

Supporting Information:

Graphene Scaffolds Enhanced Photogenerated Electron Transport in ZnO Photoanodes for High-Efficiency Dye-Sensitized Solar Cells

Feng Xu,^{*,†,#} Jing Chen,^{‡,#} Xing Wu,^{†,#} Yi Zhang,[†] Yuxi Wang,[†] Jun Sun,[†] Hengchang Bi,[†] Wei Lei,[‡] Yaru Ni[§], and Litao Sun^{*,†}

[#]These authors contributed equally to this work.

[†]SEU-FEI Nano-Pico Center, Key Laboratory of MEMS of Ministry of Education, Southeast University, Nanjing 210096, China

[‡]Jiangsu Information Display Engineering Research Center, School of Electronic Science and Engineering, Southeast University, Nanjing 210096, China

[§]State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing University of Technology, Nanjing 210009, China

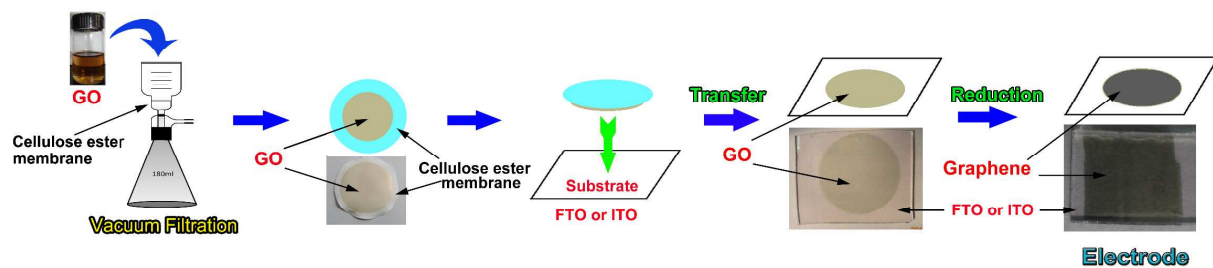
Experimental Section of synthesis of graphene oxide and ZnO HSNs

Graphene oxide (GO) was prepared by chemically exfoliating expandable graphite (EG)^{1,2} based on a modified Hummers method by us.³ All of the other chemicals were of analytical reagent grade and used without further purification. Briefly, EG (2 g) was added slowly into concentrated H₂SO₄ (46 mL) with stirring in an ice-water bath. After this, about NaNO₃ (1 g) was also poured into the mixture. Then, KMnO₄ (6 g) was added gradually under stirring over 1 h and kept stirring for another 2 h, which also was carried out in an ice-water. Subsequently, the mixture was stirred unceasingly for 15 h at room temperature. Whereafter, distilled water (DW, 92 mL) was added slowly into the mixture. After stirring at 98 °C for 15 min, the reaction was terminated by in sequence adding DW (280 mL) and 30 wt % H₂O₂ (15 mL), and another 2 h stirring at room temperature was carried out. The product was separated by centrifugation at 20000 rpm and washed with 5 wt % HCl solution until sulphate could not be detected with BaCl₂ solution. After this, the product was also washed 7 times with DW for eliminating chloridion. Finally, according to experiment request, GO aqueous solutions with different concentrations were prepared by concentrating the as-synthesized product.

ZnO HSNs were synthesized by the solvothermal process of zinc salt in polyol medium at 160 °C, similar to the method reported by Jezequel et al.⁴ The typical synthesis procedure was described as follows: 0.03 mol of zinc acetate dehydrate (ZnAc·2H₂O) was added to 300 mL of diethylene glycol (DEG) with stirring. The mixed solution was heated to 160 °C in an oil bath at a rate of 5 °C/min and then refluxed for 5 h. The as-prepared colloidal solution was centrifuged at a rate of 5000 rpm for 0.5 h. Subsequently, the ZnO product precipitated at the bottom of the centrifugation tubes were redispersed in ethanol by sonication for 0.5 h. This procedure of centrifugation and sonication was repeated several times in order to remove the supernatants. At last, the resultant ZnO colloids were dried at 100 °C and saved in vacuum.

* To whom correspondence should be addressed. Phone: +86-25-83792632. Fax: +86-25-83792939. E-mail: fxu@seu.edu.cn (F. Xu); slt@seu.edu.cn. (L. T. Sun).

[#]These authors contributed equally to this work.



Scheme S1. Schematic steps for the preparation of graphene/ITO or graphene/FTO electrodes by a filtration-transfer-reduction method.

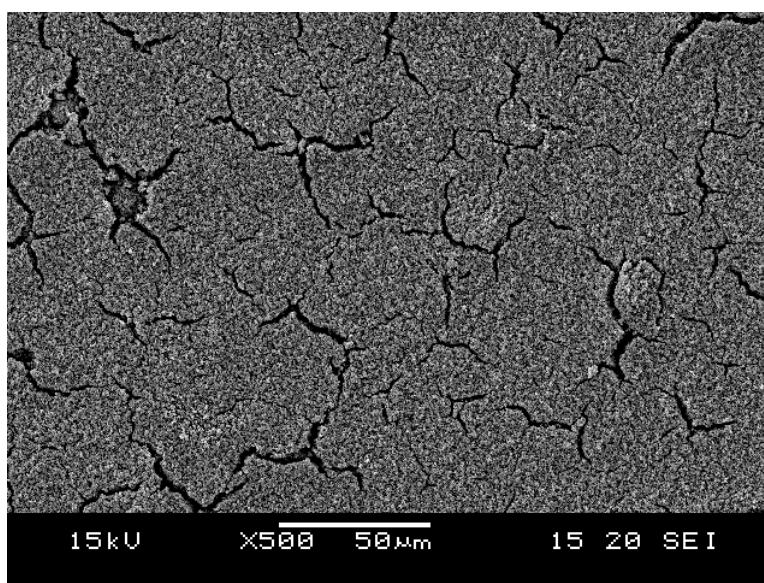


Figure S1. Plan-view SEM image of graphene/ZnO HSN composite photoanode with 4.0 wt% graphene loading. A mass of large cracks resulted from the overmuch release of H_2O and N_2H_4 during the reduction of graphene oxide.

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