Synthesis of Ultra-long Hollow Mercury Selenide (HgSe) Chalcogenide Nanofibers from Co and Ni Sacrificial Nanofibers

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Authors' contributions

*This work was carried out in collaboration between all authors. Authors NGNA and NVM designed the
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ABSTRACT

A general synthetic method has been used to fabricate Co and Ni nanofibers. By using the
electrospinning technique followed by galvanic displacement reaction, we have successfully
prepared ultra-long hollow chalcogen and chalcogenide nanofibers. The outstanding features of
this approach to get ultra-long sacrificial nanofibers with controlled dimensions and morphology,

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thereby imparting control over the composition and shape of the nanostructures evolved during galvanic displacement reaction are its simplicity, effectiveness and ease of assembly. The aim of this study is to exploit the structural and compositional changes during the formation of HgSe chalcogenide with a view of fabricating a mercury sensor.

1. INTRODUCTION

The key synthetic methodologies to get 1D magnetic nanostructures developed so far include template assisted electrodeposition [1], metallization of DNA [2], nanolithography [3], organometallic precursors decomposed in solution [4], between catalyzed and high-temperature growth via the vapour- liquid- solid (VLS) mechanism [5], solvothermal synthesis [6] and direct electrochemical precipitation [7]. A low cost and high- efficiency electrospinning technique has been used to synthesize and assemble ferromagnetic metal nanofibers with diameters of about 20 nm and lengths longer than 100 um. It is a simple and effective method for fabricating ultra-thin nanofibers, either oriented or laid in a random fashion as a fibrous mat [8-12]. Elecrospun nanofibers exibit a range of unique features and properties that distinguish themselves from 1D nanostructures fabricated using other techniques, for example the nanofiber is highly charged after it has been ejected from the nozzle, and therefore it is possible to control its trajectory electrostatically by applying an external electric field. Compared with 1D nanostructures synthesized or fabricated using other chemical or physical methods, electrospun nanofibers are extremely long [13]. Because electrospinning is a continuous process, the fibers could be long after kilometers.

These long fibers can be assembled into a three-dimensional, non woven mat as a result of bending instability of the spinning jet. Such a porous mat can be immediately used for various applications. For example, Pawlowski et al demonstrated that lightweight using skins for a micro-air vehicle could be directly formed by electrospinning polymer nanofibers on a wing frame [14]. Galvanic displacement reaction (GDR) is a simple and versatile yet powerful technique for selectively changing the composition and /or morphology of nanostructures. It takes place via a spontaneous electrochemical reaction driven by the difference in redox potentials between the solid material to be displaced and the ions in the electrolyte and is well suited to high-through put processing under nearly ambient conditions [15]. It has been utilized to create metal nanostructures with hollow interiors exhibiting a spectrum of geometries and multi-walled metal nanoshell [16] and to coat Si with metal films/ nanoparticles [17]. In this work, we combined electrospinning and galvanic displacement reaction to demonstrate cost-effective high throughput 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 potentials, thereby imparting control over the composition and shape of the nanostructures that evolved during galvanic displacement reaction. Selenium and Mercuric Chloride were selected as proof of concept materials because they possess unique electrical and optical properties with a remarkable electron mobility [18] and has n-type behaviour [19]. It can be used as an ohmic contact to wide-gap II-VI semiconductor such as zinc selenide or zinc oxide.

2. EXPERIMENTAL

Polyvinylpyrrolidone (PVP, MW=360,000) was purchased from Sigma Aldrich as polymer matrix. Nickel acetate tetrahydrate (Ni-acetate, $Ni(CH_3COO)_2.4H_2O$ was purchased from Acros Organics to be utilized as the Ni precursor. Cobalt acetate tetrahydrate (Co-acetate, $Co(CH_3COO)_2.4H_2O$ was purchased from J.T Baker Chemical Company. Selenium oxide (SeO_2) was obtained from Alfa Aesar, Mecuric Chloride $(HgCl_2)$ and Hydrochloric acid (HCl) were obtained from Fisher Scientific, respectively, for galvanic displacement deposition. All chemicals were used as received. Ni and Co nanowires were synthesized based on electrospinning process. PVP, Ni and 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 3 g of DI-water, while Co solution was prepared with a concentration of cobalt acetate of 4 mmol in 3 g of de-ionized (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 continous stirring only at 40°C for 30 minutes. The mixed 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 electrospinning setup, the solution was fed at a constant rate of 0.5 ml/hr using syringe pump (Perfusor compact S, B. Braun). Applied voltage of 10 to 16 kV was applied 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 was 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_xSe_y nanotubes. The electrolyte utilized to make Hg_xSe_y nanotubes by galvanic displacement reaction was prepared by dissolving SeO_2 in 2M hydrochloric acid, followed by addition of $HgCl_2$. After uniform mixing the resulting solution was diluted with DI water. The final concentration of the electrolytes were 2 mM $HSeO^{2+}$, 1.5mMHg^{2+} and 2 M HCl, for the Hg_xSe_y nanofiber from Ni sacrificial nanofiber and 2 mM $HSeO^{2+}$, 2mMHg^{2+}, 2M HCl for Hg_xSe_y nanofiber from the Co sacrificial nanofiber. To perform 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 vortex 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_xSe_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 [21].

3. CHARACTERIZATION

The deposited products (Ni acetate/PVP, Co acetate/PVP, NiO, CoO, Ni and Co nanowires and the synthesized HgxSey nanotubes) were characterized by FE-SEM and the compositions by electron dispersive X-ray spectroscopy (EDS)

4. RESULTS AND DISCUSSION

Hg_xSe_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) Co acetate/PVP (b) CoO and (c) Co nanofibers and (d) Hg_xSe_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 [20]. For example, when nickel nanofibers are immersed into an acidic nitric solution containing only $HSeO_2^-$ ions, nickel nanofiber are galvanically displaced by $HSeO_2^+$ ions due to the difference in the reduction potential of Ni^{2+}/Ni^0 (E = 0-257 V Vs SHE) and $HSeO_2^+$/SeO (E = 0.551V Vs SCE) as described in equation 1.

$$HSeO_2^+ (aq) + 3H^+ (aq) + 2Ni^0 (s) \longrightarrow$$
$$Se^0(s) + 2H_2O + 2Ni^{2+} \quad (1)$$
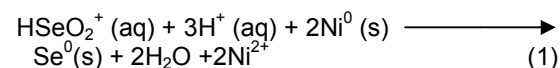
In the electrolyte containing both Hg^{2+} and $HSeO_2^+$ ions, Se is galvanically displaced by Nickel following spontaneous under potential deposition of Hg on Se to form HgSe due to the negative Gibbs free energy of HgSe formation:

$$3Hg^{2+}(aq) + 3 HSeO_2^+ + 9Ni^0 + 9 H^+(aq) \longrightarrow$$
$$3HgSe(s) + 9 Ni^{2+} + 6H_2O(aq) \quad (2)$$
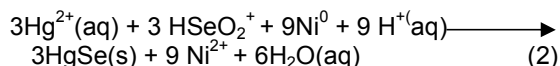
Based on thin film results from previous works [9, 20-21] the deposited Hg content measured by energy dispersive X-ray spectroscopy (EDS) initially increases linearly with the log of the [Hg^{2+}]/[$HTeO^{2+}$] ratio greater than 0.2 for the Co sacrificial material (Fig. 3a) and also for the Ni sacrificial material (Fig. 4a) Hg_xSe_y hollow nanofibers from Co sacrificial material (Fig. 3a) and Hg_xSe_y hollow nanofibers from Ni sacrificial material (Fig. 4a) were formed after galvanic displacements.
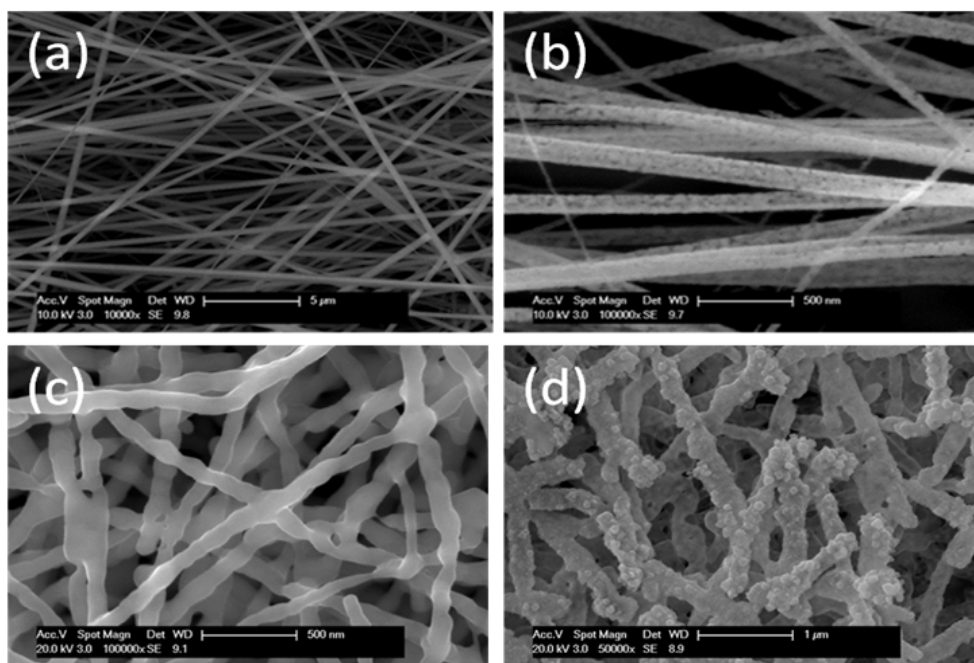
Fig. 1. FE-SEM images of (a) electrospun PVP/Co acetate nanofibers, (b) CoO nanofibers after thermal oxidation at 500°C in air, (c) Co nanofibers after thermal reduction at 400°C in 5% H_2/N_2, and (d) Hg_xSe_y hollow nanofibers after galvanic displacement
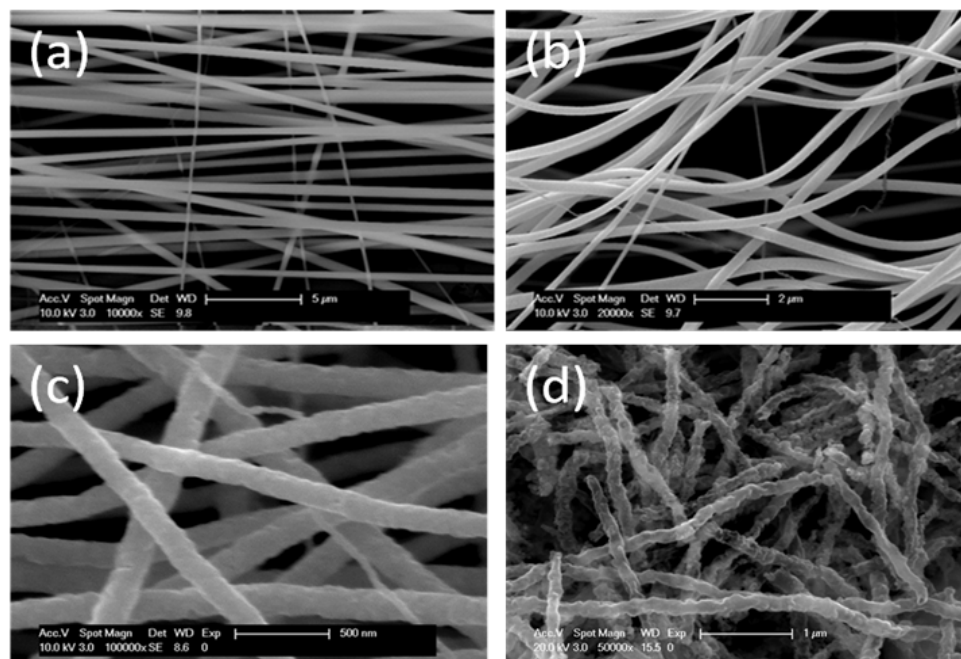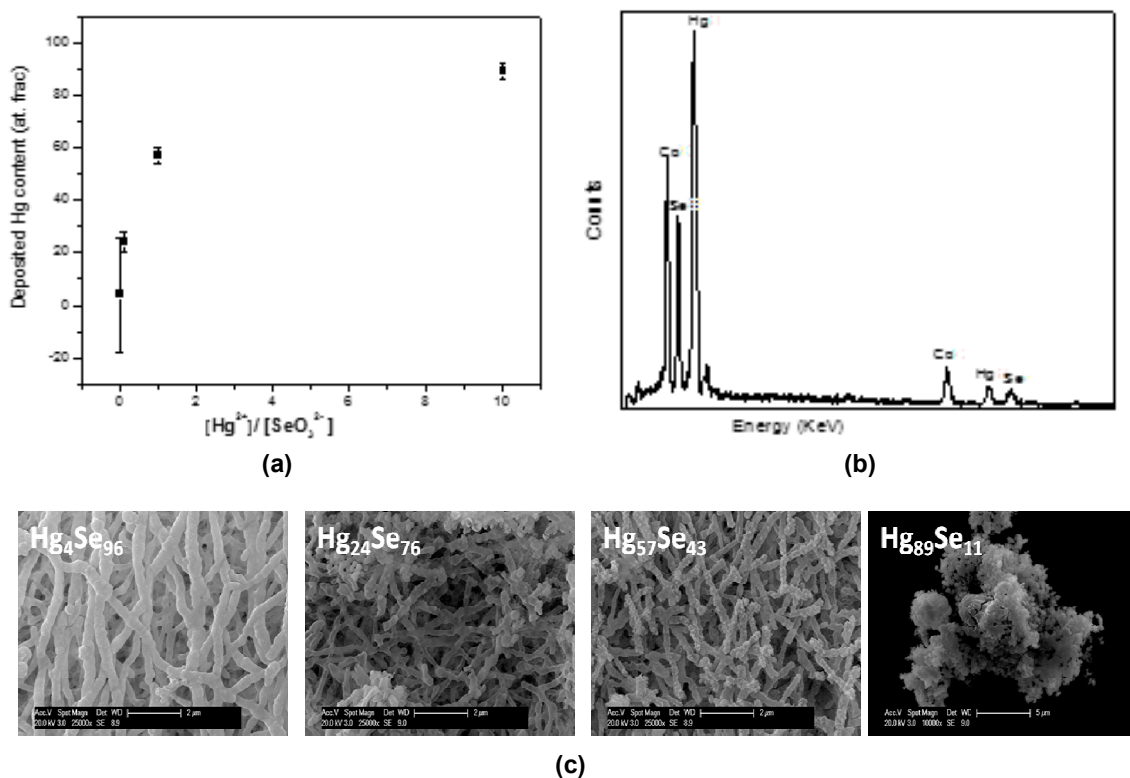
Fig. 2. FE-SEM images of (a) electrospun PVP/Ni acetate nanofibers, (b) NiO nanofibers after thermal oxidation at 500°C in air, (c) Ni nanofibers after thermal reduction at 400°C in 5% H_2/N_2, and (d) Hg_xSe_y hollow nanofibers after galvanic displacement
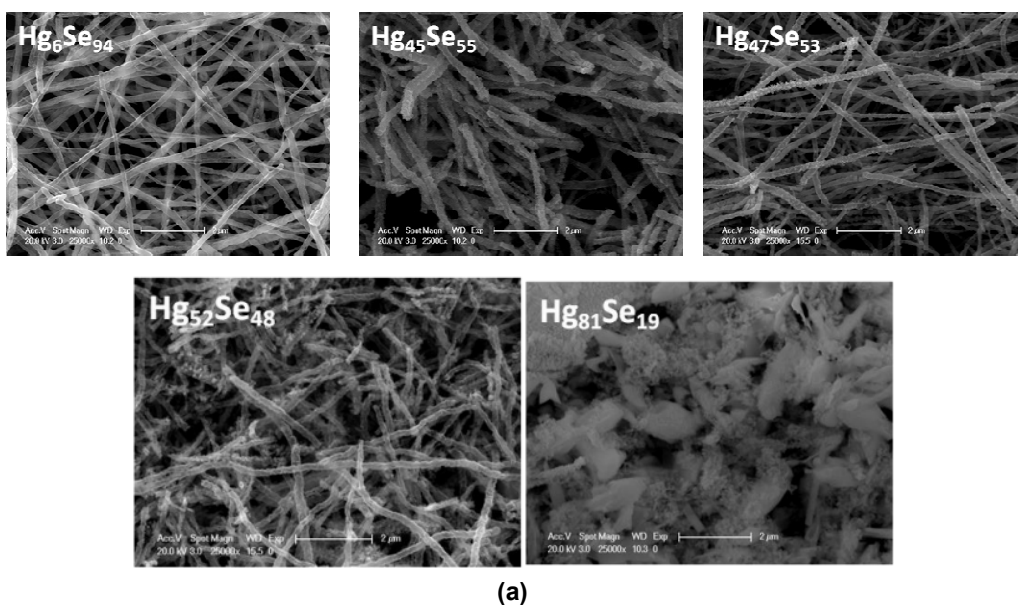
(a)

(b)

(c)

Fig. 3. (a) Dependence of the deposited Hg content of Hg_xSe_y nanofibers as a function of $[Hg^{2+}]$ ratio. $[Hg^{2+}]$ was varied from 0.01 mM to 1.0mM while fixing the $[SeO_2]$ and $[HCl]$ at 1 mM and 1 M, respectively at 25°C. (b) Typical EDS spectra of synthesized Hg_xSe_y nanofibers from Co nanofibers. (c) Morphology changes using different $[Hg^{2+}]$

The best Hg_xSe_y hollow nanostructure obtained were those closest to the 50:50 stoichiometric ratio of Hg and Se. The mechanism for creating these hollow nanostructures by galvanic displacement reactions has been described previously by Xia's group [5-7,10].
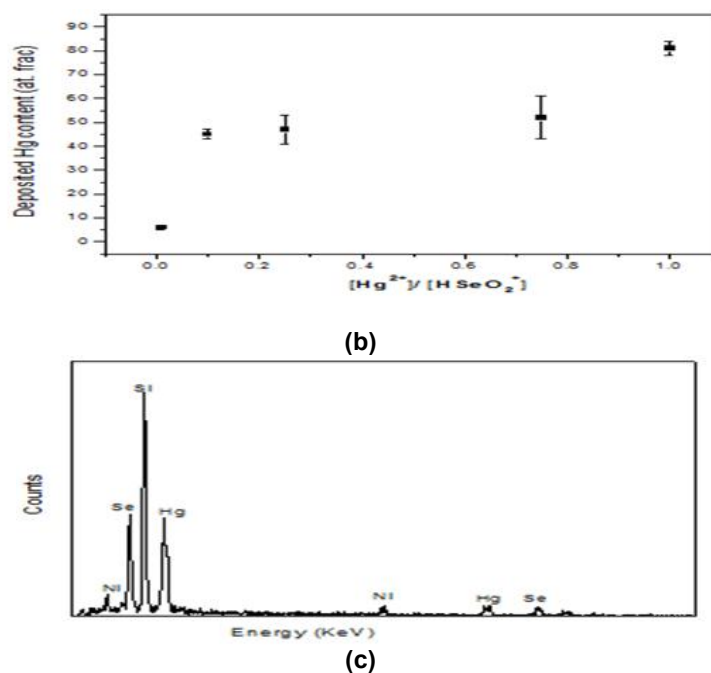

(a)

(b)

(c)

Fig. 4. (a) changes in morphology using different [Hg^{2+}]. (b) Dependence of the deposited Hg content of Hg$_x$Se$_y$ nanofibers as a function of [Hg^{2+}] ratio. [Hg^{2+}] was varied from 0.01 mM to 1.0 mM while fixing the [SeO$_2$] and [HCl] at 1 mM and 1 M, respectively at 25°C. (c) typical EDS spectra of synthesized Hg$_x$Se$_y$ nanofibers from ni nanofibers
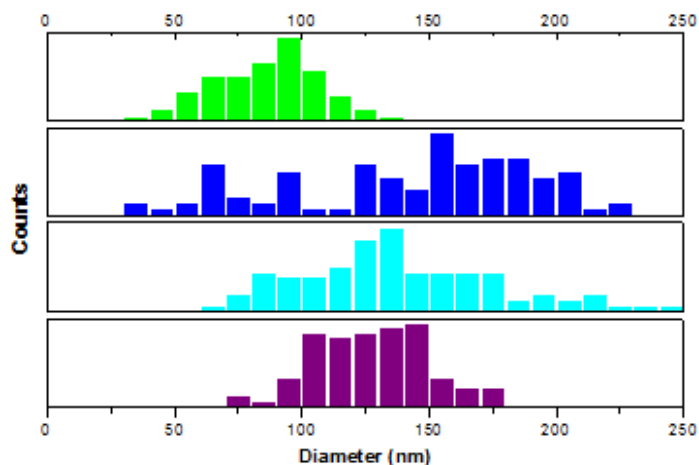

Fig. 5. Diameter distribution of the synthesized nanofibers from top to bottom: PVP/ Co acetate, Co$_3$O$_4$, Co and Hg$_{57}$Se$_{43}$

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 sheat. As the shell fills in, diffusion across the casing allows for continued oxidation/dissolution of the sacrificial metal. The end result is a hollow nanostructured with an interior roughly resembling the exterior of the sacrificial metal. The ratio of the diameter distribution for the synthesized Hg$_{57}$Se$_{43}$ nanofibers from Co sacrificial material is shown in Fig. 5 while that for the synthesized Hg$_{52}$Se$_{48}$ nanofibers is shown in Fig. 6.
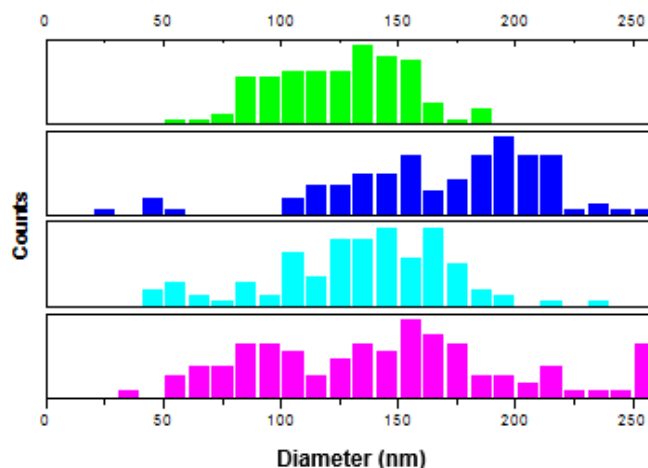
Fig. 6. Diameter distribution of the synthesized nanofibers from top to bottom: PVP/ Ni acetate, NiO, Ni and Hg$_{52}$Se$_{48}$

5. CONCLUSION

Electrospinning and galvanic displacement reaction were combined to synthesize Mercury Selenide 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 material can be extended (semiconductor) metal core-shell and branched to new and exotic nanofibers.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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