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Fast, Scalable, and Eco-Friendly Fabrication of Energy Storage Paper Electrode

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Abstract

Recent progress in portable and wearable electronics has promoted a growing demand for high-performance and flexible energy-storage devices that are abundant and affordable. Because reduced graphene oxide (rGO), originating from inexpensive graphite, serves as higher-performance energy-storage electrode than conventional activated carbons and carbon nanotubes, research and development of rGO/polymer composite electrodes for flexible supercapacitors have become a center of attraction. However, the fabrication of rGO-based flexible electrodes frequently requires long time with high-temperature treatment or toxic chemical treatment, resulting in the lack of scalability and eco-friendliness. Here we show fast, scalable, and environment-compatible route to fabricate high-performance rGO/cellulose paper supercapacitor electrode. Single-layer graphene oxide (GO) sheets and recycled waste pulp fibers were successfully fabricated into a paper composite by a well-established scalable papermaking process, followed by a room-temperature, additive-free, and millisecond-timescale flash reduction process. The as-prepared rGO/paper electrode had high specific capacitance, up to 212 F g^{-1}, for an all paper-based flexible supercapacitor, comparable to those of state-of-the-art rGO-based electrodes, while dramatically decreasing the reduction time of GO from the conventional hour timescale to milliseconds. This work will pave the way for green, flexible, and mass-producible energy-storage papers in future wearable electronics.

Introduction

Since the invention of paper approximately 2000 years ago, it has been traditionally fabricated from an aqueous suspension of cellulose fibers by papermaking, which is a sequential process of filtration, dewatering, and drying. The current papermaking process enables high-speed and large-area fabrication of paper materials up to 18,000 m^2 min^{-1}. Therefore, paper materials are mass-producible and inexpensive, and they have been used for many purposes, such as writing, printing, and packaging applications, in daily life. Recently, the application of paper has been extended to electronics;[1,2] electronic devices have been fabricated on paper substrates, including inorganic[3,4] and organic transistors,[5] complementary metal oxide semiconductors,[6,7] triboelectric nanogenerators,[8] memory,[9,10] transparent conductive films,[11,12] and antennas.[13,14] Paper electronics provides new possibilities for next-generation devices with flexible, biodegradable, biocompatible, and eco-friendly electronics.

Recent years have seen remarkable progress in wearable electronics;[15,16] portable consumer electronics are becoming flexible, lightweight, and even wearable. Because wearable electronics essentially require energy-storage devices with thin, lightweight, flexible, and conformable properties, such flexible energy-storage devices have become the focus of major research.[17–19] Of various energy-storage devices, supercapacitors have attracted much attention because of their high power density, long life cycle, and environmental friendliness.[20,21] Because electrode materials play essential roles in energy-storage devices, enormous efforts have been devoted to the research and development of high-capacitance electrodes for flexible supercapacitors. Reduced graphene oxide (rGO), which can be obtained by the reduction of graphene oxide (GO) extracted from inexpensive graphite, offers much higher specific capacitance than conventional activated carbons and carbon nanotubes.[22,23] Thus, flexible rGO/polymer composites have emerged as one of the most promising electrodes for future supercapacitors.[24–31]

The forthcoming widespread use of portable and wearable electronics will provide a strong demand for making flexible energy-storage devices more abundant and affordable. It is therefore highly desired to develop mass production processes for low-cost and high-performance rGO-based electrodes for flexible supercapacitors. Paper serves as a favorable matrix for flexible binder-free rGO electrodes[24–28] because of its high affinity for nanocarbons *via* a CH-π interaction between the axial plane of the cellulose and the graphene π-conjugated system,[11,32] as well as its excellent availability. The papermaking process can also boast excellent scalability and benefit from techniques and equipment common in the established paper industry. However, the fabrication of rGO remains challenging to processing speed, scalability, and environmental compatibility because the reduction of GO frequently requires hour-scale time with high-temperature treatment[24–26,29,30,33] or toxic chemical treatment.[22,23,27,28,31,34,35] Here, we show the high-speed, scalable, and eco-friendly fabrication of rGO/cellulose paper composite electrodes for flexible supercapacitors using a combination of papermaking and flash reduction techniques. First, single-layer GO sheets were effectively composited with virgin pulps or recycled waste pulps to prepare a flexible GO/cellulose paper composite by a scalable papermaking process. Then, room-temperature, additive-free, and millisecond-timescale reduction of GO was achieved *in situ* in the paper composite by high-intensity pulsed light irradiation. The rapidly reduced GO/cellulose paper composite electrodes achieved high specific capacitance, up to 212 F g^{-1}, and were successfully applied for an all paper-based flexible supercapacitor.

Results and discussion

Fabrication of the rGO/cellulose paper composite by a combination of papermaking and flash reduction

Fast fabrication of the rGO/cellulose paper composite was carried out by papermaking with a filtration time of 4 s and successive flash reduction for 0.036 s (**Fig. 1**). First, an aqueous dispersion of negatively charged single-layer GO sheets (**see Supplementary Information Table S1**) with widths of

10–30 μm, which were extracted from graphite powder according to the modified Hummer's method,[36] was mixed with an aqueous suspension of virgin cellulose pulp fibers with widths of several 10 μm and lengths of several millimeters. Because pulp fibers have weakly negative charges on their surfaces (**Table S1**), the brown-colored GO and white-colored pulp fibers were then clearly separated from each other in water as a result of electrostatic repulsion. For preparation of the paper composite by the papermaking process, the resulting aqueous mixture was filtered through a #300 wire mesh. While the pulp fibers were effectively retained on the wire mesh, most of the GO dropped through the mesh because of its small size, suggesting that a simple mixture of GO and pulp fibers presents significant difficulty in fabricating uniform composites using the papermaking process. To overcome this difficulty, in this study, a branched polymer with high-density positive charges, *i.e.*, polyethylenimine (PEI), was added in the mixture to connect nano-dispersed GO with pulp fibers through electrostatic interaction (**Fig. 1** and **Table S1**). Subsequently, the prepared aqueous suspension of the brown-colored GO/pulp fiber composite was rapidly dewatered through the mesh within 4 s with excellent retention of nearly 100%. The wet paper obtained was dried by hot pressing to prepare a GO/cellulose paper composite with paper-like flexibility. The process time for this sequential procedure was as short as the conventional papermaking process for preparation of cellulose paper, indicating the potential for industrial-level scalability. Finally, the GO/cellulose paper composite was treated with high-intensity pulsed light using xenon flash lamps (light intensity: 0.986 J cm^{-2}) for 0.036 s under ambient conditions, while maintaining its flexibility.

Flash reduction of GO to rGO was confirmed by Fourier transform infrared attenuated total reflection (FT-IR/ATR) analysis. FT-IR/ATR spectra of GO without the cellulose paper matrix before and after the irradiation of high-intensity pulsed light are shown in **Fig. 2a**. After pulsed light irradiation for 0.036 s, most of the peaks derived from oxygen functional groups of the original GO[37] disappeared, and the C=C stretching vibration peak at ca. 1600 cm^{-1} for the GO shifted to 1560 cm^{-1}, indicating the formation of rGO.[37] Thus, the millisecond-scale rapid reduction of GO was successfully conducted at atmospheric conditions using high-intensity pulsed light. The *in situ* flash reduction of GO in the cellulose paper matrix was also achieved to prepare the flexible rGO/cellulose paper composite while keeping the crystalline structure of native cellulose (cellulose I[38]) (**Fig. 2b**). Then, GO sheets with widths of 10–30 μm, which were embedded in the paper matrix (**Fig. 2c, see also Supplementary Information Fig. S1**), formed porous structures after the flash reduction (**Fig. 2d**), as reported by Cote et al.[39] The flash reduction mechanism of GO could involve photo-thermal ultrafast heating[39] and/or electron supply from photo-ionized moisture.[40]

Flash-reduced GO/cellulose paper electrode for a flexible supercapacitor

The prepared flash-reduced GO/cellulose paper composite was applied as an electrode material for a flexible supercapacitor. The electrical conductivity and specific capacitance of the rGO/cellulose paper composite were evaluated as a function of the pulsed-light irradiation time (**Fig. 3a**). The electrical conductivity of the paper composite increased with increasing irradiation time because of the conversion of electrically insulating GO to conductive rGO by the flash reduction. Then, the rGO/cellulose paper composite with thickness ca. 100 μm was conductive in 3D, indicating that the flash-reduced GO formed a percolation network not only on the surface but also inside the paper composite. The conductivity reached 172 mS cm^{-1} after the flash reduction for 0.072 s. Thus, the rGO/cellulose paper composite was free-standing and 3D conductive and could be used as a flexible electrode material, without any additives, for a supercapacitor. It should be noted that the maximum specific capacitance of 212 F g^{-1} (areal capacitance: 24 mF cm^{-2}, volumetric capacitance: 2.4 F cm^{-3}) was recorded at a flash reduction time of 0.036 s, while the specific capacitance values decreased over 0.036 s (**see also Supplementary Information Fig. S2**). To elucidate this phenomenon, electrochemical impedance spectroscopy measurements were conducted to discuss the electrical resistance and ion-transport behavior of the rGO/cellulose paper electrodes. **Fig. 3b** shows Nyquist plots of the rGO/cellulose paper electrodes prepared by the flash reduction for 0.036 s and 0.072 s. The equivalent series resistance (ESR), the charge-transfer resistance, and the diffusion resistance of electrolyte ions in the electrode materials can be separated by the complex plane plots corresponding to different frequency regions. In general, the intersection of the curve at the real resistance (Z') axis represents the ESR, which determines power density of the supercapacitors. The charge-transfer resistance at the electrode-electrolyte interface is determined by the width of semicircle plotted at higher frequencies. The inclined line with a slope of 45° to the Z' axis at lower frequencies is related to the diffusion of electrolyte ions, which is called the Warburg impedance. Then, the projected length of the Warburg line on the Z' axis (Warburg length) represents the diffusion resistance of electrolyte ions in the electrode materials.[24] As shown in **Fig. 3b**, the Warburg length of the rGO/cellulose paper electrode prepared at a flash-reduction time of 0.036 s was shorter than that of the rGO/cellulose paper electrode prepared at a flash-reduction time of 0.072 s, while there were no large difference between their ESR values (ca. 8 Ω). These results suggested that the excess irradiation of the pulsed light could cause the increased diffusion resistance of electrolyte ions inside the paper electrode possibly due to the aggregation of rGO by π-π re-stacking and the damage to the paper structure (**see also Supplementary Information Fig. S3**), resulting in a decrease in the specific capacitance. It is well known that nano-dispersed GO sheets suffer from severe re-stacking after reduction, and the resulting rGO loses its excellent functionalities.[22, 36] Lee et al. has recently addressed the chronic re-stacking issues of rGO by doping with melamine resin monomers to enlarge the interlayer spacing between rGO sheets, achieving efficient ion diffusion and an improvement in the specific capacitance from 110 to 210 F g^{-1} at 0.5 A g^{-1}.[30] Thus, it is implied that the *in situ* flash-reduction of GO immobilized inside the paper matrix, demonstrated in this study, can suppress the re-stacking of GO sheets to some degree by controlling the flash-reduction time. The rGO/cellulose paper composite prepared at the optimum flash-reduction time (0.036 s) demonstrated a rectangular-shaped cyclic voltammetry (CV) curve with slight distortion (**Fig. 3c**) and somewhat non-linear charge-discharge curves (**Fig. 3d**), indicating electric double-layer capacitor behavior with slight pseudo-capacitance possibly due to the presence of a few oxygencontaining functional groups.[37] Based on the charge-discharge curves, the specific capacitance values were plotted as a function of current density (**Fig. 3e**). The rGO/cellulose paper composite prepared using virgin pulp fibers achieved high specific capacitances ranging from 212 to 100 F g^{-1} with current densities ranging from 0.5 to 10 A g^{-1}. In addition, the paper composite electrodes offered excellent charge-discharge cyclic durability; the retention of the specific capacitance was ca. 94%, even after 14,000 cycles (**Fig. 3f**). As shown in **Fig. 4a**, an all paper-based flexible supercapacitor was also successfully prepared using two pieces of the rGO/cellulose paper composite electrode and one piece of the paper separator; the specific capacitance of a single paper electrode was estimated to be 177 F g^{-1} at a current density of 1.0 A g^{-1} (**Fig. 4b**). **Fig. 4c** shows Ragone plot for the paper-based supercapacitor. The specific energy density and specific power density at a voltage of 1.0 V of the paper-based supercapacitor were 24.6 Wh kg^{-1} and 503 W kg^{-1}, respectively. These results suggest that the flash-reduced GO/cellulose paper composite is promising for energy-storage paper devices in portable, flexible, and wearable electronics.

Eco-friendly fabrication of the paper supercapacitor electrode by using recycled waste pulps

Efficient recycling of waste paper materials has a significant role in sustainable development because it contributes to low-cost, low-energy consumption, and environmentally benign paper industries. Compared with virgin pulps, recycled pulps from waste paper can save ca. 17 trees, 3.3 cubic yards of landfill space, 360 gallons of water, 100 gallons of gasoline, 60 pounds of air pollutions, and 10,401 kW of electricity per production of one ton of paper.[41] In this study, as shown in **Fig. 5**, the high electrode performances of the paper composite were achieved even when prepared using recycled waste pulps from newspapers instead of virgin pulps. In conjunction with a well-established scalable papermaking process, therefore, the use of recycled waste pulps can contribute to eco-friendly fabrication of more affordable GO/cellulose paper composites. Furthermore, the flash-reduction process achieved a drastic shortening of the GO reduction time from the conventional hour timescale to milliseconds; after reduction, the flash-reduced GO/cellulose paper composite in this study offered high specific capacitance, comparable to those of state-of-the-art rGO-based electrodes prepared by chemical reduction,[22,23,27,28,31,34,35] thermal reduction,[24–26,29,30,33] and flash and successive thermal reduction,[37] including matrix-free rGO,[22,23,33–35,37] paper-based rGO,[24–28] and other polymer-based rGO electrodes[29–31] (**Fig. 6**). In addition, our paper supercapacitor electrode achieved higher capacitance (212 F g^{-1}) than previously reported carbon nanotube-based supercapacitor electrode (51 F g^{-1})[42]. It has been reported that the flash-lamp irradiation process can be extended to large-area and roll-to-roll photonic sintering and manufacturing of metal nanoparticle conductive lines printed on flexible substrates.[43–46] Thus, the combination of papermaking and flash reduction is expected to be a promising approach for the high-speed and roll-to-roll production of high-capacitance and flexible rGO-based electrodes.

Conclusions

In conclusion, we have demonstrated the fast and scalable fabrication of high-performance rGO/cellulose paper electrodes by combining papermaking and *in situ* flash-reduction techniques. Both virgin pulps and recycled waste pulps can be used as a flexible matrix for GO to prepare GO/cellulose paper composites by a facile papermaking process. Then, room-temperature, additive-free, and millisecond-timescale flash-reduction of GO was successfully performed *in situ* in the paper matrix, providing the paper electrodes with a specific capacitance up to 212 F g^{-1} for a flexible supercapacitor. These findings open up a new window for green and mass production of energy-storage papers towards future wearable electronics.

Experimental

Materials

Virgin pulps (never-dried softwood dissolving sulfite pulps), which were provided by Nippon Paper

Group. Inc., Japan, and recycled waste pulps obtained from newspapers were used as cellulose pulp fibers. PEI (average molecular weight: 1800) and an aqueous dispersion of single-layer GO sheets (GO-TQ2, 1 wt%, width: 10-30 μm) were purchased from Wako Pure Chemical Industries, Ltd., Japan and NiSiNa materials, Co. Ltd., Japan, respectively. The aqueous GO dispersion (0.5 g) was diluted with distilled water (15 mL), followed by sonication for 4 min using an ultrasonic homogenizer equipped with a 7-mm probe tip (US-300T, Nihon Seiki, Co. Ltd., Japan) before use. All reagents were used without further purification.

Preparation of the GO/cellulose paper composite using a papermaking technique

An aqueous suspension of cellulose pulp fibers (0.15 wt%, 200 mL) was mixed with an aqueous dispersion of GO (0.032 wt%, 15.5 mL, GO content: 5 mg) and an aqueous solution of polyethylenimine (1.0 wt%, 0.4 mL) in that order, with each step being carried out at an interval of 10 min. The resulting suspension of the GO/pulp fiber composites was dewatered for 4 s by suction filtration through a #300 wire mesh. The wet paper on the wire mesh was sandwiched between a hydrophobic glass plate and paper towel and dried by hot pressing at 110 °C for 10 min (1.1 MPa). The obtained sample was then peeled from the wire mesh to prepare the GO/cellulose paper composite with a diameter of 75 mm and thickness of ca. 100 μm.

Flash reduction of the GO/cellulose paper composite

The GO/cellulose paper composite was subjected to a flash reduction process at room temperature in air using a PurseForge 3300 equipped with xenon flash lamps (Novacentrix Corp., USA). Typically, the irradiation of high-intensity pulsed light for 0.0018 s was carried out 10 times at a frequency of 2

Hz for each surface of the paper composite (light intensity: 0.986 J cm^{-2}; net time of pulsed light irradiation: 0.036 s).

Analyses

The conductivity and sheet resistance values were measured using a resistivity meter with a four-point probe (Loresta-GP, MCP-T610, Mitsubishi Chemical Analytech Co., Ltd., Japan). Surface observations of the paper composites were conducted using a field-emission scanning electron microscope (JSM-6700F, JEOL Ltd., Tokyo, Japan) at an accelerating voltage of 1.0 kV. FT-IR/ATR spectra were obtained using a KJP-05120S instrument (PerkinElmer Co. Ltd., Japan). X-ray diffraction patterns were recorded using a Rigaku MiniFlex600 with a scanning angle (2θ) range of 10–35°, at 40 kV and 15 mA. The zeta potential values of GO, cellulose pulp fibers, PEI, and GO/pulp/PEI composite were measured using a Zeta-potential & Particle size Analyzer ELSZ-2000N (Otuska Electronics, Co. Ltd., Japan).

Electrochemical measurements

The electrochemical measurements were conducted using a conventional three-electrode system with an aqueous electrolyte (1 M Na_2SO_4). The rGO/cellulose paper composite was set on Al foil as a current collector and was used as the working electrode. A platinum electrode and Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively. The weight and dimensions of the active material (GO) in the working electrode were 0.113 mg and 1.0 cm^2, respectively. Cyclic voltammetry at a scan rate of 20 mV s^{-1} and galvanostatic charge-discharge behavior at an operation voltage range of 0–1.0 V were performed using a potentio/galvanostat (1255WB, Solartron Co. Ltd., UK). Specific capacitance values were calculated based on the galvanostatic discharge curve and the weight of the active material. Electrochemical impedance spectroscopy was recorded from 1 MHz to

0.1 Hz at 0 V with an amplitude of 10 mV. For evaluation of the paper-based supercapacitor, a cellulose nanofiber paper separator with a thickness of 50 μm, which was prepared according to a previous report,[47] was sandwiched between the rGO/cellulose paper electrodes on the Al-foil current collector, followed by soaking with the aqueous electrolyte (1 M Na_2SO_4) and setting into a cell (TBH3-CELL, Toyo Corp., Japan). The specific energy density and specific power density were calculated by using $E = CV^2/2$ and $P = E/\Delta t$, respectively, where C is the specific capacitance, V is the cell voltage, Δt is the discharge time in the galvanostatic charge/discharge curves.[48]

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Electronic Supplementary Information (ESI) available: Zeta potential values of GO, cellulose pulp fibers, polyethylenimine, and their composite; Field-emission scanning electron microscope images of the cellulose paper and the rGO/cellulose paper prepared at a flash reduction time of 0.072 s; Electrode performance of the rGO/cellulose paper prepared at a flash reduction time of 0.072 s. See DOI: 10.1039/x0xx00000x

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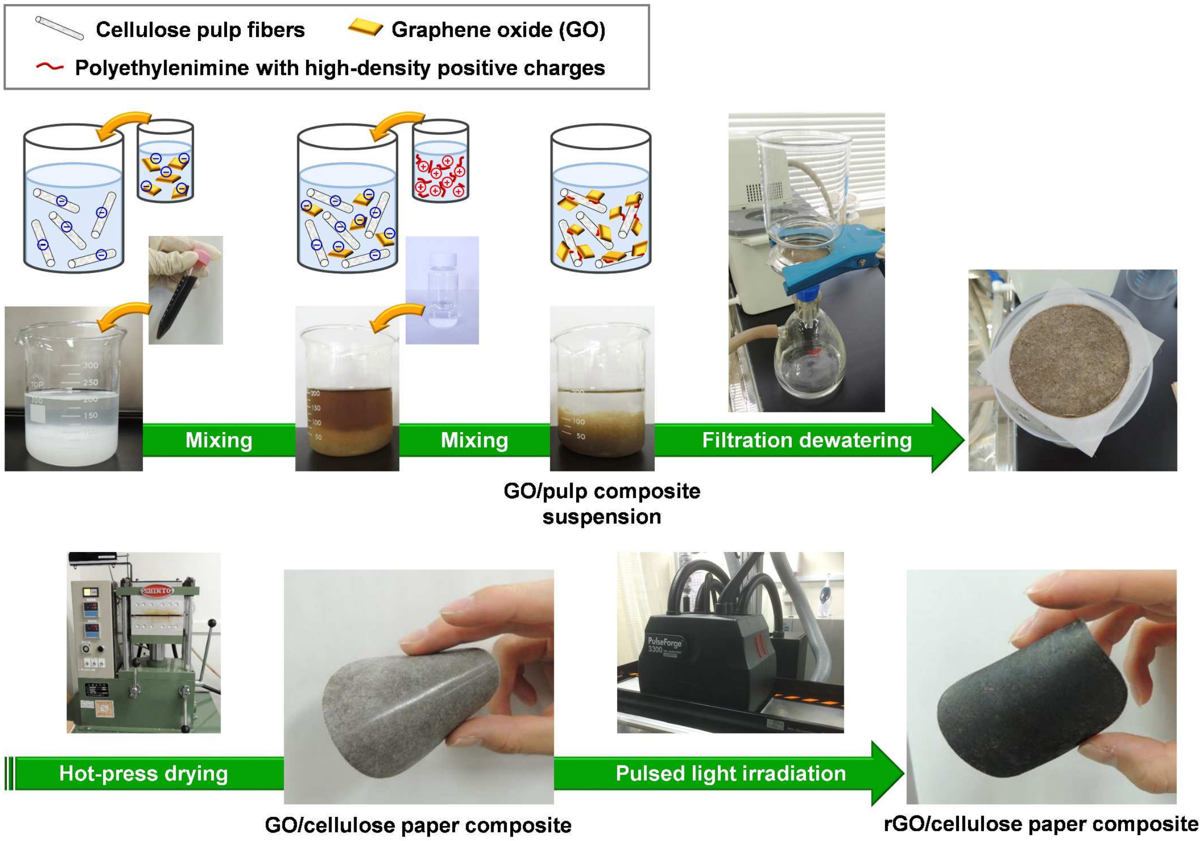

Fig. 1 Preparation procedure for the rGO/cellulose paper composite by papermaking and successive flash-reduction processes. Size of the paper composite: 75 mm in diameter, 100 µm in thickness.

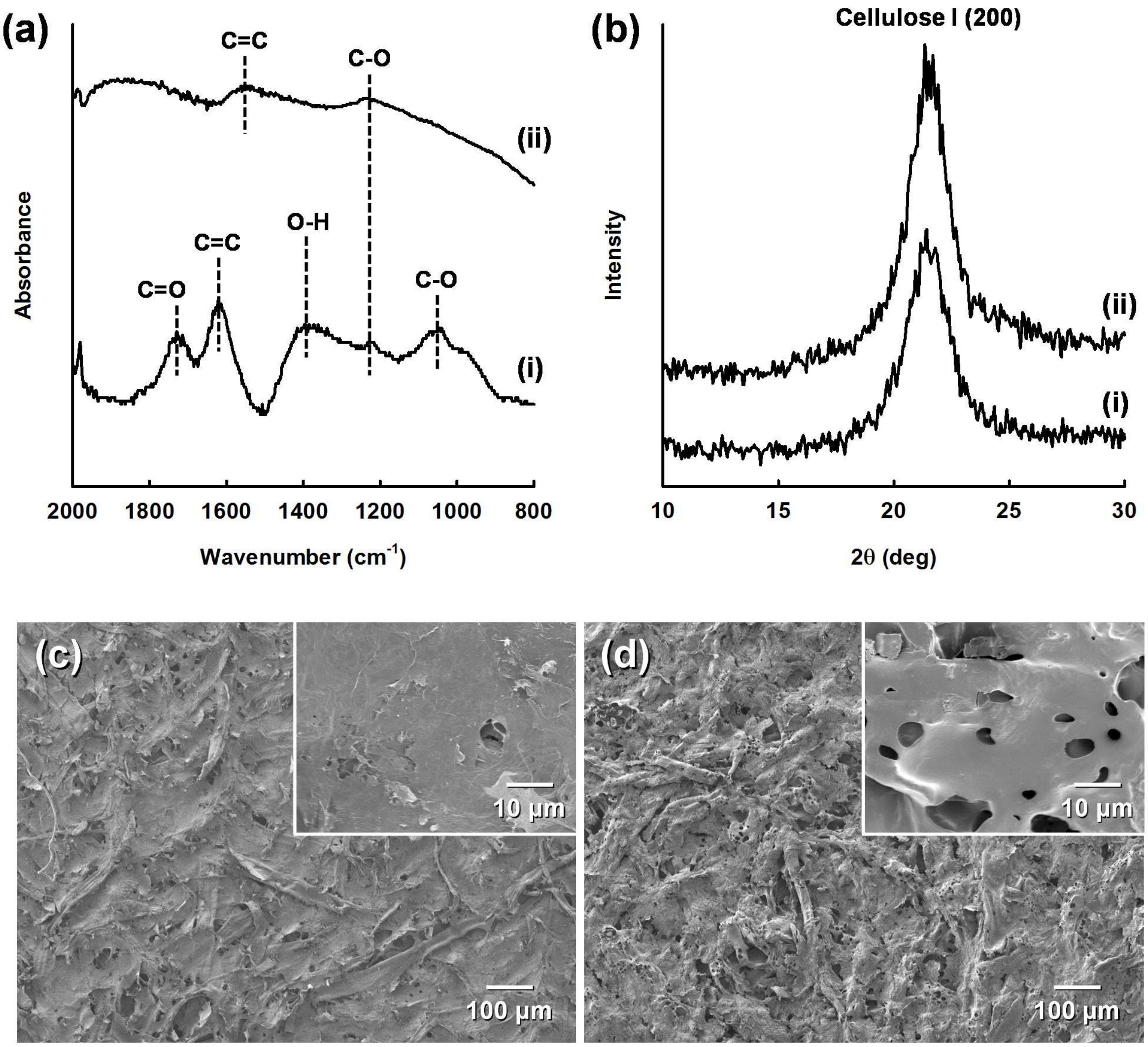

Fig. 2 Characterization of the flash-reduced GO/cellulose paper composite. (a) FT-IR/ATR spectra of GO without cellulose paper matrix (i) before and (ii) after pulsed light irradiation, (b) X-ray diffraction spectra and (c, d) field-emission scanning electron microscope images of the GO/cellulose paper composite (i) before and (ii) after pulsed light irradiation. Light intensity: 0.986 J cm^{-2}. Irradiation time: 0.036 s.

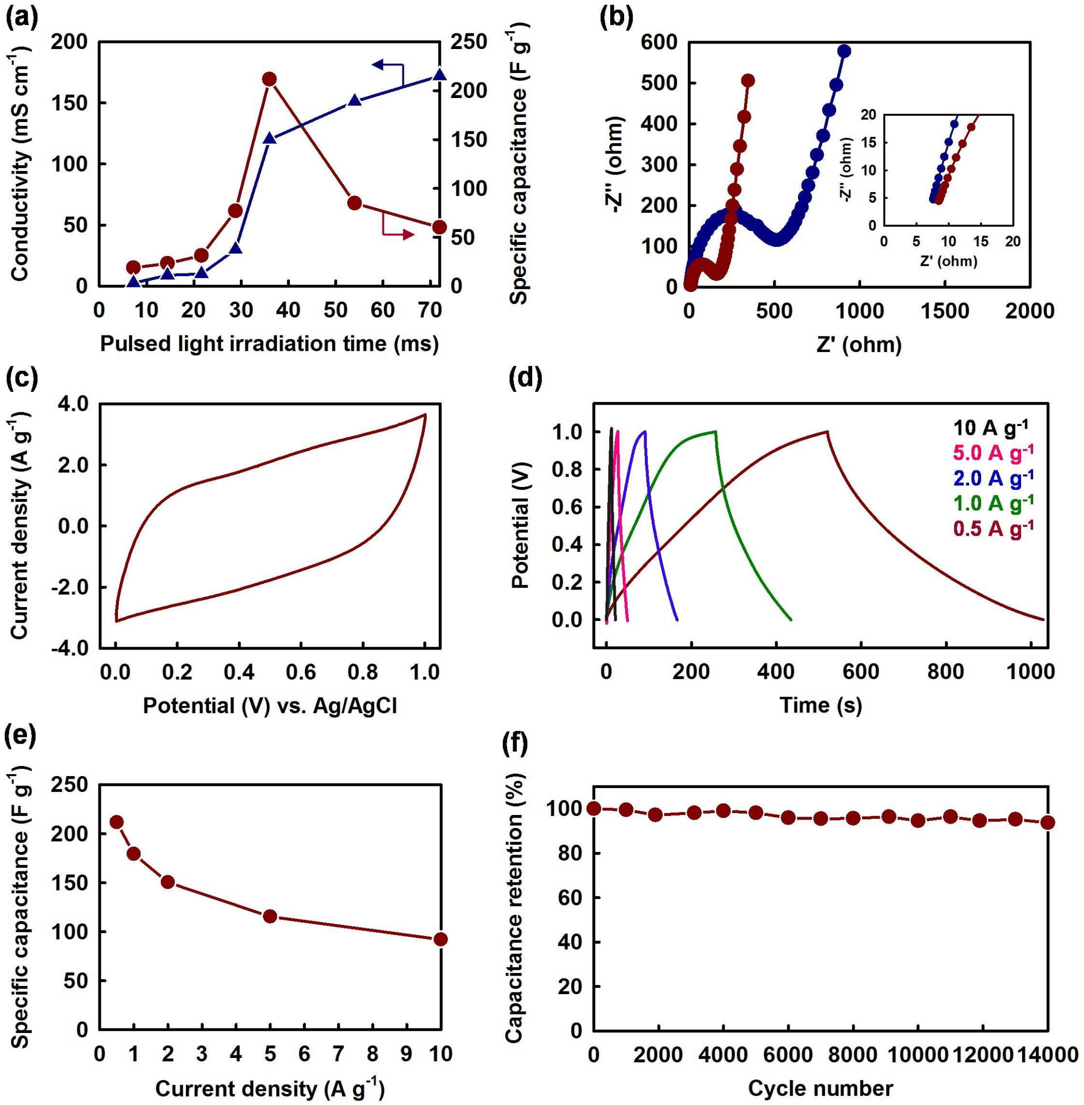

Fig. 3 Flash-reduced GO/cellulose paper electrode for flexible supercapacitor. (a) Electrical conductivity and specific capacitance at a current density of 0.5 A g^{-1} of the rGO/cellulose paper composite as a function of pulsed-light irradiation time, (b) Nyquist plots of the rGO/cellulose paper electrode prepared by pulsed light irradiation for 0.036 s (red) and 0.072 s (blue), (c) CV curve at a scan rate of 20 mV s^{-1} and (d) charge-discharge curves at current densities of 0.5–10 A g^{-1} for the rGO/cellulose paper electrode prepared by pulsed light irradiation for 0.036 s, (e) specific capacitance versus current density for the rGO/cellulose paper electrodes prepared using virgin pulps, (f) specific capacitance retention of the rGO/cellulose paper composite as a function of the charge-discharge cycle number at a current density of 10 A g^{-1}. Light intensity: 0.986 J cm^{-2}.

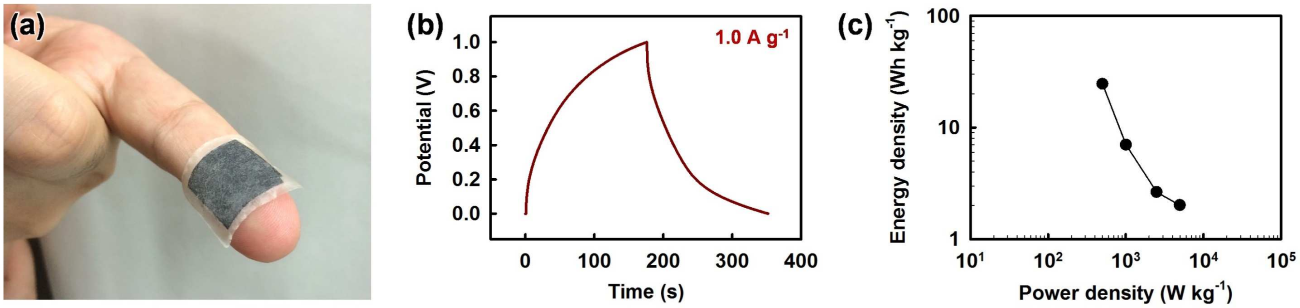

Fig. 4 All paper-based flexible supercapacitor. (a) An optical image of the all paper-based flexible supercapacitor, (b) Charge-discharge curve at a current density of 1.0 A g^{-1} for the paper-based supercapacitor, (c) Ragone plot at a voltage of 1.0 V for the paper-based supercapacitor.

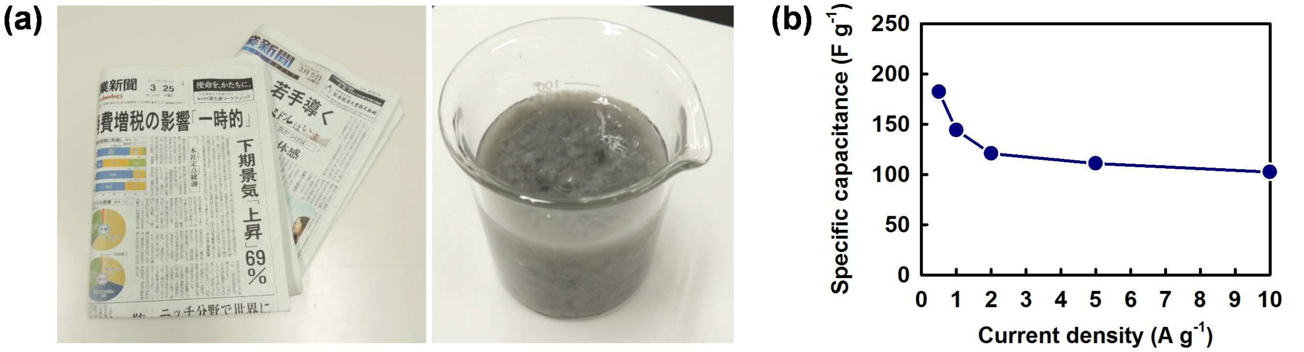

Fig. 5 Paper supercapacitor electrode prepared using recycled waste pulps. (a) Optical images of Japanese newspapers (left) and an aqueous suspension of their recycled waste pulps (right), (b) specific capacitance versus current density for the rGO/cellulose paper electrodes prepared using recycled waste pulps.

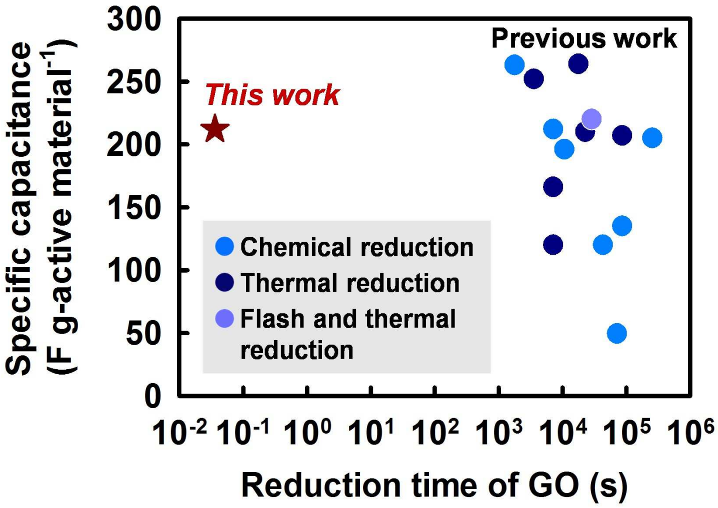

Fig. 6 Specific capacitance versus reduction time of GO for the state-of-the-art rGO-based electrodes.