Light-Controlled Conductance Switching in Azobenzene-Containing MWCNT−Polymer Nanocomposites

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Ⓢ Supporting Information

ABSTRACT: We report on reversible light-controlled conductance switching in devices consisting of multiwalled carbon nanotube (MWCNT)−polymer nanocomposites blended with azobenzene molecules and photoisomerization of the latter. Both the azobenzene molecules and MWCNT, which are functionalized with carboxyl groups (MWCNT-COOH), are embedded independently in a poly(methyl methacrylate) matrix, and thin films are prepared by using a simple spin-coating technique. We demonstrate the feasibility of the present concept with a photocurrent switching amplitude of almost 10%.
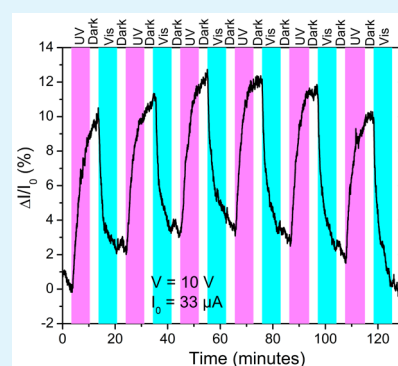
KEYWORDS: photoswitching, conductance switching, carbon nanotube, polymer, nanocomposite, azobenzene

■ INTRODUCTION

Organic devices containing chromophores have been under extensive research for several decades because of applications in the next generation of organic electronics and optoelectronics ranging from nonlinear-optical devices and optical switches to information storage.[1−3] Light-controlled electrical property changes of molecular devices based on chromophore molecules have been studied recently.[4−12]

Several investigations involved the use of diarylethene molecules,[4−7,13−16] which were pioneered by Irie and co-workers.[7] These molecules change their conductance by suitable light illumination. UV-light irradiation leads to a closed-ring conductive state, whereas visible-light irradiation leads to an open-ring nonconducting state.[4−7,13−16] A fundamental problem here was that the molecules lost their reversible photoisomerization functionality once connected to a gold electrode surface, which was a result of strong electronic coupling between the molecules and metal.[13−16] The same effect was reported by Whalley et al. and Ashraf et al. for bridged carbon nanotube (CNT) contacts.[17,18]

Van der Molen et al. overcame this difficulty by employing diarylethene switches with cross-conjugated methaphenyl end groups as molecular bridges between gold nanoparticles in a two-dimensional nanoparticle array.[5] The investigation showed reversible optical conductance switching but suffered from strongly decreasing modulation amplitudes with time. The authors related this phenomenon to photodecomposition due

to excessive UV illumination and the building of photostationary states.

Recently, we reported a new concept to produce light-induced conductance switching devices without using molecules whose conductivity can be switched intrinsically. We used an azobenzene−polymer nanocomposite with embedded metal nanoparticles near the percolation threshold.[19] The mechanism was proposed as being mainly due to a change of the metal nanoparticle separation as the azobenzene molecules undergo the isomerization process and thus change their shape. A pronounced change of the tunneling current was expected, which depends exponentially on the nanoparticle separation. Although the observed reproducibility of the switching amplitude was significantly better and the drift was smaller compared to the results reported by Van der Molen et al.,[5] the switching amplitude was less than 1%.[19]

The most attractive candidates to improve the performance of these devices are CNTs, which have received special attention in designing percolative nanocomposites because of their excellent electrical properties.[20,21] Exploring their hollow core, large surface area, small size, and excellent mechanical and electronic properties, during the last decades, many reports have also shown the capabilities of CNTs as gas sensors

through the charge-transfer or capacitance change by gas adsorption.[22−27]

Recently researchers have utilized the photoisomerization of chromophores to optically modulate conduction in individual nanotube transistors.[8−12,28−30] Mostly the azobenzene molecules are attached covalently or noncovalently with a spacer or linker to single-walled or few-walled CNTs.[8,9,29] In these reports, the conductance of the devices is switched on only by UV irradiation[8,9] or only by visible irradiation (400−650 nm).[29] Back-switching is observed immediately after the light is switched off because of the rapid cis-to-trans thermal reversibility. The light-controlled conductance switching of a multiwalled carbon nanotube covalently linked spironaphthoxazine (MWCNT-SPO) composite film has been reported by Cheong et al.[12] Although the devices are able to be switched in two directions by alternating UV and visible irradiation, the conductivity considerably decreases in the dark, where the merocyanine form converts back to the spironaphthoxazine form once the UV light is turned off.[12] The same result has already been reported by Guo et al.[11] using spiropyran and a single-walled carbon nanotube (SWCNT). More recently, Sciacia et al. published a percolative CNT photochromic polymer blend, where intrinsic conductivity changes of the diarylethene polymer intercalating SWCNTs resulted in switching ratios of up to 3.[31]

In this paper, we demonstrate the feasibility of reversible light-controlled conductance switching of devices based on MWCNT−polymer nanocomposites doped with azobenzene molecules. Our devices are able to switch between two stable conductance states by alternating exposure to 370 nm of UV light and 480 nm of visible light. Using a simple spin-coating technique, we were able to fabricate devices with a photocurrent switching amplitude of almost 10% change. The photoswitching directions in the present MWCNT−polymer nanocomposites are opposite to the behavior observed in our previous work on metal−polymer nanocomposites and reflect a different switching mechanism.

■ EXPERIMENTAL PART

1. Materials. To fabricate our samples, we used carboxyl-group-functionalized multiwalled carbon nanotubes (MWCNT-COOH), which were supplied by Arry International and were directly used without further treatment. The tubes had a diameter of 20−30 nm and a length of 15 μm. The purity was >95 wt % with 0.5−3 wt % −COOH and <1.5 wt % ash content according to the supplier. The azobenzene molecule that we used was 4′-hexylphenyl[4-(propylbutoxy)phenyl]diazene (Figure 1), which has a branched carbon chain to prevent crystallization and aggregation.[32] Poly(methyl methacrylate) (PMMA) powder was used for the polymer matrixes of the devices and was supplied by Polymer Source Inc. with an average molecular weight of 9850 g mol^{-1} (M_w/M_n = 1.09). Polystyrene (PS) was used to provide a dispersed solution of MWCNT-COOH and was supplied by Fluka Chemie GmbH with a molecular weight of 200000 g mol^{-1}. Toluene, which was supplied by Sigma-Aldrich GmbH with purity 99.8%, was used as a solvent without further purification.

2. Sample Fabrication. We applied two different procedures of sample fabrication. The first type of sample (referred to as S1) was produced by direct spin coating of 0.5 wt % MWCNT-COOH, 50 wt % azobenzene molecules, and PMMA, which were mixed together in a toluene solution using a Bandelin Sonorex RK 52 bath sonicator for 30 min. This solution was spin-coated on a glass substrate with two sputtered 1-mm-wide gold contacts with a 0.3 mm gap using a model P6700 series spin coater from Specialty Coating Systems, Inc. The thickness of the dried film, measured with a DEKTAK8000 profilometer, was 150 nm. The same procedure was used to fabricate
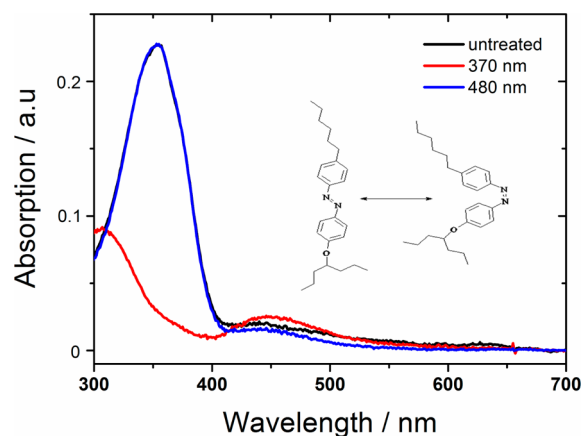
Figure 1. Absorbance spectra showing fully reversible photo-isomerization of PMMA with 40 wt % of the azobenzene moiety 4′-hexylphenyl[4-(propylbutoxy)phenyl]diazene.

the reference sample, which contained 1 wt % MWCNT-COOH and PMMA.

The second type of sample (referred to as S2) was produced by first depositing a precursor film of MWCNT-COOH on a glass substrate with sputtered-on 0.3-mm-gap gold contacts. The dispersion of 3 wt % MWCNT-COOH, 50 wt % azobenzene molecules, and PS in toluene was produced using a Bandelin Sonorex RK 52 bath sonicator for 30 min. The film was prepared by spin coating this dispersion on a glass substrate. Afterward, the matrix was washed away using toluene to remove the azobenzene−polymer blend and leaving the CNTs on top of the glass substrate. This procedure was repeated at least three times until a conductive CNT network was formed. (A sequence of SEM pictures for these preparation steps can be found in Figures S2−S4 in the Supporting Information, SI.) After washing and drying, 40 wt % azobenzene molecules and PMMA in a toluene solution was drop-casted onto this MWCNT-COOH template. The drop was put in the gap of the gold contacts. The sample was then dried in open air and degassed in a vacuum oven overnight.

3. Characterization. Concerning the details of the optical investigations of the azobenzene−PMMA composite, analyzed by UV/vis spectroscopy (Laser2000), we refer to our previous investigations.[19,32,33] The electrooptical investigations were carried out using a homemade setup partially purchased from Newport including a 500 W xenon lamp, a monochromator (bandwidth 20 nm), an energy detector, and a self-mounted sample holder for in situ electrooptical measurements. The measurement parameters were controlled using a *LabView* program. The changes in conductance were measured in situ with a picoampere meter (Keithley model 6485 integrated voltage source; setup leakage currents on the order of 10^{-10}). If not noted otherwise, the irradiation conditions were 370 nm (3 mW cm^{-2}) for UV light and 480 nm (9 mW cm^{-2}) for visible light.

■ RESULTS AND DISCUSSION

A typical UV/vis absorption spectrum of an as-prepared nanocomposite sample containing 40 wt % azobenzene molecules in a PMMA matrix and typical spectra after UV and visible irradiation are shown in Figure 1. The stable configuration of the azobenzene moiety prior to light exposure is the trans state, indicated by a maximum absorption peak at 350 nm. Upon alternation of UV and visible irradiation, the molecule shows a fully reversible and reproducible switching from trans to cis to trans configuration. The illumination wavelengths for this reversible transition are typically chosen close to the two absorption maxima, as shown in Figure 1. The details of the investigations on the switching behavior of this composite were previously reported.[19,32,33]

Figure 2 shows a scanning electron microscopy (SEM) image of a sample of type S1, which was prepared by direct spin
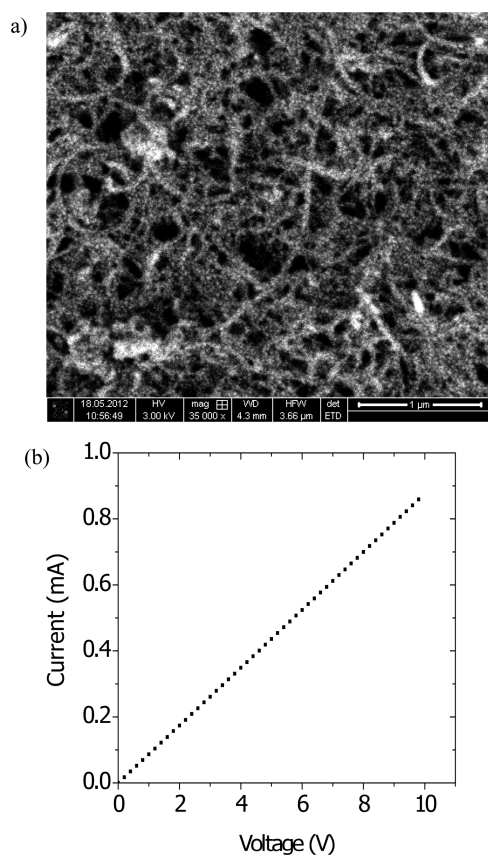

Figure 2. (a) SEM image showing the formation of a dense network of MWCNTs in a sample of type S1 prepared by direct spin coating of a solution containing a mixture of 0.5 wt % MWCNT, 50 wt % azobenzene molecules, and PMMA. (b) $I-V$ curve obtained from a typical region with a dense MWCNT network.

coating of a dispersion containing MWCNT-COOH, azobenzene molecules, and PMMA. One observes the formation of a dense network of MWCNTs. We note that, on a millimeter scale, regions of very low MWCNT density were observed between regions with a dense MWCNT network. In the present measurements, the contacts were always bridged by dense MWCNT networks. An optical microscopy image showing a larger sample section is displayed in Figure S1 in the SI.

The $I-V$ curve of the sample in Figure 2a is shown in Figure 2b. The high current and linear behavior clearly show that the MWCNTs form a percolating network of MWCNTs. Apparently, electron hopping through the polymer matrix at MWCNT–polymer–MWCNT junctions is not rate-limiting; otherwise, the $I-V$ curve would be nonlinear because of the increase in the tunneling current with increasing voltage.[34]

Figure 3 shows the photoswitching behavior of a sample of type S1. One notes that the current increases upon UV irradiation by about 2% and decreases again upon visible irradiation. Unlike in the aforementioned photoswitching device of Van der Molen et al.,[5] the switching amplitude does not decrease upon repeated switching.

To ensure that the photoswitching effect is due to the presence of the azobenzene molecules, we also measured the photocurrent effect of the reference sample without chromo-
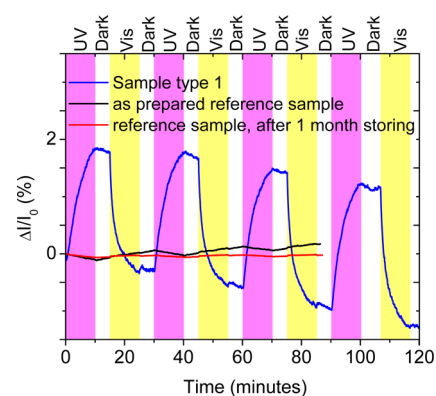
Figure 3. Photoswitching behavior of the sample of type S1 containing 0.5 wt % MWCNT-COOH and 50 wt % azobenzene molecules in PMMA, together with an as-prepared reference sample without chromophores and a reference sample stored for 1 month at ambient conditions in the dark. The sample with chromophores was stored for 3 days. The measurements were carried out at 1 V and 0.061 mA.

phores. As seen in Figure 3, the as-prepared reference sample shows a very small response during illumination cycles. The current slightly decreases upon UV irradiation and increases upon visible irradiation. In the dark, the current increases at almost the same rate as the current increase upon visible irradiation. In any case, the different directions and magnitudes of the current change observed in the sample and reference sample demonstrate that the photoswitching of the sample is due to the presence of the azobenzene molecules. The origin of the drifts present in both sample types will be discussed below.

It has to be pointed out that the light-induced conductance switching seen in Figure 3 is opposite to the behavior of our aforementioned azobenzene–polymer nanocomposites with embedded metal nanoparticles near the percolation threshold,[19] where the conductance dropped upon UV irradiation and increased upon visible irradiation. In the nanocomposites with embedded nanoparticles, the switching mechanism was discussed in terms of a geometrical effect, where the photoisomerization process changes the separation between the metal nanoparticles and, hence, the tunneling distance. The opposite switching direction and linear $I-V$ curves in the present MWCNT-based devices clearly rule out a similar geometrical effect resulting from a change in the nanoparticle separation and rather suggests an electronic effect due to the different electronic interactions between the MWCNTs and chromophores in the cis and trans states.

There are indeed papers that discuss the electronic interaction between azobenzene-containing photoswitchable molecules and CNTs for conductance switching applications.[9,29] Simmons et al.,[9] for instance, discuss the effect of a change in the dipole moment upon photoisomerization on the conductivity of a field-effect transistor containing CNTs that were noncovalently functionalized with azobenzene using a linker to anchor the azobenzene molecules on the CNT side wall. Azo dyes are known to have an electrical dipole moment in their cis form, which is greatly reduced when the chromophore is switched to the thermodynamically stable trans isomer.[35] Like in the present work, the authors measured a current increase after trans-to-cis isomerization similar to that of our devices. However, the chromophores used by Simmons et al. were not stable in the cis state and exhibited an immediate thermal back-isomerization after UV irradiation was switched

off.[9] Jung et al.[36] and Jacob et al.[37] found reduced lifetimes for the excited state of azobenzene "platform" molecules compared to solutions when these molecules are adsorbed via their platform π system on gold surfaces. The authors explained this effect with strong electronic coupling between the molecular platform molecules and gold substrate. Whether this effect could be reduced by adding an isolating spacer group between the platform and photoswitchable unit is currently under investigation.[36] For this reason, we did not attach the azobenzene molecules directly to the CNTs, e.g., via pyrene units as CNT-philic groups.[38] Our approach to circumvent the problem of fast thermal back-switching is to distribute the molecules in a polymer matrix that is surrounding the CNT network. We showed recently that the dielectric properties of a highly doped polymer film can be reversibly switched by photochromic molecules on the order of 50% because of the different dipole moments in the trans and cis states, respectively.[33] The ohmic $I(V)$ dependence observed by us clearly identifies a percolating MWCNT network. Therefore, a contribution of the two azobenzene isomers as an integral part of the conduction path between the CNT tubes can be ruled out. This is supported by the observation that the conductivity of PMMA samples with 50 wt % azo content with no MWCNTs added showed no conductivity in the range of our setup. We thus also attribute the reversible photoswitching with stable amplitude observed in our samples to the large change in the dipole moment of the azobenzene moiety upon isomerization due to the reasons mentioned above. We cannot completely rule out that other mechanisms contribute also to the observed conductivity changes, and thus further investigations are needed to fully clarify the switching mechanism.

To further support our view, we tested another type of sample. We expect that increased interaction of azobenzene molecules with CNTs results in a higher photocurrent switching amplitude. This implies that the CNT should be dispersed very well to increase the interaction area. In order to obtain a better dispersion, we prepared samples by first dispersing the CNTs on a glass substrate and afterward dropping the azobenzene molecule containing PMMA solution on it (see the section on sample preparation for samples of type S2). In our experiments, several approaches for the CNT network creation were used. CNT and CNT/PS dispersions in toluene were some of those approaches. However, the best results were achieved with the method mentioned in the S2 procedure. Further we point out that no photoswitching was observed for samples after washing with toluene prior to deposition of the PMMA/azobenzene solution.

The resulting photoswitching behavior is shown in Figure 4. One notes a strong increase in the photoswitching amplitude, which is now as large as 10%. The above-mentioned baseline drift is also seen for the samples of type S2. One has to point out, however, that the switching amplitude is stable, as for the S1 type samples, and does not change from cycle to cycle.

Without azobenzene molecules, the CNT also seems to exhibit a weak response to UV and visible light, as seen from the curves of the reference sample in Figure 3. The slight current change in this figure could be due to the adsorption and desorption processes of oxygen, as suggested by Collins et al.[22] Because of the high electron affinity of oxygen and the hole-type characteristic of MWCNTs,[23,25] the adsorbed oxygen withdraws electrons from the CNTs and thus leads to an increase in the conductivity. UV-light irradiation induces a current decrease in the sample due to a molecular photo-
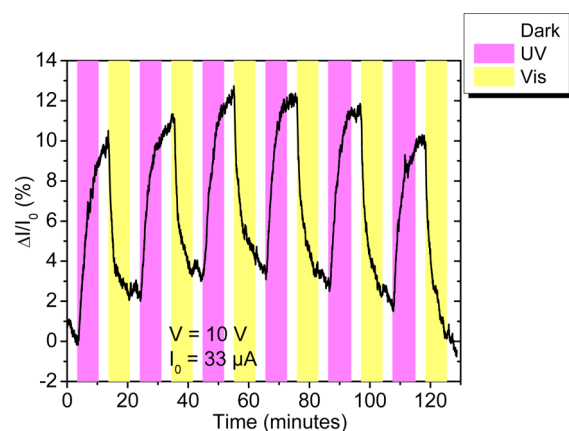
Figure 4. Photocurrent change of a sample of type S2 prepared by dispersing a PMMA solution containing 40 wt % azobenzene molecules on a MWCNT-COOH film on a glass substrate.

desorption effect from the CNT.[25,39] When the UV light is switched off, the CNT, again, adsorbs the molecules in air, which leads to the conductivity increase.

This photodesorption process is one of the origins for drifts found in Figure 3. The second is related to the measurement. We found that our devices respond to currents that are directed through the sample. For a photoresponse of our devices on the order of several percent, the devices had to be measured at a minimum at the 10^{-5}–10^{-6} A current range to stay above the detection limit of our setup. However, in this current range, drifts are present in our devices, as can be seen in Figure 5. A
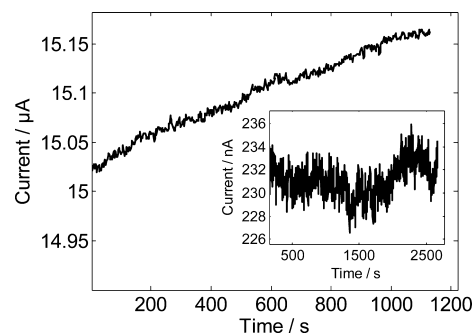
Figure 5. Drifts present in the samples without illumination as a response to different currents directed through the devices. The voltage in the main graph was 1 V. The inset shows the behavior at 0.02 V.

sample was prepared similarly to the device in Figure 3 and subjected to two different voltages of 1 and 0.02 V without any illumination. At 1 V, we see a clear drift, while the direction of the drift to higher currents is not representative because the opposite case could also be measured. At lower currents, the resistance of the device seems to be stable (see inset in Figure 5). The origin of this effect is unclear but is very likely due to modifications of the microstructure in the composite because locally the current densities can reach large values and cause temperature gradients.[40,41]

■ CONCLUSIONS

We demonstrated light-induced conductance switching in percolated MWCNT−polymer nanocomposites containing azobenzene-based chromophores, which do not exhibit intrinsic

switchability of the conductivity. In contrast to approaches based on diarylethenes and other chromophores with intrinsically switchable conductivity, no decrease of the switching amplitude was observed from cycle to cycle. The switching amplitude is strongly enhanced compared to metal−polymer nanocomposites containing the same chromophores. In contrast to the latter, the switching effect does not result from a geometrical effect but appears to be due to a photoswitchable interaction of the CNT network with the azobenzene dipoles in the dielectric polymer film.

■ ASSOCIATED CONTENT

ⓢ Supporting Information
Microscope image of composite S1 and an SEM sequence of the preparation steps for S2-type samples. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b01319.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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