

Communication

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Removable and Recyclable Conjugated Polymers for Highly Selective and High-Yield Dispersion and Release of Low-Cost Carbon Nanotubes

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Supporting Information Placeholder

ABSTRACT: High-purity semiconducting single-walled carbon nanotubes (s-SWNTs) with little contaminations are desired for high-performance electronic devices. Although conjugated polymer wrapping has been demonstrated as a powerful and scalable strategy for enriching s-SWNTs, this approach suffers from significant contaminations by polymer residues and high cost of conjugated polymers. Here, we present a simple but general approach using removable and recoverable conjugated polymers for separating s-SWNTs with little polymer contamination. A conjugated polymer with imine linkages was synthesized to demonstrate this concept. Moreover, the SWNTs used are without pre-purifications and very low cost. The polymer exhibits strong dispersion for large-diameter s-SWNTs with high yield (23.7%) and high selectivity (99.7%). After s-SWNT separation, the polymer can be depolymerized into monomers and be cleanly removed under mild acidic conditions, yielding polymer-free s-SWNTs. The monomers can be almost quantitatively recovered to re-synthesize polymer. This approach enables isolation of "clean" s-SWNTs and, at the same time, greatly lowers costs for SWNT separation.

Single-walled carbon nanotubes (SWNTs) are promising materials for next-generation electronics, such as field-effect transistors, photovoltaics, bio/chemical sensors.¹ In particular, SWNT networks are solution-processable and are of great interest for flexible and stretchable electronics.² Most of these applications specifically require semiconducting (s-) SWNTs with minimal metallic (m-) SWNT impurities. However, large-scale synthetic methods for SWNTs always produce a mixture of semiconducting and metallic SWNTs. Recently, various methods for the separation of s-SWNTs and m-SWNTs, including DNA wrapping, density gradient ultracentrifugation, and gel chromatography techniques, have been reported.³ However, these methods are either timeconsuming or not easily scalable.

Conjugated polymers have been intensively studied for enriching s-SWNTs, because they allow extraction of s-SWNT via simple sonication and centrifuge steps within a few hours.⁴ Additionally, conjugated polymers with certain molecular design can selectively extract a specific chirality (n, m) of s-SWNTs.⁵ Although conjugated polymer wrapping provides a fast, low-cost and scalable method for SWNT separation, this method has two major drawbacks: (1) the purified s-SWNTs retain a substantial amount of conjugated polymers on their surface. Removal of the polymers is difficult due to tight polymer wrapping and strong poly-

mer/SWNT interactions. (2) The amount of polymers used is about the same weight as the unpurified SWNTs. However, the costs of most conjugated polymers are comparable or even higher than those of SWNTs. For example, poly(9,9-di-ndodecylfluorenyl-2,7-diyl) (PFDD) and regioregular poly(3dodecylthiophene-2,5-diyl) (r-P3DDT), two widely used polymers for SWNT seperation,^{4c,4f} cost \$729/g and \$642/g from Sigma-Aldrich, respectively; whereas the large-diameter SWNTs cost about 10-35/g for the grade with -30% SWNT content, and $45\sim280/g$ for the grade with $\sim70\%$ SWNT content (Table S1). Thus, conjugated polymers can account for a large fraction of the cost for purification. Additionally, their presence lowers the electrical performance of SWNT networks due to the lower conduction of the polymers compared with SWNTs. To address these issues, three strategies have been reported: (1) releasing SWNTs using conformational switchable polymers;⁶ (2) employing noncovalently linked supramolecular polymers, which break into small units by acid;⁷ (3) irreversible depolymerization into small units.⁸ Strategy (1) requires special molecular design and has not demonstrated good selectivity for s-SWNTs so far. Strategy (2) requires multi-step synthesis of non-covalent bonding moieties, and in situ polymerization during sorting process makes it harder to independently optimize the sorting conditions. In addition, an excessive amount of acid is needed to depolymerize, which may cause p-doping of s-SWNTs.⁹ Strategy (3) does not allow the polymer to be recycled and the sorting selectivity and yield achieved so far still need much improvement. An ideal polymer used for SWNT separation should be low-cost, removable, recyclable, high selectivity and cause little damage to SWNTs. However, it is challenging to fulfill all these criteria.

Polyimines, also known as polyazomethines or Schiff-base polymers, are a family of conjugated polymers constructed from imine bonds (C=N) in backbone and have been used for some optoelectronic applications and covalent organic frameworks (Figure 1a).¹⁰ The conjugated aromatic imine bonds are relatively stable,¹¹ however, imine bonds break readily with exposure to catalytic amount of acid.^{10b} Gerstel et al. reported the use of iminebased polymer for dispersing s-SWNTs.^{5c} However, they did not show the important "removable" and "recyclable" advantages of imine polymers and only used the polymers for dispersing smalldiameter SWNTs. Here we take advantage of the imine bonds to design conjugated polymers for the separation of large-diameter semiconducting SWNTs with little polymer contaminations while lower polymer costs by recycling the monomers (Figure 1b). An imine-based polymer poly[(9,9-di-n-dodecyl-2,7-fluroendiy]-



Figure 1. Imine-based conjugated polymers for SWNT separation. (a) A general design for removable conjugated polymers. (b) Proposed separation cycle. The polymer is removable and recyclable, giving polymer-free s-SWNTs. Inset photos show the polymer solution, sorted s-SWNT solution, and s-SWNT solution after depolymerization and release. (c) Synthesis of polymer PF-PD.

dimethine)-(1,4-phenylene-dinitrilomethine)] (PF-PD) was synthesized to prove this concept (Figure 1c).Compared with smalldiameter s-SWNTs, large-diameter s-SWNTs (1.2~1.7 nm) are more desired for electronic devices due to their smaller Schottky barrier for good electrical contacts and higher current density.^{1d,12} To realize low-cost for separated s-SWNTs, a cheap raw SWNT starting material is needed. Here, we use one of the lowest priced SWNTs available commercially with diameters of 0.9-1.5 nm and a purity of 30% SWNT content (RN-020, \$10/g from Raymor Industries Inc). All other reports typically employ higher purity SWNT starting materials with 50~70% SWNT content.^{4c,4e,7b} Nevertheless, PF-PD exhibited high yield and high selectivity for dispersion of large-diameter s-SWNTs even with low-cost SWNT raw materials. After separation, the wrapping polymers can be removed by depolymerization into monomers with catalytic amount of acid and subsequently recycled, thus demonstrating a new scalable and low-cost approach for separating high-purity polymer-free s-SWNTs.

Polyfluorenes are one of the most widely used polymers for SWNT sorting.^{4a,4d} Fluorene monomers are readily synthesized at low-cost and thus used as the building block to demonstrate our concept. Starting from a commercially available building block 9,9-didodecyl-2,7-dibromofluorene (1), two aldehyde groups were introduced with a high yield of 88%. Polymer PF-PD was synthesized through a direct condensation of the dialdehyde monomer with *p*-phenylenediamine in dry toluene under the catalysis by p-toluenesulfonic acid (5% eq.). An internal drying agent anhydrous CaCl₂ was employed to remove the generated H₂O and thereby increase the molecular weight of the polymers (Figure 1b). Compared with traditional conjugated polymers that usually synthesized with cross-coupling reactions (e.g. Suzuki or Stille coupling),^{4c} PF-PD was synthesized without any noble metal catalysts or toxic phosphorous ligands. Thus the synthesis of imine polymers is economical and environmentally friendly. Additionally, they are stable under ambient conditions with decomposition temperature above 400 °C (Figure S1), and no polymer degradation was observed for over six-month storage. Upon an addition of catalytic amount of acid, PF-PD depolymerizes quickly, usually within several minutes (Figure 2a). After depolymerization, the absorption of the polymer at longer wavelengths completely disappears and the spectrum is almost identical as that of the monomer, suggesting a quantitative depolymerization.

A high concentration solution of large-diameter s-SWNTs with barely detectable metallic peaks in the M₁₁ region (Figure 2b) can be readily obtained with 1 hour of processing time (see Supporting Information). The optical density (OD) at 939 nm for PF-PD sorted SWNTs is up to 2.498 in a 1 cm path-length cuvette, corresponding to a SWNT concentration of 0.0705 mg/mL. The OD value is significantly higher (2~100 times) than many reported polymer sorting methods used for large-diameter SWNTs,4c,4e,13 indicating the strong dispersion ability of PF-PD. Compared with previous sorting methods using more expensive pre-purified SWNTs (50~70% purity, prices are usually 4~8 times higher, Table S1),^{4c,4e,7b} our results demonstrate that the as-produced raw SWNTs (30% purity) can be directly used together with our polymer sorting process without affecting the sorting yield and selectivity (Figure S3). The pre-purification processes of as-produced SWNTs typically involve strong acidic and/or harsh oxidative conditions,14 which are costly and also give rise to chemical defects. Thus the ability to sort raw SWNTs is beneficial in terms of cost and may additionally provide better electronic properties.¹⁵

Polymer/SWNT ratio and concentration are important factors that strongly affect the sorting yield and selectivity (Figure S4 and Figure S5). The sorting yield was determined by absorption intensity of the S₂₂ peak (see Supporting Information).^{4c,4d} The selectivity was evaluated based on ϕ value, which is defined by the ratio of peaks and background area of both S22 and M11 absorptions.4c Higher ϕ values indicate higher s-SWNT purities, and ϕ values > 0.40 were correlated to purities > 99%.^{4c,7b} Figure S4 plots the relationship between the yield and selectivity for different polymer/SWNT ratios. Compared with literature reports that high ϕ values > 0.40 usually resulted in low yields (< 5%) for largediameter SWNTs,4c,7b polymer PF-PD simultaneously demonstrated both a high ϕ value of 0.407 and a high yield of 23.7% (vs. theoretical s-SWNTs in the starting SWNTs) (Figure S4b), suggesting the strong dispersion ability and high selectivity of this polymer. Reducing the polymer/SWNT ratio led to an even higher selectivity with a ϕ value up to 0.445 and a relatively lower yield of 13.6%. Polymer concentrations were also varied from 0.2 mg/mL to 2 mg/mL (Figure S5). Under the same polymer/SWNT ratio (1:1), a higher concentration resulted in a slightly higher selectivity but a lower yield. This inverse relationship between yield and selectivity was also observed in many other polymer systems.^{4c,7b,16} We also compared the absorption spectrum

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Figure 2. (a) Absorption spectrum changes in the PF-PD depolymerization process. (b) Absorption spectra of the raw SWNTs dispersed by PF-PD and NMP (1 cm cuvette). Inset photo shows the high concentration solution. (c) Raman spectra of the raw SWNTs and PF-PD sorted SWNTs (785 nm). (d) PLE map of SWNTs dispersed by the PDPP4T-2 polymers. (e) Absorption spectra of the as-sorted SWNTs, sorted SWNTs redispersed in NMP and surfactant sodium cholate (SC) (1% aqueous), monomer (F-CHO) after depolymerization, and polymer PF-PD. (f) XPS results for the PF-PD wrapped SWNTs (red) and released SWNTs (black).

of PF-PD sorted s-SWNTs with that of the commercially available 99.9% s-SWNTs (Figure S6). PF-PD sorted s-SWNTs showed even higher selectivity as indicated by the "deeper valley" in the M_{11} region (600~760 nm). To further validate the enrichment of s-SWNTs, Raman spectra of the pristine SWNTs and the polymer sorted SWNTs were measured (Figure 2c and Figure S7). Under 785 nm excitation, strong radial-breathing-mode (RBM) peaks of metallic tubes in the range of 140~190 cm⁻¹ were observed for the pristine SWNTs. After sorting, this peak almost completely disappeared. Other laser excitations (532 and 633 nm) also confirmed the removal of m-SWNTs. To determine the diameters of the sorted SWNTs, photoluminescence excitation (PLE) mapping was used (Figure 2d). At least 10 different chiralities with diameters in the range of 1.25–1.38 nm were observed.

The dialdehyde monomer F-CHO cannot disperse any SWNTs (Figure S8), suggesting its weak interactions with SWNTs. To release the s-SWNTs, a small amount of trifluoroacetic acid (TFA, 0.1% v/v) and one drop of water was added to the sorted solution. The solution was sonicated for 30 mins to ensure completion of the hydrolysis reaction. s-SWNT precipitates were formed after depolymerization (Figure 1c, inset photo). The s-SWNT precipitates were centrifuged and collected by filtration through a 0.2 µm PTFE membrane. The absorption spectra of the filtrate only showed the monomer absorption, indicating that all the enriched s-SWNTs were quantitatively collected (Figure 2e). The filtered s-SWNTs can be redispersed in NMP or in aqueous solutions using surfactants, providing similar absorption features in both M11 and S₂₂ region (Figure 2e), indicating that the sorted SWNTs can also be used for NMP or aqueous based deposition methods.^{2c,17} No polymers or monomers can be detected by absorption spectroscopy for the redispersed SWNTs in NMP and aqueous solution, demonstrating the quantitative removal of the polymers. This result was further confirmed by X-ray photoelectron spectroscopy (XPS) measurement, where the N 1s peaks attributed to the N atoms in the polymers almost disappeared in the released SWNT samples (Figure 2f). We found that a large fraction of the conjugated polymers (about 1/2 to 2/3) were absorbed by the sediment containing undispersed s-SWNTs, m-SWNTs, and amorphous carbons. Thus, to fully recycle the polymer, polymers in sediment were depolymerized and collected using similar methods as described above. The filtrates can be collected and purified by running a short flash column chromatography to obtain the pure fluorene dialdehyde monomer, which was then used for polymer resynthesis. We did not attempt to collect and purify the *p*phenylenediamine co-monomer as it is readily available commercially at low cost. Absorption spectrum measurement indicates that the monomer F-CHO was almost quantitatively recycled (> 98%). After column purification, we determined the recycling yield to be 93% and the purity is sufficient for polymerization.

Absorption spectroscopy cannot be used to quantify high purity tubes due to the complicated nature of SWNT absorption spectrum.^{3e,18} To further substantiate the purity comparison, FET devices with channel length of 500 nm were fabricated on SiO₂ (36 nm)/Si wafers. Since most of the sorted tubes exhibited tube lengths in the range of 0.5 to 2 μ m, the short channel devices used here will short if there are m-SWNTs bridging directly across the channel. 190 devices were measured with 8 shorted devices (Figure 3a and Figure S9). Each device contains on average ~12 tubes, as characterized using scanning electron microscope (SEM) images. Thus ~2300 tubes were measured. We assume that any shorted devices were caused by one m-SWNT because of the high purity of our sorted tubes. Thus the purity of PF-PD sorted s-SWNT is estimated to be 99.7% $[(1-8/2300) \times 100\% = 99.7\%]$, which is one of the highest purity values reported to date for polymer sorted large-diameter s-SWNTs characterized by direct electrical measurement.4a-e,13

Thin-film transistors (TFTs) were also fabricated by dropcasting the PF-PD sorted SWNT solution on patterned Au (source-drain)/SiO₂ (300 nm)/doped Si substrates. The devices were then rinsed with toluene containing a small amount (0.1 % v/v) of TFA to remove polymer residues and annealed at 200 °C for 20 min. Toluene rinsing was used to degrade and remove the polymer residues. Annealing led to better tube-tube junctions and improved source/drain contacts. Figure S10 displays the atomic force microscopy (AFM) image showing a SWNT network with a tube density ca. 50 tubes/ μ m². TFT devices with various channel lengths from 5 to 30 μ m all showed good on/off ratios (Figure S11). High hole mobilities in the range of 20–49 cm² V⁻¹ s⁻¹ with on/off ratios > 10⁶ were obtained for devices with channel lengths > 10 μ m (Figure 3b). Compared to the unsorted raw SWNTs with on/off ratios lower than 10, the high on/off ratios further confirmed the high purity of the sorted s-SWNTs.



Figure 3. (a) Electrical characterization of PF-PD sorted SWNTs using short channel devices with a channel length of 0.5 um. Inset: SEM image of a device. (b) Transfer characteristics of a typical TFT device measured in vacuum (L = 20 um W = 400 um).

In summary, an imine-based conjugated polymer has been developed for selective dispersion of s-SWNTs. PF-PD exhibits strong dispersion ability for large-diameter s-SWNTs with high yield (23.7%) and high selectivity (99.7%). After separation, the polymers can be depolymerized, removed, and recycled, providing polymer-free high-purity s-SWNTs. Compared with other sorting methods, our approach offers significant advantages, such as low-cost, high-selectivity, removable, recyclable, and less-damage to SWNTs, yet only uses cheap and versatile building blocks. More importantly, both dialdehyde and diamine groups can be readily introduced to other π -conjugated structures, thus demonstrating a general approach for low-cost separation of "clean" s-SWNTs.

ASSOCIATED CONTENT

Supporting Information

Polymer synthesis, SWNT dispersion/characterization, device fabrication and supplementary figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(1) (a) Franklin, A. D. Science 2015, 349, 704; (b) Cao, Q.; Kim, H.-s.; Pimparkar, N.; Kulkarni, J. P.; Wang, C.; Shim, M.; Roy, K.; Alam, M. A.; Rogers, J. A. Nature 2008, 454, 495; (c) Cao, Q.; Han, S.-j.; Tulevski, G. S.; Zhu, Y.; Lu, D. D.; Haensch, W. Nat. Nano. 2013, 8, 180; (d) Brady, G. J.; Joo, Y.; Wu, M.-Y.; Shea, M. J.; Gopalan, P.; Arnold, M. S. ACS Nano 2014, 8, 11614; (e) Jain, R. M.; Howden, R.; Tvrdy, K.; Shimizu, S.; Hilmer, A. J.; McNicholas, T. P.; Gleason, K. K.; Strano, M. S. Adv. Mater. 2012, 24, 4436; (f) Ye, Y.; Bindl, D. J.; Jacobberger, R. M.; Wu, M.-Y.; Roy, S. S.; Arnold, M. S. Small 2014, 10, 3299; (g) Snow, E. S.; Perkins, F. K.; Houser, E. J.; Badescu, S. C.; Reinecke, T. L. Science 2005, 307, 1942.

(2) (a) Liang, J.; Li, L.; Chen, D.; Hajagos, T.; Ren, Z.; Chou, S.-Y.; Hu, W.; Pei, Q. Nat. Commun. 2015, 6, 7647; (b) Chen, H.; Cao, Y.; Zhang, J.; Zhou, C. Nat. Commun. 2014, 5, 4097; (c) Wang, C.; Hwang, D.; Yu, Z.; Takei, K.; Park, J.; Chen, T.; Ma, B.; Javey, A. Nat. Mater. 2013, 12, 899. (3) (a) Hersam, M. C. Nat. Nano. 2008, 3, 387; (b) Tu, X.; Manohar, S.; Jagota, A.; Zheng, M. Nature 2009, 460, 250; (c) Arnold, M. S.; Green, A. A.; Hulvat, J. F.; Stupp, S. I.; Hersam, M. C. Nat. Nano. 2006, 1, 60; (d) Moshammer, K.; Hennrich, F.; Kappes, M. Nano Res. 2009, 2, 599; (e) Tulevski, G. S.; Franklin, A. D.; Afzali, A. ACS Nano 2013, 7, 2971; (f) Liu, H.; Nishide, D.; Tanaka, T.; Kataura, H. Nat. Commun. 2011, 2, 309. (4) (a) Samanta, S. K.; Fritsch, M.; Scherf, U.; Gomulya, W.; Bisri, S. Z.; Loi, M. A. Acc. Chem. Res. 2014, 47, 2446; (b) Nish, A.; Hwang, J.-Y.; Doig, J.; Nicholas, R. J. Nat. Nano. 2007, 2, 640; (c) Ding, J.; Li, Z.; Lefebvre, J.; Cheng, F.; Dubey, G.; Zou, S.; Finnie, P.; Hrdina, A.; Scoles, L.; Lopinski, G. P.; Kingston, C. T.; Simard, B.; Malenfant, P. R. L. Nanoscale 2014, 6, 2328; (d) Mistry, K. S.; Larsen, B. A.; Blackburn, J. L. ACS Nano 2013, 7, 2231; (e) Gomulya, W.; Costanzo, G. D.; de Carvalho, E. J. F.; Bisri, S. Z.; Derenskyi, V.; Fritsch, M.; Fröhlich, N.; Allard, S.; Gordiichuk, P.; Herrmann, A.; Marrink, S. J.; dos Santos, M. C.; Scherf, U.; Loi, M. A. Adv. Mater. 2013, 25, 2948; (f) Lee, H. W.; Yoon, Y.; Park, S.; Oh, J. H.; Hong, S.; Liyanage, L. S.; Wang, H.; Morishita, S.; Patil, N.; Park, Y. J.; Park, J. J.; Spakowitz, A.; Galli, G.; Gygi, F.; Wong, P. H. S.; Tok, J. B. H.; Kim, J. M.; Bao, Z. Nat. Commun. 2011, 2, 541; (g) Jakubka, F.; Schießl, S. P.; Martin, S.; Englert, J. M.; Hauke, F.; Hirsch, A.; Zaumseil, J. ACS Macro Lett. 2012, 1, 815; (h) Berton, N.; Lemasson, F.; Tittmann, J.; Stürzl, N.; Hennrich, F.; Kappes, M. M.; Mayor, M. Chem. Mater. 2011, 23, 2237.

(5) (a) Ozawa, H.; Fujigaya, T.; Niidome, Y.; Hotta, N.; Fujiki, M.; Nakashima, N. J. Am. Chem. Soc. 2011, 133, 2651; (b) Akazaki, K.; Toshimitsu, F.; Ozawa, H.; Fujigaya, T.; Nakashima, N. J. Am. Chem. Soc. 2012, 134, 12700; (c) Gerstel, P.; Klumpp, S.; Hennrich, F.; Poschlad, A.; Meded, V.; Blasco, E.; Wenzel, W.; Kappes, M. M.; Barner-Kowollik, C. ACS Macro Lett. 2014, 3, 10.

(6) (a) Liang, S.; Zhao, Y.; Adronov, A. J. Am. Chem. Soc. 2014, 136, 970;
(b) Zhang, Z.; Che, Y.; Smaldone, R. A.; Xu, M.; Bunes, B. R.; Moore, J. S.; Zang, L. J. Am. Chem. Soc. 2010, 132, 14113; (c) Umeyama, T.; Kawabata, K.; Tezuka, N.; Matano, Y.; Miyato, Y.; Matsushige, K.; Tsujimoto, M.; Isoda, S.; Takano, M.; Imahori, H. Chem. Commun. 2010, 46, 5969.

(7) (a) Toshimitsu, F.; Nakashima, N. Nat. Commun. 2014, 5, 5041; (b) Pochorovski, I.; Wang, H.; Feldblyum, J. I.; Zhang, X.; Antaris, A. L.; Bao, Z. J. Am. Chem. Soc. 2015, 137, 4328; (c) Llanes-Pallas, A.; Yoosaf, K.; Traboulsi, H.; Mohanraj, J.; Seldrum, T.; Dumont, J.; Minoia, A.; Lazzaroni, R.; Armaroli, N.; Bonifazi, D. J. Am. Chem. Soc. 2011, 133, 15412.

(8) (a) Wang, W. Z.; Li, W. F.; Pan, X. Y.; Li, C. M.; Li, L.-J.; Mu, Y. G.; Rogers, J. A.; Chan-Park, M. B. *Adv. Funct. Mater.* **2011**, *21*, 1643; (b) Lemasson, F.; Tittmann, J.; Hennrich, F.; Sturzl, N.; Malik, S.; Kappes, M. M.; Mayor, M. *Chem. Commun.* **2011**, *47*, 7428.

(9) Geng, H.-Z.; Kim, K. K.; So, K. P.; Lee, Y. S.; Chang, Y.; Lee, Y. H. J. Am. Chem. Soc. 2007, 129, 7758.

(10) (a) Hu, B.; Zhu, X.; Chen, X.; Pan, L.; Peng, S.; Wu, Y.; Shang, J.;
Liu, G.; Yan, Q.; Li, R.-W. J. Am. Chem. Soc. 2012, 134, 17408; (b)
Belowich, M. E.; Stoddart, J. F. Chem. Soc. Rev. 2012, 41, 2003.
(11) Yang C. J.; Ianekhe S. A Macromolecules 1995, 28, 1180

(11) Yang, C.-J.; Jenekhe, S. A. Macromolecules 1995, 28, 1180.

(12) Tulevski, G. S.; Franklin, A. D.; Frank, D.; Lobez, J. M.; Cao, Q.; Park, H.; Afzali, A.; Han, S.-J.; Hannon, J. B.; Haensch, W. ACS Nano **2014**, *8*, 8730.

(13) Tange, M.; Okazaki, T.; Iijima, S. J. Am. Chem. Soc. 2011, 133, 11908.

(14) Wang, Y.; Huang, L.; Liu, Y.; Wei, D.; Zhang, H.; Kajiura, H.; Li, Y. Nano Res. 2009, 2, 865.

(15) Neophytou, N.; Kienle, D.; Polizzi, E.; Anantram, M. P. Appl. Phys. Lett. 2006, 88, 242106.

(16) Lei, T.; Lai, Y.-C.; Hong, G.; Wang, H.; Hayoz, P.; Weitz, R. T.; Chen, C.; Dai, H.; Bao, Z. Small **2015**, *11*, 2946.

(17) Geier, M. L.; McMorrow, J. J.; Xu, W.; Zhu, J.; Kim, C. H.; Marks, T. J.; Hersam, M. C. Nat. Nano. **2015**, *10*, 944.

(18) Kim, W.-J.; Lee, C. Y.; O'brien, K. P.; Plombon, J. J.; Blackwell, J. M.; Strano, M. S. J. Am. Chem. Soc. **2009**, 131, 3128.

