

Facile deposition of [60]fullerene and carbon nanotubes on ITO electrode by electrochemical oxidative polymerization of ethylenedioxythiophene †

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It was found that [60]fullerene encapsulated in *p*-sulfonatocalix[8]arene and single-walled carbon nanotubes (SWNTs) solubilized by sodium dodecylsulfate can be readily deposited on the ITO electrode by electrochemical oxidative polymerization of ethylenedioxythiophene (EDOT) without chemical modification of these carbon clusters. The driving force for the deposition is an electrostatic interaction between the anionic complexes and the cationic charges of poly(EDOT) formed in the oxidative polymerization process. The surface morphology was thoroughly characterized by scanning electron micrograph: the [60]fullerene/poly(EDOT) film is covered by nano-particles with 20–100 nm diameters whereas the SWNTs/poly(EDOT) film is covered by nanorods with several μm length and *ca.* 100 nm diameter. The results indicate that the anionic complexes act as nuclei for the polymer growth in the oxidation polymerization. Interestingly, when these modified ITO electrodes were photoirradiated, the appearance of a photocurrent wave was observed. The action spectra showed that the photoexcited energy of [60]fullerene or SWNTs is efficiently collected by the electroconductive poly(EDOT) film and transferred to the ITO electrode.

Introduction

The ready availability of [60]fullerene and its homologues as novel electron-pool π -systems has increasingly invited exploration of their outstanding new physical and chemical properties. In particular, the preparation of fullerene or carbon nanotube thin films is of great interest from both a fundamental and a practical point of view.^{1,2} However, the challenge has been in overcoming the high aggregation tendency of these carbon spheres.³ One approach to overcome this problem is to introduce either thin-layer-forming substituents (such as long aliphatic groups)^{4,5} or surface-adsorptive substituents (such as trimethoxysilyl or mercapto groups)^{6,7} into these carbon spheres. These derivatives may be deposited on electrode surfaces as monolayers by means of Langmuir–Blodgett (LB) techniques and self-assembly. In the case of fullerene derivatives, monolayer systems comprised of covalently-linked donor–acceptor molecules can result in high light-to-photocurrent conversion values, because the fullerene layers tend to generate long-lived charge-separated states.⁸ However, only a few studies have so far been reported for these systems because of the synthetic difficulty in covalently linking all of the thin-layer-forming substituents in one molecular system.⁸ It thus occurred to us that a self-assembly method which is easily prepared by alternate adsorption of donor and acceptor layers will offer a promising prospect for the formation of a multilayer photocurrent generation system on an electrode.⁹ Previously, we reported that a hexacationic homooxocalix[3]arene–[60]fullerene 2 : 1 complex^{10,11} can be deposited on anion-coated gold surfaces as a monolayer or as a component of a bilayer with a porphyrin-containing anionic polymer: as expected, these membranes showed an efficient redox response in cyclic voltammetry (CV) and a photoelectrochemical response under

visible light irradiation.¹¹ Here, we report our new findings that [60]fullerene encapsulated in anionic *p*-sulfonatocalix[8]arene (**1**) and single-walled carbon nanotubes (SWNTs) solubilized by sodium dodecylsulfate (SDS) is readily deposited on the electrode through electrochemical oxidative polymerization of ethylenedioxythiophene (EDOT). The main characteristics of the present system are (1) unmodified [60]fullerene and SWNTs can be assembled as a film because of the encapsulation in anionic calix[8]arenes or in anionic micelles, so that sufficient π -conjugate systems necessary for efficient electron transfer are retained, (2) all [60]fullerene molecules are insulated from each other by encapsulation, (3) further coagulation of SWNTs is suppressed and (4) the photoexcited state energy is efficiently transduced to the electrode through the electroconductive poly(EDOT).¹²

Results and discussion

Deposition of [60]fullerene and its electrochemical response

The [60]fullerene·**1** complex was prepared using a high-speed vibration milling apparatus according to Komatsu's method.¹³

The oxidative polymerization of EDOT in the presence of $3.0 \times 10^{-5} \text{ mol dm}^{-3}$ [60]fullerene·**1** complex was carried out in a CV cell in a voltage range of 0–0.9 V (vs. Ag/AgCl) with a scan rate of 50 mV s^{-1} at 25 °C. After 40 redox cycles, the ITO electrode was subjected to UV–VIS measurements (Fig. 1).

The spectral patterns of both the oxidized state and the reduced state are very similar to those of poly(EDOT) in reference 14 except for a new peak at 330 nm. This peak was not found in the reference ITO electrode prepared from EDOT in the absence of the [60]fullerene·**1** complex. Thus, one may assign this new peak to the [60]fullerene·**1** complex deposited in the thin poly(EDOT) layer through the oxidative polymerization. In fact, the [60]fullerene·**1** complex gives the same λ_{max} at 330 nm in aqueous solution. The peak intensity scarcely

† Electronic supplementary information (ESI) available: SEM images. See <http://www.rsc.org/suppdata/ob/b3/b303828a/>

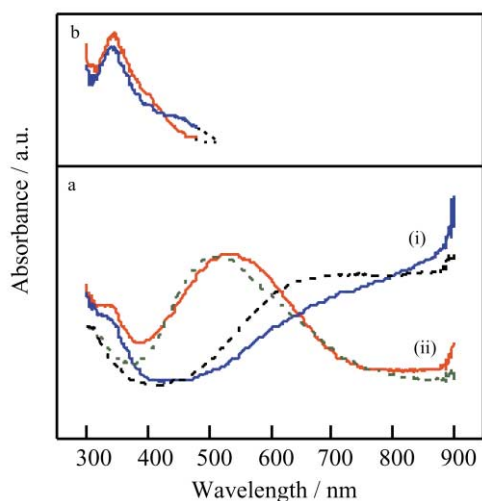


Fig. 1 (a) UV-VIS absorption spectra of [60]fullerene-1 complex-deposited film (—) and poly(EDOT) film (---) and (b) difference absorption spectra of [60]fullerene-1 complex-deposited film and poly(EDOT) film at the oxidized state and the reduced state: 0.05 mol dm⁻³ LiCl aqueous solution; applied potential, (i) 0.8 V, (ii) -0.6 V vs. Ag/AgCl; 25 °C.

decreased even after the electrode was rinsed with deionized water at 25 °C.

Further evidence for the deposition of the [60]fullerene-1 complex was obtained by the CV measurements. As shown in Fig. 2, a clear redox peak appears at -0.73 V (vs. Ag/AgCl). This value is more negative by -0.13 V than that reported for the similar [60]fullerene-deposited electrode.¹⁵ We consider that this negative shift is due to the electrostatic effect of the anionic calix[8]arene on the encapsulated [60]fullerene. From the oxidation peak area, the amount of deposited [60]fullerene was estimated to be 1.3×10^{-9} mol cm⁻².

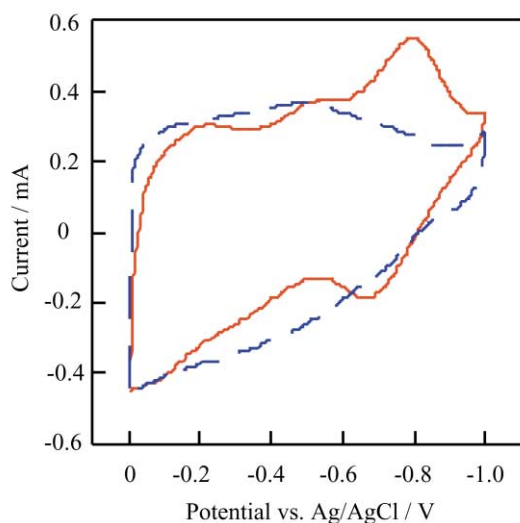


Fig. 2 CV of [60]fullerene-1 complex-deposited film (—) and poly(EDOT) film (---): 0.05 mol dm⁻³ LiCl aqueous solution; under argon atmosphere; scan rate 0.05 V s⁻¹; 25 °C.

The foregoing findings consistently support the view that poly(EDOT) carries the cationic charge in the electrochemical polymerization process,¹⁶ which acts as a driving force to deposit the anionic [60]fullerene-1 complex.

Deposition of SWNTs and their electrochemical response

The SWNTs solubilized using SDS were prepared by sonication.¹⁷ EDOT was electrochemically polymerized in an aqueous solution containing SWNTs-SDS complex ([SWNT] = 10 μg ml⁻¹). The reaction conditions were basically the same as those

used for the electrochemical oxidation of EDOT in the presence of [60]fullerene-1 complex. The UV-VIS absorption spectrum of SWNTs-SDS complex-deposited poly(EDOT) film obtained after 25 redox cycles is shown in Fig. 3. It is seen from Fig. 3 that the film has a broad absorption band at $\lambda > 400$ nm. This spectral shape is very similar to that obtained by electrochemical polymerization of EDOT in the presence of SDS micelles and therefore, it is very difficult to judge whether or not SWNTs are really deposited on the ITO electrode. We thus tried to detect them by Resonance Raman spectroscopy. It is known that SWNTs have a characteristic Raman peak at 1593 cm⁻¹.¹⁸ As shown in Fig. 4, the SWNTs-SDS complex-deposited poly(EDOT) film gives a weak but perceptible peak at 1591 cm⁻¹, which is not observed for the SDS-deposited poly(EDOT) film at all. Although it is still difficult to determine the amount of deposited SWNTs quantitatively, the Raman spectral data support the view, at least qualitatively that a significant amount of SWNTs is deposited on the ITO electrode through oxidative polymerization of EDOT.

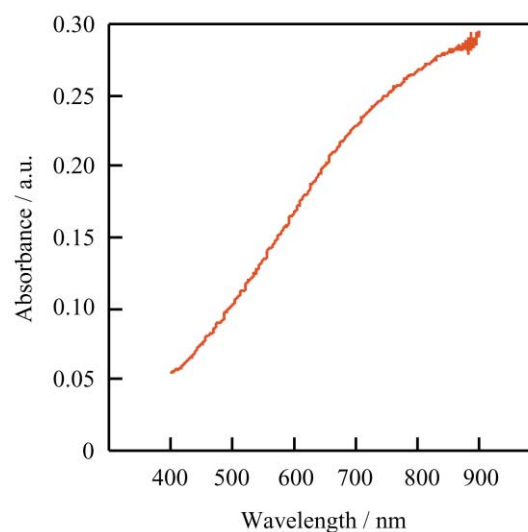


Fig. 3 UV-VIS absorption spectrum of SWNTs-SDS complex-deposited poly(EDOT) film.

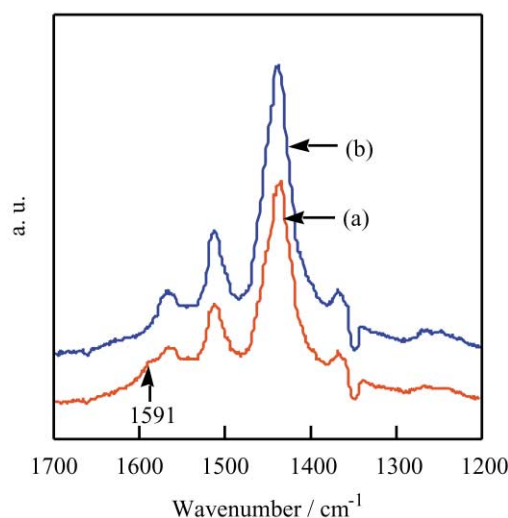


Fig. 4 Raman spectra of (a) SWNTs-SDS complex-deposited poly(EDOT) film and (b) SDS-deposited poly(EDOT) film.

Surface morphology as observed by scanning electron micrograph (SEM)

The SEM image of the [60]fullerene-1 complex-deposited film is shown in Fig. 5. It is seen from Fig. 5 that the surface is covered by nano-particles with 20–100 nm diameters. Since the

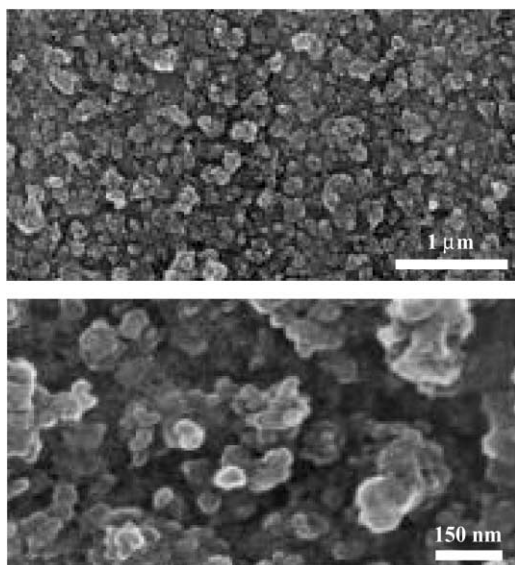


Fig. 5 SEM images of the surface of [60]fullerene·1 complex-deposited film.

poly(EDOT) surface prepared in the absence of the complex is smoother without such nano-particles (Fig. S1 †), one may regard the anionic complex acting as a nucleus of polymer growth in the oxidative polymerization.

On the other hand, SEM images obtained from the SWNTs·SDS complex-deposited film are more impressive (Fig. 6). One can recognize many ‘nanorods’ with several μm length and *ca.* 100 nm diameter. This morphology is very different from that of SDS-deposited poly(EDOT) film which is much smoother (Fig. 6b). As an alternative possibility, we suspected that this structure might result from adsorption of

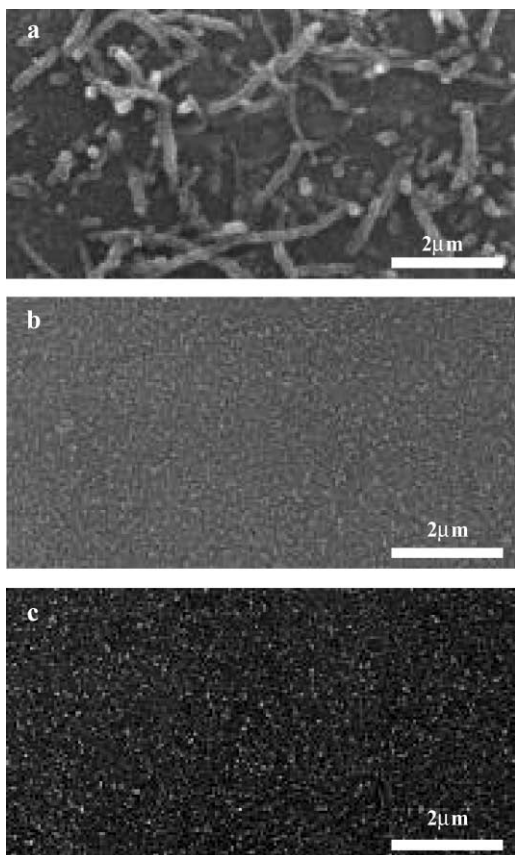


Fig. 6 SEM image of (a) SWNTs·SDS complex-deposited poly(EDOT) film, (b) SDS-deposited poly(EDOT) film, and (c) SDS-deposited poly(EDOT) film immersed in an aqueous solution containing SWNTs·SDS complex.

SWNTs·SDS complexes onto the SDS-deposited poly(EDOT) film on the ITO electrode. Thus, we first carried out oxidation polymerization of EDOT in the presence of SDS micelles and then immersed the resultant modified ITO electrode into an aqueous solution containing SWNTs·SDS complexes. The film thus obtained showed no significant structure as detected by SEM (Fig. 6c). Furthermore, we tested whether or not the bare ITO electrode surface can adsorb the SWNTs·SDS complex. The SEM image showed that the bare ITO electrode surface is not modified at all by this treatment (Fig. S2 †), indicating that there is no affinity between SWNTs·SDS complex and the ITO electrode surface. The foregoing results consistently support the view that SWNTs·SDS complex is bound to the poly(EDOT) polymer owing to the electrostatic attractive force¹⁹ and eventually deposited onto the ITO electrode as a poly(EDOT) film. One may consider, therefore, that SWNTs play a role of template to create electroconductive ‘nanorods’.

Generation of a photocurrent wave

When the [60]fullerene·1 complex-deposited ITO electrode was photoirradiated at 400 nm at -0.1 V bias voltage, the appearance of a large photocurrent wave (*ca.* 100 nA cm^{-2}) was observed (Fig. 7). This photoresponsive phenomenon could be repeated many times reversibly. In contrast, the working electrode which deposited only the poly(EDOT) film did not show such a photochemical response at all (Fig. 7). Since the action spectrum is comparable with the UV–VIS absorption spectrum of the [60]fullerene·1 complex (Fig. 8), it is undoubted that the photoexcited energy of [60]fullerene is efficiently collected by electroconductive poly(EDOT) and transferred to the ITO electrode.²⁰ The quantum yield estimated at 400 nm²¹ and -0.1 V bias voltage was 3.7%. Taking the convenience of the electrode preparation method into account, one may propose that the attained quantum yield is considerably high.

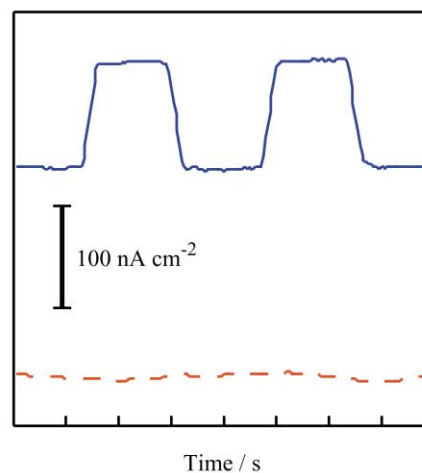


Fig. 7 Photoelectrochemical response of [60]fullerene·1 complex-deposited electrode (—) and poly(EDOT) electrode (---): $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ and $1 \times 10^{-3} \text{ mol dm}^{-3}$ methylviologen; argon atmosphere; light irradiation at 400 nm (0.16 mW cm^{-2}); bias voltage -0.1 V vs. Ag/AgCl; 25°C .

Very interestingly, we found that the SWNTs·SDS complex-deposited poly(EDOT) film on the ITO electrode also generates a photocurrent wave under photoirradiation (Fig. 9). A survey of the literature teaches us that SWNTs and poly(thiophene) films are photoexcited at $220 < \lambda < 400$ nm and $\lambda > 440$ nm, respectively, and generate a current of electricity.^{22,23} When irradiation of $220 < \lambda < 400$ nm was carried out, the electric current observed for the SWNTs·SDS complex-deposited poly(EDOT) system was much larger than that observed for the SDS-deposited poly(EDOT) system. To obtain clear evidence that this difference is ascribable to the presence of SWNTs, we

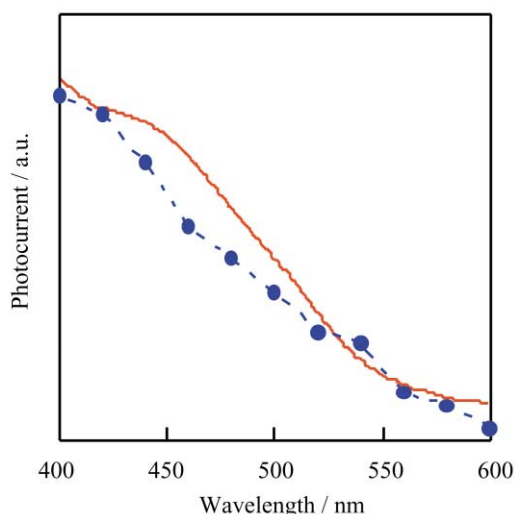


Fig. 8 Action spectrum of [60]fullerene·1 complex-deposited electrode (---) and the UV-VIS absorption spectrum of [60] fullerene·1 complex in aqueous solution (—): for the action spectrum, $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ and $1 \times 10^{-3} \text{ mol dm}^{-3}$ methylviologen; argon atmosphere; bias voltage $-0.1 \text{ V vs. Ag/AgCl}$; 25°C .

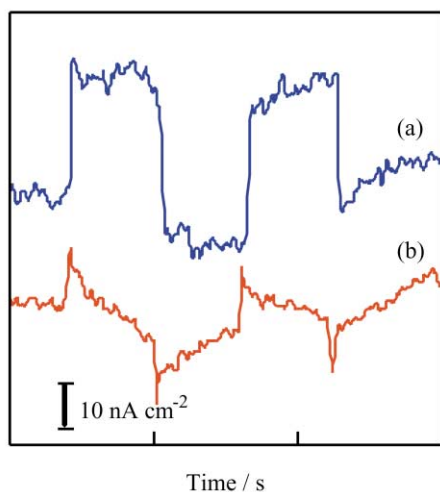


Fig. 9 Photoelectrochemical response of (a) SWNTs·SDS complex-deposited poly(EDOT) electrode and (b) SDS-deposited poly(EDOT) electrode.

photoirradiated these modified electrodes at different wavelength regions (Fig. 10). When they were irradiated at $220 < \lambda < 400 \text{ nm}$ where SWNTs are mainly photoexcited, the difference in the photocurrent intensity was 4.7-fold. On the other hand, when they were irradiated at $\lambda > 440 \text{ nm}$ where poly(EDOT) is mainly photoexcited, the difference was reduced to 3.1-fold. One may regard, therefore, that when the SWNTs·SDS complex-deposited poly(EDOT) film on the ITO electrode was photoirradiated at $220 < \lambda < 400 \text{ nm}$, the excitation of SWNTs plays an important role in the photocurrent generation.

Conclusion

In conclusion, the present paper demonstrates that unmodified [60]fullerene and SWNTs can be easily deposited on the electrode by encapsulation in anionic calix[8]arenes or solubilization in SDS micelles followed by *in situ* electrochemical polymerization of EDOT. It is unambiguous that the driving force for this novel and facile deposition is an electrostatic interaction between the anionic complexes and the cationic charges in poly(EDOT) formed through the oxidative polymerization. As expected, the films generate a photocurrent response to photoirradiation with a moderate quantum yield. Further applications of these new light-to-photocurrent

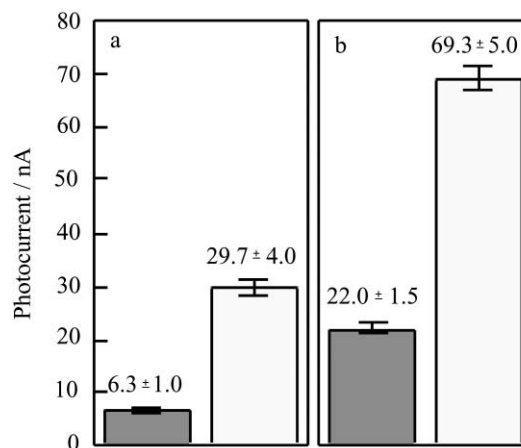


Fig. 10 Influence of glass filters on the photocurrent: (a) $220 < \lambda < 400 \text{ nm}$, (b) $\lambda > 440 \text{ nm}$. The values are the average of three measurements. Clear entry: SWNTs-SDS complex deposited poly(EDOT) electrode, shaded entry: SDS-deposited poly(EDOT) electrode.

conversion systems are currently being investigated in these laboratories. In addition, we believe that the present method is useful to create new morphological structures of conductive polymers using ‘anionic’ superstructures as templates.

Experimental

Chemicals

C_{60} (>99.5%) was purchased from MER corporation. 3,4-Ethylenedioxythiophene (EDOT, Aldrich), *p*-sulfonatocalix[8]arene (Sugai Co.), sodium dodecylsulfate (SDS, Wako Ind. Japan), lithium chloride (Kishida Co. Japan) and single-walled carbon nanotubes (SWNTs, Carbon Nanotechnologies Inc. Texas, USA) were used as purchased. Water used as a solvent was deionized water.

Electrochemical polymerization

A triethylene glycol solution (100 μl) containing EDOT (10 mg) was dispersed in 10 ml of deionized water by sonication. To this aqueous solution were added LiCl (21 mg). The concentrations were $[\text{EDOT}] = 7.1 \times 10^{-3} \text{ mol dm}^{-3}$ and $[\text{LiCl}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$. The [60]fullerene·1 complex solution or the SWNTs·SDS complex solution were added into the polymerization solution. Cyclic voltammometry (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 0–0.9 V (vs. Ag/AgCl) with a scan rate of 50 mV^{-1} at 25°C .

Polymer film analysis

UV-VIS and Raman spectra were measured on a Shimadzu UV-2500PC spectrophotometer and a JASCO NRS-2000 laser Raman spectrometer, respectively. Scanning electron microscopy (SEM) studies were carried out on a Hitachi S-5000. CV was performed with a three-electrode configuration in aqueous solution containing supporting electrolyte (LiCl, 0.05 mol dm^{-3}). The modified ITO electrode was used as the working electrode, the counter electrode being a platinum wire. An Ag/AgCl electrode was used as the reference electrode. The scan rate was 50 mV s^{-1} . All measurements were carried out under nitrogen and at 25°C .

Photoelectrochemical measurements

A 500 W Xe arc lamp (Ushio XB-50101AAA, XS-50102AAA) was used as a light source in the photoelectrochemical studies

and a monochromator (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 an aqueous Na₂SO₄ (0.1 mol dm⁻³) or LiCl (0.05 mol dm⁻³) solution by using a three-electrode photoelectrochemical cell, consisting of the modified ITO electrode. Quantum efficiency was calculated based on the number of photons absorbed by the chromophore on the ITO electrode at each wavelength using the input power (0.16 mW cm⁻²), the photocurrent density and the absorbance determined from the absorption coefficient of [60]fullerene-1 in aqueous solution and the amount of deposited [60] fullerene. The glass filters set on the light source were UV-D33S (220 < λ < 400 nm; Toshiba, Japan) and Y-44 (λ > 440 nm; Toshiba, Japan).

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- The contribution of the hydrophobic force is not ruled out. However, SWNTs-CTAB (cetyltrimethylammonium bromide) complex is scarcely deposited on the ITO electrode by the present oxidative polymerization of EDOT. We therefore consider that the electrostatic force plays the primary role.
- The UV-VIS absorption spectrum (Fig. 1a) is the sum of poly(EDOT), and [60]fullerene whereas the photocurrent is generated only from [60]fullerene. This is the reason why the action spectrum (Fig. 8) is somewhat different from the UV-VIS absorption spectrum.
- For the determination of the quantum yield see 11.
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