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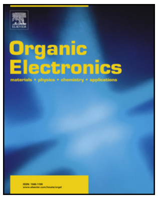

Highly-efficient organic light-emitting devices based on poly(*N*,*N*′-bis-4-butylphenyl-*N*,*N*′-bisphenyl)benzidine:octadecylamine-graphene quantum dots

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ABSTRACT

Organic light-emitting devices (OLEDs) with a poly(*N*,*N*′-bis-4-butylphenyl-*N*,*N*′-bisphenyl)benzidine (poly-TPD):octadecylamine (ODA)-graphene quantum dots (GQDs) hole transport layer (HTL) were fabricated to enhance their efficiency. Photoluminescence (PL) and PL excitation spectra showed that the optical energy bandgap of the ODA-GQDs was 2.7 eV, and ultraviolet photoelectron spectroscopy spectra demonstrated that the edge of the highest occupied molecular orbital of the ODA-GQDs was 5.3 eV below the Fermi level. While the operating voltage of the OLEDs with a PVK:ODA-GQD (9.77 V, 0.25 wt%) HTL at 10 mA/cm^2 was 0.8 V lower than that of the OLEDs with a poly-TPD HTL (10.57 V), their current efficiency was larger by more than 20% than that of the OLEDs with poly-TPD (32.88 cd/A) due to an increase in the number of holes injected from the ITO to the HTL. The number of injected holes was increased due to a reduction of the energy barrier and an increase in the conductivity.

1. Introduction

Organic light-emitting devices (OLEDs) have been receiving considerable attention for potential applications in flexible displays and solid-state lighting [1–4]. The prospect for promising applications of OLEDs has led to substantial research and development efforts to decrease their operating voltage and to enhance their efficiency [5,6]. The optimization of the charges injected from the electrode into the emitting layer is designed to achieve a low operating voltage and a high efficiency due to the low intrinsic carrier concentration of the organic materials [7]. However, the large energy barrier between the work function of the indium-tin oxide (ITO) and the highest occupied molecular orbital (HOMO) of the hole transporting layer (HTL) restricts the efficient flow of the injected holes from the ITO to the HTL [8,9]. A variety of routes have been proposed to facilitate hole injection utilizing the advantages of special materials such as tungsten oxide, molybdenum trioxide, vanadium oxide, and nickel oxide [10–14]. However, almost all of the oxides are relatively toxic to both humans and the environment. In particular, when nanoparticles of metal oxides are synthesized, the toxicity of the metal oxides may pose some serious problems [15].

Graphene quantum dots (GQDs) are graphene fragments with sizes less than 20 nm and with special quantum confinement effects and edge effects [16]. Recently, GQDs have been used extensively as carrier acceptors due to the ultrafast injection of carrier through the GQDs from the carrier extraction layer to the active layer of the photovoltaic (PV) cells [17]. When the GQDs are inserted into the hole transport layer of the PV cells, the carrier conductance of the PEDOT:PSS layer is increased, and its light scattering length is extended [18]. Furthermore, GQDs have excellent physical properties: non-zero band-gap, strong excitation luminesce due to the quantum confinement and the edge effects, simple band-gap tuning, low toxicity, high chemical stability, and excellent carrier transport mobility [19–23]. However, the existence of numerous oxygenous functional groups and defects in the GQDs decreases their electron mobility, and because of the hydrophilic behavior of the GQDs, they are not uniformly dispersed in the hydrophobic HTL solution, resulting in limited HTL material selection [24].

In this paper, we demonstrate enhancement of the current efficiency for OLEDs using a poly(*N*,*N*′-bis-4-butylphenyl-*N*,*N*′-bisphenyl)benzidine (poly-TPD):octadecylamine (ODA)-GQD HTL formed by using a simple solution method. The ODA-GQDs have high conductivity and good dispersal properties with a poly-TPD solution. Also, because the highest occupied molecular orbital (HOMO) level of the ODA-GQDs is located between the work function of the ITO and the HOMO level of the poly-TPD, the poly-TPD:ODA-GQDs were used as the HTL of the OLEDs. The efficiency enhancement of the OLEDs with ODA-GQDs is

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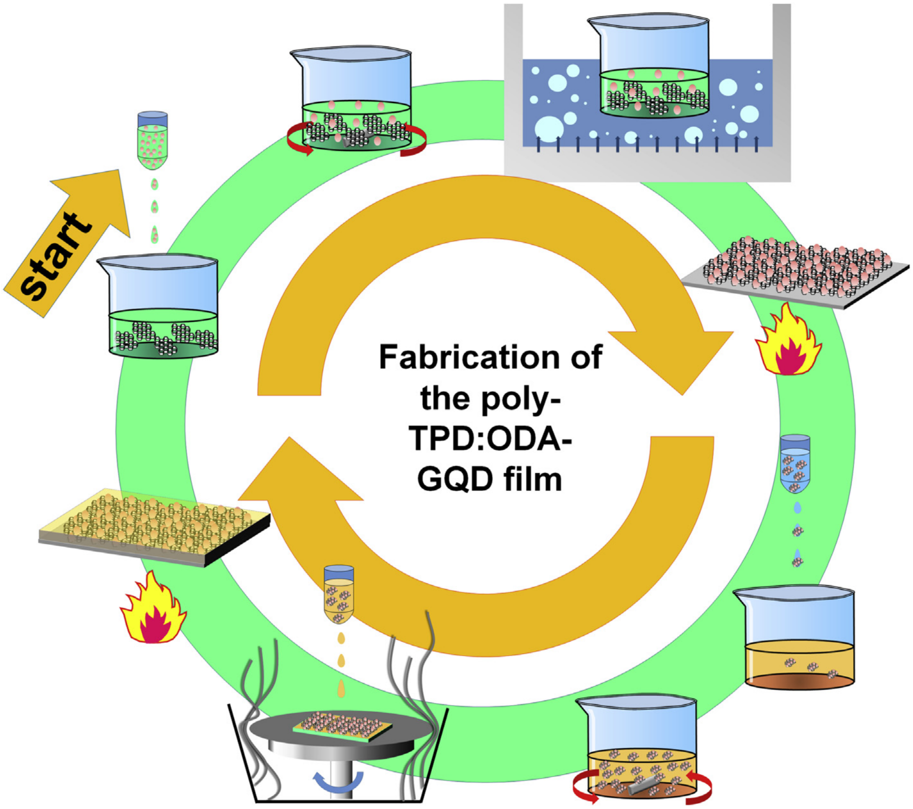

Fig. 1. Schematic diagram of the formation process for the poly-TPD:ODA-GQD film.

attributed to the improved efficiency for injecting holes from the anode to the active layer, resulting in a higher current efficiency [25]. Transmission electron microscopy (TEM) measurements were performed to investigate the microstructural properties of the ODA-GQDs. X-ray photoelectron spectroscopy (XPS) was performed to investigate the nucleophilic substitution in the ODA-GQDs. Ultraviolet photoelectron spectroscopy (UPS) and photoluminescence (PL) measurements were carried out to investigate the optical properties of the ODA-GQDs. Current density - voltage - luminance (J-V-L) measurements were carried out to investigate the electrical and the optical properties of the OLEDs fabricated utilizing ODA-GQDs.

2. Experimental details

Fig. 1 shows a schematic diagram of the method used in this research to fabricate the poly-TPD:ODA-GQD films. The details of the process for fabricating the ODA-GQDs are given elsewhere [26]. A mixed powder of ODA and reduced graphene oxide (rGO) was dissolved in methanol at a weight ratio of 20:1. After the mixed solution had been stirred for 24 h by using a spin-bar, an ODA-rGO flakes were formed due to nucleophilic substitution. The ODA-rGO flakes were washed with methanol to remove the residue. The ODA-rGO flake powder was dried at 100 °C. The ODA-rGO powder was dissolved in a mixed solution of chlorobenzene and methanol with a volume ratio of 50:1. Next, the ODA-rGO solution was mixed for 3 h by using an ultrasonic method, resulting in the formation of the ODA-GQDs. After this solution had been centrifuged, the upper portion of the liquid in the centrifuge tube was extracted. The poly-TPD was dissolved in the ODA-GQDs solution, and the mixed solution was stirred for 10 h by using a spin-bar. The poly-TPD:ODA-GQD solution was deposited onto an ITO-coated glass substrate, resulting in the formation of a poly-TPD:ODA-GQD film.

The sheet resistivity and the thickness of the ITO thin films coated on the glass substrates were 15 Ω/square and 150 nm, respectively. The ITO-coated glass substrates were cleaned in acetone and methanol at 25 °C for 20 min each by using an ultrasonic cleaner and were thoroughly rinsed in de-ionized water. After the chemically-cleaned ITO-coated glass substrates had been dried by using N_2 gas with a purity of 99.9999%, the surfaces of the ITO-coated glass substrates were treated with an ultraviolet-ozone gas for 20 min at room temperature. The poly-TPD:ODA-GQD solution was deposited onto the ITO-coated glass substrate by spin-coating at 5000 rpm for 61 s and was then annealed at 145 °C for 15 min in a glove box. After the samples had been transferred into an evaporation chamber, the organic layers and the electrodes were deposited at a substrate temperature of 25 °C and a system pressure of 1.7×10^{-4} Pa. The deposition rates of the organic layers and the metal layer were approximately 1.0 and 2.0 Å/s, respectively.

The TEM images were measured by using a JEM 2100F transmission electron microscope operating at 200 kV. The XPS and the UPS spectra were measured by using a theta probe base system purchased from the Thermo Fisher Scientific Co. The UPS spectra were obtained at a system pressure of 6.7×10^{-10} Pa with a HeI 21.2-eV source. The Raman measurements were obtained by using an IS50 model spectrometer. The PL measurements were performed by using an X-ray fluorescence spectrometer (TCSPC-FL920) equipped with a pulsed laser operating at 365 nm. The current-voltage characteristics were measured on a programmable electrometer with built-in current and voltage measurement units (M6100, McScience). The brightness intensities were measured by using a brightness meter, and the electroluminescence (EL) spectra were measured by using a luminescence spectrometer (CS-1000, Minolta). All measurements of the electrical characteristics for the OLEDs were carried out at 25 °C under atmospheric conditions.

3. Results and discussion

Fig. 2 shows (a) low-resolution and (b) high-resolution TEM images of the ODA-GQDs. The diameter of the ODA-GQDs was approximately 40 nm, as shown in Fig. 2 (a). The TEM image demonstrated that GQDs had been embedded in the ODA nanoparticles, resulting in the