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Hybrid materials of upcycled Mn_3O_4 and reduced graphene oxide for a buffer layer in organic solar cells

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ABSTRACT

Mn_3O_4 on reduced graphene oxide (r-GO) was easily synthesized by upcycling process of wasting manganese ions which were generated during oxidation reaction from graphite to GO. The yellow-brown GO suspension under acid media before neutralization immediately became black precipitates when the suspension was titrated into the concentrated NaOH solution. The method could convert the wasting manganese ions up to ~91 wt% to Mn_3O_4 to optimize work function in a hole transport layer (HTL) for organic solar cells. The hybrid materials exhibited an ideal electronic structure suitable for HTL, leading to the excellent power conversion efficiency of ~3.23%.

Introduction

In recent years, there have been great advances in the synthesis and application technologies of graphene. In particular, chemically converted graphene (CCG), which represented graphene oxide (GO) and reduced graphene oxide (r-GO), has been widely and deeply studied due to the potential for mass production. However, the CCG has lots of structural defects that originated from severely toxic environments to expand the inter-layer distance of graphite even though modified Brodie, Staudenmaier, and Hummers methods have been persistently developed [1–3]. In the case of modified Hummer's method that has widely used, excessive hydrogen peroxide with the high toxicity should be used to neutralize the extremely strong acid conditions. In addition, manganese ions as a by-product have been thrown out for the preparation of the CCG. The amount of the waste is generally four times higher than that of the produced CCG [4]. Green and facile routes such as metal ion intercalation, sonication, and hydrothermal method have been reported, to overcome the drawbacks [5–9]. However, these methods have been limited to the mass production yet. Therefore, facile and environmental friendly approaches to minimize the waste should be developed on the basis of the widely used method with the most practical potential.

Transition-metal oxides (TMOs) showed a universal energy alignment with several organic semiconductors due to a broad range of work function from 2 to 7 eV [10–13]. In particular, TMO have been tried to use an efficient charge extraction interlayer in organic solar cells (OSCs). However, the interlayer was generally prepared using vacuum deposition system for an energy alignment with each diverse semiconductor. A conventional polymer based material for hole transport layer (HTL) in OSCs is poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), which has inherent problems such as hygroscopic and acidic properties, results in corrosion of ITO and contamination of an

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active layer even though the OSCs with PEDOT:PSS show excellent a hole extraction performance. Therefore, hybrid functional materials combining graphene and metal oxides such as zinc oxide (ZnO), vanadium oxide (V_2O_5), and molybdenum oxide (MoO_3) have been studied to replace conventional PEDOT:PSS, because of their high stability to moisture, proper pH value, and suitable band-gap [14–17]. To the best of our knowledge, however, there is no experimental attempt for electronic application of manganese oxide.

Here, we introduce a simple and cost-effective synthetic route for Mn_3O_4 particles on r-GO, designated as MnG, from graphite using a single reductant of NaOH without any other complicated processes. In this approach, manganese ions as by-products from the process of graphite oxidation could be recycled as Mn_3O_4 precursors. In addition, the use of NaOH allows a one-step reduction of GO and spontaneous functionalization of Mn_3O_4 particles onto graphene frameworks. The wasteful manganese ions could be upcycled to demonstrate the feasibility of hybrid materials in electronic device applications. Therefore, we fabricated the OSC with the synthesized MnG as a HTL. As a result, the highly desirable power conversion efficiency (PCE) was achieved in the OSC using the MnG HTL, which is quite comparable to that of conventional OSC with PEDOT:PSS.

Experimental

Synthesis of Mn_3O_4 and r-GO composite

MnG was synthesized by NaOH treatment during an oxidation of graphite using a modified Hummers method. Briefly, a mixture of graphite flake (4 g) and sulfuric acid (120 ml) in a round-bottom flask was stirred for 30 min. After then, potassium permanganate of 12 g was added for 3 h to prevent an increase of temperature and the mixture was heated up to 40 °C and maintained for 6 h. Subsequently, deionized water (DI) of 150 ml and hydrogen peroxide of 17 ml were slowly added. Then, the suspension was injected to saturated NaOH solution using a pipette. Finally, approximately 11.1 g of black precipitates were obtained by filtering and washed for 3–4 times using DI water.

Characterizations

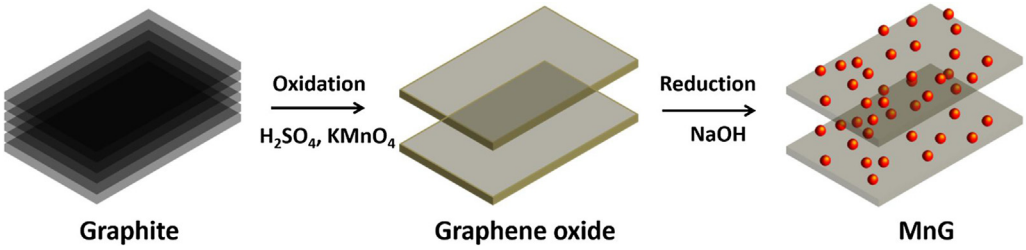
The chemical structure and composition of MnG and GO were investigated using a XPS (Thermo fisher, Multilab 2000) and a XRD (Rigaku, SmartLab). The XPS was measured using a Al Ka radiation (hv = 1000 eV). The work function and roughness values of ITO, MnG, and GO were measured using an ultraviolet photoelectron spectroscope (UPS) with a He 1 (hv = 21.2 eV) excitation source (AXIS Ultra DLD, Kratos Inc.) under ~10^{-8} Torr and using a AFM (Veeco, Digital Instruments Nanoscope IIIA), respectively. An electrical surface resistance values were obtained using a four-point probe measurement system (FPP-RS8, Dasol Eng.).

Fabrication and evaluation of organic solar cells

After a patterned indium tin oxide (ITO, ~10 Ω/sq) substrate was cleaned and UV/O_3-treated for 30 min, MnG (1 mg/ml) solution was spin-coated using a gradient spin-rpm from 700 to 3500 rpm for 45 s, followed by drying at 120 °C for 10 min. A conventional PEDOT:PSS (Clevios™ P VP AI 4083) film as a reference anode buffer layer was also fabricated using spin-coating at 5000 rpm for 40 s followed by drying at 120 °C for 10 min. Subsequently, blended solution with a 1 ml P3HT (25 mg) and $PC_{61}BM$ (25 mg) in 1,2-dichlorobenzene (DCB) was coated on buffer layer at 700 rpm for 60 s, and then a annealing treatment was performed for 2 h followed by thermal annealing at 110 °C for 10 min in an N_2-filled glove box. Finally, a thermal evaporation was used for a cathode fabrication of Ca/Al (20/100 nm) with an active area of 4.64 mm^2 under a pressure of 10^{-6} Torr. Photocurrent density–voltage (J–V) curves were recorded using a Keithley 2400 instrument under a standard 100 mW/cm^2 illumination and AM 1.5 G condition after accurate calibration using a standard Si-based solar cell certified by the International System of Units (SRC-1000-TC-KG5-N, VLSI standards, Inc).

Results and discussion

A facile synthetic procedure of MnG is schematically described in Scheme 1. Firstly, suspended GO in a mixture of deionized water (DI) and hydrogen peroxide was prepared by modified Hummer's method. And then, the suspension was titrated into the saturated NaOH solution to reduce the wasteful Mn ions to the Mn oxide particles on the GO. A detail procedure was described in experimental section. Chemical compositions of as-synthesized MnG were examined by X-ray photoelectron spectroscopy (XPS) in comparison with those of GO. As shown in Fig. 1a, the deconvoluted the C 1s spectra for MnG reveals that oxygen functional groups such as hydroxyl, epoxide, carbonyl, and carboxyl groups were significantly eliminated, indicating an effective reduction of GO through NaOH treatment [18]. In addition, Mn 2p peaks in the MnG appeared after NaOH treatment as shown Fig. 1b. The difference of binding energies between Mn $2p_{1/2}$ and Mn $2p_{3/2}$ is approximately 11.9 eV, which is evident that a chemical structure of manganese oxide in the MnG is Mn_3O_4 [19]. A typical Mn_3O_4 crystal structure could be also confirmed by XRD diffractogram of MnG as shown in Fig. 1c. The average width and height of the Mn_3O_4 particles on r-GO exhibited ~210 and ~70 nm, respectively (Fig. 1d and e). It is believed that the Mn_3O_4 particles were biaxially grown on the planar r-GO surface similar to a coin shape with a high aspect ratio [20]. An atomic ratio of oxygen calculated from XPS spectra decreased from 44.9–36.4% for GO and MnG, respectively (Table 1). Considering the chemical structure of Mn_3O_4 and the atomic ratio of Mn (12.2%) in the MnG, oxygen content of 16.3% in the MnG would stem from the Mn_3O_4, and thus, the residual oxygen functional groups on r-GO in the MnG would



Scheme 1. Schematic of simple synthetic steps for the MnG.

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