MISSION INNOVATION ITALY

MINISTERO DELL'AMBIENTE
E DELLA SICUREZZA ENERGETICA

D4.27 - Database con le proprietà di foto-ricarica e delle interfacce degli elettrodi sviluppati

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Consiglio Nazionale delle Ricerche

Report MI21-24/170

D.4.27 - DATABASE CON LE PROPRIETÀ DI FOTO-RICARICA E DELLE INTERFACCE DEGLI ELETTRODI SVILUPPATI

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Report MISSION INNOVATION

Ministero dell'Ambiente e della Sicurezza Energetica - ENEA
Mission Innovation 2021-2024 - III annualità

Progetto: Piattaforma accelerata per i Materiali per l'Energia
Work package: WP4 – Materiali per Fotovoltaico
Linea di attività LA4.12 Realizzazione di dispositivi integrati fotovoltaico-accumulo a 2 terminali
Responsabile del Progetto: Massimo Celino (ENEA)
Responsabile della LA: Dr.ssa Alessandra Sanson (ISSMC-CNR)

WO_3IJP-PEDOT/MIP asymmetric integrated photovoltaic/storage device with gel state $LiClO_4$ electrolyte

SUMMARY

Photo-rechargeable tests	☒
Interfaces	☒
Stability in laboratory	☒
Stability outdoor	☒

FILM DEPOSITION ANDE DEVICE ASSEMBLY

Reagents

Substrate: Fluorine doped tin oxide coated glass (FTO, Sigma Aldrich, surface resistivity 7 Ω/sq.) with dimension of 2.5x2.5 cm^2.
Screen printing WO_3-based ink, containing active material between 15 and 20 wt.%, produced by using α-terpineol and cellulose derivates (Sigma Aldrich).
Inkjet printing ink formulated starting from the Avantama P-10 commercial suspension and using additives, with viscosity and surface tension equal to 6.50 mPa*s and 24.59 mN/m respectively.
3,4 ethylenedioxythiophene (EDOT, 97% Sigma Aldrich), $LiClO_4$ (ACS Reagent, Sigma Aldrich), water with MQ grade, oxalic acid di-hydrate (>99.5%, Merck), water MQ grade.
$LiClO_4$ salt (ACS Reagent, Sigma-Aldrich) 0.1M water MQ solution and poly-vinyl alcohol (PVA) 10% wt.

Procedure

Thick films based on WO_3 were prepared by semi-automatic screen-printing machine, AUREL 900 (Aurel Automation S.p.A., Italia), with speed of 45 mm/s and ten consecutive depositions. A mean thickness close to 22 µm and an active area of 0.25 cm^2 were achieved. Between each deposition, a drying treatment in IR oven at 80°C was applied. Finally, the thermal consolidation of the films was obtained by treating them at 450°C for 30'. Inkjet printing decoration was performed on the previous films, by using a multiple-deposition techniques station (XCEL, Aurel Automation s.p.a., Italy) equipped with a drop-on-demand inkjet printing head, MD-K-140 (microdrop Technologies GmbH, Germany) that has the possibility to heat up the nozzle. A specific pattern, a wavy line, was realized by printing at 20 mm/s and heating up the nozzle at 45°C. The film drying was realized at 95°C for 90''on a hot plate while the final consolidation was obtained by treating the samples at 120°C for 60' in a common oven with an oxidative atmosphere. For supporting electrode preparation, Poly-3,4 ethylenedioxythiophene (PEDOT) film was deposited by electro-polymerization in a three electrodes cells (working: FTO, reference: SCE, counter: platinum foil) using 3,4 ethylenedioxythiophene 5 mM in $LiClO_4$ 0.5M in water MQ and 25 mM of oxalic acid. Applied potential equal to +1.05 V vs SCE with a total amount of charge equal to 0.1 C, active area deposited equal to 0.25 cm^2. The final device was completed by adding PVA gel between two electrodes and sealed with a thermoplastic sealant, epoxy glue and protective UV-filter.

PHOTO-RECHARGEABLE TESTS

Galvanostatic charge-discharge tests (CD) featuring a charge at current density of 0.32 mA cm^{-2} applied under illumination with different intensities (1000 W m^{-2} or 500 W m^{-2} calibrated with reference cell) and discharge at different current densities in the dark.

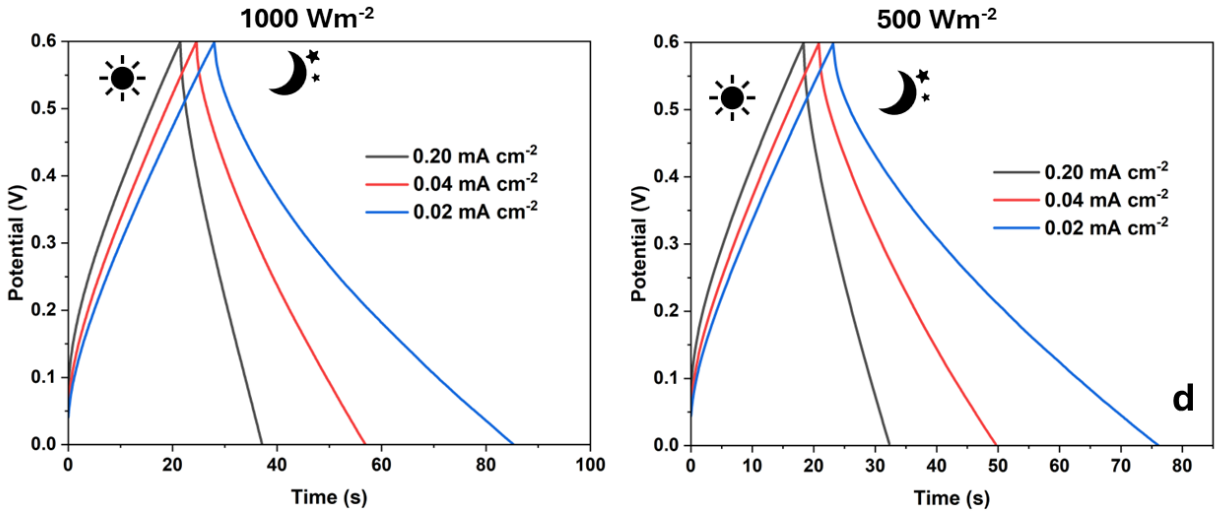
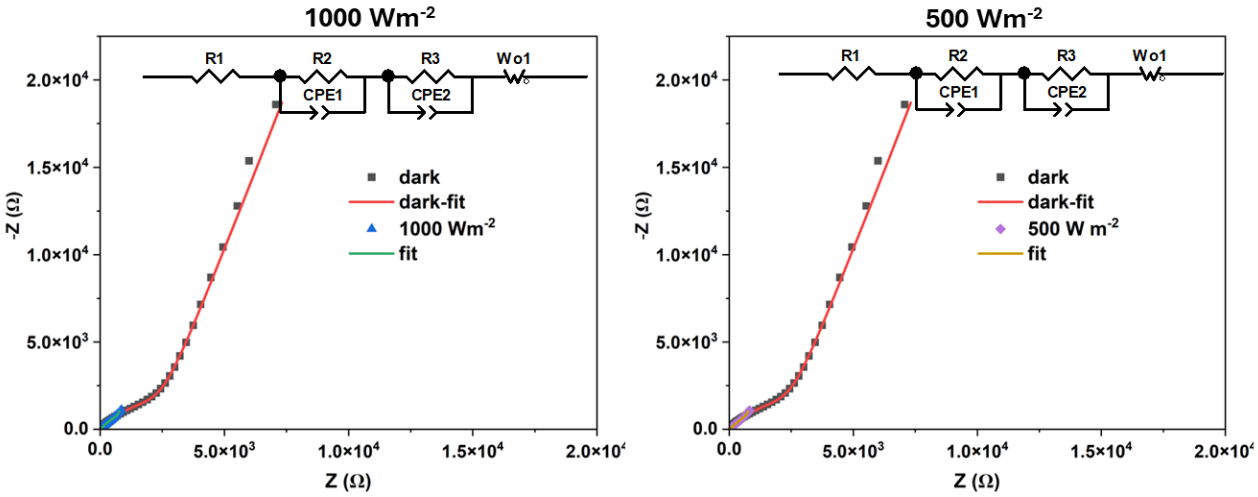


Photo-rechargeable parameters

- Specific capacitance of 5.2, 2.2 e 1.9 mF cm^{-2} at 0.02, 0.04 e 0.2 mA cm^{-2} current densities under illumination (1000 W m^{-2}).
- Specific capacitance of 4.6, 1.9 e 1.7 mF cm^{-2} at 0.02, 0.04 e 0.2 mA cm^{-2} current densities under illumination (500 W m^{-2}).

INTERFACE PROPERTIES

Electrochemical Impedance Spectroscopy in frequency range between 100 kHz e 0.01 Hz with signal amplitude of 10 mV and potential applied equal to 0 V in the dark and under illumination with different intensities (1000 W m^{-2} or 500 W m^{-2} calibrated with a reference cell).

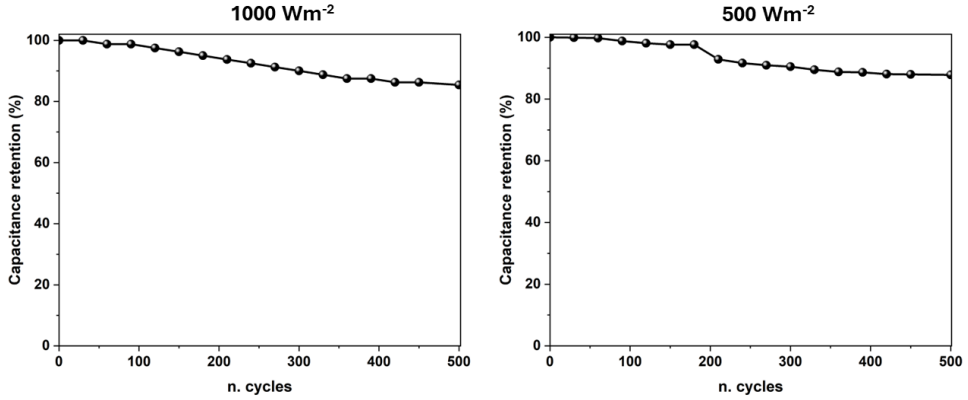


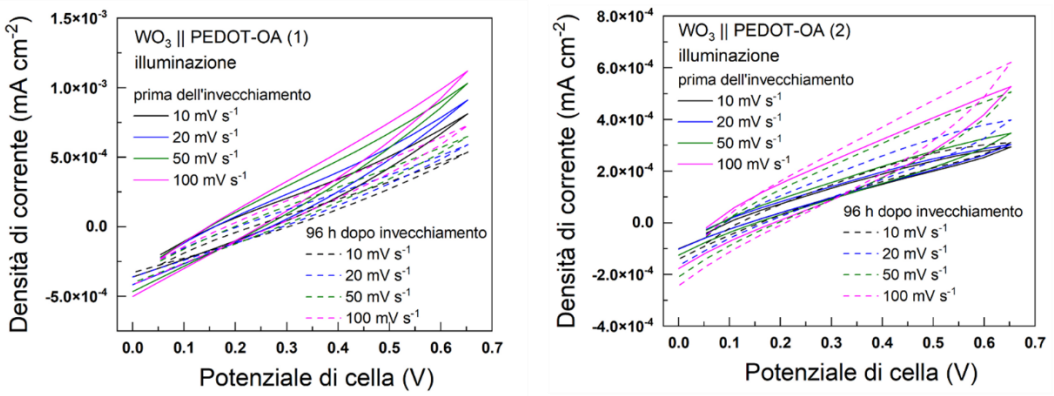
Interfaces Properties

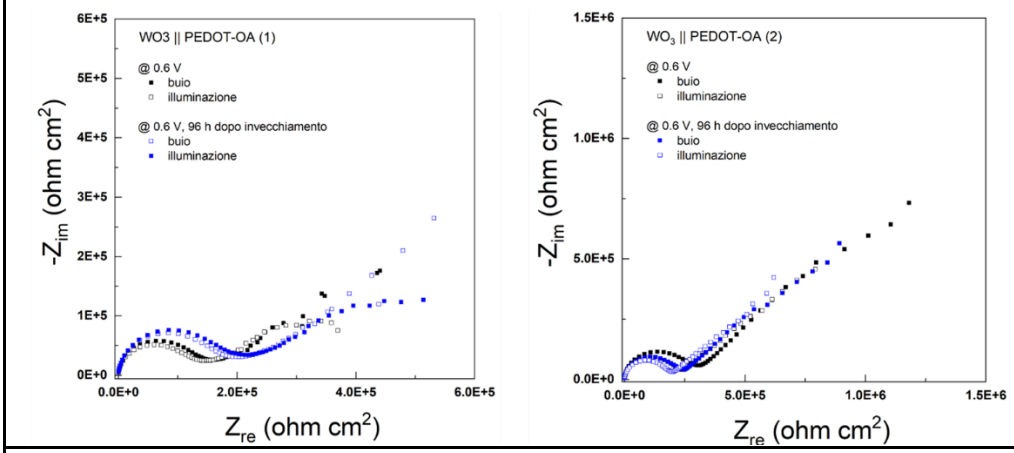
- Electrical resistance under 1000 W m^{-2} of 14 Ω.
- Electrical resistance under 500 W m^{-2} of 14 Ω.
- Charge transfer resistances at the electrode/electrolyte interfaces equal to 30 Ω (R2) and 1440 Ω (R3) under illumination at 1000 W m^{-2}.
- Charge transfer resistances at the electrode/electrolyte interfaces equal to 45 Ω (R2) and 1404 Ω (R3) under illumination at 500 W m^{-2}.

STABILITY IN LABORATORY ENVIRONMENT

Stability test with galvanostatic charge-discharge: 500 cycles of charge and discharge cycles at 0.4 mA cm^{-2} under illumination with different intensities (1000 W m^{-2} or 500 W m^{-2} calibrated with a reference cell).
Stability test in humid static chamber: Cyclic voltammetry at different scan rates (10, 20, 50 e 100 mV s^{-1}) and Electrochemical Impedance Spectroscopy (100 kHz – 0.1 Hz, ac 10 mV) performed at 0.6 V in dark and under illumination with Xenon-lamp Oriel 6258 (300 W) before and after 96 in humid static chamber (Memmert HCP 153) at 40 °C with relative humidity of 40%.





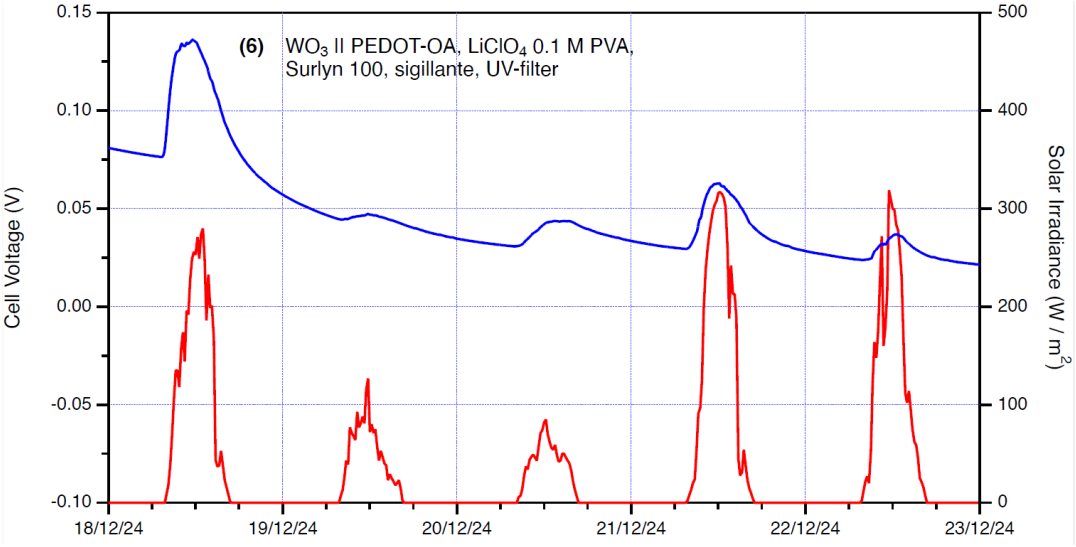


Interfaces Properties

- Capacitance retention of 82% under 1000 W m^{-2}
- Capacitance retention of 85% under 500 W m^{-2}

STABILITY IN REAL ENVIRONMENT (OUTDOOR TESTS)

Stability outdoor tests: Device tested with 35° angle, irradiance value acquired every 5 min by thermal sensors at high resolution S405C Thorlabs, with interface PM100USB, driven by Optical Power Monitor (OPM) software. The cell voltage was monitored continuously every 30 s by Keithley mod. 2400.



WO_3IJP-rGO asymmetric integrated photovoltaic/storage device with water-based $LiClO_4$ electrolyte

SUMMARY

Photo-rechargeable tests	☒
Interfaces	☒
Stability in laboratory	☒

WO_3 AND PEDOT-OA FILM DEPOSITION AND DEVICE ASSEMBLY

Reagents

Substrate: Fluorine doped tin oxide coated glass (FTO, Sigma Aldrich, surface resistivity 7 Ω/sq.) with dimensions of 2.5 × 2.5 cm^2.
Substrate: Fluorine doped tin oxide coated glass (FTO, Sigma Aldrich, surface resistivity 7 Ω/sq.) with dimension of 2.5x2.5 cm^2.
Screen printing WO_3-based ink, containing active material between 15 and 20 wt.%, produced by using α-terpineol and cellulose derivates (Sigma Aldrich).
Inkjet printing ink formulated starting from the Avantama P-10 commercial suspension and using additives, with viscosity and surface tension equal to 6.50 mPa*s and 24.59 mN/m, respectively.
Graphene oxide suspension (GO, 4 mg/mL in water, Sigma Aldrich), Nafion (Nafion® 5 wt % in alcohol and water), Na_2SO_4 (ACS Reagent ≥99.5%, Sigma-Aldrich), water MQ grade.
$LiClO_4$ salt (ACS Reagent, Sigma-Aldrich) 0.1M water MQ solution.

Procedure

Thick films based on WO_3 were prepared by semi-automatic screen-printing machine, AUREL 900 (Aurel Automation S.p.A., Italia), with speed of 45 mm/s and ten consecutive depositions. A mean thickness close to 22 µm and an active area of 0.25 cm^2 were achieved. Between each deposition, a drying treatment in IR oven at 80°C was applied. Finally, the thermal consolidation of the films was obtained by treating them at 450°C for 30 min. Inkjet printing decoration was performed on the previous films, by using a multiple-deposition techniques station (XCEL, Aurel Automation S.p.A., Italy) equipped with a drop-on-demand inkjet printing head, MD-K-140 (microdrop Technologies GmbH, Germany) that has the possibility to heat up the nozzle. A specific pattern, a wavy line, was realized by printing at 20 mm/s and heating up the nozzle at 45°C. The film drying was realized at 95°C for 90 son a hot plate while the final consolidation was obtained by treating the samples at 120°C for 60 min in a common oven with an oxidative atmosphere.
For supporting electrode preparation, an ink formulation based on GO 83% vol. e 17 % vol. Nafion was prepared and deposited by dro-by-drop deposition (150 µL) on FTO substrate. After that, this film was reduced electrochemically in a three electrodes cells (working: FTO, reference: SCE, counter: platinum foil) using Na_2SO_4 0.1 M water solution using cyclic voltammetry method. The potential range was set between +0.750 V and -1.4 V vs SCE with a scan rate of 50 mV s^{-1} for 50 cycles. Active area deposited was equal to 0.25 cm^2. The final device was completed adding liquid electrolyte between two electrodes (by holes on supporting electrode) and sealed with a thermoplastic sealant, epoxy glue.

PHOTO-RECHARGEABLE TESTS

Galvanostatic charge-discharge tests (CD) featuring a charge at current density of 0.32 mA cm^{-2} applied under illumination with different intensities (1000 W m^{-2} or 500 W m^{-2} calibrated with reference cell) and discharge at different current densities in the dark.

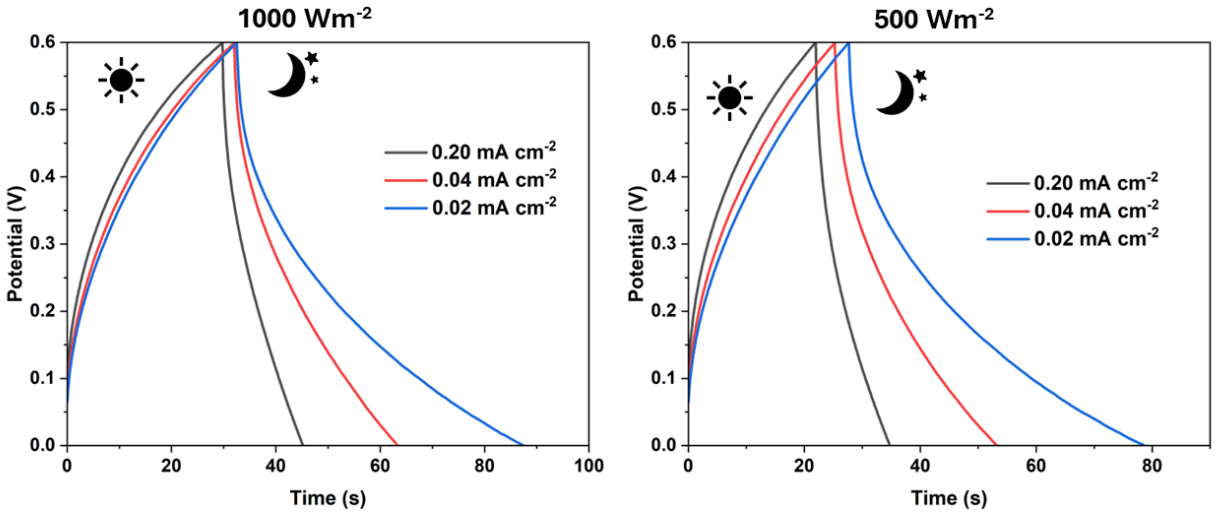
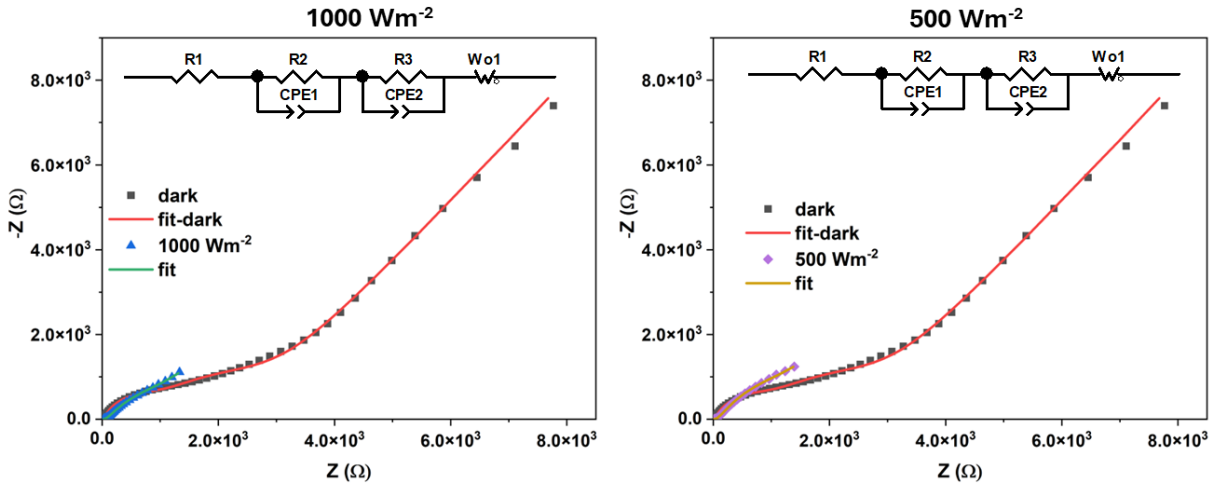


Photo-rechargeable parameters

- Specific capacitance of 5.1, 2.1 e 1.8 mF cm^{-2} at 0.02, 0.04 e 0.2 mA cm^{-2} current densities under illumination (1000 W m^{-2}).
- Specific capacitance of 4.2, 1.8 e 1.7 mF cm^{-2} a 0.02, 0.04 e 0.2 mA cm^{-2} current densities under illumination (500 W m^{-2}).

INTERFACE PROPERTIES

Electrochemical Impedance Spectroscopy in frequency range between 100 kHz e 0.01 Hz with signal amplitude of 10 mV and potential applied equal to 0V in the dark and under illumination with different intensities (1000 W m^{-2} or 500 W m^{-2} calibrated with a reference cell).

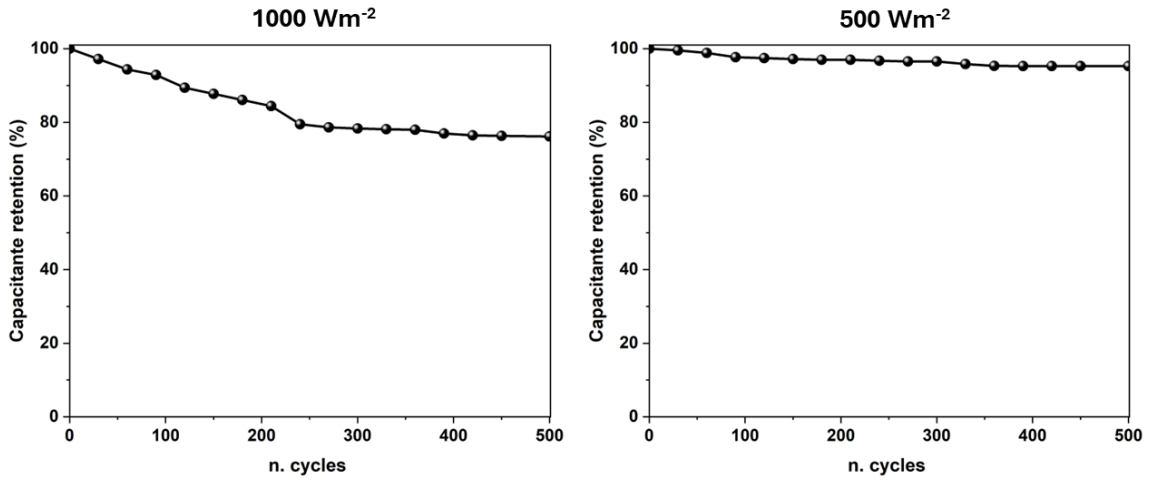


Interfaces Properties

- Electrical resistance under 1000 W m^{-2} of 20 Ω.
- Electrical resistance under 500 W m^{-2} of 13 Ω.
- Charge transfer resistances at the electrode/electrolyte interfaces equal to 33 Ω (R2) and 333 Ω (R3) under illumination at 1000 W m^{-2}.
- Charge transfer resistances at the electrode/electrolyte interfaces equal to 38 Ω (R2) and 440 Ω (R3) under illumination at 500 W m^{-2}.

STABILITY IN LABORATORY ENVIRONMENT

Stability test with galvanostatic charge-discharge: 500 cycles of charge and discharge cycles at 0.4 mA cm^{-2} under illumination with different intensities (1000 W m^{-2} or 500 W m^{-2} calibrated with reference cell).



Stability Properties

- Capacitance retention of 75% under 1000 W m^{-2}
- Capacitance retention of 97% under 500 W m^{-2}

WO_3IJP-rGO asymmetric integrated photovoltaic/storage device with acetonitrile-based $LiClO_4$ electrolyte

SUMMARY

Photo-rechargeable tests	☒
Interfaces	☒
Stability in laboratory	☒

WO_3 AND PEDOT-OA FILM DEPOSITION AND DEVICE ASSEMBLY

Reagents

Substrate: Fluorine doped tin oxide coated glass (FTO, Sigma Aldrich, surface resistivity 7 Ω/sq.) with dimension of 2.5 × 2.5 cm^2.
Substrate: Fluorine doped tin oxide coated glass (FTO, Sigma Aldrich, surface resistivity 7 Ω/sq.) with dimension of 2.5x2.5 cm^2.
Screen printing WO_3-based ink, containing active material between 15 and 20 wt.%, produced by using α-terpineol and cellulose derivates (Sigma Aldrich).
Inkjet printing ink formulated starting from the Avantama P-10 commercial suspension and using additives, with viscosity and surface tension equal to 6.50 mPa*s and 24.59 mN/m respectively.
Graphene oxide suspension (GO, 4 mg/mL in water, Sigma Aldrich), Nafion (Nafion ® 5 wt % in alcohol and water), Na_2SO_4 (ACS Reagent ≥99.5%, Sigma-Aldrich), water MQ grade.
$LiClO_4$ salt (ACS Reagent, Sigma-Aldrich) 0.1M acetonitrile-based solution.

Procedure

Thick films based on WO_3 were prepared by semi-automatic screen-printing machine, AUREL 900 (Aurel Automation S.p.A., Italia), with speed of 45 mm/s and ten consecutive depositions. A mean thickness close to 22 µm and an active area of 0.25 cm^2 were achieved. Between each deposition, a drying treatment in IR oven at 80°C was applied. Finally, the thermal consolidation of the films was obtained by treating them at 450°C for 30'. Inkjet printing decoration was performed on the previous films, by using a multiple-deposition techniques station (XCEL, Aurel Automation s.p.a., Italy) equipped with a drop-on-demand inkjet printing head, MD-K-140 (microdrop Technologies GmbH, Germany) that has the possibility to heat up the nozzle. A specific pattern, a wavy line, was realized by printing at 20 mm/s and heating up the nozzle at 45°C. The film drying was realized at 95°C for 90''on a hot plate while the final consolidation was obtained by treating the samples at 120°C for 60' in a common oven with an oxidative atmosphere.
For supporting electrode preparation, an ink formulation based on GO 83% vol. e 17 % vol. Nafion was prepared and deposited by drop by drop deposition (150 µL) on FTO substrate. After that, this film was reduced electrochemically in a three electrodes cells (working: FTO, reference: SCE, counter: platinum foil) using Na_2SO_4 0.1 M water solution using cyclic voltammetry method. The potential range was set between +0.750V and -1.4 V vs SCE with a scan rate of 50 mV sec^{-1} for 50 cycles. Active area deposited was equal to 0.25 cm^2. The final device was completed adding liquid electrolyte between two electrodes (by holes on supporting electrode) and sealed with a thermoplastic sealant, epoxy glue.

PHOTO-RECHARGEABLE TESTS

Galvanostatic charge-discharge tests (CD) with charge with current density of 0.32 mA cm^{-2} applied under illumination with different intensities (1000 W m^{-2} or 500 W m^{-2} calibrated with a reference cell) and discharge at different current densities in the dark.

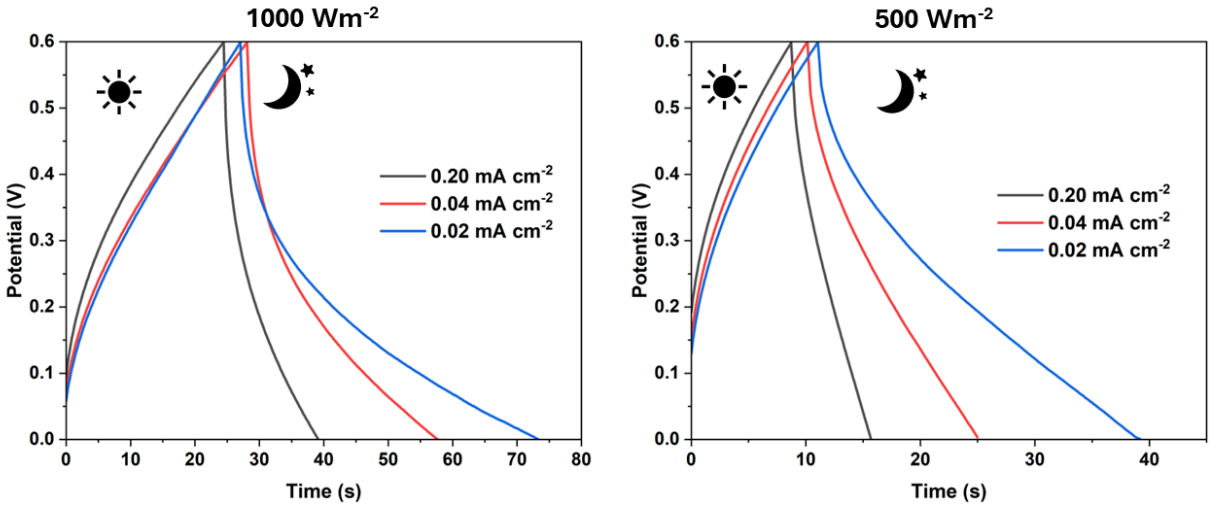
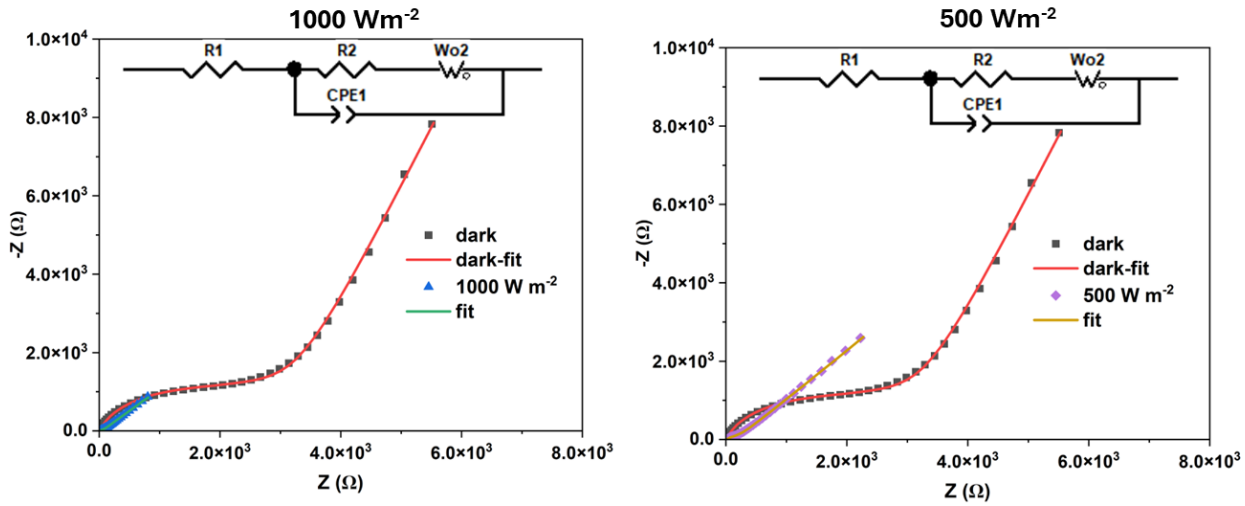


Photo-rechargeable parameters

- Specific capacitance of 4.9, 2.0 e 1.5 mF cm^{-2} a 0.02, 0.04 e 0.2 mA cm^{-2} current densities under illumination (1000 W m^{-2}).
- Specific capacitance of 2.3, 0.9 e 0.7 mF cm^{-2} a 0.02, 0.04 e 0.2 mA cm^{-2} current densities under illumination (500 W m^{-2}).

INTERFACE PROPERTIES

Electrochemical Impedance Spectroscopy in frequency range between 100 kHz e 0.01 Hz with signal amplitude of 10 mV and potential applied equal to 0 V in the dark and under illumination with different intensities (1000 W m^{-2} or 500 W m^{-2} calibrated with reference cell).

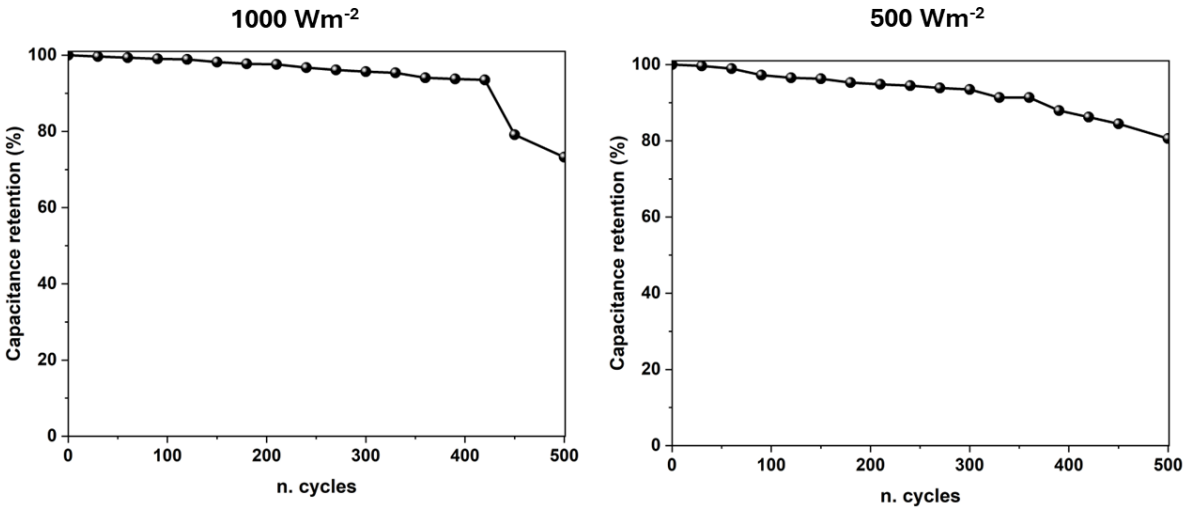


Interfaces Properties

- Electrical resistance under 1000 W m^{-2} of 11 Ω.
- Electrical resistance under 500 W m^{-2} of 17 Ω.
- Charge transfer resistance at the electrode/electrolyte interface equal to 274 Ω under illumination at 1000 W m^{-2}.
- Charge transfer resistance at the electrode/electrolyte interface equal to 305 Ω under illumination at 500 W m^{-2}.

STABILITY IN LABORATORY ENVIRONMENT

Stability test with galvanostatic charge-discharge: 500 cycles of charge and discharge cycles at 0.4 mA cm^{-2} under illumination with different intensities (1000 W m^{-2} or 500 W m^{-2} calibrated with a reference cell).



Stability Properties

- Capacitance retention of 65% under 1000 W m^{-2}
- Capacitance retention of 80% under 500 W m^{-2}

TiO_2IJP-N3-PEDOT-PEDOT/MIP asymmetric integrated photovoltaic/storage device with gel state $LiClO_4$ electrolyte

SUMMARY

Photo-rechargeable tests	☒
Interfaces	☒
Stability in laboratory	☒
Stability outdoor	☒

FILM DEPOSITION ANDE DEVICE ASSEMBLY

Reagents

Substrate: Fluorine doped tin oxide coated glass (FTO, Sigma Aldrich, surface resistivity 7 Ω/sq.) with dimension of 2.5x2.5 cm^2.
Screen printing TiO_2-based ink 18NR-T (Greatcell Solar Materials), with viscosity between 40-55 Pa*s.
Inkjet printing ink formulated starting from 18NR-T paste and including some additives, with viscosity and surface tension equal to 37.66 mPa*s and 32.55 mN/m, respectively.
Dye N3 (cis-Bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II), Sigma Aldrich) 0.3 mM in Absolute Ethanol.
3,4 ethylenedioxythiophene (EDOT, 97% Sigma Aldrich), $LiClO_4$ (ACS Reagent, Sigma Aldrich), water with MQ grade, oxalic acid di-hydrate (>99.5%, Merck), water MQ grade.
0.1M water MQ solution and poly-vinyl alcohol (PVA) 10% wt.

Procedure

Thick films based on TiO_2 were prepared by a semi-automatic screen-printing machine, AUREL 900 (Aurel Automation S.p.A., Italia), with a speed of 90 mm/s and three consecutive depositions. A mean thickness of 11.84 µm and an active area of 0.25 cm^2 were achieved. Between each deposition, a drying treatment in IR oven at 80°C was applied. Finally, the thermal consolidation of the films was obtained by treating them at 450°C for 30'.
Inkjet printing was performed on the previous films, by using a multiple-deposition techniques station (XCEL, Aurel Automation s.p.a., Italy) equipped with a drop-on-demand inkjet printing head, MD-K-140 (microdrop Technologies GmbH, Germany) that has the possibility to heat up the nozzle. A specific pattern, a wavy line, was realized by printing at 40 mm/s and heating up the nozzle at 35°C. The film drying was realized at 85°C for 60 seconds on a hot plate while the final consolidation was obtained treating the samples at 450°C for 30 min in a common oven.
The as obtained film was sensitized overnight in 0.3 mM N3 dye solution and the excess of dye was removed by absolute ethanol. On top of this film, Poly-3,4 ethylenedioxythiophene (PEDOT) film was deposited by electro-polymerization in a three electrodes cells (working: FTO, reference: SCE, counter: platinum foil) using 3,4 Ethylenedioxythiophene 5 mM in $LiClO_4$ 0.5M in water MQ with applied potential equal to +1.05 V vs SCE and with a total amount of charge equal to 0.1 C. For supporting-electrode preparation, Poly-3,4 ethylenedioxythiophene (PEDOT) MIP film was deposited by electro-polymerization in a three electrodes cells (working: FTO, reference: SCE, counter: platinum foil) using 3,4 ethylenedioxythiophene 5 mM in $LiClO_4$ 0.5M in water MQ and 25 mM of oxalic acid. Applied potential equal to +1.05 V vs SCE with a total amount of charge equal to 0.1 C, active area deposited equal to 0.25 cm^2. The final device was completed adding PVA gel between two electrodes and sealed with a thermoplastic sealant, epoxy glue and protective UV-filter.

PHOTO-RECHARGEABLE TESTS

Galvanostatic charge-discharge tests (CD) with charge with current density of 0.08 A g^{-1} applied under illumination with different intensities (1000 W m^{-2} or 500 W m^{-2} calibrated with a reference cell) and discharge at different current densities in the dark.

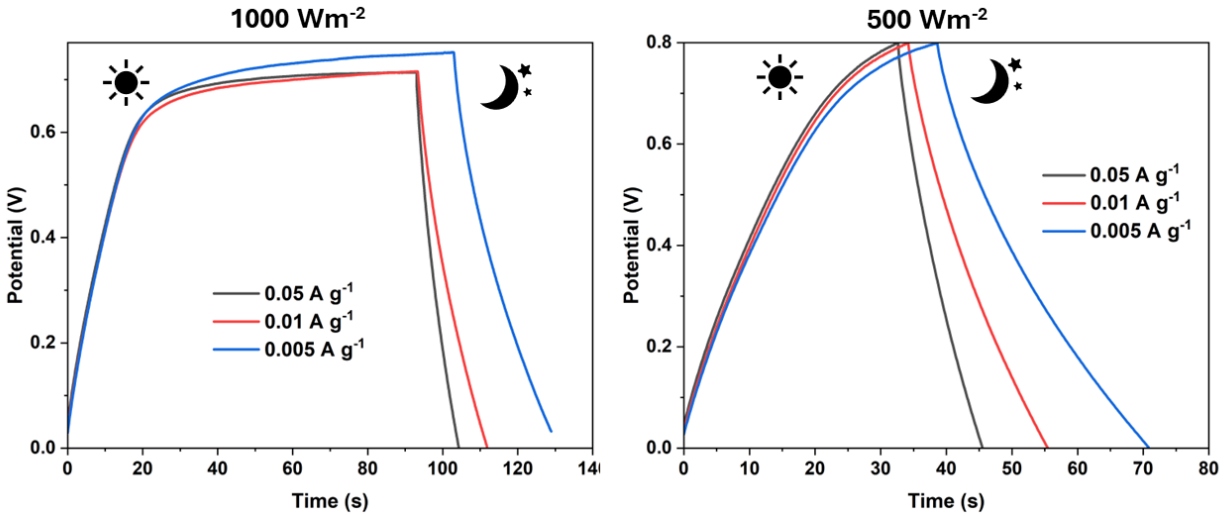
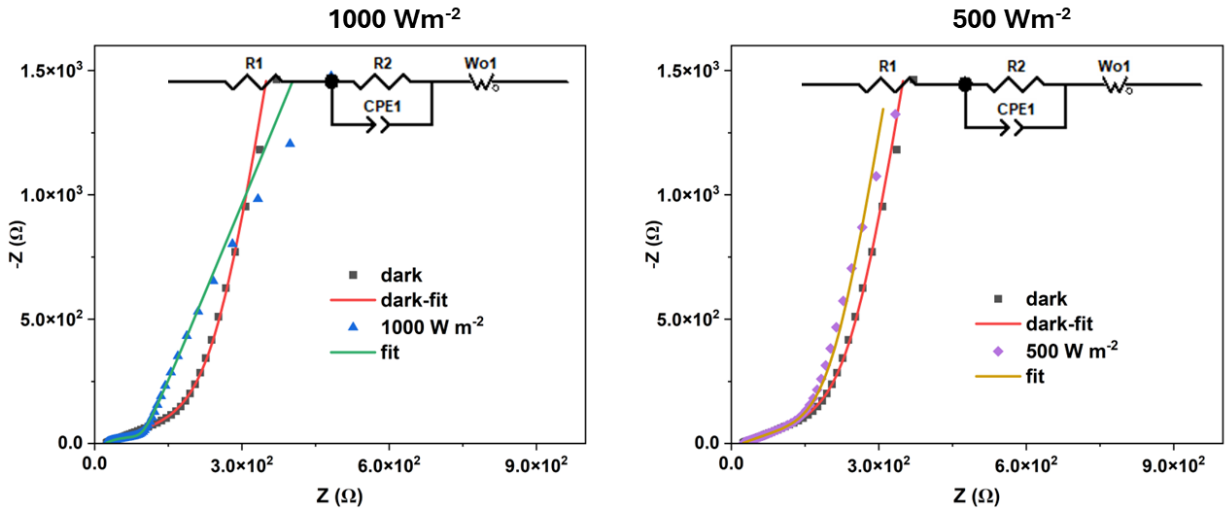


Photo-rechargeable parameters

- Specific capacitance of 0.72, 0.23 e 0.16 F g^{-1} at 0.005, 0.01 e 0.05 A g^{-1} current densities under illumination (1000 W m^{-2}).
- Specific capacitance equal to 0.83, 0.27 e 0.20 F g^{-1} at 0.005, 0.01 e 0.05 A g^{-1} current densities under illumination (500 W m^{-2}).

INTERFACE PROPERTIES

Electrochemical Impedance Spectroscopy in frequency range between 100 kHz e 0.01 Hz with signal amplitude of 10 mV and potential applied equal to 0 V in the dark and under illumination with different intensities (1000 W m^{-2} or 500 W m^{-2} calibrated with a reference cell).

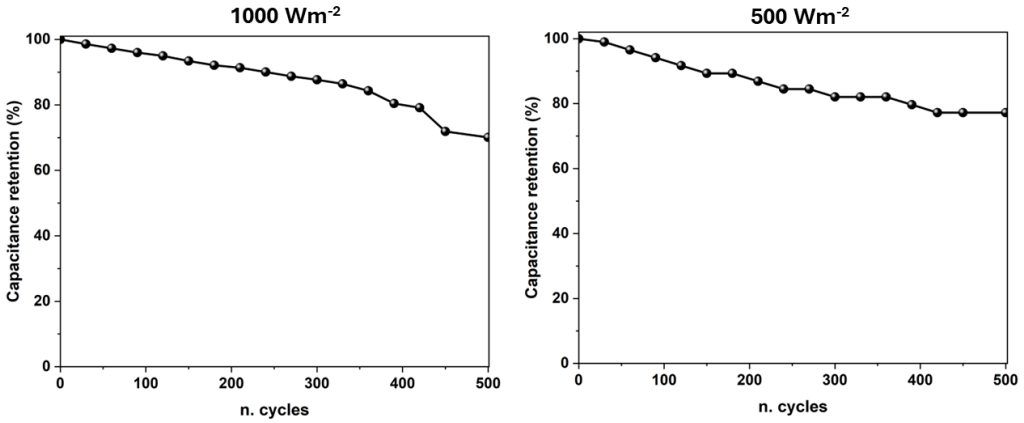


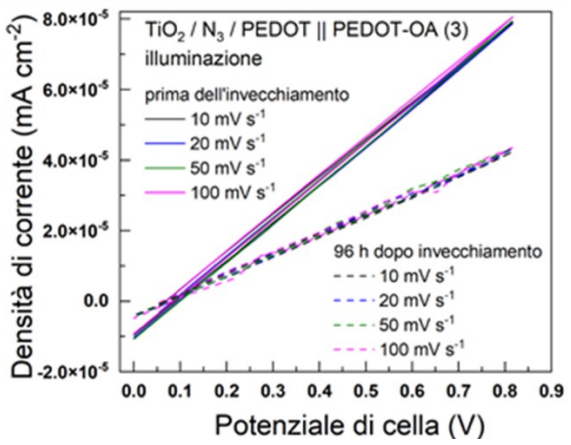
Interfaces Properties

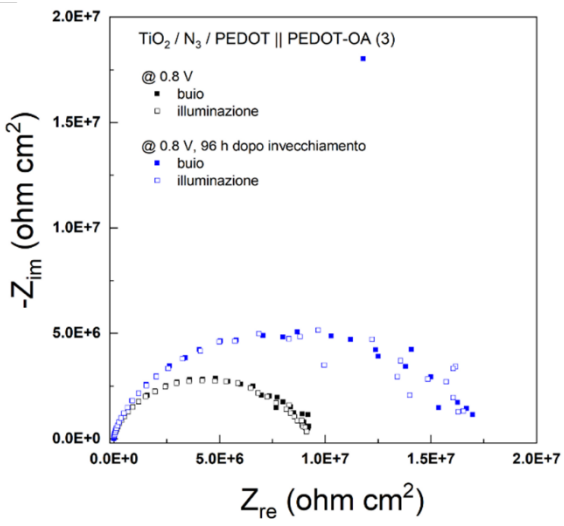
- Electrical resistance under 1000 W m^{-2} of 22 Ω.
- Electrical resistance under 500 W m^{-2} of 22 Ω.
- Charge transfer resistance at the electrode/electrolyte interface equal to 76 Ω under illumination at 1000 W m^{-2}.
- Charge transfer resistance at the electrode/electrolyte interface equal to 224 Ω under illumination at 500 W m^{-2}.

STABILITY IN LABORATORY ENVIRONMENT

Stability test with galvanostatic charge-discharge: 500 cycles of charge and discharge cycles at 0.1 A g^{-1} under illumination with different intensities (1000 W m^{-2} or 500 W m^{-2} calibrated with a reference cell).
Stability test in humid static chamber: Cyclic voltammetry at different scan rates (10, 20, 50 e 100 mV s^{-1}) and Electrochemical Impedance Spectroscopy (100 kHz – 0.1 Hz, ac 10 mV) with different bias applied under illumination with Xenon-lamp Oriel 6258 (300 W) before and after 96 in humid static chamber (Memmert HCP 153) at 40 °C with relative humidity of 40%.





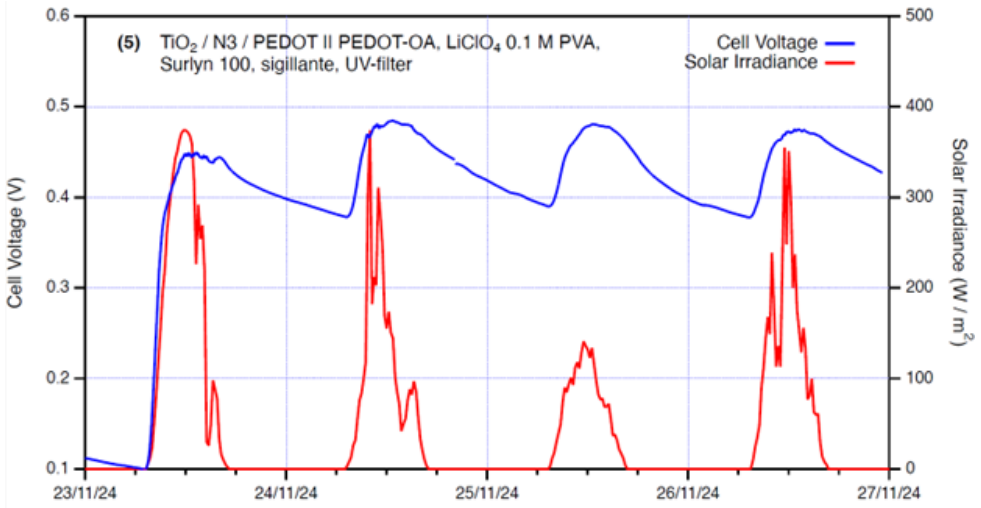


Stability Properties

- Capacitance retention of 65% under 1000 W m^{-2}
- Capacitance retention of 78% under 500 W m^{-2}

STABILITY IN REAL ENVIRONMENT (OUTDOOR TESTS)

Stability outdoor tests: Device tested with 35° angle, irradiance value acquired every 5 min by thermal sensors at high resolution S405C Thorlabs, with interface PM100USB, driven by Optical Power Monitor (OPM) software. The voltage was monitored continuously every 30 s by Keithley mod. 2400.



TiO_2IJP-AD418-PEDOT-PEDOT/MIP asymmetric integrated photovoltaic/storage device with gel state $LiClO_4$ electrolyte

SUMMARY

Photo-rechargeable tests	☒
Interfaces	☒
Stability in laboratory	☒
Stability outdoor	☒

FILM DEPOSITION ANDE DEVICE ASSEMBLY

Reagents

Substrate: Fluorine doped tin oxide coated glass (FTO, Sigma Aldrich, surface resistivity 7 Ω/sq.) with dimension of 2.5x2.5 cm^2.
Screen printing TiO_2-based ink 18NR-T (Greatcell Solar Materials), with viscosity between 40-55 Pa*s.
Inkjet printing ink formulated starting from 18NR-T paste and including some additives, with viscosity and surface tension equal to 37.66 mPa*s and 32.55 mN/m, respectively.
Dye AD418 (molecular formula $C_{43}H_{44}N_2O_4S_2$) 0.3 mM in Ethanol:THF.
3,4 ethylenedioxythiophene (EDOT, 97% Sigma Aldrich), $LiClO_4$ (ACS Reagent, Sigma Aldrich), water with MQ grade, oxalic acid di-hydrate (>99.5%, Merck), water MQ grade.
0.1M water MQ solution and poly-vinyl alcohol (PVA) 10% wt.

Procedure

Thick films based on TiO_2 were prepared by semi-automatic screen-printing machine, AUREL 900 (Aurel Automation S.p.A., Italia), with a speed of 90 mm/s and three consecutive depositions. A mean thickness of 11.84 µm and an active area of 0.25 cm^2 were achieved. Between each deposition, a drying treatment in IR oven at 80°C was applied. Finally, the thermal consolidation of the films was obtained by treating them at 450°C for 30 min.
Inkjet printing was performed on the previous films, by using a multiple-deposition techniques station (XCEL, Aurel Automation S.p.A., Italy) equipped with a drop-on-demand inkjet printing head, MD-K-140 (microdrop Technologies GmbH, Germany) that has the possibility to heat up the nozzle. A specific pattern, a wavy line, was realized by printing at 40 mm/s and heating up the nozzle at 35°C. The film drying was realized at 85°C for 60 seconds on a hot plate while the final consolidation was obtained treating the samples at 450°C for 30 min in a common oven.
The obtained film was sensitized overnight in 0.3 mM AD418 dye solution and the excess of dye was removed by absolute ethanol. On top of this film, Poly-3,4 ethylenedioxythiophene (PEDOT) film was deposited by electro-polymerization in a three electrodes cells (working: FTO, reference: SCE, counter: platinum foil) using 3,4 ethylenedioxythiophene 5 mM in $LiClO_4$ 0.5 M in water MQ with applied potential equal to +1.05 V vs SCE and with a total amount of charge equal to 0.1 C. For supporting-electrode preparation, Poly-3,4 Ethylenedioxythiophene (PEDOT) MIP film was deposited by electro-polymerization in a three electrodes cells (working: FTO, reference: SCE, counter: platinum foil) using 3,4 Ethylenedioxythiophene 5 mM in $LiClO_4$ 0.5 M in water MQ and 25 mM of oxalic acid. Applied potential equal to +1.05 V vs SCE with a total amount of charge equal to 0.1 C, active area deposited equal to 0.25 cm^2. The final device was completed adding PVA gel between two electrodes and sealed with a thermoplastic sealant, epoxy glue and protective UV-filter.

PHOTO-RECHARGEABLE TESTS

Galvanostatic charge-discharge tests (CD) featuring a charge at current density of 0.08 A g^{-1} applied under illumination with different intensities (1000 W m^{-2} or 500 W m^{-2} calibrated with a reference cell) and discharge at different current densities in the dark.

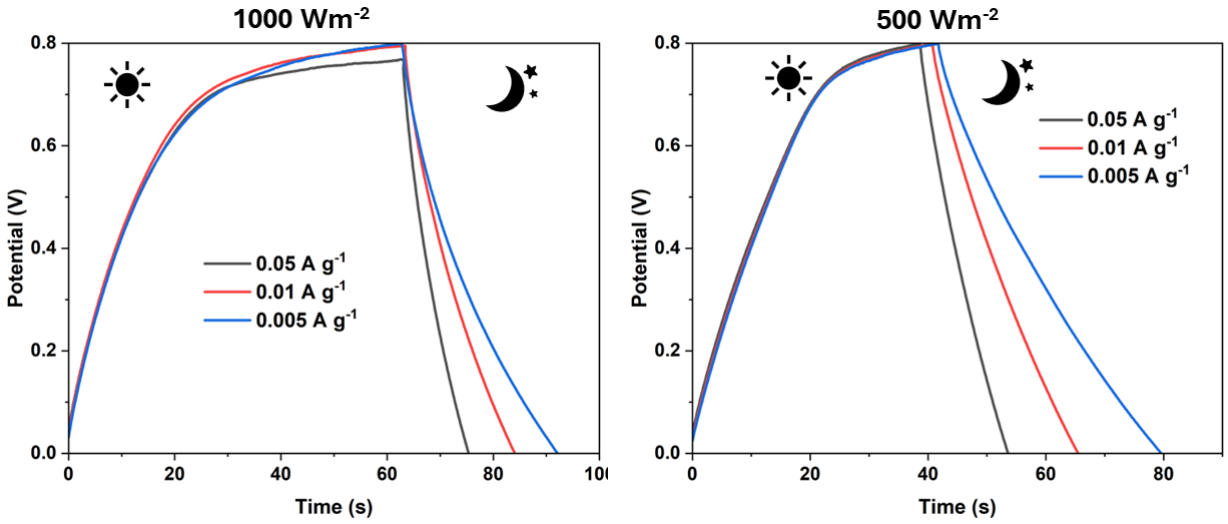
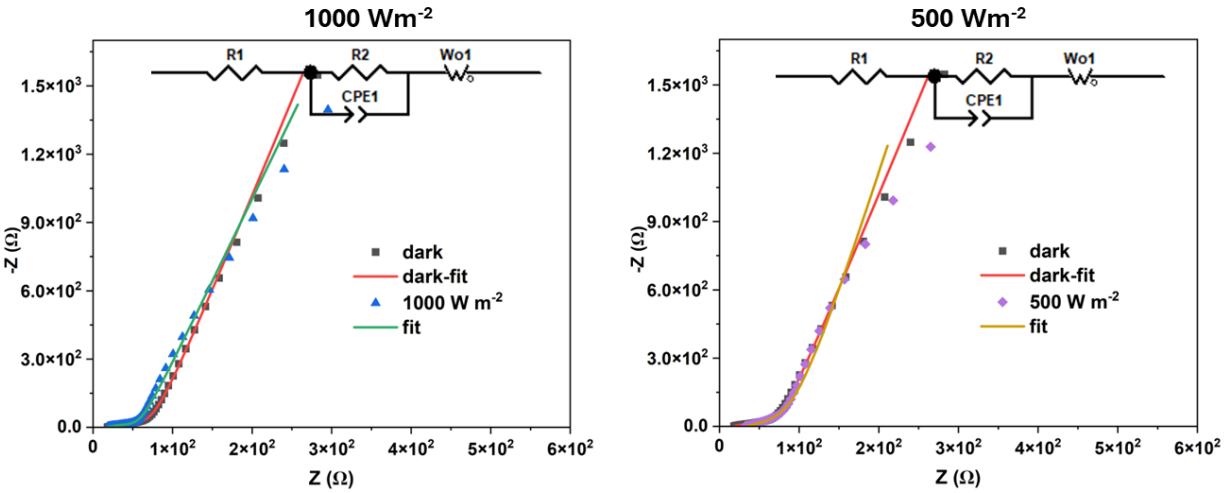


Photo-rechargeable parameters

- Specific capacitance of 0.79, 0.26 e 0.18 F g^{-1} at 0.005, 0.01 e 0.05 A g^{-1} current densities under illumination (1000 W m^{-2}).
- Specific capacitance equal to 0.95, 0.31 e 0.24 F g^{-1} at 0.005, 0.01 e 0.05 A g^{-1} current densities under illumination (500 W m^{-2}).

INTERFACE PROPERTIES

Electrochemical Impedance Spectroscopy in frequency range between 100 kHz e 0.01 Hz with signal amplitude of 10 mV and potential applied equal to 0 V in the dark and under illumination with different intensities (1000 W m^{-2} or 500 W m^{-2} calibrated with a reference cell).

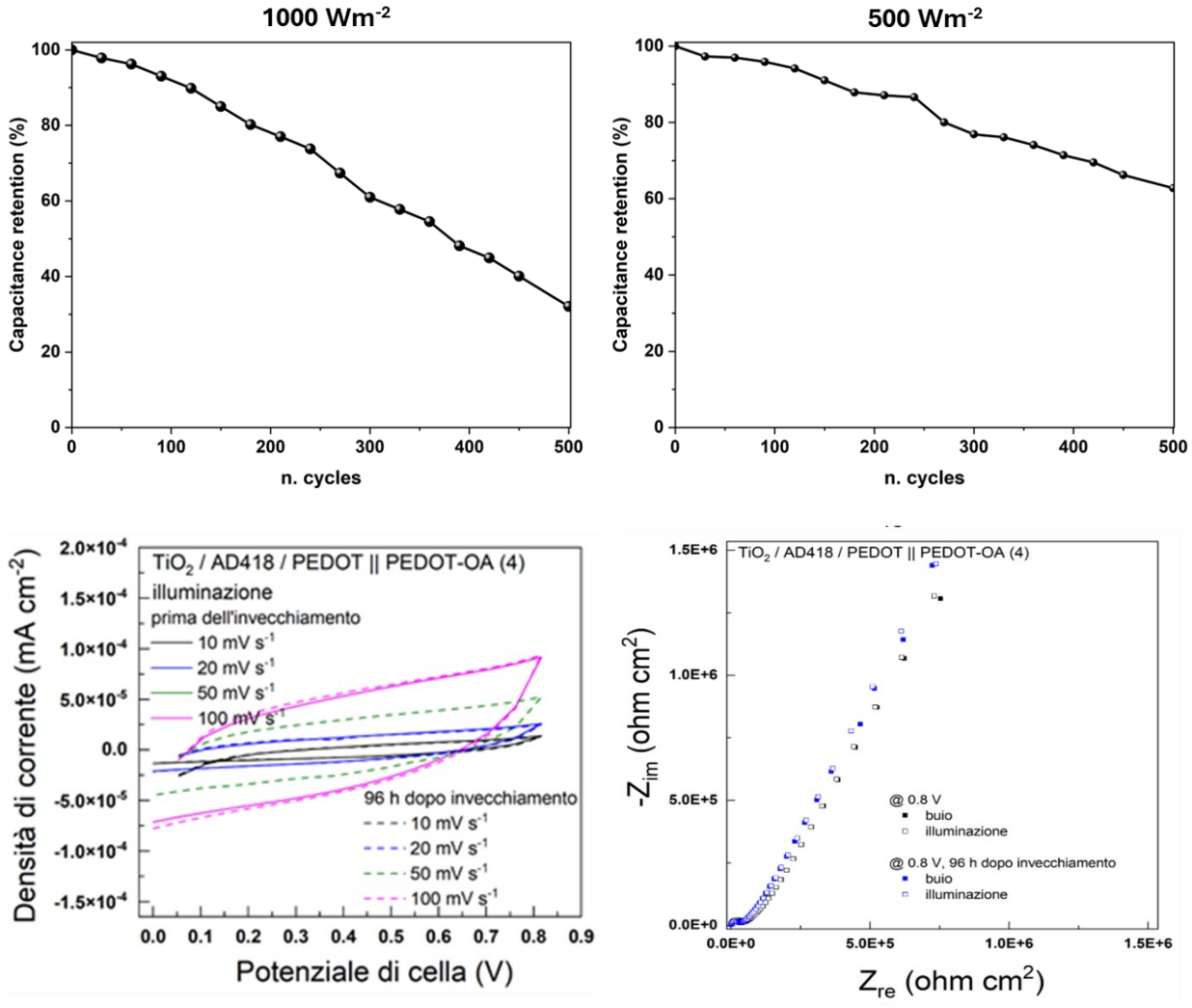


Interfaces Properties

- Electrical resistance under 1000 W m^{-2} of 17 Ω.
- Electrical resistance under 500 W m^{-2} of 33 Ω.
- Charge transfer resistance at the electrode/electrolyte interface equal to 47 Ω under illumination at 1000 W m^{-2}.
- Charge transfer resistance at the electrode/electrolyte interface equal to 77 Ω under illumination at 500 W m^{-2}.

STABILITY IN LABORATORY ENVIRONMENT

Stability test with galvanostatic charge-discharge: 500 cycles of charge and discharge cycles at 0.1 A g^{-1} under illumination with different intensities (1000 W m^{-2} or 500 W m^{-2} calibrated with a reference cell).
Stability test in humid static chamber: Cyclic voltammetry at different scan rates (10, 20, 50 e 100 mV s^{-1}) and Electrochemical Impedance Spectroscopy (100 kHz – 0.1 Hz, ac 10 mV) with different bias applied under illumination with Xenon-lamp Oriel 6258 (300 W) before and after 96 in humid static chamber (Memmert HCP 153) at 40 °C with relative humidity of 40%.



Stability Properties

- Capacitance retention of 30% under 1000 W m^{-2}
- Capacitance retention of 62% under 500 W m^{-2}

STABILITY IN REAL ENVIRONMENT (OUTDOOR TESTS)

Stability outdoor tests: Device tested with 35° angle, irradiance value acquired every 5 min by thermal sensors at high resolution S405C Thorlabs, with interface PM100USB, driven by Optical Power Monitor (OPM) software. The cell voltage was monitored continuously every 30 s by Keithley mod. 2400.