Electrochemical fabrication of single-walled carbon nanotubes– DNA complexes by poly(ethylenedioxythiophene) and photocurrent generation by excitation of an intercalated chromophore †

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It was found that single-walled carbon nanotubes (SWNTs) solubilized into water by complexation with DNA (salmon testes) can be readily deposited on the ITO electrode by electrochemical oxidative polymerization of ethylenedioxythiophene (EDOT). The driving force for this novel deposition is an electrostatic interaction between the anionic charges of wrapping DNA and the cationic charges of poly(EDOT) formed in the oxidative polymerization process. The presence of poly(EDOT), SWNTs and DNA in the composite was confirmed by measurements of UV-Vis, IR, resonance Raman spectra, cyclic voltammetry (CV) and confocal laser scanning microscopy (CLSM). The composite adsorbed a DNA intercalator (ethidium bromide: EB) very efficiently, which is regarded to be further evidence for inclusion of DNA. The surface morphology, characterized by CLSM, SEM and AFM, featured the network structure consisting of 0.5–*ca.* 10 μm nanorods. Very interestingly, we found that photoexcitation of EB bound to the DNA generates the photocurrent, indicating that the excited energy of EB is injected into SWNTs, which is collected by the electroconductive poly(EDOT) film on the ITO electrode. We believe, therefore, that the present system is a very convenient method to explore new materials related to redox and photochemical functions.

Introduction

Recently, we and others have explored a new method to transcribe a variety of organic superstructures into inorganic materials by a sol-gel reaction of metal alkoxides ('sol-gel transcription'), by which one can precisely control the morphology of inorganic compounds and create various new superstructural inorganic materials.[1–7] It is known that in particular, when superstructures comprised of molecular assemblies constituted from low molecular-weight gelators in the gel phase[8] are used as templates and sol-gel polycondensation of tetraethoxysilane is applied to their fabrication, the organic template architectures are scrupulously transcribed into the silica. The primary driving force operating in these sol-gel transcription systems is considered to be an electrostatic interaction between 'anionic' silica nanoparticles and 'cationic' organic assemblies acting as templates. These examples provoked us into a new idea that 'anionic' superstructures would also be useful as templates to transcribe them into some 'cationic' polymer-forming materials. Thus, it occurred to us that the morphology of conductive polymers obtained from pyrrole, thiophene, aniline, *etc.* would be controllable, applying this template method to their electrochemical polymerization processes;[9] as oxidative polymerization of these monomers produces 'cationic' intermediates, the 'anionic' assemblies should act as appropriate templates due to the mutual electrostatic attractive force. Poly(ethylenedioxythiophene: EDOT) is a well-known conductive polymer easily obtained by electrochemical polymerization of EDOT.[9] Despite the convenience of the preparation method, however, the applications have been

rather limited. One major reason is the serious drawback related to the difficulty in controlling the morphology in the polymerization process. Only a few examples have been reported; for example, it is known that the presence of anionic micelles affects the resultant poly(aniline) morphology.[10,11] To the best of our knowledge, however, there was no precedent for such a general concept to control the morphology of these conductive polymers until we recently proposed this idea.[12,13] In fact, the morphology of the superstructure acting as the template had never been strictly compared with that of the resultant polymer in order to clarify whether the fine transcription is really attained or not. So far, we have demonstrated that a [60]fullerene-*p*-sulfonatocalix[8]arene complex (low molecular-weight compound), a self-assembled 5,10,15,20-tetrakis (4-sulfonatophenyl) porphyrin (molecular assembly) and a SDS-single-walled carbon nanotube (SWNTs) composite (supramolecular complex) are useful as templates for transcribing their specific superstructures into the conductive polymers.[13]

Here, we noticed that an 'anionic' polymeric template which is not yet applied to this system but would be the most attractive candidate is a '*polynucleotide*' (DNA). It is known, however, that the higher-order structure of DNA is sensitively affected by the medium conditions and may not act as an appropriate template. Very recently, Nakashima *et al.* demonstrated that double stranded DNA is capable of wrapping SWNTs to dissolve them into aqueous solution.[14] Because of the rigid nature of the complex, it should be suitable for the template of the present system. We have found that the complex is readily deposited onto an ITO electrode by electrochemical polymerization of EDOT. Furthermore, when ethidium bromide bound to DNA was photoexcited, a signicant amount of photocurrent was generated.

† Electronic supplementary information (ESI) available: CV and UV/VIS spectra. See http://www.rsc.org/suppdata/ob/b4/b402044h/

Results and discussion

Fabrication of the SWNTs·DNA complex

The SWNTs·DNA complex was prepared from SWNTs (1–10 μm length) and salmon testes DNA according to the method prepared by Nakashima *et al.*[14] This aqueous solution was mixed with a LiCl solution of EDOT: the final concentrations were [EDOT] = 10 μmol dm^{-3}, [LiCl] = 50 mmol dm^{-3}, [DNA] = 0.113 mg ml^{-1} and [SWNT] = 0.0165 mg ml^{-1}. The oxidative polymerization of EDOT was carried out in a cyclic voltam-mometry (CV) cell in a voltage range of −0.5–1.0 V (*vs.* Ag/AgCl) with a scan rate of 50 mV s^{-1} at 25 °C. With the increase in the scanning cycle the magnitude of the CV redox waves increased, indicating that the poly(EDOT) film is constructed on an ITO electrode (ESI: Fig. S1 †). The CV pattern is similar to that obtain from electrochemical polymerization of EDOT itself under the same reaction conditions (ESI Fig. S2 †).[13] The oxidized and reduced states of an obtained poly(EDOT) film deposited onto the ITO electrode was characterized by UV-Vis spectroscopy. The oxidized state showed a weak absorption band in the visible region and a strong absorption band in the near-IR region, whereas the reduced state showed a broad absorption band at 450–550 nm because of the π→π* electronic transition (Fig. 1). The CV waves and UV-Vis spectral change were very similar to those of the poly(EDOT) system. The results indicate that the composite film comprised of SWNTs·DNA complex and poly(EDOT) is deposited onto the ITO electrode.
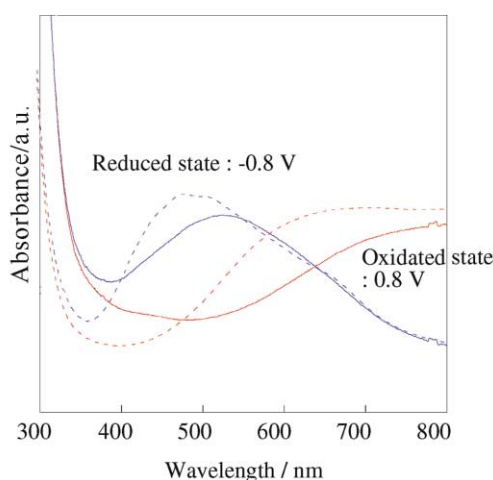

Fig. 1 UV-Vis absorption spectra of poly(EDOT) film (dashed line) and SWNTs·DNA/poly(EDOT) composite film (solid line).

To confirm the deposition of SWNTs in poly(EDOT), we measured the resonance Raman spectroscopy, because it is known that SWNTs have a characteristic Raman peak at 1593 cm^{-1}.[15] As shown in Fig. 2, the SWNTs·DNA/poly(EDOT) composite film gives a weak but perceptible peak at 1591 cm^{-1}, in addition to peaks at 1432 and 1512 cm^{-1} (C=C stretching) and 1366 cm^{-1} (C–C stretching). To find evidence for inclusion of DNA is more difficult. One line of evidence was obtained from the FT-IR spectrum: the SWNTs·DNA/poly(EDOT) composite film gives the peak at 1639 cm^{-1} and 984 cm^{-1} which are attributable to C=O and P–O stretching bands, respectively. These peaks are not found in the poly(EDOT) film. Further evidence was obtained from the binding of ethidium bromide (EB), a cationic intercalator. The modified ITO electrode was immersed in an aqueous solution containing EB (0.5 mg ml^{-1}) for 64 h at 25 °C. Then, the modified ITO electrode was rinsed with water for 30 min. As shown in Fig. 3, a new absorption maximum appeared at 485 nm, which is ascribable to EB. Since (i) further rinsing treatment did not decrease the absorbance of EB and (ii) poly(EDOT) film itself did not bind EB, one can
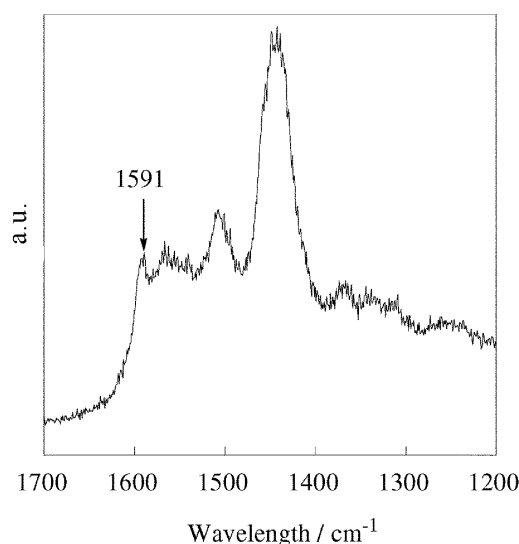

Fig. 2 Raman spectrum of SWNTs·DNA/poly(EDOT) composite film.
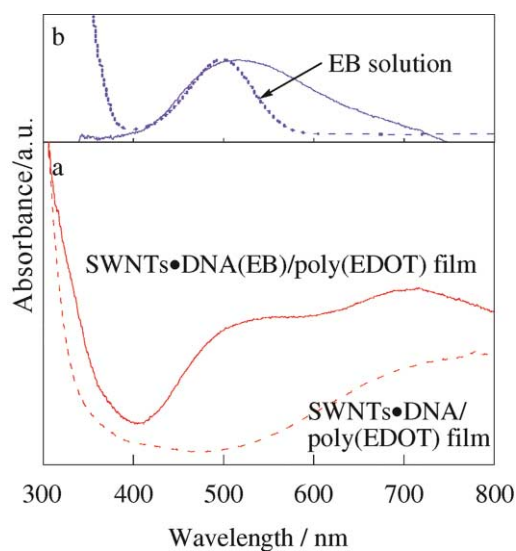

Fig. 3 UV-Vis absorption spectra: (a) SWNTs·DNA/poly(EDOT) film (dashed line) and SWNTs·DNA(EB)/poly(EDOT) composite film (solid line), (b) differential spectrum of (a) spectra (solid line) and absorption spectrum of EB in water (dashed line).

attribute this EB binding to intercalation of EB into DNA included in the composite.

On the basis of the foregoing findings, one can conclude that the SWNTs·DNA complex can be efficiently fabricated by poly(EDOT) through electrochemical polymerization.

Surface morphology as observed by CLSM (confocal laser scanning micrograph), TEM and AFM

Since the SWNTs·DNA/poly(EDOT) composite film is able to bind EB, a fluorescent intercalator, the morphology is directly observable by CLSM. As shown in Fig. 4b, the CLSM image features an entangled aggregate of structures, which is totally different from the rod-like or circular aggregates observed for the DNA/poly(pyrrole) composite film (without SWNTs).[16] When the red spot was photoexcited at 488 nm, the corresponding fluorescence spectrum gave a fluorescence maximum at around 595 nm (Fig. 4a). The finding indicates that these fibers include EB-binding DNAs. In the optical microscope, only SWNTs show up as a black shadow in the screen. As can be seen in Fig. 4c, the black shadow constructs the same pattern as that in Fig. 4b. It is without doubt, therefore, that these fibrous structures are constructed by SWNTs·DNA/poly-(EDOT) composites; that is, SWNTs play a primary role in
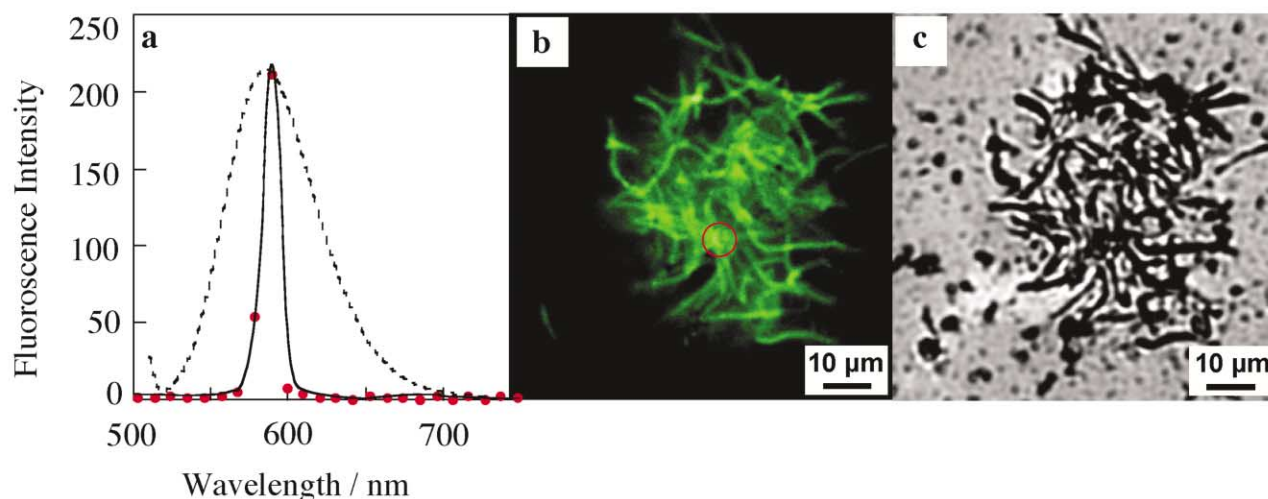
Fig. 4 CLSM images of SWNTs·DNA(EB)/poly(EDOT) composite film: (a) fluorescence spectrum obtained by excitation of the red spot at 488 nm (solid line) and that of EB in aqueous solution (dashed line), (b) fluorescence image, (c) optical microscope image.

determining the observed fibrous structure and DNA wrapping the SWNTs acts as a 'glue' to attach them to poly(EDOT).

Fig. 5 shows a SEM image of the ITO electrode surface covered by the SWNTs·DNA/poly(EDOT) composite film. One can recognize the presence of fibrous structures with 0.5–*ca.* 10 μm length and 50–100 nm diameter. The length is comparable with that of used SWNTs (1–10 μm) and the morphology is similar to that observed for the SWNTs·DNA complex reported by Nakashima *et al.*[14] Although the diameter is much larger than that of used SWNTs (0.8–1.2 nm), the difference is readily rationalized in terms of wrapping by DNA and subsequent fabrication by poly(EDOT).
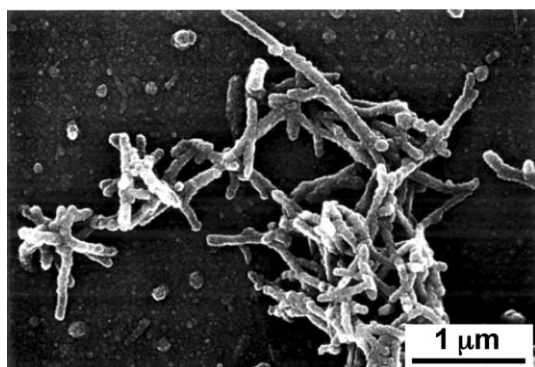

Fig. 6 AFM image of SWNTs·DNA/poly(EDOT) composite fibers obtained from the electrolyte solution.

Fig. 5 SEM image of the surface of SWNTs·DNA/poly(EDOT) composite film.

After redox treatment of 100 cycles in an electrochemical cell, the electrolyte solution was subjected to extensive dialysis. The resultant solution was cast on a mica and the surface was observed by AFM. As shown in Fig. 6, one can recognize the presence of fibrous structures with 1–2 μm length and *ca.* 20 nm height. From the similarity with the structure observed by SEM for the ITO electrode surface, we consider that they are also SWNTs·DNA/poly(EDOT) composite fibers which are not deposited on the ITO electrode. Since the length is a little shorter and the diameter (which should be comparable with the height in AFM) is significantly smaller than those observed for the ITO electrode surface, one may consider that the longer SWNTs·DNA/poly(EDOT) composites are preferably deposited over the shorter ones and subsequent electrochemical polymerization proceeds predominantly on the surface.

Generation of a photocurrent wave

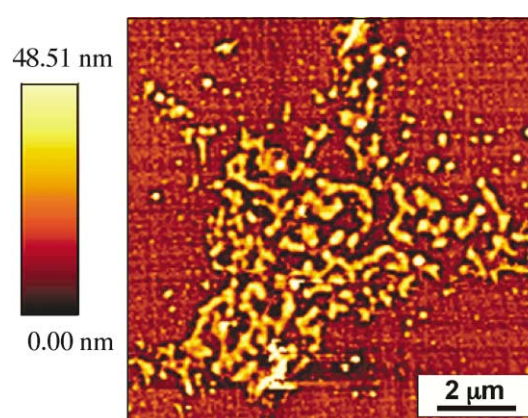In relation to photochemical properties of SWNTs, DNA and poly(EDOT), it is known that (i) SWNTs yield the excited species when they are photoirradiated at 220–400 nm,[13,17] (ii) DNA binding certain dyes (intercalators) generates photocurrent when the dyes are photoexcited[18] and (iii) poly(EDOT) is also photoexcited by irradiation at around 400 nm to generate photocurrent.[13] Based on these foregoing findings, one may envisage a novel, very intriguing photocurrent generation system consisting of EB → SWNTs → poly(EDOT) → ITO electrode for the EB-binding composite film, *i.e.*, SWNTs·DNA(EB)/poly(EDOT). However, concurrent cascades which do not include all of these three components (EB, SWNTs and poly(EDOT)) should be also taken into consideration.

Firstly, we evaluated whether the photoexcited energy of EB is really transferred to SWNTs in homogeneous phosphate buffered saline (PBS, pH = 6.98): [PBS] = 50 mmol dm^{-3}. The absorption band of EB (λ_{max} 488 nm) was reduced to about a half by the addition of DNA (ESI Fig. S3†). The absorbance in the presence of the SWNTs·DNA complex was scarcely changed from that in the presence of DNA (Fig. S3)†, although the absorbance of EB in the presence of DNA was somewhat decreased from that in the absence of DNA due to the stacking of EB with a DNA base pair.[19] On the other hand, the fluorescence spectra were largely changed (Fig. 7). The fluorescence intensity of EB (Em_{max} 595 nm) was increased when it was bound to DNA. This is due to the hydrophobic environment provided by DNA. In the presence of the SWNTs·DNA complex, the fluorescence intensity was drastically decreased nearly to zero (Fig. 7). The difference in the additive effect between DNA and the SWNTs·DNA complex is clearly seen in Fig. 8. These results support the view that the photoexcited energy of EB is efficiently transferred to SWNTs.
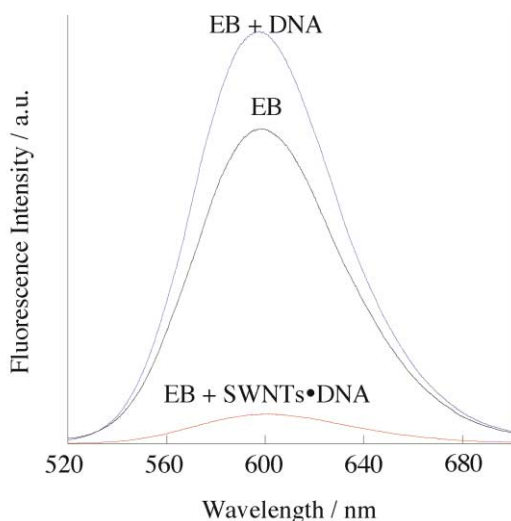
Fig. 7 Fluorescence spectra of EB, EB + DNA and EB + SWNTs·DNA complexes in 50 mmol dm^{-3} phosphate buffered saline (pH 6.98) at 25 °C; [EB] = 50.7 μmol dm^{-3}, [DNA] = 1.33 mmol dm^{-3} (base unit), [SWNT] = 2.97 μg dm^{-3}, excitation 485 nm.
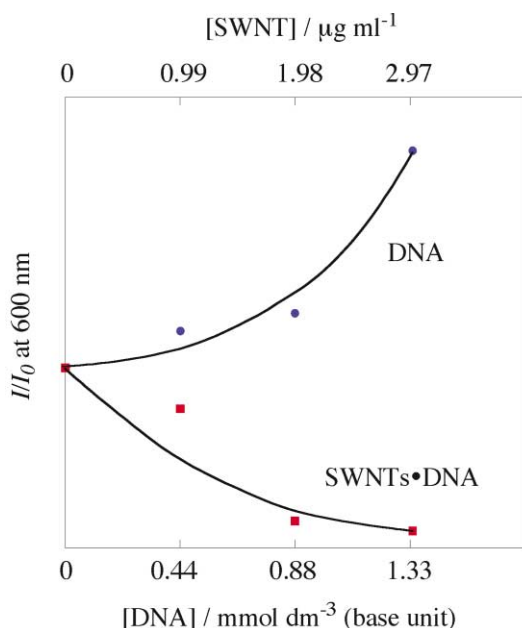

Fig. 8 Plots of relative fluorescence intensity *vs.* DNA or SWNTs concentration: excitation 490 nm.

Secondly, we measured action spectra for the SWNTs·DNA/poly(EDOT) and SWNTs·DNA(EB)/poly(EDOT) composite films (Fig. 9). It is seen from Fig. 9 that the SWNTs·DNA/poly(EDOT) composite film gives rise to a cathodic photocurrent which increases with shifting to shorter wavelengths. In the SWNTs·DNA(EB)/poly(EDOT) composite film, on the other hand, a large photocurrent maximum appears at 520 nm. To further confirm the contribution of EB, we photoirradiated these composite films at 375 nm (where SWNTs and poly-(EDOT) are mainly photoexcited) and 520 nm (where EB and poly(EDOT) are mainly photoexcited). At 375 nm, the presence of EB does not induce any significant difference in the efficiency of photocurrent generation (*ca.* 45 nA: Fig. 10a). At 520 nm, on the other hand, the photocurrent increases from 97 nA in the absence of EB to 210 nA in the presence of EB (Fig. 10b). From these results, it is clear that EB plays an important role in the mechanism of photocurrent generation. Thirdly, we evaluated the contribution of SWNTs. To do this experiment, we separately prepared a DNA(EB)/poly(EDOT) composite film by electrochemical polymerization of EDOT in the presence of
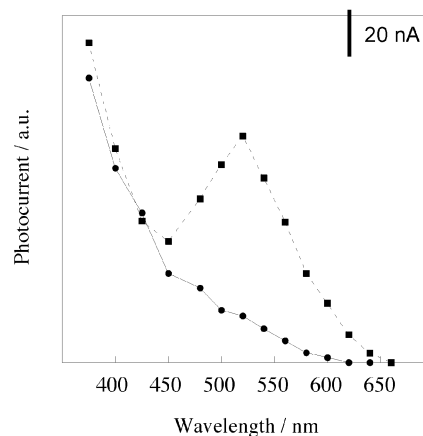

Fig. 9 Action spectra of a SWNTs·DNA/poly(EDOT) composite film ● and a SWNTs·DNA(EB)/poly(EDOT) composite film ■: 50 mmol dm^{-3} LiCl, argon atmosphere, bias voltage −0.2 V *vs.* Ag/AgCl, 25 °C.
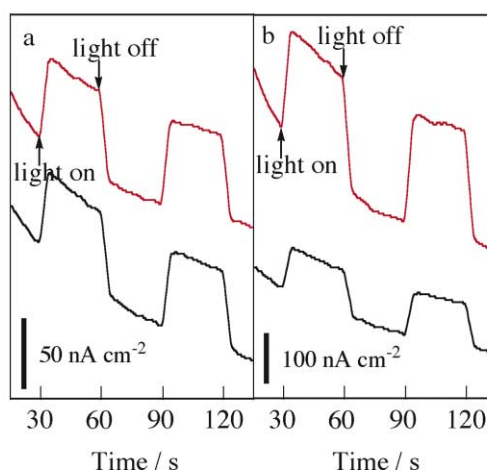

Fig. 10 Photochemical response of a SWNTs·DNA/poly(EDOT) composite film (black line) and a SWNTs·DNA(EB)/poly(EDOT) composite film (red line): (a) excited at 375 nm, (b) excited at 520 nm.

EB-binding DNA. By comparison of the UV-Vis absorption spectra, the concentration of deposited EB was controlled to the same level as that of SWNTs·DNA(EB)/poly(EDOT). In 375 nm excitation, we could detect photocurrent generation of 45 nA and 33 nA for SWNTs·DNA(EB)/poly(EDOT) and DNA(EB)/poly(EDOT) composite films, respectively (Fig. 11a).
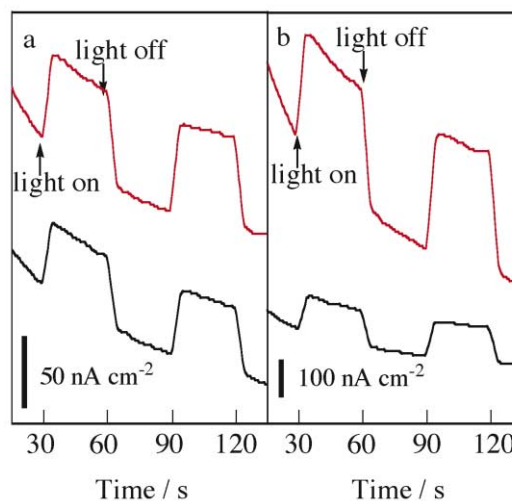

Fig. 11 Photochemical response of a DNA(EB)/poly(EDOT) composite film (black line) and a SWNTs·DNA(EB)/poly(EDOT) composite film (red line): (a) excited at 375 nm, (b) excited at 520 nm.

Since the difference is relatively small, one may consider that photocurrent generation mediated by SWNTs excitation is, if any, in the negligible level. When the composite films are photoexcited at 520 nm, the systems largely differ in the photocurrent efficiency (92 nA and 210 nA: Fig. 11b). This large difference supports the presence of a route including SWNTs, *i.e.*, EB → SWNTs → poly(EDOT) → ITO electrode and/or EB → SWNTs → ITO electrode (Fig. 12).
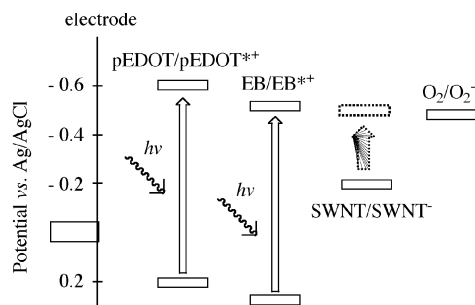

Fig. 12 Energy diagram of SWNTs·DNA(EB)/poly(EDOT) composite film in contact with 50 mmol dm^{-3} LiCl aqueous solution. Anothor hole-transfer process *via* photo-excitation of poly(EDOT) is also possible,[13] which is not shown here for clarity.

Conclusion

It has been expected that when SWNTs are fabricated by electron-conductive polymers, the resultant composites would provide new electrochemical and photochemical functions. So far, however, there is no convenient method to prepare these attractive functional materials. The present study demonstrated that SWNTs wrapped by DNA are useful as templates to carry out electrochemical oxidation of EDOT. The fibrous morphology of SWNTs·DNA/poly(EDOT) composites is novel, reflecting that of SWNTs. Furthermore, the ability of the DNA to bind an intercalator was retained. This ability has enabled us to evaluate energy transfer from the intercalator to SWNTs in the ternary composite. In this system, therefore, all functions of SWNTs, DNA and electron-conductive poly(EDOT) are cooperatively and efficiently utilized. We believe that this fabrication method as well as the resultant composites will be useful in the design of novel functional materials.

Experimental

Materials

SWNTs·DNA (salmon testes DNA) complex solution was prepared according to the method reported by Nakashima *et al.*[14] 3,4-Ethylenedioxythiophene (EDOT, Aldrich), lithium chloride (LiCl, Kishida Co. Japan), ethidium bromide (EB, Wako Pure Chemical Industries, Ltd.), sodium dihydrogen phosphate (anhydrous, Wako Pure Chemical Industries, Ltd.) and disodium hydrogenphosphate (Wako Pure Chemical Industries, Ltd.) were used as purchased. PBS (phosphate buffered saline) was prepared with sodium dihydrogen phosphate and disodium hydrogenphosphate. Deionized water from a Millipore purification system was used for the preparation of the solutions.

Electrochemical polymerization

CV experiments were performed using a one-compartment, three electrode electrochemical cell driven by an electrochemical analyzer (BAS 100B). The oxidative polymerization of EDOT was carried out in a CV cell using an ITO electrode as the working electrode, a Pt counter electrode and an Ag/AgCl reference electrode. The redox was repeated in a voltage range of −0.5 ~ 1.0 V (*vs.* Ag/AgCl) with a scan rate of 50 m V^{-1} at

25 °C. The typical concentrations employed for electrochemical oxidation are as follows: [EDOT] = 10 μmol dm^{-3}, [LiCl] = 50 mmol dm^{-3}, [DNA] = 0.113 mg ml^{-1} and [SWNT] = 0.0165 mg ml^{-1} (scan cycles: 100 cycles).

Apparatus for spectroscopic measurements

UV-Vis spectra were measured on a Shimadzu UV-2500 PC spectrophotometer. Fluorescence spectral measurements were performed using a Hitachi F-4500 spectrometer. It is photoexcited at an excitation wavelength of 490 nm.

SEM observations

Scanning electron microscopy (SEM) was used for observing the morphology of the films. The prepared film was cutted by a glass cutter. The film was dried by a vacuum pump for 1 day. The obtained film was shielded with platin for 30 s. SEM observations were carried out on a Hitachi S-5500. The accelerating voltage of SEM was 25.0 kV and the emission current was 10 μA.

AFM observations

A morphology investigation of the solutions before and after electrochemical polymerization was carried out using atomic force microscopy (AFM). The solution was cast on a mica film and then dried by a vacuum pump for 1 h. The surface was examined by Topometrix TMX-2100 (non-contact mode).

CLSM measurements of films

Confocal laser scanning microscope (CLSM) was used for taking the fluorescence spectra. The film was sandwiched by cover glasses and fixed by an adhesive. CLSM studies were carried out on a BIO-RAD Radiance 2000 AGR3. Excitation wavelength was 470 nm or 510 nm (argon laser with a reflector turrnet).

Photoelectrochemical measurements

A 500W Xe arc lamp (Ushio XB-50101AAA, XS-50102AAA) was used as a light source in the photoelectrochemical studies and a monochrometer (Shimadzu SPG 120IR) was used to obtain desired wavelengths. The intensity of the light was measured with an energy and power meter (Advantest TQ8210). Photocurrent measurements were carried out in LiCl (50 mmol dm^{-3}) solution by using a three-electrode photoelectrochemical cell, consisting of the modified ITO electrode.

Acknowledgements

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