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journal homepage: [www.elsevier.com/locate/jiec](http://www.elsevier.com/locate/jiec)Hybrid materials of upcycled  $\text{Mn}_3\text{O}_4$  and reduced graphene oxide for a buffer layer in organic solar cellsCheol-Ho Lee<sup>a,b</sup>, Sungho Lee<sup>a,c</sup>, Jun-Seok Yeo<sup>a</sup>, Gil-Seong Kang<sup>a,b</sup>, Yong-Jin Noh<sup>d</sup>, Sae-Mi Park<sup>d</sup>, Doh C. Lee<sup>b</sup>, Seok-In Na<sup>d,\*</sup>, Han-Ik Joh<sup>e,\*</sup><sup>a</sup> Carbon Composite Materials Research Center, Korea Institute of Science and Technology, 92 Chudong-ro, Bongdong-eup, Wanju-gun, Jeollabuk-do 55324, Republic of Korea<sup>b</sup> Department of Chemical and Biomolecular Engineering (BK21+ Program), KAIST Institute for the Nanocentury, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Republic of Korea<sup>c</sup> Department of Nano Material Engineering, Korea University of Science and Technology, 217 Gajeong-ro, Yuseong-gu, Daejeon 34113, Republic of Korea<sup>d</sup> Professional Graduate School of Flexible and Printable Electronics, Polymer Materials Fusion Research Center, Chonbuk National University, 567 Beakjedaero, Deokjin-gu, Jeonju-si, Jeollabuk-do 54896, Republic of Korea<sup>e</sup> Department of Energy Engineering, Konkuk University, 120 Neungdong-ro, Gwangjin-gu, Seoul 05029, Republic of Korea

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## ABSTRACT

$\text{Mn}_3\text{O}_4$  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  $\text{Mn}_3\text{O}_4$  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%.

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## 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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