Solution-Processable Graphene Oxide as an Efficient Hole Injection Layer for High Luminance Organic Light-Emitting Diodes

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1. EXPERIMENTAL SECTION

Preparation of Graphene Oxide (GO): The graphite flakes (10g) and concentrated H_2SO_4 (230 mL) were placed in a flask. The flask was stirring continuously and placed in an ice bath. KMnO₄ (30 g) was added gradually with stirring and cooling, so that the temperature of the mixture was not allowed to rise to 20° C. After adding KMnO₄ completely, the mixture was stirred for 2h at 35° C. Then after, about 460 mL of deionized (DI) water was added to the mixture and continued stirring for 1 h. The reaction was terminated by the addition of about 1.4 L of DI water and 25 mL of 30 % H₂O₂ solution, causing violent effervescence and an increase of temperature to about 100° C. Then the color of the reaction mixture changes to bright yellow. The obtained graphene oxide (GO) suspension was filtered and washed with a large amount of HCl (1:10) solution (2.5 L) to remove metal ions followed by deionized water. Then, the obtained GO paste was dried in vacuum oven at 60° C until the agglomerate appeared. Finally, the obtained GO was dissolved in DI water by ultrasonication and centrifuged at 4000 rpm for 30 min. to remove any unexfoliated GO. The GO platelets were obtained by dehydration at 60° C in air.

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Device fabrication and characterization: Pre-patterned ITO substrates were bought with the sheet resistance of $9\sim15 \Omega/sq$, ITO thickness of 1200 ~1600 Å, and the substrate size of $20\times20\times0.7$ mm. ITO substrates were first cleaned in an ultrasonic bath with acetone and isopropanol consecutively for 10 minutes. These were then blow dried with a nitrogen gun, and followed by oxygen plasma treatment for 5 minutes. The GO solution had ultrasonic treatment for 10 minutes before spin-coating on oxygenplasma precleaned ITO substrates. The spin-coating was done at 1000 rpm for 1 minute, then films were dried on a hot plate at 160°C for 5 minutes to remove any solvents, and finally ITO substrates were loaded into the evaporator chamber for device fabrication. The device structure is anode/TPD (20 nm)/Alq₃ (60 nm)/LiF (1.0 nm) or Li₃N (0.5 nm)/Al (150 nm). The TPD layer was first evaporated (deposition rate 0.1-0.2 nm/s) onto the anode, then the Alq₃ layer was evaporated at a rate of 0.2-0.4nm/s, and a thin layer of LiF (1.0 nm) or Li₃N was deposited on Alq₃/TPD/anode at a rate of 0.01 nm/s, and finally a 150-nm Al electrode deposited on top at a rate of 0.6–1.0 nm/s with a shadow mask. The active area of the devices was 3.9 mm^2 . All evaporations were conducted under a vacuum of 4×10^{-6} torr. The deposition rates were controlled by a quartz oscillating thickness monitor. The current densityvoltage-luminance characteristics were measured using Keithley (2400 and 2100) sources with a calibrated silicon photodiode. All measurements were performed without encapsulation in an ambient atmosphere. The morphology was characterized by Atomic force microscopy (AFM) (Veeco Dimension 3100) in tapping mode. All measurements were performed without encapsulation in an ambient atmosphere. The XPS and UPS measurements were carried out using a Scienta ESCA 200 spectrometer at a base pressure of 10^{-10} mbar, using monochromatized Al (K_a) X-rays (1486.6 eV) and He I radiation (21.2 eV), respectively. The experimental conditions were such that the full width at half maximum of the Au 4f7/2 line was 0.65 eV.

2. XRD

The crystalline structure was investigated by x-ray diffraction using a Philips diffractometer with a monochromatic Cu $K_{\alpha 1}$ incident beam ($\lambda = 0.154056$ nm). Figure s1 shows the XRD pattern of the sample in $\theta/2\theta$ geometry. Only the peak at around 12° corresponding to the (001) plane family of the

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graphene oxide phase can be observed. This suggested that the sample is crystalline with a preferred (001) orientation, with an interplane distance of 7.37 Å [1]. However, the XRD peak is broadening, which is due to the small grain size of the sample. The crystallites average size was estimated from the full width at half maximum (FWHM) of the most intense diffraction peak (001) using the Debye-Scherrer's formula. The average grain size is calculated to be approximately around 4 nm.



Figure S1. X ray diffraction pattern of grapheme oxide samples

3. Raman spectroscopy

Raman spectroscopy is a widely used tool for the characterization of carbon products. Raman spectra were recorded with the LabRam Aramis HR (Jobin-Yvon) system, using a laser excitation line at 532 nm (Nd–YAG) in the range of 1000–2000 cm⁻¹. A power of 0.9 mW was used with 1µm focus spot in order to avoid photodecomposition of the films. The acquisition time for the Raman spectrum was 15 s for each spectrum. The G band is broadened and shifted to 1603 cm⁻¹ compared with graphite whereas the D band at 1352 cm-1 becomes the prominent feature in the spectrum testifying to indicating the creation of sp3 domains due to the extensive oxidation [2,3]. These results were confirmed by different batches of GO and different regions in one sample.



Figure S2. Raman spectroscopy of GO on silicon substrate

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