A facile approach to fabricate functional 3D macroscopic silica microtube networks using *N*,*N*′-methylenediacrylamide organogel as template†

Yu Xia, Yu Wang, Kai Chen and Liming Tang*

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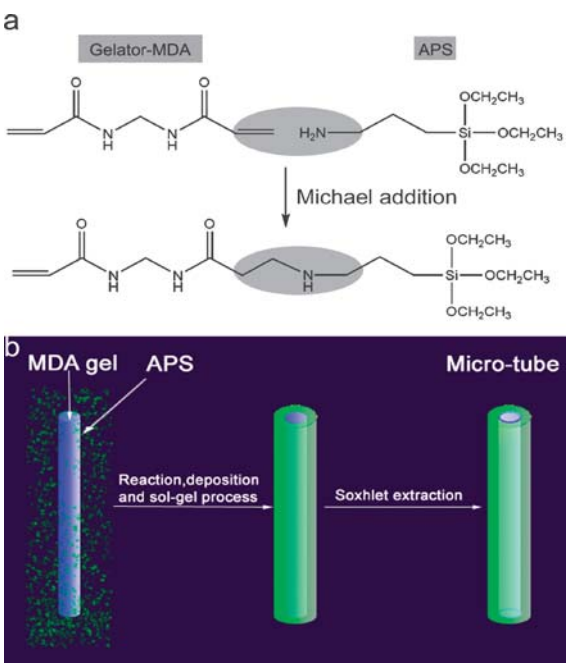
Using *N*,*N*′-methylenediacrylamide organogel as a template and γ-aminopropyltriethoxysilane as the precursor, functional silica microtube networks (MTNs) with adequate mechanical strength and different surface groups were prepared by an easy and effective approach.

Supramolecular gels deriving from the building blocks of low molecular weight gelators (LMWGs) have gained considerable attention recently. In a gel system, the solvent is trapped by the networks of numerous nanofibers or microfibers which are formed by gelators. Owing to huge specific surface area and porous structure for easy transport of solvents and other molecules, these gels display potential applications as materials responding to external stimuli,[1] electrooptics/photonics,[2,3] biomedical materials,[4] chemical sensors[5] and as templates for the preparation of porous inorganic materials.[6] However, many applications of the gels, especially as skeletons and functional materials in catalysis, separation, molecular imprinting and so on, are limited or undeveloped, though some research groups have explored the application for LMWG systems as skeletons of tissue engineering,[7] artificial enzymes[8] and biomaterials.[9] Those applications are restricted due to two disadvantages of LMWGs, which are poor mechanical properties (easily broken) and difficulty to be functionalized (synthesis and purification processes would break the gel structure).

Recently, Shinkai and co-workers[6] and other groups[10–12] tried to obtain inorganic materials by using organogels as templates, in which different LMWGs were used, such as carbohydrate derivatives, amphiphilic glucopyranoside derivatives, cyclohexane-based gelators, cholesterol gelators, crown-appended cholesterol gelators and charge-transferred gelators. Based on different transcription processes,[13,14] many novel inorganic microscopic structures, including fibers, lotus-shaped nanotubes, double helical nanotubes, chiral nanotubes, double-walled nanotubes, hollow particles and so on, were successfully achieved. In those studies, the authors paid their attention mainly on obtaining various and fascinating inorganic microscopic structures. However, the gelators they used were artificially synthesized, leading to additional costs. The macroscopic morphologies of the modified organogels were not provided and the functional potentiality of their products was rarely mentioned. These works inspired us in that through achieving functional inorganic materials in the gel system, we might solve the two problems.

In the present paper, we found that a cheap and easily obtained reagent, *N*,*N*′-methylenediacrylamide (MDA) was able to gel chloroform at low concentration. Using MDA organogel as template, silica functional microtubes were prepared from γ-aminopropyltriethoxysilane (APS) *via* a simple procedure.‡ The microtubes network obtained have sufficient mechanical strength to support the whole skeleton during chemical reaction and the microscopic and macroscopic morphology are almost the same as that of the gel system. We also investigated different kinds of functional groups on the tubes, which make the MTNs possible for further modification and functionalization.

The preparation procedure is outlined in Scheme 1, in which APS reacted first with MDA on the surface of the gel fibers *via* Michael addition. As more APS deposited on the fibers and subsequently participated in the sol–gel reaction, a silica layer



Scheme 1 (a) Chemical structures of MDA, APS and their Michael addition reaction; (b) preparation procedure for MTNs using MDA organogel as template.

Laboratory of Advanced Materials, Department of Chemical Engineering, Tsinghua University, Beijing, 100084, P. R. China. E-mail: tanglm@tsinghua.edu.cn; Fax: (+86) 10-6278-0304

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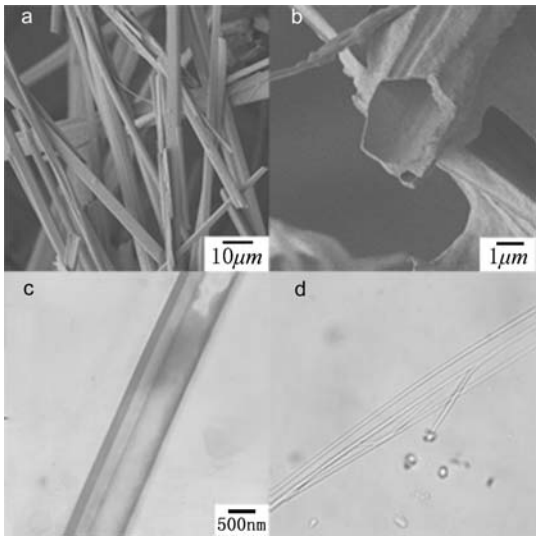


Fig. 1 (a) SEM image of the MDA gel before modification; (b) SEM image of a silica microtube; (c) TEM image of a silica microtube; (d) optical microscope image of microtubes (1000×).

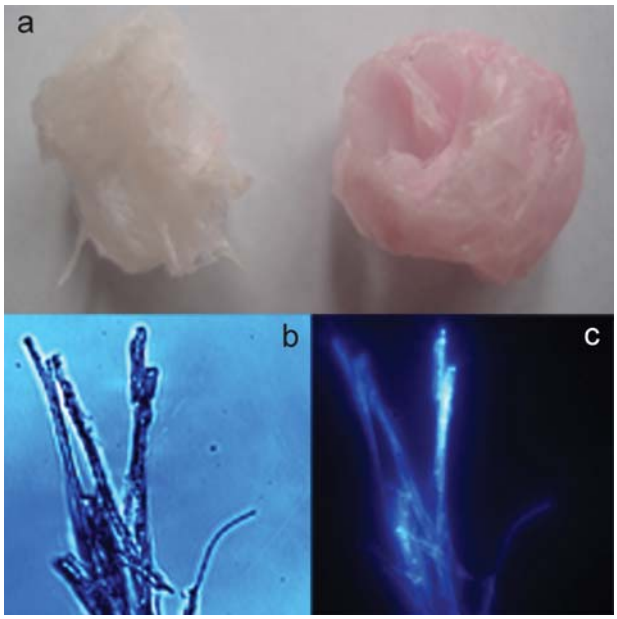


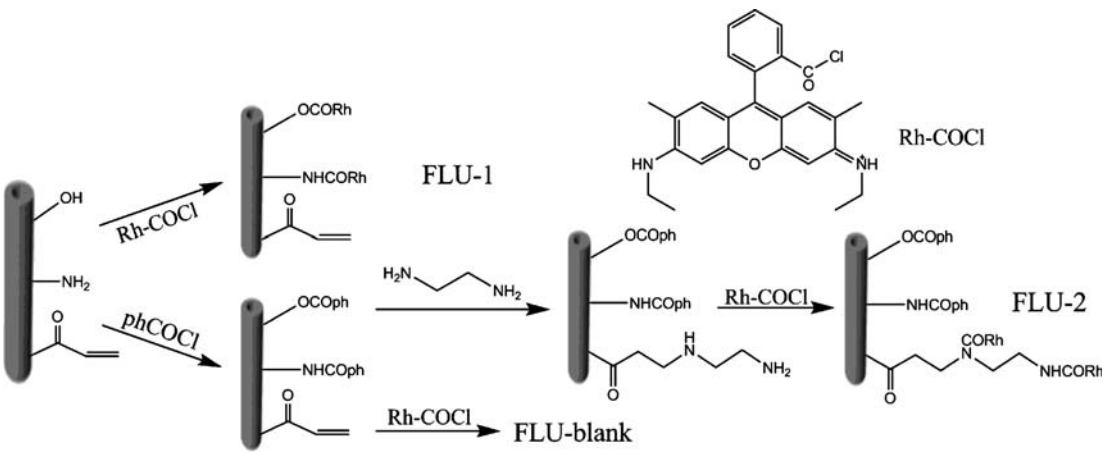
Fig. 2 (a) Optical image of FLU-blank (left) and FLU-2 (right); optical image (b) and fluorescent image (c) of FLU-1 under a fluorescent microscope (1000×).

was formed surrounding the fiber. After Soxhlet extraction, the microtubes were obtained. In contrast, no such microtubes were formed when tetraethyl orthosilicate (TEOS) was used instead of APS, which was attributed to the lack of reaction between TEOS and the gel. To the best of our knowledge, this is the first example of silica tubes being formed by introducing a covalent reaction between gelator and the precursor, rather than the non-covalent interactions most widely employed.

The MDA based gel and xerogel can not be removed from the vial due to the low mechanical strength, which is a common feature of organogels. After modification by APS, the resulting silica microtubes however possess improved strength. The sample can then be taken out of the vial, maintaining the shape of original gel.

The microscopic morphologies of the MDA xerogel and the silica microtubes were investigated by SEM, TEM and optical microscopy. From Fig. 1(a), the xerogel consists of MDA fibers with average width of *ca.* 3 μm. Fig. 1(b) shows a single silica microtube, which possesses a polygonal cavity. The diameter of the cavity is about 3 μm and the thickness of the tube wall ranges from several tens to several hundreds of nm, corresponding to the width of the original fibers, which suggests that the tubular structure is imprinted from the fibers.

Due to the difficulty for electron beams to penetrate large sized fibers (with diameter of several μm), we selected a smaller fiber for TEM observation to investigate the inner structure. Fig. 1(c) is the TEM image of a single silica microtube with diameter of 1 μm. Comparing the deep and shallow parts of the sample, it is clearly observed that hollow structure is presented all along the fiber. However, the deep part is not distributed uniformly throughout the tube, which should be ascribed to the irregular formation of a silica layer outside the MDA fiber (also see Fig. 1(b)). Fig. 1(d) is an optical microscopic picture of silica microtubes, from which one can see the whole structure of the microtubes. The microtubes have several biforked structures and very large aspect ratio. Also, the thickness of the microtubes walls are not uniform.



Scheme 2 The dyeing process of MTNs.

According to the fabrication procedure, there should be three kinds of functional groups on the microtubes: hydroxyl groups of the silicon dioxide network, amino groups of unreacted APS and acrylate groups of MDA. To prove the existence of the functional groups, the MTNs sample was treated by different approaches shown in Scheme 2: (1) the MTNs were reacted directly with Rh-COCl (acyl chloride product of Rhodamine 6G, a fluorescent dye) to give FLU-1. (2) After treating the MTNs successively with excess benzoyl chloride and ethylenediamine, the resulting sample was further modified by Rh-COCl to give FLU-2. (3) After treating the MTNs with excess benzoyl chloride, the resulting sample was modified by Rh-COCl to give the blank sample (FLU-blank). After each reaction, the sample was washed carefully with methanol to remove residual reagents.

The samples of FLU-2 and FLU-blank are compared in Fig. 2(a). It is clear that FLU-blank is almost white and its fluorescent signal was very weak and bleached rapidly under fluorescent microscope observation, which means that only a trace amount of dyes are physically absorbed on the sample. However, FLU-1 and 2 are both bright red, indicating considerable amount of dyes being incorporated. Meanwhile, the fluorescent signals of FLU-1 and -2 were both very strong, far beyond the absorption amount of the dye.

The result of fluorescence analysis of FLU-1 is shown in Fig. 2(b) and (c) in which both optical and fluorescent images demonstrate the hollow structure of the microtubes. The same results were obtained for FLU-2. These results indicate that there are different kinds of functional groups on the tube walls and they readily participate in various reactions.

This study has proved that the problems of traditional organogel systems can be solved by a simple procedure, therefore making the products suitable for many applications. For example, by introducing a thin layer of molecular imprinting polymers on the microtubes, the resulting material is expected to provide fast molecular exchanging speed. Such work is now under investigation in our lab. Also, catalysts may be recovered effectively when MTNs serve as the carrier. Furthermore, because different functional groups of MTNs can be modified by different chemicals, respectively, MTNs also have the possibility to be applied in the area of asymmetric catalysis and micro-reactors.

In summary, we have developed a simple approach to achieve functional microtubes with MDA gel as template. The adequate mechanical properties and different functional groups make the MTNs suitable for further modification and functionalization. It should be noted that the low cost and facile preparation procedure make such materials promising for practical uses.

Notes and references

‡ Preparation procedure of microtube networks (MTNs): A mixture of 45 mg (1.5 wt%) MDA and 9 mg (0.3 wt%) APS was added into 3 g chloroform in a vial. The suspension was heated at 60 °C for 1 min to obtain a transparent solution. A supramolecular gel was formed after cooling the vial at room temperature for about 5 min. After storage at room temperature for 24 h, the gel was exposed in air for another 24 h to volatilize the solvent slowly. During this period, APS reacts and deposits on the surface of the gel fibers based on the Michael-addition between amino group and acrylate group. Then the xerogel was transferred into a container saturated with water and small amount of triethylamine (as a catalyst) and stored at room temperature for 24 h and then at 60 °C for another 24 h. As expected, the silica microtubes were finally obtained after extracting the xerogel by methanol in Soxhlet apparatus.

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