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Facile deposition of [60]fullerene on the electrode by electrochemical oxidative polymerization of thiophene†

Tsukasa Hatano,[a] Masayuki Takeuchi,[a] Atsushi Ikeda[bc] and Seiji Shinkai*[a]

[a] *Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka 812-8581, Japan. E-mail: seijitcm@mbox.nc.kyushu-u.ac.jp; Fax: +81-92-642-3611*

[b] *Graduate School of Materials Science, Nara Institute of Science and Technology, Ikoma, Nara 630-0101, Japan*

[c] *PRESTO, Japan Science and Technology Corporation, Ikoma, Nara 630-0101, Japan*

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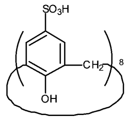
It was found that [60]fullerene encapsulated in anionic calix[8]arenes can be readily deposited by electrochemical oxidative polymerization of ethylenedioxythiophene: the resultant electrode generates a photocurrent wave (*ca.* 100 nA cm^{-2}) in response to visible light irradiation.

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 thin films is of great interest from both a fundamental and a practical point of view.[1,2] However, the challenge has lain in overcoming the high aggregation tendency of the carbon sphere.[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 fullerenes. These fullerene derivatives can be deposited on electrode surfaces as monolayers by means of Langmuir–Blodgett (LB) techniques and self-assembly. In these approaches, 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. 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 absorption 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 homooxacalix[3]arene·[60]fullerene 2 : 1 complex[9,10] 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 voltammometry (CV) and a photoelectrochemical response under visible light irradiation.[11] Here, we report that [60]fullerene encapsulated in anionic calix[8]arene (**1**) 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 can be assembled as a film because of the encapsulation in anionic calix[8]arenes, so that sufficient π-conjugate system of [60]fullerene necessary for efficient electron transfer is retained in the fullerene film, (2) all [60]fullerene molecules are insulated from each other by encapsulation and (3) the photoexcited state energy is efficiently transduced to the electrode through the electroconductive poly(EDOT).



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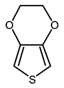

EDOT

The [60]fullerene·**1** complex was prepared using a high-speed vibration milling apparatus according to Komatsu's method.[12] 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 an aqueous [60]fullerene·**1** complex solution (200 μl) and LiCl (21 mg). The final concentrations were [complex] = 3.0×10^{-5} mol dm^{-3}, [EDOT] = 7.1×10^{-3} mol dm^{-3} and [LiCl] = 5.0×10^{-2} mol dm^{-3}. 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 a 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 s^{-1} at 25 °C. After 40 cycles, the ITO electrode was subjected to the 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 the reference[13] except 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 was scarcely decreased even after the electrode was rinsed with deionized water at 25 °C.

The deposition of the [60]fullerene·**1** complex is further evidenced 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

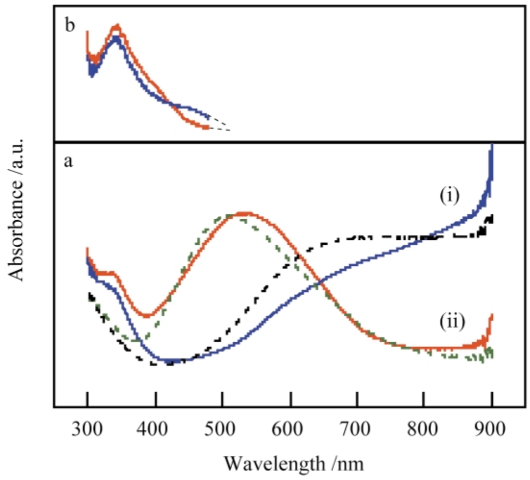

Fig. 1 (a) UV-VIS absorption spectra of [60]fullerene·**1** complex-deposited film (—) and poly(EDOT) film (----) and (b) difference absorption spectra of [60]fullerene·**1** complex-deposited film and poly(EDOT) film at the oxidized state and the reduced state: 0.05 mol dm^{-3} LiCl aqueous solution;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

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† Electronic supplementary information (ESI) available: SEM images and action spectrum. See http://www.rsc.org/suppdata/cc/b2/b210433d/

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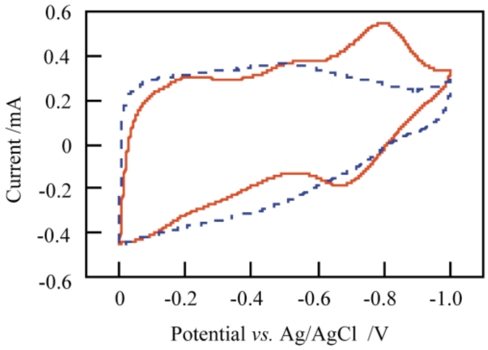

Fig. 2 CV of [60]fullerene·**1** complex-deposited film (—) and poly(EDOT) film (----): 0.05 mol dm^{-3} LiCl aqueous solution; under argon atmosphere; scan rate 0.05 V s^{-1}; 25 °C.

[60]fullerene-deposited electrode.[14] We consider that this negative shift is due to the electrostatic effect of the anionic calix[8]arenes including [60]fullerene. From the oxidation peak area, the amount of deposited [60]fullerene was estimated to be 1.3×10^{-9} mol cm^{-2}.

The foregoing findings consistently support the view that poly(EDOT) carrys the cationic charge in the electrochemical polymerization process,[15] which acts as a driving force to deposit the anionic [60]fullerene·**1** complex. The SEM image of the [60]fullerene·**1** complex-deposited film is shown in Fig. 3.

It is seen from Fig. 3 that the surface is covered by particles with 20–100 nm diameters. Since the poly(EDOT) surface prepared in the absence of the complex is smoother without such particles (Supplementary Fig. 1), one may regard that the anionic complex acts as a nucleus of the polymer growth in the oxidative polymerization. When the [60]fullerene·**1** complex-deposited ITO electrode was photoirradiated at 400 nm at −0.1 V bias voltage, the appearance of a photocurrent wave (*ca.* 100 nA cm^{-2}) was observed (Fig. 4).

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. 4). Since the action spectrum is comparable with the UV-VIS spectrum of the [60]fullerene·**1** complex (Supplementary Fig. 2), it is undoubted that the photoexcited energy of [60]fullerene is efficiently collected by electroconductive poly(EDOT) and transferred to the ITO electrode.[16] The quantum yield estimated at 400 nm[17] 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.

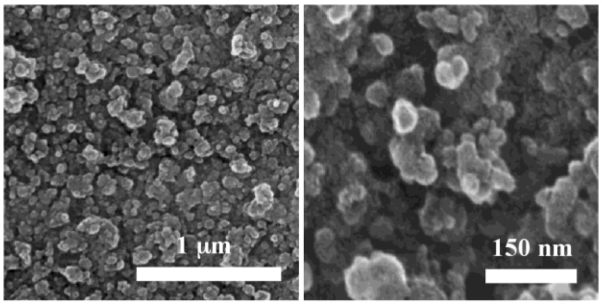

Fig. 3 SEM images of the surface of [60]fullerene·**1** complex-deposited film.

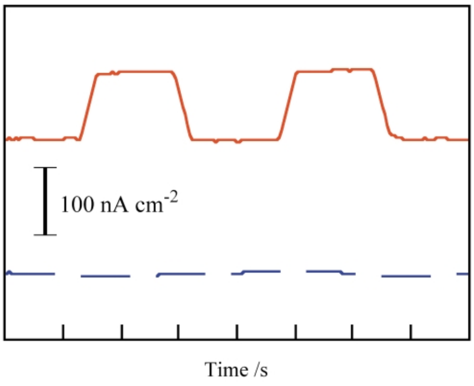

Fig. 4 Photoelectrochemical response of [60]fullerene·**1** complex-deposited electrode (—) and poly(EDOT) electrode (----): 0.1 mol dm^{-3} Na_2SO_4 and 1×10^{-3} mol dm^{-3} methylviologen; argon atomosphere; light irradiation at 400 nm (0.16 mW cm^{-2}); bias voltage −0.1 V *vs.* Ag/AgCl; 25 °C.

In conclusion, the present paper demonstrates that unmodified [60]fullerene can be easily deposited on the electrode by encapsulation in anionic calix[8]arenes followed by *in situ* electrochemical polymerization of EDOT. As expected, the film generates a photocurrent response to visible light irradiation with a moderate quantum yield. Further applications of this new light-to-photocurrent conversion system are currently being investigated in these laboratories.

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16 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 (Supplementary Fig. 2, see ESI†) is somewhat different from the UV-VIS absorption spectrum.
17 For the determination of the quantum yield see ref. 10.