Energy Conversion

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A Twisted Wire-Shaped Dual-Function Energy Device for Photoelectric Conversion and Electrochemical Storage**

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Abstract: *A wire-shaped energy device that can perform photoelectric conversion and electrochemical storage was developed through a simple but effective twisting process. The energy wire exhibited a high energy conversion efficiency of 6.58% and specific capacitance of 85.03 $\mu F cm^{-1}$ or 2.13 $mF cm^{-2}$, and the two functions were alternately realized without sacrificing either performance.*

It is well recognized that electronic devices with the same function, such as photoelectric conversion or electrochemical storage, generally consist of similar materials and structures. More specifically, photoactive materials are sandwiched between anodes and cathodes to produce organic solar cells,[1–6] while electrochemically active materials are incorporated between two electrodes to form electrochemical capacitors.[7–12] A lot of studies have been conducted to develop new materials and optimize structures for high performances in either solar cells or electrochemical capacitors.[13–20] However, to the best of our knowledge, no reports are available on the realization of both energy harvesting and storage in one device with the same material and structure, even though it would be very beneficial to achieve this goal with regard to low costs and high efficiencies that are required in electronics.

We herein report the development of a wire-shaped energy device that serves as both a dye-sensitized solar cell with high energy conversion efficiency and an electrochemical capacitor with high specific capacitance. The wire-shaped device can be further woven into flexible energy textiles by the well-developed textile technology. These bi-functional energy wires and textiles meet the pressing requirements for low weight and high flexibility in modern electronics.

A typical wire-shaped energy device was produced by twisting two fiber electrodes, with one being composed of a titanium wire modified with titanium dioxide nanotubes and the other being composed of a multi-walled carbon nanotube (CNT) fiber, followed by incorporation of a redox electrolyte containing an I_3^-/I^- redox ion couple (Figure 1a). This wire-shaped device serves as a dye-sensitized solar cell to convert solar energy to electric energy (Figure 1b). Under illumination, the dye molecules (red dots) are excited and inject photoelectrons into the conduction band of titanium dioxide.

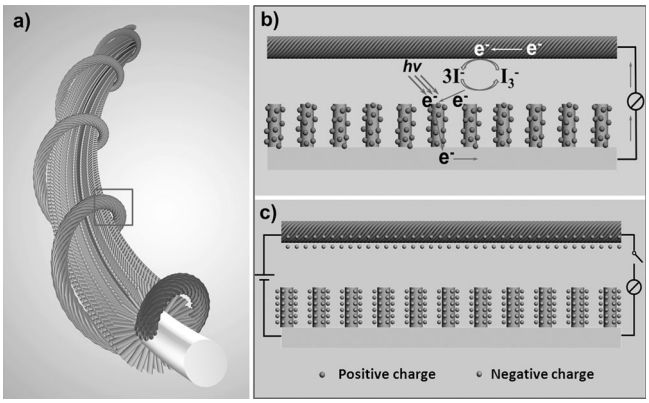

Figure 1. a) Structure of the wire-shaped energy device. b) Working mechanism as a dye-sensitized solar cell. c) Working mechanism as an electrochemical capacitor. (b) and (c) are cross-sections of the rectangle in (a).

The generated photoelectrons are then transported to the titanium wire, travel through the external circuit and reach the counter electrode. The I_3^- ions that receive the electrons are reduced to I^- ions, and the dye cations are reduced to the neutral state by I^- ions with the generation of I_3^- ions.[6] This wire-shaped device can also function as an electric double-layer capacitor to store the electric energy when a direct current is connected to the two electrodes (Figure 1c). The electrolyte includes Li^+ and imidazolium cations and I_3^- and I^- anions.

The CNT fiber and TiO_2-nanotube-modified Ti wire were investigated by scanning electron microscopy (SEM). The CNT fiber was uniform along the axial direction with a diameter of approximately 40 μm (Figure 2a), and the CNTs were highly aligned to enable high tensile strength and electrical conductivity (Figure S2). TiO_2 nanotubes with uniform sizes, including inner diameter and wall thickness, were perpendicularly grown on the surface of the Ti wire (Figure 2b). Because of the high flexibility, the aligned CNT fiber could be closely and stably wound onto the modified Ti wire

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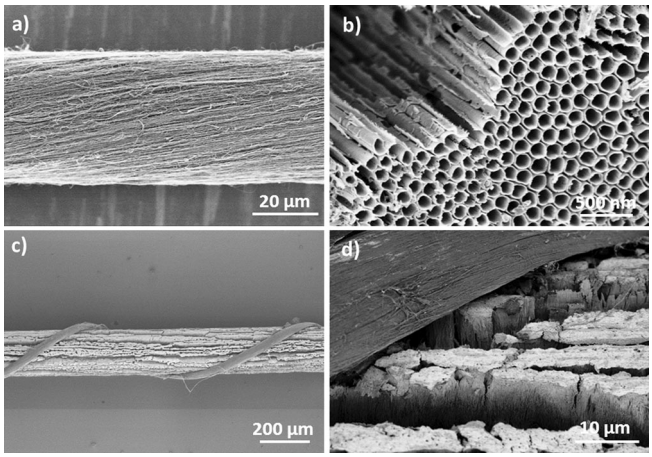

Figure 2. Structures of the wire-shaped energy device. a) CNT fiber with a diameter of 40 μm. b) Aligned TiO_2 nanotubes perpendicularly grown on a Ti wire. c,d) CNT fiber twisted with a TiO_2-nanotube-modified Ti wire to produce the device, shown at low and high magnifications, respectively.

(Figure 1a, Figure 2c and d). The pitch distances of the two twisted fiber electrodes could be controlled by varying the twisting angle, and a typical pitch distance of 0.8 mm was used in this work.

The dependence of the energy conversion efficiency and specific capacitance on the length of the TiO_2 nanotubes and diameter of the CNT fiber were carefully explored to optimize the wire-shaped energy device. First, TiO_2 nanotubes with increasing lengths from 11 to 38 μm, controlled by increasing the anodic oxidation time from 1 to 8 h, were compared. Here the effective area of the wire-shaped device as a dye-sensitized solar cell was calculated by multiplying the length and diameter of the TiO_2-nanotube-modified Ti wire. The energy conversion efficiencies were increased with the increasing length from 11 to 28 μm, as longer TiO_2 nanotubes could absorb more dye molecules to generate a higher number of photoelectrons under the same illumination (Figure 3a). However, the energy conversion efficiencies decreased with a further increase in length of the nanotubes to 38 μm, as the charge recombination became dominating because the diffusion length of photoelectrons became longer, thus decreasing the collection efficiency of electrons. To realize the best performance at the solar-cell part, TiO_2 nanotubes with a length of 28 μm were mainly studied below.

On the other hand, the CNT fiber was used to catalyze the redox reaction of I_3^- to I^- in the case of a solar cell or store charges as an electrochemical capacitor. CNT fibers with increasing diameters from 18 to 50 μm were employed as counter electrodes and inspected by cyclic voltammetry. Two pairs of oxidation/reduction peaks were observed in all curves, with the left one corresponding to the redox reaction of I_3^-/I^- (Figure S4). It is known that both a larger peak current and smaller peak-to-peak voltage separation (V_{pp}) indicate a higher catalytic activity of the counter electrode.[21] The peak currents were gradually increased, while the V_{pp} values gradually decreased with the increasing diameter, thus showing that larger CNT fibers exhibited high catalytic activities. In addition, larger CNT fibers showed lower electrical resistances. For instance, for the same length of 0.5 cm, the electrical resistances of aligned CNT fibers were decreased from 466, 245, and 176 to 125 Ω with the increasing diameters from 18, 30, and 40 to 51 μm, respectively. Here the CNT fibers were wound onto the same modified Ti wire with a diameter of 163 μm. As a result, the energy conversion efficiencies were increased as a result of an improved fill factor (FF) and short-circuit current (J_{SC}) with the increasing CNT fiber diameters from 18 to 41 μm (Figure 3b). However, with the further increase to 51 μm, although the FF was increased, the J_{SC} and the energy conversion efficiency were decreased (Figure 3b and c). The decreased J_{SC} may be explained by the fact that a larger CNT fiber shields more incident light with a decreasing number of photoelectrons. The specific length capacitances were increased from 39.1 to 71.89 $\mu F\,cm^{-1}$ at a scan rate of 10 $mV\,s^{-1}$ (Figure 3c). As a result, the CNT fibers with a diameter of 41 μm will be mainly used in the following discussion.

For the optimized fiber electrode, the energy conversion efficiency and specific capacitance of the wire-shaped energy device achieved 5.69% under simulated AM1.5 solar light and 64.9 $\mu F\,cm^{-1}$ or 1.65 $mF\,cm^{-2}$ at a scan rate of 10 $mV\,s^{-1}$. Figure 3d shows cyclic voltammetric curves with increasing scan rates from 50 and 100 to 500 and 1000 $mV\,s^{-1}$. The redox peaks correspond to the reversible redox reactions of I^- and I_3^-. Galvanostatic charge–discharge tests were conducted at increasing current densities of 0.43, 0.64, 1.28, 1.70, and 2.13 $mA\,cm^{-2}$ (Figure 3e). A high reversibility was produced at a wide current range during the charge and discharge processes. The wire-shaped energy device also exhibited a high cyclic stability (Figure 3f), and the capacitances retained approximately 98% after 5000 cycles at a charge–discharge current density of 0.64 $mA\,cm^{-2}$. The high stability as a capacitor can be attributed to the aligned TiO_2 nanotubes and CNTs in two fiber electrodes. TiO_2 nanoparticles were widely found to be easily peeled off from the substrate during use and under bending. In contrast, the aligned TiO_2 nanotubes were grown on the Ti wire with much improved stability. Figure S5 compares the aligned TiO_2 nanotubes before and after 5000 charge–discharge cycles, and the morphology was well maintained. It has been widely reported that the alignment of CNTs is a key to realize remarkable properties of CNT bulk materials.[22] Herein, the aligned CNTs are also expected to show high mechanical and thermal stabilities. In fact, Figure S5 compares the aligned CNT fiber before and after 5000 charge–discharge cycles, and the original aligned structure was also well maintained in the fiber. Moreover, according to our previous studies,[22] aligned CNTs exhibited better performance in electrical and thermal conductivities compared with randomly dispersed CNTs, which will contribute to the long-term stability of the device.

As a result of the introduction of the semiconducting TiO_2 layer that separated the two fiber electrodes, no short circuit was observed for the wire-shaped energy device. For instance, the electrical resistance between the Ti wire and CNT fiber was measured on a reasonable level, for example, 9.6 kΩ compared with 0.16 kΩ where a CNT fiber was twisted onto the Ti wire without the growth of the TiO_2 nanotubes on the

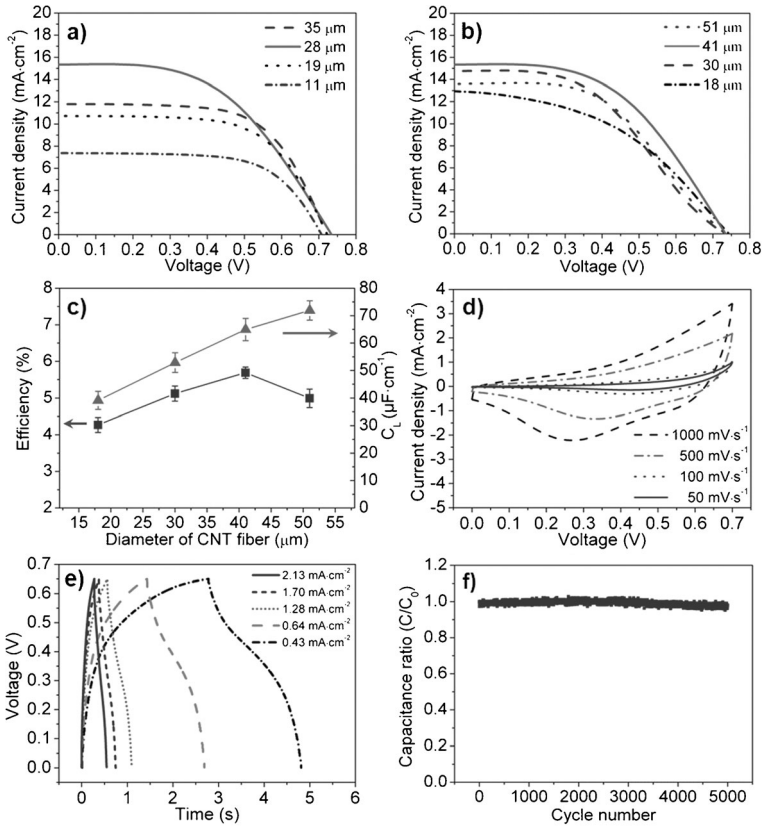

Figure 3. a) *J–V* curves of the wire-shaped devices with different lengths of TiO_2 nanotubes, but the same diameter (41 μm) of CNT fibers . b) *J–V* curves of the wire-shaped devices with different diameters of CNT fibers, but the same modified Ti wire (length of 28 μm for TiO_2 nanotubes). c) Dependence of energy conversion efficiency and specific length capacitance on CNT fiber diameter. d,e) CV and galvanostatic charge–discharge curves of the wire-shaped device derived from the TiO_2 nanotube with a length of 28 μm and the CNT fiber with a diameter of around 40 μm at increasing scan rates and current densities, respectively. f) Specific capacitances in 5000 charge–discharge cycles when the wire-shaped energy device was used as a capacitor. The specific capacitance was calculated from the charge–discharge curve at a current density of 0.64 $mA\,cm^{-2}$.

surface under the same conditions (length of 12 mm). The dye has also played an important role for the efficient energy device. For the use as an electrochemical capacitor, we compared the wire-shaped energy device without and with the adsorbed dye under the same condition by recording galvanostatic charge–discharge curves (Figure S6). At the same charge–discharge current density of 1.28 $mA\,cm^{-2}$, the wire-shaped device could be effectively charged and discharged. In contrast, it failed to work without the dye.

To further improve the performance in both photoelectric conversion and energy storage, polyaniline (PANI) that showed high electrical conductivity, catalytic activity and pseudocapacitance was incorporated into aligned CNT fibers. For the resulting composite fiber, the CNTs remained highly aligned and were uniformly deposited with a thin layer of PANI (Figure 4a), which was further verified by Raman spectroscopy (Figure S7). Cyclic voltammograms of a bare CNT and PANI/CNT (PANI weight percentage of 30%) were compared in Figure S8. The composite fiber exhibited larger peak current and smaller V_{PP} than the bare CNT fiber under the same conditions, indicating a higher catalytic activity for the I_3^-/I^-. *J–V* curves based on different counter electrodes were further compared in Figure S9. The composite fiber showed much a higher FF of 0.560 and a J_{SC} of 16.13 $mA\,cm^{-2}$, compared with 0.506 and 14.70 $mA\,cm^{-2}$ for the bare CNT fiber, respectively. Here the wire-shaped device based on the PANI/CNT composite fiber achieved an energy conversion efficiency of 6.58%. To the best of our knowledge, it represents the highest energy conversion efficiency of a wire-shaped solar cell based on a platinum-free counter electrode.[23] The high energy conversion efficiency can be explained by the aligned structures of TiO_2 nanotubes at the working electrode and CNTs at the composite counter electrode. Compared with the generally used TiO_2 nanoparticles in the conventional planar device, the TiO_2 nanotubes that were designed to be perpendicular to the outer surface of the Ti wire could enable a more rapid transport for charges. In addition, as previously reported, the aligned CNT/PANI composite fiber demonstrated a high electrical conductivity.[24]

The stable electrochemical performance of the "energy wire" based on the aligned CNT/PANI composite fiber was verified by the charge and discharge curves at a wide current density range (Figure S10). In addition, the specific capacitance of the wire-shaped device on the basis of the composite fiber reached 85.03 $\mu F\,cm^{-1}$ or 2.13 $mF\,cm^{-2}$ (scan rate of 10 $mV\,s^{-1}$), which is approximately 30% higher than that with the bare CNT fiber (Figure 4b and S11). Electrochemical impedance spectroscopy was further conducted to investigate the wire-shaped energy device (Figure S12). The high-frequency region is attributed to the porous structure of PANI/CNT composite fiber, while the low-frequency region indicates the capacitive behavior. The equivalent series resistance was measured to be 94.5 Ω or 6.59 $\Omega\,cm^2$, comparable to the previous report.[25] The leakage discharge current of the energy wire was measured to be 2.1 μA after two hours (Figure S13).

The high performance of the wire-shaped energy device was also studied by alternative operations on photoelectric conversion and electrochemical storage. For instance, after the wire-shaped device was continuously charged and discharged for 50, 100, 150, 200, 300, 400, 500, and 1000 cycles at a current density of 0.64 $mA\,cm^{-2}$, the energy conversion efficiencies between two neighboring periods were measured (Figure 5a and b). Obviously, for both bare CNT and PANI/CNT composite fibers, no obvious decrease was observed in the energy conversion efficiency and the specific capacitance. In other words, the wire-shaped energy device can be alternately used as an effective solar cell and electrochemical capacitor without sacrificing either performance. The long-term stability of the solar-cell part was also investigated. (Figure S14). For both bare CNT and PANI/CNT composite

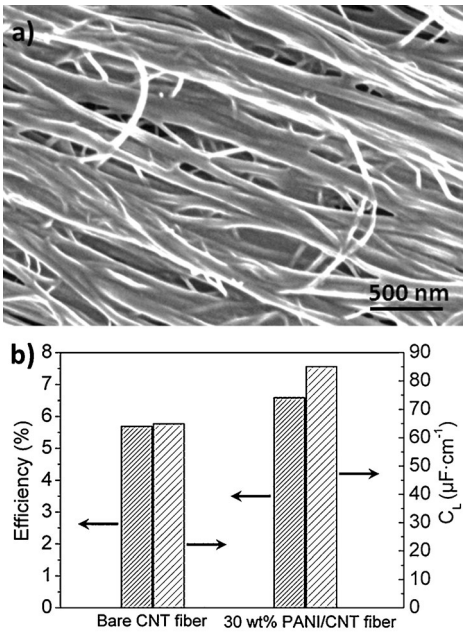

Figure 4. Wire-shaped devices based on the PANI/CNT composite fiber. a) SEM image of a PANI/CNT composite fiber. b) Comparison of energy conversion efficiencies and specific length capacitances based on the bare and composite fiber. The weight percentage of PANI was 30% in the composite fiber.

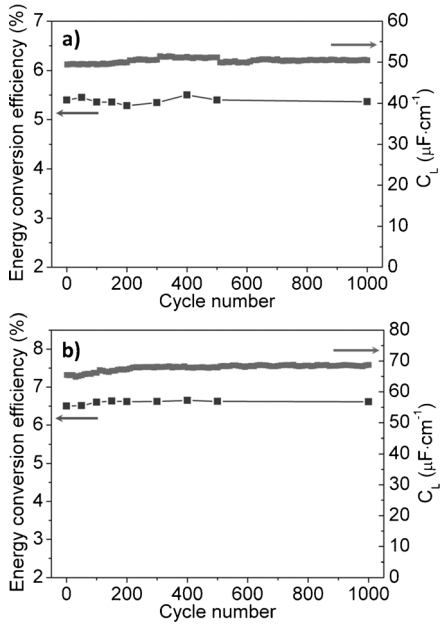

Figure 5. A wire-shaped energy device being alternately operated as a solar cell and electrochemical capacitor for continuous 1000 cycles based on the modified Ti wire (length of 28 μm for TiO_2 nanotubes) as one electrode and a bare CNT fiber (a) or PANI/CNT composite fiber with the PANI weight percentage of 30% (b) as the other. The galvanostatic charge–discharge was conducted at a current density of 0.64 mA cm^{-2}.

fibers, the energy conversion efficiency was first slightly decreased and then maintained, indicating a good stability of the solar-cell part of the energy wire; as expected, the specific capacitances of the two energy wires were also well maintained.

The dye was stable during the continuous and alternate operations as an electrochemical capacitor and solar cell. Both energy storage and photoelectric efficiencies remained almost unchanged after alternate operations for 1000 cycles (Figure 5). If the dye was peeled off during the cyclic use, the photoelectric efficiencies severely decreased. In addition, a comparing experiment was further conducted to investigate whether the dye would hinder the adsorption of the ions during the use as a capacitor. TiO_2-nanotube-modified Ti wires with or without absorption of the dye were used to fabricate dual-functional wire-shaped devices. For the dye-absorbed device, the specific capacitance was not decreased compared with the case without the dye, so the dye should not hinder the adsorption of ions on the TiO_2 nanotube.

Note that the same two CNT-based hybrid fibers were previously twisted to form a symmetrical capacitor.[26] However, it can be used for the electrochemical storage but cannot function as a solar cell to realize the photoelectric conversion. In addition, compared with the conventional planar device, the wire-shaped device demonstrates a unique and promising advantage for the possibility to be woven into clothes or various other flexible structures, aiming at the widespread use in the rapidly developing area of portable and wearable electronics. To this end, the wire-shaped devices as well as the resulting woven textiles should be strong enough to bear the generated tensile force during use, for example, movements of bodies. Although individual CNTs have been widely studied to be very strong, the wire-shaped capacitor from two twisted CNT-based hybrid fibers could bear a maximal tensile force of only around 0.15 N (Figure S15). In contrast, the Ti wire provided the dual-functional wire-shaped energy device to bear the tensile force up to 2.8 N (Figure S15).

The wire-shaped "energy wires" were lightweight, flexible, and weaveable, which made them particularly suitable for portable electronic textiles. For instance, the energy conversion efficiency and specific capacitance were well maintained after bending (Figure S16). Here, eight wire-shaped energy devices in series were woven into an electronic textile that well retained the stable structure and performance (Figure 6). The energy textile was used to power a commercial red light emitting diode (LED) lamp. Once the indoor lights were turned off and the energy textile was illuminated by the simulated sunlight, the red LED lamp was immediately lightened up by the electric power generated from the energy textile (Figure S17a and S17b). Figure S17c and S17d exhibited the energy textile that served as an energy storage module. An electrochemical workstation was used to charge the energy textile with a charging current of 0.64 mA cm^{-2}. The voltage exceeded 5.6 V in 1.5 seconds. Once connected with an LED lamp, the energy textile could also lighten up the lamp successfully. Note that both dye and electrolyte were stable at this high voltage. As shown in Figure 5, the energy wire serves as a capacitor with a charging current density of 0.64 mA cm^{-2} without sacrificing the performance as the solar cell, indicating the survival of the dye. In addition, eight energy wires were connected in series to share the voltage of 5.6 V, that is, 0.7 V for each one. Therefore, the electrolyte can

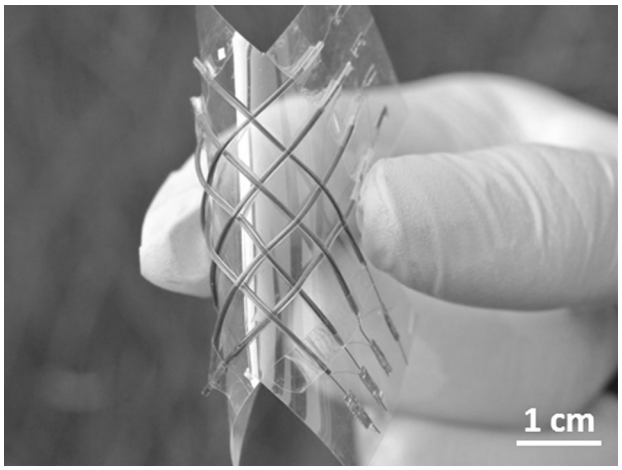

Figure 6. Photograph of the wire-shaped device being woven into a flexible textile.

also survive. Therefore, the wire-shaped energy device as well as the resulting energy textile can be used to power various electronic facilities as a solar cell at day time and an electrochemical capacitor at night. These dual-functional energy devices are particularly promising for various miniature and wearable electronic facilities.

In conclusion, a concept to produce a single electronic device with dual functions, that is, energy conversion and storage, has been proposed and realized to provide a novel platform in the development of energy materials and devices. This bifunctional device was fabricated by twisting two fiber electrodes that were composed of aligned inorganic nanotubes for both high energy conversion efficiencies and capacitances, that is, maximal energy conversion efficiency and specific capacitance of 6.58% and 85.03 $\mu F\,cm^{-1}$, respectively. In addition, it appeared in a novel wire shape that enabled unique advantages of low weight, flexibility, and weavability. The wire-shaped energy devices were further woven into an electronic textile that could light up a commercial LED lamp either as a solar cell or electrochemical capacitor. This work also provides a new strategy in designing and developing efficient electronic devices for future electronics.

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