Microstructures and photovoltaic properties of fullerene-based organic-inorganic hybrid solar cells

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Abstract. C_60-based bulk heterojunction solar cells were fabricated, and the electronic and optical properties were investigated. C_60 were used as n-type semiconductors, and copper oxides, CuInS_2 and diamond were used as p-type semiconductors. Electronic structures of the molecules were investigated by molecular orbital calculation, and energy levels of the solar cells were discussed. Nanostructures of the solar cells were investigated by transmission electron microscopy, electron diffraction and X-ray diffraction, which indicated formation of mixed nanocrystals.

1. Introduction
Fullerene-based solar cells have been investigated and reported recently. These organic solar cells have a potential for use in lightweight, flexible, inexpensive, and large-scale solar cells. However, significant improvements of photovoltaic efficiencies are mandatory for use in future solar power plants. One of the improvements is donor-acceptor proximity in the devices by using blends of donor-like and acceptor-like molecules or polymers, which are called donor-acceptor bulk-heterojunction solar cells [1-3]. Organic-inorganic hybrid structures would be other improvements for the organic solar cells [4].

The purpose of the present work is to fabricate and characterize fullerene-based organic-inorganic hybrid solar cells by using different organic polymers. In the present work, CuInS_2, diamond, and copper oxides were used for p-type semiconductors, and C_60 was used for n-type ones. Device structures were produced, and efficiencies and optical absorption were investigated. Electronic structures were also investigated by molecular orbital calculations.

2. Experimental procedures
Cu_2O and CuO layers were prepared on pre-cleaned indium tin oxide (ITO) glass plates by an electrodeposition method using platinum counter electrode. Copper (II) sulfate (CuSO_4, 0.4 mol/L, Wako 97.5%) and l-lactic acid (3 mol/L, Wako) were dissolved into distilled water. The electrolyte pH was adjusted to 12.5 by adding NaOH. The electrolyte temperature was kept at 65 °C during electrodeposition. The electrodeposition of Cu_2O and CuO layers were carried out at voltages of -0.35 and +0.70, respectively, and quantity of electric charges of 2.2 Ccm^{-2} [4].

C_60 layers with thickness of ~100 nm were prepared on the Cu_2O and CuO layers by vacuum evaporation from C_60 powder (Material Technologies Research, 99.98 %). For all the present copper oxides semiconductor solar cells, aluminum (Al) metal contacts of thickness ~100 nm were deposited as top electrodes, and annealed at 140 °C for 20 min in N_2. The present solar cells were denoted as ITO/Cu_2O/C_60/Al and ITO/CuO/C_60/Al as shown in Fig. 1.
CIS solution for p-type semiconductors was also produced by dissolving CuI (Sigma Aldrich Corp., 99.99%) and InCl₃ (Sigma Aldrich Corp., 99.99%) in a mixture of triphenylphosphite (1 mL) (Sigma Aldrich Corp., 97%) and acetonitrile (2 mL) (Nacalai Tesque, Inc., 99.5%), dropping bis(trimethylsilyl)sulfide (Tokyo Chemical Industry Co., Ltd., >95%) [5,6]. The solution for n-type semiconductors was prepared by dissolving C₆₀ in o-dichlorobenzene. A thin layer of polyethylenedioxythiophene doped with polystyrene-sulfuric acid (PEDOT:PSS) (Sigma Aldrich) was spin-coated on a pre-cleaned fluoride tin oxide (FTO) glass plate (Asahi Glass, ~9.3 Ω/□). Then, semiconductor layers were prepared on a PEDOT:PSS layer by spin coating, and annealed at 120 °C for 10 min in N₂ atmosphere. The FTO was used because of the high temperature annealing process. The thickness of the blended device was ~150 nm. Al metal contacts were evaporated as a top electrode, and annealed at 140 °C for 20 min in N₂ atmosphere.

A diamond:C₆₀ BHJ solar cell was also prepared by spin coating using a mixed solution of C₆₀ (Material Technologies Research, 99.98%) and diamond powder (New metals & Chemicals Co. Ltd., >95%) in 1,2-dichlorobenzene. Although the diamond powder did not have high purity, the impurities would not be activated, and the carrier concentration would be low. Total weight of diamond:C₆₀ was 18 mg, and weight ratio of diamond:C₆₀ was 1:8.

Current density-voltage (J-V) characteristics were measured (Hokuto Denko Corp., HSV-100), both in the dark and under illumination at 100 mWcm⁻² using an air mass (AM) 1.5 solar simulator (San-Ei Electric, XES-301S). The solar cells were illuminated through the substrate side, with an illuminated area of 0.16 cm². Optical absorption of the solar cells was investigated by means of UV-visible absorption spectroscopy (Hitachi Ltd., U-4100). The microstructures of the copper oxides thin films were investigated by X-ray diffractometry (XRD, Philips X’Pert-MPD System) with CuKα radiation at 40 kV operating voltage and 40 mA operating current. Transmission electron microscopy (TEM, Hitachi H-8100, 200 kV operating voltage) were also carried out for nanostructure analysis. Thermodynamical calculations for the copper oxide reactions were carried out by HSC Chemistry (Outokumpu Research Oy. Poli, Finland).

![Device structure of solar cells.](image)

3. Results and discussion

J-V characteristics of the present solar cells under illumination showed photocurrents with short-circuit currents and open-circuit voltages. Measured parameters of the present solar cells are summarized in Table 1. Cu₂O/C₆₀ structures fabricated by the electrodeposition method provided better power conversion efficiency (η) of ~4×10⁻³ % compared to CuO/C₆₀ solar cells. The Cu₂O/C₆₀ solar cell prepared by the electrodeposition gave an η of 4.2×10⁻³ %, a fill factor (FF) of 0.25, short-circuit current density (J_Sc) of 67 µAcm⁻² and open-circuit voltage (V_OC) of 0.20 V.
Table 1. Measured parameters of the present solar cells.

| Sample          | \( V_{OC} \) (V) | \( J_{SC} \) (\( \mu A cm^{-2} \)) | FF  | \( \eta \) (%) |
|-----------------|------------------|-----------------------------------|-----|----------------|
| CuO/C\(_60\)    | 0.24             | 1.8                               | 0.25| 9.0 \times 10^{-5} |
| Cu\(_2\)O/C\(_60\) | 0.20             | 67                                | 0.25| 4.2 \times 10^{-3} |
| CuInS\(_2\):C\(_60\) | 0.18             | 16                                | 0.28| 8.0 \times 10^{-4} |
| Diamond:C\(_60\) | 0.023            | 5.3                               | 0.35| 4.3 \times 10^{-5} |

Figure 2. (a) Optical absorption of Cu\(_2\)O/C\(_60\) solar cells. (b) XRD patterns of Cu\(_2\)O and CuO thin films prepared by electrodeposition.

Figure 3. (a) TEM image of Cu\(_2\)O and (b) electron diffraction pattern of C\(_60\) heterojunction layer.

Figures 2(a) show optical absorption of the Cu\(_2\)O/C\(_60\) and CuO/C\(_60\) solar cells. The solar cells prepared by the electrodeposition indicated higher absorption in the range of 300-700 nm compared to those by spin-coating, which would be due to the film thickness. Absorption peak at \(~360\) nm and \(~500\) nm were due to copper oxides, and peaks at \(~340\), \(~440\) and \(~610\) nm corresponded to C\(_60\).
Crystalline components in the Cu_2O and CuO thin films were investigated by XRD, as shown in Fig. 2(b). Diffraction peaks corresponding to Cu_2O and CuO were observed for the Cu_2O and CuO thin films, and they consisted of cuprite phase with cubic system (space group of Pn3m and lattice parameters of a = 0.4250 nm) and cupric phase with monoclinic system (space group of C2/c and lattice parameter of a = 0.4653 nm, b = 0.3410 nm, c = 0.5018 nm, β = 99.48°) [7]. The particle sizes were estimated using Scherrer’s equation: D = 0.9λ/Bcosθ, where λ, B, and θ represent the X-ray wavelength, full width at half maximum, and Bragg angle, as listed in Table 1. The crystallite sizes of Cu_2O and CuO produced by the electrodeposition are ~40 nm, which are larger compared to those prepared by spin-coating. The increase of crystallinity which was due to the thicker film thickness led to an increase in open-circuit voltage. Crystallite sizes of Cu_2O and C_{60} of the Cu_2O:C_{60} bulk heterojunction thin film were determined to be 7.2 nm and 25.7 nm, respectively.

Figure 3(a) and 3(b) are a TEM image and a selected area electron diffraction pattern of a Cu_2O layer prepared by the electrodeposition, respectively. The TEM image indicated Cu_2O nanocrystal structures with sizes of 40–50 nm, which agreed well with the calculated XRD results. The comparatively larger crystallite sizes of the Cu_2O resulted in unclear Debye-Scherrer rings in Fig. 3(b), which indicated the higher crystallinity of the Cu_2O nanoparticles.

Ellingham diagram of copper oxides for an O_2 gas molecule (per mol) was investigated by thermodynamical calculation. The copper element would be oxidized to CuO and Cu_2O completely by annealing at elevated temperatures, and Cu_2O would be more stable compared to CuO from the Ellingham diagram [4].

![Figure 4](image.png)

**Figure 4.** (a) Optical absorption spectra of heterojunction and bulk heterojunction solar cells. (b) X-ray diffraction pattern of CIS:C_{60} thin film.

Figure 4(a) shows a measured optical absorption of the solar cells based on CIS. These solar cells show a wide optical absorption range from 400 to 800 nm, and the heterojunction solar cell show as higher optical absorption range from 350 nm to 550 nm than that of the bulk heterojunction. Since the FTO substrate was set as an incident side, the optical absorption of the CIS layer was high for the heterojunction structure. On the other hand, optical absorption of the bulk heterojunction would be lower compared to that of the heterojunction structure because C_{60} were mixed with the CIS layer [6].

An X-ray diffraction pattern of CIS:C_{60} bulk heterojunction is shown in Fig. 4(b). Several diffraction peaks are observed, which correspond to 112, 204 of CIS and 111, 220, 311, 222, 422, 511 of C_{60}. The average particle sizes of CuInS_2 and C_{60} were calculated from Scherrer’s formula to be 5
nm and 13 nm, respectively. The 204 peak of CIS is too small to be used for the calculation of the CIS grain size, and only one peak of 112 was used for the calculation.

Figure 5(a) is a TEM image of CIS, and many CIS particles are observed. Figure 5(b) is an electron diffraction pattern of CIS. Debye-Scherrer rings are observed in the diffraction pattern, which shows crystallite structures of CIS particles. An interfacial structure of CIS and C60 was observed by TEM. Filtered Fourier transform of the HREM image of CIS:C60 bulk heterojunction layer is shown in Fig. 5(c). Figure 5(d) is an inverse Fourier transform of (c), and arrows show the interface of CIS and C60. Lattice fringes of \{101\} of CIS and \{111\} of C60 were observed. The enlarged image of a part of C60 in (b) is shown in Fig 5(e). Arrangements of C60 molecules are observed in the image. CIS and C60 have size distribution, and the crystal sizes of them observed in the TEM image are larger compared to the averaged sizes.

Optimization of the nanocomposite structure with CIS and C60 would increase the efficiencies of the bulk heterojunction solar cell. From the present TEM observation, CIS and C60 were not mixed in a molecular scale. If the mixture structure of CIS and C60 is improved to a nanoscale, it is believed that the area of the p-n junction interfaces is increased, and the efficiency would be improved. In addition, it is important to search the most suitable mixture ratio of the p-type and n-type semiconductors for bulk heterojunction solar cells.

![Figure 5](image_url)

**Figure 5.** (a) TEM image of CIS nanoparticles and (b) electron diffraction pattern of CIS. (c) Filtered Fourier transform of HREM image of CIS:C60 bulk heterojunction layer. (d) Inverse Fourier transform of (c). (e) Enlarged image of a part of C60 in (d).
Figure 6. (a) Optical absorption spectra of diamond:C$_{60}$ layer. (b) X-ray diffraction patterns of diamond powder.

Figure 7. (a) TEM image, (b) enlarged image of a part of (a) and (c) electron diffraction pattern of diamond:C$_{60}$ layer.

Figure 6(a) shows optical absorption spectra of the nanodiamond-based thin films. In Figure 6(a), the diamond:C$_{60}$ nanocomposite structure provided photo-absorption in the range of 350 to 500 nm, and shows high absorption at 339, 402 and 506 nm, which correspond to 3.7, 3.1 and 2.5 eV, respectively. Absorption peaks of the C$_{60}$ were confirmed within the range from 300 to 400 nm, and an absorption peak of 506 nm corresponds to the diamond.

Figure 6(b) shows X-ray diffraction patterns of diamond powder. In Fig. 6(b), diffraction peaks of the diamond powder were confirmed as 111, 220 and 311 of the diamond structure. A grain size of diamond powder was determined to be 12 nm, which was calculated by Scherrer’s equation. An increase of photo-absorption above ~600 nm would be due to the nanostructure of diamond particles, which will be discussed later.

A TEM image, an enlarged image and an electron diffraction pattern of the diamond:C$_{60}$ composite layer are shown in Fig. 7(a), 7(b) and 7(c), respectively. Diamond powder has an fcc structure with a lattice parameter of a=0.357 nm. C$_{60}$ has also an fcc structure with a lattice parameter of a=1.42 nm. In the electron diffraction pattern of Fig. 7(c), expansion of C$_{60}$ reflections was observed, which indicates a disordered structure of the composite layer. In the present TEM observation, diamond and C$_{60}$ were not mixed well in nanoscopic scale, and the fabricated thin film would show low conversion efficiency.
Energy level diagram of ITO/Cu$_2$O/C$_6$0/Al and ITO/CuO/C$_6$0/Al solar cells is shown in Fig. 8(a) and (b), respectively, in which previously reported values of energy levels were used [8,9]. Separated holes could transfer from the valence band of the Cu$_2$O to the ITO, and separated electrons could transfer from the conduction band of the Cu$_2$O to the Al electrode, respectively. It has been reported that $V_{OC}$ is nearly proportional to the semiconductor bandgap [10], control of the energy levels is important for increasing cell efficiency. Compared with a Si semiconductor with an indirect transition band structure, Cu$_2$O and CuO have direct transition bandgaps and greater optical absorption. Thus, ultrathin films of copper oxide layers could potentially provide efficient charge injection.

In the present study, Cu$_2$O and CuO were selected as a p-type semiconductor oxide for solar cells. These copper oxides are advantageous as a low-cost reagent with a simple fabrication process. Their lower conversion efficiencies compared to the Si may have been due to presence of heterogeneous grain size copper oxides in the active layer. Defects produced by inadequate crystallinity may have caused carrier recombination, and the formation of higher quality copper oxide thin films may overcome this problem.

An energy level diagram of CIS/C$_6$0 solar cells is shown in Fig. 8(c). Previously reported values were used for the energy levels of the figures by adjusting them to the present work [8]. When light is incident from the FTO side, excitation by the light absorption happens in the p-n interface, and electrons and holes are produced by charge separation. Carriers would transport from -4.5 eV to -4.3 eV by hopping conduction. Improvement of the present bulk heterojunction solar cells would be possible by the introduction of a buffer layer, change of annealing conditions, and the improvement of the microstructure is also necessary to obtain high efficiency.

Figure 8. Energy level diagram of (a) Cu$_2$O/C$_6$0, (b) CuO/C$_6$0, (c) CIS/C$_6$0 and diamond/C$_6$0 solar cells.
The evaporation method provided high quality thin films, but a high vacuum and high temperature process are necessary. Although CISCuT method is a productive process, it requires a high temperature process [11]. On the other hand, the present spin coating method is simpler compared to the other formation methods. In addition, we can apply the spin coating method to plastic substrates without high vacuum and high temperature processes.

An energy level diagram of nanodiamond-based solar cells is shown in Fig. 8(d). Previously reported values were also used for the energy levels [12]. An energy gap of diamond estimated from Fig. 6(a), which corresponds to absorbance of 506 nm, is used for the model. From a theoretical calculation [13], nanodiamonds are composed of three layers; a diamond core (sp$^3$), a middle core (sp$^{2+x}$) and a graphitized core (sp$^2$). Therefore, a band gap of the nanodiamond is decreased by the existence of the sp$^{2+x}$ bonding [14].

4. Conclusions

C$_{60}$-based solar cells with copper oxides, CuInS$_2$ and diamond were fabricated and characterized. Devices based on the Cu$_2$O/C$_{60}$ structure were fabricated by an electrodeposition method, which provided better η of ~4×10$^{-3}$ % compared to CuO/C$_{60}$ solar cells. XRD and TEM results indicated the presence of Cu$_2$O and CuO nanoparticles. Formation of higher quality copper oxide thin films, introduction of a new electrode and optimization of deposition condition would improve the efficiencies of the solar cells. Energy level diagram was proposed, and separated holes could transfer from the valence band of the Cu$_2$O to the ITO, and separated electrons could transfer from the conduction band of the Cu$_2$O to the Al electrode, respectively.

Chalcopyrite/fullerene solar cells were also fabricated and characterized. A device of bulk heterojunction structure based on CuInS$_2$ and C$_{60}$ provided η of 8.0×10$^{-4}$ %, FF of 0.28, Voc of 0.18 V, which is better than those of the heterojunction structure. The present solar cells showed a high optical absorption in the range of 300 nm to 800 nm. Microstructures of the solar cells were observed by TEM and XRD, which indicated average particle sizes of CuInS$_2$ and C$_{60}$ of 5 nm and 13 nm, respectively. A carrier transfer mechanism was discussed by the energy level diagram.

Nanodiamond-based solar cells were fabricated and characterized. Diamond:C$_{60}$ nanocomposite structure provided photo-absorption in the range of 350 to 500 nm, and provided η of 4.3×10$^{-5}$%, FF of 0.35, J$_{sc}$ of 5.3 μA/cm$^2$ and V$_{oc}$ of 0.023V. Nanostructures of the thin films were investigated by TEM and X-ray diffraction, and the grain size of diamond were determined to be 12 nm. Optimization of blended structures with diamond would increase the efficiencies of the thin films. Photovoltaic behavior including charge transfer and mobility can be described on the basis of the energy diagram of the bulk heterojunction solar cells from the present J-V measurements, optical absorption and microstructure analysis. Optimization of blended structures with C$_{60}$ would increase the efficiencies of solar cells.

References

[1] Yu G, Heeger A J, 1995 J. Appl. Phys. 78 4510
[2] Padinger F, Ritterberger R S, Sariciftci N S, 2003 Adv. Funct. Mater. 13 85
[3] Oku T, Noma T, Suzuki A, Kikuchi K, Kikuchi S, 2010 J. Phys. Chem. Solids 71 551
[4] Oku T, Motoyoshi R, Fujimoto K, Akiyama T, Jeyadevan B, Cuya J, 2011 J. Phys. Chem. Solids 72 1206
[5] Arici E, Sariciftci N S, Meissner D, 2003 Adv. Funct. Mater. 13 165
[6] Takeda A, Oku T, Suzuki A, Kikuchi K, Kikuchi S, 2009 J. Ceram. Soc. Jpn. 117 967.
[7] Park N G, Kang M G, Ryu K S, Kim K M, Chang S H, 2004 J. Photochem. Photobiol. A 161 105.
[8] Oku T, Nagaoka S, Suzuki A, Kikuchi K, Hayashi Y, Inukai H, Sakuragi H, Soga T, 2008 J. Phys. Chem. Solids 69 1276
[9] Oku T, Takeda A, Nagata A, Noma T, Suzuki A, Kikuchi K, 2010 Energies 3 671.
[10] Green, M A, Emery K, King D L, Hishikawa Y, Warta W, 2006 Photovolt. Prog. Res. Appl. 2
14, 455

[11] Winkler M, Griesche J, Konovalov I, Penndorf J, Wienke J, Tober O. 2004 Solar Energy 77 705

[12] Nagata A, Oku T, Kikuchi K, Suzuki A, Yamasaki Y, Ōsawa E, 2010 Prog. Nat. Sci. Mater. Inter. 20 38

[13] Korobova M V, Avramenko N V, Bogachev A G, Rozhkova N V, Ōsawa, E, 2007 J. Phys. Chem. C 111 7330

[14] Ōsawa E, Ho D, Huang H, Korobov M V, Rozhkova N N 2009 Diam. Rel. Mater. 18 904.