Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.


Supporting Information

**Rational design and fabrication of sulfur-doped porous graphene with enhanced performance as counter electrode in dye-sensitized solar cells**

*Xiangtong Meng,*[‡] *Chang Yu,*[‡] *Xuedan Song, Zhiqiang Liu, Bing Lu, Ce Hao, and Jieshan Qiu**

State Key Lab of Fine Chemicals, Liaoning Key Lab for Energy Materials and Chemical Engineering, PSU-DUT Joint Center for Energy Research, Dalian University of Technology, Dalian 116024, China.

E-mail: jqiu@dlut.edu.cn

[‡] These authors contributed equally to this work.

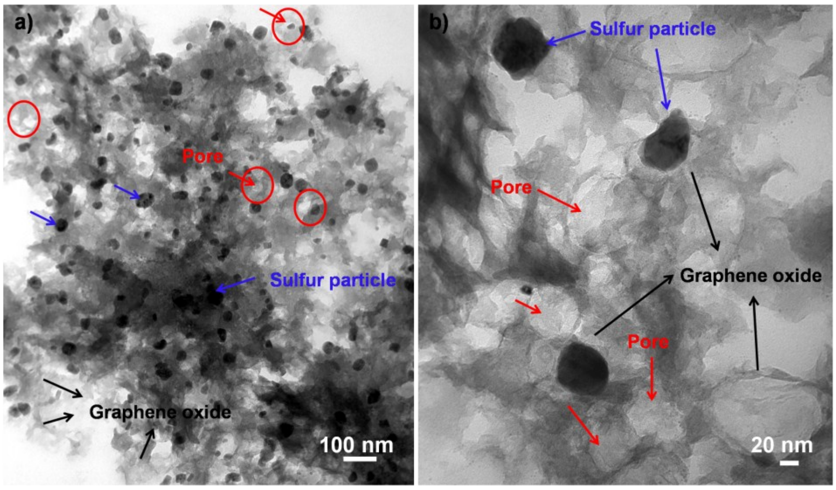


**Fig. S1.** TEM images of the composites made of GO and sulfur treated by ball milling.

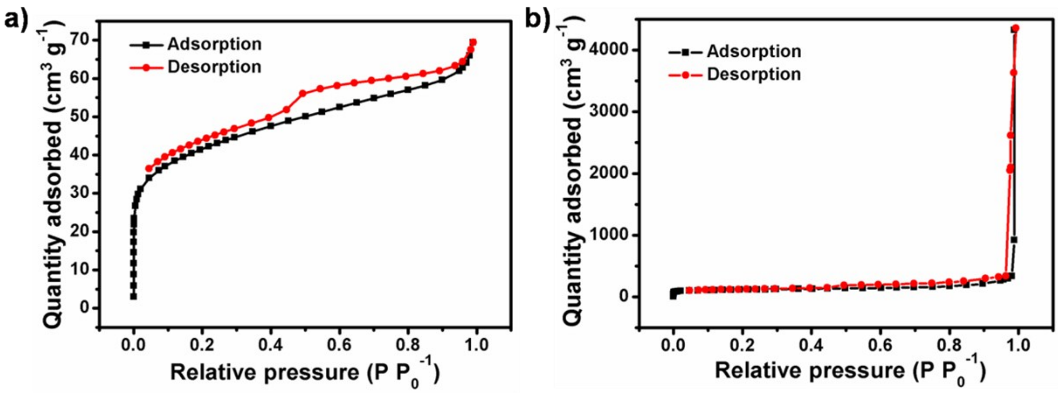


**Fig. S2.** Nitrogen adsorption–desorption isotherms of a) G and b) SPG.

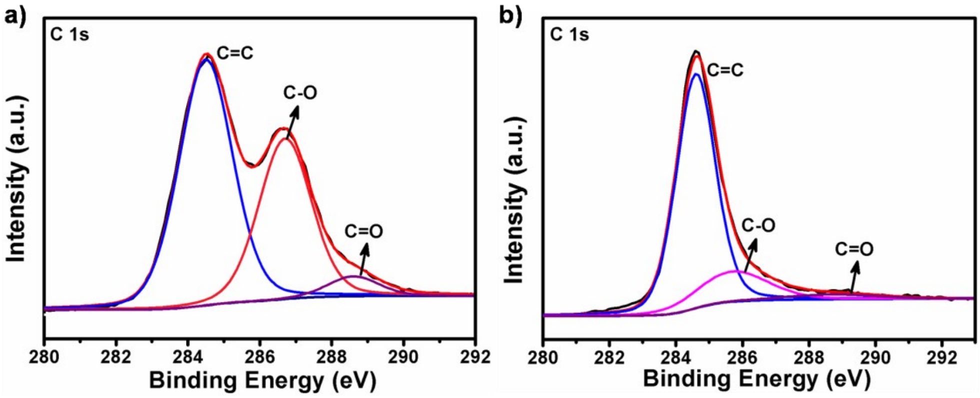


**Fig. S3.** High resolution C1s XPS spectra of a) GO and b) G.

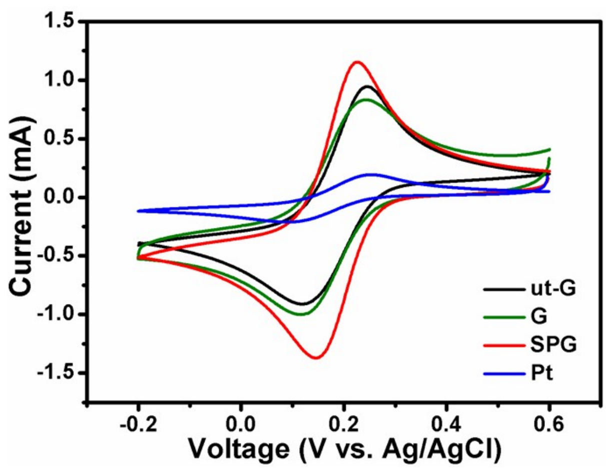


**Fig. S4.** CV curves of ut-G, G, SPG, and Pt CEs in 5 × $10^{-3}$ M $K_3Fe(CN)_6$/0.1 M KCl solution, scan rate: 50 mV $s^{-1}$.

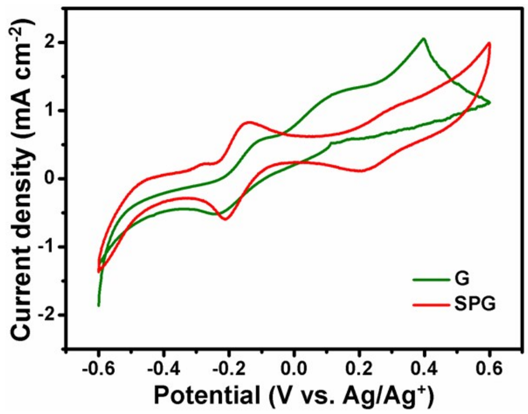


**Fig. S5.** CV curves of G and SPG CEs, scan rate: 5mV $s^{-1}$.

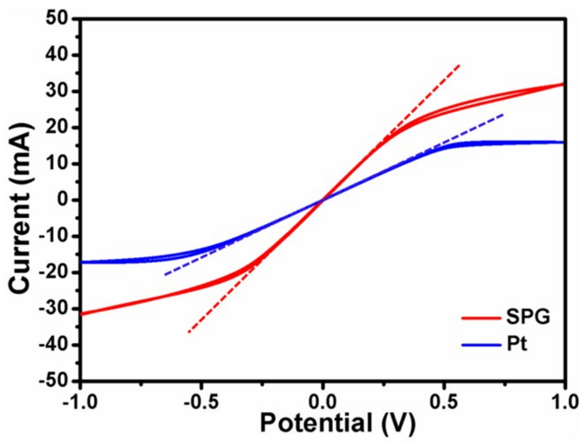


**Fig. S6.** CV curves of dummy cells with $I_3^-/I^-$ in acetonitrile solution based on SPG and Pt CEs, scan rate: 50 mV $s^{-1}$.

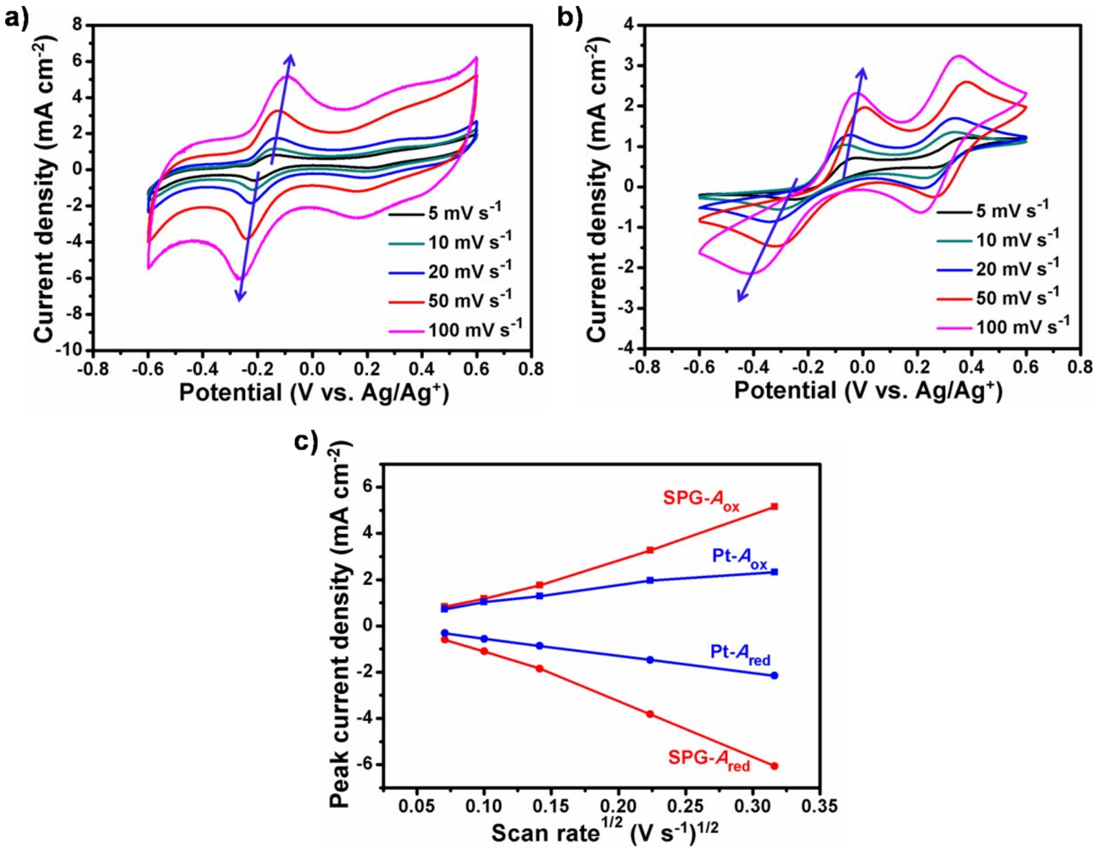


**Fig. S7.** CV curves of a) SPG CE and b) Pt CE at various scan rates. c) Relationship between the peak current densities for redox reaction of $I_3^-/I^-$ and the square root of scan rates for SPG and Pt CEs.

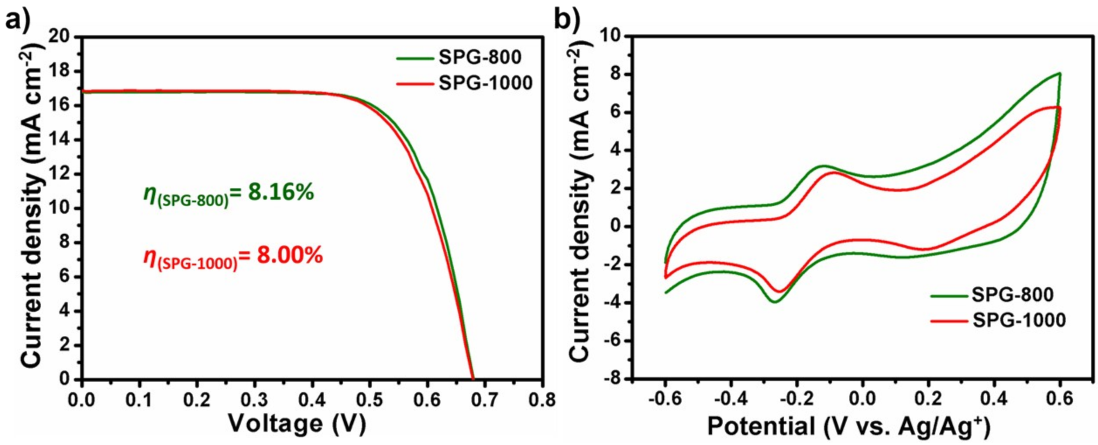


**Fig. S8**. a) *J-V* curves and b) CV results of DSSCs with SPG CEs annealed at different temperature.

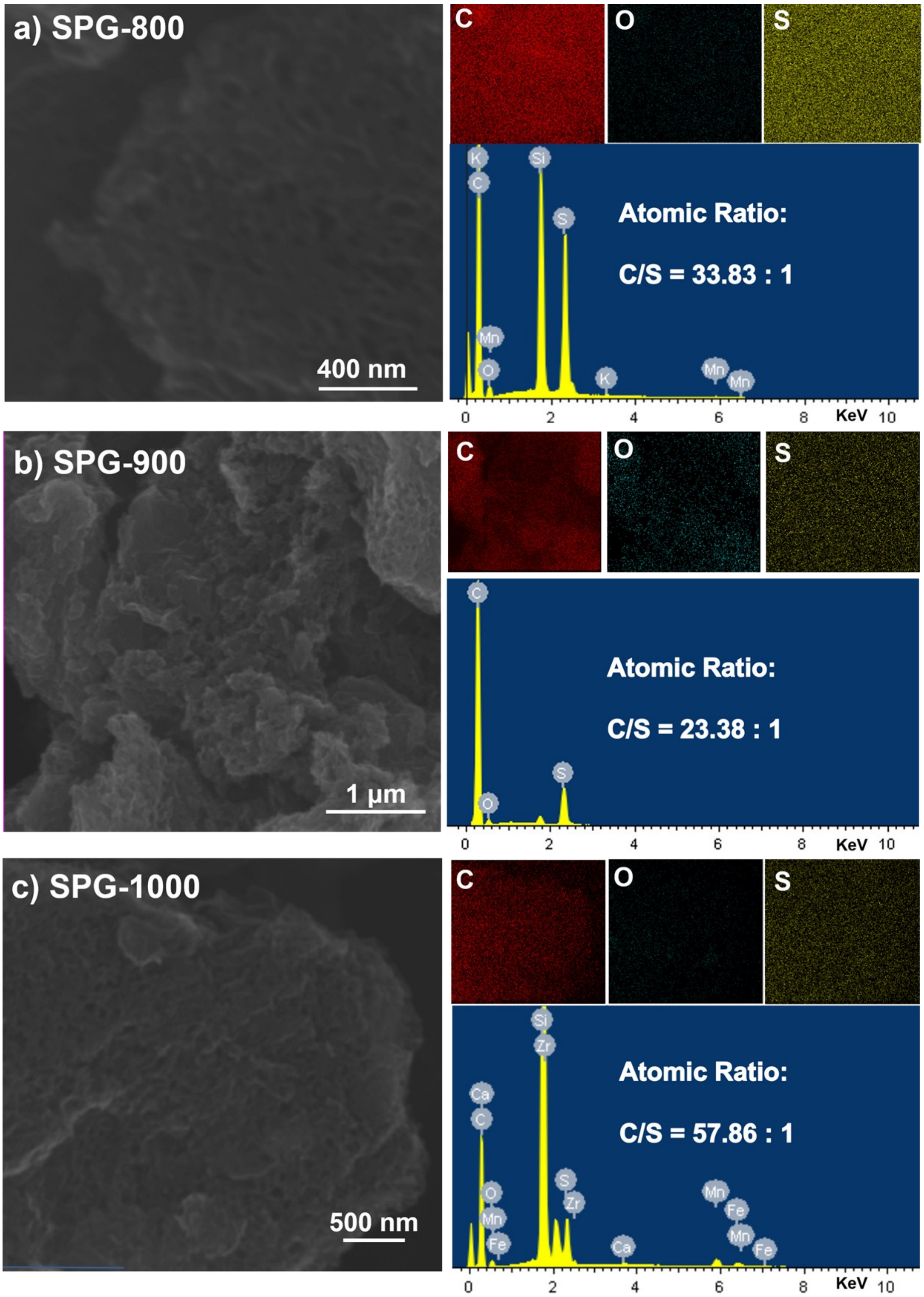


**Fig. S9**. SEM images and corresponding EDS mappings for a) SPG-800, b) SPG-900, and c) SPG-1000.

**Table S1.** The chemical compositions of as-made samples measured via element analysis.

| Samples | | $GO^a$ | $GO^b$ | G | SPG |
|---|---|---|---|---|---|
| Content (wt. %) | C | 44.25 | 55.44 | 79.28 | 77.54 |
| | S | 1.14 | 1.12 | 0.53 | 11.48 |
| | O | 51.06 | 40.89 | 18.65 | 10.13 |
| | N | 0.37 | 0.46 | 0.66 | 0.42 |
| | H | 3.18 | 2.09 | 0.88 | 0.43 |

a: GO before ball milling treatment, b: GO after ball milling treatment.

**Table S2.** The atomic ratios of different S species for SPG derived from XPS analysis.

| Type | Thiol-S (-S-H) | Thiophene-S | | Sulphone-S (-C-$SO_2$-C-) |
|---|---|---|---|---|
| | | $2p_{3/2}$ | $2p_{1/2}$ | |
| Area | 448.90 | 6665.72 | 4010.60 | 1089.48 |
| Atomic ratio (at. %) | 3.68 | 54.57 | 32.83 | 8.92 |

**Table S3.** Calculated electroactive surface areas ($S_e$) of different counter electrodes*

| CEs | G | SPG | Pt |
|---|---|---|---|
| $S_e$ (cm$^2$) | 1.597 | 2.189 | 0.337 |

*The tested area is 0.25 cm$^2$ (0.5×0.5 cm$^2$), and the electroactive surface area was calculated using the Randles-Sevcik equation:

$$A = \frac{I_{\text{peak}}}{2.69\times10^5 \times n^{3/2} \times D^{1/2} \times V^{1/2} \times C}$$

Where, $A$ is the electroactive surface area (cm$^2$), $I_{peak}$ is the peak current ($A$), n is the electron transfer number, here, $n$=1, $D$ is the diffusion coefficient of the solute, and $D = 4.34\times10^{-6}$ (cm$^2$ s$^{-1}$), $V$ is the scan rate (V s$^{-1}$), and $V$=0.05 V s$^{-1}$, $C$ is the concentration (mol mL$^{-1}$).

**Table S4.** Electrochemical parameters for SPG and Pt CEs.

| Samples | $E_{pp}$ (V) | $R_s$ (Ω cm$^2$) | $R_{ct}$ (Ω cm$^2$) | $Z_N$ (Ω cm$^2$) | $Z_{pore}$ (Ω cm$^2$) |
|---|---|---|---|---|---|
| SPG | 0.12 | 1.78 | 0.10 | 0.60 | 0.24 |
| Pt | 0.32 | 3.97 | 1.14 | 0.44 | \ |

**Table S5.** The ionization energy ($E_i$) for five kinds of simulated graphene slabs.

| Species | Graphene | Thiol-S | Thiophene-S | Sulfone-S |
|---|---|---|---|---|
| $E_i$ ( kcal mol$^{-1}$) | 130.29 | 128.34 | 128.21 | 125.10 |