



Layer-by-layer deposition films of copper phthalocyanine derivative; their photoelectrochemical properties and application to solution-processed thin-film organic solar cells

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ARTICLE INFO

Article history:

Received 11 December 2007
Received in revised form 16 September 2008
Accepted 26 September 2008
Available online 11 October 2008

Keywords:

Layer-by-layer deposition films
Phthalocyanine
Orientation
Light harvest
Hole transport
Thin-film organic solar cells

ABSTRACT

Ultrathin films serving as a light-harvesting and hole-transporting material were fabricated by layer-by-layer deposition of a water-soluble phthalocyanine derivative, copper(II) phthalocyanine-3,4',4'',4'''-tetrasulfonic acid tetrasodium salt (CuPcTS), and poly(diallyldimethylammonium chloride). The blue-shift of absorption peak and the absorption dichroism of the Q band indicated that CuPcTS molecules in the layer-by-layer films form cofacial dimers or oligomers and that their molecular planes take a three- or two-dimensional orientation in a direction parallel to the substrate depending on a drying process of the film during the deposition. The diffusion constant of hole carriers among CuPcTS molecules in the film was evaluated to be $6.5 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ in an acetonitrile solution from potential step chronoamperometry measurement. Solution-processed thin-film organic solar cells with a triple-layered structure were developed by combining a hole-transporting layer made of poly(3,4-ethylenedioxythiophene) oxidized with poly(4-styrenesulfonate), a light-harvesting layer of CuPcTS, and an electron-transporting layer of fullerene, in this sequence. Photovoltaic properties of the cells strongly depended on the thickness of CuPcTS films and can be maximized by controlling the thickness at ca. 10 nm.

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1. Introduction

Phthalocyanine (Pc) and its derivatives have been extensively studied as attractive materials for application to photovoltaic, electrochemical, gas-sensing, and data-storage devices [1,2]. Owing to the extended and delocalized π -electron system, Pc derivatives can absorb visible light efficiently and serve as an ambipolar conducting material depending on doping conditions. Because of these photoelectrochemical advantages and thermal and chemical stability, they have often been employed in thin-film organic solar cells [2].

Historically, the first Pc-based solar cell was a simple device called Schottky junction, which was composed of a Pc film sandwiched between two different electrodes [3]. The introduction of p - n heterojunction structure by Tang overcame the poor quantum efficiency of charge generation in the Schottky junction devices and improved the power conversion efficiency (η_p) to 1% [4]. Recently, Forrest et al. increased η_p by careful purification of organic materials and precise design of device structures [5–9]. They controlled the thickness of each active layer and the layered structures on a scale of angstrom by sequential vacuum (co)deposition of small molecules, resulting in η_p as high as 3.6% even for a simple planar p - n heterojunction device composed of copper phthalocyanine (CuPc) and fullerene (C_{60}) [6]. In addition to η_p , the well-designed layered structures in the planar

heterojunction devices can provide valuable fundamental information on primary processes such as exciton diffusion and charge collection [5].

On the other hand, wet-process fabrications such as spin-coating, dip-coating, and screen-printing have attracted much attention because they are suitable for producing large-area devices with low cost at ambient temperature and pressure, and because these techniques are easily applicable to flexible devices [10,11]. However, it is difficult to construct well-defined multi-layered structures using wet-processes such as solvent casting and printing techniques. Several studies have focused on the Langmuir–Blodgett (LB) technique to vary precisely the thickness of the organic layer. Hua et al. fabricated Schottky junction devices using a Pc-based LB film [12]. The pioneering work demonstrated that the layer thickness can be precisely controlled even by a wet-process to optimize photovoltaic structures although the photovoltaic performance was poor. Alternatively, the layer-by-layer deposition method has been developed as a simple technique for fabricating a multi-layered structure in the direction normal to the substrate and controlling the thickness of each functional layer with nanometer precision [13–15]. This technique is based on electrostatic adsorption of oppositely charged materials such as polycations, polyanions, and charged small molecules. Until now, many studies have been carried out on the fabrication and characterization of ultrathin films of Pc derivatives using this technique [16–24]. However, only a few studies dealing with thin-film organic solar cells have been reported [24]. Previously, our group fabricated light-harvesting ultrathin polymer films bearing tris

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(2,2'-bipyridine)ruthenium(II) moieties [25] and hole-transporting films [26] bearing ferrocene moieties, respectively, by the layer-by-layer deposition technique. Photocurrent generation was also observed for a heterostructured film composed of ruthenium complex and ferrocene moieties [27]. Recently, we also reported that ultrathin conducting polymer films of poly(3,4-ethylenedioxythiophene) oxidized with poly(4-styrenesulfonate) (PEDOT:PSS) can be fabricated by the layer-by-layer deposition technique and the films exhibited an excellent diffusion constant of hole carriers as high as that of spin-coat films of PEDOT:PSS [28]. In this study, layer-by-layer deposition films were fabricated with a water-soluble Pc derivative, copper(II) phthalocyanine-3,4',4'',4'''-tetrasulfonic acid tetrasodium salt (CuPcTS). Thin-film organic solar cells with the CuPcTS film as a light-harvesting layer were developed by combination with a hole-transporting layer with PEDOT:PSS and an electron-transporting layer with C₆₀.

2. Experimental details

2.1. Materials

Copper(II) phthalocyanine-3,4',4'',4'''-tetrasulfonic acid, tetrasodium salt (CuPcTS, Aldrich) and poly(3,4-ethylenedioxythiophene) oxidized with poly(4-styrenesulfonate) (PEDOT:PSS, Aldrich, 1.3 wt.% dispersion in H₂O, conductive grade) were used as an anionic molecule and a polyanion, respectively. Poly(diallyldimethylammonium chloride) (PDDA, Aldrich, $M_w = 10,000$ – $20,000$) and poly[(2-(methacryloyloxy)ethyl)trimethylammonium chloride] (PCM) were used as polycations. PCM was prepared by a radical polymerization of 2-(methacryloxy)ethyl trimethylammonium chloride (Aldrich) initiated by 2,2'-azobisisobutyronitrile (AIBN, Wako) in a degassed ethanol solution at 333 K and purified by reprecipitation from an ethanol solution into acetone three times. Chemical structures of polyelectrolytes and CuPcTS used in this study are shown in Fig. 1. CuPcTS and polyelectrolytes aqueous solutions were prepared using ultrapure water, which was purified by deionization, distillation, and passing through a filtration system (Barnstead, Nanopure II). The concentrations of CuPcTS and the polyelectrolytes aqueous solutions were adjusted to be 1 and 10 mM, respectively. The concentration of the polyelectrolytes was based on the molecular weight of their repeated units. CuPcTS and PEDOT:PSS aqueous solutions were ultrasonicated with an ultrasonic disruptor (Tomy Seiko Co., Ltd., UR-200P) for 2 min and filtered through a 0.45 μm membrane filter (Millipore, PVDF) before the layer-by-layer deposition. Polystyrene (PS, Aldrich, $M_w = 280,000$) was used after purification by the reprecipitation from a toluene solution into methanol three times. Fullerene (C₆₀) was purchased from Frontier Carbon Co. Ltd. Tetrabutylammonium tetrafluoroborate (Aldrich), anhydrous acetonitrile (Aldrich), *o*-dichlorobenzene (Wako, guaranteed reagent), toluene (Nacalai Tesque, extra pure reagent), acetone (Nacalai Tesque, extra pure reagent), and ethanol (Nacalai Tesque, extra pure reagent) were used as received.

2.2. Substrate preparation

Quartz plates (12 × 32 × 1 mm³) and indium–tin–oxide (ITO)-coated glass plates (76 × 26 × 0.88 mm³, 10 Ω/square) were used as a substrate for absorption and AFM measurements, and as an electrode for electrochemical and current density–voltage (*J*–*V*) characteristics measurements, respectively. They were cleaned by ultrasonication in toluene, acetone, and ethanol for 15 min each in this order and then dried with a N₂ flow. These cleaned substrates were additionally cleaned with UV–O₃ (Nippon Laser & Electronics Lab., NL-UV253S) for 60 min.

2.3. Preparation of layer-by-layer films

Layer-by-layer deposition films consisting of PCM and PEDOT:PSS (PCM/PEDOT:PSS) were prepared as described previously [28].

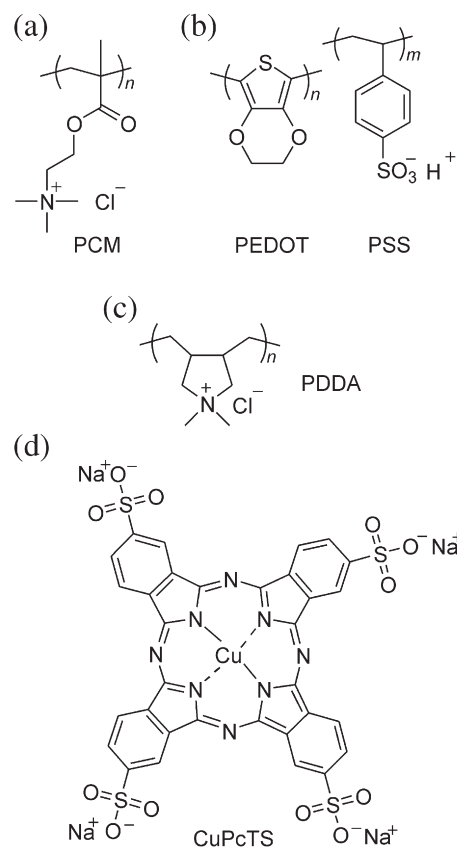


Fig. 1. Chemical structures of polyelectrolytes and CuPcTS used in the layer-by-layer deposition: (a) PCM (polycation), (b) PEDOT:PSS (polyanion), (c) PDDA (polycation), and (d) CuPcTS.

Layer-by-layer deposition films of a pair of ionic species, PDDA and CuPcTS (PDDA/CuPcTS), were prepared on quartz, ITO-coated glass, and the PCM/PEDOT:PSS films by the repetitive immersion cycles of the substrates into solutions in the following order: substrates were immersed first in an aqueous solution of PDDA for 5 min, rinsed in ultrapure water for 3 min, then immersed in an aqueous solution of CuPcTS for 5 min, and rinsed again in ultrapure water for 3 min: this cycle gives a one-bilayer film. The substrates were dried completely under the airflow for 5 min after each rinse. All of the experiments were carried out under atmosphere at a temperature of 294 K.

2.4. Preparation of photovoltaic cells

A PDDA/CuPcTS film with *n* bilayers was deposited onto the PCM/PEDOT:PSS film (100 nm, 20 bilayers) preliminarily prepared on an ITO-coated glass. A blend solution of C₆₀ (24 mg) and PS (6 mg) in *o*-dichlorobenzene (1 mL) was spin-coated on the top of the PDDA/CuPcTS films at a spin rate of 400 rpm for 10 s and then 1000 rpm for 99 s. The thickness of the C₆₀-dispersed film was ~50 nm. Finally, Al electrode about 50 nm in thickness was thermally deposited at 3.3×10^{-4} Pa on the top of the C₆₀-dispersed film through a shadow mask with an active device area of 0.1 cm² (0.2 × 0.5 cm²). The layer structures of photovoltaic cells built up by these processes were described as ITO|PCM/PEDOT:PSS|(PDDA/CuPcTS)_{*n*}|C₆₀|Al in this report.

2.5. Measurements

UV–visible absorption spectra of the films were measured with a spectrophotometer (Hitachi, U-3500). The thickness and the surface morphology of the films were measured by atomic force microscopy (AFM, Shimadzu, SPM-9500J) in the contact mode. For absorption

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