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Template Synthesis of Freestanding Nanostructural Membrane of Polyaniline

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A reactive template method was used to synthesize large, flexible, freestanding nanostructural membranes of a conductive polymer, polyaniline. The resulting membranes are constructed of textured nanofibers with diameters about 100 nm. Such a flexible nanostructural membrane has great potential in applications in supercapacitors, lithium batteries, sensors, memories, and artificial muscles.

Nanostructural membranes, a kind of freestanding nanoporous paperlike film combining the advantages of thin film and self-assembled nanowires/sheets, have received intensive attention during the past two years. Examples include carbon nanotubes (CNTs),[1,2] MnO_2,[3,4] and graphene oxide membranes.[5] These membranes show great potential for practical applications with various excellent functional properties, such as superstrength,[1] superabsorption,[4] and surface properties switchable by electric field.[6] At the same time, as one of the most important conducting polymers,[7–14] nanostructured polyaniline (PAni) materials have been used as the key activation components in energy devices such as supercapacitors,[14,15] lithium ionic batteries, and intelligent devices such as sensors, memories,[12] and artificial muscles, due to the large specific surface area, controllable surface modification, fast charge and ion transport and so on. Nevertheless, the powder or block nanostructured PAni materials have many limitations for practical applications. Naturally, we are eager to bring important advances in paperlike PAni materials.

So far, fabricating a freestanding membrane from PAni has been stymied by several obstacles: 1) No synthetic method is available for preparing long PAni fibers (at least several hundred microns) to form the textured structures of a nanostructural membrane. 2) Individual PAni fibers show severe shrinkage during drying. 3) PAni is usually brittle due to its rigid molecular chain. Herein, we present a large area, flexible, and freestanding PAni membrane composed of nanotubes, produced by using a nanostructural MnO_2 membrane reported by Yuan et al.[3,4] as the template and by the reactive template methods proposed by our group.[8] Figure 1 shows a photograph of the large area, freestanding nanostructural PAni membrane. The final PAni membrane shows high conductivity and large specific surface area, suggesting an innovative material for use in energy storage, electronic, electromechanical, and hybrid electronic/biological applications.

A typical synthesis process is illustrated in Scheme 1. Membrane composed of MnO_2 nanowires was used as a template for the formation of nanostructural PAni membrane, which is produced according to a reported method.[3,4] The MnO_2 template membrane was immersed in a solution of aniline monomer and perfluorooctanesulfonic acid (PFOSA) in 1-butyl-3-methylimidazolium tetrafluoroborate, a room-temperature ionic liquid (RTIL). During the formation of the membrane, the color of the material turned from dark brown to black with a slight greenish tint. Here, PFOSA supplied H^+ ions and acted as the doping acid for PAni in the reaction. MnO_2 nanowires played the roles of both the template and the oxidative initiator for PAni polymerization, since the electrode potential of MnO_2 in acidic conditions is higher than that of aniline polymerization.

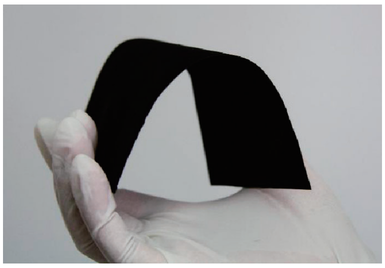
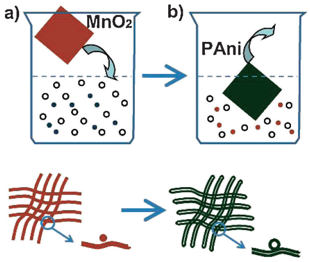


Figure 1. A large size, flexible membrane of PAni.



Scheme 1. Formation mechanism of nanostructural polyaniline membrane.

$$MnO_2 + 4H^+ + 2e \rightarrow Mn^{2+} + 2H_2O\ (1.23\,\mathrm{V}) \qquad (1)$$

During the reactive template reaction, the MnO_2 nanowires were converted into PAni nanofibers and simultaneously removed in the form of soluble Mn^{2+} ions.[8] The in situ template method stringently controls the micromorphology of PAni because the reaction happens only at the interface between solid phase and liquid phase and finally results in an intact sheet of membrane constructed of PAni nanotubes. Herein, the use of doping acid PFOSA for PAni is important for the formation of large and flexible PAni membrane, because PFOSA forms soft molecular side chains by doping on PAni, which transforms the brittle nature of PAni into a flexible material. The conductivity of the membrane was found to be $0.983\,\mathrm{S\,cm^2}$ by standard four-probe method, which can be increased to $10.335\,\mathrm{S\,cm^2}$ by mixing 5% carbon nanotubes (CNTs) in the initial MnO_2 membrane and forms a complex membrane of PAni and CNTs.

Figure 2a shows a scanning electron microscopy (SEM) image of the surface morphology of the produced membrane.

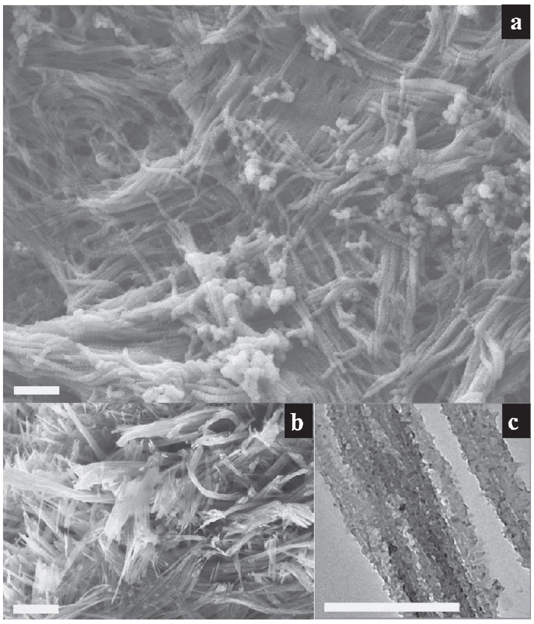


Figure 2. Structural characterization of the PAni membrane. a) SEM image show surface morphology of the PAni membrane and the textured structure of nanowires; b) SEM image of cross-sectional area of the membrane; c) TEM image reveals the nanotube structure of PAni fibers. Scale bar: 1 µm.

Note the in situ template method for converting a MnO_2 membrane into PAni should just be necessary for fabricating PAni membrane, the MnO_2 nanowires close in space were merged to develop crosslinked texture of PAni nanofibers. The crosslinked and stacked structures are clearly visible and are composed of bundles of long PAni fibers with diameters about 30–120 nm. It is the crosslinked and stacked structures of long PAni fibers that ensure the anticracking and solution-tolerant properties of the membrane. In addition, energy-dispersive X-ray spectroscopy (EDX) analysis indicated that the membrane contains no residual Mn. Figure 2b shows the cross-sectional morphology of the membrane observed via SEM: the PAni fibers are interconnected to form a randomly stacked nanowire structure. Further investigation by transmission electron microscopy (TEM) of fibers separated by ultrasonication in solution from the membrane is shown in Figure 2c, which reveals that most of the PAni fibers are nanotubes with inner diameter about 10–30 nm.

Figure 3 shows Raman spectra of PAni membrane and initial MnO_2 membrane template. The peaks located at 515 and 638 cm^{-1} in curve b correspond to cryptomelane-type manganese oxide (OMS-2), which are not presented in curve a, indicating that MnO_2 has been removed in the reaction to form the final polymer membrane. In the spectrum of PAni membrane shown in the curve a, C–H bending of the quinoid/benzenoid ring at 1162 cm^{-1}, C–C stretching of the benzenoid ring at 1558 and 1612 cm^{-1}, and $C–N^{\bullet+}$ stretching around 1339 cm^{-1} were observed, indicating the presence of acid-doped PAni structures. In addition, the PAni is doped with PFOSA, which is indicated by the presence of stretching peaks of $–CF_2–$ at 1218 cm^{-1}, $–CF_3$ bending at 742 cm^{-1}, and skeletal bending involving FCF and CCF at 522 cm^{-1}.[16]

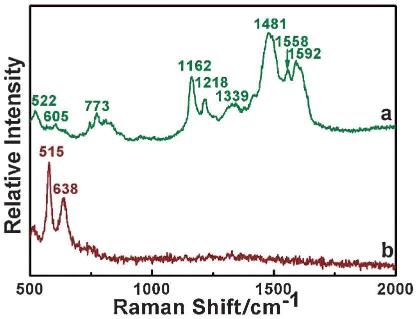


Figure 3. Raman spectra of PAni membrane (curve a), and template membrane of MnO_2 nanowires (curve b).

In summary, large sheets of flexible PAni paper have been produced by using a nanostructured MnO_2 membrane with reactive template methods. The in situ template method converted the MnO_2 membrane of nanowires into nanostructural PAni membrane composed of long nanotubes. Most importantly, the long PAni nanotubes were crosslinked in the reaction, which prevented cracking during drying and enhanced the stability of PAni membrane in solvents. The doping acid PFOSA was used to form flexible molecular side chains on PAni to achieve good flexibility of the final nanostructural membrane. The freestanding nanostructured membrane form of the paper is more compatible with applications in energy and intelligent devices than powder samples of PAni and shows most promising applications in flexible electronics.

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