

Supplementary Information

Super Proton / Electron Mixed Conduction in Graphene

Oxide Hybrids by Intercalating Sulfate Ions

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Experimental Section

A graphene oxide (GO) suspension was prepared by a modified Hummers' method.¹ GO films intercalated with sulfate ions (sGO) were prepared by mixing the GO suspension (10 mL, 0.8 g L⁻¹) with a H₂SO₄ solution (0.83 mL, 0.18 mol L⁻¹) and dropping the mixture on comb electrodes (width: 2 μm, interval: 2 μm, 65 pairs; BAS Ltd.), followed by drying under vacuum.

The photoreduction was carried out in air using a 500 W high pressure mercury lamp (USHO, SX-U1501HQ), which emits ultraviolet light with emission lines at 436, 405 and 365 nm. We confirmed that the sample temperature was less than 40 °C during the photoirradiation. Thermal reduction was carried out using an incubator (ESPEC, SH-241) from 70 to 150 °C for 1 h. We used AFM (Bruker, Digital Instruments Nanoscope V) for determining the morphology and thickness of reduced sGO (r-sGO) films deposited on the comb electrodes. Layer distances of sGO and r-sGO films were measured on a powder X ray diffractometer (Rigaku RINT 2500) using Cu Kα ($\lambda = 0.154$ nm) radiation. The content of elements and oxygen functional groups of the samples were analyzed by an XPS analyzer (Thermo Scientific, Sigma Probe). The Nyquist plots of the samples were measured by an impedance / gain phase analyzer (Solartron 1260) in the frequency range from 1 MHz to 1 Hz with a perturbation voltage amplitude of 50 mV. The electron conductivities of the samples were measured by two- and four-probe DC method using a potentiostat with a function generator (IVIUM TECHNOLOGIES, CompactStat). We confirmed that electrical resistances measured by these two different techniques were found to be very close within the experimental error. Thus, we used the two-probe DC method to determine the electrical conductivity of samples. The proton conductivities were obtained by the subtraction of the electron conductivity from the total conductivity. The AC and DC measurements were performed under controlled temperature and humidity using an incubator (ESPEC, SH-241). The details regarding the calculation of conductivities were described in our previous report.²

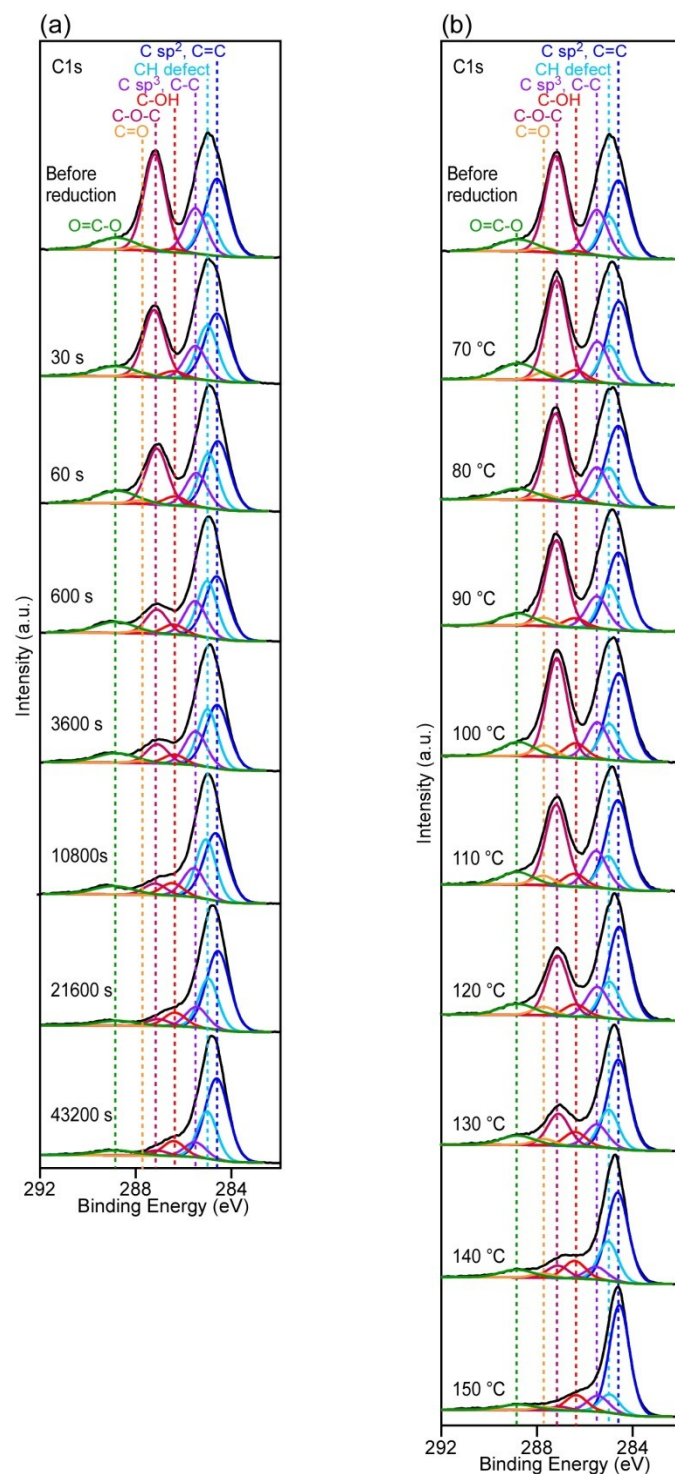


Figure S1. C 1s XPS spectra of sGO and r-sGO films after (a) the photo-reduction for 30-43200 s and (b) the thermal-reduction at 70-150 °C. The C 1s XPS spectra were split up into 7 groups ($-\text{COOH}$, $\text{C}=\text{O}$, $\text{C}-\text{O}-\text{C}$, $\text{C}-\text{OH}$, sp^3 $\text{C}-\text{C}$, $\text{C}-\text{H}$ defect, and sp^2 $\text{C}=\text{C}$ bonds) according to our previous report.³ The $\text{C}-\text{O}-\text{C}$ peak intensities drastically decreased after the photo- and thermal-reduction processes.

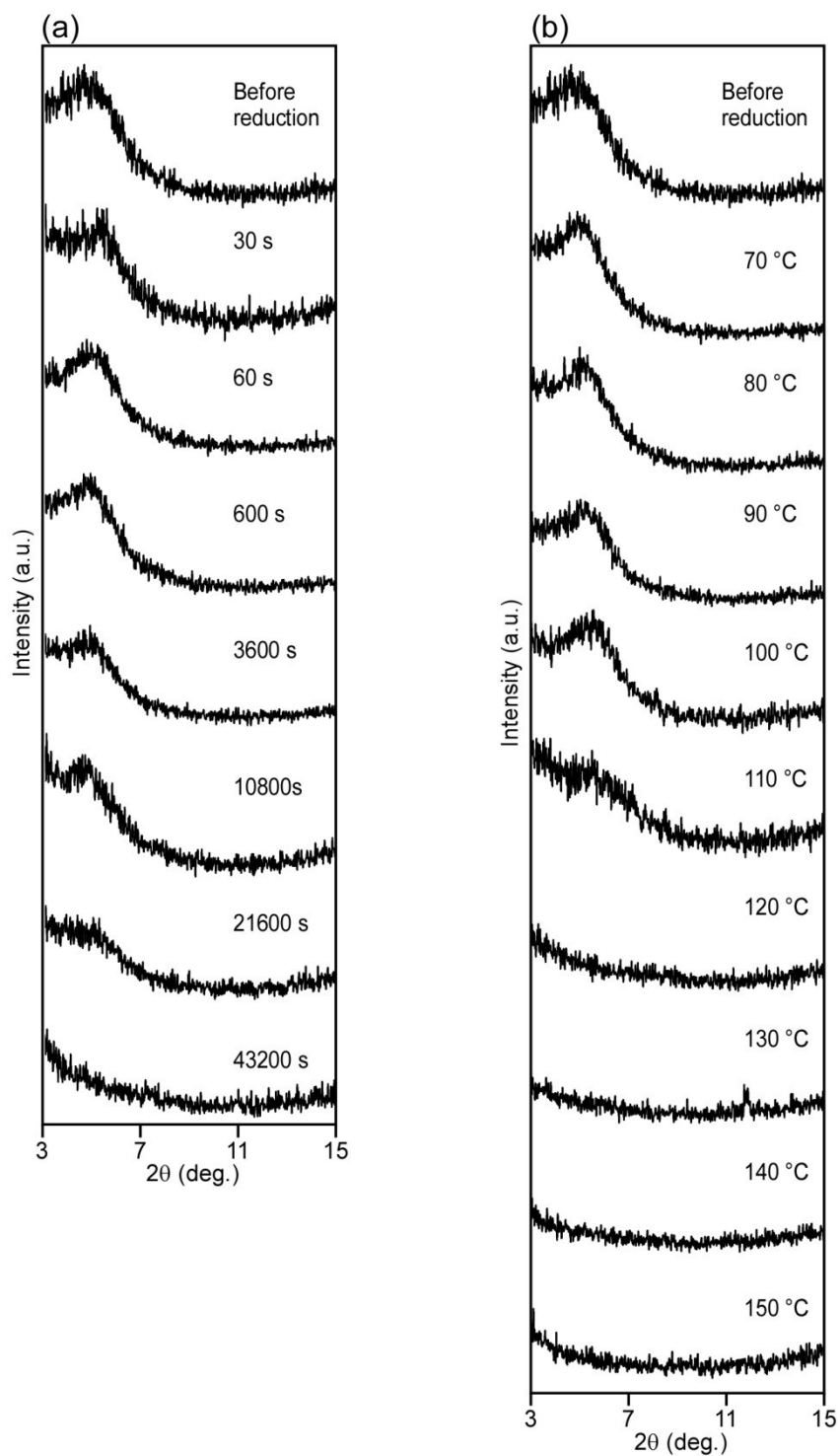


Figure S2. XRD patterns of the sGO and r-sGO films after (a) the photo-reduction for 30-43200 s and (b) the thermal-reduction at 70-150 °C. The positions of diffraction peaks barely changed after the reduction processes. However, the diffraction peak intensity and width gradually became weaker and wider, respectively, as the reduction proceeded. Finally, the diffraction peaks disappeared.

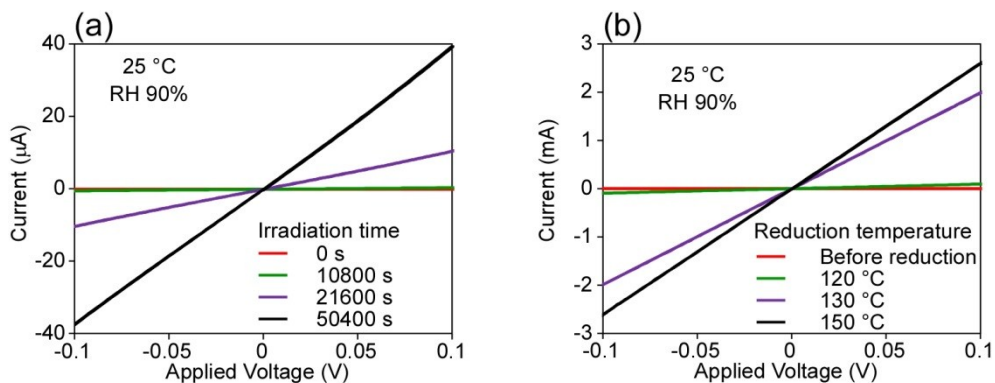


Figure S3. Typical I - V curves of the sGO and r-sGO films after (a) the photo-reduction for 10800-50400 s and (b) the thermal-reduction at 120-150 °C. The electron conductivities of the sGO and r-sGO films were determined by the slopes of these I - V curves.

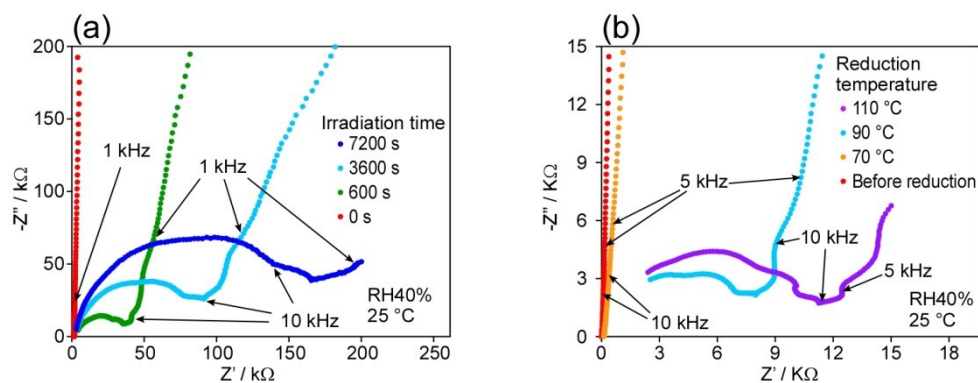


Figure S4. Typical Nyquist plots of the sGO and r-sGO films after (a) the photo-reduction for 600-7200 s and (b) the thermal-reduction at 70-110 °C. The total conductivities of the sGO and r-sGO films were determined from these Nyquist plots. Because the sGO and r-sGO films were highly sensitive to humidity, fluctuations in plots were observed. Note that RH in an incubator fluctuated in the order of $\pm 1\%$.

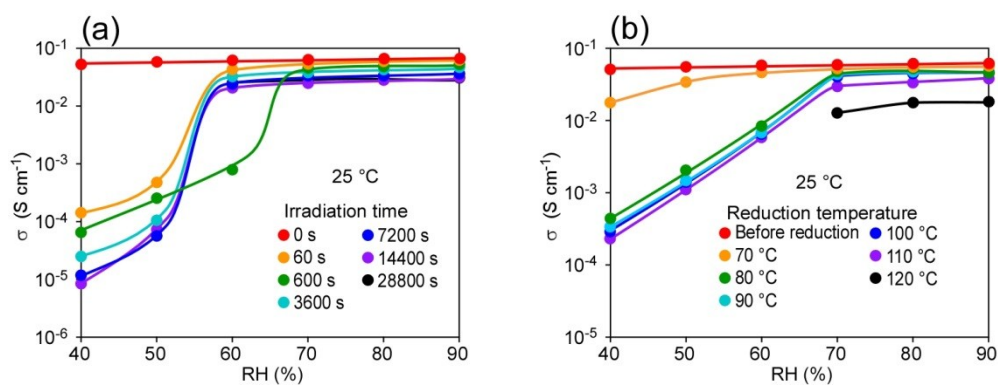


Figure S5. RH dependence of the total conductivities of the sGO and r-sGO films after (a) the photo-reduction for 60-28800 s and (b) the thermal-reduction at 70-120 °C.

References

- 1 M. Koinuma, C. Ogata, Y. Kamei, K. Hatakeyama, H. Tateishi, Y. Watanabe, T. Taniguchi, K. Gezuhara, S. Hayami, A. Funatsu, M. Sakata, Y. Kuwahara, S. Kurihara and Y. Matsumoto, *J. Phys. Chem. C*, 2012, **116**, 19822-19827.
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