Effects of Magnetic Processing on Electrochemical and Photoelectrochemical Properties of Electrodes Modified with Nanoclusters of a Phenothiazine-C$_{60}$ Linked Compound

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Abstract. Effects of magnetic processing on morphological, electrochemical, and photoelectrochemical properties of electrodes modified with nanoclusters of a phenothiazine-C$_{60}$ linked compound with four methylene group (Ph(4)C$_{60}$) were examined in the absence and presence of magnetic processing with three different magnetic environments due to strong magnetic field. The AFM measurements indicated that the morphologies of nanostructures of Ph(4)C$_{60}$ varied with magnetic environments as comparison with that in the absence of magnetic processing. At top position (5.6 T ; -940 T$^2$/m) with hypogravity, large spherical nanoclusters (60~70 nm diameter) were observed as comparison with those (ca. 20 nm diameter) in the absence of magnetic processing. At middle position (15 T ; 0 T$^2$/m) with normal gravity, the fiber-like nanostructure was observed. At bottom position (9.8 T ; +1070T$^2$/m) with hypergravity, the rod-like nanostructure was observed. The interesting results might be ascribed to the different solvent properties due to the different rates of evaporation of two solvents in the toluene-acetonitrile mixed solvent during drying process under various magnetic environments. First reduction peaks due to C$_{60}$ moiety of Ph(4)C$_{60}$ nanostructures in the presence of magnetic processing at three different positions were negative-shifted as comparison with that in the absence of magnetic processing. Potential dependencies of the photocurrents of the electrodes modified with Ph(4)C$_{60}$ nanostructures in the presence of magnetic processing at three different positions were also different from that in the absence of magnetic processing. The magnetic field effects in AFM, and electrochemical and photoelectrochemical measurements are most likely ascribed to the difference of the reduction potentials due to C$_{60}$ clusters between the absence and presence of magnetic processing due to the morphological change of Ph(4)C$_{60}$ nanostructures.
1. Introduction

Applying strong magnetic fields to materials induces huge magnetic field effects (MFEs). It is expected to create highly functional nanomaterials containing new physical and chemical properties, since new interfaces or nanostructures are constructed by strong magnetic fields. [1]

Magnetic orientation of crystals [2-4], polymers [5,6], fibrin fiber [7,8], and carbon nanotubes [9-11] by strong magnetic fields due to a superconducting magnet has been widely investigated. 2D- or 3D-patterns of silver dendrites in a strong magnetic field were reported by Mogi et al. [12,13] and Katsuki et al. [14,15]. Significant morphological changes induced by magnetic fields were interpreted in terms of magnetohydrodynamic (MHD) mechanism, in which Lorentz force affects the motions of ions in a magnetic field, and/or by magnetic force which is caused by a gradient magnetic field. MFEs on growth morphology in electropolymerization, photoelectrochemical reactions, and redox behaviors of polypyrrole as a conducting polymer have been reported by Mogi et al. [16-18] The MFEs were explained by the diamagnetic orientation of the polymers. Recently, Tanimoto et al. reported attractive 3D morphological chirality in membrane tubes prepared by a silicate garden reaction using strong magnetic field. [19,20]

It has also been reported that C_{60} and its derivatives formed optically transparent microscopic clusters in some mixed solvents. [21,22] The clustering behavior of C_{60} is associated with the strong hydrophobic interactions among the C_{60} units. Photoinduced electron-transfer and photoelectrochemical reactions using the C_{60} clusters have been reported because of their interesting properties. [21,22] Recently, we examined photoinduced electron-transfer reactions and MFEs on the dynamics of a radical pair that was generated from the intermolecular electron-transfer reaction between a C_{60} cluster and methyl phenothiazine (MePH) (Figure 1). [23] A fullerene derivative containing a positive charge (a monopyrrolidinium salt) (C_{60}N^{+}) (Figure 1) forms optically transparent clusters in the THF/H_{2}O mixed solvent. Also, transient absorption spectra of the clusters of C_{60}N^{+}-MePH system following laser excitation at 355 nm indicated that the photoinduced intermolecular electron-transfer from the triplet excited state of phenothiazine (PH) to C_{60}N^{+} cluster (C_{60}N^{+})_{n} occurred and the yield of the escaped phenothiazine cation radical (PH•^{+}) increased with increase of magnetic field. These MFEs can be explained by spin-lattice relaxation mechanism in radical pair mechanism and most likely ascribed to the nanoclusters of C_{60}N^{+}.

We also reported MFEs on the photoelectrochemical reactions of photosensitive electrodes modified with nanoclusters containing of C_{60}N^{+} and MePH, intended for utilization of C_{60} as photofunctional nanodevices. [24] Photosensitive electrodes with the nanoclusters of C_{60}N^{+} and MePH were fabricated on the electrodes modified with a self-assembled monolayer of HS(CH_{2})_{2}SO_{3}Na^{+} on a gold substrate. The photocurrents increased with increasing an external magnetic field, typically 3 % at 0.5 T. The MFEs are ascribable to the contribution of triplet radical pair that are generated by photoinduced intermolecular electron-transfer from MePH to triplet excited state of nanocluster of C_{60}N^{+}, and can be explained in terms of spin-lattice relaxation mechanism in radical pair mechanism.

Besides the MFEs in photochemistry and photoelectrochemistry, we recently reported the effects of magnetic processing on morphological, electrochemical, and photoelectrochemical properties of electrodes modified with nanoclusters of C_{60}N^{+} and MePH in the absence and presence of magnetic processing due to strong magnetic field. [25] In the study, we used a superconducting magnet with horizontal direction of magnetic field. We demonstrated that the morphology of nanostructures, electrochemical, and photoelectrochemical properties in the electrodes modified with nanoclusters of C_{60} are controlled by applying strong magnetic field. The morphological effects of applying magnetic fields are probably ascribed to MHD mechanism and/or the convective flow of suspension produced by magnetic force, since the C_{60}N^{+}-MePH clusters has positive charge.

In this study, we examined effects of magnetic processing on morphological, electrochemical, and photoelectrochemical properties of electrodes modified with nanostructures of a phenothiazine-C_{60} linked compound with four methylene group (Ph(4)C_{60}) in the absence and presence of magnetic processing in three different magnetic environments with hypogravity, hypergravity, and normal gravity due to strong magnetic field with vertical direction of magnetic field. In the study, the MHD
mechanism due to Lorentz force is ineffective in the effects of magnetic processing, since the nanostructures consisting of Ph(4)C₆₀ possess no charge.

2. Experimental

A phenothiazine-C₆₀ linked compound (Ph(4)C₆₀) (Figure 1) was prepared according to the previous paper. [26] The structure of Ph(4)C₆₀ was confirmed by ¹H-NMR and MALDI-TOF MS spectra and elemental analysis. ¹H-NMR spectra were measured on a JEOL model JNM-GSX 400. Mass spectra were measured by a MALDI-TOF-MS instrument (PE Biosystems Voyager DE). Steady-state absorption spectra were recorded on a Shimadzu UV-3150 spectrometer. Toluene (Dojindo, spectrosol or Wako, for Spectrochemical Anal.) and acetonitrile (CH₃CN) (Dojindo, spectrosol or Wako, for Spectrochemical Anal.) were used as received. Water was deionized with a Milli-Q system (Milipore).

Clusters of Ph(4)C₆₀ were prepared by dissolving in the toluene-CH₃CN (1:1) mixed solvent due to first injection methods. [22-25] Ph(4)C₆₀ formed optically transparent clusters by the following procedure. First, the toluene solution of Ph(4)C₆₀ was sonicated for 15 minutes. Next, the toluene solution of Ph(4)C₆₀ was injected into CH₃CN with a syringe. After sonication of the sample for 15 minutes, the solution became optically transparent in the mixed solvent (toluene:CH₃CN = 1:1) solvent.

Magnetic processing of the samples was carried out using an experimental setup as shown in Figure 2. A superconducting magnet (Japan Superconductor Technology, JMTD-LH15T40) with vertical direction of magnetic field was used as reported in the previous papers. [19,20] It has a room temperature bore tube with of 40 mm. The distribution of the magnetic field is reported in the previous papers. [19,20] The maximum field (B_max(vertical)) and field (B) ×gradient field (dB/dz) were 15 T and 1500 T²/m, respectively, where z is the distance from the center of the bore tube along the tube. Three samples were placed at the positions in the bore tube, of which B and dB/dz were 5.6 T and -940 T²/m for the top position, 15 T and 0 T²/m for the middle position, and 9.8 T and +1070 T²/m for the bottom position and one was placed outside of the tube as a control.

The toluene-CH₃CN (1:1) mixed solution (50 µM) of Ph(4)C₆₀ was dropped on a freshly cleaved mica or an ITO electrode (10 Ω). The samples were placed at three positions in the strong magnetic field and outside magnetic field as shown in Figure 2. Magnetic field was applied vertical to surface of the mica or the ITO electrode at room temperature. After drying the solvent at room temperature under atmospHERIC pressure, AFM measurements of the sample on the mica and electrochemical and photoelectrochemical measurements of the sample on the ITO electrode, so that the electrode modified with Ph(4)C₆₀ nanostructures, were carried out. In the AFM measurements, the AFM images of Ph(4)C₆₀ nanostructures on the mica were recorded in tapping mode using a Nanoscope IIIa (Digital Instrument).
Electrochemical and photoelectrochemical measurements were carried out by using a three electrode cell containing the electrode modified with Ph(4)C₆₀ nanostructures as a working electrode, a platinum electrode as a counter electrodes, and a Ag/AgCl electrode as a reference electrode. Na₂SO₄ (0.1 M) was used as a supporting electrolyte according to previous paper [25].

3. Results and Discussion

3.1. Effects of magnetic processing on morphological properties of Ph(4)C₆₀ nanostructures

The absorption spectrum of Ph(4)C₆₀ in toluene is shown in Figure 3(a). The spectrum in the region of 400-800 nm is essentially identical with 6,6-closed mono-functionalized C₆₀ derivative, because PH moiety in Ph(4)C₆₀ has no absorption band above 400 nm. [26] For a contrast, the absorption spectrum of Ph(4)C₆₀ in the toluene-CH₃CN (1:1) mixed solvent is shown in Figures 3(b) and 3(c). The absorption in the 400-800 nm regions in Figure 3(b) and 3(c) were broadened as compared with that in Figure 3(a). In addition, the spectrum changed with elapsed time after sample preparation and became same after 135 min. The peaks were slightly blue-shifted and the absorbance increased slightly with elapsed time. The results including the hyperchromic effect suggest the formation of clusters of Ph(4)C₆₀ in the toluene-CH₃CN (1:1) mixed solvent as reported previously. [23-25]

The formations of clusters of Ph(4)C₆₀ were also examined by AFM measurement. From the AFM image on mica placed in the absence of magnetic field at room temperature (Figure 4(a)), many small sphere-like nanoclusters were clearly observed. The results were similar to those of the clusters of C₆₀N⁺-MePH in the previous papers. [24,25] The diameters of the clusters of Ph(4)C₆₀ were estimated to be ca. 20 nm. However, the diameters (ca. 20 nm) of the clusters of Ph(4)C₆₀ was shorter than those (ca. 100 nm) of nanoclusters of C₆₀N⁺-MePH [25].

![Figure 3. Absorption spectra of Ph(4)C₆₀ (50 µM) in (a) toluene (green dotted line) and in toluene-CH₃CN (1:1) mixed solvent after preparation of sample at 0 min (b) (blue unbroken line) and 135 min (c) (red dash-dotted line) at room temperature.](image)

![Figure 4. AFM images of Ph(4)C₆₀ nanostructures obtained from Ph(4)C₆₀ (50 µM) in toluene-CH₃CN (1:1) mixed solvent on mica placed in the absence (a), and the presence of magnetic processing at (b) top, (c) middle, and (d) bottom positions at room temperature.](image)

Morphological effects of applying magnetic fields on Ph(4)C₆₀ nanostructures on mica were also examined by AFM measurements. The AFM images at various magnetic environments at top, middle, and bottom positions are shown in Figures 4 (b)-(d). The AFM images indicated that the morphologies of Ph(4)C₆₀ nanostructures in the presence of magnetic processing (Figures 4(b), (c), and (d)) were different from that in the absence of magnetic processing (Figure 4(a)). The morphologies in all AFM images were different each other (Figure 4). In the AFM images placed in the presence of magnetic
processing at middle and bottom positions, nonspherical clusters were observed (Figures 4 (c) and (d)).

At top position with hypogravity (5.6 T ; -940 T²/m), the large spherical nanoclusters (diameter ; 60~70 nm) were observed (Figure 4(b)) and the size of the nanoclusters was much larger than those (diameter ; ca. 20 nm) in the absence of magnetic processing (Figure 4(a)). At middle position with normal gravity (15 T ; 0 T²/m), the fiber-like nanostructure (height; ca. 20 nm) was observed. Finally, at bottom position with hypergravity (9.8 T ; +1070 T²/m), the rod-like nanostructure (short axis :150~200nm, long axis ; 500~600 nm, height; ca. 10 nm) was observed.

The effects of magnetic processing on morphologies of Ph(4)C₆₀ nanostructures are very interesting. In previous paper, we reported that the morphological effects of applying magnetic fields are mainly ascribed to MHD mechanism and/or the convective flow of suspension produced by magnetic force since the C₆₀N⁺-MePH clusters has positive charge. [25] In the present study, the MHD mechanism due to Lorentz force is ineffective in the effects of magnetic processing (Figure 4), since Ph(4)C₆₀ possess no charge.

Many possible mechanisms for the effects of magnetic processing on the morphologies can be considered. We suggest one of the plausible mechanisms on the basis of the results in previous papers and a preliminary results. In previous some papers, it was reported that self-assembly of C₆₀ derivative in different solvents including mixed solvents results in the formation of nanostructures. [27-29] Therefore, though we used same the mixed solvent, the interesting results might be ascribed to the different solvent properties due to the different rates of evaporation of two solvents (toluene and CH₃CN) in the toluene and CH₃CN (1:1) mixed solvent during drying process under various magnetic environments including hypogravity, normal gravity, and hypergravity at top, middle, and bottom positions. The difference of evaporation rates between toluene and CH₃CN in the absence of magnetic processing might be verified with magnetic environments at top, middle, and bottom positions.

We preliminarily examined the effects of reduced pressure on morphology of Ph(4)C₆₀ nanostructures on a mica at the absence of magnetic processing in the preparation of sample. The AFM images obtained under reduced pressure was similar to those under atmosphere pressure in the absence of magnetic processing (Figure 4(a)). In other words, many small sphere-like nanoclusters were clearly observed similar to those in Figure 4(a). It suggested that magnetic field seems to play an important role for the difference of Ph(4)C₆₀ nanostructures (Figure 4). The composition (toluene/CH₃CN) ratio in the mixed solvents may change by the interactions between two solvents and strong magnetic field. Further investigations are necessary to clarify the novel effects of magnetic processing on morphology of Ph(4)C₆₀ nanostructures.

3.2. Effects of magnetic processing on electrochemical properties of the modified electrodes with Ph(4)C₆₀ nanostructures

Redox potentials of ITO electrodes modified with Ph(4)C₆₀ nanostructures were measured by cyclic voltammetry and differential pulse voltammetry measurements in the absence and presence of magnetic processing (Figures 5 and 6).

In the cyclic voltammogram (CV) in the absence of magnetic processing (Figure 5), the peak currents due to the reduction of C₆₀ in the first scan were larger than those in the later scans. The peak currents due to the reduction of C₆₀ were clearly observed as comparison with those due to the re-oxidation of C₆₀⁺. The results can probably be ascribed to electron migration from C₆₀⁺ to a neighbouring C₆₀ molecule. [25] In contrast, the oxidation peaks of PH or the re-reduction peaks of PH⁺ were not clearly observed in Figure 5. The results in CVs in the presence of magnetic processing at top, middle, and bottom positions were similar to those as shown in Figure 5.

Differential pulse voltammetry measurements of ITO electrodes modified with Ph(4)C₆₀ nanostructures were also carried out. Differential pulse voltammograms (DPVs) for ITO electrodes modified with Ph(4)C₆₀ nanostructures are shown in Figures 6 (a) and (b). In the case of the reduction of Ph(4)C₆₀ nanostructures in the absence of magnetic processing, the peak due to the first reduction of C₆₀ in Ph(4)C₆₀ nanostructures was observed at -500 mV vs. Ag/AgCl (Figure 6 (a), (-1200 ← 0
mV), while the peaks due to re-oxidation of C_{60}^{••} (-508 mV vs. Ag/AgCl) and re-oxidation form C_{60}^{••} to C_{60}^{•} (-902 mV vs. Ag/AgCl) were observed (Figure 6 (a), (-1200 → 0 mV)). In contrast, in the absence of magnetic processing, the peaks due to the first reduction of C60 were negative-shifted at top (-764 mV vs. Ag/AgCl), middle (-758 mV vs. Ag/AgCl), and bottom (-600 mV vs. Ag/AgCl) positions (Figure 6 (a), (-1200 → 0 mV)) as comparison with that (-500 mV vs. Ag/AgCl) in the absence of magnetic processing. The peaks due to re-oxidation of C_{60}^{•} at top (-922 mV vs. Ag/AgCl), middle (-910 mV vs. Ag/AgCl), and bottom (-902 mV vs. Ag/AgCl) positions were also negative-shifted as as comparison with that (-508 mV vs. Ag/AgCl) in the absence of magnetic processing (Figure 6 (a), (-1200 → 0 mV)). The effects of magnetic processing on the first reduction of C_{60} of electrodes modified with Ph(4)C_{60} nanostructures was similar to those of electrodes modified with C_{60}N^{+}-MePH nanoclusters [25].

On the other hand, in the case of the oxidation of Ph(4)C_{60} nanostructures, the peak due to the first oxidation peak of PH moiety was observed at 466 mV vs. Ag/AgCl in the absence of magnetic processing, while those were positive-shifted in the presence of magnetic processing at top (714 mV vs. Ag/AgCl), middle (736 mV vs. Ag/AgCl), and bottom (876 mV vs. Ag/AgCl) positions ((Figure 6 (b), (0 mV → 1000 mV)). However, the peaks due to the re-reduction of PH^{•+} were not appreciably observed in both the absence and presence of magnetic processing ((Figure 6 (b), (0 mV → 1000 mV)). Previously, in electrodes modified with C_{60}N^{+}-MePH mixed nanoclusters, the peak due to first oxidation of PH in MePH was hardly influenced by magnetic processing. [25] The effects of magnetic processing on the peak due to first oxidation of PH moiety in Ph(4)C_{60} nanostructures was similar to those on the peak due to the first reduction of C_{60} in Ph(4)C_{60} nanostructures ((Figure 6 (a)) as

**Figure 5.** CV curves of Ph(4)C_{60} nanostructures on ITO electrodes in the absence of magnetic processing. (Scan direction 0 → -1200 → 1000 → -1200 → 1000 → -1200 mV vs Ag/AgCl).

**Figure 6.** DPV curves of Ph(4)C_{60} nanostructures on ITO electrodes in the absence (a) (blue unbroken line) and presence of magnetic processing at (b) top (orange dash-dotted line), (c) middle (green dotted line), and (d) bottom (red broken line) positions.
described above, however, was different from those on the peak due to the first oxidation of PH in MePH in the C$_{60}$N$^+$-MePH mixed nanoclusters [25]. The linkage between PH and C$_{60}$ moieties in Ph(4)C$_{60}$ is most likely responsible for the difference of the effects of magnetic processing in the electrodes modified with between the Ph(4)C$_{60}$ nanostructures and the C$_{60}$N$^+$-MePH mixed nanoclusters.

In the previous paper, we examined electrochemical and photoelectrochemical reactions of gold electrodes modified with C$_{60}$N$^+$-MePH clusters due to electrostatic interaction between self-assembled monolayer of HS(CH$_2$)$_2$SO$_3$Na$^+$ on the gold electrode and C$_{60}$N$^+$-MePH clusters with a positive charge. [24] The two broad reduction peaks (-400 mV vs. Ag/ACL) due to the first and second reductions of the nanocluster of C$_{60}$N$^+$ were observed, while the oxidation peak (750 mV vs. Ag/ACL) due to the first oxidation of PH moiety was obtained. In addition, in the electrodes modified with C$_{60}$N$^+$ clusters, the only first reduction peak due to the nanocluster of C$_{60}$N$^+$ (-400 mV vs. Ag/AgCl) was observed. The reduction peaks (-400 and -800 mV vs. Ag/AgCl) of nanocluster of C$_{60}$N$^+$ and the oxidation peak (750 mV vs. Ag/AgCl) of MePH were different of those in present modified electrode. The difference is most likely ascribed to that of the preparation of the modified electrode.

In addition, Kamat et al. reported that the two reduction peaks (-400 and -800 mV vs. Ag/AgCl) due to the first and second reductions of the C$_{60}$ nanocluster were obtained in the CV of the C$_{60}$ cluster film electrophoretically deposited on the ITO electrodes. [30] Therefore, the reduction peaks in the modified electrodes in DPVs (Figure 5) are attributable to the reduction of C$_{60}$ clusters in Ph(4)C$_{60}$ nanostructures. The method of preparation of the electrodes was different from that in the present study. The electrochemical responses in the other electrodes in previous papers [24,25,30] were similar to those in the modified electrode in the present study, though the reduction potentials in the other electrodes were different from those in the modified electrode in the present study. The result may be ascribed to the difference of morphology of the nanostructures of Ph(4)C$_{60}$ and/or the fabrication methods of the electrodes among the modified electrodes.

Nakashima et al. reported that the DPVs due to the reduction of C$_{60}$ were influenced by the kind of cation electrolyte in the cast films of C$_{60}$ lipids on electrodes. [31] The results showed the importance of the cationic charge of lipids and the microenvironments in the films for electrochemistry of C$_{60}$. The negative-shifts due to magnetic processing in the electrodes modified with the C$_{60}$N$^+$-MePH mixed nanoclusters can be explained by the above considerations in the previous paper [25]. Therefore, the negative-shifts of reduction of C$_{60}$ moiety and the positive-shifts of oxidation of PH moiety in Ph(4)C$_{60}$ due to magnetic processing (Figure 6(b)) are mostly likely explained by the same mechanism. In other words, Coulomb interaction between C$_{60}$$^*$ and Na$^+$ cation of electrolyte, or PH$^*$ and SO$_4^{2-}$ anion of electrolyte are mostly likely responsible for the remarkable negative- or positive-shifts in the present study, since the interaction between the anion of C$_{60}$$^*$ and Na$^+$ cation or PH$^*$ and SO$_4^{2-}$ anion was changed by the morphology of Ph(4)C$_{60}$ nanostructures. The MFEs on the electrochemical properties of Ph(4)C$_{60}$ nanostructures are in good agreement with the morphological effects of applying magnetic fields on the AFM images (Figure 4).

3.3. Effects of magnetic processing on photoelectrochemical properties of the modified electrodes with Ph(4)C$_{60}$ nanostructures.

Photoelectrochemical properties of ITO electrodes modified with Ph(4)C$_{60}$ nanostructures were also measured in the absence and presence of magnetic processing. In the absence and presence of magnetic processing, the photoirradiation of all modified electrodes afforded anodic photocurrents. Figure 7 shows the photocurrent action spectrum of ITO electrode modified with Ph(4)C$_{60}$ nanostructures in the absence magnetic processing at 0 volt vs. Ag/AgCl. The photocurrent action spectrum was in fair agreement with the absorption spectrum (Figure 3(b)) of Ph(4)C$_{60}$ in the toluene-CH$_3$CN (1:1) mixed solvent. Similar photocurrent action spectra were observed in the presence of magnetic processing at top, middle, and bottom positions. These results indicate that the photocurrents
are caused by photoexcitation of C_{60} clusters in Ph(4)C_{60} nanostructures in the absence and presence of magnetic processing. The results in the photocurrent action spectra were in fair good agreement with those in the ITO electrode modified with the C_{60}N^{+}-MePH mixed nanoclusters in previous papers [24,25].

Potential dependencies of the photocurrents of the modified electrodes were examined in all ITO electrodes modified with Ph(4)C_{60} nanostructures in the absence and presence of magnetic processing (Figure 8). Potential dependencies of the photocurrents of the modified electrodes in the presence of magnetic processing at top, middle, and bottom positions (Figures 8(b)-(d)) were appreciably different from that in the absence of magnetic processing (Figure 8(a)). The potentials at zero photocurrent in the presence of magnetic processing at top position (Figure 8(b)) were remarkably negative-shifted as comparison with that in the absence of magnetic processing (Figure 8(a)). Also, the potentials at zero photocurrent in the presence of magnetic processing at middle position (Figure 8(b)) were negative-shifted as comparison with that in the absence of magnetic processing (Figure 8(a)). The magnitude of negative-shift at top position was larger than that at middle position. In contrast, the potential at zero photocurrent in the presence of magnetic processing at bottom position (Figure 8(d)) was slightly negative-shifted as comparison with that in the absence of magnetic processing (Figure 8(a)).

The reaction scheme of the photoelectrochemical reactions of the ITO electrodes modified in the absence and presence of magnetic processing is shown in Figure 9. On the basis of the reaction scheme (Figure 9), the effects of magnetic processing on the potential dependencies (Figure 8) are most likely ascribed to the difference of the first reduction potentials of C_{60} clusters in Ph(4)C_{60} nanostructures in the absence and presence of magnetic processing and are in good agreement with those in the electrochemical properties (Figures 6 (a)-(d)). The mechanism for the effects of magnetic processing on the photoelectrochemical reactions is similar to that in the previous paper [25]. The difference of the first oxidation of PH moiety in Ph(4)C_{60} nanostructures in the absence and presence of magnetic processing are probably responsible for the magnitude of photocurrent, but not for the negative-shifts of the potential at zero photocurrent.

4. Conclusion
A phenothiazine-C_{60} linked compound with four methylene group (Ph(4)C_{60}) formed optically transparent clusters (ca. 20 nm diameter) in a toluene-CH_{3}CN (1:1) mixed solvent via the use of first injection methods, as was verified from absorption measurements and AFM in the absence of
magnetic processing. The effects of magnetic processing on the morphological, electrochemical, and photoelectrochemical properties of electrodes modified with Ph(4)C₆₀ nanostructures were examined in the absence and presence of magnetic processing using three different magnetic environments including hypogravity, normal gravity, and hypergravity induced using a strong magnetic field by AFM, and electrochemical (CV and DPV) and photochemical measurements.

The AFM measurements indicated that the Ph(4)C₆₀ nanostructures on mica in the absence and presence of magnetic processing at top, middle, and bottom positions were different each other. In the electrochemical measurements, the first reduction peaks corresponding to the C₆₀ clusters of Ph(4)C₆₀ nanostructures in the presence of magnetic processing were markedly negatively shifted in comparison with that in the absence of magnetic processing. The potential dependences of the photocurrents of the electrodes modified with Ph(4)C₆₀ nanostructures in the presence of magnetic processing at top, middle, and bottom positions were also different from that in the absence of magnetic processing.

The MFEs in electrochemical and photoelectrochemical measurements can most likely be ascribed to the difference of the reduction potentials due to the C₆₀ clusters between in the absence and presence of magnetic processing using the morphological change of Ph(4)C₆₀ nanostructures.

We have demonstrated that the morphology of nanostructures, electrochemical, and photoelectrochemical properties in the electrodes modified with nanostructures of the Ph-C₆₀ linked compound (Ph(4)C₆₀) can be controlled by applying a strong magnetic field. The present study provides useful information for designing novel nanodevices whose photofunctions can be controlled by a magnetic field. Further investigation are necessary to verify the mechanism for the effects of magnetic processing on the morphological, electrochemical, and photoelectrochemical properties of electrodes modified with Ph(4)C₆₀ nanostructures. The magnetic processing using in the horizontal direction of the magnetic field and Ph(n)C₆₀ (n=10) with ten methylene group as a long spacer are now in progress.

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