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# Biotemplated MnO/C microtubes from spirogyra with improved electrochemical performance for lithium-ion batterys

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ABSTRACT

Biotemplates from microbial origin have been used as a new source of inspiration for designing and fabricating novel functional materials. Herein, we reported a novel MnO/C microtubes prepared by using spirogyra, a green algae growing widely in natural water, as the template. Due to the unique filamentous shape and abundant organism of spirogyra, a porous carbon tube with wrinkle surface has been fabricated. The MnO nanoparticles are set and embedded into the porous carbon matrix, which leads to the tube-like MnO/C composite materials. The as-prepared spirogyra-templated MnO/C microtubes exhibit a reversible electrochemical lithium storage capacity as high as 610 mAh $g^{-1}$ at 200 mA $g^{-1}$ after 60 cycles, and an excellent rate capability of 350 mAh $g^{-1}$ at a high current density of 2 A $g^{-1}$. Considering the vast options of natural materials, this green, facile and economic biotemplating method will provide considerable freedom in structural and functional variability which can be extended to other promising high performance anode materials for the future development of novel energy storage materials.


## 1. Introduction

Lithium-ion batteries (LIBs) have attracted much attention due to the versatile, clean, and promising power source applying in portable electronic devices and electric vehicles [1–5]. The commercial anode material of graphite with low cost, good cyclic stability and low electrochemical potential has been widely used for LIBs. Unfortunately, owing to the relatively low theoretical capacity (372 mAh $g^{-1}$), graphitic carbon could not meet the increasing demands for large energy and power density of future lithium-ion batteries. Therefore, tremendous efforts have been made to improve the performance of LIBs anode materials [6–10]. In this context, transition metal oxides, including $Co_3O_4$ [11–14], $Fe_2O_3$ [15–17], $Fe_3O_4$ [18–20], $Mn_3O_4$ [21–24], $SnO_2$ [25–27], and NiO [28], have been extensively exploited as new anode materials for high performance LIBs due to their higher capacities than that of graphite. Among them, MnO is one of the most promising anodes because of its high capacity, worldwide abundance, low cost, and environmental benignity [29–31]. Despite the marvelous features it has, MnO is still limited by the low rate capability arising from the poor conductivity and rapid capacity fading resulting from large volume expansion and severe collapse of the electrode during the cycle process [32–35]. At present, more efforts have been made to circumvent these drawbacks. An efficient strategy is to downsize metal oxides into nanoscale with special morphology, and thus shorten the diffusion distance of $Li^+$ [29,36–38]. Another approach is preparing MnO/C nanocomposites by coating or mixing with carbon mass [2,39,40], which can effectively improve the electronic conductivity and maintain a stable structure during charge/discharge cycles and increase ion/electron transport in the electrode.

Nowadays, template-based synthesis has been commonly employed in fabricating anode or cathode materials since its advantages in controlling micro/nanostructures and constructing novel carbon matrix. Of them, biotemplates with unique structure and rich carbon source attract considerable interests due to the advantages associated with low-cost, renewable, and environmentally compatibility. Meanwhile, the three-dimensional periodic architectures with multiple sizes ranging from nanoscale to macroscale materials found in nature usually provide the possibility for fabricating advanced anode materials with controlled micro/nanostructures. Consequently, many biomaterials (such as microalgaes, DNA, viruses, etc.) have been successfully used to create hierarchical nanostructured architectures, which exhibit excellent electrochemical performance for LIBs. For examples, Zhang's group fabricated hollow porous MnO/C composites templated by microalgaes, which exhibit the reversible specific capacity of 700 mAh $g^{-1}$ at 0.1 A $g^{-1}$ after 50 cycles [40].

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Dong-Wan Kim reported a porous cobalt oxide nanostructure using Gram-positive bacteria as the soft templates, showing a high surface area and exhibiting an excellent electrochemical performance for rechargeable Li-ion batteries [41]. Mitlin's group created MnO/C composites with 3D carbon network obtained from hemp bast fiber as template, displaying a high reversible discharge capacity of 900 mA h $g^{-1}$ at a current density of 2 A $g^{-1}$ after 500 cycles [42]. Guo's group reported that $\alpha$-$Fe_2O_3$@C composites with 3D porous hollow secondary structures were prepared by directly burning the cotton containing the iron salt, which delivers a high reversible capacity of 990 mAh $g^{-1}$ at 0.1 A $g^{-1}$ after 50 cycles [43]. Clearly, the above successes have shown the great prospects of the biotemplating method in fabricating anode materials with hierarchical structures and superior property. Considering numerous inexpensive and renewable natural materials, however, the corresponding work on this aspect is rather inadequate and limited to date.

Inspired by this, our present attention is focused on fabricating metal oxides@carbon anode materials via more nature resources as the templates. The filamentous spirogyra belongs to green algae, which is distributed extensively in the ponds, pools, small streams with abundant amounts. Each filament of spirogyra consists of an extensive chain of tube-like cells, which measure approximately 40 to 100 $\mu$m in width and may stretch centimeters long. Each cell of the filaments features a large central vacuole, within which the nucleus is suspended by fine strands of the helical chloroplast and other organic substance (fatty acids, sterols etc.) [44]. Owing to its unique filamentous shape and abundant organisms, spirogyra can be considered as an ideal template for designing and preparing novel micro/nanostructures. In this work, hierarchically tube-like porous MnO/C composites were successfully synthesized via a facile biotemplating method using natural spirogyra as both the carbon source and template. Owing to the 3D hierarchically porous structure, the as-prepared MnO/C electrode materials exhibit a high reversible capacity, significantly improved rate and cycling performance as an anode material for LIBs.

## 2. Experimental section

### 2.1. Preparation of materials

In a typical procedure, the live spirogyra was washed carefully with deionized water to remove the unwanted materials, and then vacuum freeze-dried. 3.16 g of $KMnO_4$ (0.02 mol) and 2.84 g of $Na_2SO_4$ (0.02 mol) were dissolved into 100 mL of deionized water. And then, 2 g spirogyra was added to the solution. After magnetically stirred for 1 h at room temperature, the color of spirogyra was changed from green to dark brown due to the biosorption and spontaneous redox deposition of metal ions on the spirogyra surface. The dark brown products were filtered and washed with deionized water for several times, and then freeze-dried for future use. The as-treated sample was loaded in an alumina crucible and annealed in a tube furnace at 500 °C for 8 h under a mixed atmosphere of Ar (95%) and $H_2$ (5%). In order to clarify the effect of the carbon matrix for MnO on electrochemical performances, pure MnO was synthesized. Fabrication of pure MnO was similar to MnO/C except for the concentration of initial solution (0.4 M) and the time of immersion (12 h).

### 2.2. Material characterization

The X-ray diffraction (XRD) patterns were obtained of the composites from a German Bruker D8 Advanced X-Ray Diffractometer using Cu K$\alpha$ radiation ($\lambda$ = 15406 nm). The thermogravimetric analysis (TGA) was tested on an SDT600 apparatus with a heating rate of 10 °C $min^{-1}$ from room temperature to 700 °C in air flow. Measurements of Raman spectra were performed on a micro-Raman spectrometer (Raman, Jobin-Yvon LabRAM HR800) with a radiation of 532 nm. The Brunauer-Emmett-Teller (BET) surface area was measured using a Belsorp-max surface area detecting instrument. Scanning electron microscope (Philip XL30) was used to investigate the microstructure of the sample. Transmission electron micrographs (TEM) were got using a JEOL JEM-2010 transmission electron microscope.

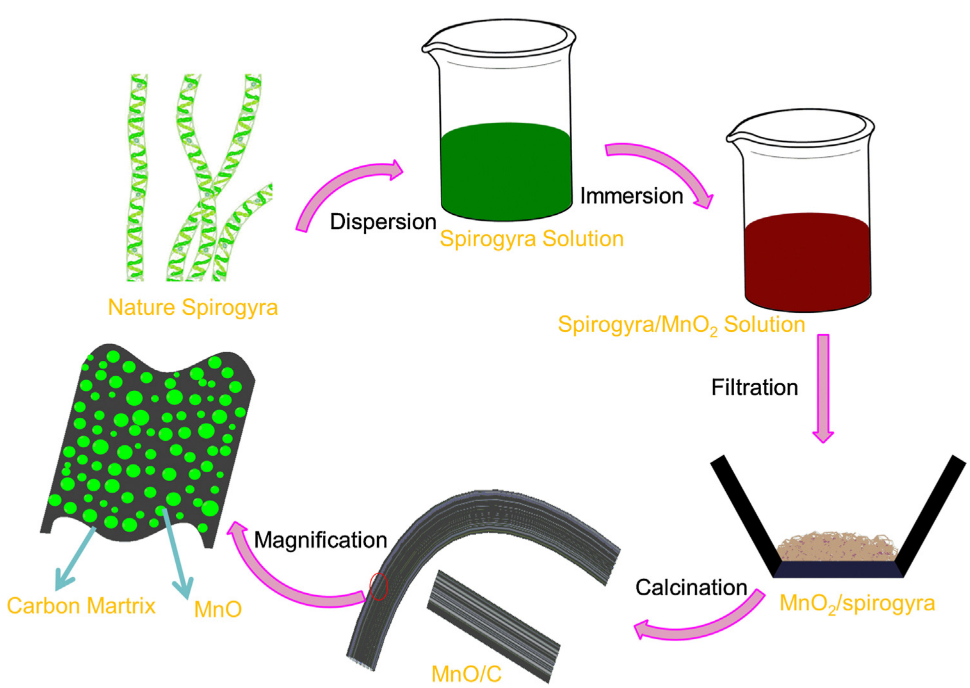


**Fig. 1.** Schematic illustration of the fabrication process of spirogyra-templated MnO/C microtubes.