

## Supporting Information

### Tunable Graphene Oxide Proton/Electron Mixed Conductor that Function at Room Temperature

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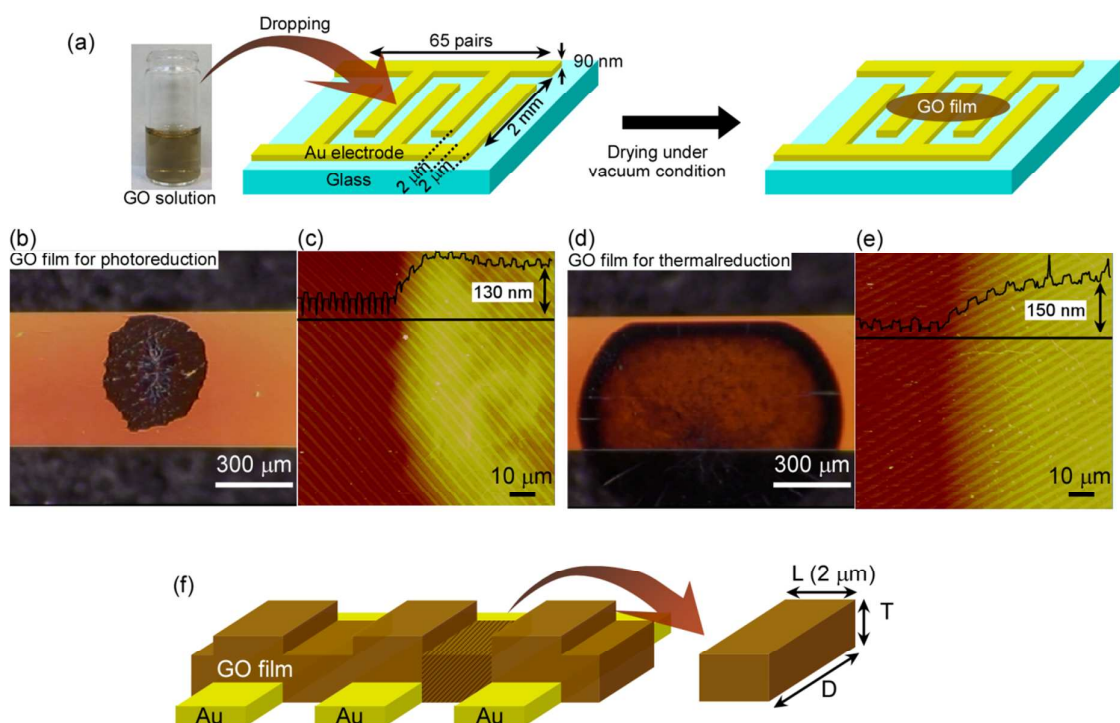
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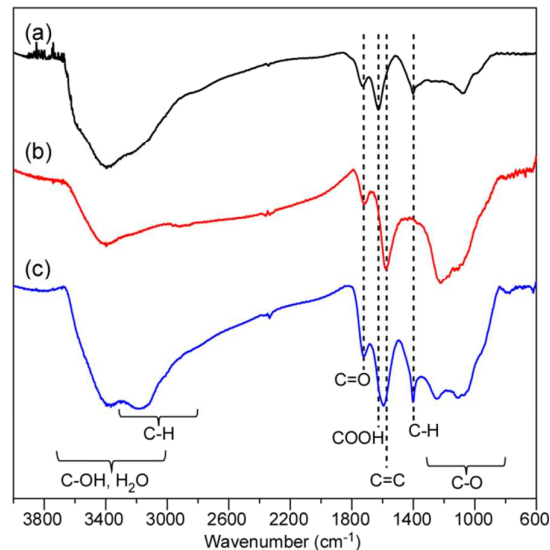
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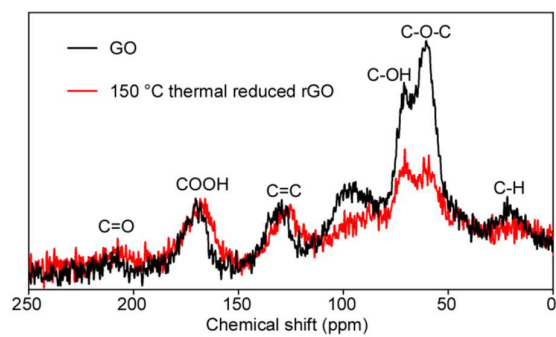


**Figure S1.** (a) Schematic illustration of the fabrication process of the GO films on comb electrodes. The comb electrode (width: 2 μm, interval: 2 μm, 65 pairs) was used for AC and DC measurement. (b) CCD camera image and (c) AFM image and height profile of GO film for photoreduction on comb electrode. (d) CCD camera image and (e) AFM image and height profile of GO film for thermal reduction on comb electrode. (f) Schematic of GO film on comb electrode and L, D and T (in the formula  $\sigma = L / (R \times T \times D)$ ) positions.

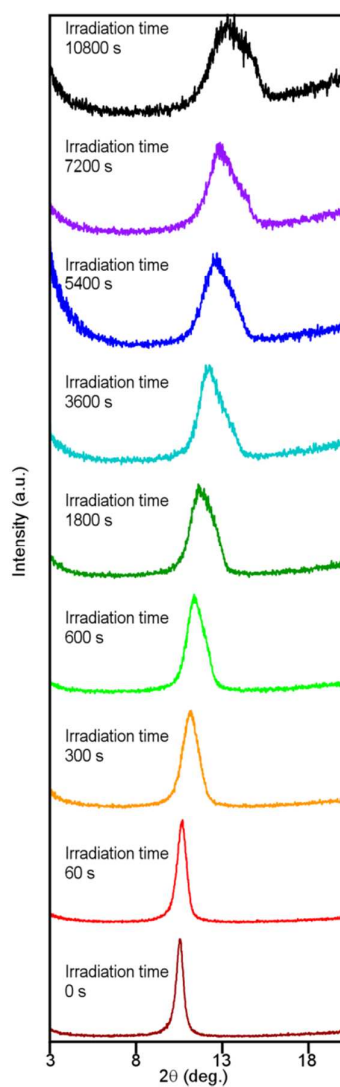


**Figure S2.** FT-IR spectra of (a) GO, (b) thermally reduced rGO (at 150 °C), and (c) photoreduced rGO (after 3 h).

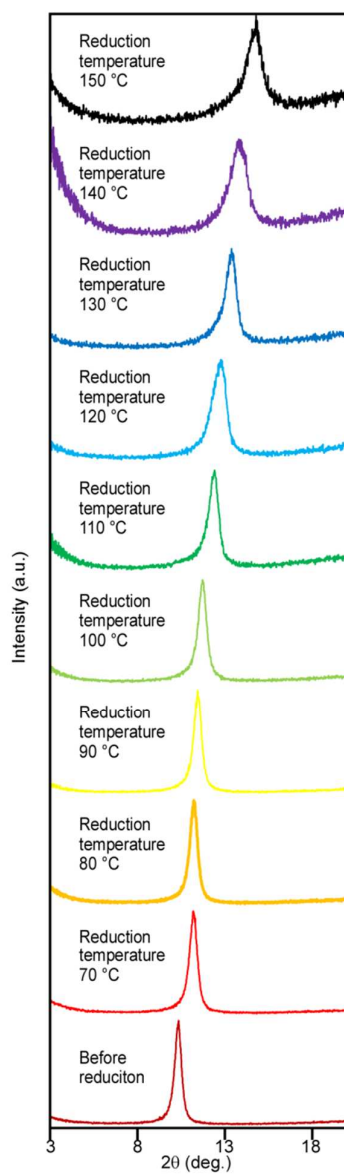
There are stretching vibrations of C–OH and H<sub>2</sub>O at 3000–3700 cm<sup>−1</sup>,<sup>1</sup> C–H stretching at 2800–3300 cm<sup>−1</sup>,<sup>2</sup> C=O vibrations at 1750–1850 cm<sup>−1</sup>,<sup>1</sup> COOH vibrations at 1600–1750 cm<sup>−1</sup>,<sup>1</sup> in-plane stretching of C=C at 1500–1600 cm<sup>−1</sup>,<sup>1</sup> C–H bending vibrations at 1375–1480 cm<sup>−1</sup>,<sup>2-5</sup> and the C–O region (C–O–O, C–OH, etc.) at 800–1330 cm<sup>−1</sup>.<sup>1</sup> The absorption bands of 3200 cm<sup>−1</sup> and 1400 cm<sup>−1</sup> are based on the C–H that disappeared due to thermal reduction, but are relatively increased by the photoreduction in intensity. These results relating to C–H are in good agreement with those of the XPS analysis in Figures 2 and 3.



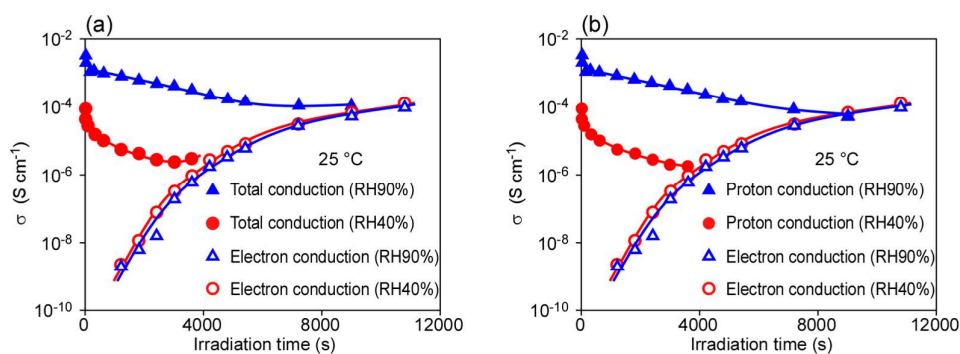
**Figure S3.**  $^{13}\text{C}$  SSNMR spectra of GO and thermally reduced rGO. The peak intensities of C–O–C decreased by thermal reduction. These results are in agreement with those of the XPS analysis in Figure 3.



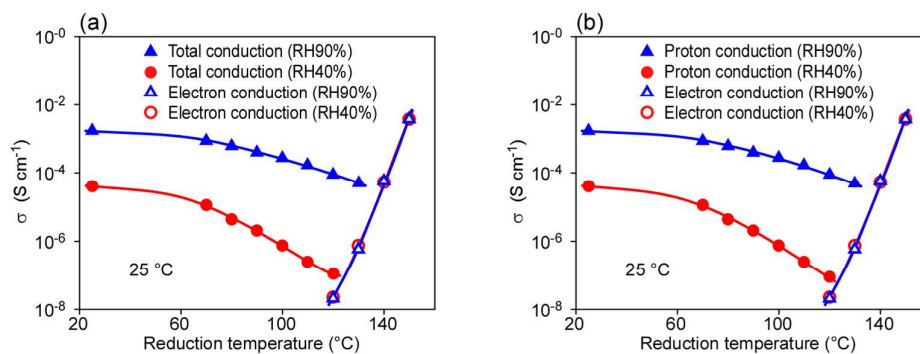
**Figure S4.** XRD patterns of the GO films prepared using various irradiation times. The diffraction peaks shifted to higher angles and broadened after the photoreduction process. The layer distances of the GO films decreased from 0.84 before photoreduction to 0.67 nm after photoreduction.



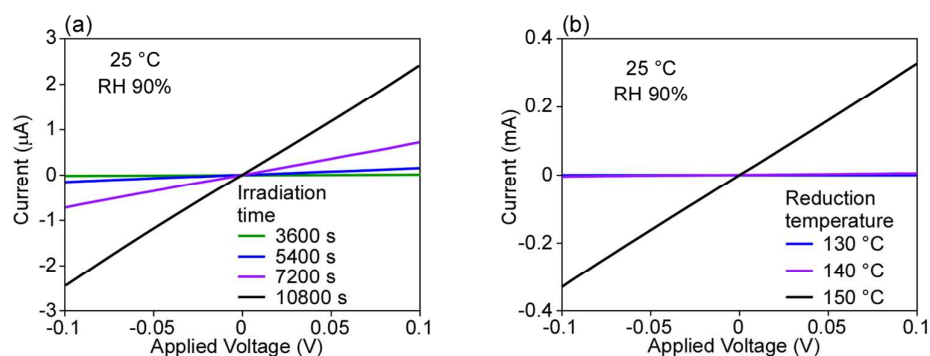
**Figure S5.** XRD patterns of the GO films prepared using various reduction temperatures. The diffraction peaks shifted to higher angles keeping sharp peaks after the thermal reduction process. The layer distances of the GO films decreased from 0.85 before thermal reduction to 0.60 nm after thermal reduction.



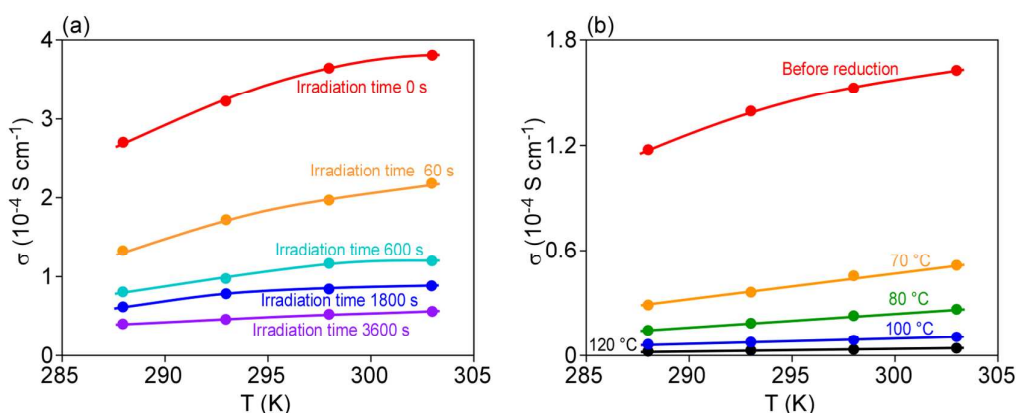
**Figure S6.** (a) Total and electron conductivities as a function of irradiation time. Total conductivities were obtained from cole-cole plots. (b) Proton and electron conductivities as a function of irradiation time (same as Figure 4a). Proton conductivities were calculated using the formula  $\sigma_{\text{total}} = \sigma_{\text{proton}} + \sigma_{\text{electron}}$ , where  $\sigma_{\text{total}}$ ,  $\sigma_{\text{proton}}$  and  $\sigma_{\text{electron}}$  are the total, proton and electron conductivities, respectively.



**Figure S7.** (a) Total and electron conductivities as a function of the reduction temperature. Total conductivities were obtained from cole-cole plots. (b) Proton and electron conductivities as a function of the reduction temperature (same as Figure 4b). Proton conductivities were calculated using the formula  $\sigma_{\text{total}} = \sigma_{\text{proton}} + \sigma_{\text{electron}}$ .



**Figure S8.** Typical  $I$ - $V$  curves of (a) photo and (b) thermally reduced rGO films obtained by a two-probe DC method. The linear relationships between  $I$  and  $V$ , and independent on RH (Figure S6 and Figure S7, Supporting Information) indicate the obtained resistances are based on only the electron conductivity.



**Figure S9.** Temperature dependence of the proton conductivity of rGO films (60% RH). (a) The rGO film prepared using various irradiation times. (b) The rGO film prepared using various reduction temperatures.

## References

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