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**SYNTHESIS OF ULTRA-LONG HOLLOW MERCURY TELLURIDE (HgTe)
CHALCOGENIDE NANOFIBERS FROM Co AND Ni SACRIFICIAL NANOFIBERS**

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ABSTRACT

This paper describes a procedure based on electrospinning for generating sacrificial Co and Ni nanofibers with control dimensions and morphology. We have combined electrospinning and galvanic displacement reaction to fabricate ultra-long hollow chalcogen and chalcogenide nanofibers in a cost-effective and high through put manner. This technique is a general route of forming various ultra-long hollow semiconducting nanofibers. The aim of this study is to exploit the structural and compositional changes during the formation of HgTe chalcogenide with a view of fabricating a mercury sensor.

KEYWORDS: Electrospinning, Co nanofiber, Ni nanofiber, Galvanic displacement, HgTe chalcogenide

INTRODUCTION

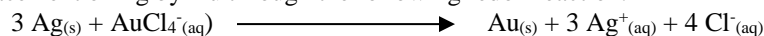
One dimensional (1D) nanostructures of metal oxides and related materials have been a subject of intense research because of their potential applications in many areas that include electronics, photonics, mechanics and sensing [1].

A number of synthetic methods for generating nanoscale wires, belts and tubes from various metal oxides have been demonstrated. Notable examples include those based on the vapour-solid (VS), [2], Vapour-Liquid-Solid (VLS) [3], solution-solid, [4] and solvothermal [5]. Among these methods, electrospinning seems to provide the simplest approach to nanofibers with both solid and hollow interiors that are exceptionally long in length, uniform in diameter and diversified in composition [6]. Unlike other methods for generating 1D nanostructures, the formation of a thin fiber via electrospinning is based on the uniaxial stretching or elongation of a viscoelastic jet derived from a polymer solution or melt. It is better suited for generating fibers with much thinner diameters, since the elongation can be accomplished via a contactless scheme through the application of an external electric field. The morphology and the diameter of electrospun fibers are dependent on the intrinsic properties of the solution such as the type of polymer, the conformation of polymer chain, viscosity or concentration, elasticity, electrical conductivity and the polarity and surface tension of the solvent.

It also depends on the operational conditions such as the strength of the applied electric field, the distance between spinneret and collector and the feeding rate of the polymer solution [6]. In addition to these variables, the humidity

and temperature of the surroundings may also play an important role in determining the morphology and diameter of the electro spun nanofibers.

Galvanic displacement reaction is a chemical transformation between solid metals and metal ions. It is a single-step reaction based on the difference in standard electrode potentials of various metals. The reaction leads to the deposition of a more noble metal and dissolution of a less noble metal. For example the standard reduction potential of $\text{AuCl}_4^-/\text{Au}$ (0.99V vs SHE) is higher than that of Ag^+/Ag (0.8V vs SHE). The reduction potential difference drives the replacement of Ag by Au through the following redox reaction:



Xia and co- workers have utilized the reaction to transform various Ag nanostructures into Au or Au/ Ag alloy nanomaterials [7, 8].

In this work, we combined electrospinning and galvanic displacement reaction to demonstrate cost-effective high through put fabrication of ultra-long hollow chalcogen and chalcogenide nanofibers. This procedure exploits electrospinning to fabricate ultra-long sacrificial nanofibers with controlled dimensions, morphology and crystal structures, providing a large material database to tune electrode potential thereby imparting control over the composition and shape of the nanostructures that evolved during galvanic displacement reactions. Tellurium and Mercuric Chloride were selected as proof of concept materials because they possess unique electrical, optical and chemical properties [9] which lead to many potential application including sensors, thermoelectric and non-volatile phase change memory, solar cells and infra-red detectors. For example elemental tellurium (Te) is a p-type semiconductor with electrical properties that depend on the orientation [10]. HgTe is naturally p-type due to mercury vacancies. P-type doping can also be achieved in HgTe by introducing Zn, Cu, Ag and Au. It is a semi-metal related to the II-VI group of semiconductor materials. It occurs in nature as the mineral form coloradoite- a rare telluride ore associated with metallic deposit (especially gold and silver). It is also used in photo optic applications.

MATERIALS AND METHODS

Polyvinylpyrrolidone (PVP, MW = 360,000) was purchased from Sigma Aldrich as polymer matrix. Nickel acetate tetrahydrate (Ni-acetate, $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) was purchased from Acros Organics to be utilized as the Ni precursor. Cobalt acetate tetrahydrate (Co- acetate, $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) was purchased from J.T Baker chemical company. Tellurium oxide (TeO_2) was obtained from Alfa Aesar, mercuric chloride (HgCl_2) and hydrochloric acid (HCl) were obtained from Fisher Scientific, respectively, for galvanic displacement deposition. All chemicals were used as received.

Synthesis:

Ni and Co nanowires were synthesized based on electrospinning process. PVP/Ni and PVP/Co solutions were prepared separately. The PVP solution was prepared to 10 g using PVP and anhydrous ethanol with a weight ratio of 1:9. The Ni solution was prepared with a concentration of nickel acetate of 12 mmol in 3g of DI-water, while the Co solution was prepared with a concentration of cobalt acetate of 4 mmol in 3g of DI-water. The prepared solutions were allowed to stir for 30 minutes. Once the solutions were prepared, the PVP and Ni solutions were mixed under continuous stirring at 60 °C for 1 hour to create a homogenous solution, while the PVP and Co solutions were mixed under continuous stirring only at 40 °C for 30 minutes. The mixed PVP/Ni or PVP/Co solution was loaded into a plastic syringe connected to a nozzle connector with a capillary tip (0.31 mm diameter) placed at the end of it. At this time, the nozzle connector was also connected to a high voltage power supply (High voltage AC-DC, Acopian). After assembling the electrospinning setup, the solution was fed at a constant rate of 0.5 ml/hr using a syringe pump (Perfusor compact S, B. Braun). An applied voltage of 10 to 16 kV was connected between the capillary tip and the collectors (two half of 4" highly doped Si wafers with controlled gap of 25 mm) which was grounded to protect the setup from electrostatic discharge. A SiO_2/Si substrate (1.5 x 1.5 cm) was positioned between the collectors. Upon applying the voltage, a fluid jet was drawn from the capillary tip and the solvent evaporated rapidly. Highly aligned Ni acetate/PVP or Co acetate/PVP nanowires were deposited on Si/ SiO_2 for 1 hour. The calcinations of the aligned Ni acetate/PVP or Co acetate/PVP nanowires were achieved by thermal treatment at 500 °C for 3 hours in air, with a heating rate of 3 °C/min to form NiO or CoO nanofibers. Finally ultra long and aligned Ni or Co nanofibers were reduced by annealing in forming gas (5% H_2 + 95% N_2) for 3 hours at 400 °C.

Aligned Ni and Co nanowires were employed in galvanic displacement reaction to synthesize ultra high long highly aligned Hg_xTe_y nanotubes. The electrolyte utilized to make Hg_xTe_y nanotubes by galvanic displacement reaction was prepared by dissolving TeO_2 in 2M hydrochloric acid, followed by addition of $HgCl_2$. After uniform mixing the resulting solution was diluted with DI water. The final concentrations of the electrolytes were 2mM $HTeO^{2+}$, 0.2mM Hg^{2+} and 2 M HCl for the Hg_xTe_y nanofiber from Ni sacrificial nanofiber and 2 mM $HTeO^{2+}$, μ mM Hg^{2+} and 2M HCl for Hg_xTe_y nanofiber from the Co sacrificial nanofiber. To perform the galvanic displacement reaction, 0.5 ml highly aligned Ni nanofibers suspension in DI water was added to 0.5 ml of the electrolyte solution. The resulting mixture which was in a 1.5 ml centrifuge tube was vortexed for 10 seconds and placed on a rotor in the refrigerator at 25 °C for 1 hour and rinsed with DI water. The effects of Hg^{2+} concentration on Hg_xTe_y nanofibers composition from both the Ni and Co sacrificial nanofibers were performed by altering the $[Hg^{2+}]$ from 0.01 mM to 10 mM.

Characterization

The morphologies of the Ni acetate/PVP, Co acetate/PVP, NiO, CoO, Ni and Co nanowires and the synthesized Hg_xSe_y nanotubes from both Ni and Co sacrificial nanofibers were investigated by FE-SEM. The compositions of Ni, Co and Hg_xSe_y nanotubes synthesized from both Ni and Co nanofibers were analyzed by electron dispersive X-ray spectroscopy (EDS).

RESULTS AND DISCUSSION

Results

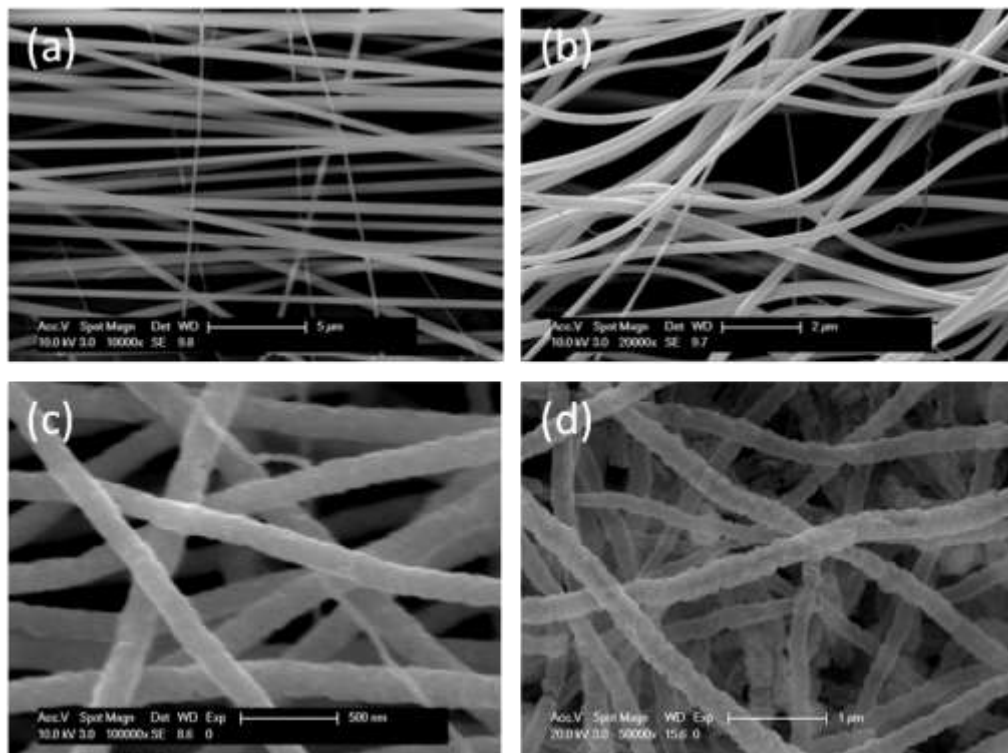


Figure 1: FE-SEM images of (a) electrospun PVP/Ni acetate nanofibers, (b) NiO nanofibers after thermal oxidation at 500°C in air, (c) Ni nanofibers after thermal reduction at 400°C in 5% H₂/N₂, and (d) Hg_xTe_y hollow nanofibers after galvanic displacement.

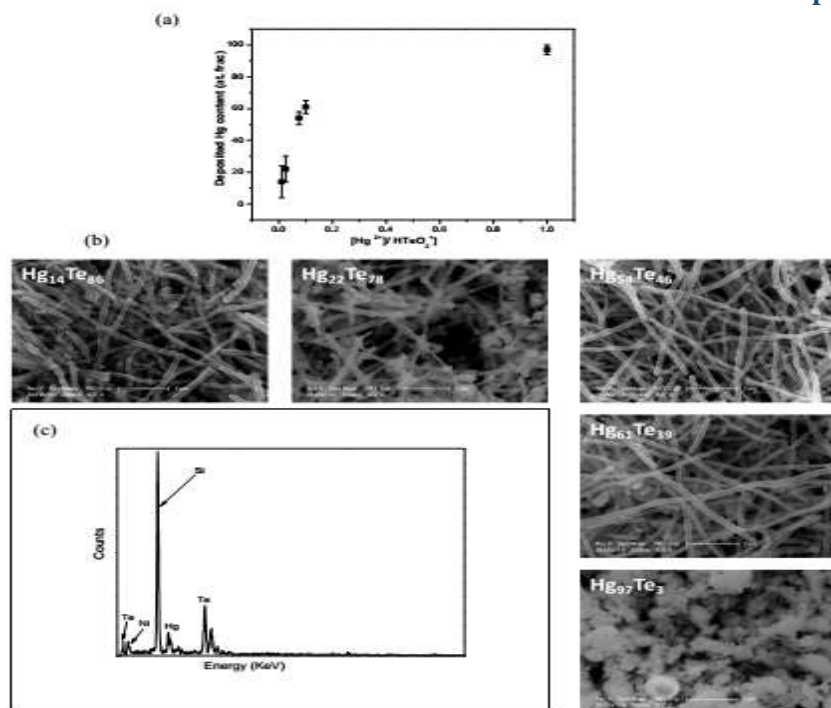


Figure 2: (a) Dependence of the deposited Hg content of Hg_xTe_y nanofibers as a function of $[Hg^{2+}]$ ratio. $[Hg^{2+}]$ was varied from 0.01 mM to 1.0 mM while fixing the $[Te^{2+}]$ and $[HCl]$ at 0.1 mM and 1 M, respectively at 25°C. (b) Changes in morphology using different $[Hg^{2+}]$. (c) Typical EDS spectra of synthesized Hg_xTe_y nanofibers from Ni nanofibers

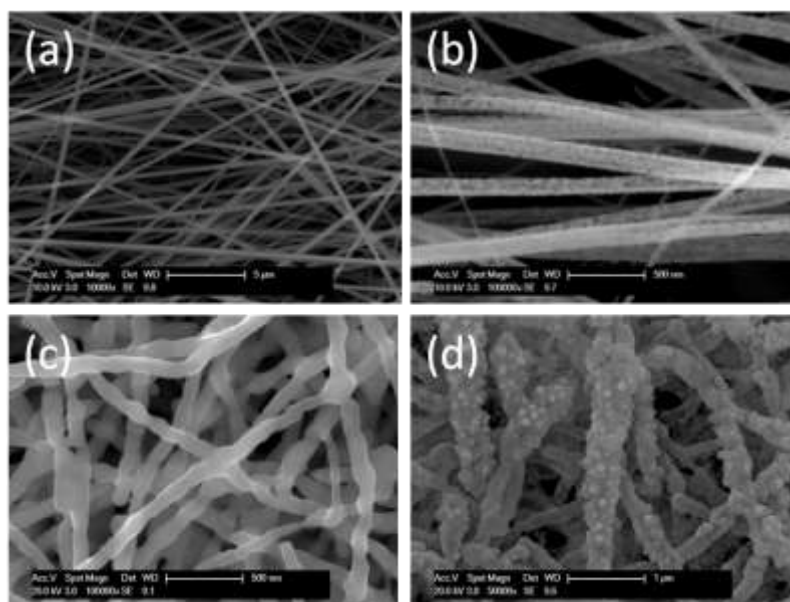


Figure 3: FE-SEM images of (a) electrospun PVP/Co acetate nanofibers, (b) Co_3O_4 nanofibers after thermal oxidation at 500°C in air, (c) Co nanofibers after thermal reduction at 400°C in 5% H_2/N_2 , and (d) Hg_xTe_y hollow nanofibers after galvanic displacement.

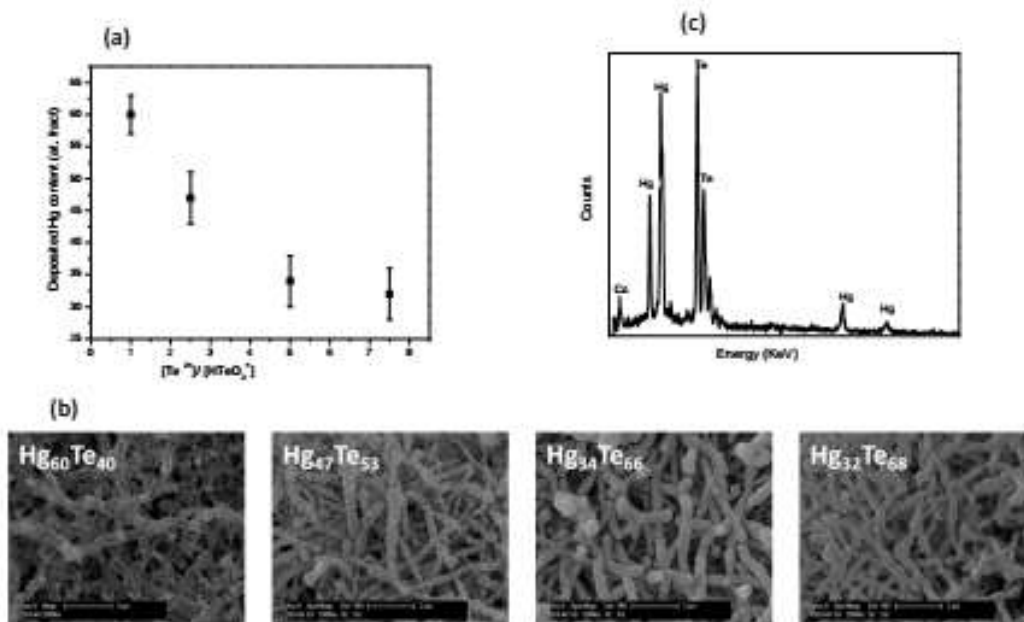
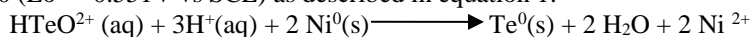


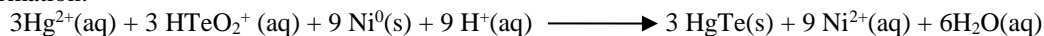
Figure 4: (a) Dependence of the deposited Hg content of Hg_xTe_y nanofibers as a function of $[Te^{2+}]$ ratio. $[Te^{2+}]$ was varied from 1 mM to 7.5 mM while fixing the $[Hg^{2+}]$ and $[HCl]$ at 1 mM and 1 M, respectively at 25°C. (b) Changes in morphology using different $[Te^{2+}]$ (c) Typical EDS spectra of synthesized Hg_xTe_y nanofibers from Co nanofibers

Discussion

Hg_xTe_y hollow nanofibers were synthesized by galvanic displacement reaction of electrospun nickel nanofibers at room temperature. Nickel nanofibers were synthesized by calcinating Ni acetate PVP nanowires at 500°C for 3 hours in air to form NiO nanofibers, followed by thermal reduction at 400°C for 3 hours in reducing environment (5% H_2 + 95% N_2) to form Ni nanofibers. Fig 1 shows the morphologies of synthesized (a) Ni acetate / PVP nanofibers, (b) NiO nanofibers, (c) Ni nanofibers and (d) Hg_xTe_y hollow nanofibers after galvanic displacement. Fig 2 shows the morphologies of synthesized (a) Co acetate / PVP, (b) Co_3O_4 , (c) Co nanofibers and (d) Hg_xTe_y hollow nanofibers after galvanic displacement. The driving force for galvanic displacement reactions is the difference in redox potentials, a fundamental electrochemical process which is the basis of battery technology [11]. For example, when nickel nanofibers are immersed into an acidic nitric solution containing only $HTeO_2^+$ ions, nickel nanofibers are galvanically displaced by $HTeO_2^+$ / Te^0 ($E_0 = -0.551V$ vs SCE) as described in equation 1.



In the electrolyte containing both Hg^{2+} and $HTeO_2^+$ ions, Te is galvanically displaced by nickel following spontaneously under potential deposition of Hg on Te to form HgTe to the negative Gibbs free energy of HgTe formation:



Based on thin film results from previous works [12], the deposited Hg content, measured by energy dispersive X-ray spectroscopy (EDS) initially increased linearly with the log of the $[Hg^{2+}]/[HTeO_2^+]$ ratio and plateaued for the $[Hg^{2+}]/[HTeO_2^+]$ ratio greater than 0.2 for the Ni sacrificial material (fig 3a) and decreases linearly for the Co sacrificial material (fig 4a). $Hg_{54}Te_{46}$ hollow nanofibers from Ni sacrificial material (fig 3a) and $Hg_{47}Te_{53}$ hollow nanofibers from Co sacrificial material (fig 4a) were formed after galvanic displacement. The best Hg_xTe_y nanostructure obtained were those closest to the 50:50 stoichiometric ratio of Hg and Te. The mechanism for creating these hollow nanostructures by galvanic displacement has been described previously by Xia's group [13- 16]. The generalized scheme starts with particle nucleation and growth of the more noble material on the surface of the sacrificial metal nanostructure, forming

a thin porous sheath. As the shell fills in, diffusion across the casing allows for continued oxidation / dissolution of the sacrificial metal. The end result is a hollow nanostructure with an interior roughly resembling the exterior of the sacrificial metal.

CONCLUSION

Electrospinning and galvanic displacement reactions were combined to synthesize mercury telluride hollow nanofibers in a cost-effective manner. This approach is believed to be a general route to form ultra-long hollow semiconducting nanofibers as numerous electrospun nanofibers can be utilized. Moreover, by exploiting the redox potential dependent reactions of galvanic displacement, nanofiber materials can be extended (semiconductor / metal core-shell and branched) to new and exotic nanofibers.

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