Co-Electrospun Lead Selenide/Titania-Core/Sheath Nanowires for Photovoltaic Applications

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16. Abstract

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Co-Electrospun Lead Selenide/Titania-Core/Sheath Nanowires for Photovoltaic Applications

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This study presents a novel, low-cost, all-inorganic lead selenide-titania (PbSe/TiO$_2$) nanowire heterostructure material synthesis for photovoltaic applications. PbSe nanorods (NRs) have been co-electrospun within a TiO$_2$ nanotube with high connectivity for highly efficient charge carrier flow and electron-hole pair separation. This material has been characterized by Transmission Electron Microscopy (TEM), Energy Dispersive X-ray Spectroscopy (EDX), and Photovoltaic testing.

Introduction

Co-electrospinning is a quick, simple, way to produce nanowires that can be easily controlled and modified. Control of this process depends on many factors, including formation of the Taylor cone (or coaxial jet) due to the electrostatic attraction overcoming the surface tension of the solvent, stretching of this co-axial jet, preventing clogging and breakup of the jet, inducing a high-voltage surface charge on a conducting polymer solution [1], the distance between the spinneret tip and the collector, as well as, the type of collection method [2]. Modification and manipulation of these parameters allows control over the nanowire inner and outer diameter, wall thickness, and alignment [2, 3]. Electrospun nanowires have applications in such fields as nanoelectronics [4, 5], photovoltaics [6], bio-molecule encapsulation [7], microfluidics[1, 8], as well as being possible candidates for hydrogen storage, tissue engineering scaffolds, and drug delivery systems [9].

The core material of these nanowires is the narrow-band-gap IV-VI semiconducting lead selenide (PbSe) nanowires which have shown particularly interesting photovoltaic properties due to their highly efficient multi-exciton generation (MEG) processes [10-15]. Schaller *et al.* has reported an extraction of up to 7 excitons/photon absorbed, which corresponds to a 700% external quantum efficiency [16]. This advanced extraction could greatly improve the photo-conversion and efficiency in quantum solar cells. Lead selenide has access to a much wider range of the electromagnetic spectrum than most organic dyes and other semiconducting nanostructures, due to its easily tunable bandgap [17]. PbSe, with a bulk bandgap (E$_g$) of about 0.27eV, has been found to absorb photons and exhibit multi-exciton generation strongly in the infrared region, and well into the visible region. The cutoff for multi-exciton generation depends on many factors, including: the crystallinity of the nanocrystals, the size of the nanocrystals, electron-hole Coulomb interactions, the exciton-Bohr radius of the particular nanocrystal, charge-carrier separation, electron-hole recombination (Auger recombination, which begins to compete with MEG at about 3E$_g$, λ= 1531 nm), electron-phonon relaxation rates (crystal lattice vibrations), and alignment of the nanocrystals' structure.

The sheath material of these co-electrospun nanowires is titanium dioxide

(titania-TiO$_2$), which is widely used in photovoltaic materials [18-21]. Wide band-gap TiO$_2$ has exhibited strong charge-carrier separation [18], semiconducting properties [22], a low reflectance [23], and absorbance in the ultraviolet region ranging into the visible region [18, 19]. Titania is the ejected electron acceptor and its uni-axial tube-like structure makes it a fine candidate for charge flow.

These core/sheath PbSe/TiO$_2$ nanowires have many advantages over hybrid organic-inorganic dye-sensitized solar (DSSC or Grätzel) cells including their resistance to photobleaching, their thermal stability, and their general robustness - being entirely inorganic. As stated before, these core/sheath nanowires will exhibit an increased efficiency over DSSC's, due to their MEG and access to a much wider range of the electromagnetic spectrum than organic dyes because of their easily tunable bandgap (controlled by particle size). The presented nanocomposite will have a high charge carrier separation (electron ejecting) due to the quantum size effects and strong confinement, and the slightly higher conductance band of lead selenide compared to titania. It will also exhibit a high surface-area to volume ratio for maximum loading of lead selenide on the titania's inner surface. This, along with efficient absorbance through the ultraviolet, visible, and infrared electromagnetic spectrum make this technique a novel and scalable synthesis for a novel PbSe/TiO$_2$ photovoltaic material via use of a solvothermal route for the stacked PbSe nanorods, which are then co-electrospun within a titania nanotube.

2. Experiments

2.1. Chemicals

Tri-*n*-octylphosphine (TOP), selenium powder, lead acetate trihydrate, oleic acid, *n*-tetradecylphosphonic acid, and diphenyl ether were purchased from Sigma-Aldrich for the synthesis of the lead selenide nanowire structures. Titanium iso-propoxide (TIP), absolute ethanol, acetic acid (AA), and poly(vinyl pyrrolidone) (PVP,) were purchased for electrospinning through Sigma-Aldrich.

2.2 Core and Sheath Solutions Preparation

2.2.1 Core- PbSe NWs

All syntheses were done under dry nitrogen. The synthesis of the PbSe nanorods followed an existing synthesis route [24] with a few minor modifications. A 1.0 M stock solution of TOPSe was prepared by adding 7.86 g of selenium to 100 mL of TOP and mixing for 2 hours at 50° C. Lead oleate was formed in-situ by mixing 0.76 g of lead acetate trihydrate with 2 mL of oleic acid in 10 mL diphenyl ether and heating for 30 minutes at 150° C for 30 minutes under nitrogen flow via a bubbler. The lead oleate solution was then cooled to 60° C and 4 mL of TOPSe is added to this solution. This solution is referred to as the lead oleate-TOPSe solution.

In a separate jar, 0.2 g of n-tetradecylphosphonic acid is added to 15 mL of diphenyl ether and this solution is heated to 250° C with vigorous stirring. The lead oleate-TOPSe solution is added to the solution of n-tetradecylphosphonic acid in diphenyl ether. The final solution is heated for 50 seconds at 250° C and then cooled to room temperature. While the solution cools down, the solution turns cloudy, indicating the formation of the PbSe nanorods. Finally, 31 mL of hexane is added to this solution. The PbSe nanorods can be centrifuged and re-suspended in different solvents such as chloroform, water, and THF. They are left in hexane for the purposes of electrospinning.

2.2.2 Sheath- Titania

The sheath solution is made by mixing the following two solutions in a capped vial:

(1) 3 mL of ethanol mixed with 3 mL acetic acid and 1.5 g TIP and (2) 7.5 mL ethanol and 0.45 g PVP. Once the two solutions are combined, cap and mix rigorously with magnetic stirrer for 1 hour. If using again after allowing the solution to sit for a period of time, additional mixing or sonication is required.

2.3 Electrospinning Setup and Conditions
The electrospinning setup, which can be seen in **Figure 1.**, follows reference [2], with modifications to the working conditions. During typical procedures, a voltage of 12 kV was applied between the 9cm gap between the needle tip and the 2" x 2" aluminum foil collector. The core solution was pumped at a rate of 0.6 mL/hr and the sheath solution was pumped at a rate of 0.38 mL/hr, both through Harvard Apparatus syringe infusion pump 22. Once complete, the nanowires were left on the collector in air overnight to allow the TIP to hydrolyze and then calcined at 400ºC for 30 minutes, then increased every thirty minutes by 50ºC, all the way up to 550ºC, where it was held for 4.5 hours. Once calcined, the samples were ready for characterization.

2.4 Characterization
Transmission electron microscopy (TEM) and energy dispersive x-ray spectroscopy (EDX) of the PbSe/TiO$_2$ nanowires was done on a JEOL JEM 2100 instrument operated at 200 keV using copper 100/200 square mesh grids (Electron Microscopy Sciences). Electrical testing, as seen in references [12, 25], of these photovoltaic nanowires was performed on a fabricated device, as shown in **Figure 4.**, and data was collected using a digital multimeter and a Vernier LabPro data collection device connected to a PC.

3. Results and Discussion
3.1. Transmission Electron Microscopy
Transmission electron microscopy (TEM) of the titania nanowires shows that they are indeed hollow as seen in **Figure 3. (a)**, which shows the titania nanowires with lead selenide nanorods deposited on the inner walls. In this micrograph, one may see the ends of some of the nanowires, which clearly show that they are hollow. **Figure 2. (a-d)** show that the nanowires are of a fairly uniform outer and inner diameter of about 150 nm and 140 nm, with a wall thickness of about 5 nm. This small wall thickness maximizes the surface area of which lead selenide can be loaded onto the inner wall of these nanowires and lowers the thickness of the titania, which will help to reduce electron-hole recombination as the hot electrons will be transported through the titania to the electrodes.

3.2 Energy Dispersive X-ray Photospectroscopy
The energy dispersive x-ray spectroscopy (EDX) analysis is shown in **Figure 3. (b)** and shows both major and minor peaks of: Titanium (Kα=4.5 keV, Lα=0.4 keV), Oxygen (Kα=0.5 keV), Lead (Lα=10.5 keV, Mα=2.3 keV), and Selenium (Kα=11.2 keV, Lα=1.3 keV), suggesting the presence of both titania and lead selenide. The copper and carbon peaks are due to the TEM grid.

3.3 Photovoltaic Testing
To demonstrate these nanowires photovoltaic application, a device was fabricated as seen in the inset of **Figure 4**. These current-voltage (I-V) curves show that there is a clear difference between the dark-current (un-illuminated) and the photo-current (illuminated with UV-Vis-IR) samples of the nanowires. It is clear that the sample illuminated under UV, visible, and IR wavelengths generates the highest current and

shows somewhat linear behavior. Illuminated under only IR wavelengths, the sample showed a slightly lower photo-generated current and also behaved somewhat linearly. This is expected, as the lead selenide can produce excitons in both the IR and visible regions. When under only visible wavelengths, however, the sample generated a very low current, only being slightly higher than the dark-current. This could be expected as lead selenide generates excitons in the visible region, but has been shown to produce them, primarily, at IR wavelengths. Ultraviolet photo-currents were not displayed as they were practically the same as the dark-currents. These nanocomposite wires I-V curves are compared to the photo-generated current of titania electrospun nanowires with the same configuration, without the lead selenide. These samples showed much lower photo-generated currents and illumination of any wavelength did not seem to show a difference from the dark-current curve. This shows that the synthesized core/shell nanowires are indeed photovoltaic, and a photo-generated current can be collected from them easily.

4. Conclusions

This work has shown that co-electrospinning can be used as an effective nanocomposite photovoltaic simple material synthesis route. These synthesized $PbSe/TiO_2$ core/sheath nanowires have shown that photo-generated current extraction is easily obtained through a simple device and under further characterization and optimization these nanocomposite wires have potential to have an increased quantum efficiency and efficient charge-carrier extraction. Further experimentation could include use of different collectors for better alignment, as well as reducing or increasing the dimensions of the nanowires to obtain an optimum size.

Transportation consumes about 25% of the world's energy, and about 60% of all the oil being produced today. It is now accepted that fossil fuels cannot remain the primary mode of energy supply for transportation in the future. This is dictated by the fact that the demand is outstripping the available supply, and the environmental burden of using fossil fuels is not sustainable. Alternate ideas for long-term, sustainable energy use in transportation are developing rapidly. One such idea is the use of photovoltaic cells, which uses abundantly available energy from the sun and converts that into clean 'fuel' - electricity. Such sources can be used directly in cars and other transportation modes, or generate off-grid sources of power that can be stored to recharge electric vehicles.

The key technical problem behind the use of solar cells is their low efficiency - only 15% of the sun's energy is actually converted to useful electrical energy. This low efficiency makes the current generation of solar cells economically infeasible for practical applications. This project is focused on structuring lead-selenide nanowires within a titania porous matrix to increase the efficiency of a photovoltaic cell. Our unique process for synthesis of these nanostructured materials allows more efficient separation of the electrons and holes at lead-selenide/titania interfaces than current designs, and transport of electrons and holes through the respective phases without recombination. Given the worldwide demand for alternate energy sources, we expect that even a small (2-5%) increase in photovoltaic cell efficiency will have a dramatic impact in the future. Our preliminary data in this area has not yet shown this target increase in efficiency, but we are currently working on strategies to improve the materials for photovoltaic cells.

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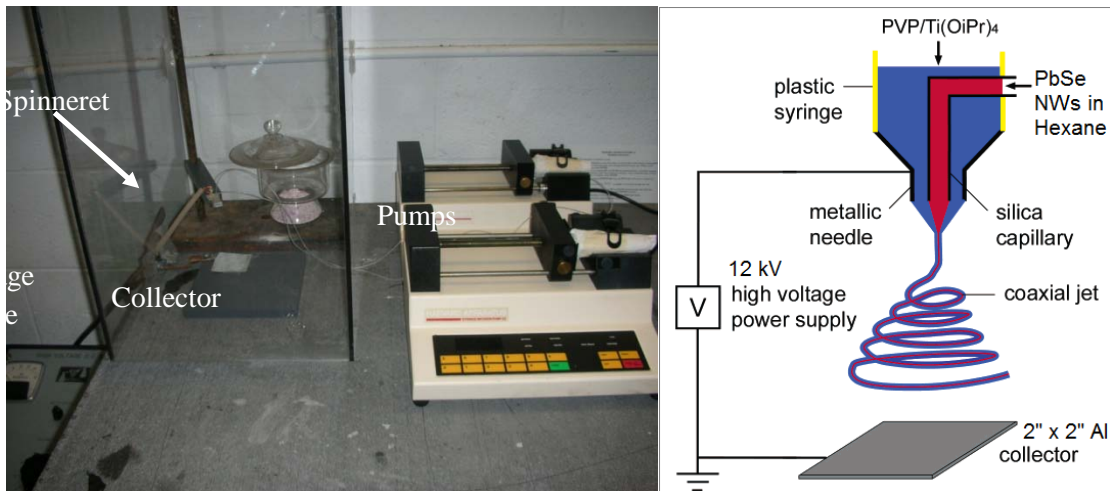
Figures

Figure 1. **(a)** Photograph showing the setup used and **(b)** a schematic illustration of the co-axial spinneret adapted from reference [2]
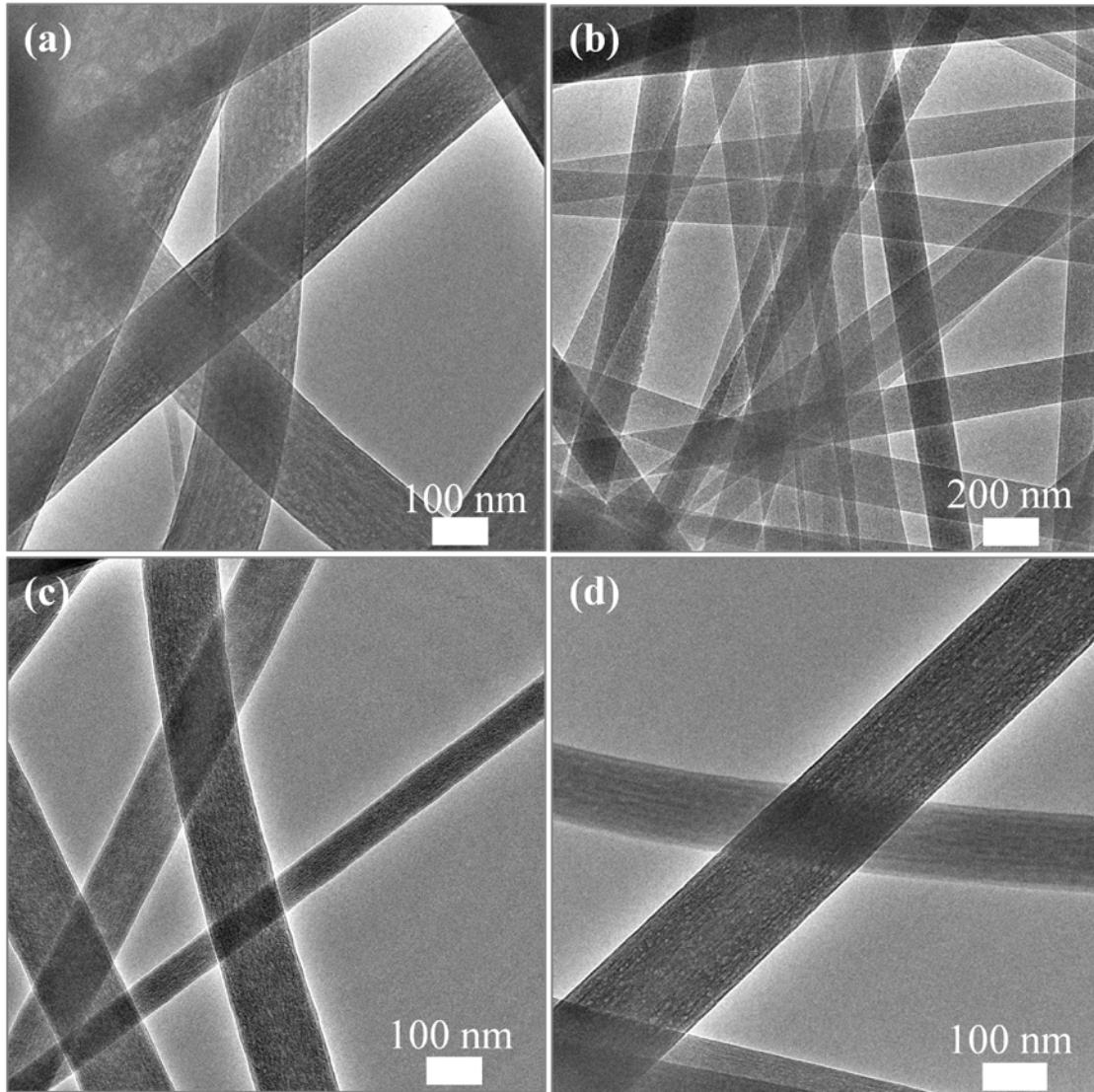
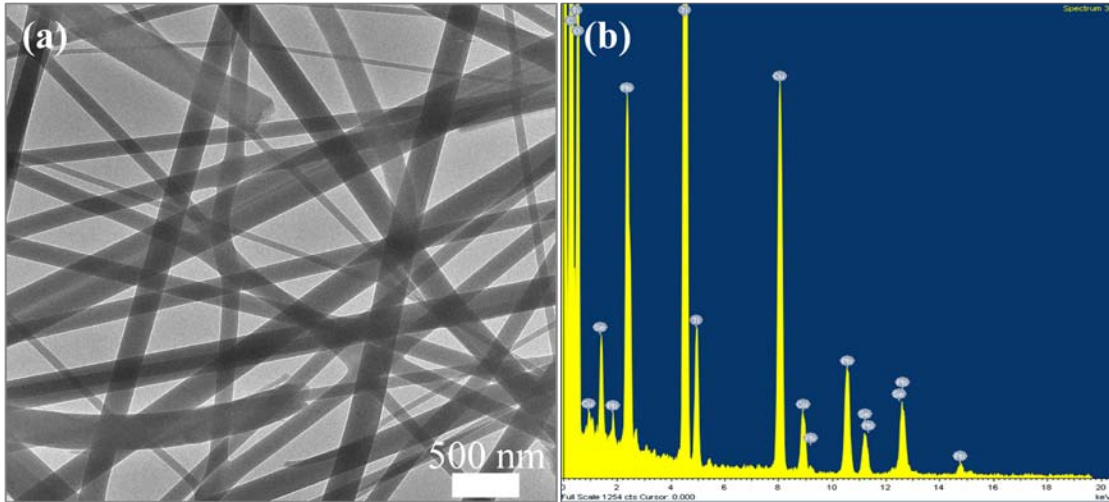**Figure 2.** TEM micrographs of the PbSe/TiO$_2$-core/sheath nanowires

Figure 3. **(a)** TEM image showing some of the ends of the hollow TiO$_2$ nanowires with the PbSe nanorods within them and **(b)** EDX analysis of the PbSe/TiO$_2$ nanowires
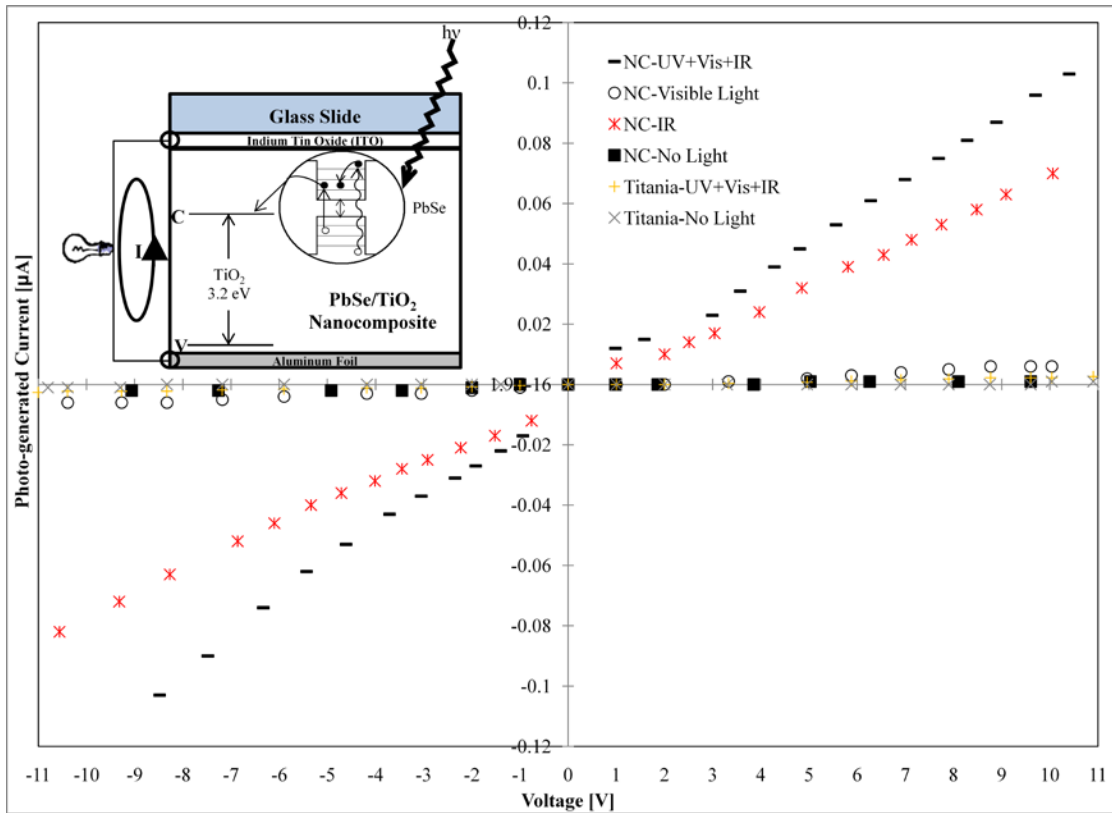

Figure 4. I-V curves for dark-current and photo-current testing of the electrospun nanocomposite compared to electrospun titania (inset shows device setup for testing