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# Graphene transparent conductive electrodes doped with graphene quantum dots-mixed silver nanowires for highly-flexible organic solar cells

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ABSTRACT

Recent active studies on flexible photovoltaic cells strongly call for matchable flexible transparent electrodes. Graphene (GR) is one of the promising candidates as transparent conductive electrodes (TCEs) for flexible photovoltaic cells, but high sheet resistance of GR limits the efficiency of the cells. Here, we first fabricate GR TCEs doped with graphene quantum dots (GQDs)-mixed silver nanowires (Ag NWs) on polyethylene terephthalate substrates for highly-flexible organic solar cells (OSCs). With increasing doping concentration of GQDs to 0.03 g/L, the sheet resistance of the Ag NWs/GR TCE decreases to ~92 Ω/sq whilst its work function increases to ~4.53 eV, resulting in 3.66% power-conversion efficiency (PCE). In addition, the GQDs enhance the bending flexibility of the Ag NWs/GR TCEs, thereby maintaining the initial PCE of the OSCs over 90% even after 1000 bending cycles at a curvature radius of 4 mm.



## 1. Introduction

Over the past two decades, flexible organic solar cells (FOSCs) have received considerable attention due to their low cost, highly-scalable roll-to-roll preparation, light weight, and excellent mechanical flexibility [1–9]. One of the major issues in the studies of FOSCs is how to maintain their performance even after repeated bending tests at various curvature radius (R) [10–13]. For achieving this purpose, the electrode as well as the photoactive medium is required to be highly flexible with their excellency in conductivity and transparency. Graphene (GR) has been proposed as a promising material for transparent conductive electrodes (TCEs) of FOSCs due to its mechanical/chemical robustness, excellent electrical and optical properties, and potentially low-cost fabrication processes [14–16]. Several studies have demonstrated the feasibility of GR-TCE-based optoelectronic devices [17,18], including organic solar cells (OSCs) [19,20], but high sheet resistance ($R_s$) of bare GR cannot meet the requirement for high-efficiency OSCs.

Various methods, such as chemical doping [21–23] and formation of metal nanoparticles or metal nanowires (NWs) [24–26], have been developed to reduce $R_s$ of GR sheets, Among them, Ag NWs are attractive as a dopant for GR, especially in GR-based solar cells, because Ag NWs reduce the reflectance as well as enhance the absorption [25–27]. Recently, the performance of the FOSCs was also improved by employing Ag NWs/GR TCEs [20], whose $R_s$ increased by repeated bending tests [28,29], resulting in the deterioration of the power-conversion efficiency (PCE). Very recently, hybrid TCEs made of Ag NWs-GR oxide composite materials [30] were employed for Si-based solar cells, but not for flexible devices. Graphene quantum dots (GQDs) have been regarded as a rising material in optoelectronic applications due to their tunable band gap, low toxicity, environmental compatibility, and chemical inertness [31–33]. With GQDs, it may be possible to increase the ultra violet-visible absorption and thus further increase the PCE of Ag NWs/GR TCE-based FOSCs. In this work, we employ Ag NWs mixed with GQDs as a dopant to reduce $R_s$ of GR TCEs and enhance their flexibility, thereby improving the performance of the FOSCs. The FOSCs exhibit a maximum PCE of 3.66% at a GQD concentration ($n_G$) = 0.02 g/L. In addition, the FOSCs become much more flexible by containing GQDs in the Ag NWs/GR TCEs, as demonstrated by bending tests at various R. We also analyze the photovoltaic parameters based on the structural, electrical, and optical properties of the Ag NWs/GR TCEs with/without GQDs.

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## 2. Experimental

Single-layer GR layers were grown on Cu foils by chemical vapor deposition, and transferred onto polyethylene terephthalate (PET) substrates in the same manner as previously reported [34]. Ag NWs powder was dissolved in isopropyl alcohol to prepare a 0.1 wt% Ag NWs solution. The Ag NWs solution was coated on the GR/PETs at 1500 rpm for 1 min, and then dried on a hot plate at 100 °C for 2 min. GQDs solution for $n_G = 0.01–0.03$ g/L was subsequently spin-coated on the Ag NWs/GR/PETs at 4000 rpm for 1min, and air-dried at room temperature. To prepare the FOSCs, PEDOT:PSS was spin-coated on the Ag NWs/GR films with/without GQDs at 3000 rpm for 60s, and subsequently annealed at 130 °C for 15 min in air. This process was repeated two times to obtain continuously-smooth film. Then, a blend solution of 25-mg P3HT and 25-mg PCBM in 1-ml 1,2-dichlorobenzene was spin-coated onto the PEDOT:PSS layers at 700 rpm for 60 s under a nitrogen atmosphere. The devices were then treated by solvent annealing at 120 °C for 2 h, and further annealed at 110 °C for 10 min. Finally, Al electrodes were deposited on the devices using a thermal evaporator at a pressure of $10^{-6}$ Torr.

The transmittance, sheet resistance, and work function of GR were measured by ultraviolet–visible-near IR optical spectroscopy (Varian, Cary 5000), 4 probe van der Pauw method (Dasol eng, model FPP-HS8-40K), and Kevin probe force microscopy (Park systems, model XE100), respectively. Photoluminescence (PL) spectra were measured at room temperature using a 325 nm line of the HeCd laser as the excitation source. The morphologies of GQDs were analyzed by transmission electron microscopy (TEM). Surface morphology of the doped GR was analyzed by field-emission scanning electron microscopy (FE-SEM) equipped with energy dispersive X-ray spectroscopy (EDX) system. The surface of the PEDOT:PSS on TCEs were measured by atomic force microscopy (AFM). The current density-voltage ($J–V$) characteristics of the FOSCs were measured using a solar simulator under illumination of 1 Sun (100 mWcm$^{-2}$ AM 1.5G). External quantum efficiency (EQE) was measured under short circuit conditions while the cells were illuminated by a light source system with monochromator. The illumination area was fixed to 4.52 mm$^2$.

## 3. Results and discussion

The FE-SEM image in Fig. 1a shows hybrid formation of Ag NWs and GQDs on a GR sheet, and the inset image demonstrates high flexibility/transparency of the hybrid TCE (For $n_G$-dependent SEM images, see Supporting Information Figs. S1a–c). The diameter of the GQDs was measured to be about 7 nm by using high-magnification TEM (Supporting Information Fig. S1d). The optical absorption and PL spectra of the GQDs aqueous solution are peaked at 356 and 450 nm, respectively, (Supporting Information Fig. S1e), as can be expected from previous reports [35,36]. The well formation of the Ag NWs on the GR surface was further confirmed by EDX analysis. Fig. 1b shows a clear Ag peak near 3 keV in the EDX spectrum. Fig. 1c compares optical transmittance spectra of GR and Ag NWs/GR without/with GQDs on PET substrates for various $n_G$. The transmittance of the Ag NWs/GR TCEs with GQDs is smaller than that of bare GR TCE or the Ag NWs/GR TCE without GQDs, but is still near 90% in the visible range. The Ag NWs/GR TCEs with GQDs have a specific absorption peak at around 350 nm, as shown in Fig. 1c, resulting from the GQDs [32,33], also demonstrating well formation of the GQDs on the Ag NWs/GR TCEs. The yellow brackets

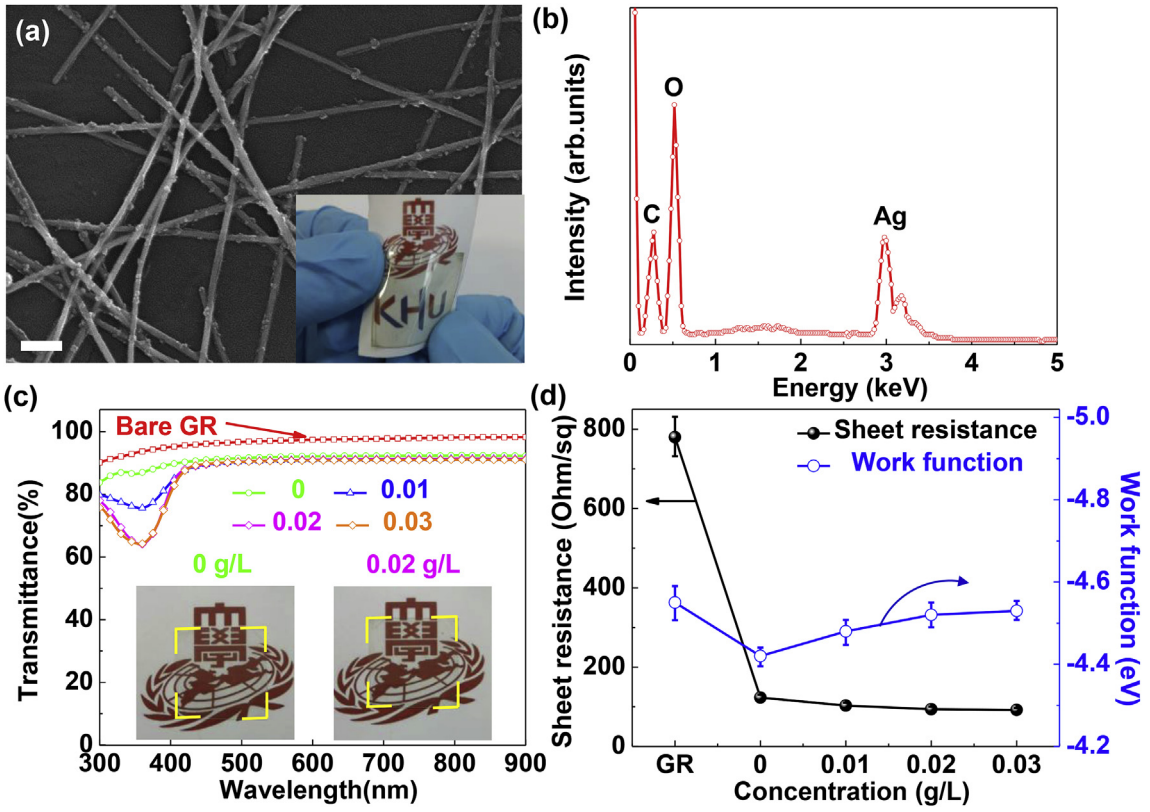


**Fig. 1.** (a) FE-SEM image and (b) EDX spectrum of GQDs-mixed Ag NWs/GR TCE at $n_G = 0.02$ g/L. The inset in (a) shows a real image of the TCE. (c) Optical transmittance spectra, (d) sheet resistances, and work functions of GR, Ag NWs/GR, and GQDs-mixed Ag NWs/GR TCEs. Here, $n_G$ is varied from 0.01 to 0.03 g/L. The yellow brackets in the inset of (c) show real images of the Ag NWs/GR TCEs with/without GQDs, indicating their excellent transparency. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)