A Simple and Low Cost Method for Fabrication of Nanochannels Using Water Soluble Nanowires

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ABSTRACT

Nanowires (NW) of $K_2Mo_3O_{10}.4H_2O$ with high yield were synthesized in 15 min using simple chemical method at room temperature. SEM shows NWs with length ranging from 10-30 μm and diameter of ~300 nm and XRD revealing orthorhombic structure. Solubility rate of the NWs in water was determined to be ~ 30 nm/min. Fabrication process of nanochannels with the obtained NWs begins with mounting two metal electrodes spaced few μm apart, followed by isolation and alignment of single NW using DEP(dielectrophoresis). PDMS (poly(dimethyl siloxane)) was casted over the aligned NW, cured at 60ºC for 3.5 h and demolded from the substrate with NW bridged between two electrodes. The NW embedded in the PDMS was then etched by continuous flow of de-ionized water, resulting in formation of a nanochannel. The reported process demonstrates fabrication of nanochannels using a simple, rapid, reproducible and importantly a low cost approach as compared to conventional techniques.

Keywords: Nanochannel, dielectrophoresis, poly(dimethyl siloxane, nanowire.

1 INTRODUCTION

Nanofluidics, an emerging field leads to various devices like nanofluidic diodes, perm selective membranes, biomolecular separation, nanochannels, etc. Nanofluidic devices facilitate isolation, manipulation and analysis of single biomolecules such as DNA and proteins, essential functions in the newly emerging field of nanobiotechnology
[1-5]. Consequently, this has stimulated various fabrication methodologies for constructing nanofluidic devices. Nanochannels, one of crucial component in nanofluidic chip, are fabricated with conventional methods employing nanolithography, nanoimprinting and successive etching. In a recent report Gong et. al. [6] reported fabrication of nanochannel using water dissolvable nanowires. In their approach, they have used nanowires as a template and nanochannels were fabricated using standard photolithographic process and thin film techniques. In another paper by Chu et. al. [7], monolithic polymer based nanochannels were reported. The fabrication process uses nanowires as a template and further steps include designing of nanowire based FET structure followed by casting polyimide film over a device. Polyimide layer was removed using focused ion beam (FIB) process. Nanowire residing in polyimide layer was removed by HF to produce a nanochannel. Further, highly precise triangular shaped nanochannels were fabricated by Choi et. al. [8] using electron beam lithography (EBL) employing hydrogen silsesquioxane as a resist material. Although, all these finding offer significant flexibility in design and structure of nanochannel, the processes adopted are quite cumbersome and involve multi-step approach. Additionally, these conventional methods are time consuming and requires expensive instruments like mask-aligner, e-beam lithography, reactive ion etching (RIE) and focused ion beam (FIB) milling, thereby raising the cost of fabrication. This introduces necessity of development of simple, rapid process for fabricating nanochannels with a low cost approach.

In the present study we propose a simple, quick and most notably a low cost fabrication scheme for construction of a nanochannels. Nanowires (NWs) of $K_2Mo_3O_{10}.4H_2O$ were synthesized using a simple chemical method at room temperature. After purification, these wires were used as a sacrificial template for fabrication of nanochannel. An attempt has been made to grow nanowires inside a microchannel to achieve uniformity as well as monodispersivity. For preparation of nanofluidic device, aluminum electrodes spaced few tens of micron apart were prepared. It is noteworthy that electrodes were prepared without any arduous deposition/fabrication process. To start with , a microgap was created by placing aluminium foil on glass substrate and making an incision on its surface using a scalpel blade. To have a control over the creation of gap between electrodes, unconventional masking process was used. In this method, a glass substrate was masked using silk thread having width in range of few tens of micron followed by deposition of aluminum. NW was aligned dielectrophoretically across electrode gap and PDMS elastomer was further casted. After curing of PDMS layer, NW was etched in deionized (DI) water to form a nanochannel.

2 EXPERIMENTAL

Fabrication strategy for nanochannels consist of synthesis of nanowires, preparation of microelectrodes, isolation and alignment of nanowire over electrodes followed by

transferring pattern into PDMS membrane and succesive etching of nanowire in water. The schematic illustrating fabrication steps is given in Fig 1.

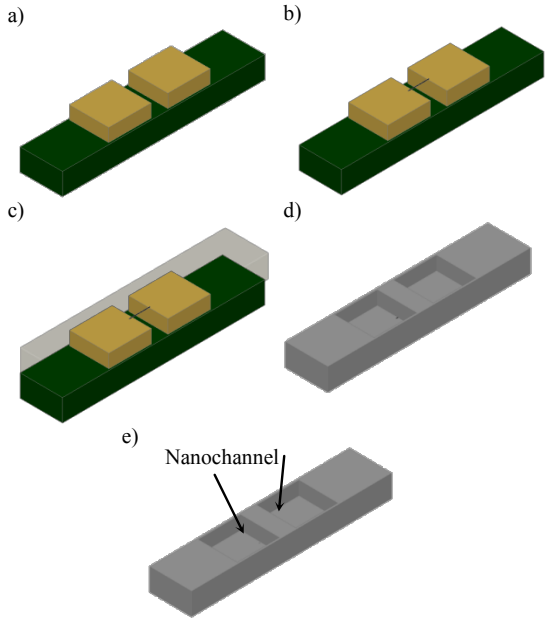

Fig 1: Schematic illustrating fabrication steps for nanochannels. a) Fabrication of metal electrodes spaced few tens of micron. b) Alignment of NW between electrodes using DEP process. c) Casting of PDMS solution over NW device. d) Demolding PDMS with formation of reservoirs bridged by a nanowire. e) Formation of nanochannel after dissolution of nanowires in de-ionized water.

2.1 Synthesis of $K_2Mo_3O_{10}.4H_2O$ nanowires

Nanowires of $K_2Mo_3O_{10}.4H_2O$ were synthesized using aqeous precursors $(NH_4)_6Mo_7O_{24}.4H_2O$ and KCl. Powders of pure $(NH_4)_6Mo_7O_{24}.4H_2O$ and KCl were dissolved separately in DI water, and further mixed together in 3:1 mass ratio [9]. This ratio of precursors was considered as it produced best quality nanowires in terms of uniformity and purity in phase. The reaction was conducted at room temperature under normal atmospheric conditions. Nanowires were obtained as white floccule like precipitates in reaction vials in 15 min. The products were cleaned by repeated cycles of centrifuging and rinsing by deionized water. The morphology and composition of nanowires was characterized using scanning electron microscope (SEM) and x-ray diffraction (XRD).

2.2 Synthesis of nanowires in microchannel

To attain more uniformity in size of NWs, the synthesis was conducted in a microchannel. For this purpose, the precursor solutions were micropipetted in microchannel with 400 µm diameter and the reaction was carried out at room temperature.

2.3 Preparation of microelectrodes

In our proposed scheme microelectrodes were prepared without using any strenuous process. In this technique focus was given to avoid any laborious deposition and patterning process and develop a rapid and low cost scheme. The electrodes were fabricated by attaching aluminium foil on glass substrate and microgap was created by cutting foil using sharp scalpel blade. With this method a microgap of 20-30 µm was achieved. However the repeated fabrication processes resulted in variation in microgap of order of ± 10 µm. To gain precision in fabrication process further, a new method was explored. In this approach, a simple silk thread was used as a masking material, it was tightly fixed onto a clean glass substrate. The substrates were then placed in evaporation chamber and aluminum was evaporated. Wires were attached on aluminium electrodes using silver paste for making contacts for DEP process.

2.4 Alignment of nanowire across microelectrodes

A droplet with volume 2 µl, containing a dilute dispersion of nanowires (2 µl/1ml DI water) was placed on the electrodes and NWs were aligned using dielectrophoresis (DEP) technique. Signal generator from Agilent with 1Hz-20 MHz frequency and maximum of 10 V peak to peak amplitude was used. The electrodes were kept at 20 MHz signal with 10 V peak to peak amplitude.

2.5 Transfer of aligned nanowire into polymer membrane

DEP process produced a device consisting of a nanowire bridged across microelectrodes. The device was further molded in polydimethylsiloxane (PDMS) layer. For this purpose liquid PDMS solution (Sylgard 184, dow corning) was prepared using PDMS elastomer and curing agent mixed together in 10:1 mass ratio and degassed for 20 min in vacuum desiccator. This solution was poured on microelectrodes containing aligned wire and cured at 65 ºC for 3.5 h. The layer was then demolded from substrate with nanowire embedded in PDMS layer.

2.6 Dissolution study of nanowires

The wires synthesized in this work are reported to be soluble in water. To study dissolution of NWs, a very dilute dispersion of NWs was prepared and a small volume ~ 2 µl was dropped in a closed reservoir and enclosed with a cover slip to avoid evaporation of water.The dissolution rate of wire was studied by monitoring change in length of a specific wire over time scale.

2.7 Fabrication of nanochannel by etching of nanowire

The wire trapped in PDMS mould was dissolved by immersing PDMS membrane in DI water bath under constant magnetic stirring. The aluminium traces attached to

wire surfaces were removed by KOH solution. When NW gets totally dissolved in DI water, a nanochannel is formed in PDMS with dimensions as that of wire.

3 RESULTS AND DISCUSSION

Nanowires of $K_2Mo_3O_{10}.4H_2O$ were synthesized at room temperature as reported earlier [9]. In the present study we could produce NWs faster at room temperature without use of magnetic stirring during synthesis. Optical microscope (Biotech labs) with a resolution of ~ 2 μm was used initially to observe products obtained. The precipitate obtained in reaction revealed formation of clusters of nanowires when it was imaged under optical microscope (Fig 4). The detailed morphology was examined under SEM using a dispersed sample on glass substrate. The typical SEM image of nanowire is given in Fig 2 with dimensions of ~300 nm (Fig 2b) in diameter and length ranging from 10-30 μm.

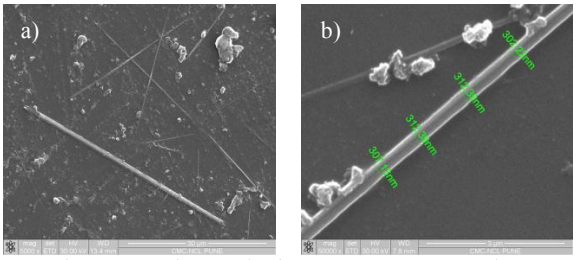

Fig 2: SEM micrograph of $K_2Mo_3O_{10}.4H_2O$ nanowires synthesized at room temperature. a) bunch of nanowires b) isolated nanowire.

Crystal structure of nanowires was characterized using XRD technique. The diffraction pattern shown in Fig 3 was found to match with previously reported data [9,10]. Various planes associated with standard structure of NWs were identified and observed peak values were found to be close to standard data. The results indicate pure orthorhombic phase of $K_2Mo_3O_{10}.4H_2O$ nanowires. Purified sample showed single crystalline structure as compared to that of as synthesized sample as evident from Fig 3. This might be due to removal of all impurities attached to nanowire surfaces leading to highly pure structure of NWs. High degree of crystallinity for molybdate nanowires is reported for the first time.

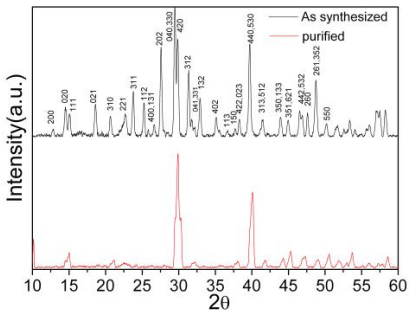

Fig 3: XRD pattern of as synthesized and purified NWs.

NWs synthesized in microchannel were viewed under optical microscope. Fig 4 depicts optical micrograph of NWs showing nucleation and further growth with the length of ~15-20 μm and diameter ~300 nm. The growth mechanism of nanowires is unclear and additional study is underway.

Fig 4: Optical micrograph of NWs inside microchannel.

The etch rate of nanowire was studied by taking a very dilute dispersion of nanowire in a closed reservoir. Using optical microscope a specific nanowire was identified and the total change in length with time was observed. The etch rate was calculated repeatedly for different wires and an average of etch rates was considered. The typical representation of etch profile monitored is shown in Fig 5. The initial etch rate of nanowire was in the range of 37 nm/min, which subsequently increased to 46 nm/min. This might be attributed to dissolved portion of nanowire in DI water leading to increase in its pH value due to hydroxyl group associated with NW structure. It is reported that the aqeous solution with high pH increases etch rate of the nanowire [6]. The etch rate reduced subsequently to a constant value of order of 13 nm/min possibly due to saturation of water as a result of the increased concentration of dissolved segments of NW.

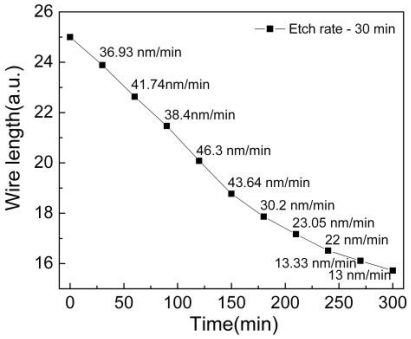

Fig 5: Etch profile of nanowire monitored at 30 min time interval.

Nanowires synthesized were used as a sacrificial template for fabrication of nanochannel. The fabrication process as mentioned in the experimental section consisted of deposition of aluminium electrodes spaced few tens of micron apart. The thickness of electrodes was ~200 nm. Fig

6a shows image of these electrodes viewed under optical microscope (Nikon-MM 40) with total spacing between electrodes of order of 20 µm. DEP process was used to isolate and align nanowire across the microelectrodes. Optical microscope images of electrodes after DEP revealed deposition of single nanowire aligned between two electrodes and middle segment was suspended as seen in Fig 6b.

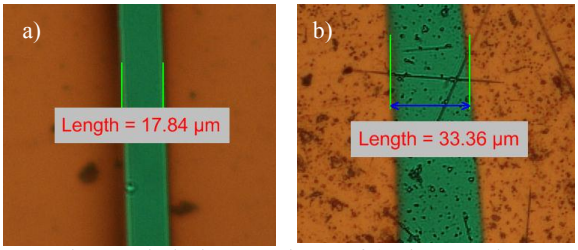

Fig 6: Optical microscope image of a) microspaced electrodes.b) Aligned wire across electrodes using DEP.

Next, 10:1 base to curing agent PDMS solution was drop-casted on the NW device and cured. After curing the layer was demolded from the substrate and viewed under microscope. The results showed nanowire transferred to PDMS along with aluminum attached to its ends. The residual aluminum on nanowire was removed by washing PDMS with KOH solution, which also helps in exposing nanowire to etching solution. The nanowire embedded in PDMS layer was dissolved by immersing PDMS in deionized water bath under constant magnetic stirring at room temperature. It was viewed under optical microscope after certain time intervals to check dissolution of wire until nanowire is completely dissolved. The etch profile of individual nanowires as obtained previously was utilized for estimating the total duration of dissolution of NW over time scale. After completion of etching process a nanochannel of similar dimensions as that of nanowire is obtained. The optical micrograph of hollow channel produced inside PDMS layer is shown in Fig 7.

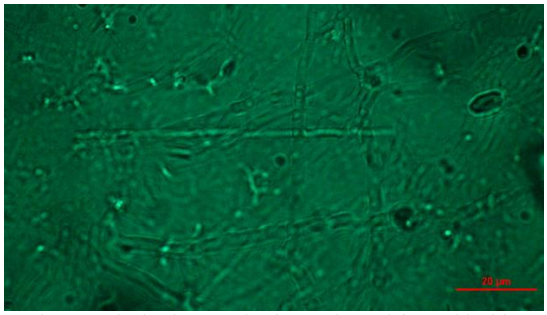
Fig 7: Optical Micrograph of nanochannel formed inside PDMS layer by etching nanowire.

4 CONCLUSION

A simple method to synthesize pure, well defined and highly crystalline nanowires at room temperature within few minutes and their application for fabrication of nanochannels has been demonstrated. The reported fabrication process produces PDMS nanochannels using simple fabrication steps obviating necessity of any expensive instruments. Likewise, present approach provides a time and cost effective method of nanochannel fabrication as compared to those reported using conventional techniques.

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