MISSION INNOVATION ITALY

Ministero dell'Ambiente e della Sicurezza Energetica

MISSION INNOVATION

accelerating the clean energy revolution

POA MATERIALI AVANZATI PER L'ENERGIA

PROGETTO IEMAP - Piattaforma Italiana Accelerata per i Materiali per l'Energia

D4.22 "Database: Sviluppo di un database con le proprietà delle interfacce degli elettrodi sviluppati con dati da inviare alla piattaforma IEMAP, implementata nel WP1"

Autori: A. Sanson (ISSMC), N. Sangiorgi (ISSMC), A. Sangiorgi (ISSMC)

Consiglio Nazionale delle Ricerche

Report MI21-24/48

TITOLO: D4.22 “Database: Sviluppo di un database con le proprietà delle interfacce degli elettrodi sviluppati con dati da inviare alla piattaforma IEMAP, implementata nel WP1”

Autori: A. Sanson (ISSMC), N. Sangiorgi (ISSMC), A. Sangiorgi (ISSMC)

M13-M24 (12/05/2022-11/05/2023)

Maggio 2023

Report MISSION INNOVATION

Ministero dell’Ambiente e della Sicurezza Energetica - ENEA
Mission Innovation 2021-2024 - II annualità
Progetto: Italian Energy Materials Acceleration Platform - IEMAP
Work package: *WP4 – Materiali per Fotovoltaico*
Linea di attività: *LA4.11 Ottimizzazione di tecniche di deposizione facilmente automatizzabili e struttura di elettrodi per dispositivi integrati fotovoltaico-accumulo a 2 terminali*
Responsabile del Progetto: Massimo Celino (ENEA)
Responsabile della LA: Dr.ssa Alessandra Sanson (ISSMC-CNR)

Indice

1 ELECTRODE FOR STORAGE BASED ON ELECTROCHEMICALLY REDUCED GRAPHENE OXIDE

ELECTRODE FOR STORAGE BASED ON ELECTROCHEMICALLY REDUCED GRAPHENE OXIDE

SUMMARY

Interfaces properties	☒

FILM DEPOSITION

Reagents

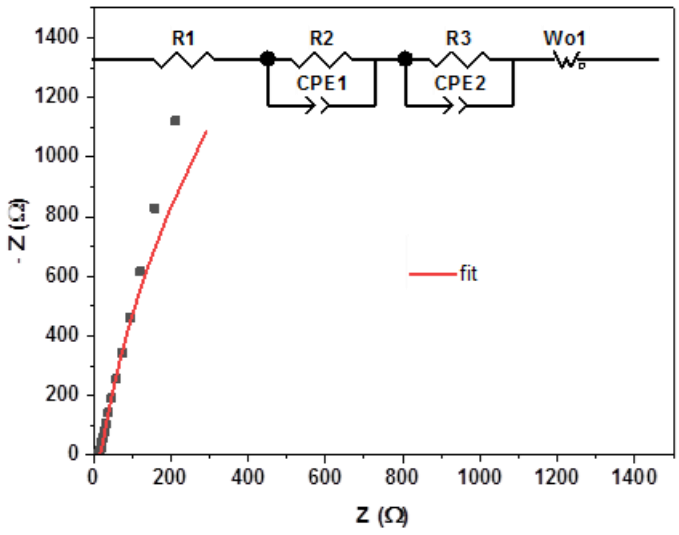
Substrate: Fluorine doped tin oxide coated glass (FTO, Sigma Aldrich, surface resistivity 7 Ω/sq.) with dimension of 2.5x2.5 cm^2.
Graphene oxide suspension (GO, 4 mg/mL in water, Sigma Aldrich), Nafion (Nafion ® 5 wt % in alcohol and water), Na_2SO_4 (ACS Reagent ≥99.5%, Sigma-Aldrich), water MQ grade.

Procedure

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.

PHOTO-ELECTROCHEMISTRY

Eectrochemical Impedance Spectroscopy in a three-electrodes cell with working electrode: FTO+film; counter-electrode: platinum foil; reference electrode: SCE; electrolyte: H_2SO_4 1 M in H_2O MQ. Frequency range between $1x10^5$ Hz e 0.01 Hz with signal amplitude of 10 mV and potential applied equal to 0V vs Ag/AgCl.



Interfaces Properties

- Electrical resistance under illumination of 3 Ω.
- Charge transfer resistance electrode/electrolyte interface under illumination equal to 8186 Ω.

2 ELECTRODE FOR STORAGE BASED ON MOLECULAR IMPRINTED POLY-3,4 ETHYLENEDIOXYTHIOPHENE WITH OXALIC ACID

ELECTRODE FOR STORAGE BASED ON MOLECULAR IMPRINTED POLY-3,4 ETHYLENEDIOXYTHIOPHENE WITH OXALIC ACID

SUMMARY

Interfaces properties	☒

FILM DEPOSITION

Reagents

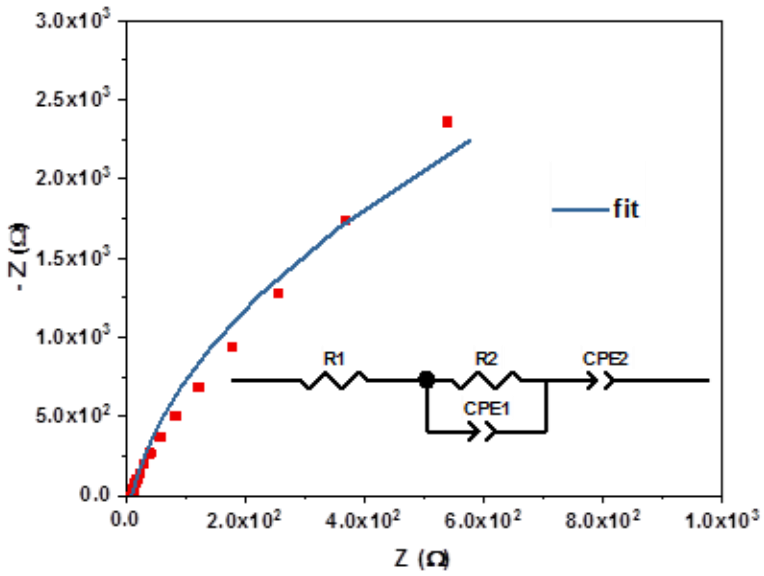
Substrate: Fluorine doped tin oxide coated glass (FTO, Sigma Aldrich, surface resistivity 7 Ω/sq.) with dimension of 2.5x2.5 cm^2.
3,4 Ethylenedioxythiopene (EDOT, 97% Sigma Aldrich), $LiClO_4$ (ACS Reagent, Sigma Aldrich), water with MQ grade, oxalic acid di-hydrate (>99.5%, Merck), water MQ grade.

Procedure

Poly-3,4 Ethylenedioxythiopene (PEDOT) film was deposited by electro-polymerization in a three electrodes cells (working: FTO, reference: SCE, counter: platinum foil) using 3,4 Ethylenedioxythiopene 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.

PHOTO-ELECTROCHEMISTRY

Eectrochemical Impedance Spectroscopy in a three-electrodes cell with working electrode: FTO+film; counter-electrode: platinum foil; reference electrode: SCE; electrolyte: H_2SO_4 1 M in H_2O MQ. Frequency range between $1x10^5$ Hz e 0.01 Hz with signal amplitude of 10 mV and potential applied equal to 0V vs Ag/AgCl.



Interfaces Properties

- Electrical resistance under illumination of 9 Ω.
- Charge transfer resistance electrode/electrolyte interface under illumination equal to 6437 Ω.

3 PHOTO-RECHARGEABLE ELECTRODE BASED ON TiO2 DECORED WITH INKJET PRINTING, SENSITIZED WITH AD418 DYE AND POLY-3,4 ETHYLENEDIOXYTHIOPHENE

PHOTO-RECHARGEABLE ELECTRODE BASED ON TiO_2 DECORED WITH INKJET PRINTING, SENSITIZED WITH AD418 DYE AND POLY-3,4 ETHYLENEDIOXYTHIOPHENE

SUMMARY	
Interfaces properties	☒

TiO_2 FILM DEPOSITION AND SENSITIZATION

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 TiO2-based ink 18NR-T (Greatcell Solar Materials), with viscosity between 40-55 Pa*s.
Inkjet printing ink formulated starting from 18NR-T paste and using 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 Ethylenedioxythiopene (EDOT, 97% Sigma Aldrich), $LiClO_4$ (ACS Reagent, Sigma Aldrich).

Procedure

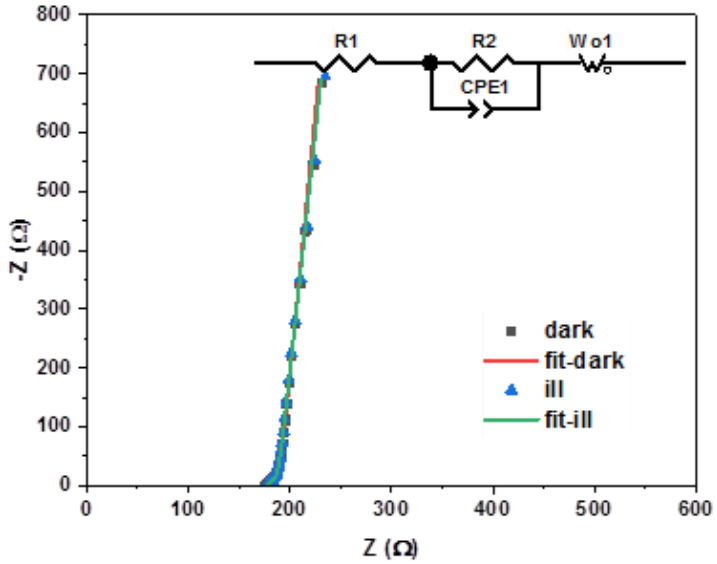
Thick films based on TiO_2 were prepared by semi-automatic screen-printing machine, AUREL 900 (Aurel Automation S.p.A., Italia), with speed of 90 mm/s and three consecutive depositions. A mean thickness of 11.84 µm and an active area of 0.25 cm^2 were achieved. Between each deposition, a drying treatment 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 since 35°C. The film drying was realized at 85°C for 60''on a hot plate while the final consolidation was obtained treating the samples at 450°C for 30' in a common oven.

The as 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 Ethylenedioxythiopene (PEDOT) film was deposited by electro-polymerization in a three electrodes cells (working: FTO, reference: SCE, counter: platinum foil) using 3,4 Ethylenedioxythiopene 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.

PHOTO-ELECTROCHEMISTRY

Eectrochemical Impedance Spectroscopy in a photoelectrochemical cell with working electrode: FTO+film; counter-electrode: platinum wire; reference electrode: aqueous Ag/AgCl (sat. KCl); electrolyte: $LiClO_4$ 0.1 M in H_2O MQ. Frequency range between $1x10^5$ Hz e 0.01 Hz with signal amplitude of 10 mV and potential applied equal to 0V vs Ag/AgCl. Dark and illumination conditions with 1000 W m^{-2} as irradiance (calibrated with a reference cell).



Interfaces Properties

- Electrical resistance under illumination of 177 Ω.
- Charge transfer resistance electrode/electrolyte interface under illumination equal to 11 Ω.

4 PHOTO-RECHARGEABLE ELECTRODE BASED ON TiO2 DECORED WITH INKJET PRINTING, SENSITIZED WITH BTD-DTP2 DYE AND POLY-3,4 ETHYLENEDIOXYTHIOPHENE

PHOTO-RECHARGEABLE ELECTRODE BASED ON TiO_2 DECORED WITH INKJET PRINTING, SENSITIZED WITH BTD-DTP2 DYE AND POLY-3,4 ETHYLENEDIOXYTHIOPHENE

SUMMARY

Interfaces properties	☒

TiO_2 FILM DEPOSITION AND SENSITIZATION

Reagents

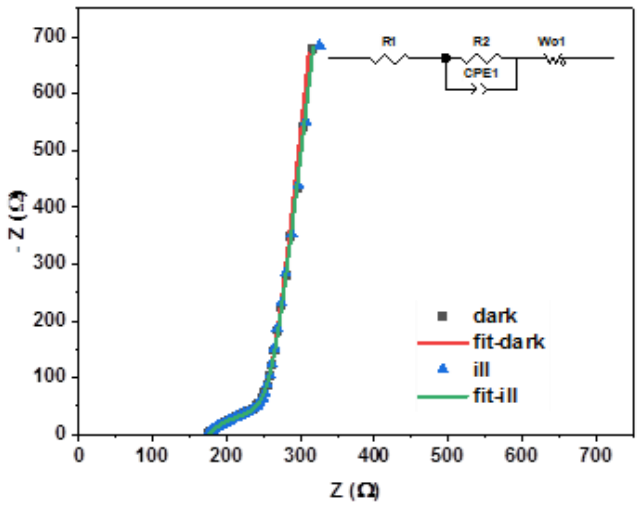
Substrate: Fluorine doped tin oxide coated glass (FTO, Sigma Aldrich, surface resistivity 7 Ω/sq.) with dimension of 2.5x2.5 cm^2.
Screen printing TiO2-based ink 18NR-T (Greatcell Solar Materials), with viscosity between 40-55 Pa*s.
Inkjet printing ink formulated starting from 18NR-T paste and using additives, with viscosity and surface tension equal to 37.66 mPa*s and 32.55 mN/m respectively.
Dye BTD-DTP2 (molecular formula $C_{64}H_{61}N_5O_4S_3$) 0.3 mM in Ethanol:THF.
3,4 Ethylenedioxythiopene (EDOT, 97% Sigma Aldrich), $LiClO_4$ (ACS Reagent, Sigma Aldrich).

Procedure

Thick films based on TiO_2 were prepared by semi-automatic screen-printing machine, AUREL 900 (Aurel Automation S.p.A., Italia), with 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 since 35°C. The film drying was realized at 85°C for 60''on a hot plate while the final consolidation was obtained treating the samples at 450°C for 30' in a common oven.
The as obtained film was sensitized overnight in 0.3 mM BTD-DTP2 dye solution and the excess of dye was removed by absolute ethanol. On top of this film, Poly-3,4 Ethylenedioxythiopene (PEDOT) film was deposited by electro-polymerization in a three electrodes cells (working: FTO, reference: SCE, counter: platinum foil) using 3,4 Ethylenedioxythiopene 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.

PHOTO-ELECTROCHEMISTRY

Eectrochemical Impedance Spectroscopy in a photoelectrochemical cell with working electrode: FTO+film; counter-electrode: platinum wire; reference electrode: aqueous Ag/AgCl (sat. KCl); electrolyte: $LiClO_4$ 0.1 M in H_2O MQ. Frequency range between $1x10^5$ Hz e 0.01 Hz with signal amplitude of 10 mV and potential applied equal to 0V vs Ag/AgCl. Dark and illumination conditions with 1000 W m^{-2} as irradiance (calibrated with a reference cell).



Interfaces Properties

- Electrical resistance under illumination of 175 Ω.
- Charge transfer resistance electrode/electrolyte interface under illumination equal to 88 Ω.

5 PHOTO-RECHARGEABLE ELECTRODE BASED ON TiO2 DECORED WITH INKJET PRINTING, SENSITIZED WITH N3 DYE AND POLY-3,4 ETHYLENEDIOXYTHIOPHENE

PHOTO-RECHARGEABLE ELECTRODE BASED ON TiO_2 DECORED WITH INKJET PRINTING, SENSITIZED WITH N3 DYE AND POLY-3,4 ETHYLENEDIOXYTHIOPHENE

SUMMARY

Interfaces properties	☒

TiO_2 FILM DEPOSITION AND SENSITIZATION

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 TiO2-based ink 18NR-T (Greatcell Solar Materials), with viscosity between 40-55 Pa*s.
Inkjet printing ink formulated starting from 18NR-T paste and using 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 Ethylenedioxythiopene (EDOT, 97% Sigma Aldrich), $LiClO_4$ (ACS Reagent, Sigma Aldrich).

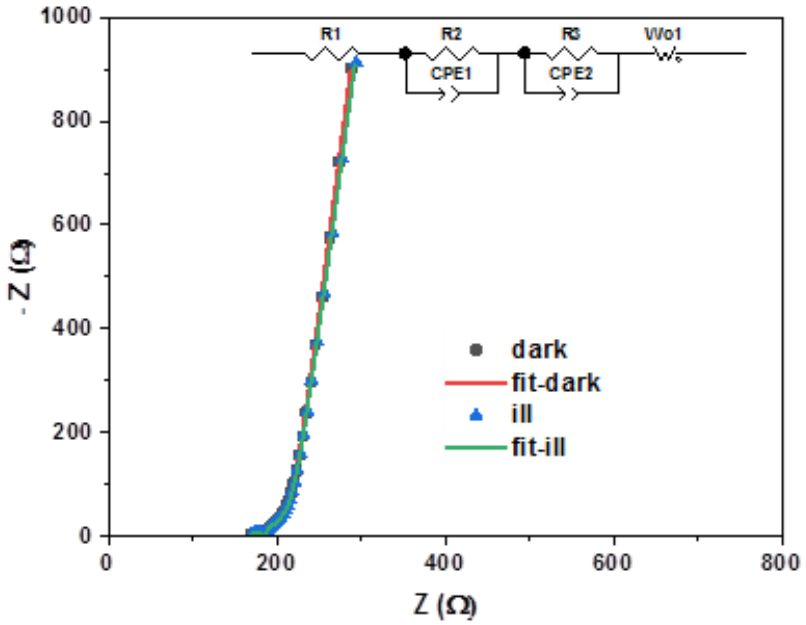
Procedure

Thick films based on TiO_2 were prepared by semi-automatic screen-printing machine, AUREL 900 (Aurel Automation S.p.A., Italia), with 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 since 35°C. The film drying was realized at 85°C for 60''on a hot plate while the final consolidation was obtained treating the samples at 450°C for 30' 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 Ethylenedioxythiopene (PEDOT) film was deposited by electro-polymerization in a three electrodes cells (working: FTO, reference: SCE, counter: platinum foil) using 3,4 Ethylenedioxythiopene 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.

PHOTO-ELECTROCHEMISTRY

Eectrochemical Impedance Spectroscopy in a photoelectrochemical cell with working electrode: FTO+film;

counter-electrode: platinum wire; reference electrode: aqueous Ag/AgCl (sat. KCl); electrolyte: $LiClO_4$ 0.1 M in H_2O MQ. Frequency range between $1x10^5$ Hz e 0.01 Hz with signal amplitude of 10 mV and potential applied equal to 0V vs Ag/AgCl. Dark and illumination conditions with 1000 W m^{-2} as irradiance (calibrated with a reference cell).



Interfaces Properties

- Electrical resistance under illumination of 168 Ω.
- Charge transfer resistance electrode/electrolyte interface under illumination equal to 34 Ω.

6 PHOTO-RECHARGEABLE ELECTRODE BASED ON WO3 DECORED WITH INKJET PRINTING AND N2 TREATMENT

PHOTO-RECHARGEABLE ELECTRODE BASED ON WO_3 DECORED WITH INKJET PRINTING AND N_2 TREATMENT

SUMMARY	
Interfaces properties	☒

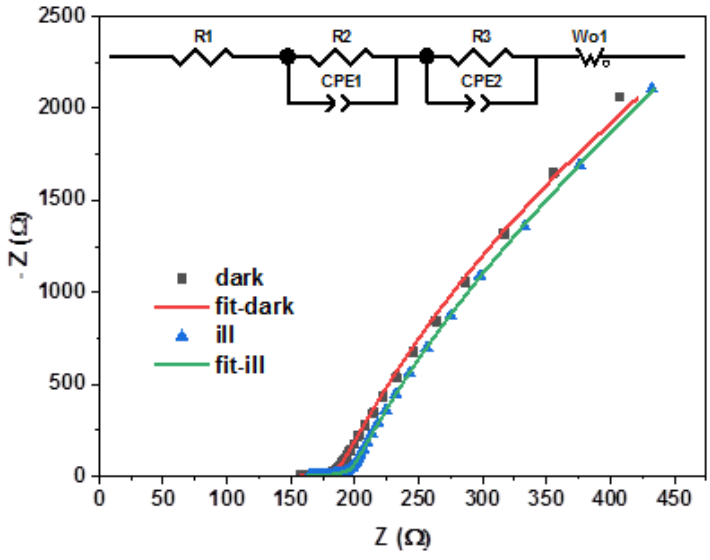
FILM DEPOSITION
Reagents

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.

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' on a hot plate under N_2 flux.

PHOTO-ELECTROCHEMISTRY

Eectrochemical Impedance Spectroscopy in a photoelectrochemical cell with working electrode: FTO+film; counter-electrode: platinum wire; reference electrode: aqueous Ag/AgCl (sat. KCl); electrolyte: $LiClO_4$ 0.1 M in H_2O MQ. Frequency range between $1x10^5$ Hz e 0.01 Hz with signal amplitude of 10 mV and potential applied equal to 0V vs Ag/AgCl. Dark and illumination conditions with 1000 W m^{-2} as irradiance (calibrated with a reference cell).



Interfaces Properties

- Electrical resistance under illumination of 159 Ω.
- Charge transfer resistance electrode/electrolyte interface under illumination equal to 3800 Ω.

7 PHOTO-RECHARGEABLE ELECTRODE BASED ON WO3 DECORED WITH INKJET PRINTING AND OVEN TREATMENT

PHOTO-RECHARGEABLE ELECTRODE BASED ON WO_3 DECORED WITH INKJET PRINTING AND OVEN TREATMENT

SUMMARY

Interfaces properties ☒

FILM DEPOSITION

Reagents

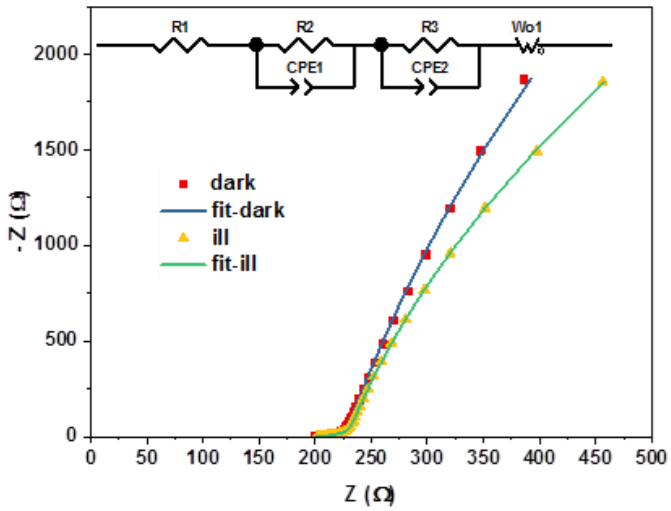
Substrate: Fluorine doped tin oxide coated glass (FTO, Sigma Aldrich, surface resistivity 7 Ω/sq.) with dimension of 2.5x2.5 cm^2.
Screen printing WO3-based ink, containing active material between 15 and 20 wt.%, produced by using α-terpineol and cellulose derivates (Sigma Aldrich).
Inkjet printing ink 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.

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.

PHOTO-ELECTROCHEMISTRY

Eectrochemical Impedance Spectroscopy in a photoelectrochemical cell with working electrode: FTO+film; counter-electrode: platinum wire; reference electrode: aqueous Ag/AgCl (sat. KCl); electrolyte: $LiClO_4$ 0.1 M in H_2O MQ. Frequency range between $1x10^5$ Hz e 0.01 Hz with signal amplitude of 10 mV and potential applied equal to 0V vs Ag/AgCl. Dark and illumination conditions with 1000 W m^{-2} as irradiance (calibrated with a reference cell).



Interfaces Properties

- Electrical resistance under illumination of 133 Ω.
- Charge transfer resistance electrode/electrolyte interface under illumination equal to 4668 Ω.