A Monolithic Silicon-Mesoporous Carbon Photosupercapacitor with High Overall Photoconversion Efficiency

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Off-grid devices require autonomous power supply systems that can be achieved via coupling a solar cell with a supercapacitor in one integrated multifunctional device that is able to harvest energy from the environment, store, and release it on demand. Herein, a straight-forward approach is proposed to realize a monolithic photosupercapacitor rechargeable under illumination by integrating a silicon (Si) solar cell with an electrochemical double-layer capacitor (EDLC) based on mesoporous N-doped carbon nanospheres (MPNC) in a three-electrode configuration, i.e., via a shared electrode. The optimized porous structure of the MPNC-EDLC electrodes results in a high storage efficiency of 95% and a superior performance compared to an activated carbon based EDLC. When monolithically integrated with a highly compatible and technologically robust Si solar cell in a photosupercapacitor, fast charging up to 0.63 V (2.5 V for a module of four photosupercapacitors connected in series) in less than 5 s is attained even under weak illumination conditions, with an outstanding peak overall efficiency of 11.8%. These results show high potential toward the development of photorechargeable and decentralized power sources for deployed smart electronic devices.

1. Introduction

The increasing trend of miniaturization, automatization and interconnection of smart devices—termed the Internet of Things (IoT)—calls for the development of an energy solution that can overcome the economic and environmental challenges associated with established systems, i.e., battery and wiring replacement and disposal.

A promising solution to this problem is to combine the IoT device with a solar cell and an electrochemical charge storage unit, such as a battery, a supercapacitor or an electrolytic cell.[1,2] Solar energy is one of the strongest candidates for being harvested on a small scale, as it is locally abundant wherever and whenever there is daylight or artificial lighting.[3] Given the intermittency of illumination conditions (due to moving shadows for instance) and the consumer device’s energy consumption, the storage unit is required as a buffer to mediate between the light source and the load of the device. This arrangement allows the power unit to supply energy on demand, in a broad range of environments.

To make the power unit as compact as possible, as well as to reduce its complexity and ohmic losses, an interesting approach is to integrate the solar cell with the storage unit in a monolithic, three-electrode configuration, where the solar cell and the storage unit share a common electrode.[4] In this architecture, during charging, the solar cell separates positive and negative photo-generated charge carriers, of which one type migrates directly through the common electrode into one electrode of the storage layer, and the other type travels through an external wire into the other electrode of the storage layer. Power can then be drawn from the device via the two electrodes of the storage device.

The intensity of ambient light can vary across multiple time scales, from hours (day/night shift, stationary artificial lighting) to seconds or less (moving shadows). Meanwhile, a typical IoT device consumes energy in short bursts on the order of seconds. This sort of short-term power fluctuation...
requires the storage unit to be efficient under fast charging and discharging—a feature more characteristic of capacitors than batteries. This is because as opposed to batteries they do not suffer from the large on-set times caused by slow solid-state diffusion and reaction processes.\[5\] Electrochemical double-layer capacitors (EDLCs), in particular, while possessing a much higher energy density than simple solid dielectric capacitors, are not limited by specific redox processes for operation and are therefore not only fast-charging but also much more flexible systems in terms of coupling to a photovoltaic system compared to batteries and pseudocapacitors.\[6,7\]

Since the recent successful proof of concept of a three-electrode photosupercapacitor, based on a dye-sensitized solar cell (DSSC) and an activated carbon EDLC,\[4\] various attempts to improve the device performance using more efficient solar cells have been made.\[8\]

Organometallic lead halide perovskite solar cells are considered as promising candidates for the integration in such hybrid devices due to their high efficiency, high open circuit voltage ($V_{oc}$) and low processing cost.\[9,10\] However, the instability of the perovskite layer against polar-based electrolytes used in supercapacitors requires implementation of additional protection layers to minimize exposure to the electrolyte. This complicates their integration and makes questionable the long-term utilization of such devices.\[11,12\]

A few works reported the successful integration of supercapacitors with emerging solar cell technologies such as organic solar cells with flexible substrates\[13,14\] and, more recently, highly efficient perovskite solar cells\[15,16,19,20\]. On the other hand, using a crystalline silicon (Si) solar cell—a highly efficient, mature and robust PV technology—allows to aim for reliable and long-lasting devices. Moreover, using a well-known, standard solar cell system allows to establish reliable measurement protocols, to investigate working principles and to benchmark the performance of such hybrid devices without the interference of side effects—such as delicate fabrication and lacking stability, which can be experienced while using emerging types of solar cells. Si solar cells offer the required chemical stability, enabling the use of aqueous electrolytes which are nontoxic, eco-friendly and cost-effective. Additionally, it makes any housing and/or encapsulation unnecessary, which reduces the device’s cost and, most importantly, facilitates scaling-up and commercialization. As silicon solar cells are currently the dominant and most accessible type of solar cells on the market, investigating their integration into a hybrid photosupercapacitor could further accelerate the development of this technology towards applications.\[17\] Additionally, a new generation of photovoltaic technology might soon be based on silicon-based tandem solar cells,\[18\] which would allow to achieve higher $V_{oc}$ and in turn enlarge energy density ($E = 0.5CV^2$, where $V = V_{oc}$, and $C$ is the capacitance) of the photosupercapacitor.

Besides working on the voltage, improving energy densities of the photosupercapacitor can be achieved by rationalization of the active material and electrodes of the supercapacitor unit to improve the capacitance. In this regard, mesoporous nitrogen-doped carbon nanospheres (MPNCs) show excellent properties as electrode materials for a variety of electrochemical energy applications, including supports for electrocatalysts, electrode materials for redox flow batteries, as well as electrochemical supercapacitors.\[19–22\] Their large specific surface area, well-defined mesopore size, shape and structure, combined with favorable N-dopants and uniform particle sizes for easy processing and 3D-percolation are all considered to be beneficial for high capacitance and improved electrolyte and ion diffusion which, in turn, leads to high energy and power density. Additionally, introducing heteroatoms such as nitrogen to the carbon matrix modifies the carbon surface with polar functionalities, rendering the surface more hydrophilic, which improves the interaction of the electrode with the polar electrolyte when compared to hydrophobic activated carbon (AC)-based electrodes (usually used for EDLCs) that suffer from poor wettability. This makes MPNC an ideal electrode material for highly efficient EDLCs.\[21\]

Only few attempts have so far been reported of combining silicon solar cells with supercapacitors in a three-electrode fashion. Westover et al. proposed to etch the backside of a multicrystalline silicon solar cell and used the formed porous silicon as one of the supercapacitor electrodes.\[23\] However, the integrated silicon-based photosupercapacitor suffered from large internal resistance and low device capacitance (14 $\mu$F cm$^{-2}$). An improvement in capacitance and energy density was achieved by Z. Ouyang et al. using a MoO$_3$-pseudocapacitor as the energy storing unit attached to the rear side of a screen-printed silicon solar cell.\[24\] However, direct deposition of the MoO$_3$ layer onto the rear aluminum contact of the solar cell again resulted in a large internal resistance. Liu et al. recently reported a photosupercapacitor based on a hybrid silicon nanowire/polymer heterojunction solar cell and a polypyrrole-based supercapacitor, which reached an overall photoconversion efficiency of 10.5%.\[25\] However, this high performance was achieved at the cost of the device simplicity. Hence, there is quite some room for improvement and there is a clear need to develop straight-forward integration approaches for hybrid energy harvesting and storage devices combining reliable solar cells with high-performance supercapacitors, and in particular for silicon solar cells.

In this work, we developed a straightforward approach for integrating a silicon solar cell with an MPNC-based EDLC. We worked on several aspects of device performance and integration, including lowering design-related ohmic losses, increasing supercapacitor efficiency and paving off the fabrication/compatibility. A device design with three electrodes was employed, with an MPNC-based symmetric supercapacitor integrated onto the rear side of a silicon solar cell via a shared Ag substrate/electrode (Figure 1). This simplified design provides a robust way of producing a monolithic free-standing photosupercapacitor.

The electrodes of the supercapacitor were assembled out of MPNC particles with a pore size of 23 nm. The MPNC synthesis is based on a hard templating approach, reported by us previously for EDLCs and other electrochemical energy applications, yielding controlled MPNC particle sizes and morphologies and well-defined mesoporous structures.\[16,19,20\] By simple doctor-blading of MPNC-inks, highly porous and perfectly percolated MPNC-electrodes with high accessible surface area were obtained. For the supercapacitor assembly, a nontoxic gel-based aqueous electrolyte was used, allowing...
a much simpler device fabrication than with liquid electrolytes, as no encapsulation step was required. Additionally, in view of a future implementation of different and potentially more efficient solar cell types, the gel-type electrolyte is better at preventing the electrolyte from reaching sensitive parts of the device. On the other hand, MPNCs have a bimodal porous structure, with large contribution of micropores that increases the specific surface areas of materials, providing more effective electrode/electrolyte interfaces, while mesopores enable more efficient infiltration and surface accessibility offering efficient ion pathways for fast kinetics (high-rate capability), leading to the optimal surface utilization, when compared to pure microporous carbons.

The integrated silicon solar cell is based on an $n^+pp^+$ device structure which shows a very linear I-V behavior over a wide illumination range, as it was designed as a reference cell for calibration purposes. This makes it an ideal device for the characterization of the overall photosupercapacitor performance. The silicon solar cell shows an instant energy output upon illumination even at weak light intensities, which results in fast charging of the supercapacitor part of the integrated device. Taking advantage of the MPNC-based EDLC's excellent storage efficiency of 95%, our photosupercapacitor shows an overall photovoltaic energy conversion efficiency of 11.8%, thereby outperforming to the best of our knowledge all previously reported silicon solar cell based photosupercapacitors. Additionally, when four photosupercapacitors are connected in series, a stable voltage output of 2.5 V was achieved, sufficient to light up an LED. This proves the feasibility of a practical application, demonstrating a high potential of the device for energy-autonomous electronic devices, e.g., as elements of the IoT.

2. Results

2.1. Working Principle of the Device

Figure 1 shows the schematic structure of the Si-MPNC-EDLC photosupercapacitor realized via integration of the silicon solar cell with the MPNC-based EDLC in a three-electrode integration mode. Here, the graphite foil performs the two functions of accepting charge carriers from the solar cell and transferring them to the active material of the supercapacitor. Figure 1a demonstrates the device's connections in the photocharging mode. Illumination of the device induces charge carrier photogeneration and separation. When short-circuiting terminals 1 and 3, the photogenerated electrons migrate through the external wire to the bottom supercapacitor electrode. At the same time, holes are collected by the middle electrode of the device (terminal 2). This results in electrode polarization of the supercapacitor and formation of the electric double layer (EDL) at the electrode/electrolyte interface, and hence device charging. Discharging of the device occurs through terminals 2 and 3 while disconnecting the solar cell front contact (terminal 1). In this way, the full process of energy harvesting, conversion, storage and release occurs: the solar energy is being harvested by the solar cell, converted to the electrochemical energy and stored in the EDL, and later released as electric energy.

2.2. Silicon Solar Cell

The $n^+pp^+$ silicon solar cell (Figure 2a) features a phosphorus-diffused $n^+$-emitter, a boron-diffused high-low junction and an excellent edge passivation avoiding shunts and edge
recombination. It exhibits a conversion efficiency of 20.5% with high open-circuit voltage (0.652 V), short circuit current (38.8 mA cm⁻²) and fill factor (81%). The shape of the IV curve is close to an ideal diode behavior with low series and high shunt resistance (Figure 2b). The cells show an excellent illumination linearity. This is the reason why this cell type was chosen rather than other cell architectures (e.g., passivated emitter and rear cells (PERC), or cells with passivated poly-Si contacts or hetero junctions) which have even higher efficiency potential but also show strong nonlinearities which would complicate a proper characterization of the photosupercapacitor. Moreover, introducing heteroatoms can enhance the electrochemical stability and provide the electrode surface with sufficient polarity for efficient electrolyte wetting. At the same time, the hierarchical 3D-percolated structure of the electrodes processed out of these mesoporous carbon materials (mostly powders) should be accessible to the electrolyte for fast ion transport throughout the entire hierarchy/structure of the electrode.

2.3. Mesoporous N-Doped Carbon Nanospheres for EDLC

The electrochemical properties of the EDLC are mostly determined by the inherent characteristics of the electrodes in the device structure, since the formation of the EDL occurs at the electrode/electrolyte interface. The composition, specific surface area, pore size distribution, pore volume, conductivity, as well as electrochemical stability of the electrodes are critical for a good capacitive performance.

Owing to their good electrical conductivity, excellent thermal and chemical stability, porous carbon materials have demonstrated great potential as active materials for electrodes in EDLCs. Advances in the morphology-controlled synthesis of carbon materials enable producing carbons with a controlled particle size, large surface area and tunable pore size in the nanometer range. Having a well-controlled interconnected porous structure with spherical mesopores allows for efficient surface utilization, which means good charge storage capabilities including enhanced ion adsorption capacity and ion diffusion rates, which in turn lead to large energy and power densities. Moreover, introducing heteroatoms can enhance the electrochemical stability and provide the electrode surface with sufficient polarity for efficient electrolyte wetting. At the same time, the hierarchical 3D-percolated structure of the electrodes processed out of these mesoporous carbon materials (mostly powders) should be accessible to the electrolyte for fast ion transport throughout the entire hierarchy/structure of the electrode.

Taking these considerations into account, we opted for MPNCs as electroactive material for our supercapacitor electrodes, as these fulfill all previously named conditions. MPNC nanospheres were synthesized using a hard-templating approach following a procedure reported by us previously. In brief, MPNCs were obtained through the self-assembly of 23 nm spherical silica nanoparticles with in situ polymerized aniline; the latter serving as both a carbon and a nitrogen source (Figure S1, Supporting Information). The procedure led to the formation of SiO₂-polyaniline nanocomposite spheres, which, after freeze-drying, carbonization at 1000 °C under inert atmosphere and SiO₂ etching, yielded spherical MPNC nanoparticles denoted as MPNC-23-1000 (where 23 stands for the obtained pore size and 1000 °C for the carbonization temperature). Using a hard template enables tuning of the MPNC porosity, e.g., size, shape and accessibility of the pores, which is crucial for our application, where a supercapacitive performance depends on the active material interaction with the electrolyte media. Besides, as can be seen from our previous reports, the developed synthesis procedure allows us to fine tune the pore wall thickness (by adjusting the ratio of silica to aniline), to adjust the nitrogen content and the graphitization degree (controlling conductivity and electrolyte wettability, as demonstrated for redox-flow-battery applications), as well as to fine tune the MPNC particle size and overall morphology.

SEM images in Figure 3a shows that the obtained MPNC nanospheres were ≈320 ± 22 nm in diameter with homogeneously distributed 23 nm pores. TEM analysis (Figure 3b,c) revealed the highly porous structure within the MPNC
particles with pores distributed homogeneously throughout the entire particle volume. Raman spectra (Figure S4a,b, Supporting Information) of the MPNC-23-1000 material showed two broad peaks at 1594 and 1352 cm−1 corresponding to the G (graphitic) and D1 (defect) band respectively, showing the still rather amorphous/nanocrystalline nature of the sample.[32] Fitting of the Raman spectra (Figure S4b, Supporting Information) allowed us to identify additional peaks at 1120 (D4), 1522 (D3), and 1640 cm−1 (D2), revealing the contribution of defects and disordered carbon. The ratio between peak intensities I_D/I_G was calculated to be 1.26 in line with a high amount of disordered carbon.[32] Higher carbonization temperatures would result in higher graphitization, and hence higher conductivity, however, it would also lead to a lower nitrogen content and decreased wettability.[19] From elemental analysis (Table S1, Supporting Information) the nitrogen content in the MPNC-23-1000 material could be determined to be as high as 3.26 wt%, which is in good agreement with our previous reports for MPNC materials carbonized at 1000 °C.[19,20]

To determine the porous structure of the material, we performed nitrogen physisorption experiments. The Brunauer–Emmett–Teller (BET) theory was used to calculate the specific surface area of 628 m² g⁻¹ with 38.5% related to the micropore area and 61.5% to the mesopore and macropore areas. Adsorption–desorption isotherms (Figure 3d) were of type IV, which is characteristic for condensation processes occurring in mesopores.[33] Figure 3e shows the pore size distribution with the main peak at 23 nm which is in line with the size of the corresponding silica template. The cumulative pore volume of 1.35 cm³ g⁻¹ was calculated using the QSDFT model, taking into account spherical pores (Figure 3f). The micropore volume was calculated to be 0.20 cm³ g⁻¹ which is 15.6% of the total pore volume (Figure 3e inset). Large mesopores together with the high specific surface area of the MPNC-23-1000 material provide efficient migration pathways for electrolyte ions. From these structural/morphological parameters large values of capacitance are anticipated.

To produce electrodes for the supercapacitor, we formulated MPNC-23-1000 inks as it is described in the experimental section. The inks were deposited onto pre-cut graphite foil substrates using doctor-blading as depicted in Figure 4a.

Figure 4b and Figure S5 (Supporting Information) show an SEM top view image of the doctor-bladed layer. As can be seen, the coating consisted of homogeneously distributed closely packed MPNC-23-1000 nanospheres across the whole surface of the electrode. A closer look at the layer (Figure 4b, inset) shows the presence of carbon black (SP) NPs (Figure S6, Supporting Information) used to improve the electrical conductivity of the coating. A cross-section of the electrode reveals its highly percolated but porous nature on the macro- and mesoscale (Figure 4c).
Prior to supercapacitor assembly, the MPNC-electrodes were soaked with a PVA-H\_2SO\_4 gel electrolyte. The supercapacitor was then assembled in a symmetric configuration via sandwiching together two electrodes with electrolyte, followed by heat treatment in order to induce solvent evaporation and gel-electrolyte solidification. Figure 4d shows a photograph of the assembled supercapacitor with copper tape as contacts for measuring the electrochemical characteristics of the device.

To test the electrochemical performance of the assembled supercapacitor, we performed cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) experiments in a potential window between 0 and 1 V. The CV and GCD profiles recorded in the potential window of 0–0.6 V matching the operation voltage of the silicon solar cell are shown in Figure S7 (Supporting Information).

Figure 5a represents CV profiles recorded by sweeping the potential with different scan rates from 1 to 300 mV s\(^{-1}\). As can be seen, the CV curves showed a rectangular symmetric shape, suggesting the prevalence of an EDL charge storage mechanism, typical for MPNC-based EDLCs reported in the literature.[21,34,35] Integrating the CV curves allowed us to estimate the dependence of capacitance on the scan rate (Figure S8, Supporting Information). Obtained values of the electrode areal capacitance were calculated to be in the range between 228 and 70 mF cm\(^{-2}\) for scan rates between 1 and 100 mV s\(^{-1}\). Increasing the scan rate induced a capacitance drop; this is because at higher scan rates, ion diffusion from the electrolyte to the pores of the MPNCs was not sufficiently fast and hence, at these conditions, the device cannot be fully charged. This indicates that CV curves measured at high scan rates are only partially representing the device’s capacitive performance.[36]

Nevertheless, even at a scan rate of 300 mV s\(^{-1}\), the corresponding CV curve was nearly rectangular, and the areal capacitance was maintained as high as 54 mF cm\(^{-2}\) proving that the mesopores represent efficient pathways for a fast ion transfer. Values of the areal capacitance obtained from CV profiles (228 mF cm\(^{-2}\) at 1 mV s\(^{-1}\) and 54 mF cm\(^{-2}\) at 300 mV s\(^{-1}\)) were higher than those reported in the literature (102 mF cm\(^{-2}\) at 1 mV s\(^{-1}\), 18 mF cm\(^{-2}\) at 200 mV s\(^{-1}\)), for instance.[37] At the same time, values of gravimetric specific capacitance (312 F g\(^{-1}\) at 1 mV s\(^{-1}\), 108 F g\(^{-1}\) at 300 mV s\(^{-1}\)) also exceeded the values reported for other carbon-based EDLCs (see Figure S9 and Table S2, Supporting Information).[38–43]

Figure 5b shows the GCD profiles obtained by recording the voltage response under different applied currents. We observed a near-linear change of the voltage yielding a near-triangular GCD shape, which supports the EDL storage mechanism. The deviation from the ideal triangular shape may have several causes. First, the restrictive ionic and electronic pathways would slow the internal distribution of charge, leading to delayed charging and discharging of parts of the capacitor.[44–46] The redistribution current increases with terminal voltage, and so at high voltages, the charging curve would be flattened while the discharging curve is steepened. Second, a voltage-proportional leakage current due to the finite shunt resistance of the capacitor would contribute a curvature to the charge and discharge traces akin to that of an exponential function. Third, there may be a pseudocapacitive contribution that comes from the presence of the nitrogen and oxygen functional groups on the MPNC surface. It is reported that the presence of nitrogen on the surface of the carbon materials triggers the surface redox reactions, contributing to the pseudocapacitance.[35,38] At the same time, the acidic character of oxygen functional groups enhances the electron-acceptor properties contributing further to the pseudocapacitance.[35] Similar behavior was reported in the literature.[21,34,38]

The GCD curves were generally quite symmetrical, indicating good reversibility. However, a certain difference between the charging and the discharging times was observed, which may be related to i) delayed internal charge redistribution, as described above, ii) heat loss from the charge distribution
channels and the shunt resistance, and iii) electrolyte decomposition. From the CVs, however, electrolyte decomposition can be excluded, which leaves the other two options. The delay of the internal charge redistribution would mean that parts of the capacitor will not fully charge during a GCD sweep, and so the current flowing to these parts impedes the charging process and accelerates the discharging process. The resistive heat loss would be due to electronic and ionic current flowing through the restrictive pathways of the porous electrode, the electrolyte and the separator.\[^{47–49}\] Its effect would be most pronounced at low GCD currents, as the energy loss increases with the time spent at $V > 0$, and indeed we see the largest asymmetry at low currents.

Also, no significant voltage step was observed at the beginning of the charging and discharging curves, indicating a low series resistance of the device (Figure 5b, Figure S8d, Supporting Information).

The dependence of the areal capacitance on the current density applied is shown in Figure 5c. The largest areal capacitance of 168 mF cm\(^{-2}\) was measured at low discharge current densities of 0.25 mA cm\(^{-2}\). As expected, with current densities increasing beyond 0.5 up to 1 mA cm\(^{-2}\), the capacitance progressively decayed to 150 and 107 mF cm\(^{-2}\), respectively (Table S3, Supporting Information). Our values of areal capacitance were in any case higher than those reported in literature for mesoporous N-doped carbons, where 22 mF cm\(^{-2}\) was

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**Figure 5.** a) Electrochemical measurements of the supercapacitor before its integration. CV curves obtained at different scan rates. b) GCD profiles measured at different current densities and c) the corresponding calculation of the areal capacitance. d) Self-discharge curve obtained after the supercapacitor was charged to 1 V at 1 mA cm\(^{-2}\). e) Capacitance retention and Coulombic efficiency as a function of the number of GCD cycles and f) the corresponding first and last GCD cycles (4 mA cm\(^{-2}\)). Values normalized to the weight of the active material on the electrode are shown in the Supporting Information (Figures S8 and S9, Table S2).
obtained at 0.2 mA cm⁻², for instance.[90] At larger currents of 9 mA cm⁻², the areal capacitance of our MPNC-EDLC remained comparatively high, i.e., at 45 mF cm⁻². Considering the MPNC active material loading (0.75 mg cm⁻²) per electrode, the calculated gravimetric capacitance shows values of 224, 200, and 163 F g⁻¹ at discharge current densities of 0.5, 1, 1.5 A g⁻¹, respectively. These values are higher than or comparable to those reported in literature for mesoporous N-doped carbon nanomaterials.[34] At 18 A g⁻¹, the electrode still delivers 60 F g⁻¹, suggesting a good rate capability of the device (Figure S8, Supporting Information). Further increase in gravimetric capacitance can be attained by using MPNCs with larger specific surface areas and smaller pore sizes (MPNC-7, with 7 nm mesopores and 825 m² g⁻¹ for instance).[36] Figure 5d shows a self-discharge curve of the device charged at 1 mA cm⁻². As can be seen, even after 20 h, the potential remains at 0.2 V (which is 20% of the maximal applied voltage of 1 V), whereas the supercapacitor reported by Liu et al. self-discharges down to 0.25 V already after 11 h.[23] The GCD cycling was performed over 5000 cycles to evaluate the stability of the supercapacitor device. As can be seen from Figure 5e, the device shows only a small performance degradation over cycling, indeed the capacitance retains 94% of its initial value. Coulombic efficiency retention was above 95% after 5000 cycles (Figure 5e). At the same time no obvious changes were observed between the first 10 GCD cycles and the last 10 cycles, confirming a robust structure of the electrodes and the whole device. Considering the thickness of the MPNC electrodes of ≈10 µm, the electrode volumetric capacitance was calculated to be 168 F cm⁻³ at 0.5 A g⁻¹, which is higher than or comparable to those reported in literature (2.21 F cm⁻³ at 1 A g⁻¹, 40 F cm⁻³ at 0.5 A g⁻¹).[50,51] For the sake of comparison and as a reference we fabricated a gel-based (H₂SO₄-PVA) EDLC using commercially available activated carbon (AC) as the electrode active material and tested its performance (Figure S10, Table S3, Supporting Information). Despite having high specific surface area (1400 m² g⁻¹), the AC has small diameters of micropore (<2 nm) which results in limited accessibility of the gel electrolyte ions to the micropore structure, slowing down the charging kinetics.[32] Indeed, the produced AC-EDLC showed a more resistive behavior of the CV curves, which deteriorated with higher scan-rates (100–300 mV s⁻¹), indicating a poor rate capability (Figure S10a,b, Supporting Information). In comparison, the MPNC-EDLC proved good rate performance: even at 300 mV s⁻¹ the capacitance was maintained as high as 72 F g⁻¹ (54 mF cm⁻²), whereas the capacitance of the AC-EDLC dropped down to 16 F g⁻¹ (24 mF cm⁻²) (Figure S10c, Supporting Information). The values of gravimetric and areal capacitance calculated from GCD profiles (Figure S10d, Supporting Information) were 95 F g⁻¹ at 0.5 A g⁻¹ and 138 mF cm⁻² at 0.25 mA cm⁻² for AC-EDLC, whereas the MPNC-EDLC demonstrated a substantially higher value of 224 F g⁻¹ at 0.5 A g⁻¹ (2.34 times higher) and 168 mF cm⁻² at 0.25 mA cm⁻² (1.2 times higher) (Figure S10e-g, Supporting Information). This only confirms that the mesoporous nature of the MPNC promotes efficient gel-electrolyte diffusion, offering larger capacitance and good rate capability.

Our MPNC-EDLC delivers large energy and power densities of 77 Wh kg⁻¹ at 71 W kg⁻¹ and 2.1 Wh kg⁻¹ at 2.4 kW kg⁻¹, which corresponds to geometric energy density of 11.6 µWh cm⁻² at a power density 106 µW cm⁻² and 3.1 µWh cm⁻² at 3.6 mW cm⁻² (Figure S10g,h, Supporting Information). These values are substantially higher compared to the values obtained for AC-EDLC (gravimetric: 3.3 Wh kg⁻¹ at 34.5 W kg⁻¹ and 0.4 Wh kg⁻¹ at 0.9 kW kg⁻¹, geometric: 9.6 µWh cm⁻² at 100 µWh cm⁻² and 1.3 µWh cm⁻² at 2.6 mWh cm⁻²) and other similar types of EDLCs reported in literature.[21,34,50,51]

2.4. Photosupercapacitor

Figure 6a,b shows the scheme of the silicon solar cell integrated with the MPNC-supercapacitor and the corresponding photographs of the device (front and back side). Measuring the voltage of the solar cell under illumination, via terminals 1 and 2, shows its fast saturation at a peak value of 0.62 V (Figure 6c, black line). A similar situation was observed when terminals 1 and 3 were short-circuited and the voltage was measured at the supercapacitor end (terminals 2 and 3, Figure 6c, blue line). This constitutes photocharging of the device. However, switching off the light leads to a different voltage behavior. In the first case, the potential drops instantly, due to the charge carrier recombination in the solar cell. In the second case, when the voltage is measured across the supercapacitor terminals, the potential decays slowly, corresponding to the EDL self-discharge. This confirms the working principle of the photosupercapacitor.

The photoelectrochemical performance of the device was determined using photocharge–galvanostatic discharge experiments. To charge the device, terminals 1 and 3 were connected and illumination was applied, as shown in Figure 6a (blue line). The voltage was recorded across terminals 2 and 3 of the supercapacitor module. Upon discharge, the light was switched off and terminals 1 and 3 were disconnected. Figure 7a shows the photocharge–discharge profiles recorded for different photocharge durations at a constant discharge current. The measurements show that the device needs less than 2 s to reach its maximal voltage. Further extension of the photocharging time did not lead to any increase in the voltage. Besides, the discharge behavior was the same over the whole range of the chosen photocharge durations (5-60 s), demonstrating an areal capacitance of 47 mF cm⁻². This indicates that the device performs efficiently even after just brief illumination. Besides, extension of the illumination time led to a slight decrease of the Si solar cell Voc caused by temperature increase during the photocharging experiments. Due to the supercapacitor at the rear side of the device, it was not possible to keep the solar cell at temperature of 25 °C as in the measurement of the solar cell alone. It is well known that the voltage of silicon solar cells is reduced by around 2.2 mV K⁻¹ with increasing temperature.[53–55] The local temperature varied depending on the duration of the measurement. For photocharge–discharge experiments shown in Figure 7a–c, the local temperatures were...
in the range of 21–35 °C; for the photocharge–discharge cycling experiment in Figure 7e, the temperature varied in the range of 21–35 °C, leading to a decrease in the \(V_{oc}\) of the solar cell (Figure S11, Supporting Information). Furthermore, we performed photocharge experiments under different light intensities, while keeping the photocharging time and the discharge current constant. As can be seen from Figure 7b, even at lower light intensities during photocharging, the voltage increases fast. At the same time, we did not observe any changes in the discharge behavior. These results point out that even under weak illumination conditions the solar cell delivers sufficient currents to fully charge the supercapacitor.

Figure 7c shows the results of photocharge–galvanostatic discharge measurements performed at different discharge currents. As can be seen, the discharge curves follow the same trend as for GCD measurements of the supercapacitor alone, where different discharge currents led to different discharge times and changes in the inferred capacitance values. Figure 7d shows the correlation between the areal capacitance and the applied discharge current densities. The areal capacitance values calculated from the photocharge–galvanostatic discharge profiles, (47, 43 to 18 mF cm−2 at 0.25, 0.5 and 10 mA cm−2, respectively) were similar to those obtained using galvanostatic charge–discharge experiments of the supercapacitor unit (Figure 5c). These values of areal capacitance were much higher than those obtained for the photosupercapacitor with porous Silicon EDLC reported by Westover et al, or for the Mo-based pseudocapacitor integrated with a Silicon solar cell reported by Ouyang et al.[23,24]

To examine the discharge behavior of the device under illumination, we performed photocharge–galvanostatic discharge experiments, where after 10 s of photocharge, we started the device discharge while keeping the light on for 10 s (Figure 7e). The light was subsequently switched off and the device was allowed to continue discharging in the dark. As can be seen, applying light during the discharge led to much slower discharge rates resulting in a discharge self-compensation provided by the photocurrent of the solar cell. As expected, switching off the light led to the same discharge behavior as in the case of Figure 7c. Figure 7d shows the cycling stability of the photosupercapacitor where it was photocharged and discharged at 2 mA cm−2 at least 15 times, confirming good operation stability of the device.

We also performed photoassisted charge–galvanostatic discharge experiments, where along with applying current to the supercapacitor terminals 2 and 3, terminals 1 and 3 were connected and the device was illuminated—the solar cell was effectively connected in parallel to the external current source. This led to a much faster device charging under illumination of 13 s compared to 50 s obtained in the case of charging the device with only an external current of 0.5 mA cm−2 applied (Figure S12, Supporting Information). This can be explained by the much higher current delivered by the solar cell. As expected, the discharging behavior was not affected and led to the same values of areal capacitance as previously (=43 mF cm−2, vide supra).

Figure 8a shows the peak overall photoelectrochemical energy conversion efficiency (\(\eta\)) versus the photocharging time, estimated for different currents as it is established in the literature.\[^{[56]}\] As can be seen, the maximal overall photoelectrochemical energy conversion efficiency value of 11.8% was obtained at 0.25 mA cm−2. Applying larger current densities led to a progressive decay in the device capacitance, which in turn resulted in lower overall photoelectrochemical energy conversion efficiency (6.7% at 10 mA cm−2). Nonetheless, all the profiles followed the same trend. Upon photocharging the curves reached their peaks after around 0.5 s. Prolonging the photocharging to >5 s led to an efficiency decrease to 1%. This is due to the saturation of the voltage in the beginning of the discharge.
photocharging process (Figure 7c). While continuing photocharging, the voltage approached the value of the solar cell’s $V_{oc}$, resulting in a decrease in photocurrent. All the energy of the photons impinging on the cell could no longer be used by the supercapacitor unit and so the efficiency, equaling stored energy divided by supplied energy, decreases. Considering the solar cell’s power conversion efficiency of 20.5%, the maximal storage efficiency was calculated to be 57.5%. Compared to the photosupercapacitor reported by Liu et.al, where the Si nanowire/polymer solar cell was monolithically integrated with a polypyrrole supercapacitor with an overall photoelectrochemical energy conversion efficiency of 10.5%, the 11.8% of our photosupercapacitor is substantially higher (Figure 8b,c and Tables S4 and S5, Supporting Information).[25] Also, compared to photosupercapacitors integrated using other photovoltaic and supercapacitor technologies (Figure 8b,c), our device showed better performance, which we attribute to the synergy between the highly efficient Silicon solar cell and the good storage ability of the MPNC-based supercapacitor used for the integration.[16,25,57–66] Our experiments serve as a proof of concept.

Figure 7. a) Performance evaluation of the integrated photosupercapacitor. Photocharge–galvanostatic discharge curves under different durations of photocharge (5–60 s) and b) different light intensities during the photocharge (highlighted by the yellow shading) performed at a discharge current of 0.25 mA cm$^{-2}$. c) Photocharge–galvanostatic discharge experiments measured at different discharge currents (0.25–10 mA cm$^{-2}$, light intensity—100 mW cm$^{-2}$, photocharge time—10 s) and d) the corresponding areal capacitance of the integrated device. e) Photocharge–galvanostatic discharge under light or in the dark showing self-compensating of the discharge while illuminating the device. f) Photocharge–galvanostatic discharge cycling at 2 mA cm$^{-2}$ showing the operation stability of the photosupercapacitor.
providing a conceptual benchmark. It should be noted that by controlling other experimental parameters, e.g. the temperature while photocharging or a higher solar cell $V_{oc}$, a higher overall photoelectrochemical energy conversion efficiency of the photo-supercapacitor would be achievable.\[67\]

The correlation between energy and power density was estimated using a Ragone plot, where photocharge-galvanostatic discharge profiles were used to calculate power and energy densities (Figure 8d). The photosupercapacitor developed by us is able to deliver energy densities of 1.25 and 0.5 $\mu$Wh cm$^{-2}$ at power densities of 59.4 and 595 $\mu$W cm$^{-2}$, respectively (or 1.30 and 0.51 Wh kg$^{-1}$ at power densities 61 and 619 W kg$^{-1}$). As can be seen from the comparative Ragone plot in Figure 8c, our device features a better performance in comparison to similar works, where a similar type of supercapacitor or/and Si solar cell is used.\[23,24\]

To assess the feasibility of practical application, a photosupercapacitor module was made, which contained four series-connected photosupercapacitor units. The capacitor parts of the four units were all connected in series, while the solar cell parts were each connected within their own unit for photocharging, as shown in Figure 1. When in the dark, the solar cells were each disconnected from their supercapacitor parts to prevent self-discharge through them. For discharge, the module was connected to an external load (such as an LED or an SMU set to galvanostatic discharge).

Illumination of the photosupercapacitor module triggered a voltage increase up to 2.5 V in less than 5 s (Figure 9a). The photocharged device was able to drive an LED in the dark (see movie in the Supporting Information). Figure 9b shows the peak overall photoelectrochemical energy conversion efficiency ($\eta$) versus the photocharging time of the photosupercapacitor module. The peak overall photoelectrochemical energy conversion efficiency value of 10.7% was obtained at 0.25 mA cm$^{-2}$ which is slightly lower than the one calculated for a single photosupercapacitor (11.8% at 0.25 mA cm$^{-2}$). We attribute this decrease in efficiency to the losses generated by the series interconnection of the photosupercapacitors and energy self-consumption by the Si solar cell. Nevertheless, these results demonstrate a prototype of an energy-autonomous power system, paving the way towards the development of off-grid powered energy-autonomous devices.

In the future, a further increase in the values of energy and power density could be attained by increasing the operation voltage of the device. This could be achieved on one hand by combining the silicon solar cell with a perovskite solar cell in a tandem configuration, which would enable a $V_{oc}$ as high as 1.8 V.\[68\] This would also allow us to use a pseudocapacitor with larger capacitance instead of an EDLC, potentially increasing the achievable voltage in combination with a suitable electrolyte, albeit losing the ease of integration/compatibility of the present approach. Work related to the coupling of

Figure 8. Overall photoelectrochemical energy conversion efficiency as a function of photocharging time calculated for different discharge currents (a). b,c) Comparison of peak overall photoelectrochemical conversion efficiencies of the fabricated photosupercapacitor with other reported works.\[23,37-46\] d) Ragone plot showing a comparison of energy density and power output between the fabricated photosupercapacitor and other reported works that use a silicon solar cell.\[23,26\] (Values of gravimetric energy and power density can be found in Table S3, Supporting Information.)
As the active material.

3. Conclusion

In this work we provide a strategy to fabricate a rigid monolithic photorechargeable supercapacitor by integrating a 20.5% efficient silicon solar cell with a mesoporous N-doped carbon based EDLC. The device demonstrates simultaneous energy harvesting, its conversion, storage and release on-demand. The silicon solar cell provides a fast charging of the device up to 0.6 V (2.5 V for the device module based on four photosupercapacitors), aided by the efficient charge storage in the optimized MPNC-based EDLC. This results in a high peak overall photoelectrochemical energy conversion efficiency of 11.8%, outperforming previously published works. Further, a prototype of an energy-autonomous power system, realized by coupling four Si-MPNC-EDLC photosupercapacitors in series into a module, was demonstrated, paving the way towards the development of off-grid powered energy-autonomous devices.

4. Experimental Section

**Chemicals and Solvents Used for Device Fabrication:** Silica (Ludox TMA, 23 nm, 34 wt% solution in H2O), hydrochloric acid (HCl, 1 m), ammonium persulfate (APS, ≥99.0%), ammonium hydrogen difluoride (NH4HF2, ≥99%), Poly(vinylidene fluoride) (PVDF, Mw = 534 000), 1-Methyl-2-pyrrolidinone (NMP, anhydrous, 99.5%), Polyvinylalcohol (PVA, Mw = 31 000) and graphite foil (1 mm, 98%, 7 µm electrical resistivity parallel to the surface) were purchased from Sigma-Aldrich. Aniline (99.5%) was purchased from AppliChem. 2-propanol, acetone and ethanol were of analytical grade and were purchased from Sigma-Aldrich. Activated carbon (AC, 1400 m2 g–1, with pore diameter <3 nm) was purchased from Nanografi. Super P conductive carbon black (SP, Timcal) was purchased from Nanografi. Silver conductive epoxy adhesive (33135) was purchased from MG Chemicals.

**Synthesis of Mesoporous N-Doped Carbon Nanospheres with 23 nm Pores (MPNC-23-1000):** MPNCs were synthesized via oxidative polymerization of aniline in the presence of Silica nanoparticles (NPs) as hard template followed by carbonization and silica etching (Figure S1, Supporting Information), according to a procedure reported by us previously.[19,20] First, 11.4 mL of Silica (Ludox TMA, 23 nm) NPs (Figure S2, Supporting Information) and 400 mL of MilliQ water were filled into a 500 mL one-neck round-bottom flask. Then 50 mL 1 m HCl were added under magnetic stirring. The procedure was followed by the injection of 4 mL of aniline.[89] To the obtained mixture, 10.02 g of APS dissolved in 20 mL of 1 m HCl was added drop-wise (over the course of ~10 min). The reaction flask was kept in an ice bath under air atmosphere. The stirring was stopped after 24 h. The resulting polyaniline composite material (PANI/SiO2, Figure S3a, Supporting Information) was separated from the liquid phase by centrifugation (9000 rpm). It is worth noting that the washing step has to be repeated at least 5 times until a neutral solution is obtained. In the following step, the precipitate was transferred into a 250 mL round-bottom flask and freeze-dried. Freeze-drying of the sample is required in order to stabilize the PANI/SiO2 morphology. The procedure was followed by sample carbonization at 1000 °C for 6 h under N2 atmosphere (heating rate of 3.3 °C min–1). This yielded an N-doped carbon/silica composite material (Figure S3b, Supporting Information). The silicon template was removed by etching with 4 m NH4HF2 solution. After etching for 3 d, the MPNCs were washed and separated from the liquid via filtration with water and ethanol. Finally, the wet filtrate was dried at 60 °C in a vacuum oven, yielding a powder of MPNC, which was denoted as MPNC-23-1000 (23 nm pore size, 1000 °C carbonization temperature).

**Preparation of MPNC-Based Electrodes:** Carbon-based inks for the supercapacitor electrodes were prepared using MPNC-23-1000 as the active material, SP as a conductive additive and PVDF as a binder in the weight% ratio of 8:1:1. First, 10 mg of PVDF was added to 1 mL of NMP. The mixture was allowed to stir for 12 h to ensure complete dissolution of the binder in the solvent. To the obtained clear solution, 10 mg of SP and 80 mg of MPNC-23-1000 powder was added. The procedure was followed by tip-sonication for 30 min until the mixture became homogeneous.

The obtained homogeneous ink was deposited onto graphite foils, used as current collectors for the symmetric supercapacitor. Prior to the ink deposition, the graphite foils were washed with 1 m NaOH solution and dried in a vacuum oven at 60 °C for at least 24 h. To ensure good adhesion of the MPNC carbon inks, the surface of the graphite foil was roughened with sand paper (P80-grade). For the ink deposition, the treated graphite foil was cut into square pieces of 2 × 2 cm and placed into a customized mask for doctor-blading. The graphite foil was sized to correspond to the active area of the silicon solar cell.

A 100 µL drop of the freshly prepared ink was used for doctor-blading each piece of the graphite foil. The blade thickness and the speed were set to 250 µm and 10 mm min–1, respectively. The resulting electrodes were dried at 60 °C under vacuum for at least 12 h. The resulting mass loading of the active material was 0.75 ± 0.01 mg cm–2.

As a reference, we used the same procedure to produce electrodes with commercially available activated carbon (AC, with a specific surface area of 1400 m2 g–1 and a pore size of 3 nm. Data provided by supplier) as the active material.

Figure 9. a) Photocharge–discharge profiles of the photosupercapacitor module fabricated from four connected in series photosupercapacitors and b) the calculated overall photoelectrochemical energy conversion efficiency as a function of photocharging time.
Electric Double-Layer Capacitor Assembly: As an electrolyte for the supercapacitor, we used a semisolid PVA-H2SO4 gel electrolyte. To prepare the electrolyte, we used a previously reported procedure.[90] In brief, 1 g of PVA and 1 g of H2SO4 were mixed in 10 mL of H2O under magnetic stirring. The mixture was heated to 80 °C for 2 h until it became transparent. Before being used, the prepared electrolyte was cooled down to room temperature. The ionic conductivity of the gel electrolyte is estimated to be 0.14 S cm−1 at a viscosity of 0.6×105 Pa s.[71,72] The supercapacitor was manufactured in a symmetric configuration, i.e., with two identical electrodes. Prior to assembly, the MPNC-electrodes were immersed into the as-prepared electrolyte for at least 15 min to ensure its infiltration into the pores of the 3D electrode and each MPNC particle. The obtained MPNC-electrodes coated with PVA-H2SO4 electrolyte were assembled face-to-face with a Whatman filter paper separator soaked with the electrolyte (overall amount of gel electrolyte used for the assembly was 0.5 mL). Exposure of the fabricated supercapacitor to heat treatment at 80 °C for 2 h resulted in evaporation of the H2O from the polymer matrix leading to the formation of a solid-state supercapacitor (denoted as MPNC-EDLC) with the geometric area of 4 cm2.[73] The same procedure was used to produce supercapacitor with AC-electrodes (denoted as AC-EDLC) as the reference.

Silicon Solar Cell Fabrication: The crystalline silicon solar cells (active area 4 cm²) were made of high-quality (100)-oriented boron-doped p-type float-zone (FZ) Si wafers with a diameter of 100 mm and a thickness of 250 μm. Photolithography took place in the clean-room facilities of Fraunhofer ISE allowing for a very low contamination level. Prior to processing, the wafers were thoroughly cleaned using an RCA cleaning sequence.[74] This cleaning step ensures that the crystalline silicon material retains a very high carrier lifetime. In the first step, a heavily doped boron back surface field (BSF) was diffused into the rear side in a BBr3 tube furnace process and a subsequent drive-in, while the front side was covered with a masking oxide. The resulting p–p+ high-low junction reduces the recombination of electrons at the rear side of the cell effectively.[75] Then, inverted pyramids were etched into the front side using a photolithographically structured mask of thermally grown oxide. Inverted pyramids are known to reduce the reflection of solar cells very effectively. Subsequently, a phosphorus diffusion in a POCl3 tube furnace process at 795 °C was performed to create an n-emitter doping profile with a sheet resistance of 100 Ω sq−1 at the front side and thus the pn-junction. This diffusion is limited to an area of 2 × 2 cm² for each of the 7 cells on the 4” wafers (emitter window). After removing the phosphorus glass and the oxide mask, the surfaces were oxidized at 1050 °C resulting in a 105 nm thick oxide layer, which provides an excellent surface passivation, an additional drive-in of the doping profiles and reasonable antireflection properties.[76] At the rear side this oxide was removed and the rear n-contact stack consisting of evaporated Al/Ti/Pd/Ag was deposited. On the front side the passivating oxide was opened using a photolithographically defined structure. The front side Ti/Pd/Ag p-metal grid was evaporated and structured by a lift-off process. A subsequent sintering step in forming gas improved the contact properties. For a better conductivity the front grid was thickened by a plating step in Ag electrolyte. The individual cells were cut from the 4” wafer using a laser process. The size of the final cells is slightly larger than 2 × 2 cm², thus the phosphorus emitter is not touching the edges of the cell, resulting in a very high shunt resistance and excellent linearity of the IV parameters.[24]

Photosupercapacitor Assembly: The photosupercapacitor was fabricated by integrating the supercapacitor onto the rear side/back contact of the silicon solar cell. Prior to the assembly, the solar cell back contact—Ag terminating layer—was cleaned with acetone and ethanol. Silver conductive epoxy was bar-coated over the whole area of the rear side of the solar cell and the supercapacitor was placed on top. The structure was placed on a hot-plate and annealed at 60 °C for 2 h to ensure bonding of the 2 modules. The procedure was done under air. Copper tape was used to contact the device’s electrodes.

Characterization: Scanning electron microscopy (SEM) measurements were carried out using a cold field emission gun high-resolution scanning electron microscope (FEI-HRSEM) SU8220 from Hitachi. The MPNC materials were imaged in transmission mode using an acceleration voltage of 30 kV and a working distance of 8.0 mm. For that, diluted MPNC dispersions were drop-cast onto carbon coated copper grids (200 mesh). MPNC-based electrodes were imaged in a scanning mode using an acceleration voltage of 2.5 kV and a working distance of 3.0 mm. High-Resolution Transmission Electron Microscopy (HRTEM) analysis was carried out using a Talos 200X electron microscope (Thermo Fisher) operated at an acceleration voltage of 200 kV. Raman spectra were recorded using a Senterra II microscope (Bruker Optics GmbH) equipped with a 532 nm laser with a laser power of 2.5 mW. Measurements were done with a wavenumber resolution of 4 cm−1. Spectra were recorded in the range of 750–2500 cm−1. The specific surface area and pore volume was determined by N2 sorption at 77 K using an Autosorb 1-C physisorption station (Quantachrome). The measurements were done from degassed powders under vacuum at 100 °C for 24 h. The specific surface area was calculated using the Brunauer–Emmet–Teller (BET) method P/Po ranging from 0.05 to 0.30. Pore size distribution was determined according to the quenched solid density functional theory (QSDFT) from the adsorption isotherms, taking into account spherical pores.

Solar Cell Measurements: The dark and illuminated current voltage (IV) characteristics of the solar cells were measured on a temperature-controlled measurement chuck at 25 °C. The 1-sun current-voltage (I-V) parameters of the solar cells were measured under standard testing conditions (STC: AM1.5G, 100 mW cm−2, 25 °C) using an Oriol 8100 sun simulator with an incident current calibration based on certified I-V measurements (Fraunhofer ISE CalLab).

EDLC Measurements: Electrochemical measurements of the supercapacitor were carried out using a VSP-140 Biologic potentiostat. We used cyclic voltammetry (CV) to identify the charge storage mechanism taking place. The CVs were recorded by sweeping the potential in the potential range between 0 and 1 V or 0 and 0.6 V at scan rates ranging from 1 to 300 mV s−1. Galvanostatic charge–discharge (GCD) profiles were used to test the supercapacitor performance. GCD curves were obtained by recording the potential change at different current densities. The upper potential limit was set to 1 V or to 0.6 V in order to match the operation voltage of the silicon solar cell.

Photosupercapacitor Measurements: The photoelectrochemical performance of the photosupercapacitor was measured using photocharge–galvanostatic discharge experiments. The measurements were carried out using the VSP-140 Biologic potentiostat and a Wavelabs SL-2 solar simulator with a light intensity that corresponds to 1 sun (100 mW cm−2). In brief, the photocharging was done by exposing the device to light illumination while short circuiting the terminals 1 and 3 (see Figure 1). The voltage response was recorded from the terminals 2 and 3 of the supercapacitor unit. When the voltage reached its maximum, the light was switched off, and the supercapacitor was discharged with the chosen current densities via terminals 2 and 3. The photoassisted galvanostatic charge–discharge experiments were performed by applying selected charge current densities while illuminating the device with terminals 1 and 3 short-circuited. The voltage window was limited by the potentiostat to 0.6 V. Further, the device was galvanostatically discharged to 0 V in the dark.

Calculations: Considering the nonlinear behavior of the charge–discharge curves of the supercapacitor, the stored energy E (W s)[77] was calculated via integration of the area under the discharge curve according to Equation (1)[90,97]

$$E = \int_{0}^{t_{d}} V dQ = \int_{0}^{t_{d}} V dt$$

(1)

where I(A) is the discharge current, t_d (s) is the discharge time, and V (V) is the potential as a function of time t (s).

The gravimetric and areal-energy densities (Wh kg⁻¹ or Wh cm⁻²) were calculated accounting for the weight of the MPNC active material on both electrodes m (g) or the supercapacitor electrode geometric area S (cm²) according to Equation (2)[90,98]
The gravimetric and areal power densities (W kg⁻¹ or W cm⁻²) were calculated according to Equation (3)[78]

\[
P_{\text{(g)}} = \frac{E_{\text{
olongdash light}} \cdot 3600}{\Delta t}
\]

Effective capacitance \( C_{\text{eff}} \) (F) of the supercapacitor was calculated from Equation (1), considering that \( E = \int_0^t I \cdot V dt = \frac{1}{2} C_{\text{eff}} V^2 \) [49,78]

\[
C_{\text{eff}} = \frac{2 \cdot \int_0^t I \cdot V dt}{V^2}
\]

Areal capacitance (F cm⁻²) normalized to the geometric area of the supercapacitor electrode (4 cm²) was calculated via Equation (5)[49,78]

\[
C_{\text{a}} = \frac{C_{\text{eff}}}{S}
\]

where \( S \) (cm²) is the geometric area of the supercapacitor electrode (4 cm²).

Coulombic storage efficiency (%) was calculated according to Equation (6)[78]

\[
\eta_{\text{Q}} = \frac{\Delta t_{\text{Q,disc}}}{\Delta t_{\text{Q,discharge current}}}
\]

where \( \Delta t_{\text{Q,disc}} \) (s) is the charge/discharge duration and \( I_{\text{Q,discharge current}} = I_{\text{Q}} \) (A) is the discharge or charge current.

The peak overall photoelectrochemical energy conversion efficiency \( \eta \) (%) was determined using following equation as the ratio between the energy extracted from the capacitor part during a full discharge in the dark and the light energy impinging on the solar cell part during a previous photocharge[46]

\[
\eta = \eta_{\text{conversion}} \cdot \eta_{\text{storage}} = \frac{E_{\text{output solar cell}}}{E_{\text{light}}} = \frac{E_{\text{storage}}}{E_{\text{light}}}
\]

\[
\eta = \eta_{\text{conversion}} \cdot \eta_{\text{storage}} = \frac{E_{\text{output solar cell}}}{E_{\text{light}}} = \frac{\int_Q V dq}{E_{\text{light}}} = \frac{0.5 \cdot C_{\text{cell}} \cdot V^2}{P_{\text{light}} \cdot \Delta t_{\text{A}} \cdot A}
\]

where \( E_{\text{light}} \) is the illumination light energy, \( P_{\text{light}} \) (W cm⁻²) is the power intensity of the incident light, \( V \) (V) is the voltage window, \( \Delta t \) (s) is the photocharge time, and \( A \) (cm²) is the photosensitive area of the solar cell (4 cm²).

The storage efficiency \( \eta_{\text{storage}} \) (%) was determined from Equation (8) taking into account maximal (peak) value of overall photoelectrochemical energy conversion efficiency \( \eta_{\text{max}} \)

\[
\eta_{\text{storage}} = \frac{\eta_{\text{storage}}}{\eta_{\text{max}}} = \frac{\eta_{\text{conversion}}}{\eta_{\text{max}}}
\]

where \( \eta \) (%) is the maximal (peak) overall photoelectrochemical energy conversion efficiency, \( \eta_{\text{conversion}} \) (%) is the solar cell conversion efficiency.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

photosupercapacitors, double-layer capacitors, silicon solar cells, mesoporous N-doped carbons, monolithic integration

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