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Hole injection enhancement of a single-walled carbon nanotube anode using an organic charge-generation layer

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ABSTRACT

We demonstrate significant hole injection enhancement of single-walled carbon nanotube (SWCNT) anodes in flexible organic light-emitting devices (OLEDs) by the insertion of a strong electron-accepting organic charge-generation layer (CGL), hexaazatriphenylene hexacarbonitrile (HAT–CN). To clarify the origin of hole injection improvement, we investigated interfacial electronic structures using *in situ* ultraviolet photoelectron spectroscopy, inverse photoelectron spectroscopy, theoretical calculations, and electrical measurements. The HAT–CN layer significantly increased the work function of SWCNT anodes and acted as an efficient CGL due to its deep-lying lowest unoccupied molecular orbital level, which arises from the strong electron-accepting characteristics of the carbonitrile endgroups. We compared the energy level alignment at the interface of the N,N′-bis(1-naphthyl)-N,N′-diphenyl-1,1′-biphenyl-4,4′-diamine (NPB) hole transport layer/HAT–CN/SWCNTs with that of NPB/SWCNTs, and found that the highest occupied molecular orbital level of the NPB changed from 1.20 to 0.40 eV with insertion of the HAT–CN layer. As a result, flexible OLEDs with the HAT–CN layer showed an order of magnitude larger current density and luminance than those without the HAT–CN layer.

1. Introduction

Single-walled carbon nanotubes (SWCNTs) have attracted interest in various fields of research due to their unique optical and electrical properties [1]. One promising application of SWCNTs is as transparent conducting electrodes in optoelectronic devices, such as organic light-emitting devices (OLEDs) and organic photovoltaic cells (OPVCs) [2–5]. Although indium tin oxide (ITO) is widely used as transparent electrodes in various optoelectronic devices, it is not used in flexible optoelectronic devices since the conductivity of ITO deteriorates significantly after mechanical bending due to

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its brittleness. In addition, the price of indium has increased due to limited resources. Therefore, it is necessary to search for an alternative to ITO for use as an electrode material. In this regard, SWCNTs are considered promising candidates, having both high conductivity and transparency.

However, the work function of SWCNTs is between that of an efficient anode and an efficient cathode, and hence must be increased for use as an anode or decreased for use as a cathode. In general, to achieve highly efficient organic optoelectronic devices, an appropriate charge injection layer is incorporated into the electrodes [6,7]. In an anode side, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is a well-known hole injection layer (HIL), providing high work function and smooth surface to the anode. However, PEDOT:PSS HIL has considerable shortcomings: It is difficult to be applied in large area devices unlike thermal evaporation because of its spin-coating process and its instability from light exposure and oxidation is an inveterate problem [8]. In addition, PEDOT:PSS absorbs the light in the visible range, and thus it shows some drawbacks to be applied in optoelectronic devices [9,10]. In this respect, transition metal oxides (TMOs), such as molybdenum trioxide (MoO_3), vanadium pentoxide (V_2O_5), and tungsten trioxide (WO_3), have been introduced into the anode for efficient hole injection in OLEDs [11–14]. Interestingly, the working mechanism of TMOs is very unique, so called "charge generation effect". We depict the hole injection mechanism when TMOs are present, the charge-generation layer (CGL), in Fig. 1. Outwardly, the hole injection barrier seems to be increased by the insertion of a TMO layer since its valence band minimum (VBM) is deeper than the highest occupied molecular orbital (HOMO) level of the hole transport layer (HTL). However, TMOs commonly have a high work function and a deep-lying conduction band minimum (CBM), which allow the electrons in the HOMO level of the HTL to be easily transferred to the Fermi level of an anode through the CBM, which is near the Fermi level of an anode when under a bias (Fig. 1(a)). Consequently, the result is equivalent to that of efficient hole injections (Fig. 1(b)). For this reason, this type of HILs is called a CGL. This unique mechanism of a CGL makes it to be used as an efficient connecting layer in the tandem-structured devices. This mechanism has been investigated by *in situ* ultraviolet photoelectron spectroscopy (UPS) and inverse photoelectron spectroscopy (IPES) experiments [15–19]. Recently, hexaazatriphenylene hexacarbonitrile (HAT–CN) has been investigated as an organic CGL since it has electronic characteristics and functionalities in devices similar to TMOs, while it can be easily evaporated at much lower temperatures [20–22]. This is an advantage with flexible substrates which are processed at low temperature, in addition to the significant hole injection improvement. However, no work has been reported on the HAT–CN application to SWCNTs.

In this regard, we investigated the hole injection enhancement of a SWCNT anode with the insertion of a HAT–CN layer in flexible OLEDs. We performed *in situ* UPS and IPES experiments to determine the energy level alignments at the interface of the *N*,*N*′-bis(1-naphthyl)-*N*,*N*′-diphenyl-1,1′-biphenyl-4,′4′-diamine (NPB, most typical HTL)/HAT–CN/SWCNTs and NPB/SWCNTs. In addition, we also performed a theoretical calculation of the electronic structures of HAT–CN and compared the results with experimental results to investigate the origin of deep-lying electronic states. We also fabricated practical flexible OLEDs and measured the current density–voltage–luminance characteristics (*J*–*V*–*L*) to ensure hole injection enhancement with insertion of the HAT–CN layer. To the best of our knowledge, this is the first investigation on the HAT–CN application to SWCNTs, as well as the first transport gap measurement on HAT–CN. This study would provide valuable scientific information to open a prospect in the SWCNT application to the transparent anode.

2. Experimental section

Transparent conducting films were prepared using SWCNTs on a flexible polyethylene naphthalate (PEN) substrate. A SWCNT powder was dispersed in sodium dodecylbenzenesulfonate (NaDDBS) aqueous solution by sonication in a bath-type sonicator. The solution was centrifuged at 8000 rpm for 10 min. The supernatant of the resulting solution was sprayed onto a PEN substrate with an argon gas brush pistol (Gunpiece GP-1). Then, the substrate was dried and washed with nitric acid to remove a surfactant of NaDDBS. To fabricate OLEDs using a SWCNT anode, the prepared SWCNT films were patterned using a conventional photolithography process with a photoresist (AZ5214E). Then, the exposed SWCNTs were removed with oxygen plasma.

An *in situ* UPS experiment was carried out using a PSP RESOLVE 120 spectrometer which was directly connected to the preparation chamber. Ultraviolet (He I, 21.22 eV) radiation was

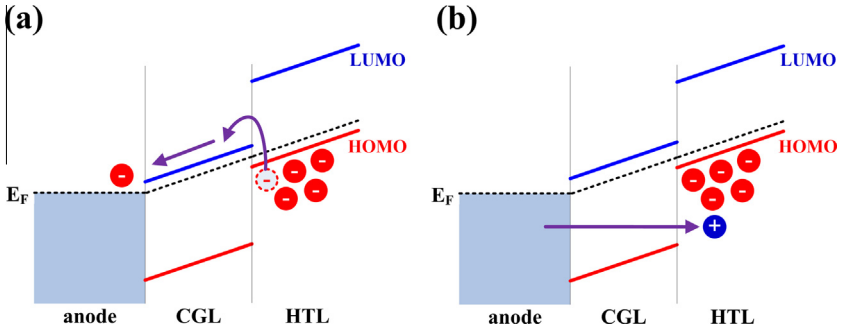

Fig. 1 – Schematic charge injection mechanism with a CGL. From the energy level alignment under a bias, it can be seen that (a) easy electron transfer from the HTL to the anode through the CGL leads to (b) efficient hole injection from the anode to the HTL. (A colour version of this figure can be viewed online.)