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

D4.21 "Database: Sviluppo di un database con le proprietà ottiche e di accumulo di cariche foto-accumulate 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 MI21-24/47

TITOLO: D4.21 “Database: Sviluppo di un database con le proprietà ottiche e di accumulo di cariche foto-accumulate 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)

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

SUMMARY

Optical properties	☒
Electrochemistry	☒
Photo-electrochemistry	☒
Photo-rechargeable tests	☒

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 2.5 × 2.5 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 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)

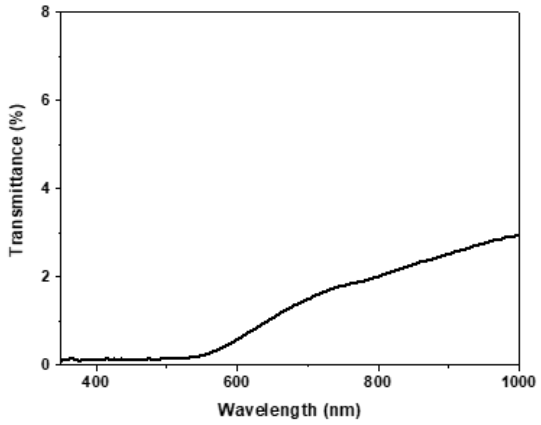
Procedure

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 to 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.

OPTICAL PROPERTIES

Transmittance spectra

Acquired in the range between 350 and 1000 nm with an integrating sphere.



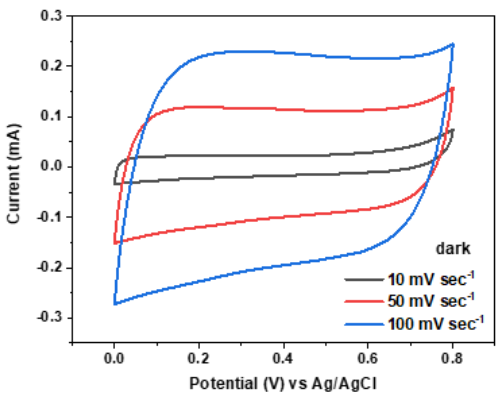
Optical parameters

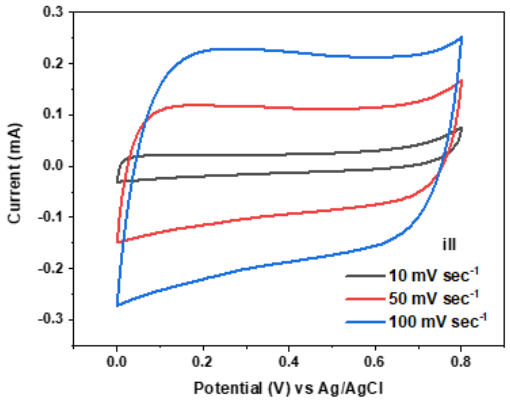
Ability to harvest light in the Visible region.

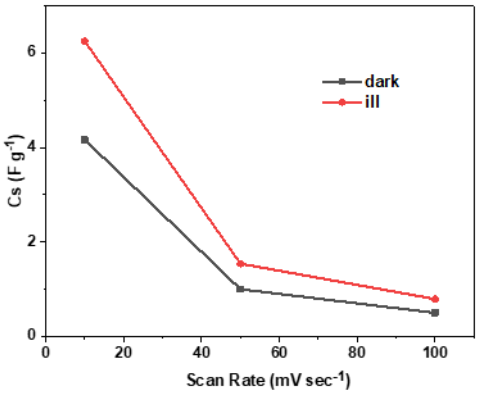
Transparency at 700 nm of 1.8%.

PHOTO-ELECTROCHEMISTRY

Cyclic Voltammetry 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. Potential applied between 0.8 V and 0 V vs Ag/AgCl and scan rate of 10, 50, 100 mV sec^{-1}. Dark and illumination conditions with 1000 W m^{-2} as irradiance (calibrated with a reference cell).







Galvanostatic charge-discharge tests 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. Potential range applied between 0 V and 0.8 V vs Ag/AgCl with current density of 0.2 A g^{-1}. Dark and illumination conditions with 1000 W m^{-2} as irradiance (calibrated with a reference cell).

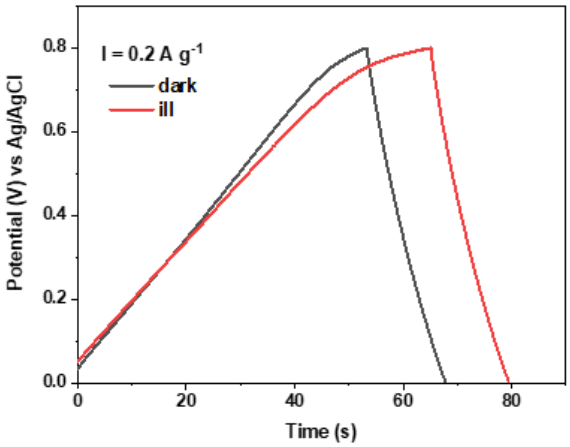


Photo-electrochemical parameters

- Specific capacitance from CV under illumination at 10 mV sec^{-1} equal to 6.2 F g^{-1};
- Specific capacitance from CD under illumination 3.6 F g^{-1} at 0.2 A g^{-1}.

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

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

SUMMARY

Optical properties	☒
Electrochemistry	☒
Photo-electrochemistry	☒
Photo-rechargeable tests	☒

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 2.5 × 2.5 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 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)

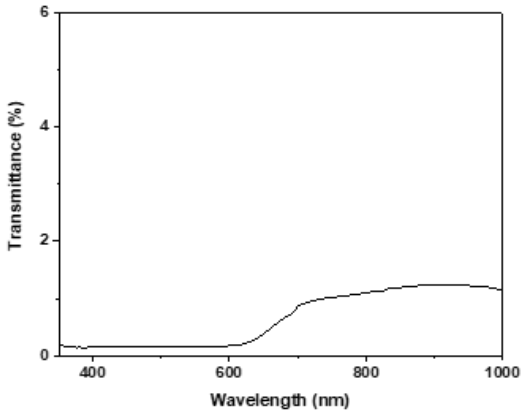
Procedure

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 at 35°C. The film drying was realized at 85°C for 60'' on a hot plate while the final consolidation was obtained by 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 0.1C.

OPTICAL PROPERTIES

Transmittance spectra

Acquired in the range between 350 and 1000 nm with an integrating sphere.



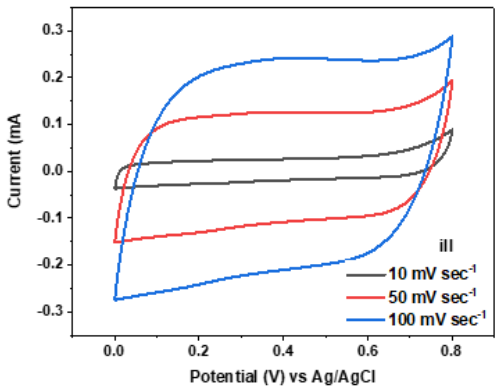
Optical parameters

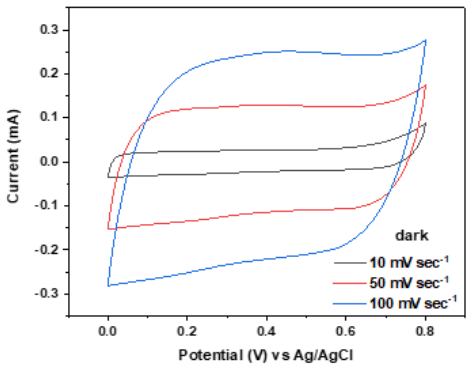
Ability to harvest light in the Visible region.

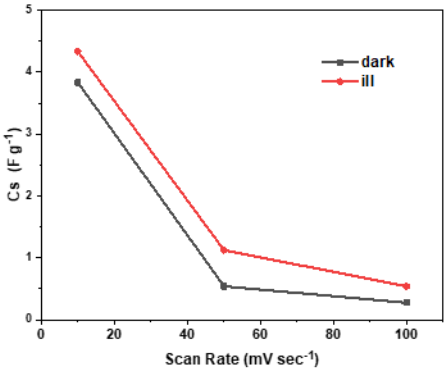
Transparency at 700 nm of 1%.

PHOTO-ELECTROCHEMISTRY

Cyclic Voltammetry 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. Potential applied between 0.8 V and 0 V vs Ag/AgCl and scan rate of 10, 50, 100 mV sec^{-1}. Dark and illumination conditions with 1000 W m^{-2} as irradiance (calibrated with a reference cell).







Galvanostatic charge-discharge tests 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. Potential range applied between 0 V and 0.8 V vs Ag/AgCl with current density of 0.2 A g^{-1}. Dark and illumination conditions with 1000 W m^{-2} as irradiance (calibrated with a reference cell).

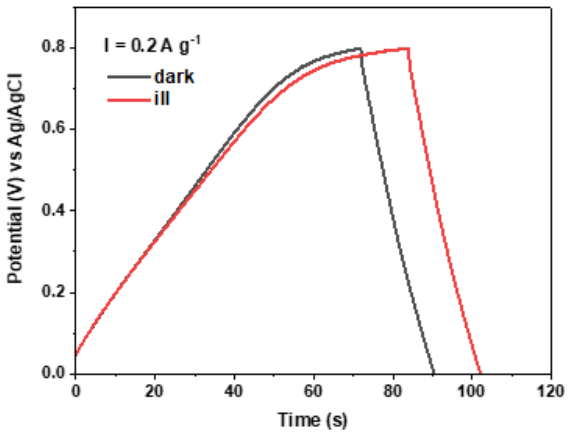


Photo-electrochemical parameters

- Specific capacitance from CV under illumination at 10 mV sec^{-1} equal to 4.3 F g^{-1};
- Specific capacitance from CD under illumination 4.5 F g^{-1} at 0.2 A g^{-1}.

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

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

SUMMARY

Optical properties	☒
Electrochemistry	☒
Photo-electrochemistry	☒
Photo-rechargeable tests	☒

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 2.5 × 2.5 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 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)

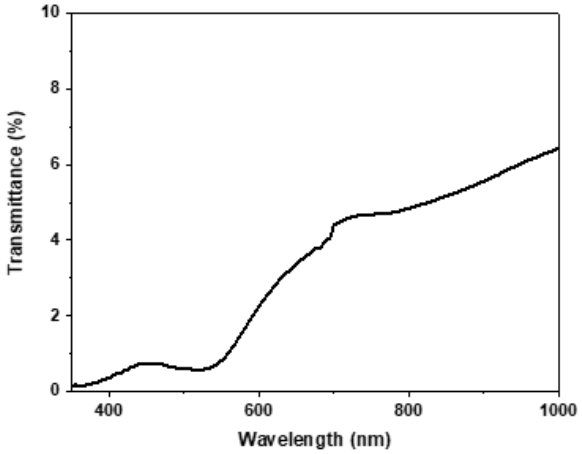
Procedure

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 at 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.

OPTICAL PROPERTIES

Transmittance spectra

Acquired in the range between 350 and 1000 nm with an integrating sphere.



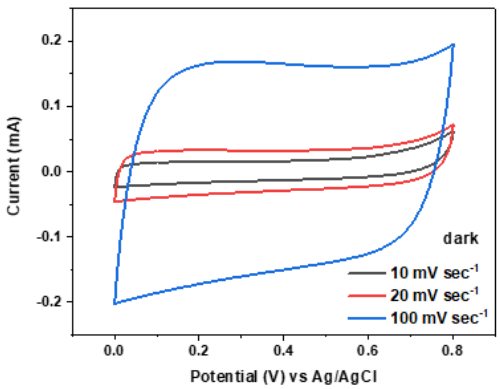
Optical parameters

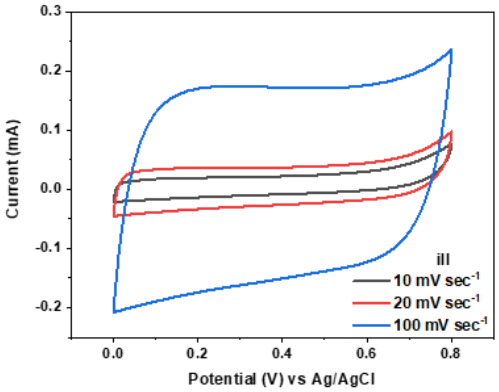
Ability to harvest light in the Visible region.

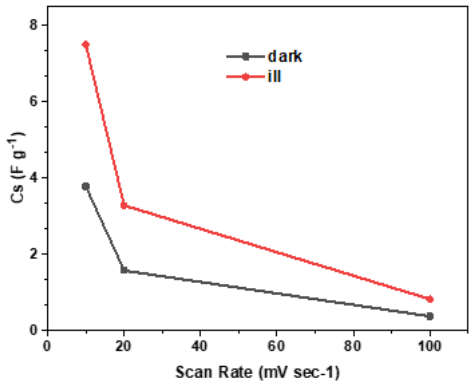
Transparency at 700 nm of 4%.

PHOTO-ELECTROCHEMISTRY

Cyclic Voltammetry 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. Potential applied between 0.8 V and 0 V vs Ag/AgCl and scan rate of 10, 20, 100 mV sec^{-1}. Dark and illumination conditions with 1000 W m^{-2} as irradiance (calibrated with a reference cell).







Galvanostatic charge-discharge tests 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. Potential range applied between 0 V and 0.8 V vs Ag/AgCl with current density of 0.2 A g^{-1}. Dark and illumination conditions with 1000 W m^{-2} as irradiance (calibrated with a reference cell).

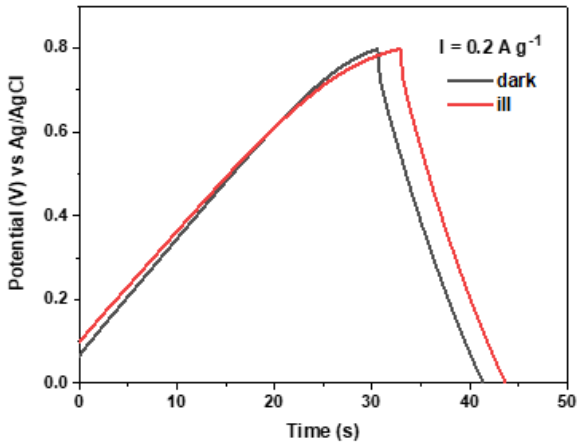


Photo-electrochemical parameters

- Specific capacitance from CV under illumination at 10 mV sec^{-1} equal to 7.5 F g^{-1};
- Specific capacitance from CD under illumination 3.1 F g^{-1} at 0.2 A g^{-1}.

4 PHOTO-RECHARGEABLE ELECTRODE BASED ON WO3 DECORATED WITH INKJET PRINTING AND N2 TREATMENT

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

SUMMARY

Optical properties	☒
Electrochemistry	☒
Photo-electrochemistry	☒
Photo-rechargeable tests	☒

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.

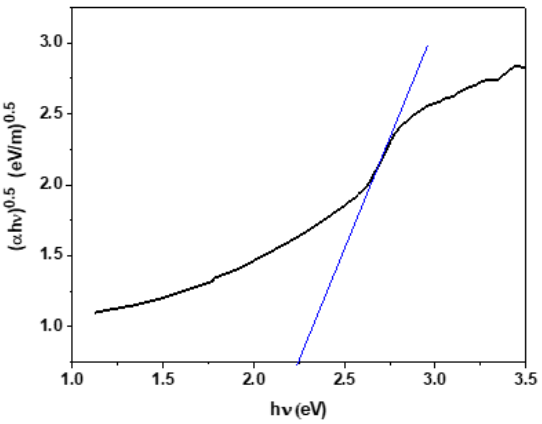
OPTICAL PROPERTIES

Transmittance spectra

Acquired in the range between 350 and 1000 nm with an integrating sphere. Tauc equation was used to determine the band gap (Eg) of the film:

$$\alpha h\nu = A(h\nu - Eg)^n$$

with exponent n=2 and α determined from transmittance spectra.

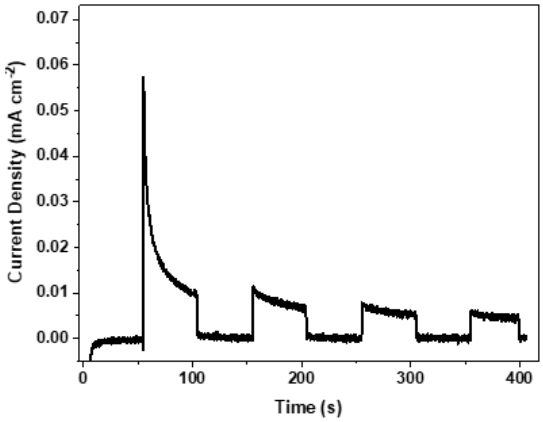


Optical parameters

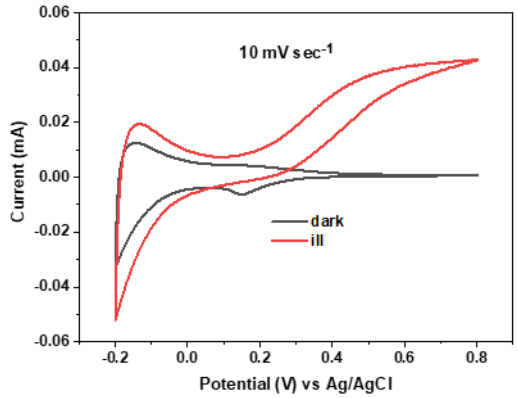
E_g= 2.25 eV

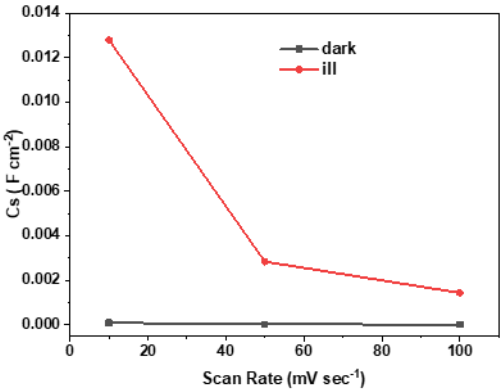
PHOTO-ELECTROCHEMISTRY

Cronoamperometry 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. Potential applied equal to 0V vs Ag/AgCl. Dark and illumination conditions with 1000 W m^{-2} as irradiance (calibrated with a reference cell).

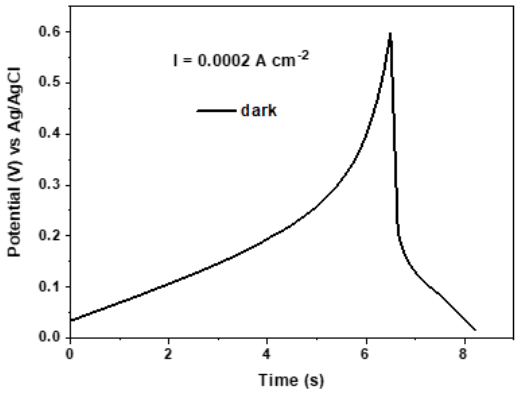


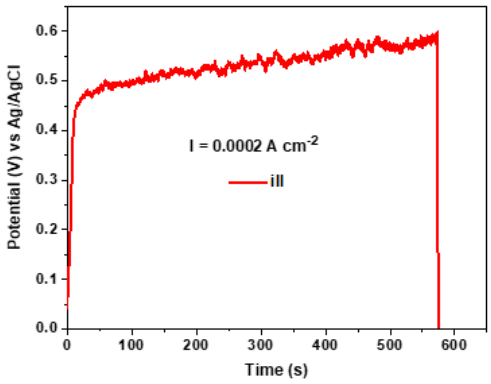
Cyclic Voltammetry (CV) in a photoelectrochemical cell with working electrode: FTO+film; counter-electrode: platinum wire; reference electrode: aqueous Ag/AgCl (sat. KCl); electrolyte: $LiClO_4$ 0.1 M in H_2O MQ. Potential applied between 0.8 V and 0 V vs Ag/AgCl and scan rate of 10, 50, 100 mV sec^{-1}. Dark and illumination conditions with 1000 W m^{-2} as irradiance (calibrated with a reference cell).





Galvanostatic charge-discharge tests (CD) 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. Potential range applied between 0V and 0.6 V vs Ag/AgCl with current density of 0.0002 A cm^2. Dark and illumination conditions with 1000 W m^{-2} as irradiance (calibrated with a reference cell).





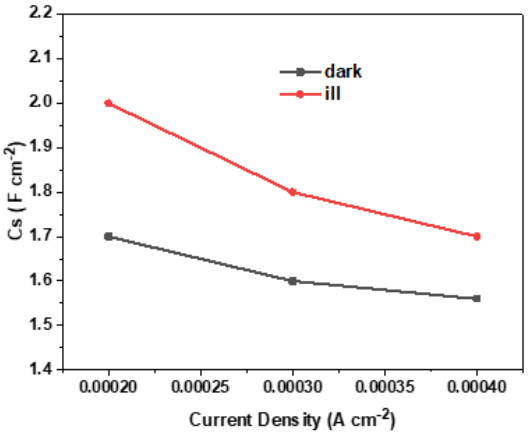


Photo-electrochemical parameters

- Photo-current equal between 0.011-0.012 mA cm^{-2};
- Areal capacitance under illumination from CV curves at 10 mV sec^{-1} equal to 12.8 mF cm^{-2};
- Areal capacitance under illumination from CD curves 2 mF cm^{-2} at 0.0002 A cm^{-2}.

5 PHOTO-RECHARGEABLE ELECTRODE BASED ON WO3 DECORATED WITH INKJET PRINTING AND OVEN TREATMENT

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

SUMMARY

Optical properties	☒
Electrochemistry	☒
Photo-electrochemistry	☒
Photo-rechargeable tests	☒

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.

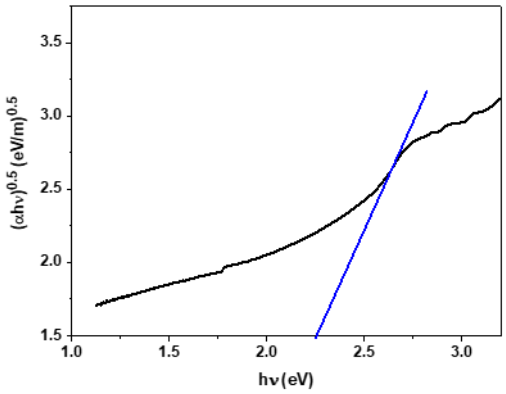
OPTICAL PROPERTIES

Transmittance spectra

Acquired in the range between 350 and 1000 nm with an integrating sphere. Tauc equation was used to determine the band gap (Eg) of the film:

$$\alpha h\nu = A(h\nu - Eg)^n$$

with exponent n=2 and α determined from transmittance spectra.

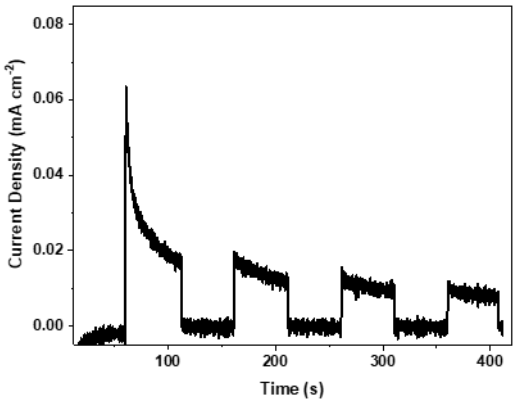


Optical parameters

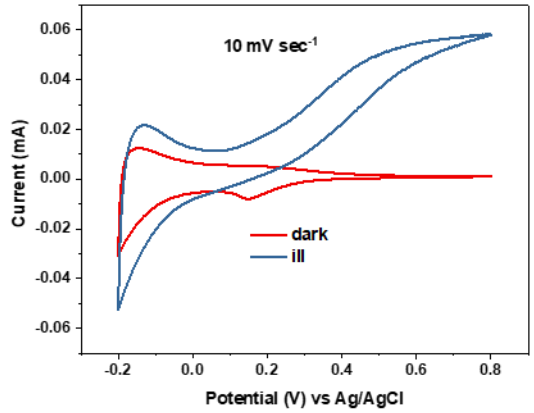
E_g= 2.26 eV

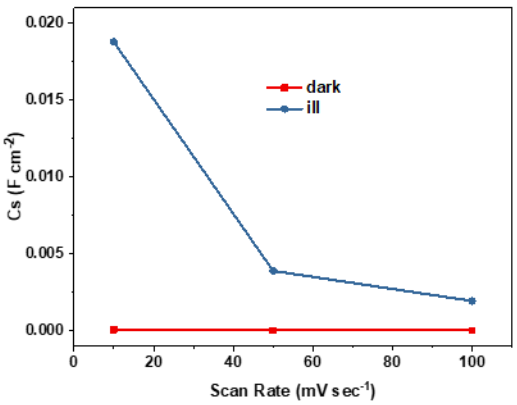
PHOTO-ELECTROCHEMISTRY

Cronoamperometry 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. Potential applied equal to 0V vs Ag/AgCl. Dark and illumination conditions with 1000 W m^{-2} as irradiance (calibrated with a reference cell).

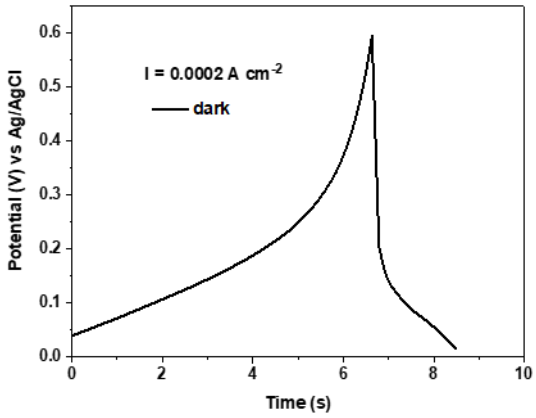


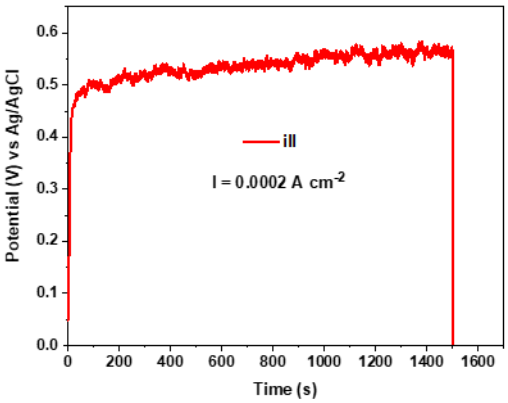
Cyclic Voltammetry (CV) in a photoelectrochemical cell with working electrode: FTO+film; counter-electrode: platinum wire; reference electrode: aqueous Ag/AgCl (sat. KCl); electrolyte: $LiClO_4$ 0.1 M in H_2O MQ. Potential applied between 0.8 V and 0 V vs Ag/AgCl and scan rate of 10, 50, 100 mV sec^{-1}. Dark and illumination conditions with 1000 W m^{-2} as irradiance (calibrated with a reference cell).





Galvanostatic charge-discharge tests (CD) 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. Potential range applied between 0V and 0.6 V vs Ag/AgCl with current density of 0.0002 A cm^{-2}. Dark and illumination conditions with 1000 W m^{-2} as irradiance (calibrated with a reference cell).





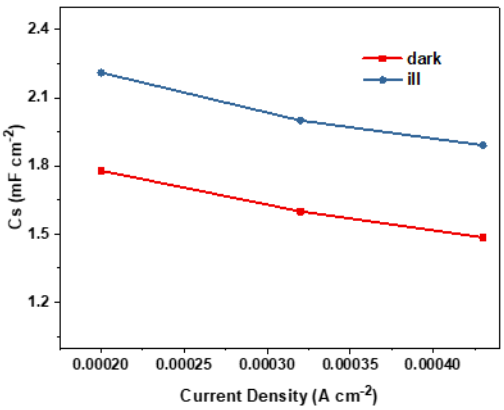


Photo-electrochemical parameters

- Photo-current equal between 0.014-0.02 mA cm^{-2}
- Areal capacitance under illumination from CV curves at 10 mV sec^{-1} equal to 18.8 mF cm^{-2}
- Areal capacitance under illumination from CD curves 2.21 mF cm^{-2} at 0.0002 A cm^{-2}.