

# Tailored Single-Walled Carbon Nanotube–CdS Nanoparticle Hybrids for Tunable Optoelectronic Devices

Xianglong Li,<sup>†,‡,\*</sup> Yi Jia,<sup>‡</sup> and Anyuan Cao<sup>†,§,\*</sup>

<sup>†</sup>Department of Mechanical Engineering, University of Hawaii, Honolulu, Hawaii 96822 and <sup>‡</sup>Key Laboratory for Advanced Materials Processing Technology, Ministry of Education, Department of Mechanical Engineering, Tsinghua University, Beijing 100084, China. <sup>§</sup>Current address: Department of Advanced Materials and Nanotechnology, Peking University, Beijing 100871, China. <sup>||</sup>Current address: Chemistry Division, Los Alamos National Laboratory (LANL), Los Alamos, New Mexico 87545.

**ABSTRACT** The integration of organic and inorganic building blocks into novel nanohybrids is an important tool to exploit innovative materials with desirable functionalities. For this purpose, carbon nanotube–nanoparticle nanoarchitectures are intensively studied. We report here an efficient noncovalent chemical route to density-controllably and uniformly assemble single-walled carbon nanotubes with CdS nanoparticles. The methodology not only promises the resulting hybrids will be solution-processable but also endows the hybrids with distinct optoelectronic properties including tunable photoresponse mediated by amine molecules. On the basis of these merits, reliable thin-film photoswitches and light-driven chemical sensors are demonstrated, which highlights the potential of tailored hybrids in the development of new tunable optoelectronic devices and sensors.

**KEYWORDS:** carbon nanotubes · nanoparticles · assembly · charge transfer · sensors

Carbon nanotubes (CNTs) and especially single-walled carbon nanotubes (SWNTs) are promising building blocks for potential applications in many fields such as nanoelectronic and optoelectronic devices due to their unique structure-dependent physical, chemical, and mechanical properties.<sup>1,2</sup> To extend and optimize applications of the CNTs in these fields, it is highly desirable to incorporate different functional molecules and to create new hybrid architectures.<sup>3–9</sup> Among these, functionalization of CNTs with a variety of inorganic nanoparticles or quantum dots has been demonstrated to have the potential to provide unique properties leading to advanced catalytic systems, highly efficient fuel cells, and very sensitive photo/chemical sensors.<sup>10–14</sup> One can also envision new approaches to managing charge, energy on the molecular or nanoscale, for example, by chemical tailoring of these nanoparticle–nanotube hybrid interfaces.

Recently, versatile tunable photosensing systems were developed based on the CNT hybrid materials. For instance, Grüner

*et al.*<sup>5</sup> modified a SWNT with pyrenecyclodextrin and demonstrated tunable photo-sensors for sensing a luminescent ruthenium complex. Guo *et al.*<sup>13</sup> combined titanium dioxide quantum dots with carbon nanotubes to make mirror photoswitches that function in opposite ways when the negative or positive gate fields are applied. These studies utilize the high specific surface areas and inherent ultrasensitivity of SWNTs to the environment and are the basis for new types of optoelectronic devices and sensors. While using an individual tube as a functional element thus yields devices that have properties different from tube to tube, macroscale thin-film ensembles of CNT<sup>15</sup> and CNT-based hybrid composites are becoming the subject of increasing interest in exploiting large-area, low-cost, and flexible electronic and optoelectronic devices.

In order to efficiently synthesize the CNT-based nanohybrids with different nanoparticles, it is necessary to activate the graphitic surface of the nanotubes that tend to be chemically inert<sup>16</sup> and introduce active binding sites for anchoring either the nanoparticles' precursors or the as-synthesized nanoparticles. Up to now, besides complex physical deposition, different scalable chemical strategies have been devised as reported elsewhere,<sup>17–22</sup> including chemical oxidation at defect sites of CNTs, polymer wrapping of CNTs, and noncovalent modification of CNTs with pyrene derivatives by  $\pi$  stacking. Most efforts, yet, were separately devoted to either control of nanoparticle loading density or dispersity on the nanotubes or solution processability of the hybrids for scalable thin-film application. Herein, we present a simple

\*Address correspondence to anyuan@pku.edu.cn, xianglongli@lanl.gov.

Received for review October 14, 2009 and accepted December 18, 2009.

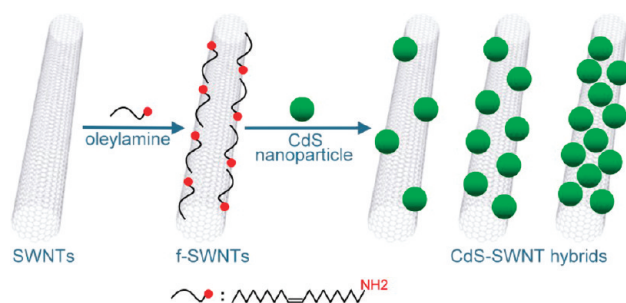
Published online December 30, 2009. 10.1021/nn901757s

© 2010 American Chemical Society

noncovalent chemical approach (Figure 1) for density-controllably and uniformly assembling the SWNTs with semiconductor nanoparticles (CdS nanoparticles, as a model, in this work), as well as efficiently solubilizing the resulting hybrid materials (CdS–SWNT). Most importantly, the assembly methodology endows tailored hybrids with extraordinary optoelectronic characteristics including tunable photoresponse mediated by amine molecules.

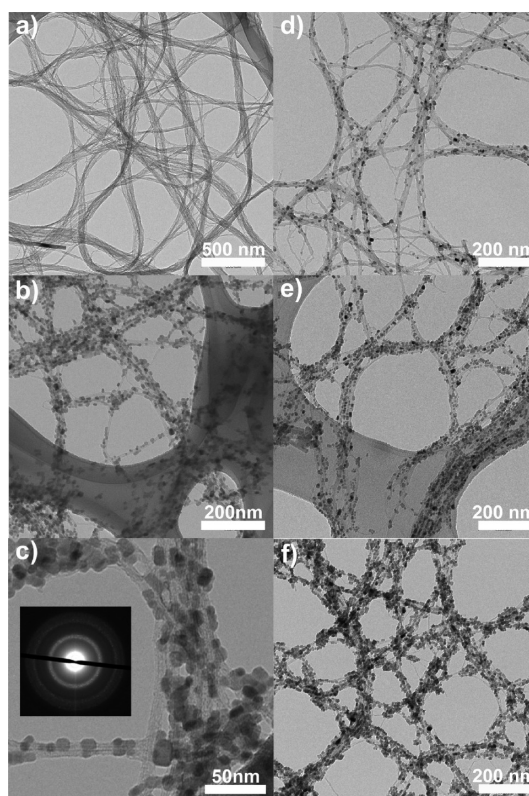
## RESULTS AND DISCUSSION

Efficient assembly of the CdS nanoparticles onto the SWNTs can be indicated in a set of typical TEM images (Figure 2). The hybrid morphology is significantly different from that of the SWNTs with a clean surface (Figure 2a). As exhibited in Figure 2b,c, the elongated (8 nm, average longitudinal size) nanoparticles with spatially isolated features uniformly decorate the surfaces of individual SWNT and/or small SWNT bundles. Furthermore, these elongated CdS nanoparticles are mostly aligned on the nanotubes, though exceptions are also observed. The corresponding selected area electron diffraction (SAED) pattern (inset of Figure 2c) taken from the hybrids validates the presence of cubic CdS of the zinc blende structure.<sup>20</sup> As a control experiment, we employed the pristine SWNTs as a support. As shown in Figure S1 in Supporting Information, large aggregates of CdS nanoparticles are randomly dispersed among the nanotubes, which implies oleylamine molecules introduced by noncovalent interaction<sup>23</sup> play an important role in uniformly anchoring the CdS nanoparticles onto the nanotubes. Without oleylamine functionalization, the CdS nanoparticles cannot be attached onto the pristine SWNTs due to the absence of active interacting points and intrinsic inertness of the nanotube surface. In contrast, as reported earlier for a similar system,<sup>24</sup> the introduced amine groups in the f-SWNTs can be employed as active binding points for anchoring the CdS nanoparticles, thus resulting in the uniform attachment of CdS nanoparticles. As for the nanoparticle alignment, similar assembly behavior has been reported for the Au nanorod–CNT system.<sup>25</sup> In that case, Au nanorods with different aspect ratios were well-aligned on the nanotubes due to the intrinsic properties of the Au nanorods themselves. In contrast to that, in our case, we assume the organized amine functionalities along the nanotubes play another role: a directing effect on the alignment of CdS nanoparticles, although the detailed mechanism is still not clear. After anchoring the nanoparticles, it is possible that the rearrangement of the anchored nanoparticles occurs relative to the orientation of the f-SWNTs. The scenario of alignment of the nanoparticles with the nanotubes favors the presence of more interacting points, thus inducing stronger interaction between amine functionalities and the CdS, as well as the formation of the stable hybrid architecture during the sonication process. It

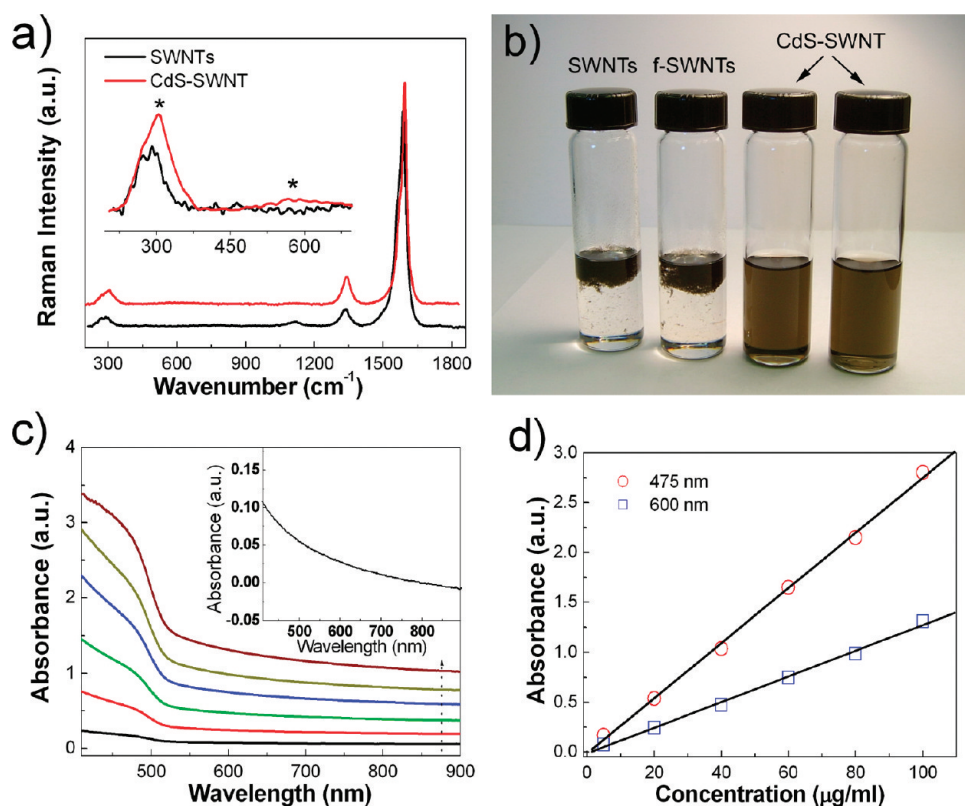


**Figure 1.** Illustration of noncovalent assembly of the CdS–SWNT hybrids with controllable nanoparticle density and dispersity.

should be noted that, in this article, we mostly focus on the hybrids with 85.7 wt % content of CdS nanoparticles (unless otherwise stated). By simply adjusting the ratio of oleylamine-functionalized SWNTs (f-SWNTs) and CdS nanoparticles, furthermore, different loading densities of the nanoparticles on the nanotubes can be controllably obtained (Figure 2d–f and also see Supporting Information Figure S2). As content of the nanoparticles increases, more CdS nanoparticles are attached onto the f-SWNTs and no free CdS aggregates can be found within the monitored TEM area even if the content of the nanoparticles increases up to 90.9 wt %. These results indicate effectiveness of this controllable assem-



**Figure 2.** Characterization of the CdS–SWNT hybrids with controlled density and dispersity. TEM images of (a) the SWNTs and (b,c) the CdS–SWNT hybrids with 85.7 wt % CdS nanoparticle content. Inset in (c): corresponding SAED pattern. (d–f) TEM images of different composition hybrids containing 50, 83.3, and 90.9 wt % CdS nanoparticle content, respectively.



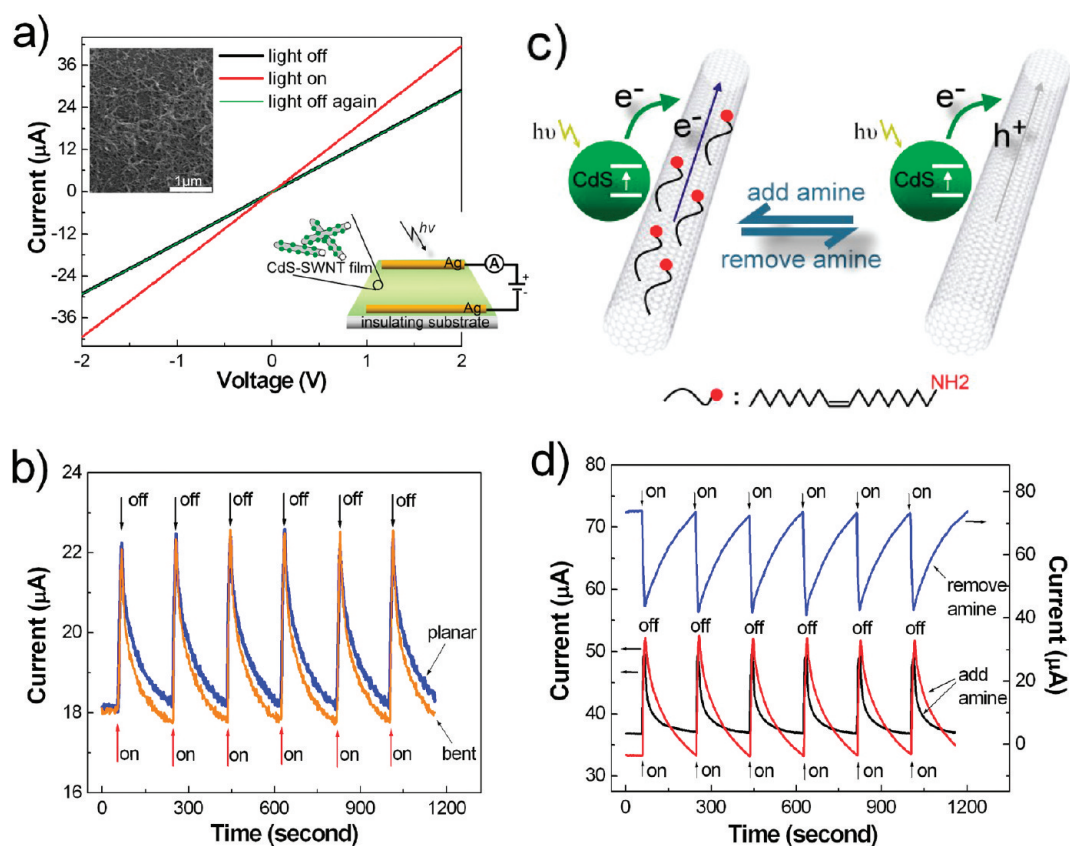
**Figure 3.** Solution properties of the CdS–SWNT hybrids. (a) Raman spectra of the SWNTs before and after assembling with CdS nanoparticles. Inset shows enlarged view of corresponding RBM region. The spectra were vertically offset for clarity. (b) Photos of (from left to right) the SWNTs in toluene, the f-SWNTs in toluene, and CdS–SWNT hybrids in toluene and THF after 2 days, showing good solubility of the hybrids in these solvents. (c) UV–vis absorption spectra of the hybrids dissolved in chloroform at room temperature and with concentrations of 10 to 100 μg/mL marked by an arrow. Inset: an absorption spectrum for the SWNTs. (d) Absorption intensities at wavelengths of 475 and 600 nm as a function of the solution concentrations.

bly route for constructing tailored nanoparticle–nanotube hybrids.

Raman spectra for the SWNTs and the hybrids are exhibited in Figure 3a. Both spectra show an intense peak at *ca.* 1588 cm<sup>-1</sup> (G mode), a small disordered-induced peak at *ca.* 1337 cm<sup>-1</sup> (D mode), and characteristic peaks of the SWNTs in the radial breathing mode (RBM) spectral region (230–340 cm<sup>-1</sup>). Compared with that for the SWNTs, the relative intensity of the D peak to G peak for the hybrids has no noticeable change, which suggests the presented route described here is a desirable nondestructive approach for hybridizing the SWNTs while preserving their electronic structures. A covalent attachment would lead to a drastic increase of D peak intensities.<sup>26</sup> Furthermore, two discernible peaks marked with asterisks are also observed at *ca.* 300 and 600 cm<sup>-1</sup> for the hybrids (inset of Figure 3a), which are respectively attributed to the longitudinal optical phonon mode (1-LO) and its overtone (2-LO) of the CdS nanoparticles<sup>27</sup> assembled onto the nanotubes. Lower intensity ratio of 2-LO to 1-LO as a result of weak electron–phonon interaction at this particle size further verifies that assembled CdS nanoparticles are of a cubic structure. While the pristine SWNTs cannot be dispersed in toluene after sonication, the f-SWNTs are

able to be well-dispersed after the same sonication process. Yet competitive van der Waals interaction between nanotubes makes dispersed f-SWNTs unstable. After assembling the nanoparticles, the hybrids can be well-solubilized in common organic solvents such as toluene, tetrahydrofuran (THF), and chloroform, as displayed in Figure 3b. It is possible that the assembled CdS nanoparticles spatially prevent functionalized/dispersed nanotubes from aggregating again and play important roles in solubilizing the hybrids. Moreover, the annealed hybrids (without oleylamine molecules) are not soluble in common organic solvents. These results indicate that the enhanced stability of the hybrids in common organic solvents should be attributed to the combined effects of both spatial blocking function of the nanoparticles and dispersing ability of the oleylamine molecule itself. Furthermore, chloroform solutions of the hybrids were prepared in different concentrations, and their UV–vis absorption spectra were investigated (Figure 3c). While their absorption spectra are similar to that for SWNTs grown by other chemical vapor deposition (CVD) process<sup>28</sup> and different from that for HiPco SWNTs,<sup>26</sup> an additional broad peak at *ca.* 475 nm could be assigned to characteristic optical transition of the attached CdS nanoparticles with an aver-





**Figure 4.** Photoresponses of the hybrid film-based devices. (a) Reversible change of  $I$ – $V$  curves of the hybrid film bridging two Ag electrodes upon exposure to white illumination. Upper inset: a typical SEM image of the hybrid film integrated into a  $\text{SiO}_2$  substrate. Lower inset: schematic of the hybrid-based thin-film photosensing device. (b) Reproducible current change with time in responding to illumination of hybrid films transferred onto a PET substrate. The curves were measured when the PET film was in a planar (blue curve) or bent (orange curve) state. (c) Model showing light-driven chemical-sensing process where analyte (e.g., oleylamine in this work) was added to or removed from the system. Note:  $e^-$  and  $h^+$  represent electron and hole, respectively;  $h\nu$  is the energy of absorbed photon. (d) Current change with time upon exposure to chopped illumination of the hybrids when amine molecules were added (black), removed (blue), and added again (red). (b,d) Bias voltage was applied at 1 and 2 V, respectively.

age size of  $\sim 8$  nm,<sup>29</sup> which fits well with the above TEM data. Most notably, the absorption spectra are dependent on the solution concentrations in a linear fashion (Figure 3d), resembling that resulting from Lambert–Beer law, which further implies the hybrids are able to be well-dissolved. The soluble character of the hybrids in a variety of common solvents enables the possibility to easily process (e.g., vacuum filtration for this work) these nanotube-based hybrids into macro-scale thin films as demonstrated later. Further, photoluminescence spectra (not shown) of the hybrids indicate that the emission of the CdS nanoparticles is totally quenched when they are assembled onto the nanotubes, which is consistent with that reported by Kamat *et al.*,<sup>30</sup> suggesting the occurrence of electron transfer from CdS quantum dots (donor) to nanotubes (acceptor) in our hybrids upon exposure to light.

To further exploit optoelectronic properties of our hybrid system, semitransparent hybrid thin films (with different thickness of 0.1–1  $\mu\text{m}$ ) were made by vacuum filtration techniques using either mixed cellulose ester or alumina filter membranes, conformally transferred onto different substrates, and integrated into desirable

optoelectronic devices (lower inset of Figure 4a). Upper inset of Figure 4a shows a SEM image of the hybrid film integrated onto a  $\text{SiO}_2$  substrate, where the morphology of the hybrid film is reasonably uniform. We investigated photoresponse of prepared hybrid film within a standard two-terminal device structure. Typical current–voltage ( $I$ – $V$ ) curves with and without light illumination (20 s, 100  $\text{mW}/\text{cm}^2$ ) are shown in Figure 4a. Both curves are of a linear feature, which should be attributed to ohmic contact between the hybrid film and metal electrodes (Al). Notably, the current increases by over 40% when light is turned on and decreases when light is turned off. It is also found that this current increase under illumination occurs for all hybrid films with different thickness, and they exhibit repeatable switching characteristics for many cycles. We also transferred the hybrid films onto flexible poly(ethylene terephthalate) (PET) membrane substrates and integrated them into similar sensing devices. A time profile of the current under chopped illumination at a bias voltage of 1 V is shown in Figure 4b. The current reproducibly responds to the turning on and off of illumination in the planar geometry, which shows that the

above-observed current change is independent of the nature of supporting substrates. After photoresponse properties of the hybrid film were tested in planar geometry, the PET substrate was bent outward into a half circle with a diameter of 0.5 cm, and the device was tested in the bending state. The highly reproducible on/off switching properties are again achieved, and no significant change under the same illumination level is observed in both states. Without regard to absolute current values, in fact, the changing values of the current are even increased a little bit in the bending state. Moreover, the reproducible photoswitching processes are repeatable for many bending cycles. These results imply that tailored hybrid materials are also potential building blocks for flexible optoelectronic sensors and devices.

Surprisingly, these phenomena of current increase upon illumination are remarkably distinct from those reported before for similar systems (e.g., CdSe–SWNT composites).<sup>31,32</sup> To clarify the photosensing behavior, comparative experiments were performed based on the SWNTs and the f-SWNTs under the same experimental conditions. We observe no discernable change in the conductivity for these two types of samples (see Supporting Information Figure S3). We also fabricated hybrid thin-film devices with their contact junctions covered by an opaque insulating layer (epoxy). These contact-junction-protected devices exhibit the same photoswitching effect as that shown in Figure 4a,b (see Supporting Information Figure S4). As a result, these control experiments suggest that the assembled CdS nanoparticles in the hybrids are mainly responsible for the current increase. Generally, the SWNTs are hole-transport material; electron transfer from the quantum dots to the nanotubes under illumination results in electron–hole recombination within the nanotubes and thus a reduction of carrier concentration and also a decrease of the current (right panel of Figure 4c). According to previous reports,<sup>33</sup> amine functionalities are capable of n-doping the nanotubes and responsible for n-type SWNT field-effect transistors. In contrast to the SWNTs, therefore, it is very likely that the introduced oleylamine molecules induce opening of the SWNT n-channel, hence making the electron a major carrier in our hybrid system. During illumination, excitons are generated in the CdS nanoparticles. While the holes would remain in the CdS nanoparticles and be mostly withdrawn *via* reactions with the environment, the process of electron transfer from the CdS nanoparticles to the f-SWNTs causes enhanced n-type conducting properties of the nanotubes and thus an increase of the hybrid conductivity (left panel of Figure 4c). Besides the enhanced n-type conducting properties under illumination, the observed behavior can also be partly attributed to a gate effect. Following the electron transfer process, the remaining positive charges in the CdS nanoparticles could also have an electrostatic influ-

ence on the nanotubes. Positive charges can drive the n-type nanotubes into the on-state, and the current flow is further increased. While the enhanced n-type conducting properties can pave a way for design and optimization of SWNT-based hybrid optoelectronic devices, these findings also imply a strong electronic coupling between the SWNTs and the CdS nanoparticles, as is expected from photoluminescence quenching phenomena in our hybrid system.

The above-proposed mechanism substantially forms the basis of new light-driven chemical sensors (e.g., for sensing amine molecules), as illustrated in Figure 4c. By adding amine molecules, the current increase under illumination can be observed due to the enhanced n-type conducting properties and the gate effect; after removing amine molecules, the major carrier in the nanotubes is the hole due to environmental doping (mostly by oxygen), and subsequent charge transfer under illumination induces electron–hole recombination, thus resulting in current decrease. The possibility and reversibility of the conceived chemical sensors are pioneeringly demonstrated in Figure 4d. While the current of assembled hybrids with oleylamine (black curve) reproducibly increases upon repeatedly chopped illumination, the annealed hybrid films without oleylamine (blue curve) show a current decrease under illumination in a manner similar to those reported previously.<sup>31,32</sup> The variance in resistances (30 and 13.5 k $\Omega$ , respectively) for assembled and annealed samples under without illumination may be related to scattering potentials induced by oleylamine and mostly attributed to modification of tube–tube contacts by oleylamine molecules in the former. After dipping the annealed devices into the ethanol solution of 0.5 % (v/v) oleylamine, the photosensing behavior can be reversibly recovered to the original state. That is, the current again increases with turning on the illumination (red curve). Thus, our devices hold two distinct and reversible photosensing behaviors for adding and removing analyte—relative increase and decrease of the hybrid conductivity under illumination, respectively. Although the sensitivity and selectivity of these sensors need to be further addressed, it is remarkable that tuning the optoelectronic properties can be realized by chemical tailoring of the hybrid interfaces.

## CONCLUSION

In conclusion, a simple and efficient noncovalent chemical approach is developed for elaborately hybridizing the nanotubes with the nanoparticles. The methodology not only enables density and dispersity-controllable assembly of the CdS nanoparticles onto the SWNT surfaces but also makes hybrid materials solution-processable. The assembly method can be easily adapted to controllably produce various nanoparticle–nanotube hybrid materials. Furthermore, on the basis of extraordinary n-type enhanced

conducting characteristics of the resulting hybrids under illumination, reliable thin-film photoswitches are obtained on both rigid and flexible substrates. The possibility of light-driven chemical sensors incorporating the hybrids is also demonstrated, which might represent a novel prototype of futuristic sensing mechanism in a complex environment. These results also highlight the importance of interface chemical engineering in understanding and manipulation of the charge transfer process between the nanoparticles and the nanotubes.

It should be also noted that it will be very interesting to investigate optoelectronic properties of the tailored hybrids in more details within a field-effect transistor (FET) device, provided that expected weaker gate coupling resulted from the blockage of assembled CdS nanoparticles and the intrinsic rigidity of the SWNTs can be overcome. Finally, this work provides us with opportunities for fundamental nanoscience research, as well as paves the way for the development of new tunable optoelectronic devices and sensors.

## MATERIALS AND METHODS

The SWNTs grown by CVD were provided by Prof. Kaili Jiang at Tsinghua University, China. CdS nanoparticles were synthesized using a procedure similar to that reported previously.<sup>34</sup>

**Preparation of the CdS–SWNT Hybrids.** The hybrids were prepared via a simple and efficient noncovalent functionalization route. Briefly, a certain quantity of the SWNTs was mildly sonicated in 10 mL of toluene solution containing 0.1% (v/v) oleylamine (Fluka) for 1 h under a nitrogen atmosphere. Then, this mixture was stirred overnight. Subsequently, the oleylamine-functionalized SWNTs (f-SWNTs) were isolated from the solution by centrifugation and washed with ethanol. As-prepared f-SWNTs with a desirable content as text indicated were again dispersed in 10 mL of toluene. Then, the THF solution (20  $\mu$ L) of CdS nanoparticles with a certain concentration was added to the above suspension. The mixture was mildly sonicated at room temperature for 1.5 h. The resulting hybrids (CdS–SWNT) were precipitated by introducing a small quantity of methanol. The hybrids prepared are highly soluble in common organic solvents.

**Fabrication and Measurements of Photosensing Devices.** A series of thin films of the hybrids were obtained using vacuum filtration techniques similar to those demonstrated elsewhere<sup>35,36</sup> and then transferred to desirable substrates followed by removal of filtration membrane using proper solvents. Here, the film dimension is dependent on the solution volume and is limited to the diameter of the filtration paper. Then, silver (Ag) paint contacts are made on the cut films with dimensions of  $1 \times 1$  or  $0.5 \times 0.5$  cm<sup>2</sup>, and dc transport between electrodes of the devices was carried out using a standard two-probe technique and was monitored by Keithley 4200 with or without white illumination (intensity = 100 mW/cm<sup>2</sup>). All measurements were carried out in air at room temperature.

**Characterization.** Samples were characterized by a LEO 912 Omega (Zeiss) transmission electron microscope (TEM) at an accelerating voltage of 100 kV and a Hitachi S-800 field emission scanning electron microscope (SEM). Raman spectra were recorded using an ALMEGA laser Raman system (Thermo Nicolet) with an excitation wavelength of 532 nm. UV–vis absorption spectra were obtained using a computer-controlled Shimadzu UV-2401PC spectrophotometer.

**Acknowledgment.** We are grateful for financial support from NSF grant CMMI-0728197, and we thank Prof. Kaili Jiang at Tsinghua University for supplying the SWNT samples.

**Supporting Information Available:** Figures S1–S4. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## REFERENCES AND NOTES

- Dresselhaus, M. S.; Dresselhaus, G.; Avouris, Ph. *Carbon Nanotubes: Synthesis, Structure, Properties and Applications*; Springer-Verlag: Berlin, 2001.
- Avouris, Ph.; Chen, Z.; Perebeinos, V. Carbon-Based Electronics. *Nat. Nanotechnol.* **2007**, *2*, 605–615.
- Kauffman, D. R.; Star, A. Carbon Nanotube Gas and Vapor Sensors. *Angew. Chem., Int. Ed.* **2008**, *47*, 6550–6570.
- Li, Y. F.; Kaneko, T.; Kong, J.; Hatakeyama, R. Photoswitching in Azafullerene Encapsulated Single-Walled Carbon Nanotube FET Devices. *J. Am. Chem. Soc.* **2009**, *131*, 3412–3413.
- Zhao, Y.; Hu, L.; Grüner, G.; Stoddart, J. F. A Tunable Photosensor. *J. Am. Chem. Soc.* **2008**, *130*, 16996–17003.
- Willinger, M.-G.; Neri, G.; Rauwel, E.; Bonavita, A.; Micali, G.; Pinna, N. Vanadium Oxide Sensing Layer Grown on Carbon Nanotubes by a New Atomic Layer Deposition Process. *Nano Lett.* **2008**, *8*, 4201–4204.
- Wang, F.; Gu, H.; Swager, T. M. Carbon Nanotube/Polythiophene Chemiresistive Sensors for Chemical Warfare Agents. *J. Am. Chem. Soc.* **2008**, *130*, 5392–5393.
- Hecht, D. S.; Ramirez, R. J. A.; Briman, M.; Artukovic, E.; Chichak, K. S.; Stoddart, J. F.; Grüner, G. Bioinspired Detection of Light Using a Porphyrin-Sensitized Single-Wall Nanotube Field Effect Transistor. *Nano Lett.* **2006**, *6*, 2031–2036.
- Guo, X.; Huang, L.; O'Brien, S.; Kim, P.; Nuckolls, C. Directing and Sensing Changes in Molecular Conformation on Individual Carbon Nanotube Field Effect Transistors. *J. Am. Chem. Soc.* **2005**, *127*, 15045–15047.
- Wildgoose, G. G.; Banks, C. E.; Compton, R. G. Metal Nanoparticles and Related Materials Supported on Carbon Nanotubes: Methods and Applications. *Small* **2006**, *2*, 182–193.
- Georgakilas, V.; Gournis, D.; Tzitzios, V.; Pasquato, L.; Guldi, D. M.; Prato, M. Decorating Carbon Nanotubes with Metal or Semiconductor Nanoparticles. *J. Mater. Chem.* **2007**, *17*, 2679–2694.
- Wu, B.; Hu, D.; Kuang, Y.; Liu, B.; Zhang, X.; Chen, J. Functionalization of Carbon Nanotubes by an Ionic-Liquid Polymer: Dispersion of Pt and PtRu Nanoparticles on Carbon Nanotubes and Their Electrocatalytic Oxidation of Methanol. *Angew. Chem., Int. Ed.* **2009**, *48*, 4751–4754.
- Liu, S.; Li, J.; Shen, Q.; Cao, Y.; Guo, X.; Zhang, G.; Feng, C.; Zhang, J.; Liu, Z.; Steigerwald, M. L.; Xu, D.; Nuckolls, C. Mirror-Image Photoswitching of Individual Single-Walled Carbon Nanotube Transistors Coated with Titanium Dioxide. *Angew. Chem., Int. Ed.* **2009**, *48*, 4759–4762.
- Lu, G.; Ocola, L. E.; Chen, J. Room-Temperature Gas Sensing Based on Electron Transfer between Discrete Tin Oxide Nanocrystals and Multiwalled Carbon Nanotubes. *Adv. Mater.* **2009**, *21*, 2487–2491.
- Grüner, G. Carbon Nanotube Films for Transparent and Plastic Electronics. *J. Mater. Chem.* **2006**, *16*, 3533–3539.
- Ellis, A. V.; Vijayamohan, K.; Goswami, R.; Chakrapani, N.; Ramanathan, L. S.; Ajayan, P. M.; Ramanath, G. Hydrophobic Anchoring of Monolayer-Protected Gold Nanoclusters to Carbon Nanotubes. *Nano Lett.* **2003**, *3*, 279–282.
- Hwang, S.-H.; Moorefield, C. N.; Wang, P.; Jeong, K.-U.; Cheng, S. Z. D.; Kotta, K. K.; Newkome, G. R. Dendron-Tethered and Templated CdS Quantum Dots on Single-Walled Carbon Nanotubes. *J. Am. Chem. Soc.* **2006**, *128*, 7505–7509.

18. Mountrichas, G.; Pispas, S.; Tagmatarchis, N. Aqueous Carbon-Nanotube-Amphiphilic-Block Copolymer Nanoensembles: Towards Realization of Charge-Transfer Processes with Semiconductor Quantum Dots. *Small* **2007**, *3*, 404–407.
19. Grzelczak, M.; Correa-Duarte, M. A.; Salgueiriño-Maceira, V.; Rodríguez-González, B.; Rivas, J.; Liz-Marzán, L. M. Pt-Catalyzed Formation of Ni Nanoshells on Carbon Nanotubes. *Angew. Chem., Int. Ed.* **2007**, *46*, 7026–7030.
20. Li, X.; Liu, Y.-Q.; Fu, L.; Cao, L.; Wei, D.; Wang, Y. Efficient Synthesis of Carbon Nanotube–Nanoparticle Hybrids. *Adv. Funct. Mater.* **2006**, *16*, 2431–2437.
21. Guldi, D. M.; Rahman, G. M. A.; Sgobba, V.; Kotov, N. A.; Bonifazi, D.; Prato, M. CNT–CdTe Versatile Donor–Acceptor Nanohybrids. *J. Am. Chem. Soc.* **2006**, *128*, 2315–2323.
22. Lu, C.; Akey, A.; Wang, W.; Herman, I. P. Versatile Formation of CdSe Nanoparticle–Single Walled Carbon Nanotube Hybrid Structures. *J. Am. Chem. Soc.* **2009**, *131*, 3446–3447.
23. Chen, R. J.; Bangsaruntip, S.; Drouvalakis, K. A.; Kam, N. W. S.; Shim, M.; Li, Y.; Kim, W.; Utz, P. J.; Dai, H. Noncovalent Functionalization of Carbon Nanotubes for Highly Specific Electronic Biosensors. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 4984–4989.
24. Olek, M.; Büsgen, T.; Hilgendorff, M.; Giersig, M. Quantum Dot Modified Multiwall Carbon Nanotubes. *J. Phys. Chem. B* **2006**, *110*, 12901–12904.
25. Correa-Duarte, M. A.; Pérez-Juste, J.; Sánchez-Iglesias, A.; Giersig, M.; Liz-Marzán, L. M. Aligning Au Nanorods by Using Carbon Nanotubes as Templates. *Angew. Chem., Int. Ed.* **2005**, *44*, 4375–4378.
26. Li, X.; Shi, J.; Qin, Y.; Wang, Q.; Luo, H.; Zhang, P.; Guo, Z.-X.; Woo, H.-S.; Park, D.-K. Alkylation and Arylation of Single-Walled Carbon Nanotubes by Mechanochemical Method. *Chem. Phys. Lett.* **2007**, *444*, 258–262.
27. Sivasubramanian, V.; Arora, A. K.; Premila, M.; Sundar, C. S.; Sastry, V. S. Optical Properties of CdS Nanoparticles upon Annealing. *Phys. E* **2006**, *31*, 93–98.
28. Liu, M.; Yang, Y.; Zhu, T.; Liu, Z. Chemical Modification of Single-Walled Carbon Nanotubes with Peroxytrifluoroacetic Acid. *Carbon* **2005**, *43*, 1470–1478.
29. Weller, H. Colloidal Semiconductor Q-Particles: Chemistry in the Transition Region between Solid State and Molecules. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 41–53.
30. Robel, I.; Bunker, B. A.; Kamat, P. V. Single-Walled Carbon Nanotube–CdS Nanocomposites as Light-Harvesting Assemblies: Photoinduced Charge-Transfer Interactions. *Adv. Mater.* **2005**, *17*, 2458–2463.
31. Hu, L.; Zhao, Y.; Ryu, K.; Zhou, C.; Stoddart, J. F.; Grüner, G. Light-Induced Charge Transfer in Pyrene/CdSe–SWNT Hybrids. *Adv. Mater.* **2008**, *20*, 939–946.
32. Juárez, B. H.; Klinker, C.; Kornowski, A.; Weller, H. Quantum Dot Attachment and Morphology Control by Carbon Nanotubes. *Nano Lett.* **2007**, *7*, 3564–3568.
33. Shim, M.; Javey, A.; Kam, N. W. S.; Dai, H. Polymer Functionalization for Air-Stable n-Type Carbon Nanotube Field-Effect Transistors. *J. Am. Chem. Soc.* **2001**, *123*, 11512–11513.
34. Yong, K.; Sahoo, Y.; Swihart, M. T.; Prasad, P. N. Shape Control of CdS Nanocrystals in One-Pot Synthesis. *J. Phys. Chem. C* **2007**, *111*, 2447–2458.
35. Wu, Z.; Chen, Z.; Du, X.; Logan, J. M.; Sippel, J.; Nikolou, M.; Kamaras, K.; Reynolds, J. R.; Tanner, D. B.; Hebard, A. F.; Rinzler, A. G. Transparent, Conductive Carbon Nanotube Films. *Science* **2004**, *305*, 1273–1276.
36. Zhou, Y.; Hu, L.; Grüner, G. A Method of Printing Carbon Nanotube Thin Films. *Appl. Phys. Lett.* **2006**, *88*, 123109-1–123109-3.