Self-Assembled Carbon Nanotube Honeycomb Networks Using a Butterfly Wing Template as a Multifunctional Nanobiohybrid

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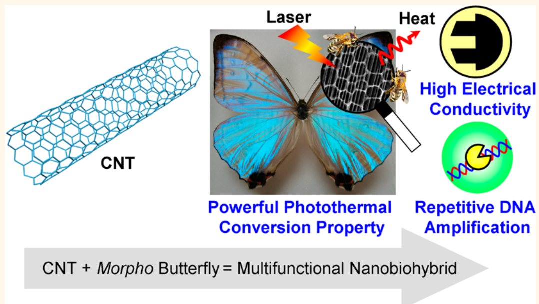
ABSTRACT Insect wings have many unique and complex nano/microstructures that are presently beyond the capabilities of any current technology to reproduce them artificially. In particular, *Morpho* butterflies are an attractive type of insect because their multifunctional wings are composed of nano/microstructures. In this paper, we show that carbon nanotube-containing composite adopts honeycomb-shaped networks when simply self-assembled on *Morpho* butterfly wings used as a template. The unique nano/microstructure of the composites exhibits multifunctionalities such as laser-triggered remote-heating, high electrical conductivity, and repetitive DNA amplification. Our present study highlights the important progress that has been made toward the development of smart nanobiomaterials for various applications such as digital diagnosis, soft wearable electronic devices, photosensors, and photovoltaic cells.



KEYWORDS: biomaterial · biomimetics · carbon nanotube · laser · nanotechnology · self-assembly

During evolutionary history, human beings have made efficient use of natural products by establishing symbiotic relationships with Nature. In particular, various biomaterials sourced from insects (for example, *Bombyx mori*,[1] *Apis mellifera*,[2] *Drosophila melanogaster*,[3] and *Photinus pyrali*[4]) have offered many benefits not only for the advancements in modern molecular biology but also for enhancing human health and improving the quality of life. In the last few decades, information about the structure and mechanical properties of the different parts of insects resulted of particular interest for various industrial applications. Insect wings, for example, have many unique and complex nano/microstructures that any current technology is not presently capable of reproducing artificially.[5] Among them, *Morpho* butterflies are an attractive type of insects owing to their multifunctional wings that are endowed with characteristic properties, including structural color,[5,6] superhydrophobicity,[5,6] self-cleaning properties,[5,6] directional adhesive functions,[7] and chemical-sensing capabilities.[8] Understanding the structure and features of light, thin, and flexible *Morpho* butterfly wings can inspire the design of novel artificial materials.[9,10] However, conducting additional bioengineering research is absolutely imperative to develop an ultimate nanobiomaterial that is based on structures found in insects. In contrast, nanomaterials are potentially highly promising for numerous scientific and technological applications in various fields.[11] In particular, carbon nanotubes (CNTs) offer a unique combination of electrical, mechanical, thermal, and optical properties that make them highly promising materials for numerous applications.[12−16] We have been investigating the use of laser-induced CNTs as a powerful photothermal

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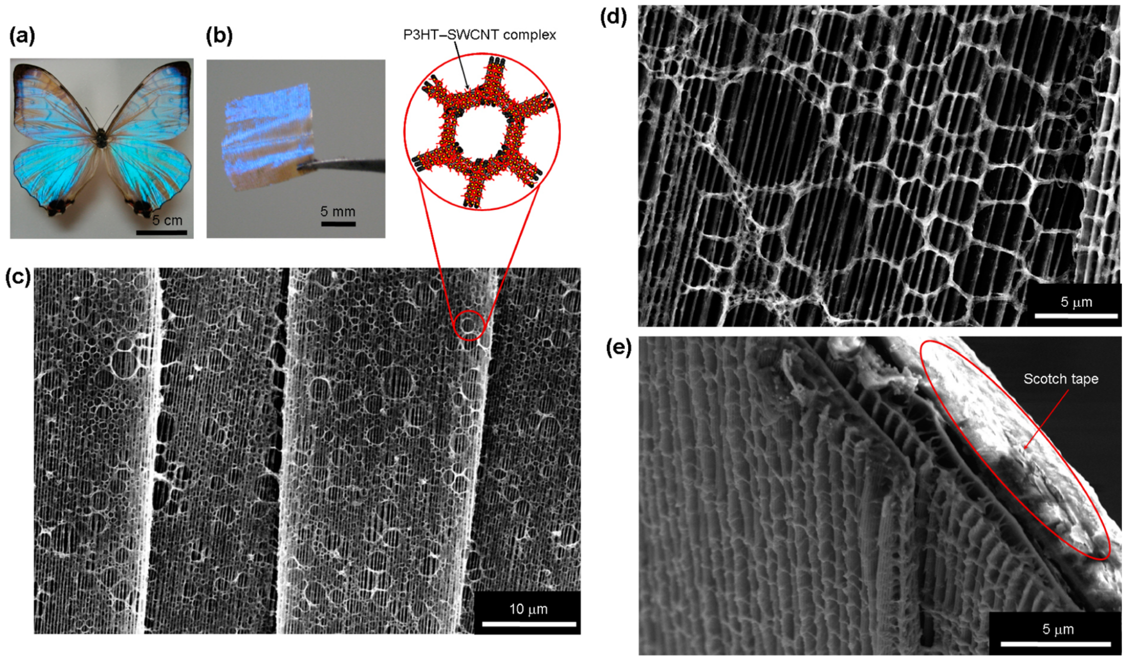

Figure 1. Structural characterization of the CNT−butterfly wing composite. (a) Image of the *M. sulkowskyi* butterfly. (b) Image of the CNT−butterfly wing composite. (c) and (d) SEM images of the CNT−butterfly wing composite and its close-up view. Inset: a schematic illustration of the honeycomb-shaped microstructure based on P3HT−SWCNT complexes. (e) SEM images of the cross-sectional CNT−butterfly wing composite. Scotch tape was used for reinforcement of the composite during the observation of the structures by SEM.

nanomaterial in various heat-based applications.[17−21] Creation of new type of photothermal materials will open doors for diverse thermal applications. In addition, there is currently a growing interest in the improvement of physical properties of CNTs by the use of patterning processes to design functional CNT composites with relevant configurations and sizes.[22,23] However, clear results showing an effective patterning of CNTs for the enhancement of their chemico-physical properties are not available yet. The final goal of our research is to develop innovative multifunctional nano/microstructures of CNT composites underlying natural functions of biomaterials sourced from a variety of insects. For that purpose, we combined the CNTs with a *Morpho* butterfly wing as the first step to create a novel biomaterial. Strategic approaches for the functionalization of CNTs with *Morpho* butterfly wing are very important in the fields of CNT composites, biomimetic and bioinspired materials.

In our study, we demonstrate that (1) a honeycomb-shaped network containing CNTs can be readily formed on a *Morpho* butterfly wing using a simple self-assembly technology; (2) the CNT functionalized *Morpho* butterfly wing (CNT−butterfly wing) composite successfully expresses multiple functions such as laser-induced remote heating and high electrical conductivity, because of the photothermal property of CNTs and highly rooted, conductive CNT honeycomb networks; and (3) the light-driven CNT−butterfly wing composite effectively illustrates the repetitive DNA amplification with the use of photothermal, water-shedding, and self-cleaning features of the composite. This type of smart nanobiomaterial systems is tremendously useful for enabling new biotechnological tools,[24,25] such as soft, wearable devices,[26] high-sensitivity photosensors,[9] and sustainable light batteries.[10] We believe that our work proposes an important progress for application of CNT biocomposite because applications and physical properties of CNT-based nanohybrids have not been satisfactorily investigated. We would like to highlight that CNT biocomposite is one of the most attractive materials. Furthermore, this study reports for the first time an improvement of photothermal properties of CNTs by a patterning process on a natural substrate. Our CNT patterning method will also shed light on creation of new types of biomimetic and bioinspired materials.[27−32]

RESULTS AND DISCUSSION

Structural Characterization of CNT−Butterfly Wing Composite. The *Morpho sulkowskyi* butterfly[5] (Figure 1a) was used in this study as a model of natural material to create a multifunctional nanobiohybrid. This butterfly is commercially available, and the high transparency of its wings is useful for the characterization of the optical performances of CNTs such as the photothermal properties and the absorbance spectra. The nanobiohybrid was based on the self-assembly of CNTs on the butterfly wings. Single-walled CNT (SWCNTs) were produced by arc plasma jet (APJ). Since pristine CNTs have a strong tendency to aggregate, thus hampering their dispersibility in different solvents,[33] we used poly(3-hexylthiophene) (P3HT)-modified-SWCNT complex [abbreviated as P3HT−SWCNT (APJ)], obtained by noncovalent self-assembly.[34] P3HT was adsorbed onto the graphitic surfaces of carbon nanotubes *via* van der Waals and hydrophobic interactions.[34] The preparation of the CNT−butterfly wing composite was very simple. A dispersion of P3HT−SWCNT (APJ) complex was added onto the butterfly wing and dried at room temperature for several minutes (see Methods for details). The color of the prepared CNT−butterfly wing composite did not change from the original one (Figure 1b). We discovered that CNT honeycomb networks were readily formed on the butterfly wing. Figure 1c−e presents the scanning electron microscopy (SEM) images of the CNT−butterfly wing composite, which have bridging structures with different sized honeycomb-like networks. The honeycomb structures of the CNT complex spread over the scales of the butterfly wing film. It is interesting to note that P3HT−SWCNT (APJ) complex showed a better-defined network structure among a variety of nanocarbons that were used in the present study (Figures S1−S3).

Photothermal Property and Electrical Conductivity of CNT−Butterfly Wing Composite. Discoveries about butterfly wings show that multilayer structures on the wing surfaces are effective solar energy collectors.[35] The scales on butterfly wings are biologically tuned to absorb solar energy efficiently and to warm them up, enabling the insect to survive in colder or higher-altitude environments.[36] More excitingly, scientists found that the honeycomb-like pattern of the scales of the same butterfly wings takes advantage of refraction to trap light, much like a fiber-optic cable.[37] Herein, we investigated the photothermal effect of our different nanocarbon−butterfly wing composites using 785 nm near-infrared (NIR) laser irradiation (Figure 2). Under laser irradiation, the temperature of the P3HT−SWCNT (APJ) functionalized-butterfly wings increased more significantly with the irradiation power than in the case of the other carbon materials [*i.e.*, P3HT−SWCNT (HiPco), P3HT−CNH, and P3HT−SWCNT (CoMoCAT)]. On the other hand, P3HT−MWCNT, P3HT, and the control butterfly wing without carbon nanomaterials showed lower temperature increases (Figure 2a,b). The effect of surface density of P3HT−SWCNT (APJ) on the capacity to form honeycomb-network structures and the photothermal conversion behavior were investigated (Figure S4). The temperature difference (ΔT) increased with the surface density of SWCNTs on the butterfly wing after laser irradiation (Figure S4b). Indeed, the absorbance of light increases with the amount of SWCNTs (Figure S4a). The surface density of SWCNTs also influenced the formation of the honeycomb networks (Figure S4c−e). We also investigated the photothermal conversion behaviors of two matrices without honeycomb networks, namely, P3HT−SWCNT (APJ) complexes on a glass substrate and octadecylamine (ODA) modified-SWCNT (ODA−SWCNT)/butterfly wing composite. The temperature of these matrices did not increase after laser irradiation compared with honeycomb structured P3HT−SWCNT (APJ)/butterfly wing composite (Figures S5 and S6). The high photothermal conversion of P3HT−SWCNT (APJ)/butterfly wing composite derived from the high photothermal conversion efficiency of the honeycomb-like networks of SWCNTs formed on the butterfly wing and the good dispersibility in organic solvent necessary for the SWCNT honeycomb formation.[20,21] Furthermore, defined honeycomb-shaped P3HT−SWCNTs (APJ) networks on the butterfly wing have a large light receiving area that probably absorbs laser light very efficiently.[20,21] The photothermal conversion behavior of the laser-induced CNT−butterfly wing composite can be applied both in air and under vacuum (Figure 2c). This result shows that heat is originally generated from CNTs themselves, and oxygen is not necessary to heat the composite with laser light. Indeed, the photothermal property of nanocarbons can be attributed to their physical properties, such as the release of substantial vibrational energy after exposure to laser radiation.[39,40] The liberation of this energy within a composite produces localized heating. The generation of excessive heat by the laser-induced CNT−butterfly wing composite with honeycomb structure allowed it to ignite a match or a nitrocellulose membrane (Figure 2d and Supporting Information Movie 1). In the control experiments (without nanocarbons, and in the presence of P3HT and P3HT−MWCNT), ignition did not occur at all even after 5 min of laser irradiation. In the cases of the P3HT−SWCNT (HiPco), P3HT−SWCNT (CoMoCAT), and P3HT−CNH, much time was also necessary to catch fire (*i.e.*, over 1 min for a match and over 30 s for a nitrocellulose membrane). These results definitely confirm that only honeycomb networks derived from CNT complexes were efficient on the butterfly wing as powerful photothermal converters. We believe that these readily formed CNT honeycomb networks also create synergy between the photothemal nanotube property[17−21] and the heat collecting function by multilayer structures of the butterfly scales.[37] Another interesting feature of the CNT−butterfly wing composite was its superior electrical conductivity (Figure S7 and Table S1).

Repetitive DNA Amplification by CNT−Butterfly Wing Composite. *Morpho* butterfly wings are covered by hierarchical scales creating a superhydrophobic and self-cleaning surface that repels water and contaminants away from the body.[6,38] These superhydrophobic and self-cleaning properties are the most attractive features of this type of butterfly wings. This property can be exploited in the context of a chemico-physical manipulation technology of droplets deposited on a solid surface.[25] To expand the inherent functions of the

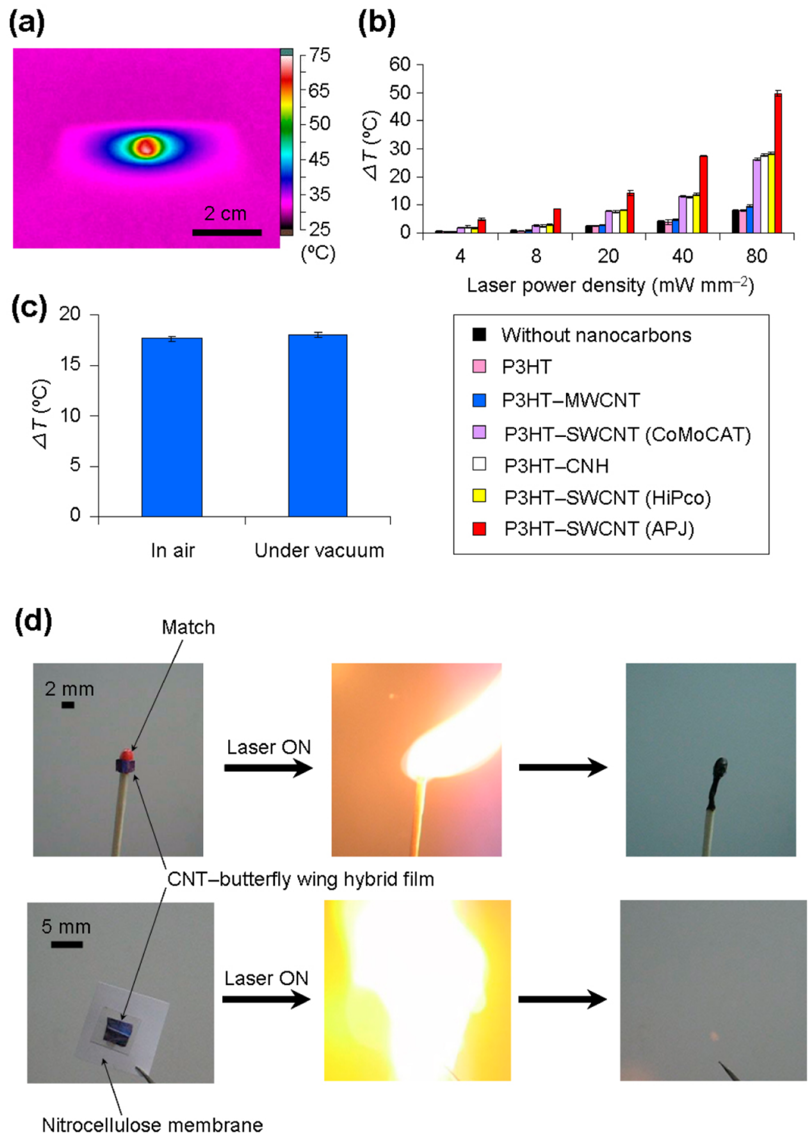

Figure 2. Photothermal conversion of the CNT−butterfly wing composite. (a) Thermographic images on the surface of the CNT−butterfly wing composite using a 785 nm NIR laser at 1000 mW (*ca.* 80 mW/mm^2). (b) Photoinduced temperature elevation on the composites at various laser powers (*ca.* 4, 8, 20, 40, and 80 mW/mm^2). (c) Photoinduced temperature changes on the composites using a 785 nm NIR laser at 1000 mW (*ca.* 80 mW/mm^2) in air or under vacuum. (d) Fire tests of the photoinduced CNT−butterfly wing composite. Laser wavelength = 785 nm. Laser power = 1000 mW (*ca.* 80 mW/mm^2).

natural *Morpho* butterfly wings and their possible applications in advanced functional tools (Figure 3), we decided to investigate repetitive DNA amplification using a photothermal property of CNT−butterfly wing composite. Photoinduced loop-mediated isothermal amplification (LAMP) of DNA was applied in this system. The LAMP reaction is a convenient nucleic acid amplification method, and it is performed under isothermal conditions (*ca.* 60−65 °C).[41] The repetitive DNA amplification mechanism is illustrated in Figure 3a, and comprised the following phases: (1) The enzymatic solution was deposited onto the CNT−butterfly wing composite because of water repellence (Figure 3b). The contact angle (CA) of the solution droplet was about 138°. This CA value is almost identical to that of the native butterfly wing.[38] (2) The enzymatic solution was irradiated with a 785 nm NIR laser for 10 min. The optimal temperature of this reaction is about 60 °C, as mentioned above. Therefore, laser power levels were adjusted to bring the temperature to 60 °C, according to a thermographic measurement. (3) An overall bright-green-colored fluorescent droplet, derived from the DNA amplification, was observed at 485 nm. This real-time LAMP reaction was monitored using calcein, which in complex with Mn^{2+} is not fluorescent (Figure S8). As the DNA amplification proceeded, the generated pyrophosphate ions (PPi) deprived the solution of manganese ions, restoring the fluorescence of calcein.[42] In addition, the fluorescence emission was enhanced by binding free calcein to magnesium ions present in the reaction mixture. According to these biochemical principles, we could observe the shiny,

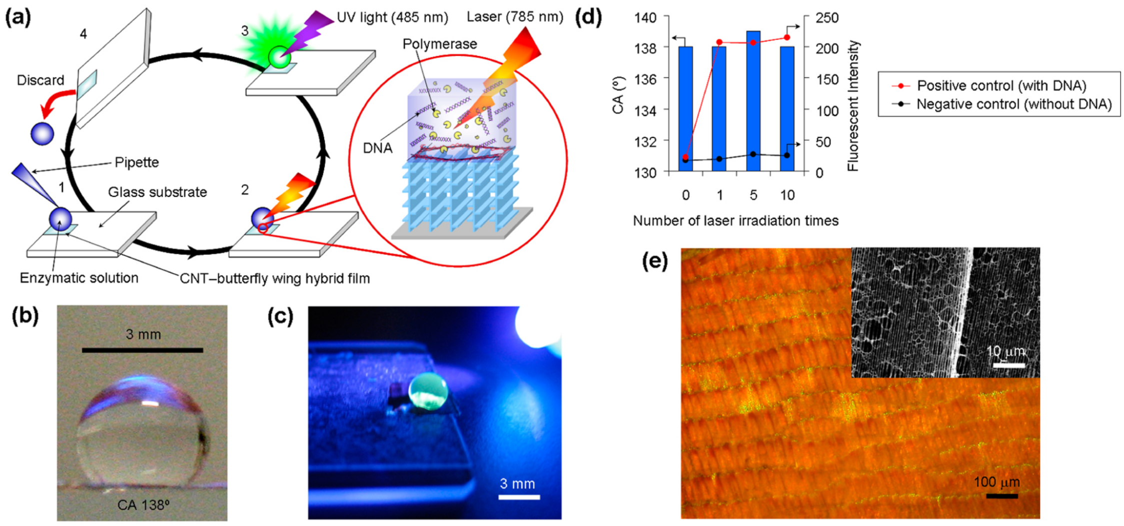

Figure 3. Repetitive DNA amplification by photoinduced CNT–butterfly wing composite. (a) A schematic illustration of repetitive DNA amplification: (1) dropping enzymatic solution onto the CNT–butterfly wing composit; (2) NIR laser irradiation (785 nm); (3) direct observation of DNA amplification using 485 nm UV light; (4) discarding of the enzymatic solution. (b) Image of a water droplet on the CNT–butterfly wing composite. (c) The visual green fluorescence of DNA amplification using 485 nm UV light. (d) The effect of the number of laser irradiations on the CA and fluorescent intensity. (e) An optical microscopic and SEM images of the CNT–butterfly wing composite after 10-times laser irradiation (total irradiation time: 100 min).

green fluorescence of an enzymatic droplet with the naked eye (Figure 3c). This result clearly proves that DNA amplification was successfully achieved. Finally, (4) the enzymatic solution was easily discarded by water repellence of the CNT–butterfly wing composite. Therefore, we could continuously reiterate this process (Supporting Information Movie 2). We also investigated how the number of times that laser irradiation was applied affected the CA and fluorescent intensity of the droplet (Figure 3d). The fluorescent intensity of the enzymatic droplet increased in the presence of positive control DNA, while background fluorescence of the droplet was not affected in the DNA-free positive control, regardless of the number of applied laser irradiations. In addition, the changes to the contact angle and the fluorescence intensity by the subsequent laser irradiations were insignificant. Finally, the morphology of the CNT–butterfly wing composite was not modified by the long laser irradiation time (total irradiation time = 100 min), probably because the water droplets very quickly dissipated the produced heat and the boiling point of water is relatively low (100 °C) (Figure 3e). We also confirmed by fluorescence microscopy that DNA molecules were not absorbed into the CNT–butterfly wing composite (Figure S9). These results clearly indicate that the laser-induced CNT–butterfly wing composite can be used repeatedly for DNA amplification exploiting the photothermal, water shedding and self-cleaning properties of the composite. Our developed laser-triggered remote heating system, which is based on the photothermal property of CNT honeycomb networks, can easily heat only a targeted area in a noncontact manner using an external highly focused laser beam. One of the most important advantages of our CNT-based photodynamic heating system in comparison to other light-driven systems[43] is the possibility to heat at various wavelengths of light because CNTs have strong absorbance over a wide range in the optical region. In addition, water droplets on the composite can be manipulated easily and rapidly without contamination by water shedding and self-cleaning properties of the composite. According to these advantages, we believe that the CNT–butterfly wing composites might be applied to the next generation of full automatic DNA manipulation devices[24] by the use of digital microfluidics,[25] in which pico-/microliter-sized droplets are manipulated on arrays of electrodes.

CONCLUSION

We developed a nanobiomaterial based on nanocarbons and *Morpho* butterfly wings. Honeycomb-shaped CNT networks were assembled on CNT-functionalized *Morpho* butterfly wing composite using a simple self-assembly technique and the wings as a template. This unique nano/microsturucture of the composite exhibits multifunctional properties, such as laser-triggered remote heating, high electrical conductivity, and repetitive DNA amplification, by combining the powerful photothermal characteristics and high electroconductivity of CNTs with the inherent functions of the *Morpho* butterfly wings. The applications of biomimetic and bioinspired materials are currently an exciting field of research. This study also represents an important advance in using external laser irradiation to create programmable and adaptable nanobiosystems. Our technology is positioned to offer novel possibilities for future developments in various applications such as digital diagnosis, soft wearable electronic devices, photosensors, and photovoltaic cells.

METHODS

CNT−Butterfly Wing Composite. The P3HT−SWCNT (APJ) was prepared as follows. APJ SWCNT (1 mg) [Arc plasma jet, purity >90%, diameter ≈ 1.4 nm, length ≈ 1−5 μm; Meijo Nano Carbon] and P3HT (1 mg) (regioregular, Mn ≈ 87 000; Aldrich) were suspended in chloroform (3 mL) and sonicated for 10 min on ice (<8 °C) using an ultrasonication bath (USD-2R; AS ONE) to obtain a uniform dispersion. The P3HT−SWCNT (APJ) dispersion was centrifuged (10 000 rpm, 10 min, 4 °C) (3500; Kubota) to remove aggregates. The supernatant was collected after centrifugation. The quantity of SWCNTs dispersed in the chloroform by P3HT molecules was determined by UV−vis-NIR spectrometer (UV-3100; Shimadzu) and resulted in about 238 μg of SWCNT/mL of chloroform. Other P3HT−nanocarbon complexes were prepared in the same way as P3HT−SWCNT (APJ). The following nanocarbons were used in this study: HiPco SWCNTs (superpurified SWCNTs, purity >95%, diameter ≈ 0.8−1.2 nm, length ≈ 0.1−1.0 μm; Unidym), CoMoCAT SWCNTs (CG-100, purity >90%, diameter ≈ 0.7−1.3 nm, length ≈ 0.45−2.3 μm; SouthWest Nano Technologies), CVD MWCNTs [(purity >95%, diameter ≈ 10−40 nm, length < 3 μm; Meijo Nano Carbon) and carbon nanohorns (CNHs) (purity >95%, average particle diameter ≈ 80−100 nm, metal-free; NEC). Small pieces, ∼0.5 × 0.5 cm^2 dried *M. sulkowskyi* butterfly wings (Nature Shop) were cut and fixed onto a glass substrate with double-sided tape. The butterfly wings were modified by applying the different P3HT−nanocarbon solutions (10 μL) onto the photonic dorsal side of the wing and allowing them to air-dry for several minutes. Surface density was calculated by dividing weight of SWCNT by area of butterfly wing. The CNT functionalized-artificial butterfly wing composites were prepared by the same method employed for the CNT-based composite by using a nanofabricated silicon wafer (DTM-2−2; Kyodo International). To prepare chitin-coated silicon wafer, 0.1 wt % of chitin powder from crab shells (Sigma) was dissolved in 30% NaOH solution. A nanofabricated silicon wafer was dipped into the chitin solution overnight and was then dried for 12 h in air. Finally, the silicon wafer was washed with distilled water to remove excess chitin.

Structural Characterization of CNT−Butterfly Wing Composite. The CNT−butterfly wing composites were characterized using SEM (JSM-6510; JEOL), a UV−vis-NIR spectrophotometry (UV-3600; Shimadzu), and optical microscopy (IX70; Olympus). The thickness of the composites from SEM images was measured by image analyzing software (Mex ver. 5.1; Alicona).

Temperature Assay. The CNT−butterfly wing composites were irradiated using a 785 nm NIR laser (spot diameter ≈ 4 mm) (BRM-785-1.0-100-0.22-SMA; B&W Tek) at various power levels (50, 150, 300, 500, 700, and 1000 mW, and 4, 8, 20, 40, 80 mW/mm^2). The temperatures of the composites were measured by IR thermography (Ti10; Fluke) and/or a temperature sensor (AD-5601A; A & D). Before performing these experiments, the indicators for measuring the temperatures were calibrated to obtain accurate temperature values. In the case of the experiments under vacuum conditions, the composites were placed in a polystyrene-type transparent vacuum desiccator (AS ONE). After lowering the atmospheric pressure (about 10^{-3} Pa), the temperatures of the composites were measured by a temperature sensor during laser irradiation.

Fire Test. A small piece of the CNT−butterfly wing composite (0.5 × 0.5 cm^2) was attached to a match (Kanematsu Nissan Norin) or to a nitrocellulose membrane (Hybond ECL; Amersham Pharmacia Biotech) using double-sided tape and it was irradiated using a 785 nm NIR laser at 1000 mW. Ignition behavior was videographed with a digital camera (IXY 3; Canon).

Electrical Conductivity Test. The electrical conductivity of the CNT−butterfly wing composite was investigated by the four-probe DC current method (Potentio/Galvanostat HA-151 model; Hokuto Denki) using a galvanostat mode connected to a wave generator (FC220; Yokogawa Electric). A linear sweep of current was applied with the two outer probe electrodes and the voltage was detected by the two inner probe electrodes. The conductivity of the CNT−butterfly wing composite was calculated by the slope of the current−voltage curve.

Repetitive DNA Amplification. The enzymatic reaction was typically performed using the DNA amplification kit (Eiken). Positive control DNA (10 μL), primer mixture solution [Forward Inner Primer (FIP) (160 pmol), Backward Inner Primer (BIP) (160 pmol), F3 (20 pmol), and B3 (20 pmol)] (10 μL), and Bst DNA polymerase (8 units/mL; 10 μL) were added in the buffer [40 mM Tris-HCl (pH 8.8), KCl (20 mM), $MgSO_4$ (16 mM), $(NH_4)_2SO_4$ (20 mM), Tween 20 (0.2%), betaine (1.6 M) and dNTPs (2.8 mM each)] (50 μL) on ice. The positive control DNA was a plasmid DNA that was inserted with a Hind III fragment (6557 bp) of λ phage DNA. For fluorescence studies, the calcein [bis[*N*,*N*-bis(carboxymethyl)-aminomethyl]fluorescein] in an aqueous solution (50 μM; 2 μL) (Eiken) was added to the solution on ice. The prepared solution (50 μL) was put onto the CNT−butterfly wing composite. The solution was then irradiated with a 785 nm NIR laser for 10 min. Laser power levels were adjusted to bring the temperature to 60 °C, as this is the optimal temperature for the amplification reaction. The fluorescent intensity of the DNA amplification was observed by the naked eye using a 485 nm blue LED (Akizuki Denshi), and it was analyzed using the imaging software (ImageJ; NIH). Contact angles were measured on a contact-angle goniometer (CA-D; Kyowa Interface Science) at room temperature. The DNA adsorption test was performed using fluorescence microscopy. The λ phage DNA (32 mDa, 48 502 bp; Toyobo) solution (90 μL, 16 μg/mL) was mixed with 1× GelRed solution (10 μL) (Wako) as an intercalator. After each laser irradiation time (10, 50, and 100 min), the prepared DNA solution (50 μL) was placed onto the CNT−butterfly wing composite for several minutes and then it was discarded. The composite was then observed using a fluorescence microscope (IX70; Olympus) equipped with a color-charge-coupled device (CCD) camera (VB-7010; Keyence).

Conflict of Interest: The authors declare no competing financial interest.

Supporting Information Available: Movies of fire test and repetitive DNA amplification (Quicktime) and additional experimental materials (PDF). This material is available free of charge *via* the Internet at http://pubs.acs.org.

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REFERENCES AND NOTES

1. Teulé, F.; Miaob, Y.-G.; Bong-Hee Sohnc, B.-H.; Kimc, Y.-S.; Hulla, J. J.; Fraser, M. J., Jr.; Lewisa, R. V.; Jarvis, D. L. Silkworms Transformed with Chimeric Silkworm/Spider Silk Genes Spin Composite Silk Fibers with Improved Mechanical Properties. *Proc. Natl. Acad. Sci. U.S.A.* **2012**, *109*, 923–928.
2. Kamakura, M. Royalactin Induces Queen Differentiation in Honeybees. *Nature* **2011**, *473*, 478–483.
3. Ohsawa, S.; Sato, Y.; Enomoto, M.; Nakamura, M.; Betsumiya, A.; Igaki, T. Mitochondrial Defect Drives Non-Autonomous Tumour Progression through Hippo Signalling in *Drosophila*. *Nature* **2012**, *490*, 547–551.

4. Nakatsu, T.; Ichiyama, S.; Hiratake, J.; Saldanha, A.; Kobashi, N.; Sakata, K.; Kato, H. Structural Basis for the Spectral Difference in Luciferase Bioluminescence. *Nature* **2006**, *440*, 372–376.
5. Sun, J.; Bhushan, B. Structure and Mechanical Properties of Beetle Wings: A Review. *RSC Adv.* **2012**, *2*, 12606.
6. Kinoshita, S.; Yoshioka, S.; Fujii, T.; Okamoto, N. Photophysics of Structural Color in the *Morpho* Butterflies. *Forma* **2002**, *17*, 103–121.
7. Zheng, Y.; Gao, X.; Jiang, L. Directional Adhesion of Superhydrophobic Butterfly Wings. *Soft Matter.* **2007**, *3*, 178–182.
8. Potyrailo, R. A.; Ghiradella, H.; Vertiatchikh, A.; Dovidenko, K.; Cournoyer, J. R.; Olson, E. *Morpho* Butterfly Wing Scales Demonstrate Highly Selective Vapour Response. *Nat. Photonics* **2007**, *1*, 123–128.
9. Pris, A. D.; Utturkar, Y.; Surman, C.; Morris, W. G.; Vert, A.; Zalyubovskiy, S.; Deng, T.; Ghiradella, H. T.; Potyrailo, R. A. Towards High-Speed Imaging of Infrared Photons with Bio-Inspired Nanoarchitectures. *Nat. Photonics* **2012**, *6*, 195–200.
10. Lou, S.; Guo, X.; Fan, T.; Zhang, D. Butterflies: Inspiration for Solar Cells and Sunlight Water-Splitting Catalysts. *Energy Environ. Sci.* **2012**, *5*, 9195–9216.
11. Steed, J. W.; Gale, P. A. *Supramolecular Chemistry: From Molecules to Nanomaterials*; Wiley-VCH: Hoboken, NJ, 2012.
12. Iijima, S. Helical Microtubules of Graphitic Carbon. *Nature* **1991**, *354*, 56–58.
13. Singh, P.; Lamanna, G.; Ménard-Moyon, C.; Toma, F. M.; Magnano, E.; Bondino, F.; Prato, M.; Verma, S.; Bianco, A. Formation of Efficient Catalytic Silver Nanoparticles on Carbon Nanotubes by Adenine Functionalization. *Angew. Chem., Int. Ed.* **2011**, *50*, 9893–9897.
14. Okazaki, T.; Iizumi, Y.; Okubo, S.; Kataura, H.; Liu, Z.; Suenaga, K.; Tahara, Y.; Yudasaka, M.; Okada, S.; Iijima, S. Coaxially Stacked Coronene Columns Inside Single-Walled Carbon Nanotubes. *Angew. Chem., Int. Ed.* **2011**, *50*, 4853–4857.
15. Zhang, M.; Murakami, T.; Ajima, K.; Tsuchida, K.; Sandanayaka, A. S.; Ito, O.; Iijima, S.; Yudasaka, M. Fabrication of ZnPc/Protein Nanohorns for Double Photodynamic and Hyperthermic Cancer Phototherapy. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 14773–14778.
16. Kostarelos, K.; Bianco, A.; Prato, M. Promises, Facts and Challenges for Carbon Nanotubes in Imaging and Therapeutics. *Nat. Nanotechnol.* **2009**, *4*, 627–633.
17. Miyako, E.; Kono, K.; Yuba, E.; Hosokawa, C.; Nagai, H.; Hagihara, Y. Carbon Nanotube-Liposome Supramolecular Nanotrains for Intelligent Molecular-Transport Systems. *Nat. Commun.* **2012**, *3*, 122610.1038/ncomms2233.
18. Miyako, E.; Deguchi, T.; Nakajima, Y.; Yudasaka, M.; Hagihara, Y.; Horie, M.; Shichiri, M.; Higuchi, Y.; Yamashita, F.; Hashida, M.; *et al.* Photothermic Regulation of Gene Expression Triggered by Laser-Induced Carbon Nanohorns. *Proc. Natl. Acad. Sci. U.S.A.* **2012**, *109*, 7523–7528.
19. Miyako, E.; Hosokawa, C.; Kojima, M.; Yudasaka, M.; Funahashi, R.; Oishi, I.; Hagihara, Y.; Shichiri, M.; Takashima, M.; Nishio, K.; *et al.* Photo-Thermal-Electrical Converter Based on Carbon Nanotubes for Bioelectronic Applications. *Angew. Chem., Int. Ed.* **2011**, *50*, 12266–12270.
20. Miyako, E.; Nagata, H.; Hirano, K.; Hirotsu, T. Carbon Nanotube-Polymer Composite for Light-Driven Microthermal Control. *Angew. Chem., Int. Ed.* **2008**, *47*, 3610–3613.
21. Miyako, E.; Nagata, H.; Hirano, K.; Hirotsu, T. Micropatterned Carbon Nanotube−Gel Composite as Photothermal Material. *Adv. Mater.* **2009**, *21*, 2819–2823.
22. Yu, G.; Cao, A.; Lieber, C. M. Large-Area Blown Bubble Films of Aligned Nanowires and Carbon Nanotubes. *Nat. Nanotechnol.* **2007**, *2*, 372–377.
23. Jung, Y. J.; Kar, S.; Talapatra, S.; Soldano, C.; Viswanathan, G.; Li, X.; Yao, Z.; Ou, F. S.; Avadhanula, A.; Vajtai, R.; *et al.* Aligned Carbon Nanotube-Polymer Hybrid Architectures for Diverse Flexible Electronic Applications. *Nano Lett.* **2006**, *6*, 413–418.
24. Tewhey, R.; Warner, J. B.; Nakano, M.; Libby, B.; Medkova, M.; David, P. H.; Kotsopoulos, S. K.; Samuels, M. L.; Hutchison, J. B.; Larson, J. W.; *et al.* Microdroplet-Based PCR Enrichment for Large-Scale Targeted Sequencing. *Nat. Biotechnol.* **2009**, *27*, 1025–1034.
25. Abdelgawad, M.; Wheeler, A. R. The Digital Revolution: a New Paradigm for Microfluidics. *Adv. Mater.* **2008**, *20*, 920–925.
26. Tee, B. C.-K.; Wang, C.; Allen, R.; Bao, Z. An Electrically and Mechanically Self-Healing Composite with Pressure- and Flexion-Sensitive Properties for Electronic Skin Applications. *Nat. Nanotechnol.* **2012**, *7*, 825–832.
27. Qiu, L.; Liu, J. Z.; Chang, S. L.; Wu, Y.; Li, D. Biomimetic Superelastic Graphene-Based Cellular Monoliths. *Nat. Commun.* **2012**, *3*, 124110.1038/ncomms2251.
28. Sethi, S.; Ge, L.; Ci, L.; Ajayan, P. M.; Dhinojwala, A. Gecko-Inspired Carbon Nanotube-Based Self-Cleaning Adhesives. *Nano Lett.* **2008**, *8*, 822–825.
29. Avinash, M. B.; Verheggen, E.; Schmuck, C.; Govindaraju, T. Self-Cleaning Functional Molecular Materials. *Angew. Chem., Int. Ed.* **2012**, *51*, 10324–10328.
30. Ge, J.; Lei, J.; Zare, R. N. Protein-Inorganic Hybrid Nanoflowers. *Nat. Nanotechnol.* **2012**, *7*, 428–432.
31. Morin, S. A.; Shepherd, R. F.; Kwok, S. W.; Stokes, A. A.; Nemiroski, A.; Whitesides, G. M. Camouflage and Display for Soft Machines. *Science* **2012**, *337*, 828–832.
32. Wong, T.-S.; Kang, S. H.; Tang, S. K.; Smythe, E. J.; Hatton, B. D.; Grinthal, A.; Aizenberg, J. Bioinspired Self-Repairing Slippery Surfaces with Pressure-Stable Omniphobicity. *Nature* **2011**, *477*, 443–447.
33. Singh, P.; Campidelli, S.; Giordani, S.; Bonifazi, D.; Bianco, A.; Prato, M. Organic Functionalisation and Characterisation of Single-Walled Carbon Nanotubes. *Chem. Soc. Rev.* **2009**, *38*, 2214–2230.
34. Geng, J.; Kong, B.-S.; Yang, S.-B.; Youn, S. C.; Park, S.; Joo, T.; Jung, H.-T. Effect of SWNT Defects on the Electron Transfer Properties in P3HT/SWNT Hybrid Materials. *Adv. Func. Mater.* **2008**, *18*, 2659–2665.
35. Heilman, B. D.; Miaoulis, L. N. Insect Thin Films as Solar Collectors. *Appl. Opt.* **1994**, *33*, 6642–6647.
36. Vukusic, P.; Sambles, J. R.; Lawrence, C. R. Structurally Assisted Blackness in Butterfly Scales. *Proc. R. Soc. London, Ser. B* **2004**, *271*, 237–239.
37. Zhang, W.; Zhang, D.; Fan, T.; Gu, J.; Ding, J.; Wang, H.; Guo, Q.; Ogawa, H. Novel Photoanode Sructure Templated from Butterfly Wing Scales. *Chem. Mater.* **2009**, *21*, 33–40.
38. Collins, M. *Design and Nature II: Comparing Design in Nature with Science and Engineering*; WIT: Southampton, 2004.
39. Ahir, S. V.; Terentjev, E. M. Photomechanical Actuation in Polymer−Nanotube Composites. *Nat. Mater.* **2005**, *4*, 491–495.
40. Sun, X.; Yu, R. Q.; Xu, G. Q.; Hor, T. S. A.; Ji, W. Broadband Optical Limiting with Multiwalled Carbon Nanotubes. *Appl. Phys. Lett.* **1998**, *73*, 3632–3634.
41. Notomi, T.; Okayama, H.; Masubuchi, H.; Yonekawa, T.; Watanabe, K.; Amino, N.; Hase, T. Loop-Mediated Isothermal Amplification of DNA. *Nucleic Acids Res.* **2000**, *28*, 63.
42. Tomita, N.; Mori, Y.; Kanda, H.; Notomi, T. Loop-Mediated Isothermal Amplification (LAMP) of Gene Sequences and Simple Visual Detection of Products. *Nat. Protoc.* **2008**, *3*, 877–882.
43. Liu, G. L.; Kim, J.; Lu, Y.; Lee, L. P. Optofluidic Control Using Photothermal Nanoparticles. *Nat. Mater.* **2006**, *5*, 27–32.