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Light-Switchable Single-Walled Carbon Nanotubes Based on Host–Guest Chemistry

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A new type of light-switchable "smart" single-walled carbon nanotube (SWNTs) is developed by the reversible host–guest interaction between azobenzene-terminal PEO (AzoPEO) and pyrene-labeled host attached on the sidewalls of nanotubes via π–π stacking. The SWNTs hybrids not only are well dispersed in pure water, but also exhibit switchable dispersion/aggregation states upon the alternate irradiation of UV and visible light. Moreover, the SWNTs hybrids dispersion is preliminarily used as coating fluid to form transparent conductive films. The dispersant AzoPEO is removed by the contamination-free UV treatment, decreasing the resistance of the films. This kind of light-switchable SWNTs hybrids, possessing a "green" trigger and intact structure of the nanotube, may find potential applications in sensor of biomedicines, device fabrication, etc. Additionally, such a reversible host–guest interaction system may open up the possibility to control the dispersion state of SWNTs by other common polymers.

1. Introduction

As a one-dimensional carbon nanomaterial,[1] single-walled carbon nanotubes (SWNTs) have garnered much interest[2] in the past two decades, owing to their excellent optoelectronic properties, mechanical strength, and chemical stability.[3] These characteristics enable them to find various prospective applications[4] ranging from photodetectors,[5] solar cells,[6] sensors,[7] field-emission devices,[8] and components in high-performance composites,[9] to name just a few. However, SWNTs exist in the form of bundles that result from a strong tube–tube interaction energy (ca. 1000 eV),[10] which not only severely hinders their device fabrication but also limits their applications where individual tubes or small-sized bundles are often required to obtain the best performance.[11] It is well recognized that the SWNT bundles are not easily dispersed and soluble in liquid environment, especially in water, even with conventional physical approaches such as sonication and ball milling.[11d] To counter this problem, several approaches, including covalent coupling reactions and noncovalent exohedral interactions, have been exploited to make SWNTs dispersed or individualized.[12] Nevertheless, covalent chemical functionalization of the nanotube sidewalls and termini results in a change of carbon hybridization from sp^2 to sp^3, which alters the electronic structure and may impair the inherent performance.[13] Comparatively, noncovalent modification, for example, π–π stacking or hydrophobic interaction, represents a more attractive strategy as it enables SWNTs to be dispersed in solution while their intrinsic structure and properties are preserved.[12a,13] Recently, SWNTs were studied for applications such as "smart" optical sensors,[14–16] and transparent conductive films (TCFs) with "green" fabrication processes.[17] To be successfully applied, SWNTs should be not only dispersed in solvent but also sensitive to external stimulus.[7b,16–18] Functionalization of SWNTs with stimuli-responsive water-soluble polymers represents one of the choices to satisfy such requirements.

Up to date, several kinds of stimuli-responsive polymers have been used to modify SWNTs noncovalently. For example, Grunlan et al.[19,20] employed pyrene-labeled poly(N-isopropylacrylamide) (PNIPAM) and poly(N-cyclopropylacrylamide) (PNCPA) respectively, to functionalize SWNTs for temperature-responsive SWNT dispersions. Kim and co-workers[21] demonstrated the control of exfoliation and bundling of SWNTs by pH-sensitive poly(acrylic acid) (PAA). Based on the cis-to-trans structural changes of phenyl-substituted tetrathiafulvalene vinylogues (TTFV), Zhao et al.[22] developed smart SWNTs with reversible dispersing and releasing properties in organic solvents under the control of redox or pH stimuli. In view of the potential for biological application, SWNTs sensitive to temperature or pH are ideal because their responsive properties can be tailored by taking advantage of the normal body temperature and physiological environment. Nevertheless, the use of temperature as a trigger for polymers may be limited in some targeted locations such as deep sites in vitro;[23] introduced

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additive triggers based on acids, bases, oxidants, or reductants will contaminate or modify the final products.[24] Thus, we have been seeking dispersants with simpler and "green" triggers for "intelligentizing" SWNTs without damaging their inherent structure and properties. Very recently, we attempted to functionalize SWNTs with a CO_2-responsive polymer;[25] heating is still needed to drive the dispersion back to the aggregate state though reversible switchability was obtained in aqueous media upon alternate treatment of CO_2 and N_2.

Among the representative stimuli, light is promising because of the following advantages:[26] noncontact process, precise area selectivity, producing no waste products compared to chemical "fuels", independence of conventional energy sources, offering a rather high spatial and temporal resolution so as allowing for true remote control. Zhang and co-workers[27] pioneered the fabrication of light-sensitive SWNTs by using poly(ethyleneglycol)-terminate malachite green, and found the obtained SWNTs can be dispersed in water due to the π–π interaction between the aromatic malachite and the fullerene structure of SWNTs. However, the dispersion/aggregation of SWNTs only stands one recycle because of the fatigue of the photoreaction,[27] which renders the final SWNTs to be excluded from the applications where reversible properties are needed. Yi et al.[28] found that a π-conjugated polymer, poly[(*m*-phenylenevinylene)-*alt*-(*p*-phenylenevinylene)] (PmPV) can disperse SWNTs in tetrahydrofuran, and the dispersibility of SWNTs can be controlled by light based on the change in cavity spaces due to the photo-isomerization of the backbone of PmPV. Similarly, Umeyama et al.[17] also got photoresponsive SWNTs through tuning the cavity spaces of azobenzene polymers (PPAzB) upon light irradiation. Although these types of SWNTs exhibit reversible dispersibility in organic media,[17,28] the dispersants for SWNTs based on the conformation change of polymer backbone were restricted in special polymers prepared by cumbersome synthesis processes, which not only results in uncome-at-able for the SWNTs but also impedes their applications usually involved in aqueous environment. Thus, novel water-soluble photo-sensitive polymeric dispersants with unrestricted structure capable of reversible controlling SWNTs are highly desirable.

As mentioned above, azobenzene exhibits light-switchable property due to its reversible photoisomerization between trans and cis forms upon irradiation with visible (Vis) and UV light, leading to the conformational changes of PPAzB. Apart from such a feature, reversible supramolecules can be formed by azobenzene and cyclodextrins (CDs) through host–guest interaction, as azobenzene is the guest for CDs, i.e., trans-azobenzene binds strongly to α- or β-CD, while cis-azobenzene cannot or binds very weakly.[29] Inspired by the photoisomerization and supramolecular nature of azobenzene, common polymers with azobenzene moieties may reversibly interact with CD-containing SWNTs, which enables us to prepare photo-switchable SWNTs with more polymers available and even realize a desired set of properties meant to satisfy given applications involved in aqueous environment.

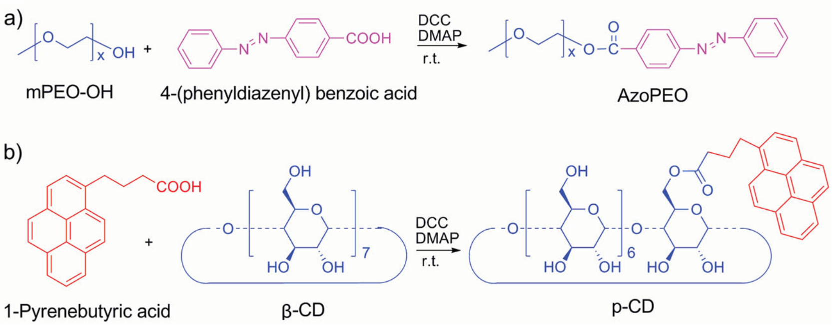
In this report, resorting to the ester condensation between carboxylic acid (-COOH) and hydroxyl (-OH), azobenzene was firstly attached to the water-soluble biocompatible polymer, poly(ethylene oxide) (PEO);[30] then, the best readily available, inexpensive, low toxic and promiscuous recognition β-cyclodextrin (β-CD), possessing a hydrophobic inner cavity and a hydrophilic outer surface,[31] was used as the host for azobenzene and modified with pyrene group to adsorb onto the sidewall of nanotube via π–π interaction.[32] In this way, light-switchable smart SWNTs can be attained by photo-controlled inclusion/exclusion between the azobenzene-containing PEO (AzoPEO) and pyrene-labelled β-CD (p-CD) that is attached onto the surface of nanotubes. This type of SWNTs can undergo reversible dispersion and aggregation induced by a polymer wrapping state to an unwrapping one upon external light stimulus, rendering them attractive in biomedical or sensory applications. In addition, we examined preliminarily the TCFs fabrication by light-induced conformation changes, i.e., yielding SWNT-based film through washing off the polymer in water, which potentially opens up a path for device fabricated environmental-benignly.

2. Results and Discussion

2.1. Synthesis

To bestow the photo-switchable property on nanotubes, AzoPEO and p-CD were synthesized through esterification (**Scheme 1**). Detailed preparation and characterization procedures can be found in the Supporting Information.

As expected, upon irradiation with UV light the absorption band around 325 nm attributable to the π–π^* transition[33,34] of the trans-azobenzene moiety of AzoPEO decreases remarkably, and concomitantly the band at around 440 nm ascribed to the n–π^* transition of cis-azobenzene[33,34] increases slightly (Figure S3, Supporting Information), indicative of the photoisomerization of azobenzene from the trans to the cis state. When irradiated by Vis (sun light) for 24 h, the π–π^* absorption increases again with a slight decrease in the n–π^* absorption, and the absorption at 325 nm recovered to 98.4% of the original value, implying the recovering change from the cis to the trans state of azobenzene group in AzoPEO.



Scheme 1. The synthesis strategies for a) azobenzene-containing PEO (AzoPEO), and b) pyrene-labelled β-cyclodextrin (p-CD).

2.2. Immobilization of p-CD onto SWNTs

To form the photo-switchable supramolecules between SWNTs and guest polymer, the host group should be immobilized onto the surface of nanotube. Thus p-CDs were attached onto the wall of the nanotubes through sonication treatment. To characterize the surface functionalization of the SWNTs, FT-IR spectroscopy was employed. As shown in **Figure 1**a, the original SWNTs are devoid of any identifiable functional groups in the IR spectrum. However, p-CD/SWCNTs show additional broad stretching bands for O–H at 3410.2 cm^{-1}, C = O at 1730.0 cm^{-1} and C–O at 1221.0–1030.0 cm^{-1}, which are assigned to the characteristic absorptions of p-CD given in Figure 1a, indicative of the successful functionalization of the SWCNTs by p-CD. To determine the relative amount of p-CD on SWNTs, thermogravimetry analysis (TGA) measurement was carried out. From the TGA curve given in Figure 1b, the weight percentage of p-CD in the p-CD/SWNTs hybrids was ca. 15.0 wt%, from which we found 1.07×10^{-4} mol of p-CD per 1 g hybrids, providing additional evidence of the complexation between p-CD and SWNTs. To further gain insight into the interactive mechanism of p-CD on SWNTs, Raman spectroscopy which is known for the sensitivity to the electronic structure of SWNTs[35] was used. As exhibited in Figure 1c, the original SWNTs show the second disordered band (D∗) at 2581.2 cm^{-1}, the tangential (G) band at 1581.0 cm^{-1}, and radial breathing mode (RBM) at 100–300 cm^{-1} (like the peak at 155.5 cm^{-1}), respectively, which are characteristic Raman peaks of SWNTs.[35] It should be noted that the original SWNTs show multiple peaks in the range of RBM, indicative of a wide diameter distribution of the tubes.[35e] These results are in good agreement with those of the previous reports,[35e,36] that is, the SWNTs prepared from chemical vapor deposition (CVD) procedure, just like what are used in this work, are always a mixture of tubes with different diameter and helicity. Compared with those of original SWNTs, the corresponding bands of the SWNTs functionalized by p-CD (p-CD/SWNTs hybrids) upshift to 2586.8, 1586.0, and 157.7 cm^{-1} due to the charge-transfer from SWNT to pyrene group absorbed on the tubes,[11d,35b–f] suggesting that a molecular-level interaction occurred between SWNTs and p-CD by π–π stacking.

2.3. Dispersibility of SWNTs in Water

The dispersibility of SWNTs in water is crucial for their applications and device fabrication.[15–17] Exhibited in **Figure 2**a is the appearance of the aqueous dispersions of pristine and modified SWNTs. It can be seen that original SWNTs are insoluble in water, and there is much sedimentation of SWNTs at the bottom of the vial. Similarly, SWNTs modified by p-CD or AzoPEO are also insoluble in water. However, SWNTs modified by both p-CD and AzoPEO (AzoPEO/p-CD/SWNT hybrids) can be dispersed in aqueous media, forming a homogeneous suspension; there was no sedimentation observed even after two months of storage (Figure 2a).

In parallel with the naked eye observation, UV–Vis–near IR (NIR) spectroscopy, a common technique for characterizing SWNT dispersions,[37] was employed to reveal the dispersion state of the ternary hybrids. As shown in Figure 2b, a strong absorbance was observed at 600–1300 nm which is the main range for observing obvious absorption of a favorable dispersion.[17] However, it should be noted that only average

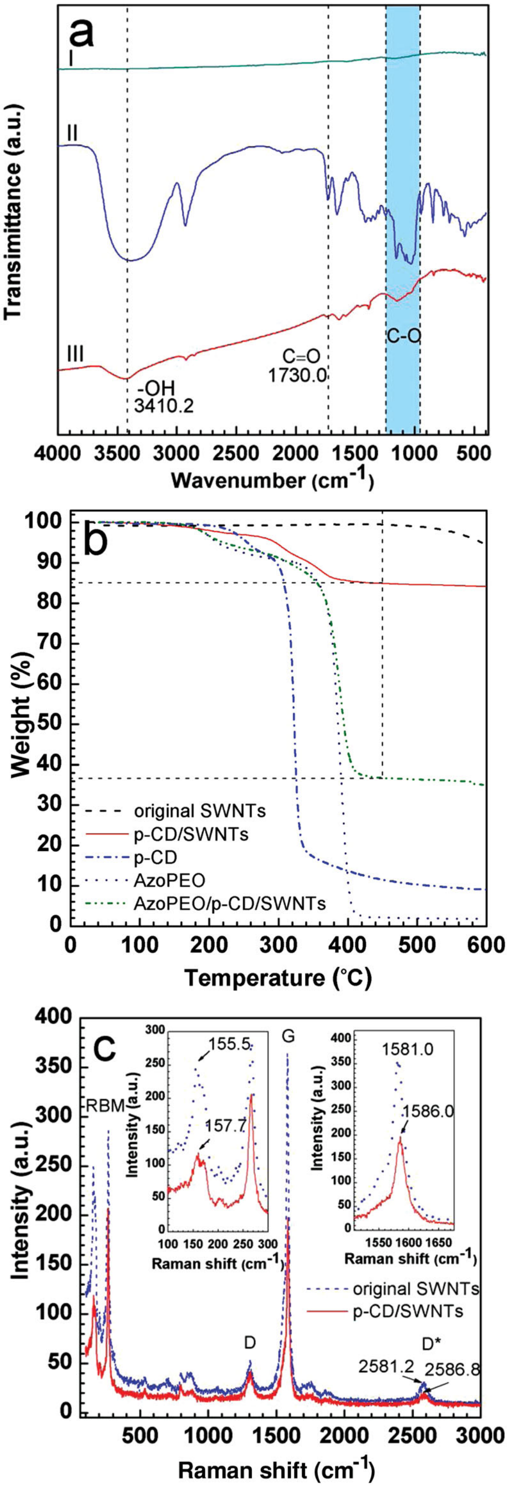


Figure 1. a) FT-IR spectra of original untreated SWNTs (I), p-CD (II), p-CD/SWNT hybrids (III). b) TGA traces for original untreated SWNTs, p-CD/SWNT hybrids, p-CD, AzoPEO/p-CD/SWNT hybrids and AzoPEO. c) Raman spectra of original untreated SWNTs and p-CD/SWNT hybrids.

spectroscopic characteristics of dispersed nanotubes were obtained because SWNTs have a wide diameter distribution as evidenced in Raman spectra. When enlarging the 750–870 nm region in the curve (inset, Figure 2b), one can find sharp peaks which are the absorption features of the van Hove transition semiconducting tubes,[37c] indicative of the exfoliated SWNTs. In order to visualize the AzoPEO/p-CD/SWNT hybrids suspended in water, transmission electron microscopy (TEM) and atomic force microscopy (AFM) observations were carried out, respectively. As given in Figures 2c and 2d, SWNTs were debundled, and the observed diameter of the individual tubes ranges from 3 to 4 nm, two times larger than that of the intrinsic tubes, implying that the nanotubes are surrounded by a thick polymer layer.

As stated above, the AzoPEO/p-CD/SWNT ternary hybrids can be dispersed while p-CD/SWNT and AzoPEO/SWNT binary ones are unable to be dispersed. Such a selective dispersibility may be attributed to the characteristics of p-CD and AzoPEO. As for p-CD, although the CD group is hydrophilic,[8,32d] the p-CD is still insoluble in water because of the incorporation of hydrophobic pyrene, leading to the poor dispersibility of p-CD/SWNT in water; AzoPEO, containing a hydrophilic PEO chain and a hydrophobic azobenzene terminal, may have weak non-covalent interaction with nanotubes via polymer wrapping, and thus is unable to stabilize SWNTs in water. In contrast, when AzoPEO was added into p-CD/SWNT suspension, the formed ternary hybrids unexpectedly showed good dispersibility owing to the host–guest interaction between azobenzene group and CD.

To confirm the host–guest interaction between p-CD/SWNT and AzoPEO, UV–Vis spectroscopy was employed to compare the difference in absorbance between the AzoPEO solution and AzoPEO/p-CD/SWNT hybrids dispersion, as the spectra are known to be very sensitive to the mutual interaction between azobenzene group and CD.[38] As shown in **Figure 3**, absorption peaks are found in the regions of 270–380 nm and 210–270 nm of AzoPEO/p-CD/SWNT hybrids and stronger than those of AzoPEO, resulting from the absorbance of SWNTs. Compared with the peak at 230 nm of AzoPEO, the maximum absorption of the SWNT hybrids is centered at 240 nm, caused by individual SWNTs.[39] It is noteworthy that the absorption peak at 270–380 nm from the ternary system was slightly blue-shifted (2 nm) compared with that of AzoPEO. Such a phenomenon was also observed in the reference systems of AzoPEO and AzoPEO/CD (Figure S7, Supporting Information), indicative of hydrophobic interaction between guest azobenzene and non-polar cavity of CD group.[38] These comparative results clearly show the existence of host–guest interaction between p-CD/SWNT and AzoPEO.

In fact, competition experiments using excess of host or guest compounds clearly demonstrate the complementary host–guest interaction.[40] As given in the inset of Figure 3, when ten equivalents of β-CD to azobenzene unit was added as competitive host, the dispersibility of AzoPEO/p-CD/SWNT hybrids significantly decreased, transforming the homogeneous suspension into aggregated SWNTs (inset b in Figure 3). This finding indicates that the excess β-CD led to the inhibition of complex formation between the CD units in p-CD/SWNTs and azobenzene group, further suggesting the occurrence of host–guest interaction between AzoPEO and p-CD/SWNTs. The weight percentage of AzoPEO in hybrids measured by TGA was ca. 48.7 wt% (Figure 1b) when deducting that of p-CD (ca. 15.0 wt%), from which we can find around 0.96×10^{-4} mol AzoPEO molecules attached onto 1 g hybrids. Such amount of AzoPEO is very close to the content of p-CD (1.07×10^{-4} mol) in 1 g hybrids, implying that each CD group contains one AzoPEO polymer molecule by host–guest interaction.

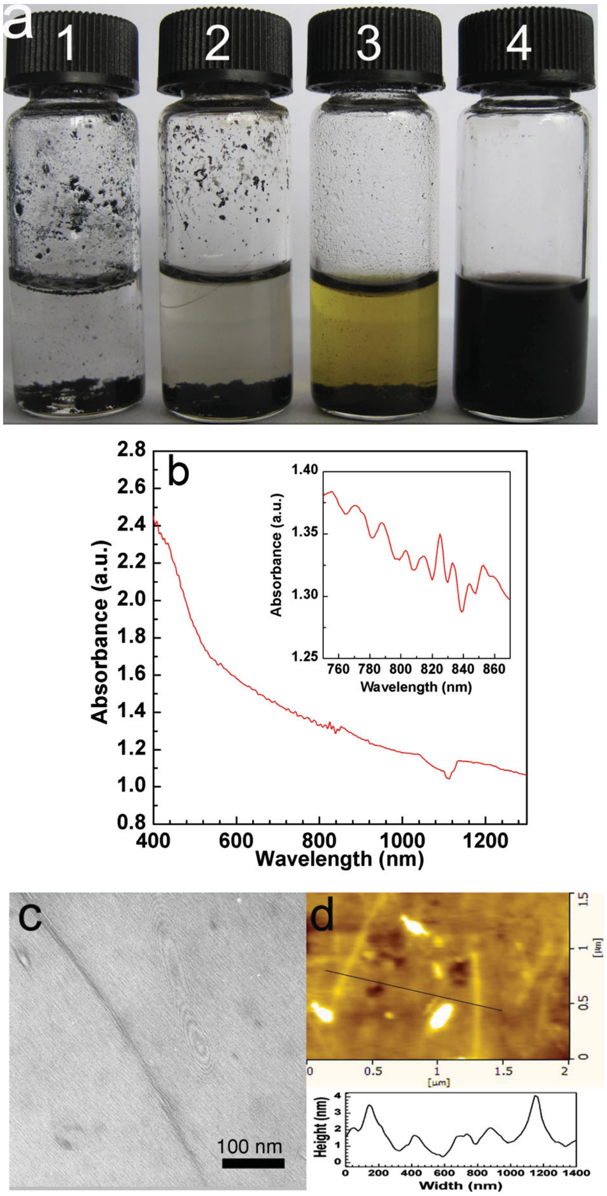


Figure 2. a) Appearances of SWNTs and SWNTs hybrids in water after two months of storage: 1) original SWNTs in H_2O; 2) p-CD/SWNT hybrids (2 mg) in 2 mL H_2O; 3) AzoPEO/SWNT hybrids containing 20 mg of AzoPEO and 2 mg SWNTs in 2 mL H_2O; 4) AzoPEO/p-CD/SWNT hybrids in H_2O (10 mg mL^{-1} of AzoPEO, 1 mg mL^{-1} of p-CD/SWNT hybrids). b) UV–Vis–NIR spectrum of AzoPEO/p-CD/SWNT hybrids (1.66 mg mL^{-1} of AzoPEO, 0.166 mg mL^{-1} of p-CD/SWNTs, 25 °C) in water. c) TEM and d) AFM images of AzoPEO/p-CD/SWNT hybrids dispersed in water.

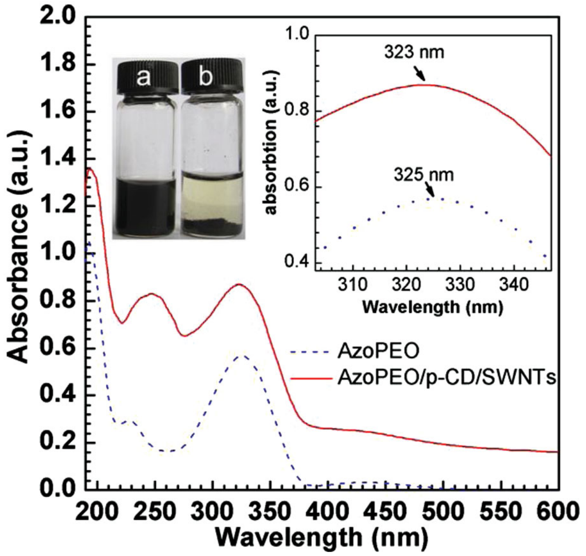


Figure 3. Comparative UV–Vis spectra of AzoPEO (0.2 mg mL^{-1}) and AzoPEO/p-CD/SWNT hybrids (0.2 mg mL^{-1} of AzoPEO, 0.02 mg mL^{-1} of p-CD/SWNT hybrids) in water. The inset images are a) AzoPEO/p-CD/SWNT hybrids dispersion and b) AzoPEO/p-CD/SWNT hybrids dispersion with 10 times of β-CD.

2.4. Light-Switchable Behavior of AzoPEO/p-CD/SWNT Hybrids

Having established that AzoPEO/p-CD/SWNT hybrids were dispersed in aqueous environment, we wondered if the dispersibility of SWNT-based hybrids could be reversibly controlled by UV–Vis irradiation, as azobenzene is known to be sensitive to the stimulus of light.[26] To address this question, the dispersion of tenary hybrids was irradiated with UV and Vis alternatively. Before the treatment with UV, AzoPEO/p-CD/SWNT hybrids exhibited good dispersion in water as described above. Nevertheless, just after 30 minutes of UV irradiation, the hybrids gradually precipitated from aqueous solution (Inset, **Figure** 4a). When the suspension was placed in sunlight for 24 h and followed by sonication for 10 min, the hybrid aqueous solution became homogeneous accordingly. Such a back-and-forth is still effective beyond three cycles of alternative UV and sunlight irradiation, suggesting that the dispersion/aggregation state of AzoPEO/p-CD/SWNT hybrids can be reversibly controlled. During the cycling process, UV–Vis spectroscopy was used to monitor the transmittance alteration of the dispersion (see Supporting Information for details). The wavelength of 600 nm in the visible region was selected to determine the transmittance to exclude the influence of aromatic rings in the polymer.[41] As shown in Figure 4a, the transmittance of the AzoPEO/p-CD/SWNT dispersion is close to "0" under visible environment, while after UV irradiation, the transmittance reaches as high as 85%, indicating that the dispersion/aggregation state of p-CD/SWNT hybrids can be reversibly switched by light.

UV–Vis–NIR spectroscopy was employed again to monitor the variation of the dispersibility of the hybrids upon alternate treatment of UV and Vis. As illustrated in Figure 4b, the sharp peaks corresponding to the absorption features of the van Hove transition semiconducting tubes in the region of 750–870 nm decreases after UV irradiation, because phase separation occurs in the dispersion and the hybrids precipitate. Meanwhile, the characteristics peaks of the SWNTs completely disappeared, indicating that bundled SWNTs were reformed. When the suspension was treated with sunlight and sonication, the characteristics sharp peaks appeared again, indicating that SWNTs were re-dispersed. In order to get more direct information on the dispersion state of SWNTs in water, TEM and scanning electron microscopy (SEM) observations were separately performed to visualize the AzoPEO/p-CD/SWNT hybrids suspension after UV irradiation (Figure 4c,d). Upon UV irradiation, SWNTs were bundled and the observed diameter of the bundled is about 50–100 nm. After sunlight irradiation, SWNTs were separated individually into small-bundle tubes (Figure 4e), implying that the nanotubes were dispersed again.

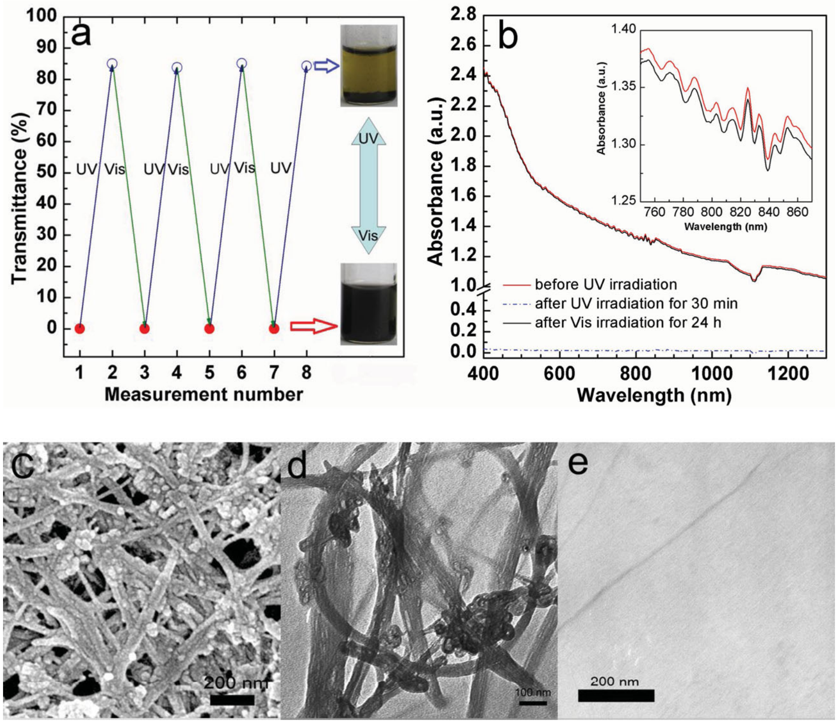


Figure 4. a) Reversible change of the transmittance of the dispersion at 600 nm upon alternative UV and Vis irradiation (10.0 mg mL^{-1} of AzoPEO, 1.0 mg mL^{-1} of p-CD/SWNT, 25 °C). The inset images of the AzoPEO/p-CD/SWNT hybrids dispersed in water refer to corresponding situations. b) UV–Vis–NIR spectrum of AzoPEO/p-CD/SWNT hybrids (1.66 mg mL^{-1} of AzoPEO, 0.166 mg mL^{-1} of p-CD/SWNT, 25°C) in water before and after UV irradiation. c) SEM and d) TEM images of the AzoPEO/p-CD/SWNT hybrids after UV radiation for 30 min. e) the TEM image of AzoPEO/p-CD/SWNT hybrids re-dispersed in water after sunlight irradiation.

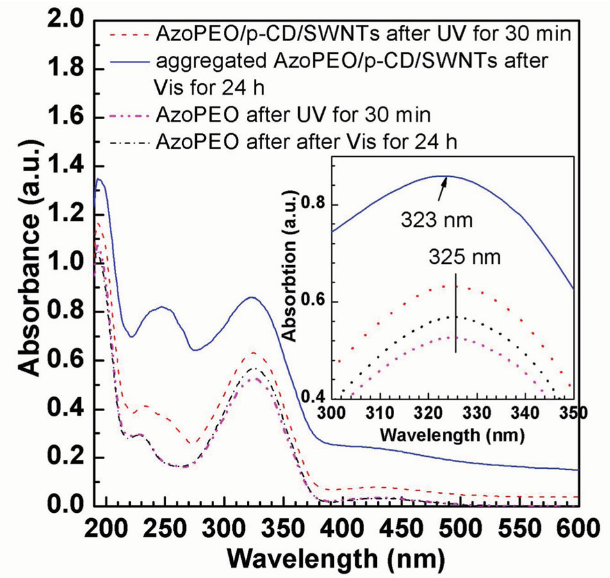
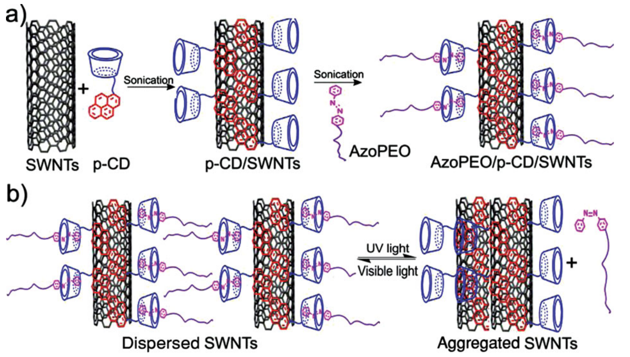


Figure 5. UV–Vis spectra of AzoPEO (0.2 mg mL^{-1}) and AzoPEO/p-CD/SWNT hybrids (0.2 mg mL^{-1} of AzoPEO, 0.02 mg mL^{-1} of p-CD/SWNT hybrids) in water during the light-responsive process.

To elucidate the dispersed/aggregated transition, UV–Vis spectroscopy was further carried out to compare the difference in UV–Vis absorbance upon UV and Vis irradiation. As described above, azobenzene absorptions around 270–380 nm of the AzoPEO/p-CD/SWNT hybrids show blue shift (2 nm) in comparison with that of pure AzoPEO, suggesting that host–guest interaction was formed. In contrast, when the AzoPEO/p-CD/SWNT hybrids were irradiated by UV light, along with the decreasing of absorbance, the characteristic peak of the SWNTs (240 nm) disappeared, reflecting that the hybrids aggregate and precipitate (**Figure 5**). At the same time, the blue-shifted phenomenon vanished, indicating that the host–guest interaction between AzoPEO and p-CD was disrupted. When the suspension was irradiated by Vis irradiation, the absorption of dispersed SWNTs and blue-shifted phenomenon was observed again, indicative of the exfoliating of SWNTs and the reforming of host–guest interaction.

On the grounds of the above results, it is reasonable to speculate that π–π stacking makes p-CD modified SWNTs form p-CD/SWNTs hybrids, and the hybrids are dispersed in water by AzoPEO through host–guest interaction (**Scheme 2**a). The light-switched dispersion of SWNTs in water is ascribed to the polymer with light-responsive azobenzene group and its host–guest interaction with CD absorbed onto surface of SWNTs. As illustrated in Scheme 2b, without UV irradiation, the azobenzene group exhibits trans form, and then SWNTs were dispersed because of the association constant (K_a) of β-CD for trans azobenzene is as high as 1700 M^{-1}.[42] However, after being treated with UV irradiation, the azobenzene group



Scheme 2. Schematic illustration of a) SWNTs modified by p-CD and AzoPEO, and b) its responses to the stimulus of UV or Vis.

is isomerized from trans to cis form,[26,34] leading to the disassembly of host–guest interaction and aggregation of SWNTs, as the K_a of β-CD for cis azobenzene is only 180 M^{-1}.[42] Thus p-CD/SWNTs hybrids aggregated and precipitated from aqueous solution. In contrast, the cis azobenzene group in AzoPEO photoisomerizes upon irradiation with Vis light presents the trans form,[26] and the host–guest interaction was reformed, resulting in dispersion again.

2.5. The Application in Transparent Conducting Films

As AzoPEO/p-CD/SWNT hybrids are sensitive to light, i.e., AzoPEO can be stripped from the SWNTs hybrids after UV treatment, it is anticipated that these hybrids can be used in SWNT-based composite films such as TCFs.[17] Thus, the dispersion of AzoPEO/p-CD/SWNT hybrids was coated onto polyethylene terephthalate (PET) substrate, and resistance measurements were then carried out to reveal the resistance of the films. As shown in **Figure 6**a, along with high transmittance (>87%), the films have high surface resistance (≈10^8 Ω/sq), and increased with increasing film transmittance. However, when the films were placed into water and treated with UV irradiation for 30 min, it was found that the surface resistance of the films was reduced by 78.0%–96.7%, ascribing to the

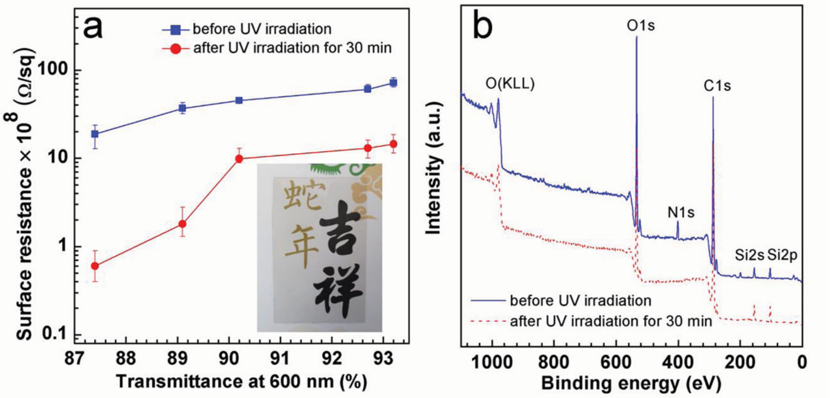


Figure 6. a) Resistance versus transmittance at 600 nm before and after UV irradiation. The inset image is the film after treating with UV. b) XPS survey spectra of the film with 87.4% transmittance before and after UV irradiation.

removal of the dispersant AzoPEO. To confirm that AzoPEO was released by UV treatment, X-ray photoelectron spectroscopy (XPS), an effective technique for surface analysis,[43] was employed to monitor the variation of elements of the coating before and after UV irradiation, respectively. Here, the film with 87.4% transmittance was chosen as an analyte. As given in Figure 6b, the coating contains C, O, N and trace of Si attributed to additives of PET substrates. The relative amount of N element is 4.49%. In addition, the N1s signals were assorted to three different types of nitrogen species (401.7 eV, 400.3 eV, and 399.4 eV) (Figure S8, Supporting Information). The peaks at 401.7 and 400.3 eV are due to the additives in the PET.[43b] The asymmetric peak at 399.4 eV is contributed by $N = N$ of azobenzene group,[43c] and the rate of integral area of the peak is 76.0%, from which we can calculate that the nitrogen content from azobenzene is 3.42%, implying that AzoPEO was present in the coating. However, when the film was treated with UV irradiation, the content of N was reduced to 0.88%, suggesting that nitrogen-containing components were washed off. Nicely, the peak at 399.4 eV almost disappeared after UV irradiation (Figure S8, Supporting Information), and the area rate is only 22.30%, i.e., the nitrogen content arising from azobenzene is 0.19%, which reflects that the dispersant AzoPEO was removed from the coating by 94.44%. Compared with those using organic solvents[17] or treatment with strong acids,[44] the removal of dispersant in water by light stimulus is "greener" and milder. Of course, it should be pointed out that the films have low conductivity because of high resistance ($\approx 10^8$ Ω/sq), which is not sufficient for the applications that need low resistance. Generally, in order to gain SWNT films with high conductivity, high abundance of metallicity, few defects and high purity on the nanotubes are desirable.[45] However, SWNTs prepared by the chemical vapor deposition (CVD) procedure, just like those used in this work, are mostly semiconductors, and have lower purity and more defects than that prepared by arc discharge (Arc), high pressure carbon monoxide (HiPCO), and laser ablation (Laser),[45] leading to the low conductivity of the films. Thus, SWNT-based TCFs with high conductivity should be fabricated by metallic SWNTs with high quality, such as Arc SWNTs or Laser SWNTs. Anyway, such a preliminary finding furnishes a potential way to fabricate SWNTs-based device environmental-benignly.

3. Conclusions

In summary, we have designed and prepared a light-switchable SWNTs aqueous system based on an azobenzene-terminal PEO and its host–guest interaction with CD attached on nanotube noncovalently. The SWNTs hybrids not only are well dispersed in pure water, but also exhibit switchable dispersion/aggregation states upon alternate irradiation with UV and visible light. In addition, we have demonstrated that the hybrid was fabricated in TCFs, and the dispersant AzoPEO can be removed from the films by contamination-free UV treatment. This kind of light-switchable SWNTs hybrids, possessing a ''green'' trigger and intact structure of the nanotube, may find potential applications in sensor of biomedicines, device fabrication, etc. Besides, such a revisable host–guest interaction system may open up the flexibility and diversity to control the dispersion state of SWNTs by other common polymers, and the strategies described in this work can also be used to functionalize graphene in a quick and easy way.

4. Experimental Section

Materials: SWNTs (purity > 90%; OD: 1–2 nm; length: 5–30 μm) prepared by the CVD procedure were kindly provided by Timesnano (Chengdu, China), and used without further treatment. Methoxy poly(ethylene oxide) (mPEO-OH, $M_n = 5.00$ kg mol^{-1}, Aldrich) was dried by azeotropic distillation in the presence of toluene. Dimethylformamide (DMF) was dried and distilled over $MgSO_4$ under reduced pressure and stored under an argon atmosphere. 1-Pyrenebutyric acid (Aldrich, 97%), β-cyclodextrin (β-CD) (Aldrich, 99%), 4-(phenyldiazenyl) benzoic acid (Aldrich, 99%), *N,N′*-dicyclohexylcarbodiimide (DCC) (Aldrich, 99%), and 4-dimethylaminopyridine (DMAP) (Aldrich, 99%), were used as received. Dichloromethane (DCM) (Guanghua Chemicals Co. Ltd., 99.9%) was stirred overnight over CaH_2 and distilled under reduced pressure prior to use. All other reagents were purchased from Shanghai Chemical Reagent Co., Ltd., and used as received unless otherwise specified.

Characterizations: ^{1}H NMR spectra were recorded at 25 °C on a Bruker AV300 NMR spectrometer at 300 MHz. Chemical shifts (δ) were reported in parts per million (ppm) with reference to the internal standard protons of tetramethylsilane (TMS).

ESI-HRMS spectra were taken on the Bruker Daltonics Data Analysis 3.2 system.

UV–Vis spectra were obtained at 25 °C on a UNICO UV–Vis 4802 spectrophotometer (Shanghai, China) with double beam of light.

Molecular weight and molecular weight distribution of the polymer AzoPEO were determined by gel permeation chromatography (GPC) systems (Water 1515-717-2414) equipped with a refractive index detector, using mono-dispersed polystyrene as the standard to get a calibration curve. GPC measurements were carried out at 30 °C using chloroform as eluent with a flow rate of 1.0 mL min^{-1}.

Infrared spectra were registered on a Nicolet MX-1E FTIR (USA) spectrophotometer in the scanning range of 4000–400 cm^{-1} using KBr pellet method.

UV–Vis–NIR measurements were carried out on a computer-manipulated dual-beam spectrophotometer (UV–Vis 4100, Hitashi, Japan) operated at a resolution of 1 nm at 25 °C. Following the previously-reported procedure,[37b] the absorbance in the wavelength range of 1600–400 nm was recorded. However, the wavelength range of 400–1300 nm was finally selected because the absorbance intensity of UV–Vis–NIR spectra of our AzoPEO/p-CD/SWNT suspensions at the wavelength higher than 1300 nm was beyond the measurement range of the instrument.

TEM observation was conducted on a Hitachi H600 electron microscope instrument operated at an acceleration voltage of 75 kV, and the specimen for TEM measurements were prepared by placing one drop of sample on copper grids coated with carbon.

AFM images were taken on a MFP-3D-BIO instrument (Asylum Research). Experiments were conducted in air tapping mode at room temperature. A driblet of the SWNTs dispersion was dropped onto a freshly-cleaved mica substrate. Then the solvent was evaporated in the air.

SEM observation was held on a JSM-7500F (JEOL, Japan).

TGA was conducted on a 299-F1 thermal analysis system (NETZSCH, Germany). Samples were heated in flowing N_2 (50 mL min^{-1}) from room temperature to 600 °C at a heating rate of 10 °C min^{-1}. To gain the sample for TGA analysis, 5 mL of p-CD/SWNT hybrids suspension and 10 mL dispersion of AzoPEO/p-CD/SWNT hybrids were filtered through a PTFE micro-porous membrane (220 nm). Those hybrids left on the membrane were then washed by DMF and water, respectively, and then freeze-dried for 24 h. Original SWNTs, AzoPEO and p-CD for TGA measurements were used without further treatment.

Raman spectra were recorded on LabRAM HR Raman Microscope (HORIBA, France) using He–Ne laser as the light source at 785 nm.

The XPS experiments were performed on a Kratos XSAM800 XPS system (Kratos Ltd.). The measurement parameters are: photon energy (Al K_α) = 1486.6 eV, P = 12 KW × 1 mA. The CASA XPS program with a Shirley background and Gaussian–Lorentzian mix function was used to analyze the XP spectra quantitatively.

A high-pressure mercury lamp with an optical fiber with output power of 500 W was used as the UV irradiation light source. The emissive wavelength was centered on 360 nm. This UV light source was used directly, without any filters. In addition, sunlight was used as visible light source, i.e., the sample sealed in transparent vial was placed outdoors for 2 days.

The surface resistance of SWNT-based transparent thin films was recorded on a SIMCO ST-3 surface resistance tester (SIMO, Japan).

Preparation of Poly(ethylene glycol)-Terminated Azobenzene Derivative (AzoPEO): mPEO-OH (2.212 g, 0.44 mmol), 4-(phenyldiazenyl) benzoic acid (0.211 g, 0.88 mmol), DCC (0.218 g, 1.06 mmol), and DMAP (0.027 mg, 0.22 mmol) were dissolved in 20.0 mL CH_2Cl_2 and added into a 100 mL one-neck round-bottomed flask equipped with a magnetic stirrer. When the solution was homogenized by stirring, it was degassed three times and sealed under argon. After 48 h of agitation at 25 °C, the precipitated solid urea was filtered off. The resultant solid was obtained as yellow solid by precipitating in diethyl ether twice dried under vacuum at room temperature for 24 h to get AzoPEO. Yield: 2.0 g (86.9%). $CHCl_3$–GPC (Figure S9, Supporting Information): M_n = 6899 g mol^{-1}, PDI = 1.46. ^{1}H NMR (300 MHz, $CDCl_3$,, δ): 8.3–7.5 (m, azobenzene H), 3.64 (br s, CH_2CH_2O), 3.37 (s, OCH_3).

Preparation of Pyrene-Labelled β-Cyclodextron (p-CD): To dry DMF solution (7.5 mL) including β-CD (0.50 g, 0.44 mmol) and 2-pyrenebutylic acid (0.10 g, 1.09 mol), DMAP (26.8 mg, 0.22 mmol) was added at 0 °C and stirred for 30 min under nitrogen atmosphere. Then DCC (95.0 mg, 0.461 mmol) was added, and the mixture was stirred at 0 °C for 2 h. Temperature of the mixture was raised to room temperature and the reaction mixture was stirred overnight. After the removal of insoluble salts by filtration, the filtrate was re-precipitated in acetone. The precipitate was washed with water several times to remove p-CD. After drying under vacuum, p-CD was obtained as yellow solid (0.11 g, 0.078 mmol, 15.45%). ^{1}H NMR (300 MHz, DMSO-d_6), δ/ppm: 2.00 (m, 2H, $-CH_2CH_2CH_2-$), 2.40 (t, 2H, $-CH_2$ CO–), 3.00–3.87 (m, β-CD and 2H, Py-$CH_2CH_2CH_2$ –), 4.32–4.44 (m, 7H, O(6)H of β-CD), 4.78–4.90 (m, 7H, CH of β-CD), 5.65–5.77 (m, 14H, OH of β-CD), 7.92–8.40 (m, 9H, pyrene group). ESI-HRMS: Calcd: 1405.4821 (p-CD·H$^+$). Found: m/z = 1405.4827.

Preparation of p-CD/SWNT Hybrids: A solution of p-CD (0.028 mM) was obtained by dissolving 80.0 mg of p-CD in 20.0 mL of DMF. 20.0 mg of SWNTs was added into the prepared solution of p-CD, followed by sonication (KQ-100, Kunshan Ultrasound Instrument Company, China) for 30 min (100 W and 40 kHz) at room temperature. Then the solution was filtered through a PTFE micro-porous membrane (220 nm). p-CD/SWNTs hybrids left on the membrane were then washed by DMF and dried under vacuum at room temperature for 48 h.

Preparation of AzoPEO/p-CD/SWNT Hybrids Dispersion: 20.0 mg of p-CD/SWNTs and 200.0 mg of AzoPEO was obtained by adding into 20.0 mL H_2O, followed by sonication (KQ-100, Kunshan Ultrasound Instrument Company, China) for 30 min (100 W and 40 kHz) at room temperature. Then the resultant suspension was then centrifuged at 4000 rpm with 80-2 centrifuge (Shanghai Medical Instruments Co. Ltd., China) for 10 min to obtain a homogeneous dispersion of SWNTs.

The Light Responses Experiments: the vial with 4 mL of the sample (i.e., AzoPEO or AzoPEO/p-CD/SWNT hybrids solution) with an ice-water cooling system was placed at a distance of 15 cm from UV source and irradiated for 30 min to cause *trans*-to-*cis* isomerization of azobenzene groups. In order to recover the change from the *cis* to the *trans* state, the sample was irradiated by sunlight for 24 h (the sample was placed outdoors for 2 days).

TCFs were fabricated following a previously reported procedure,[43b] which was held on an AFA-II automatic rod-coating system (Shanghai Pushen Chemical Machinery Co. Ltd., China). The details are as follows: about 1 mL of freshly prepared AzoPEO/p-CD/SWNT dispersion was poured onto a 50 μm thick PET substrate. Then, a Mayer rod was pulled over the fluid to form a uniform thin film of the suspensions on the PET substrate at 25 °C. The wet films were dried at 25 °C producing a thin SWNTs hybrids layer on the PET. To remove the unbound polymers, the film was further immersed into water for 2 h, followed by drying at 25 °C for resistance measurements.

UV light treatment for the SWNTs films: the films were immersed into water with an ice-water cooling system, and treated with UV irradiation for 30 min. Then, the films were dried at 25 °C for resistance measurements.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author. It includes ^{1}H NMR and UV–Vis spectra of AzoPEO and p-CD, ESI-HRMS of p-CD, and XPS N1s of the TCFs.

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