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Laminating solution-processed silver nanowire mesh electrodes onto solid-state dye-sensitized solar cells

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ABSTRACT

Solution processed silver nanowire meshes (Ag NWs) were laminated on top of solid-state dye-sensitized solar cells (ss-DSCs) as a reflective counter electrode. Ag NWs were deposited in <1 min and were less reflective compared to evaporated Ag controls; however, AgNW ss-DSC devices consistently had higher fill factors (0.6 versus 0.69), resulting in comparable power conversion efficiencies (2.7%) compared to thermally evaporated Ag control (2.8%). Laminated Ag NW electrodes enable higher throughput manufacturing and near unity material usage, resulting in a cheaper alternative to thermally evaporated electrodes.

1. Introduction

Dye-sensitized solar cells (DSCs) [1–3] are an emerging photovoltaic technology on the verge of commercialization with devices based on iodide/tri-iodide liquid electrolytes exceeding power conversion efficiencies of 11% [4]. Liquid DSCs can be made via high throughput processes because liquid based DSCs do not require vacuum deposition techniques during assembly. However, two pieces of fluorine doped tin oxide (FTO) covered glass are often used as the front and back electrodes, which represent a significant fraction of production costs for the liquid DSC. Solid-state dye-sensitized solar cells (ss-DSC), which replace the liquid electrolyte with a solid organic hole conductor (e.g. spiro-OMeTAD), have two significant manufacturing advantages over the liquid-electrolyte based DSCs: (1) solid hole conductors are easier to package and potentially more stable than volatile liquid electrolytes and (2) ss-DSCs require only one piece of transparent conducting glass used as the front electrode. However, the counter electrode of ss-DSCs are deposited via thermal evaporation of Au or Ag [5,6]. It is highly desirable to develop alternative deposition techniques to deposit reflective counter electrodes for ss-DSCs. Several groups have recently replaced thermally evaporated counter electrodes by spray coating Ag nanoparticles in solution on top of organic photovoltaic cells and achieved comparable performance [7,8]. Ag nanoparticle films deposited via spray coating usually require a 150–200 °C sintering step [9], which can crystallize the spiro-OMeTAD and dissociate the dye from the titania. It is desirable to develop Ag printing techniques that can be performed at room temperature.

It has recently been shown that films of Ag nanowires can be transferred through lamination to serve as a transparent top electrodes in organic photovoltaic devices [10,11]. Ag NWs films are first made by drop-cast from a liquid suspension in air to a host substrate and annealed to achieve sheet resistances comparable to those of transparent conducting oxides [11]. The Ag NWs films are then transferred from the host substrate to the solar cell by mechanical pressing, as shown in Fig. 1A. Thin layers of

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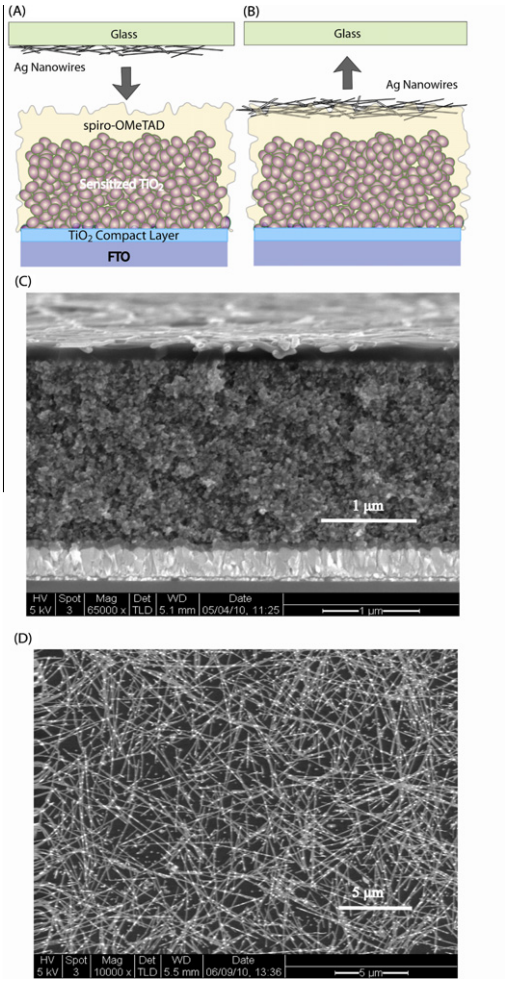

Fig. 1. Device schematic of dye sensitized solar cell (A) before and (B) after Ag NW lamination. (C) SEM side view image (65,000× magnification, 1 μm scale bar) and (D) SEM top view image (10,000× magnification, 5 μm scale bar) of solid-state DSC after Ag NW lamination.

Ag NWs show high transparency in the solar spectrum, have low sheet resistance, and can be processed with high throughput. As the nanowire concentration of the film increases, the transmission decreases and the films become more reflective. In this letter, we show that thick Ag NW meshes can be deposited on top of ss-DSCs as the reflective counter electrode without an annealing step producing comparable power conversion efficiencies versus the evaporated Ag control devices.

ss-DSCs have an empirically optimized titania film thickness of ~2.2 μm (versus >10 μm for liquid DSCs); which is likely due to higher rates of recombination [12,13]. Despite the thinner device architecture, which lowers overall light absorption, ss-DSCs have recently achieved maximum power conversion efficiencies of 6.1% [14]. ss-DSCs have the potential to match or exceed liquid based DSC performance by developing higher molar extinction coefficient dyes for increased light absorption [15–17], hole conductors with lower HOMO levels, new architectures to increase light harvesting [18–23], and tandem devices.

2. Experimental

2.1. Solid-state dye-sensitized solar cell device fabrication

Solid-state DSCs are shown schematically in Fig. 1A. ss-DSCs consist of Flourine doped SnO_2 conducting glass (Hartford Glass TEC 15) which was partially etched using zinc powder and HCl (12%) then cleaned by sonication sequentially in 10% extran, acetone, isopropanol, and water. A 50 nm compact TiO_2 layer was deposited via aerosol spray pyrolysis using air as the carrier gas [24]. Mesoporous titania films were deposited via doctor blading of commercially available paste (Dyesol 18NR-T) and slowly heated to 500 °C for 30 min in air. It should be noted, that TiO_2 paste deposition was performed in a laminar flow hood to minimize dust contamination that can affect the Ag NW transfer. Films were subsequently treated in 0.02 M $TiCl_4$ aqueous solution overnight at room temperature [25]. Samples were then heated to 450 °C for 10 min cooled to approximately 80 °C and immersed in 0.3 mM of Z907 (Solaronix SA) in a 1:1 mixture of acetonitrile and tert-butyl alcohol for 12–18 h. The organic hole conductor solution was made by dissolving 72 mg of 2,2′,7,7′tetrakis-(*N*,*N*-di-*p*-methoxyphenylamine)-9,9′-spirobifluorene (spiro-OMeTAD) in 400 μl of chlorobenzene and then adding 7 μl of tert-butylpyridine and 15 μl of 0.6 M bis(trifluoromethane)sulfonamide lithium salt (Fluka) in acetonitrile. The doped spiro-OMeTAD solution was deposited on the substrate and allowed to infiltrate the TiO_2 for 30 s prior to spin coating (2000 RPM for 40 s) and dried in a dessicator for several hours. Ag counter electrodes (200 nm) for the control devices were evaporated at 2×10^{-6} torr on half of the substrate.

2.2. Silver nanowire synthesis and lamination onto DSC

Silver nanowires were synthesized by reducing Ag nitrate in the presence of poly(vinyl pyrrolidione) in ethylene glycol which resulted in Ag NWs that were on average 8.7 μm long and have 103 nm diameters [11,26]. To create films on the host substrate, Ag NWs were deposited from methanol onto coverslip glass and annealed at 180 °C to fuse the junctions between the wires and enhance conductivity [10,11,27]. The Ag NW films were then pressed onto the spiro-OMeTAD at a pressure of 1.6×10^4 psi for approximately 30 s, as illustrated in Fig. 1A and B. Care should be taken during lamination to remove any debris on the press and align the press to consistently apply pressure across the glass surface; inconsistent pressure can cause substrate cracking. Laminated Ag NW films were roughly 2–4 nanowires thick (100–200 nm) as shown in the SEM image in Fig. 1C. During lamination >95% of the Ag NWs are transferred to the ss-DSC substrate. The overall surface coverage is relatively sparse as shown in Fig. 1D. ImageJ software was used to analyze the SEM image and determined that approximately 59% of the spiro-OMeTAD surface is covered by AgNWs. A four-point probe measurement was used to determine a sheet resistance of 4.5 Ω/□ for AgNWs counter electrode versus 1.3 Ω/□ for 200 nm of evaporated silver on inert