Synthesis of Doctoral Dissertation
Doctoral Program in Energy Engineering (35^{th} Cycle)

Integrated Energy Harvesting and Storage Systems for a Sustainable Future

By

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Novel technologies should be developed to improve the quality of life on Earth, but their development must be sustainable. The rapidly growing sector of millions of remotely connected devices promises increased automation efficiency, improved safety and security, and better health monitoring, among other things. However, now, the only solution to provide energy to these devices is through disposable or rechargeable batteries that need to be replaced or recharged periodically. This can be a significant challenge for devices that are deployed in remote areas or difficult-to-reach locations. A harvesting and storage (H&S) system is a compact and sustainable device that is able to continuously self-charge by harvesting and directly storing energy from ambient sources. Such a device would be able to work as an alternative to batteries as an energy source for distributed connected devices and Internet of Things sensor networks.

In this work, integrated H&S systems obtained by combining dye-sensitized solar cells (DSSCs) and supercapacitors (SCs) are investigated. DSSCs are still among the photovoltaic technologies with the lowest payback time and are recently attracting research interest again thanks to their extremely high conversion efficiency in indoor illumination. SCs are characterized by a long cycle life, they are safe, and more importantly, they can be directly integrated with a photovoltaic device without the need for an additional external power management system.

The work presented in the dissertation has been conducted with the precise goal of addressing some of the main limitations that could prevent integrated H&S devices to achieve a future commercialization. In each chapter, a specific aspect of the H&S device has been investigated. A description of the working mechanism of DSSC, SC and integrated H&S devices, together with the characterization techniques that have been exploited during the work has been presented in Chapter 2.
Then, in Chapter 3, the focus was put on integrating a DSSC and a SC by fabricating them on the same current collectors. In particular, a dye-sensitized solar module and an ionic-liquid-based SC were integrated on a conductive glass substrate obtaining an H&S device able to self-charge under indoor light to an output voltage higher than 3 V, making it suitable as an energy source for most low-power IoT devices (**Figure 1**).

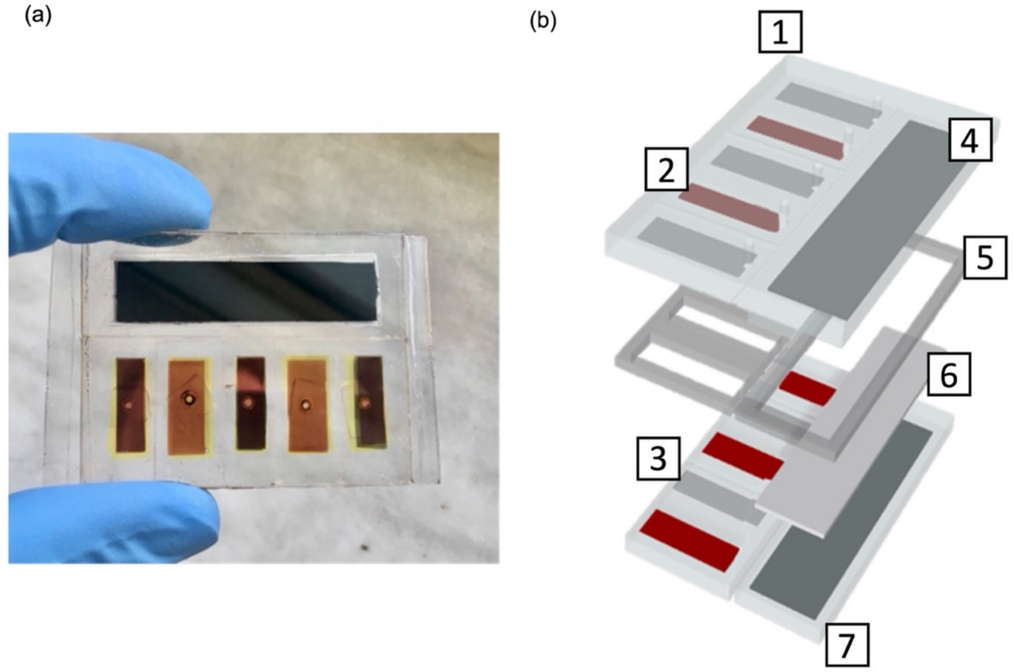

Figure 1 a) Photograph of the integrated device. b) 3D structure of the components of the device: 1) front shared current collector; 2) DSSC photoanode; 3) DSSC counter electrode; 4) SC active material; 5) thermoplastic sealant; 6) porous separator; 7) back shared current collector.

Then, in the second section of Chapter 3, a novel strategy to improve the efficiency of the DSSC is reported, which had been identified as the main limitation of the proposed device. This novel device configuration was proposed to improve the conversion efficiency of the DSSCs above the limit while keeping compatibility with the H&S device integration. It combined, in a single DSSC, the concepts of tandem and bifacial solar cells (**Figure 2**).

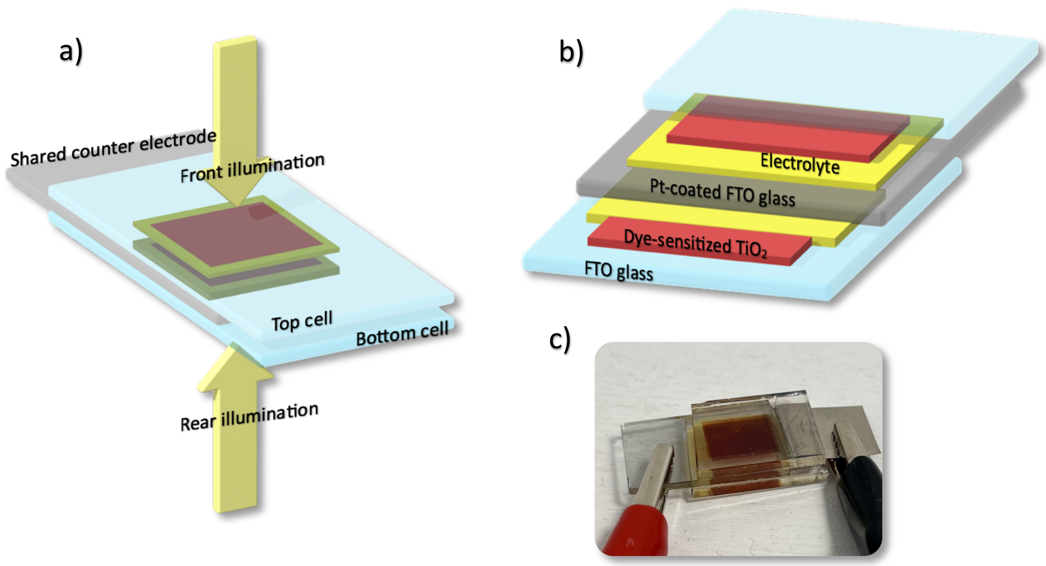

Figure 2 3D model (a), section view (b) and photograph of the proposed STB-DSSC. In panel a) the illumination condition and the half-cell definition are reported.

In Chapter 4, the possibility of extending the vacuum sealing encapsulation technique to DSSCs was presented. This never-reported solution allowed the integration of a DSSC and an SC in a flexible pouch-sealed device that proved to be stable under bending conditions (**Figure 3**)..

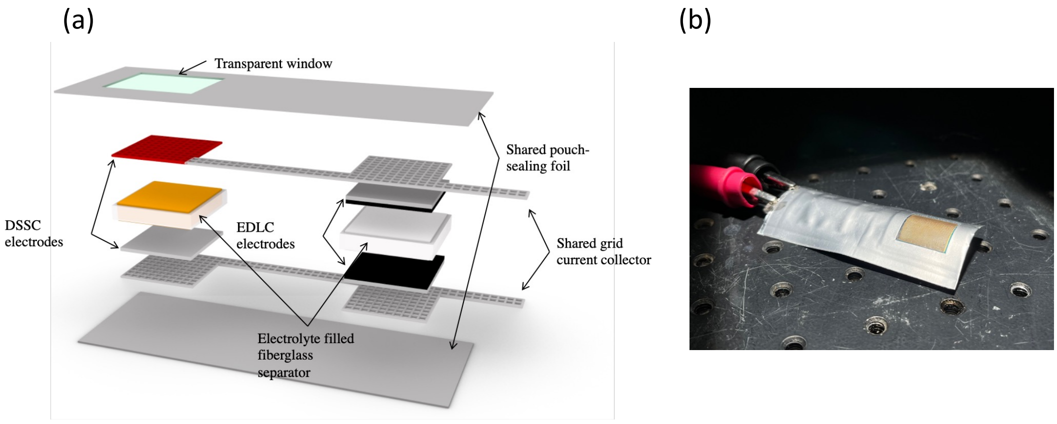

Figure 3 a) 3D rendering of the device assembly, in b) the H&S device under illumination in bent conditions.

In Chapter 5 the possibility of using laser-induced graphene both as the capacitive material for the SC and as the catalytic material at the counter electrode of the DSSC was investigated. A flexible integrated H&S device was demonstrated in which three of the four electrodes were fabricated by a one-step solvent-free laser writing process (**Figure 4**).

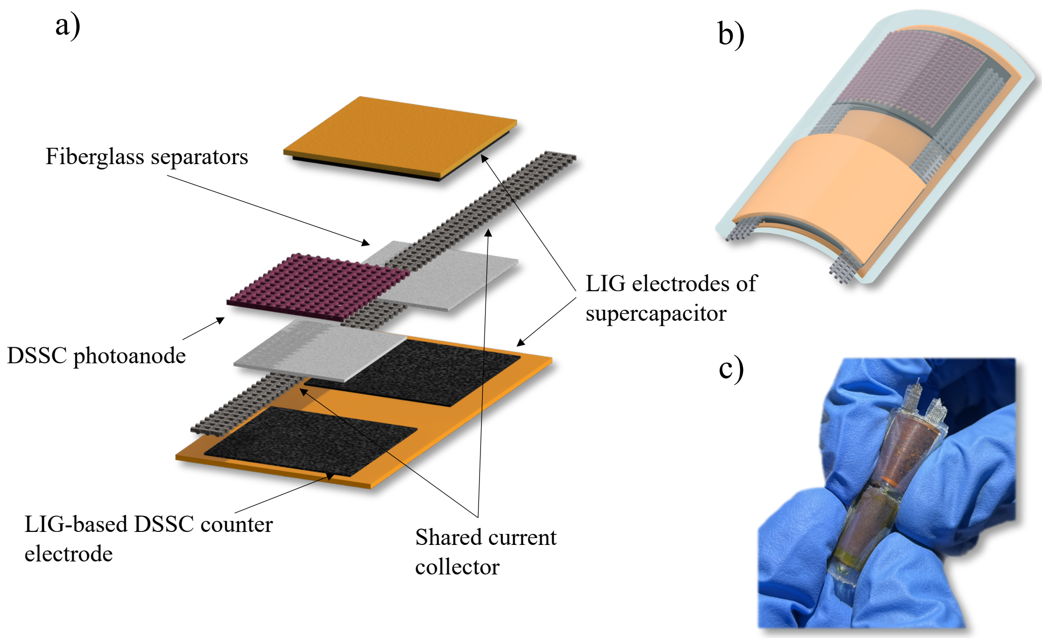

Figure 4 3D model of device assembly of the LIG-based integrated energy harvesting and storage systems integrating LIG-based dye-sensitized solar cell and a LIG-based supercapacitor.

The electrolyte of the device was addressed in Chapter 6. it was proven that γ-valerolactone is suitable as a green and sustainable solvent for the electrolyte preparation of indoor-operated DSSCs. Thanks to its compatibility as a solvent for SC electrolyte, this opens the way for a totally green integrated H&S device in which the devices' electrolytes are prepared with some shared materials.

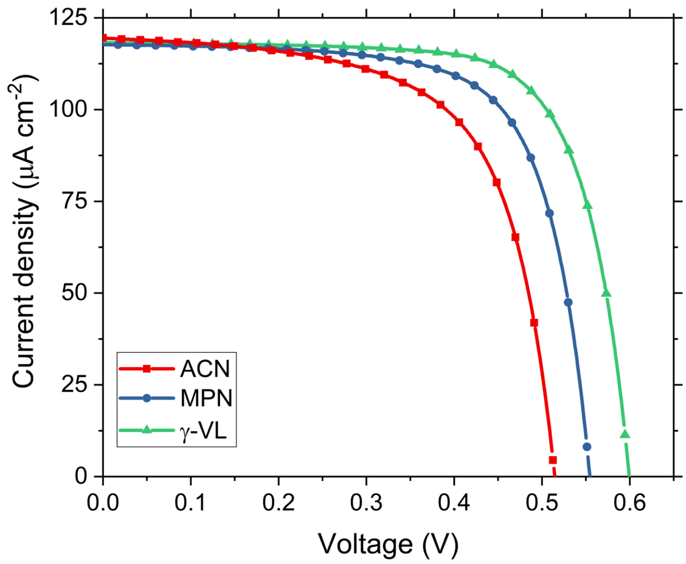

Figure Errore. Nel documento non esiste testo dello stile specificato.**.5** J-V characteristics recorded under warm LED indoor light illumination at 1000 lux (0.3 mW cm^{-2}) of DSSC fabricated with different electrolyte formulations.

Finally, a real-life application demonstration for the H&S device fabricated during this work was reported in Chapter 7, powering an temperature and humidity sensor.

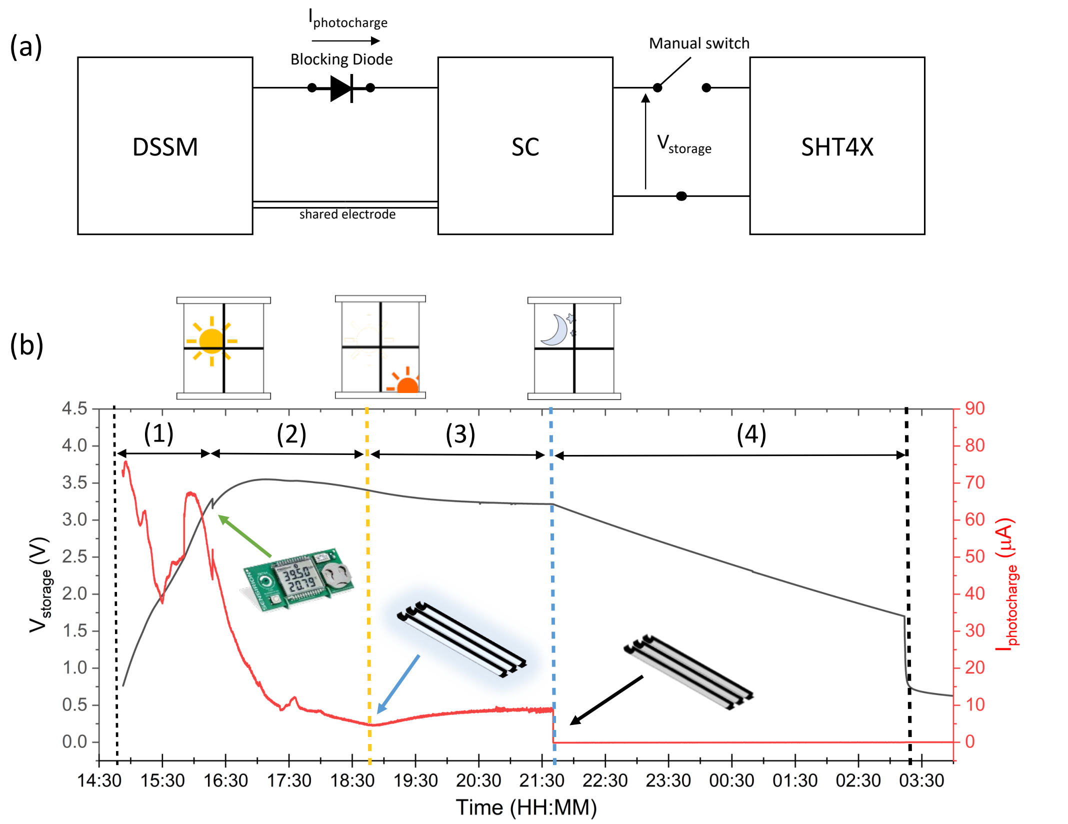

Figure Errore. Nel documento non esiste testo dello stile specificato.**.6** (a) Block diagram showing the measurement setup realized to simulate a real-life application of the integrated H&S device with the SHT4x humidity and temperature sensor. (b) Charging voltage and photocharging current time variation during the measurement.