

# Electrochemical Synthesis of Morphology-Controlled Segmented CdSe Nanowires

Nava Shpaisman, Uri Givan, and Fernando Patolsky\*

School of Chemistry, the Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, Tel Aviv 69978, Israel

Nanowires have received extensive attention as one-dimensional nanosystems due to their wide range of potential applications in nanoscale electronic, magnetic, mechanical, and sensing devices.<sup>1–4</sup> Multisegmented barcode nanowires are potential candidates for unique applications such as tagging systems for product tracking or multiplexed biodetectors.<sup>5–7</sup> An additional application of segmented nanowires may be as potential building blocks for nanoscale electronic devices, where the inclusion of semiconductor segments during their synthesis can tailor their current–voltage response.<sup>8</sup> Multisegmented nanowires commonly incorporate different materials prepared by sequential templated electro-co-deposition of several metal segments within mesoporous membranes.<sup>9–11</sup> However, the production of such multisegmented nanowires involves several time-consuming steps and requires careful control of the growth process along with replacement of the metal solutions.<sup>12</sup> Recently, Wang *et al.* published a new preparation method of multisegmented alloy nanowires using a single silver–gold mixture plating solution by applying different reduction potentials. This new versatile and easily controlled synthetic protocol leads to the formation of segmented nanowires of different Au–Ag compositions.<sup>13</sup> CdSe (groups II–VI) turned to be one of the most attractive semiconductor materials (due to its optical and electronic properties), which could be incorporated into multisegmented nanowires to create optoelectronic devices. Stoichiometrical deposition of groups II–VI semiconducting materials into porous templates is commonly performed using sweep voltammetry techniques.<sup>14–17</sup> Peña *et al.*, for in-

**ABSTRACT** Morphology, that is, the study of form comprising shape, size, and structure, is important for materials research in general. For nanostructured materials, popularly known as nanomaterials, morphology has a special significance since form, in this case, dictates physical and chemical properties. Unlike bulk materials, properties of nanomaterials are strongly correlated to form. Here, we present a novel strategy for the synthesis of morphology-controlled segmented CdSe semiconductor nanowires based on a straightforward sweep voltammetry approach of preprogrammed characteristics. It was found here that, by simply and simultaneously modulating the basic parameters of each cyclic voltammetry cycle during the nanowire growth process, scan rate, and cycle potential range, we can achieve a precise control over the morphology of the semiconductor material segment, density, and dimensions, obtained after each voltammetric cycle. The morphology of CdSe segments was found to be controlled by the extent of co-deposition of metal cadmium together with the deposition of CdSe. Thus “dense” CdSe segments and “nondense” segments can be achieved in the absence and presence of cadmium metal co-deposition, respectively. Accompanied by the density modulation achieved by the potential range applied, it was also observed that a fine control over each segment’s length, varying between few tenths to few hundred nanometers, can be achieved by simple altering the scan rate of each cycle along the wire. Also, we propose a simple mechanism that accounts for the formation of segments of controlled morphology. This is the first report on the synthesis of “segmented” CdSe nanowires of controlled morphology, density, and length of each segment, by simple single-step cycle voltammetry preprogrammed sequences from a single electrodeposition solution. In addition, this novel strategy may be applied for the synthesis of additional analogue semiconductor materials of importance (*e.g.*, CdS, CdTe, *etc.*). This segmented nanowire’s synthetic route is remarkably fast and simple, leading to a high encoding capacity with a large number of distinguishable signatures.

**KEYWORDS:** nanowires · electrochemistry · morphology · semiconductors · nanomaterials

stance, prepared segmented metal–CdSe–metal nanowires in which a nondense colloidal CdSe segment was deposited by sweeping the potential continuously between  $-400$  and  $-800$  mV at a scan rate of  $750$  mV/s.<sup>8</sup>

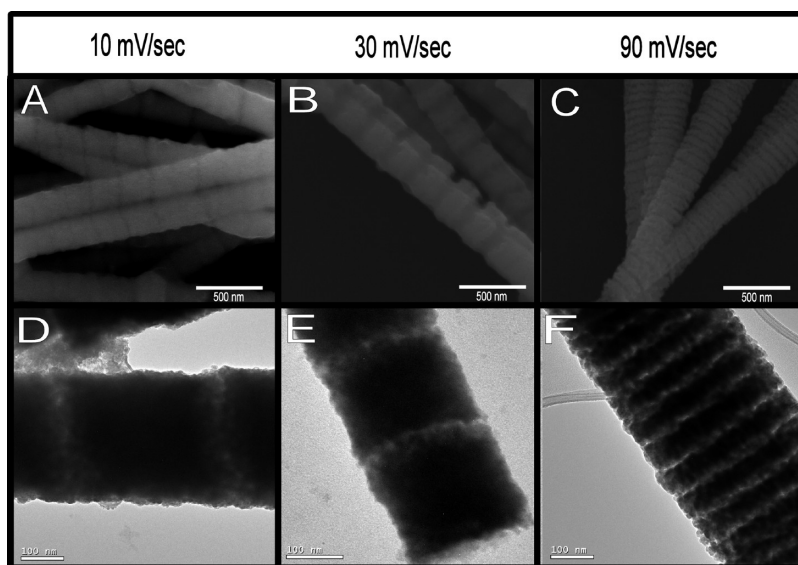
Herein, we describe template-assisted preparation of novel morphology-controlled multisegmented CdSe nanowires with uniform chemical composition and crystalline structure, where nondense CdSe layers of fixed length separate between the dense CdSe segments of controlled length. We found that, in order to form multisegmented CdSe nanowires, the

\*Address correspondence to fernando@post.tau.ac.il.

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**Figure 1.** SEM (A–C) and TEM (D–F) images of the multisegmented CdSe nanowires prepared by sweep electrodeposition at different scan rates: 10 (A,D), 30 (B,E), and 90 (C,F) mV/s.

electrodeposition process must be carried out at a relatively low scan rate. Different segment lengths could be formed by one-step electrodeposition of a single acidic plating solution containing  $\text{CdSO}_4$  and  $\text{SeO}_2$  and sweeping the potential continuously between  $-400$  and  $-800$  mV (*versus* Ag/AgCl) at a scan rate varying between 2 and 150 mV/s. Moreover, a comprehensive model is proposed which explains the segment formation and the dependence of nonlinear length on the scan rate. This is to our knowledge the first report exemplifying the control over the morphological nature (density and thickness) of similar semiconductor materials by the simple control over the voltammetric scan rate and scan range parameters.

The morphology of the semiconductor material, its density, and elemental composition (both of which can be controlled by the proposed methodology) will have a profound impact on the material physical, optical, and electrical properties. This is why the discovery of new approaches to control the final material's morphological and chemophysical properties is of great importance.

This one-step, computer-controlled preparation of CdSe nanowires with different segment lengths offers a similar number of possible combinations to that obtained by the sequential electrodeposition route, with  $n^m$  possible fingerprints, where  $n$  is the number of the used sweeping rates and  $m$  is the number of segments in the nanowire. In practice, CdSe nanowires with 10 segments that contain the products of only three different sweeping rates give 59 049 possible distinct codes.

## RESULTS AND DISCUSSION

Figure 1A–F clearly demonstrates the capability of controlling the morphology/density of the obtained CdSe along the growing axis of the nanowire by simple

scanning voltammetry method. Figure 1A–C shows SEM images of the multisegmented CdSe nanowires prepared by cyclic voltammetry electrodeposition using 10, 30, and 90 mV/s scan rates, respectively. It is clearly demonstrated that the dense CdSe segment lengths are controlled by the scan rate in an inverse manner. For example, electrodeposition at rates of 10, 30, and 90 mV/s resulted in segments length of 380, 200, and 50 nm, respectively. This finding was reinforced by TEM studies (Figure 1D–F), illustrating dense segments (dark zones) separated by nondense strips (bright zones). Furthermore, the nondense separating strips seem to be of identical length regardless the scan rate applied. The crystal structure of the multisegmented CdSe nanowires has been characterized by both X-ray powder diffraction (XRD) and HRTEM studies. Figure 2B shows the XRD pattern of the multisegmented CdSe nanowire arrays prepared by cyclic voltammetry deposition at a scan rate of 30 mV/s. All samples show the same XRD profile. The XRD pattern indicates that these nanowires correspond to the hexagonal phase of CdSe (International center for diffraction data, 00-008-0459). The peaks between  $23$  ( $2\theta$ ) and  $28.5$  ( $2\theta$ ) correspond to the (100), (002), and (101) diffraction planes, and the peaks at  $42$  ( $2\theta$ ) and  $49$  ( $2\theta$ ) correspond to the (110) and (112) diffraction planes of the hexagonal CdSe crystal. The  $c$ -axis of hexagonal crystals is preferentially aligned along the direction of the (002) plane. HRTEM analysis, as shown in Figure 2A, demonstrates that the multisegmented CdSe nanowires are polycrystalline. The interlayer distances calculated from the FFT image are 3.31, 2.05, and 3.51 Å, which correspond to the (101), (110), and (002) diffraction planes of hexagonal CdSe, respectively. Furthermore, the interlayer distances in the dense and the nondense segments are identical. The chemical composition of the

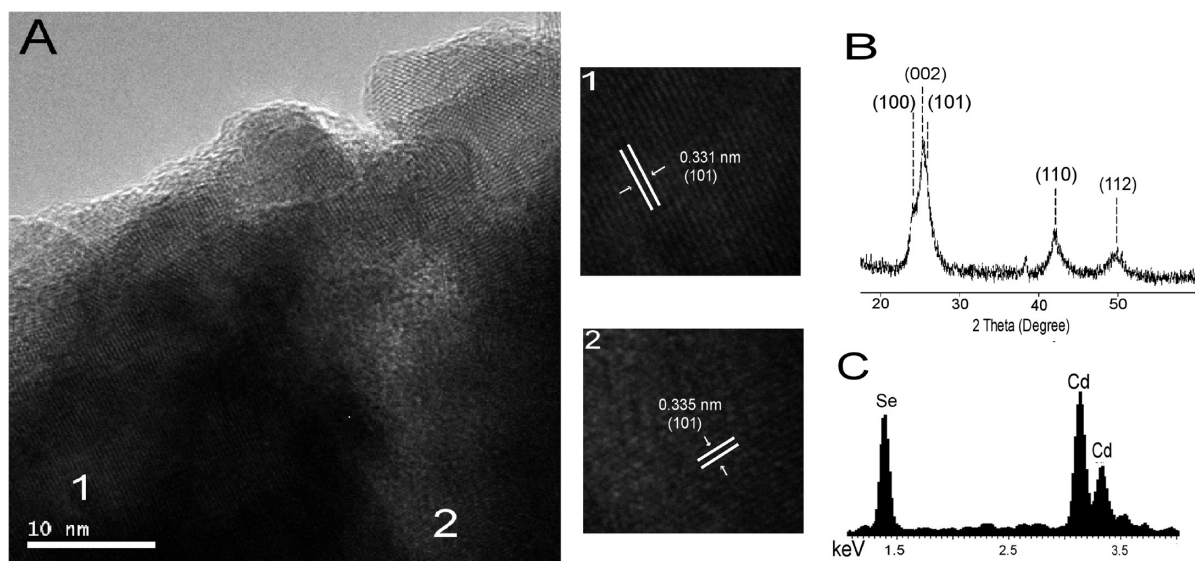
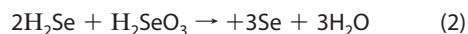
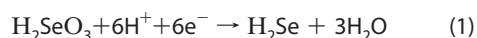


Figure 2. HRTEM images (A), X-ray diffraction results (B), and EDS spectrum (C) of the multisegmented CdSe nanowire arrays.

multisegmented CdSe nanowires determined by EDS indicates that stoichiometric CdSe is formed. Figure 2C shows three prominent peaks: Se<sub>L</sub> at 1.38 keV and Cd<sub>L</sub> at 3.14 and 3.3 keV. The Cd/Se ratio determined from the relative peaks is *ca.* 1:1.02. In addition, the elemental analysis of these multisegmented CdSe nanowires indicates that this ratio is preserved along the entire length of the nanowire, including the nondense segments.

The cathodic reactions for CdSe deposition in an acidic bath containing Cd<sup>2+</sup> and H<sub>2</sub>SeO<sub>3</sub> are as follows:<sup>14</sup>



The bath constituents, Cd and Se, have extremely different standard electrode potentials ( $E^\circ_{\text{Cd}} = -0.403$  V,  $E^\circ_{\text{Se}} = +0.74$  V (*versus* NHE)), thus, the second reaction in which an excess of Se is formed is in competition with the deposition of CdSe. In order to suppress the second reaction and achieve the above-mentioned stoichiometry, minimal quantities of selenium salt must be used.<sup>14</sup>

Cyclic voltammetry studies of CdSe deposition into the template membrane pores elucidate the mechanism of the segments formation (Figure 3A). Figure 3B presents three *I*–*V* curves for different scan rates of 10, 30, and 90 mV/s, at potential electrode sweep between –400 and –800 mV (*versus* Ag/AgCl). Regardless of scan rate, CdSe starts to be deposited in the membrane pores at a potential of –400 mV (*versus* Ag/AgCl). At the potential region between –400 and –750 mV (*versus* Ag/AgCl), any free Se which is deposited will react with the excess Cd to form CdSe<sup>14</sup> because the CdSe phase has a large negative free energy of formation ( $\Delta G^\circ_{\text{f},298\text{K}} = -141.5$  kJ mol<sup>–1</sup>).<sup>18</sup> Upon reaching

the region of higher negative potentials (–750 to –800 mV *versus* Ag/AgCl), where both depletion of the Se ion and high concentration of Cd<sup>2+</sup> occur, bulk Cd<sup>0</sup> and smaller amounts of CdSe are deposited. During the anodic positive current sweep (about halfway through the anodic part of the scan), the excess bulk Cd<sup>0</sup> is stripped back off (Cd is readily stripped in the region of its thermodynamic reduction potential<sup>19</sup>), leaving behind a colloidal nondense CdSe layer. The chemical composition of the nanowire as mentioned previously is constant along the whole length of the wire for dense/nondense stripped nanowires.

In order to confirm the above-mentioned hypothesis, a linear sweep voltammetry deposition of CdSe

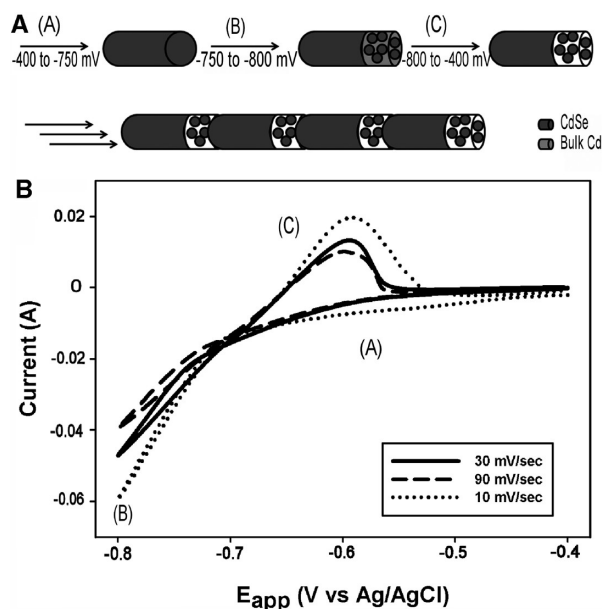
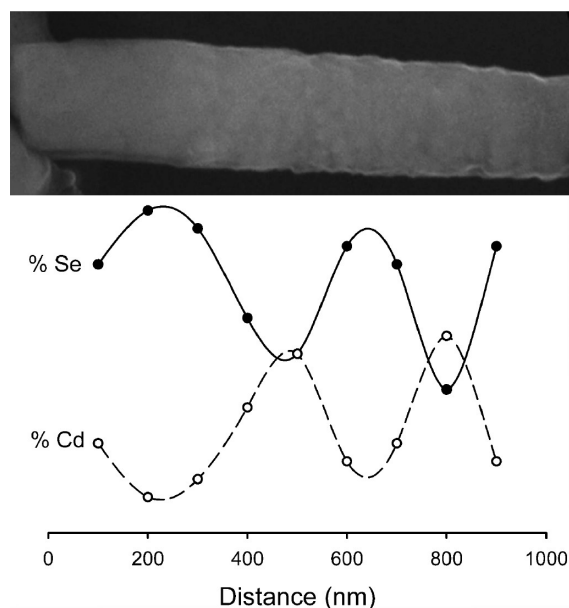
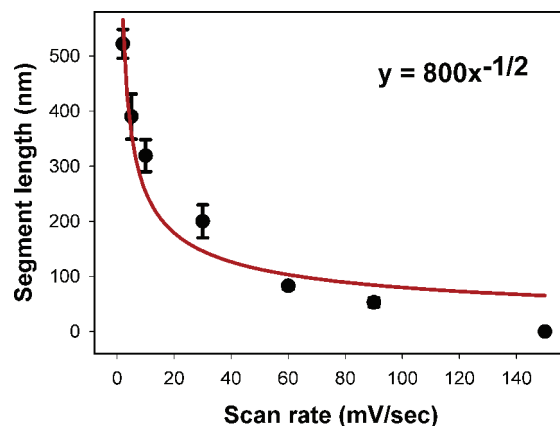


Figure 3. (A) Schematics of the mechanism proposed for the formation of the segmented CdSe nanowires. (B) Current–voltage curves obtained during cyclic voltammetry electrodeposition of CdSe into the pores of a membrane with Au back electrode.



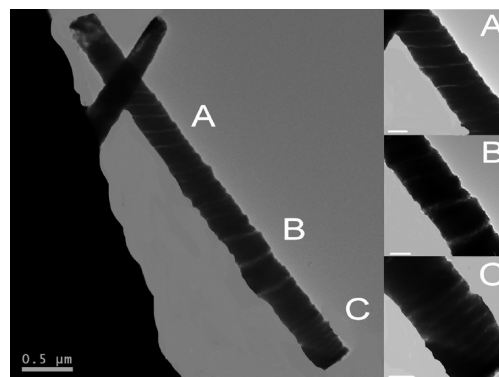
**Figure 4.** Representative SEM image and EDS measurements of a CdSe nanowire prepared by linear sweep electrodeposition with potential electrode sweep between  $-400$  and  $-800$  mV (*versus* Ag/AgCl) and scan rate of  $10$  mV/s.

nanowires was performed under the same conditions, but excluding the anodic part of the scan, at a scan rate of  $10$  mV/s for eight sweeps. This deposition process should result, based on the above-mentioned hypothesis, in a nonsegmented nanowire with a non-uniform Se/Cd ratio corresponding to the sweep length. A SEM image presented in Figure 4 indeed demonstrates that the CdSe nanowire formed by linear sweep voltammetry contains no segments. The length of a CdSe segment deposited at a potential between  $-400$  and  $-800$  mV (*versus* Ag/AgCl) at a scan rate of  $10$  mV/s was estimated to be about  $400$  nm according to Figure 1A. While the voltammetry sweep is stopped after reaching  $-800$  mV (*versus* Ag/AgCl) and the anodic way back of the cycle is omitted, the excess of elemental cadmium that deposited at the range between  $-750$  and  $-800$  mV cannot be dissolved back to cadmium ions and remains inside the nanowire. This is clearly seen and confirmed by the EDS analysis (Figure 4) that looks like a periodic fluctuation of the concentrations of Cd and Se constituents, where after each  $400$  nm an increase of Cd element is observed. These results are in good agreement with our assumptions regarding the deposition mechanism by cyclic voltammetry, where the Cd elemental excess disappears during the anodic stage of the cycle, leading to real “segmented” nanowires of constant chemical composition along their axis. The inverse dependence of the segments’ length upon scan rate, as presented in Figure 5, can be explained as follows. At high scan rates (*e.g.*,  $100$  mV/s), a relatively short segment of CdSe is formed during each cycle due to the short time of the cathodic scan (potential range  $-400$  to  $-750$  mV *versus* Ag/AgCl), while at slower scan rates (*e.g.*,  $30$  mV/s), in each cycle, a longer segment of



**Figure 5.** Calibration graph of CdSe segments’ length *versus* the sweep’s scan rate. Each point in the plot was obtained by averaging the lengths of approximately 20 segments obtained by SEM images.

dense CdSe is deposited before the deposition of the excess bulk Cd<sup>0</sup> (at potential range of  $-750$  to  $-800$  mV *versus* Ag/AgCl) and the colloidal nondense strip is formed. The plot can be divided into three scan rates regions: high ( $>150$  mV/s), low ( $>5$  mV/s), and intermediate scan rate regime. During deposition at high scan rates, the dense CdSe segment’s length becomes shorter than the nondense CdSe layer, which results in formation of nonsegmented nondense CdSe nanowires. The dense segments’ length decreases therefore to zero for scan rates above  $150$  mV. This was also found in a previous work employing high scan rates ( $700$  mV/s), which resulted in colloidal, nondense, and nonsegmented CdSe nanowires.<sup>8</sup> Since the nanowire growth is restricted to the membrane pores, the asymptotic-like behavior of the segment’s length at low scan rate depositions is limited by the membrane length ( $6$   $\mu\text{m}$ , under our experimental conditions). In addition, at very low scan rates, the segment growth might be limited by the charge transfer rate, which becomes greater than the rate of the ionic transport, thus leading to depletion of discharging Se interface region.<sup>20</sup> The segments’ length at the intermediate scan rate regime ( $2$ – $150$  mV) is proportional to the inverse square root



**Figure 6.** TEM images of representative CdSe nanowires with different segments’ lengths.



of the scan rate as can be predicted by integrating the growth rate according to Cottrell equation over the scan time.<sup>21</sup>

The capability of chemically encoding nanowires requires strict control over the length of each segment and the ability to produce variable segments of different lengths along single nanowire. Our one-step approach enables multisize segments along the nanowires simply by varying the scan rate during their growth. Figure 6 shows CdSe nanowire barcodes consisting of 25 segments, with three different segment lengths, which were produced by changing the scan rate between 10, 30, and 90 mV/s during the nanowire's growth. This combination can give up to  $8.5 \times 10^{11}$  possible distinct codes.

The effect of segmentation on the electrical transport and photoresponse was determined by comparing the  $I-V$  curves of segmented and nonsegmented CdSe nanowires taken under the same conditions. Vertical devices were made by evaporating a Au upper contact on the growth membrane, while the Au electrodeposited bottom electrode served as the bottom contact (see Experimental Section for details). Figure 7 shows  $I-V$  graphs of the vertical devices taken under dark or light conditions. Comparison of the  $I-V$  curves (inset) reveals a slight reduction of the conductivity of the segmented CdSe nanowires, and similar reduction takes place under light. On the other hand, careful examination of the photocurrent to dark current ratio shows that the segmented CdSe nanowires exhibit an enhancement of the photoresponse, which might indicate better photoabsorption of these nanostructures. In addition, we observed a clear and reproducible dependence of the conductivity on the number, and length, of nondense segments introduced into the nanowires during their synthesis.

## CONCLUSION

Novel, morphology-based, multisegmented, dense/nondense CdSe nanowires were prepared using a simple cyclic voltammetry deposition approach into the pores of a polycarbonate template membrane from a single electrodeposition solution. The dense CdSe segments are periodically separated by nondense colloidal CdSe separating segments without changing the nanowires' crystalline structure and uniform stoichiometry.

## EXPERIMENTAL SECTION

**Reagents.** Polycarbonate membranes with a specified pore diameter of 200 nm and a thickness of 6  $\mu\text{m}$  were purchased from Whatman Inc. (Cat. No. 7060-2502). Electrolyte solutions were prepared using 18 M $\Omega$  DI water and the following reagents:  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$  (98%),  $\text{SeO}_2$  (99.999%) (Sigma-Aldrich), and concentrated  $\text{H}_2\text{SO}_4$ . All other chemicals were of analytical grade purity and were used as received.

**Apparatus.** Potential controlled experiments were performed using a CHI621 A potentiostat (CH Instruments, Austin, TX). Scan-

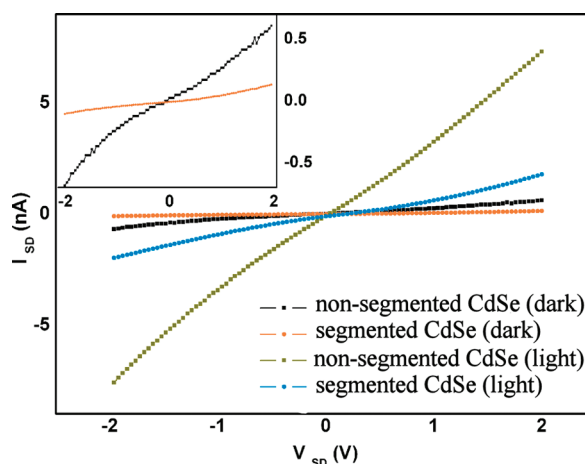


Figure 7.  $I-V$  curves of segmented (black) and nonsegmented (red) CdSe nanowires under dark conditions, and  $I-V$  curves measured under white-light exposure for the same segmented (blue) and nonsegmented (green) CdSe nanowires. The inset represents the  $I-V$  curves under dark (same colors).

etry. The formation of the nondense CdSe layer occurs due to the high concentration of  $\text{Cd}^{2+}$  ions in the plating solution, which leads to the co-deposition of a bulk  $\text{Cd}^0$ , at the high negative potential range, together with CdSe, followed by stripping off of the bulk  $\text{Cd}^0$  during the backward anodic reaction. The length of the segments can be easily controlled by changing the cycle scan rate between 2 and 150 mV/s. Electrical transport and photoresponse measurements have shown that segmentation influences the physical properties of the CdSe nanowires. The reduced conductivity and enhanced photoresponse might serve the purpose of either tailoring the semiconducting nanowire properties or for tagging applications. The porous morphology of the nondense colloidal CdSe separating segments can be used for tagging applications as well as for solid-state membranes (with the appropriate surface functionalization).<sup>22</sup> Furthermore, an excellent encoding capability can be achieved by applying sequential cycles of different scan rates. We state, to the best of our knowledge, that the formation of these segmented nanowires is the simplest and easiest method for creating multisegmented bar-coded nanowires in one step. This novel approach could be applied for analogue binary alloy nanowires as well as for electrodeposited thin films and other nanomicrostructures.

ning electron microscopy (SEM) images were obtained with FEG environmental SEM (FEG-ESEM, Quanta 200). Energy-dispersive X-ray analysis (EDS) of the nanowires was performed with an EDAX acquisition system (Ametek Inc., Mahwah, NJ) installed on the ESEM imaging instrument. Transmission electron microscopy (TEM) images were obtained with a (FEG-HRSEM, JEOL JSM-6400), at acceleration potentials of up to 200 kV.

**Preparation of CdSe Barcode Nanowires.** Polycarbonate membranes, with a pore diameter of 200 nm, were coated on one side with a 200 nm thick layer of Au by thermal evaporation to

serve as the working electrode. The membrane was then assembled in an electrochemical cell with the open pores facing a plating bath containing CdSe (0.25 M CdSO<sub>4</sub>, 0.25 M H<sub>2</sub>SO<sub>4</sub>, and 14 mM SeO<sub>2</sub>), deposition preformed at ambient temperature using a sweep technique, sweeping the potential from −400 to −800 mV at a sweep rate of 10, 30, and 90 mV/s for 20 min to form about 5 μm length CdSe nanowires. Platinum wire and Ag/AgCl (3 M NaCl) served as the counter and reference electrodes, respectively. Once the CdSe nanowires were plated, the electrolyte solution was removed and the electrochemical cell was washed with distilled deionized water (DDW) and dried with dry N<sub>2</sub>. The membrane was dissolved using methylene chloride into 1.5 mL Eppendorf tubes. The nanowires were precipitated from the solution by a 3 min centrifugation step at 2500 rpm and finally washed several times with methylene chloride.

**Preparation of Vertical Devices and *I*–*V* Measurements.** Polycarbonate membranes containing CdSe nanowires were carefully wiped and washed to remove any CdSe residues grown out of the membrane. Then, 200 nm Au contacts were thermally evaporated by a shadow mask containing an array of 400 μm diameter circles. Bottom Au electrode was attached to a conductive substrate with silver paste, in that manner the conductive substrate served as the bottom electrode for transport measurements. *I*–*V* measurements were made employing a probe station (Janis, ST-500) connected to a DAQ card (National Instruments, PCI-MIO-16XE) by computer-controlled rack-mounted breakout accessory (National Instruments, BNC 2090) via a preamplifier (DL 1211).

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$$\text{segment length} = \int_0^{\dot{t}} kt^{-1/2} dt = k_1 \sqrt{\dot{t}} = k_2 s^{-1/2}$$

where  $k_1$  and  $k_2$  are new collections of constants,  $\dot{t}$  is scan time, and  $s$  is the scan rate.

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