Electronic Supplementary Information for:

Full-solution processed, flexible, top-emitting polymer light-emitting diodes based on the printed Ag electrodes

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Experimental Section

Materials

Poly(ethylene naphthalate) (PEN) sheets with the thickness of 125 μm were used as the flexible substrates. PEDOT4083 and PH1000, two kinds of conductive Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), were purchased from Heraeus Clevios. Aqueous PH1000 solution was mixed with 5 wt%dimethyl sulfoxide (DMSO) and 0.5 wt% surfactant (Zonyl FS 300). PH1 solution was achieved from the mixed solution of PH1000 and 0.5% Zonyl FS-300. Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and Poly[2-(4-(3′,7′-dimethyloctyloxy)-phenyl)-1,4-phenylenevinylene] (P-PPV) were offered by Lijian Corporation (Guangzhou, China). ZnO nanoparticals solution and WO_3 nanoparticals solution was prepared according to the literatures.[7,9] Poly (ethylene glycol) (PEG) (Mw=4000) and potassium peroxodisulfate (KPS) were purchased from Uni-Chem. Ammonium tetrachloropalladate(II) ($(NH_4)_2PdCl_4$), [3-(methacryloyloxy)propyl] trimethoxysilane (MPS), 2-(methacryloyloxy)ethyl-trimethylammonium chloride (METAC) (80 wt.% aqueous solution), polyethylenimine (PEI), dimethylsulfoxide (DMSO) and all other chemicals were purchased from Sigma-Aldrich. A thermal crosslinkable urethane liquid rubber compound (Clear Flex 50, from Smooth-On USA, mixed at a weight ratio of 1:2 parts A:B) was used as the elastic encapsulation material, TCPU.

Fabrication of printed Ag cathodes via PAMD

PEN sheets were used directly by tearing off their protective films. They were plasma-treated for 5 min, and immersed into a 0.5 wt% MPS solution (95 wt% EtOH, wt% HAc) for 1 h, followed by rinsing. Then these substrates were immersed into an aqueous solution of 2-(methacryloyloxy)ethyl-trimethylammonium chloride (METAC) (80

wt% aqueous solution) (20 wt%) and potassium peroxodisulfate (KPS) (2.5 g/L), and heated at 60 °C for 60 min for polymerization. Screen printing of catalytic ink ($(NH_4)_2PdCl_4$, (100 mg), polyethylene glycol (PEG, 4 g, Mw=4000 g/mol) and deionised (DI) water (1.0 g)) was performed on the PMETAC-modified substrates to form the ink patterns. At the end, the ink-patterned substrates were placed in the dark for 30 min to load $PdCl_4^{2-}$ by ion exchange, followed by treating with plasma for 2 min and rinsing with DI water to remove the ink completely. The ELD of Ag was performed in a plating bath consisting of a 1:1 mixture of freshly prepared solution A and B. Solution A contains NaOH (12 g/L), and potassium sodium tartrate (29 g/L) in DI water. Solution B is a formaldehyde (40mL/L) aqueous solution. Then the activated $PdCl_4^{2-}$ loaded substrates were immersed in the Ag plating bath ([5 g/L $Ag(NH_3)_2]NO_3$ and 50 g/L potassium sodium tartrate aqueous solution) for serves minutes to achieve the printed Ag films at a thickness around 70 nm.

Fabrication of PLEDs

70 nm thick PAMD-Ag electrodes on PEN were prepared as described above. ZnO ETL was formed by spin-coating from methanol and methoxyethanol mixed solution of ZnO nanoparticles on the printed Ag electrode and then annealed for 30 min at 80°C. PEI films were made by spin-coating from its 0.5 wt% 2-methoxyethanol solution on ZnO ETL at 3500-5000 rpm for 60 s in a nitrogen-filled glove box and annealed at 80 °C for 30 min. EMLs of PLEDs were spin-coated on ZnO or PEI at different speeds in the glove box from the chlorobenzene solution of MEH-PPV or P-PPV and annealed at 60 °C for 30 min. For the devices using MEH-PPV EML, a buffer layer inserted between MEH-PPV and anode is obtained from PH1 solution. In the devices based on P-PPV, WO_3 film spin-coated on P-PPV was served as HTL. Due to the hydrophobic P-PPV, 0.5 wt% Zonyl FS-300 was doped into isopropanol solution of WO_3 to increase

wettability of the solution. Doped PH1000 was served as top anode, which was spin-coated on EML, PH1 or WO_3 at 1000 rpm for 60 s, and then annealed at 90 °C for 20 min in the glove box to finish the device fabrication. Finally, the TPLEDs were encapsulated using UV curable epoxy resin or Clear Flex 50.

Characterization

Ultraviolet photoelectron spectroscopy (UPS) was measured by ESCALAB 250Xi X-ray Photoelectron Spectrometer. Atomic force microscopy (AFM) was performed with Bruker Dimension Edge SPM System by non-contact mode. Scanning electron microscopy (SEM, JEOL JSM-6700F) was also used for surface checking. ZnO nanoparticles were characterized by using transmission electron microscopy (TEM, JEOL JEM-2000). Crystal phase of the samples was examined by X-ray diffraction (XRD) (Bruker, D8-Advance X-ray diffractometer with Cu Kα radiation, λ = 1.54056 Å, 40 kV, 40 mA) from $2\theta = 5°$ to 60° at a rate of 0.02° s^{-1} at room temperature under ambient condition. The current-voltage and light intensity measurements were done on Keithly 2400 source meter and a PR-655 Spectra Scan Spectrophotometers. The fluorescent lifetime of the samples were measured using an Edinburgh Instruments FLS920 Fluorescence Spectrometer. The devices encapsulated by Clear Flex 50 were bended in N_2 glove box with a bending radius of 5.0 mm and then the devices were test in air using a rapid test model.

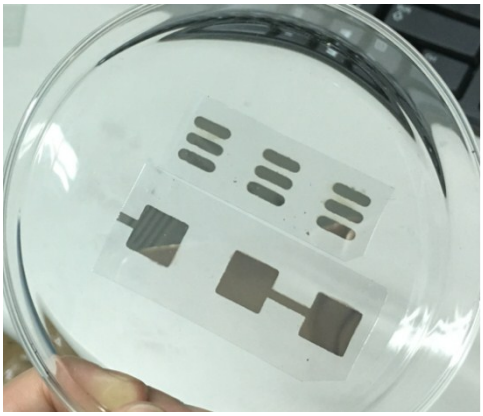

Fig. S1 Photograph of the printed Ag with different pattern fabricated on PEN sheet.

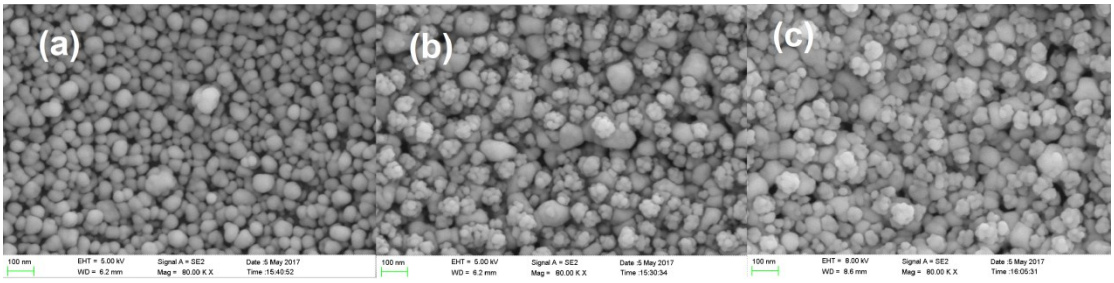

Fig. S2 SEM images of (a) Printed Ag, (b) Printed Ag/ZnO and (c) Printed Ag/ZnO/PEI.

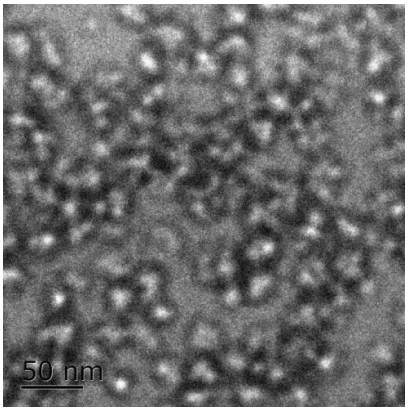

Fig. S3 TEM images of the ZnO nanoparticles

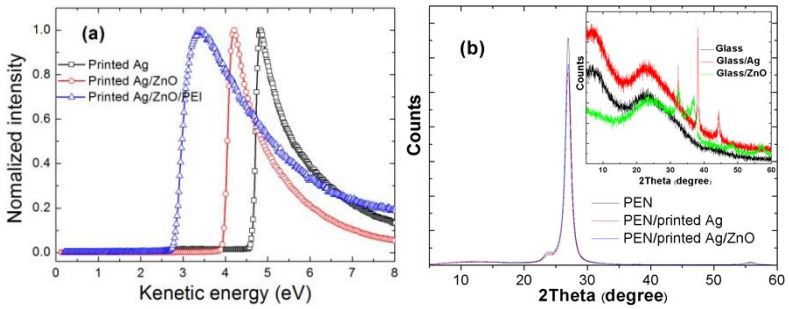

Fig. S4 (a) UPS spectra of the printed Ag W/O interface modification layers and (b) XRD spectra of the different samples.

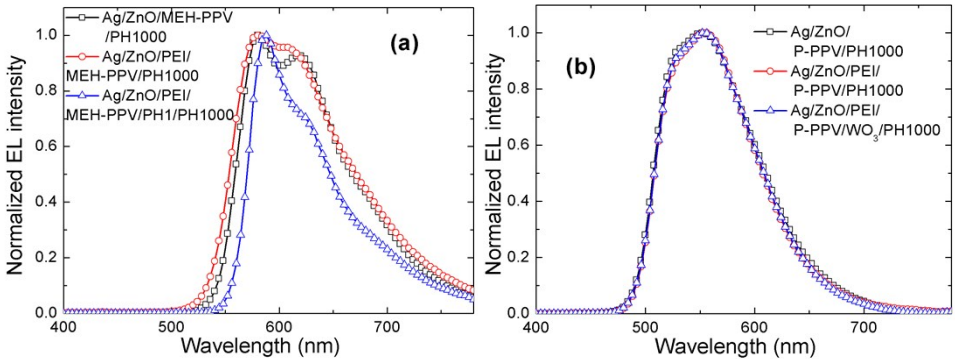

Fig. S5 EL spectra of the TPLEDs based on MEH-PPV (a) and P-PPV (b).

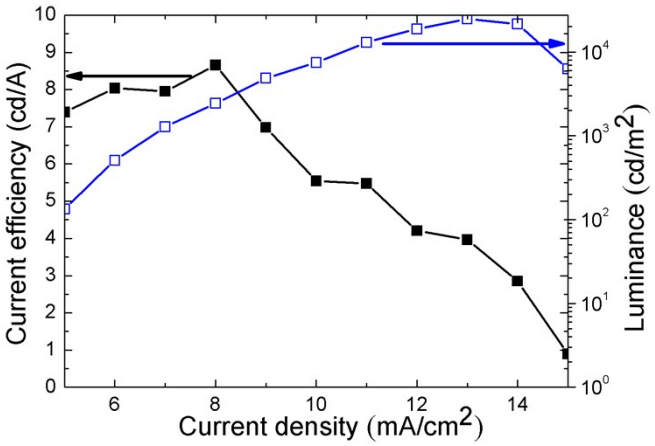

Fig. S6 Current efficiency, luminance versus current density characteristics of the PLEDs with a conventional architecture of ITO/PEDOT/P-PPV/LiF/Al.