding effect for ultraviolet. And it can be used as flash coatings, printing ink, plastics, leather, automotive topcoat, electronic and high magnetic recording materials, etc. With the extensive application of nano iron oxide, the gas-sensing and catalytic properties are attracting increasing attentions due to iron oxide's excellent effects on the forecasting, and detection of toxic and harmful gases as sensor. And iron oxide has also been widely applied in catalyze oxidation-reduction reaction. NiO has wide applications in electrical, optical and magnetic fields as catalysts, gas sensors, electrodes, electrochemical capacitors and so on. ZnO is a versatile material as a promising candidate for many applications including solar cells, photocatalysis, light emitting diodes, photodetectors, laser diodes, and transparent conductive oxides, because it's a low cost ceramic with combination properties such as electrical, optoelectronic and photochemical behaviors, and high chemical stability.

The purpose of this chapter is to study the preparation technology for wood-templated oxides with wood's hierarchical porous structures and the preparation mechanism by means of inspecting the effects of the surface chemical treatment on the microstructures especially on closed pits, investigating the flowing and diffusion mechanism of solution inside wood, analyzing the effects of processing parameters including template type, precursor solution, temperature and time on the preparation procedure to optimize the preparation technology, and studying the physiochemical transformation process and product's microstructures to verify the oxides replication of wood's hierarchical porous structures from μm to nm scale. The detailed experimental process is described as below: 8 kinds of woods were used to study the synthetic mechanism of wood-templated oxides. Paulownia, Lauan, Red beech, Manchurian ash, Cherry wood and oak belong to hardwood, while Pine and Fir belong to softwood. The chemical reagents used in experiments are analytical pure (> 98.5%) iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$), nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$), zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$), ammonia and absolute ethanol.

Fig. 1.1 shows the flow chart of the fabrication process of wood-templated oxides. Firstly, the specimens ($20 \times 10 \times 3$ mm^3) of wood were heated in boiling 5% dilute ammonia for 6 h. The extracted wood templates were washed by deionized water and dried at 80°C for 24 h. The precursor solution was distributed by nitrate (iron nitrate, nickel nitrate, and zinc nitrate) and a mixture solvent of ethanol and deionized water with the given volume ratio. Then the wood templates were infiltrated in the precursor solution at 60°C for 1 – 3 days and subsequently dried at 60°C for 24 h. After repeating the infiltration/drying steps for 1 – 5 times respectively, the samples were calcined at 600°C for 3 h in the atmosphere and air-cooled to room temperature. Ordinary oxides were fabricated with the same precursor solutions but without wood templates and used as the contrast samples.

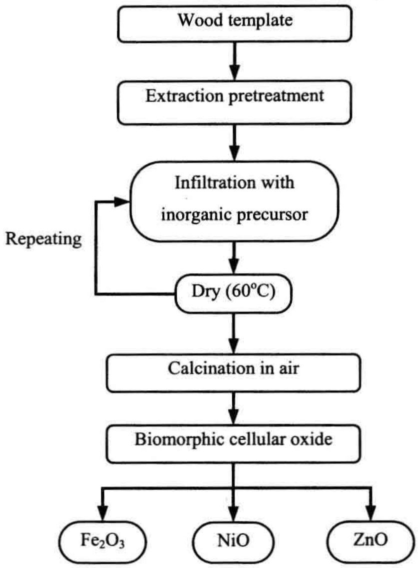

Fig. 1.1 Flow chart of the fabrication process

8 kinds of wood were used to infiltrate iron nitrate solution under the same conditions to study the wood template's influence on the infiltration capability. The infiltration rate Δ and calcinations rate δ of samples calcined at 600°C are shown in Fig. 1.2(a). According to the figure, different wood template shows different infiltration capability. Among them, the infiltration rate of softwood is generally higher than that of hardwood, because smaller density, higher porosity and better porous connectivity of softwood help solutions flow and diffuse. Among the hardwood, Paulownia has the smaller density (about 0.3 g/cm^3) than others such as oak (0.9 g/cm^3), leading to better infiltration capability. In addition, the quantity and arrangement of pits in different wood template are various.

The cutting method of wood will influence the template's infiltration capability too. Here, we use both axial and radial directions to cut Pine. The section cutting along the axial direction is cross sectional and the section cutting along the radial direction is longitudinal sectional. The infiltration rates of Pine templates through 4 times infiltration/dry processes are shown in Fig. 1.2(b). As can be seen from the figure, the infiltration rate of cross-sectional Pine is much higher than that of longitudinal-sectional Pine. And along with the increase of infiltration times, the infiltration rate of cross-sectional Pine increases much faster than that of longitudinal-sectional Pine. It is because most pores in the templates are longitudinal tracheid, and only small quantities of pores are transverse cells such as rays. So the capability and speed of solutions to flow from cross sectional to the longitudinal cells are much larger and higher than vise versa. Therefore, cutting directions can lead to very different infiltration rates in the same Pine template. The axial direction will be adopted to enable the wood template with higher infiltration rate.

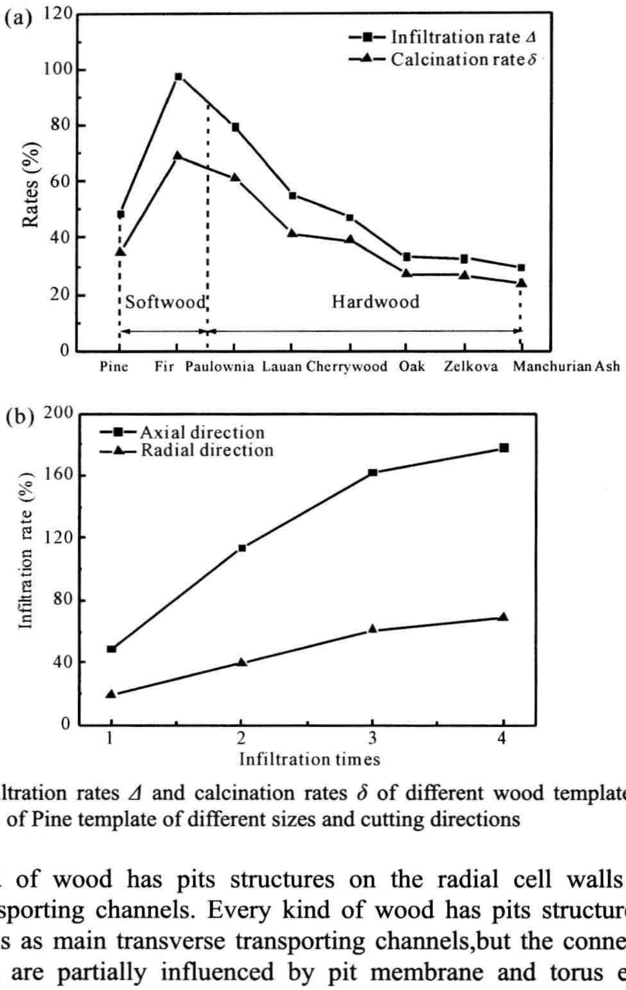

Fig. 1.2 (a) Infiltration rates Δ and calcination rates δ of different wood templates; (b) The infiltration rates Δ of Pine template of different sizes and cutting directions

Every kind of wood has pits structures on the radial cell walls as main transverse transporting channels. Every kind of wood has pits structures on the radial cell walls as main transverse transporting channels,but the connectivity of these channels are partially influenced by pit membrane and torus existed in woods. Meanwhile, inside the vessels, there always exist some obturators and extractives (Fig. 1.3) to affect the effectiveness of the capillary system to dredge the fluid. Therefore, the extraction pretreatment was added before infiltrating the precursor solution to increase infiltration efficiency and connectivity of oxides through getting rid of the pit membrane, obturators, and so on.

Some methods have been used to extract wood in former wood science research. F. C. Bao made use of the benzene-ethanol organic solvent and hot water to extract the Larch heartwood and Spruce heartwood. After the extractive process, the infiltration capability of Spruce heartwoods increased by an average of 75%, being closer to that of sapwoods. After using the pond water to infiltrate the Spruce, and thanks to bacteria decomposing the pits' membrane, the infiltration capability increased about 150% on average.

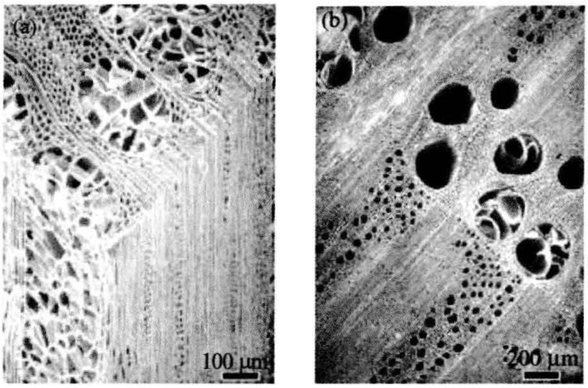

Fig. 1.3 Obturators in the hardwood's vessels: (a) osage orange; (b) white oak

In this study, wood extraction was carried out through boiling wood in dilute alkali lye for 6 h in order to dissolve and destroy the pits, thylose, extractive, etc., to improve the infiltration rate. To avoid impurities, metal ion in diluted ammonia of 5% concentration was chosen as the extraction solution. Pine and Paulownia wood with or without extraction pretreatment were used to study the extraction effect, and the results are shown in Fig. 1.4. The Pine and Paulownia wood belong to softwood and hardwood respectively. After extraction their infiltration rates were raised by about 80% and 50%. Thus, the simple extraction pretreatment can effectively improve the infiltration capability. The mechanism can be analyzed from two aspects as follows.

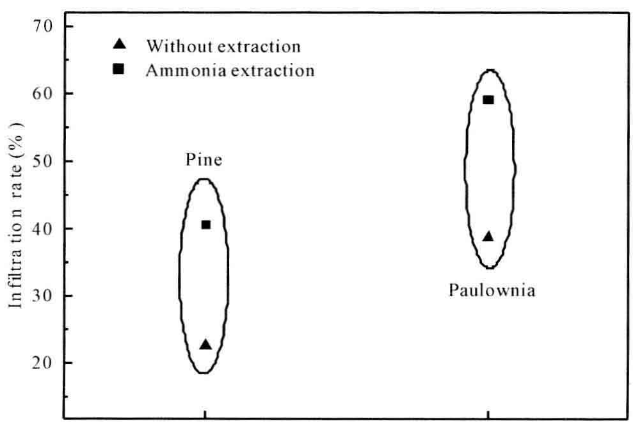

Fig. 1.4 Infiltration rates of wood templates with and without extraction pretreatment

On one hand, the alkaline environment created by dilute ammonia solution produces wood with swelling of cellulose and hemicellulose and has no obvious side effect. Limited swelling can open the hydrogen bonds on the cell wall, increase the porosity on the wall, and improve the wood's osmosis. Unlimited swelling can dissolve the cellulose, water extractives, protein, amino acid, part of hemicellulose, lignin, as well as a small amount of grease, wax, resin and essential oils, and remove the pit membrane, thylose and capillary. The higher the temperature of lye is, the larger the solubility and quantity of extractives are. So the dilute ammonia was kept at boiling status in our study.

On the other hand, after extraction, the polarity of wood enhanced and the surface tension improved to help wood adsorb solution. It is because wetting phenomenon appeared when the liquid and solid contact the surface tension. The contact angle θ is used to express the liquid's wettability to the solid. When θ<90°, it is called wetting as shown in Fig. 1.5. The smaller θ is, the better wetting property it has, and the easier to adsorb the solution the wood has, whereas it is called non-wetting. θ is expressed by:

$$\cos\theta = \frac{\gamma_{\text{s-g}}\gamma_{\text{l-s}}}{\gamma_{\text{l-g}}} \tag{1.1}$$

where them, $\gamma_{\text{s-g}}$, $\gamma_{\text{l-s}}$, and $\gamma_{\text{l-g}}$ are expressed as the surface tension of the solid, the liquid surface tension and the liquid-solid interfacial tension respectively. $\gamma_{\text{s-g}}$ is decided by the solid. The larger the $\gamma_{\text{s-g}}$ value is, the larger cosθ is, and the better the wetting property is. Therefore, the increase of the surface tension $\gamma_{\text{s-g}}$ can decrease the contact angle θ, help wood to wet the solution and help the solution to flow and be adsorbed in the wood.

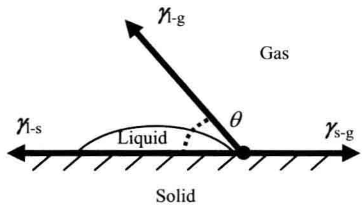

Fig. 1.5 The sketch map of wetting phenomenon

The process of infiltrating nitrate precursor solution is the dual function of the fluid to flow and diffuse in the porous materials. To fluid, wood is a natural and capillary porous colloid of limited expansion. It is a multiple capillary system composed in series and parallel connection with permanent tubular cells (macrocapillary) and instantaneous capillary-like cells (microcapillary) with all kinds of shapes, sizes, structures and connections. Fig. 1.6 shows the SEM image of wood's multiple capillary system, and the arrow at the bottom right corner points out the wood's pits on the tracheid walls, which are the channels for materials flowing among adjacent cells. Every kind of wood has all of the three capillary systems in series (as shown in Fig. 1.7): (1) capillary system in series of cell cavity and pit; (2) instantaneous capillary system in series of cell cavity and non-consecutive cell wall; (3) instantaneous capillary system of consecutive cell wall. The three capillary systems in series connect in parallel to form a uniform system. When the dried wood is infiltrated by the solution, fluid flows and osmosises occurs along the cell cavity in series with the pits and non-continuous cell wall under both outside static pressure and inside capillary force gradient. During the fluid flows, water vapor enters the surrounding cell walls in order to open up the access passage for ions. The matters in the solution are transported from the gap in the secondary wall lining uncovered by extractive to the adjacent cell wall. When the solvent evaporates, the metal ions hydrolyze to deposit and attach on the wood cell walls. Therefore, the higher the concentration of infiltration rate is, the easier it is for metal ions to be evenly distributed. At the same time, repeated infiltration allows for transported metal ions into wood's pipes to flow away from the liquid surface.

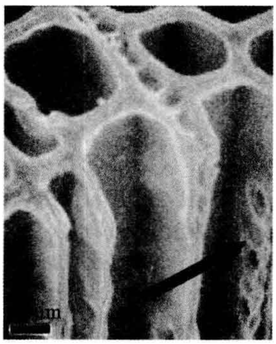

Fig. 1.6 SEM image of wood's series parallel capillary system

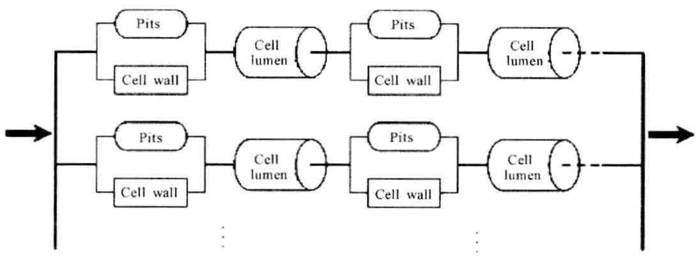

Fig. 1.7 Fluid flowing model inside softwood

Wood is assumed not to contain air, indicating no gas-liquid interface. Then fluid follows Poiseuille's equation (Eq. (1.2)) under the pressure difference, and flows and osmosizes along the capillary system in the softwood:

$$Q = \frac{N\pi r^4 \Delta P}{8\eta L} = \frac{Ar^2 \Delta P}{8\eta L} \tag{1.2}$$

Thereinto, Q is the volume flow rate of the liquid (cm^3/s), r is the capillary