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Electronic Supplementary Information

Nitrogen and sulfur co-doped graphene counter electrodes with synergistically enhanced performance for dye-sensitized solar cells

Aravindaraj G Kannan,[a] Jinxing Zhao,[a] Sung Guen Jo,[a] Yong Soo Kang,[b] and Dong-Won Kim*[a]

[a]Department of Chemical Engineering, Hanyang University, Seoul 133-791, Republic of Korea

[b]Department of Energy Engineering, Hanyang University, Seoul 133-791, Republic of Korea

*E-mail: dongwonkim@hanyang.ac.kr

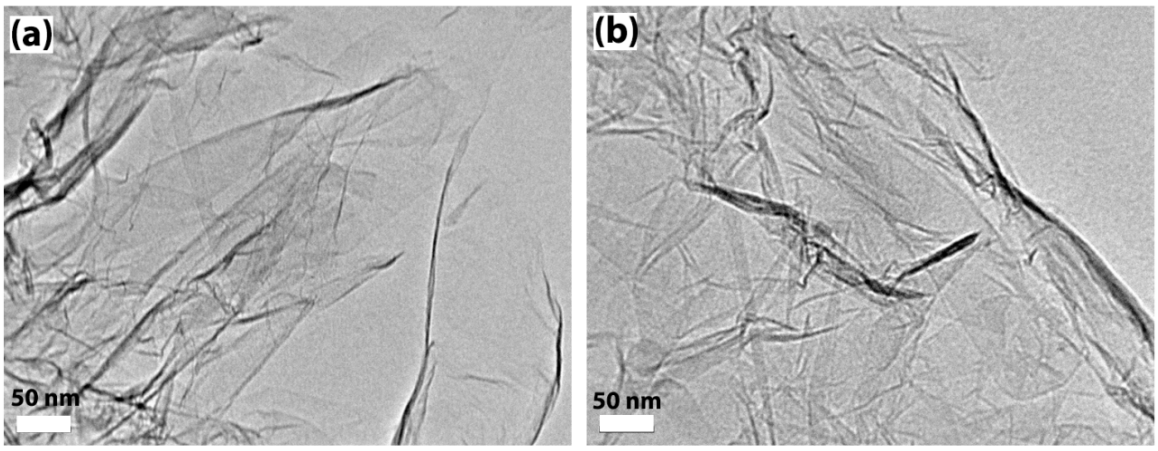

Fig. S1. TEM images of (a) NG and (b) SG control samples.

Both samples show highly wrinkled and folded morphology similar to the NSG sample.

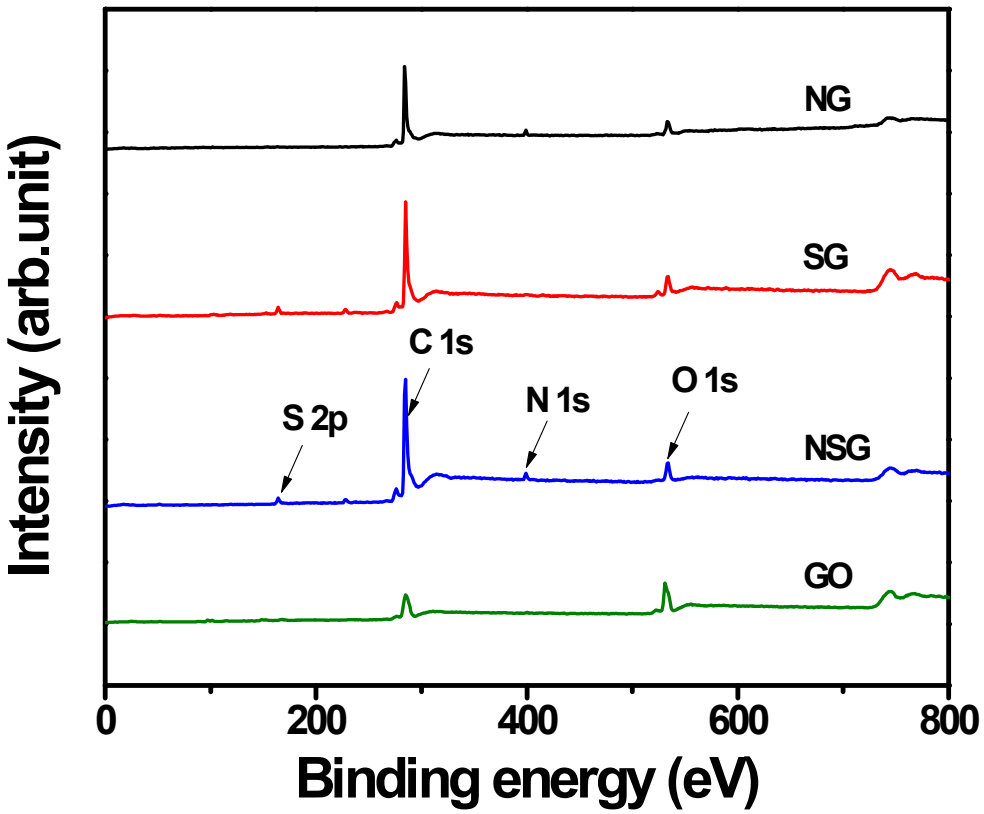

Fig. S2. XPS survey spectra of NG, SG, NSG and GO nanosheets.

The GO sample shows two peaks corresponding to C 1s and O 1s, and the NSG sample shows the presence of nitrogen and sulfur along with carbon and oxygen atoms. The SG and NG samples show the doping of only sulfur and nitrogen atoms, respectively in the graphene framework. The ratio of C/O is 1.90, 9.75, 9.32 and 9.58 for the GO, NSG, SG and NG samples, respectively. This further confirms the reduction of oxygen functional groups in graphene nanosheets during the doping process.

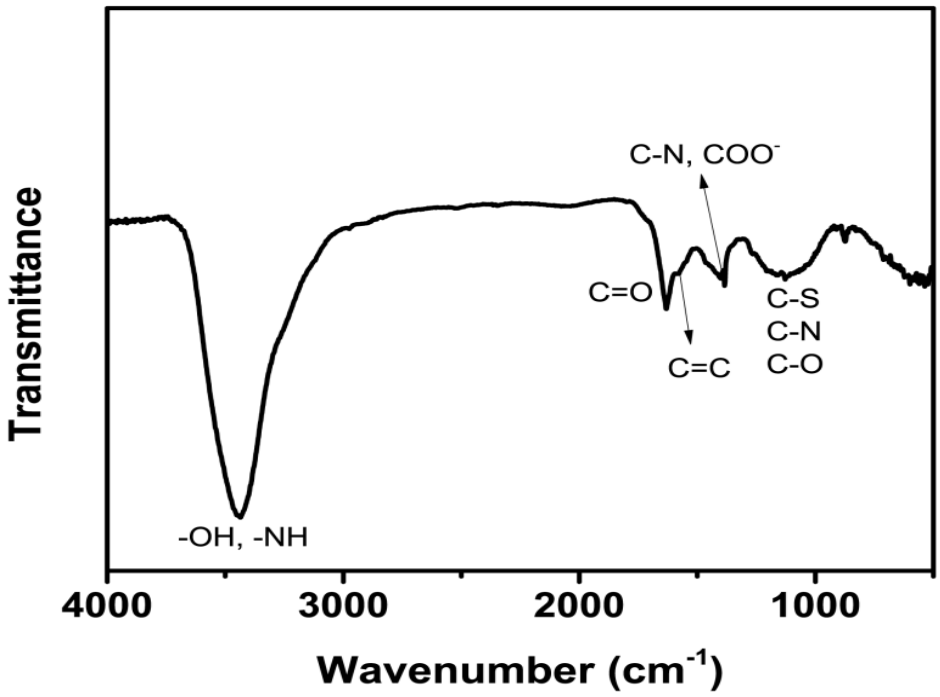

Fig. S3. FT-IR spectrum of NSG sample showing different functional groups.

FT-IR spectrum was used to identify the functional groups present in the NSG sample. A very broad transmittance band centered at 3440 cm^{-1} represents the –OH and –NH functional groups.[1] The –OH groups represent the residual hydroxyl functional groups in graphene nanosheets along with the adsorbed moisture in the sample. The band at 1635 cm^{-1} represents the C=O group and the shoulder band at 1575 cm^{-1} indicates the presence of C=C bonding.[2] A broad band centered at 1401 cm^{-1} is assigned to C-N and COO^- groups.[1] Finally, a very broad band in the range of 945 to 1290 is attributed to the presence of C-S, C-N, C-O and SOx- groups.[1,2] Thus, the FT-IR spectrum confirms the presence of C-S and C-N bonds indicating the successful doping of nitrogen and sulfur atoms in graphene nanosheets.

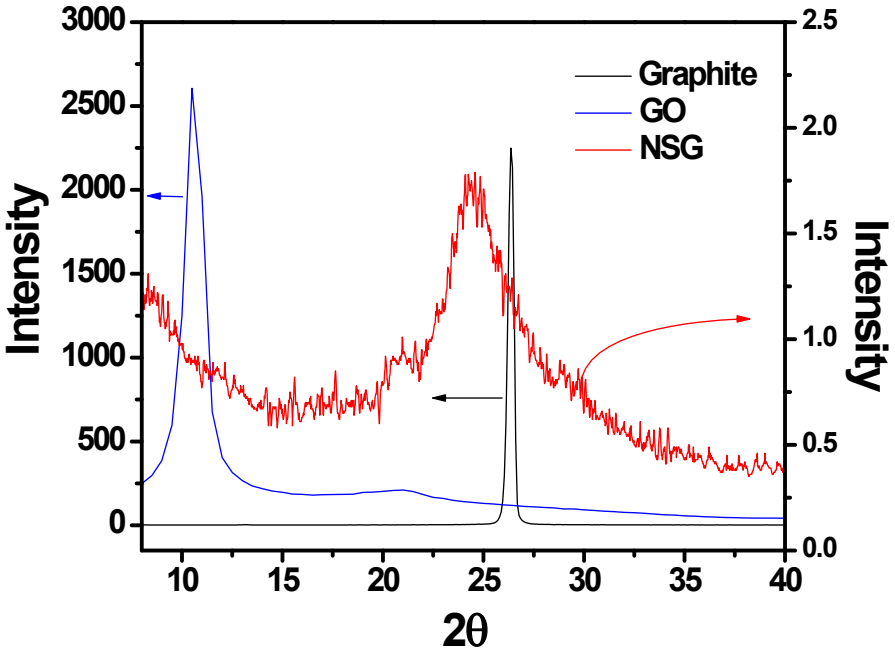

Fig. S4. XRD patterns of graphite, GO and NSG sample.

Graphite shows an intense and sharp peak at 26.4°, corresponding to the inter-sheet distance of 0.34 nm. Upon oxidation, GO shows a relatively broad and intense peak at 10.5°, corresponding to 0.84 nm, and the NSG sample shows a very broad and low-intensity peak at 24.4°, indicating the presence of mostly individual-/few-layer graphene sheets.

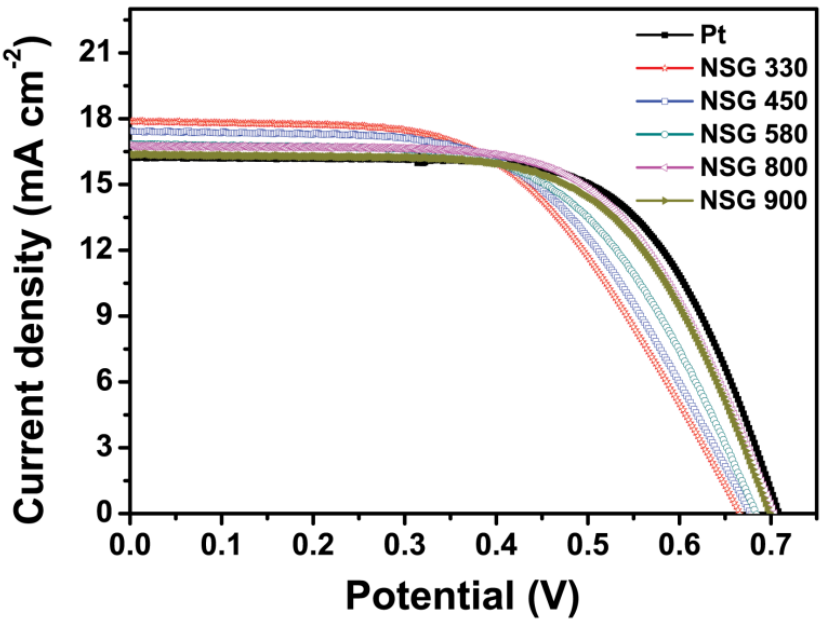

Fig. S5. Photocurrent density-voltage curves of DSSCs with NSG counter electrodes of different thickness (The number followed by NSG in the label denotes the thickness of the electrodes in nanometers).

The effect of NSG electrode thickness on the performance of DSSCs was investigated. As the thickness increased, the J_{sc} values slightly decreased and the FF value increased. It has resulted in increased cell efficiency until the electrode thickness reached 800 nm, and further increase in thickness to 900 nm resulted in decrease of J_{sc} and FF. An increase in the electrode thickness results in higher number of electrocatalytic active sites, thereby resulting in a higher FF. However, the increased thickness results in increased series resistance in the DSSCs and hence a lower J_{sc} value.[3]

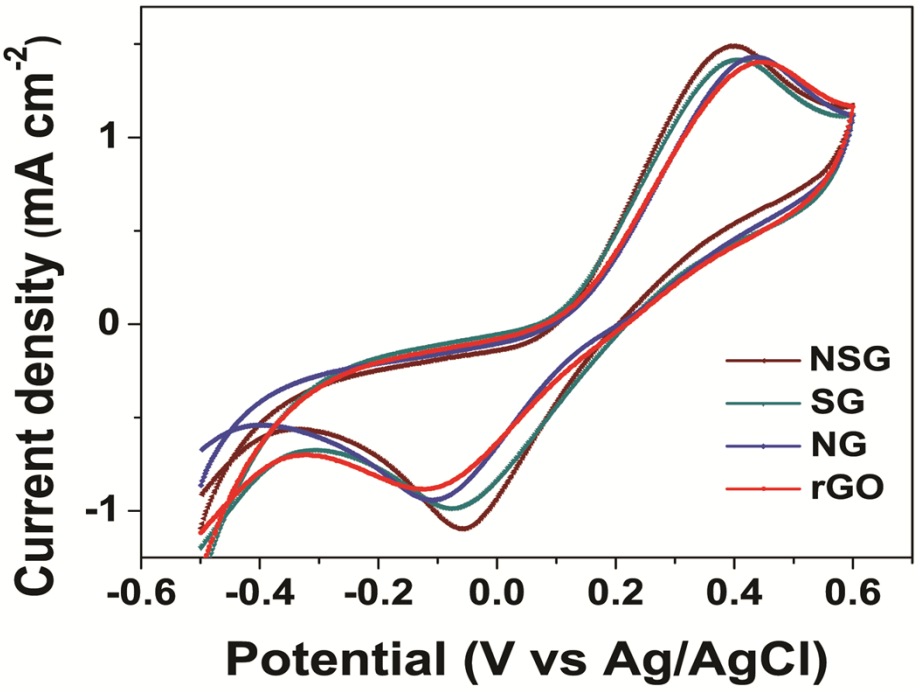

Fig. S6. CV curves of NSG, SG, NG and rGO samples obtained at a scan rate of 50 mV s^{-1} using Pt wire and Ag/Ag^{+} as counter and reference electrodes, respectively.

References

1. D. Qu, M. Zheng, P. Du, Y. Zhou, L. Zhang, D. Li, H. Tan, Z. Zhao, Z. Xie and Z. Sun, *Nanoscale*, 2013, **5**, 12272-12277.
2. D. Sun, R. Ban, P.-H. Zhang, G.-H. Wu, J.-R. Zhang and J.-J. Zhu, *Carbon*, 2013, **64**, 424-434.
3. G. Veerappan, K. Bojan and S.-W. Rhee, *Renew. Energ.*, 2012, **41**, 383-388.