doi:10.1246/cl.2010.1104

Current Generation by Fullerene in the Presence of Tetraphenylborate at a Nitrobenzene|Water Interface under Illumination with a Fluorescent Light

Shoko Furuhashi,[1] Hirosuke Tatsumi,[2] Takashi Kimoto,[3] and Teruo Hinoue*[1]
[1]*Department of Chemistry, Faculty of Science, Shinshu University, Matsumoto, Nagano 390-8621*
[2]*International Young Researchers Empowerment Center, Shinshu University, Matsumoto, Nagano 380-8621*
[3]*KIMOTO ELECTRIC Co., Ltd., Funahashi-cho, Tennoji-ku, Osaka 543-0024*

(Received July 7, 2010; CL-100614; E-mail: thinoue@shinshu-u.ac.jp)

We found that currents flowed across an interface, when a nitrobenzene solution containing fullerene, C_{60}, and tetraoctylammonium tetraphenylborate was illuminated. Expecting that a photochemical reaction of C_{60} would be responsible for the currents, we investigated its mechanism. Voltammetric and spectroscopic experiments suggested that the currents were generated through ion transfer of anions produced during the photochemical reaction and/or electron transfer between anion radical of C_{60} and oxygen. Further, we propose a galvanic cell based on the photochemical reaction.

According to theoretical calculations, two LUMOs of fullerene (C_{60}) are triply degenerated and thus C_{60} is predicted to be fairly electronegative.[1] Indeed, C_{60} has been electrochemically reduced up to the hexaanion.[2] In addition, C_{60} has been reduced to an anion radical by illuminating with visible light.[3–5] Considering such chemical properties of C_{60}, we tried voltammetric measurements at a nitrobenzene (NB)|water (W) interface illuminated with a commercial fluorescent lamp, using an NB solution containing C_{60} and tetraoctylammonium tetraphenylborate (TOATPB) as a supporting electrolyte and an aqueous solution containing LiCl. In the measurements, we observed a current flow regardless of the potential and a color change of the NB solution from violet to dark brown.[6] The current flow was against our prediction, since we expected that no currents would be observed in ion-transfer voltammetry at a liquid|liquid interface because of no charges on C_{60}. The color change led us to predict the existence of photochemical reactions. Indeed, it was due to the formation of monoanion radical of C_{60} ($C_{60}^{\bullet-}$) under illumination with visible light.[3–5] However, we could not explain mechanistically how $C_{60}^{\bullet-}$ generated the currents. In this letter, we discuss the current generation mechanism, based on data obtained by voltammetry at a liquid|liquid interface, conventional voltammetry at a Pt microelectrode, and visible (vis)/near infrared (NIR) spectroscopy. In addition, we propose a possibility of a new galvanic cell based on the mechanism.

The electrochemical system for voltammetry at the NB|W interface was as follows:

$$\mathrm{Ag|AgCl|10\,mM\ LiCl\ (W)|10\,mM\ LiCl,\ 10\,mM\ NaTPB\ (W)|}$$
$$\mathrm{1\,mM\ C_{60},\ 10\,mM\ TOATPB\ (NB)|10\,mM\ LiCl\ (W)|}$$
$$\mathrm{10\,mM\ LiCl\ (W)|AgCl|Ag\ (M = mol\,dm^{-3})} \qquad (1)$$

Here the interface between 1 mM C_{60}, 10 mM TOATPB (NB) and 10 mM LiCl (W) is a NB|W interface of interest. Voltammetry at the NB|W interface was performed with a four-electrode potentiostat (Hokuto, HA1010mM1A) controlled by a personal computer. Since the currents were very small, we used the two reference electrodes for counter electrodes. The NB solution was illuminated with a commercial fluorescent lamp (Toshiba, FL10N, 10 W), which showed a broad fluorescence band from 400 to 650 nm with sharp bright lines at 410, 440, 550, and 580 nm. Since NB serving as a solvent had an absorption limit at ca. 460 nm, C_{60} would be effectively illuminated with visible light ranging from 460 to 650 nm. Conventional voltammetry at a solid electrode was performed for NB solutions containing C_{60}, and tetrabutylammonium perchlorate ($TBAClO_4$) and TOATPB serving as supporting electrolytes. We used a Pt microelectrode of 10 µm in diameter as a working electrode and an Ag/Ag^+ (NB) electrode as a reference electrode. Spectroscopic measurements for NB solution containing C_{60} and TOATPB from 400 to 1600 nm were performed with a spectrophotometer (Ocean Optics, USB 4000).

Figure 1 shows voltammograms at the NB|W interface after the illumination. The currents increased with the illumination time over the whole potential region. If the currents arise from ion transfer, the direction of the current increase indicates either anion transfer from the NB to aqueous solution or cation transfer from the aqueous to NB solution. Since Li^+ in the aqueous solution cannot transfer across the interface, it is reasonable that the transferring ions are some anions produced in the NB solution under the illumination. However, it is also possible that the currents arise from electron transfer at the interface. On the other hand, we could not find explicit influences of pH of the aqueous solution and oxygen in the solutions on the voltammograms. Figure 2 shows conventional voltammograms of C_{60} obtained with a Pt microelectrode. The NB solution was

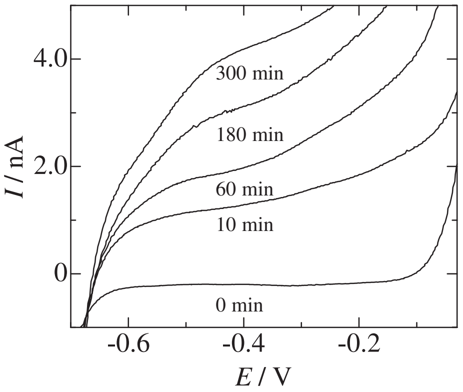

Figure 1. Voltammograms at the NB|W interface after the illumination at the illumination times shown in the figure. The NB solution contained 1 mM C_{60} and 10 mM TOATPB, and the aqueous solution contained 10 mM LiCl. The solutions were not deoxygenated.

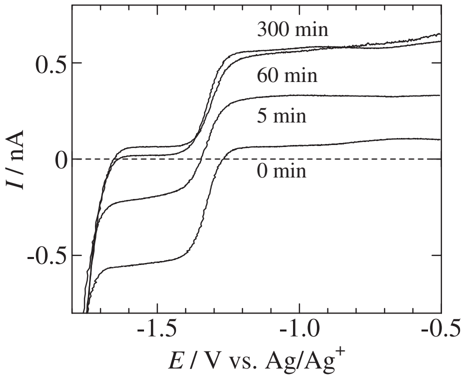

Figure 2. Time course of a conventional voltammogram of 1 mM C_{60} in NB solution. The supporting electrolyte was 10 mM $TBAClO_4$ and 10 mM TOATPB. A Pt microelectrode was used as the working electrode. The potential was scanned at 10 mV s^{-1}. The solution was purged with Ar gas.

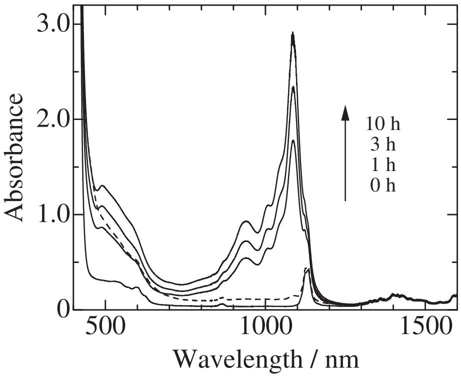

Figure 3. Time course of a vis/NIR spectrum of a NB solution containing 0.2 mM C_{60} and 2 mM TOATPB. The solution was purged with Ar gas. The broken line indicates a spectrum of the NB solution that was exposed to air after illuminating with the fluorescence light for 10 h.

deoxygenated with Ar gas. Before the illumination, the voltammogram showed a well-defined reduction wave at −1.33 V. The wave is attributable to a one-electron reduction of C_{60} to $C_{60}^{\bullet -}$. With increasing illumination time, the reduction wave wholly shifted upward and finally changed to a complete oxidation wave. In addition, when the NB solution showing the final voltammogram was sufficiently exposed to air, the voltammogram almost returned to the original one. Such changes of the voltammogram suggest that C_{60} is readily reduced to $C_{60}^{\bullet -}$ in the presence of TPB^- in the NB solution under the illumination and that the $C_{60}^{\bullet -}$ is stable in an atmosphere without oxygen and is oxidized under the presence of air. Vis/NIR spectra also supported the above photochemical reaction of C_{60} under the illumination. In the measurements of the spectra, NB solutions containing C_{60} and TOATPB were purged with N_2 gas. As can be seen in Figure 3, before the illumination, the spectrum showed two absorption bands in the wavelength ranges from 450 to 630 nm and around 1130 nm. The former band can be assigned to absorption by C_{60}[7], and the latter is a triply overtone band of C–H stretching of NB. When starting the illumination, four absorption bands grew at the wavelengths of 935, 1004, 1042, and 1077 nm, which were identical well with a vibrational structure of $C_{60}^{\bullet -}$.[8–10] Consequently, it is confirmed that $C_{60}^{\bullet -}$ is produced under the illumination. Further, when the NB solution was exposed to air, the spectrum returned to the original one. This fact indicates that the $C_{60}^{\bullet -}$ is oxidized to C_{60} under the presence of air. However, the vis/NIR spectrum did not completely return to the original one after the exposure to air (Broken line in Figure 3). From these experimental results, it is supposed that the current flowing across the NB|W interface is due to ion transfer of anions produced in the NB solution under the illumination, i.e., decomposed products of C_{60} and TPB^-, and/or electron transfer at the interface between $C_{60}^{\bullet -}$ produced in the NB solution under the illumination and oxygen remaining slightly in the aqueous solution. At present, the decomposed products and the influences of pH and oxygen of the solutions are being investigated in more detail.

Remarking that C_{60} is reduced to $C_{60}^{\bullet -}$ in the presence of TPB^- under illumination of visible light and that $C_{60}^{\bullet -}$ is stable in the absence of oxygen, we have proposed a new galvanic cell, called a photochemical electric condenser (PEC). The characteristic of PEC is the preservation of light energy in a form of a substance, i.e., $C_{60}^{\bullet -}$. The electromotive force (EMF) for the electrochemical system, Pt|10 mM $TBAClO_4$, 10 mM TOATPB, 1 mM C_{60} (NB)|10 mM TBACl (W)|Pt, increased with illumination and attained a constant value of ca. 0.76 V after ca. 30 min. After stopping the illumination, the EMF slowly decreased and increased when the illumination restarted. This must be because $C_{60}^{\bullet -}$ was slowly consumed at the anode and was produced again with re-illumination. The anode reaction is oxidation of $C_{60}^{\bullet -}$, whereas the cathode reaction may be reduction of oxygen. It is obvious that this galvanic cell needs to be improved for the commercial use as a battery. We are now developing PEC.

This work was supported by Regional Innovation Cluster Program of Nagano and by Special Coordination Funds for Promoting Science and Technology, both granted by MEXT, Japan.

References and notes

1 A. Hirsch, M. Brettreeich, *Fullerenes: Chemistry and Reactions*, Wiley-VCH, Weinheim, **2005**, pp. 49–54.
2 Q. Xie, E. Pérez-Cordero, L. Echegoyen, *J. Am. Chem. Soc.* **1992**, *114*, 3978.
3 A. Watanabe, O. Ito, *J. Phys. Chem.* **1994**, *98*, 7736.
4 O. Ito, Y. Sasaki, A. Watanabe, R. Hoffmann, C. Siedschlag, J. Mattay, *J. Chem. Soc., Perkin Trans. 2* **1997**, 1007.
5 T. Konishi, Y. Sasaki, M. Fujitsuka, Y. Toba, H. Moriyama, O. Ito, *J. Chem. Soc., Perkin Trans. 2* **1999**, 551.
6 Although we tried several supporting electrolytes, only supporting electrolytes containing TPB^- are effective for the current generation and the color change.
7 A. D. J. Haymet, *Chem. Phys. Lett.* **1985**, *122*, 421.
8 H. Kondo, T. Momose, T. Shida, *Chem. Phys. Lett.* **1995**, *237*, 111.
9 R. D. Bolskar, S. H. Gallagher, R. S. Armstrong, P. A. Lay, C. A. Reed, *Chem. Phys. Lett.* **1995**, *247*, 57.
10 T. Kato, T. Kodama, T. Shida, *Chem. Phys. Lett.* **1993**, *205*, 405.