MISSION INNOVATION ITALY

Ministero dell'Ambiente
e della Sicurezza Energetica

MISSION INNOVATION
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POA MATERIALI AVANZATI PER L'ENERGIA

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

D4.20 - Database con le caratteristiche e performance dei materiali foto-ricaricabili da utilizzare nei processi di machine learning della piattaforma

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A. Sangiorgi, M. Striccoli, C. N. Dibenedetto, M. Dell'Edera,
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Consiglio Nazionale delle Ricerche

Report MI21-24/46

D4.20 - Database con le caratteristiche e performance dei materiali foto-ricaricabili da utilizzare nei processi di machine learning della piattaforma

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Settembre 2022

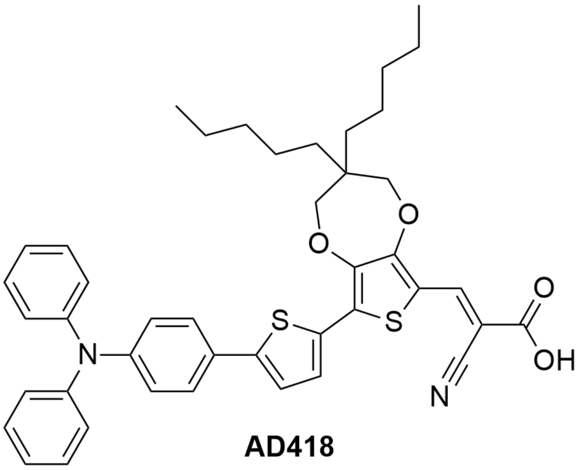
Report IEMAP D4.20

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: LA4.10 - Analisi e screening di materiali per elettrodi e trasportatori di carica per dispositivi integrati fotovoltaico-accumulo a 2 terminali
Responsabile del Progetto: Dott. Massimo Celino (ENEA)
Responsabile della LA: Dott. Alessandro Mordini (CNR-ICCOM)

Indice

1 Colorante AD418

AD418



AD418

Chemical Formula: $C_{43}H_{44}N_2O_4S_2$
Molecular Weight: 716.95

SUMMARY

^{1}H-NMR	☒	XRD	☐	Abs. spectra	☒
^{13}C-NMR	☒	TG	☐	Abs. coeff.	☒
other nuclei	☐	DTA	☐	Ems. spectra	☒
FT-IR	☒	Redox	☒	QY	☐
MS	☒	Mol. Model.	☐	LT	☐
H, C, N	☐				

SYNTHESIS

Reagents	**MW**	**d (g/mL)**	**mmol / eq**	**m (mg)**	**V (mL)**
8-(5-(4-(Diphenylamino)phenyl)thiophen-2-yl)-3,3-dipentyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4] dioxepine-6-carbaldehyde	649.90	-	0.115 / 1.0	75	-
Cyanoacetic acid	85.06	-	1.15 / 10	98	-
Ammonium acetate	77.08	-	0.46 / 4.0	35	-
Toluene	92.14	0.867	-	-	2.0
Acetic acid	60.05	1.05	-	-	2.0

Procedure

Under inert atmosphere, the aldehyde was dissolved in toluene and glacial acetic acid (1:1 v/v), then cyanoacetic acid and ammonium acetate were added. The resulting mixture was stirred at 100 °C for 4 hours, then cooled down to room temperature. After dilution with dichloromethane, the organic phase was washed twice with $HCl_{(aq.)}$ 0.3 M and the solvent evaporated.

Purification

The resulting solid was purified by washing with several portions of n-pentane and methanol, and dried under vacuum.

Yield: 92% (76 mg, 0.106 mmol)

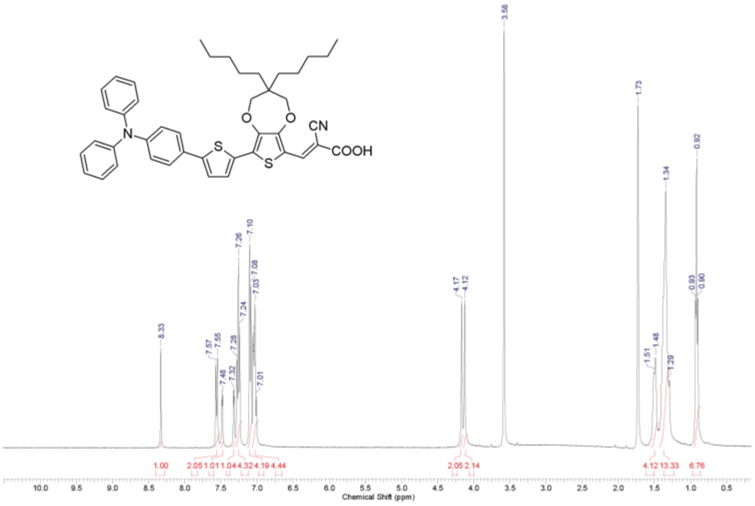
Biblio

ChemSusChem **2018**, *11*, 793 – 805

CHARACTERIZATION

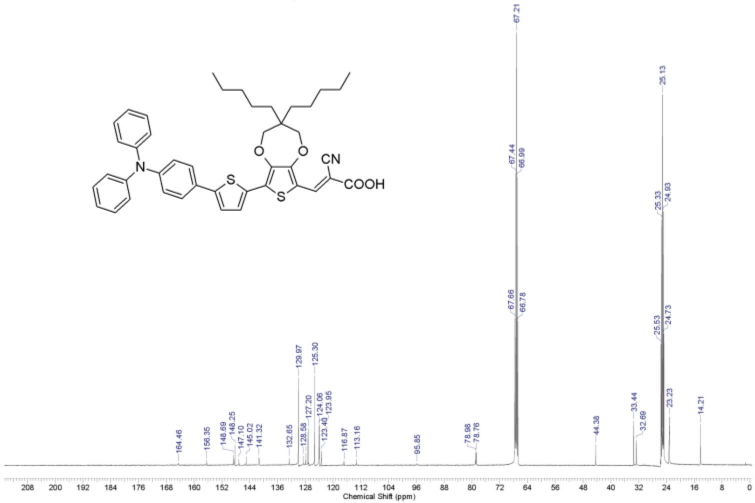
^{1}H NMR (THF-d_8, 400 MHz)

δ (ppm) = 8.33 (s, 1H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 3.3 Hz, 1H), 7.32 (d, *J* = 3.5 Hz, 1H), 7.28–7.24 (m, 4H), 7.09 (d, *J* = 7.8 Hz, 4H), 7.06–7.00 (m, 4H), 4.17 (s, 2H), 4.12 (s, 2H), 1.52–1.46 (m, 4H), 1.42–1.25 (m, 12H), 0.92 (t, *J* = 5.9 Hz, 6H).



^{13}C-NMR (THF-d_8, 100 MHz)

δ (ppm) = 164.4, 156.3, 148.7, 148.2, 147.1, 145.0, 141.3, 132.7, 130.0, 128.6, 127.8, 127.2, 127.0, 125.3, 124.1, 123.9, 123.4, 116.9, 113.2, 95.8, 79.0, 78.8, 44.4, 33.4, 32.7, 23.23, 23.17, 14.2.

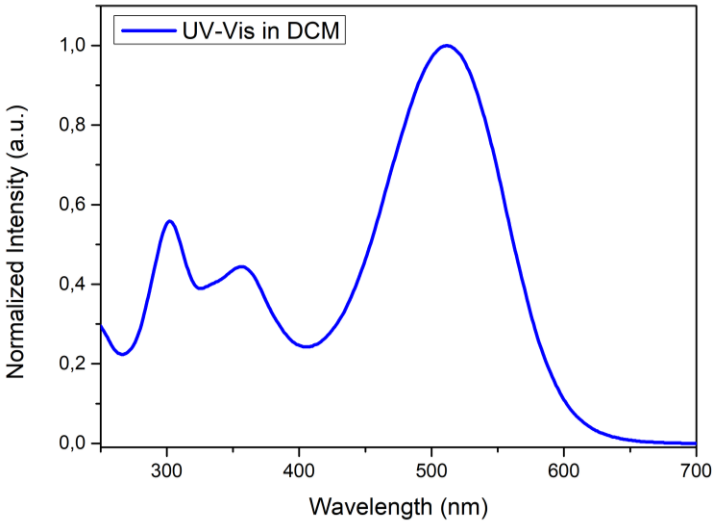


FT-IR (KBr): $\tilde{\nu}$ = 3447, 3061, 2928, 2860, 2214, 1654, 1576, 1542, 1419, 1251 cm^{-1}.

HRMS (ESI) for $C_{43}H_{44}N_4O_2S_2$ [M]$^+$: calcd: 716.2737, found: 716.2741 *m/z*.

PHOTOPHYSICS

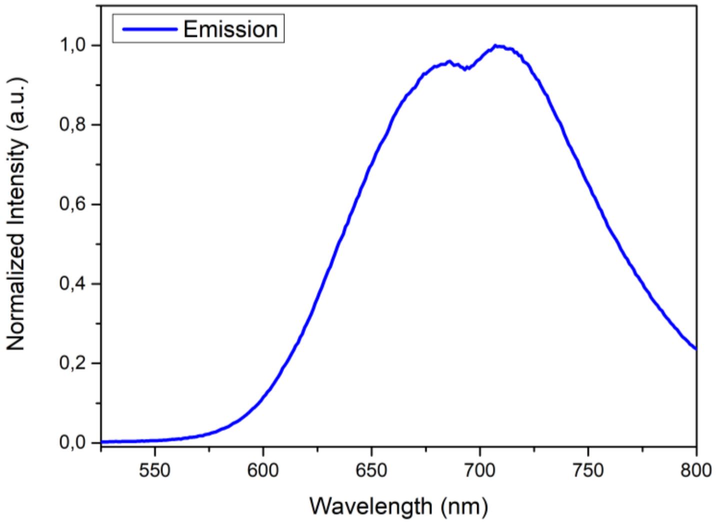
Absorption spectrum (CH_2Cl_2)



Absorption parameters

λ_{max} (CH_2Cl_2) = 512 nm (ε_{max} = 3.04 × 10^4 M^{-1} cm^{-1})
λ_{max} (@Pt/TiO_2) = 475 nm

Emission spectrum (CH_2Cl_2, λ_{exc} = 512 nm, 25 °C)



Emission parameters

λ_{max} (CH_2Cl_2) = 686, 707 nm.

ELECTROCHEMISTRY

Cyclic Voltammetry (Working electrode: glassy carbon; counter-electrode: platinum; reference electrode: aqueous Ag/AgCl (sat. KCl); supporting electrolyte: $C_{16}H_{36}NPF_6$ 0.1 M in THF; ferrocene as an external standard)

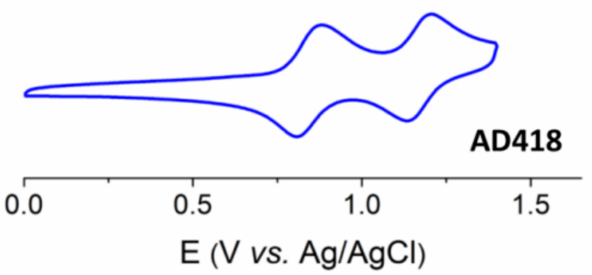
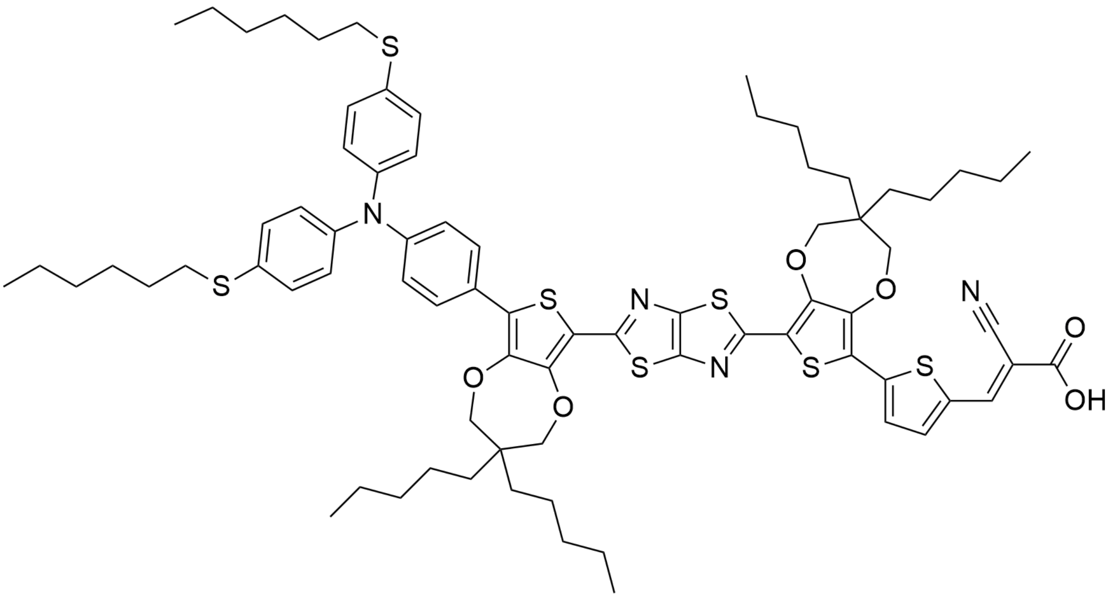


Photo-electrochemical parameters

- $E_{S+/S}$ = + 1.05 V *vs.* NHE (Values obtained using ferrocene as an external standard and assuming a reduction potential of +0.62 V for the Fc^+/Fc couple *vs.* NHE)
- E_{0-0} = + 2.07 eV (Calculated from the intersection of the absorption and emission spectra in DCM solution)
- $E_{S+/S*}$ = – 1.02 V *vs.* NHE (Calculated using the equation $E_{S+/S*} = E_{S+/S} - E_{0-0}$)

2 Colorante TTZ5

TTZ5



Chemical Formula: $C_{76}H_{94}N_4O_6S_7$
Molecular Weight: 1384.04

SUMMARY

^{1}H-NMR	☒	XRD	☐	Abs. spectra	☒
^{13}C-NMR	☒	TG	☐	Abs. coeff.	☒
other nuclei	☐	DTA	☐	Ems. spectra	☒
FT-IR	☒	Redox	☒	QY	☐
MS	☒	Mol. Model.	☐	LT	☐
H, C, N	☒				

SYNTHESIS

Reagents	MW	d (g/mL)	mmol / eq	m (mg)	V (mL)
5-(8-(5-(8-(4-(bis(4-(hexylthio)phenyl)amino) phenyl)-3,3-dipentyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepin-6-yl)thiazolo[5,4-*d*]thiazol-2-yl)-3,3-dipentyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4] dioxepin-6-yl)thiophene-2-carbaldehyde	1316.99	-	0.06 / 1.0	84	-
Cyanoacetic acid	85.06	-	0.64 / 10	54	-
Ammonium acetate	77.08	-	0.25 / 4.0	20	-
Toluene	92.14	0.867	-	-	3.0
Acetic acid	60.05	1.05	-	-	3.0

Procedure

Under inert atmosphere, the aldehyde was dissolved in toluene and glacial acetic acid (1:1 v/v), then cyanoacetic acid and ammonium acetate were added. The resulting mixture was stirred at 110 °C for 3 hours, then cooled down to room temperature. After dilution with additional toluene, the organic phase was washed twice with $HCl_{(aq.)}$ 0.3 M and the solvent evaporated.

Purification

The resulting solid was purified by washing with several portions of n-pentane, ethyl acetate, and methanol, and dried under vacuum.

Yield: 97% (85 mg, 0.06 mmol)

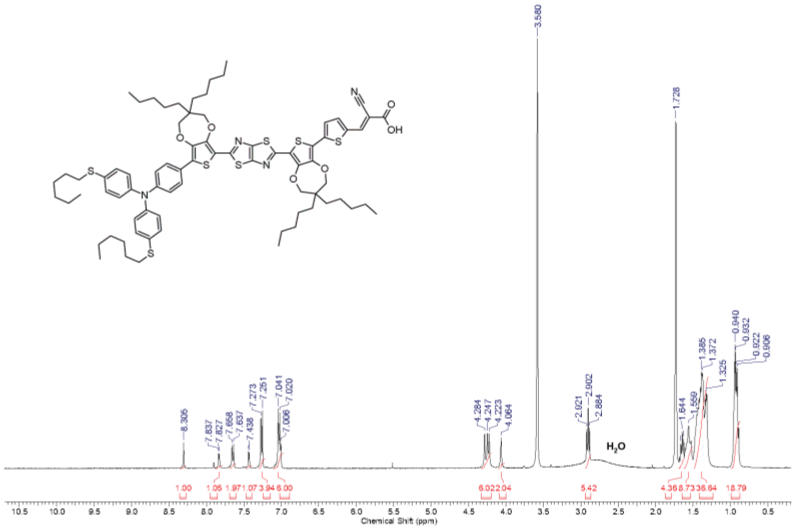
Biblio

Chem. Commun., **2014**, *50*, 13952.

CHARACTERIZATION

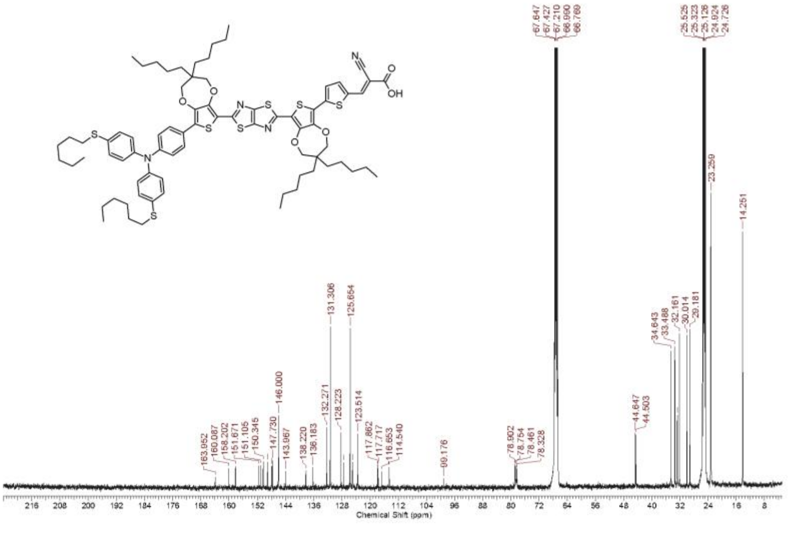
^{1}H NMR (THF-d_8, 400 MHz)

δ (ppm) = 8.30 (s, 1H), 7.83 (d, *J* = 4.0 Hz, 1H), 7.64 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 4.0 Hz, 1H), 7.26 (d, *J* = 8.5 Hz, 4H), 7.00–7.05 (m, 6H), 4.28 (s, 2H), 4.24 (s, 2H), 4.22 (s, 2H), 4.06 (s, 2H), 2.90 (t, *J* = 7.3 Hz, 4H), 1.62–1.68 (m, 4H), 1.53–1.59 (m, 8H), 1.27–1.51 (m, 36H), 0.88–0.95 (m, 18H).



^{13}C-NMR (THF-d_8, 100 MHz)

δ (ppm) = 164.0, 160.1, 158.2, 151.7, 151.1, 150.3, 149.1, 148.0, 147.7, 146.0, 145.9, 144.0, 138.2, 136.2, 132.3, 131.3, 128.2, 127.4, 125.7, 125.0, 124.9, 123.5, 117.9, 117.7, 116.7, 114.5, 99.2, 78.9, 78.8, 78.5, 78.3, 67.8, 44.7, 44.5, 34.6, 33.50, 33.49, 32.8, 32.7, 32.2, 30.0, 29.2, 23.27, 23.26, 14.3, 14.2.



FT-IR (KBr): $\tilde{\nu}$ = 3020, 2924, 2857, 2213, 1678, 1563, 1407, 1057cm^{-1}

ESI-MS: *m/z* = 1383.89 [M+1]$^+$

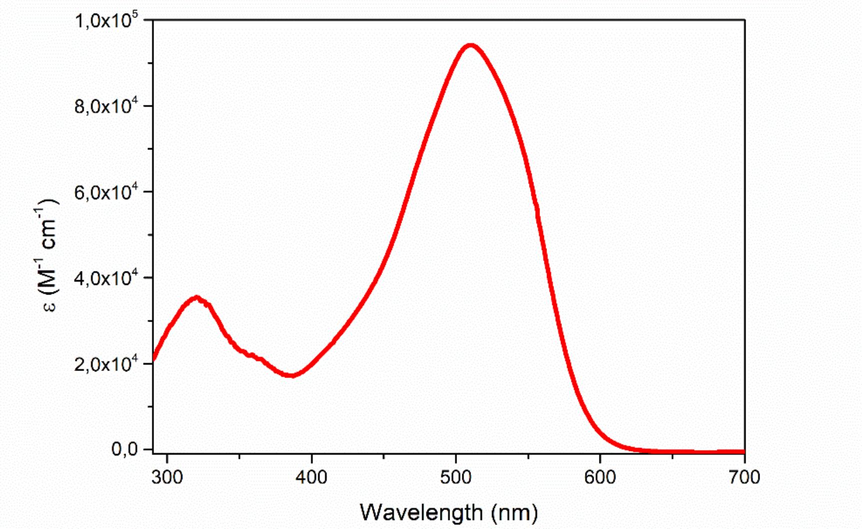
H, C, N

Calculated for $C_{76}H_{94}N_4O_6S_7$: C, 65.95; H, 6.85; N, 4.05.

Found: C, 65.69; H, 6.94; N, 4.00.

PHOTOPHYSICS

Absorption spectrum (THF)

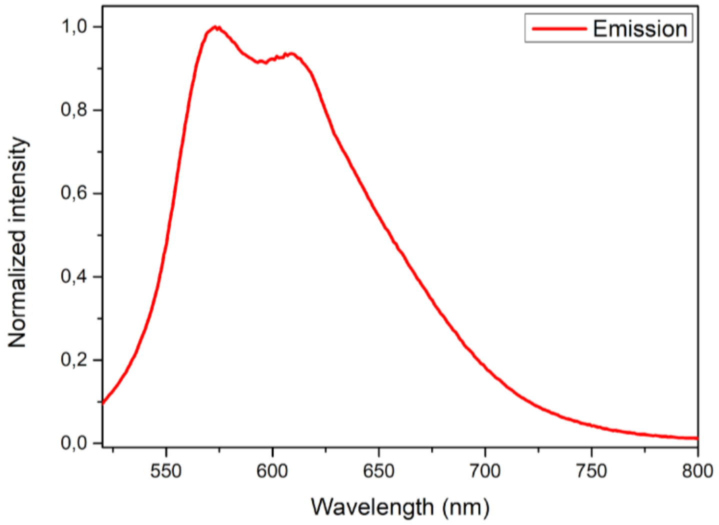


Absorption parameters

λ_{max} (THF) = 510 nm (ε_{max} = 9.41 × 10^4 M^{-1} cm^{-1})

λ_{max} (@TiO_2) = 487 nm

Emission spectrum (THF, λ_{exc} = 510 nm, 25 °C)



Emission parameters

λ_{max} (THF) = 573 nm.

ELECTROCHEMISTRY

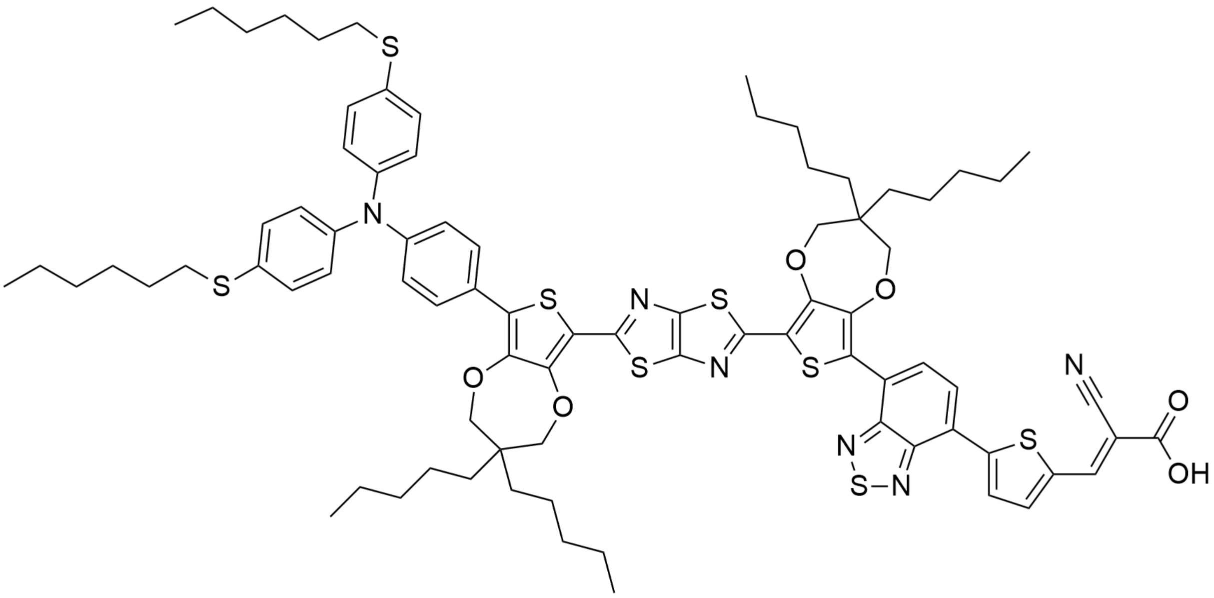
Cyclic Voltammetry (Working electrode: glassy carbon; counter-electrode: platinum; reference electrode: aqueous Ag/AgCl NaCl (3M); supporting electrolyte: $C_{16}H_{36}NPF_6$ 0.1 M in DCM; ferrocene as an external standard)

Photo-electrochemical parameters

- $E_{S+/S}$ = + 0.91 V *vs.* NHE
- $E_{0\text{–}0}$ = + 2.16 eV (Calculated from the intersection of the absorption and emission spectra in THF solution)
- E_{S+/S^*} = – 1.25 V *vs.* NHE (Calculated using the equation $E_{S+/S^*} = E_{S+/S} - E_{0\text{–}0}$)

3 Colorante TTZ9

TTZ9



Chemical Formula: $C_{82}H_{96}N_6O_6S_8$
Molecular Weight: 1518.20

SUMMARY					
^{1}H-NMR	☒	XRD	☐	Abs. spectra	☒
^{13}C-NMR	☒	TG	☐	Abs. coeff.	☒
other nuclei	☐	DTA	☐	Ems. spectra	☐
FT-IR	☒	Redox	☒	QY	☐
MS	☒	Mol. Model.	☐	LT	☐
H, C, N	☐				

SYNTHESIS

Reagents	MW	d (g/mL)	mmol / eq	m (mg)	V (mL)
5-(7-(8-(5-(8-(4-(bis(4-(hexylthio)phenyl)amino)phenyl)-3,3-dipentyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepin-6-yl)thiazolo[5,4-*d*]thiazol-2-yl)-3,3-dipentyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepin-6-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)thiophene-2-carbaldehyde	1451.15	-	0.067 / 1.0	97	-
Cyanoacetic acid	85.06	-	0.668 / 10	57	-
Ammonium acetate	77.08	-	0.267 / 4.0	21	-
Toluene	92.14	0.867	-	-	3.0
Acetic acid	60.05	1.05	-	-	1.5

Procedure

Under inert atmosphere, the aldehyde was dissolved in toluene and glacial acetic acid (2:1 v/v), then cyanoacetic acid and ammonium acetate were added. The resulting mixture was stirred at 110 °C for 3 hours, then cooled down to room temperature. After dilution with additional toluene, the organic phase was washed twice with $HCl_{(aq.)}$ 0.3 M and the solvent evaporated.

Purification

The resulting solid was purified by washing with several portions of n-pentane, ethyl acetate, and methanol, and dried under vacuum.

Yield: 85% (86 mg, 0.057 mmol)

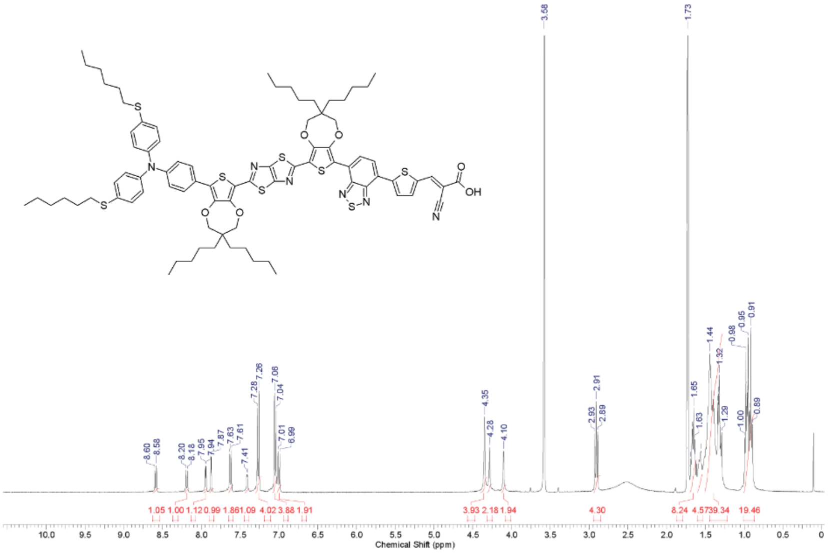
Biblio

Sustainable Energy Fuels, **2020**, *4*, 2309-2321

CHARACTERIZATION

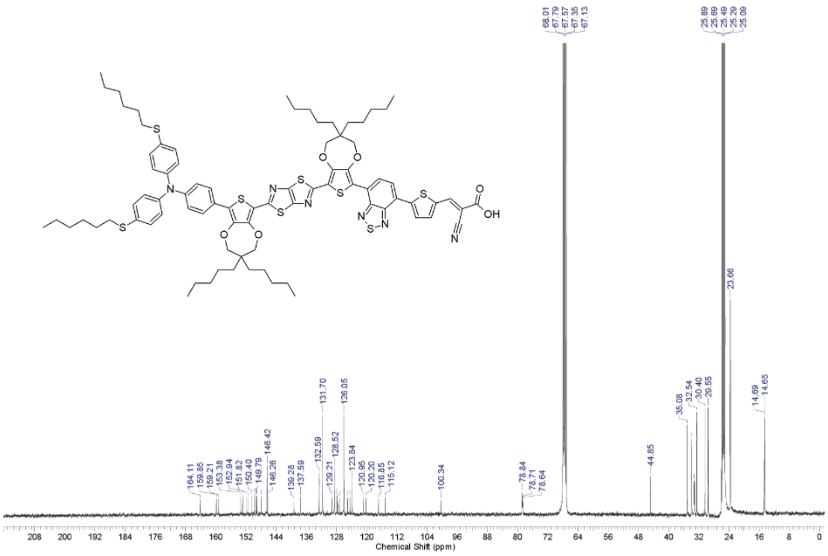
^{1}H NMR (THF-d_8, 400 MHz)

δ (ppm) = = 8.49 (d, *J* = 7.6 Hz, 1H), 8.21–8.29 (m, 2H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 4.0 Hz, 1H), 7.61 (d, *J* = 8.7 Hz, 2H), 7.27 (d, *J* = 8.7 Hz, 4H), 7.04 (d, *J* = 8.7 Hz, 4H), 6.99 (d, *J* = 8.7 Hz, 2H), 4.29 (s, 2H), 4.27 (s, 2H), 4.23 (s, 2H), 4.05 (s, 2H), 2.91 (t, *J* = 7.4 Hz, 4H), 1.60–1.70 (m, 8H), 1.26–1.58 (m, 40H), 0.93–1.02 (m, 12H), 0.91 (t, *J* = 6.9 Hz, 6H).



^{13}C-NMR (THF-d_8, 100 MHz)

δ (ppm) = 164.1, 159.9, 159.2, 153.4, 152.9, 151.8, 151.5, 150.4, 149.8, 149.3, 149.1, 147.9, 146.4, 146.3, 139.3, 137.6, 132.6, 131.7, 129.2, 128.5, 127.9, 127.7, 127.2, 126.1, 125.1, 124.4, 123.8, 121.0, 120.2, 116.9, 115.1, 100.3, 78.8, 78.7, 78.6, 44.9, 44.8, 35.1, 34.0, 33.9, 33.3, 33.2, 32.5, 30.4, 29.6, 23.7, 23.6, 14.69, 14.65, 14.57.

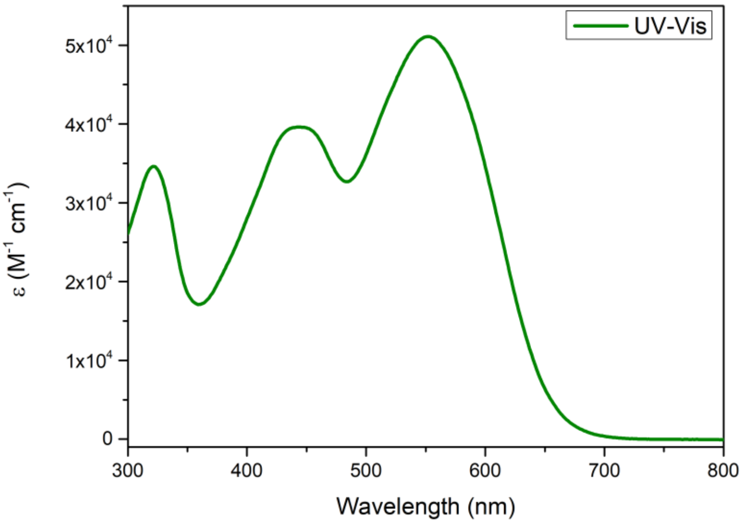


FT-IR (KBr): $\tilde{\nu}$ = 3421, 3025, 2927, 2856, 2216, 1685, 1654, 1571, 1483, 1420, 1261, 1052 cm^{-1}

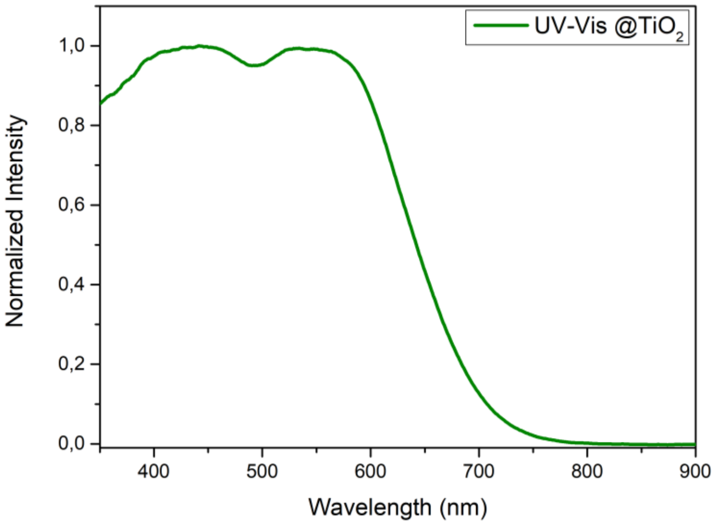
HRMS (ESI) for $C_{82}H_{96}N_6O_6S_8$ [M]$^+$: calcd. 1516.5152, found: 1516.5153 *m/z*.

PHOTOPHYSICS

Absorption spectrum (THF)



Absorption spectrum (@ TiO_2)



Absorption parameters

λ_{max} (THF) = 551 nm (ε_{max} = 5.22 × 10^4 M^{-1} cm^{-1}); 443 nm (ε_{max} = 4.05 × 10^4 M^{-1} cm^{-1}).
λ_{max} (@TiO_2) = 559, 431 nm

ELECTROCHEMISTRY

Cyclic Voltammetry (Working electrode: glassy carbon; counter-electrode: platinum; reference electrode: aqueous Ag/AgCl (sat. KCl); supporting electrolyte: $C_{16}H_{36}NPF_6$ 0.1 M in $CHCl_3$; ferrocene as an external standard)

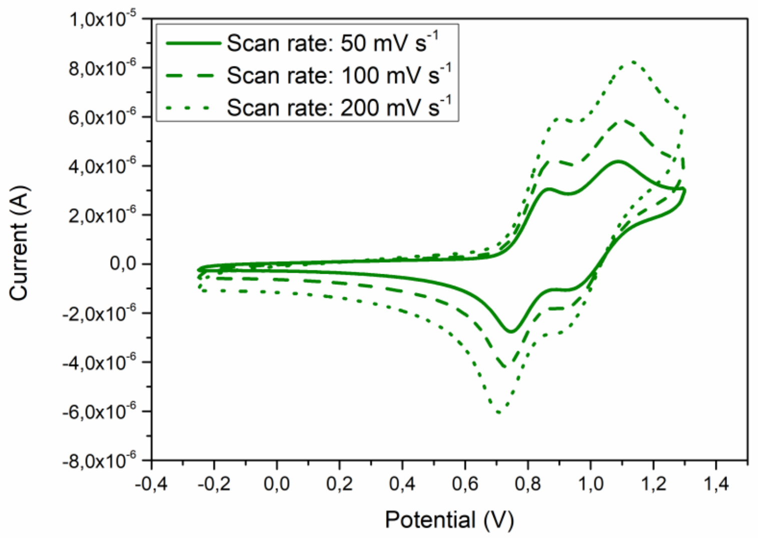
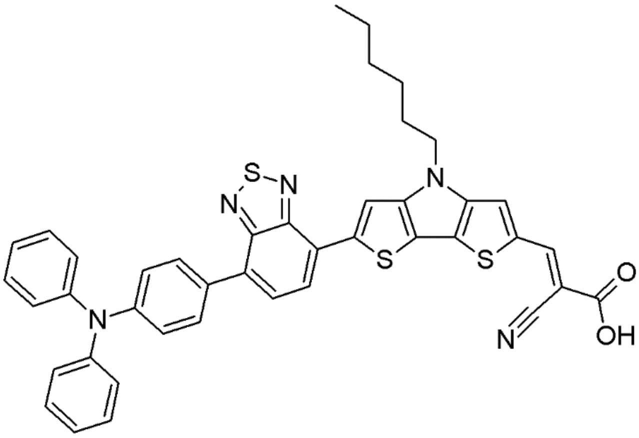


Photo-electrochemical parameters

- $E_{S+/S}$ = + 0.87 V *vs.* NHE
- $E_{0\text{–}0}$ = + 1.98 eV (Calculated from the data in THF solution, based on the corresponding Tauc plots)
- $E_{S+/S*}$ = – 1.11 V *vs.* NHE (Calculated using the equation $E_{S+/S*} = E_{S+/S} - E_{0\text{–}0}$)

4 Colorante BTD-DTP1

BTD-DTP1



Chemical Formula: $C_{42}H_{33}N_5O_2S_3$
Molecular Weight: 735.94

SUMMARY

^{1}H-NMR	☒	XRD	☐	Abs. spectra	☒
^{13}C-NMR	☒	TG	☐	Abs. coeff.	☒
other nuclei	☐	DTA	☐	Ems. spectra	☒
FT-IR	☒	Redox	☒	QY	☐
MS	☒	Mol. Model.	☐	LT	☐
H, C, N	☐				

SYNTHESIS

Reagents	**MW**	**d (g/mL)**	**mmol / eq**	**m (g)**	**V (mL)**
6-(7-(4-(diphenylamino)phenyl)benzo[*c*][1,2,5]thiadiazol-4-yl)-4-hexyl-4*H*-dithieno[3,2-*b*:2',3'-*d*]pyrrole-2-carbaldehyde	668.90	-	2.24 / 1.0	1.5	-
Cyanoacetic acid	85.06	-	11.2 / 5.0	0.954	-
Ammonium acetate	77.08	-	3.36 / 1.5	0.259	-
Toluene	92.14	0.867	-	-	20
Acetic acid	60.05	1.05	-	-	10

Procedure

Under inert atmosphere, the aldehyde was dissolved in toluene and glacial acetic acid (2:1 v/v), then cyanoacetic acid and ammonium acetate were added. The resulting mixture was stirred at 110 °C for 4 hours, then cooled down to room temperature. After dilution with additional toluene, the organic phase was washed twice with $HCl_{(aq.)}$ 0.3 M and the solvent evaporated.

Purification

The resulting solid was purified by washing with several portions of n-pentane, ethyl acetate, and methanol, and dried under vacuum.

Yield: 85% (1.41 g, 1.92 mmol)

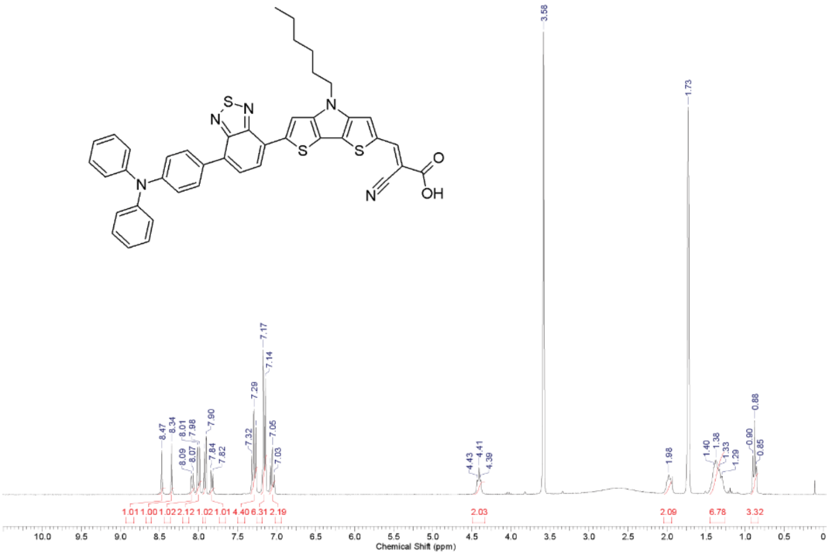
Biblio

Sustainable Energy Fuels, **2021**, *5*, 1171

CHARACTERIZATION

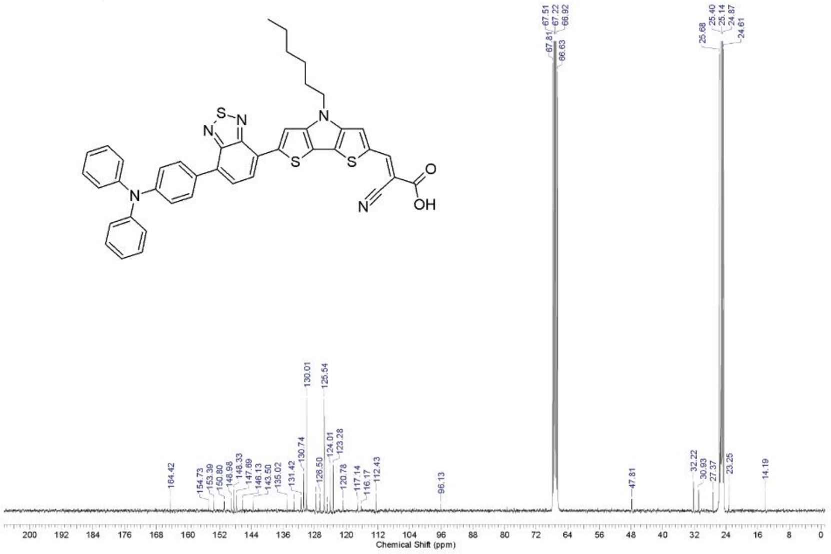
^{1}H NMR (THF-d_8, 400 MHz)

δ (ppm) = 8.47 (s, 1H), 8.34 (s, 1H), 8.08 (d, *J* = 7.3 Hz, 1H), 8.00 (d, *J* = 8.8 Hz, 2H), 7.92 (s, 1H), 7.83 (d, *J* = 7.3 Hz, 1H), 7.24–7.34 (m, 4H), 7.12–7.20 (m, 6H), 7.00–7.10 (m, 2H), 4.41 (t, *J* = 6.6 Hz, 2H), 1.94–2.04 (m, 2H), 1.26–1.44 (m, 6H), 0.83–0.94 (m, 3H).



^{13}C-NMR (THF-d_8, 100 MHz)

δ (ppm) = 164.4, 154.7, 153.4, 150.8, 149.0, 148.3, 147.7, 146.1, 143.5, 135.0, 133.2, 131.4, 130.7, 130.0, 127.6, 126.8, 126.5, 125.5, 124.8, 124.0, 123.3, 120.8, 117.1, 116.2, 112.4, 96.1, 47.8, 32.2, 30.9, 27.4, 23.3, 14.2.

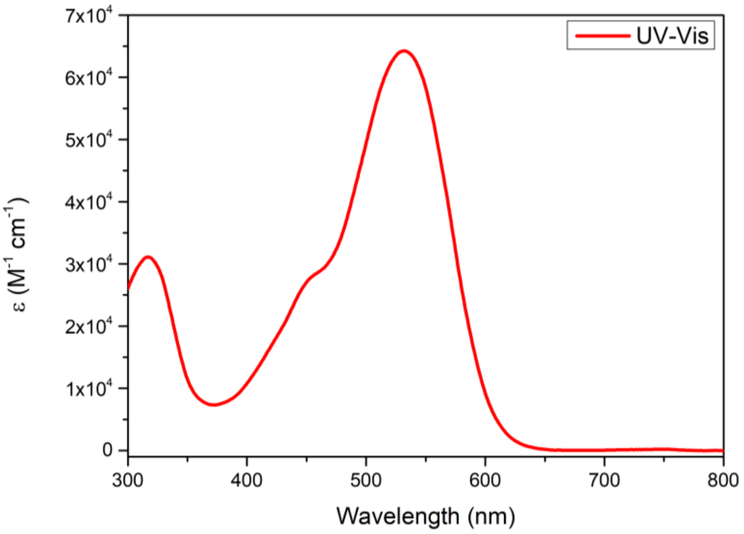


FT-IR (KBr): $\tilde{\nu}$ = 3439, 3033, 2915, 2848, 2206, 1671, 1576, 1491, 1258, 1177, 816, 694 cm^{-1}

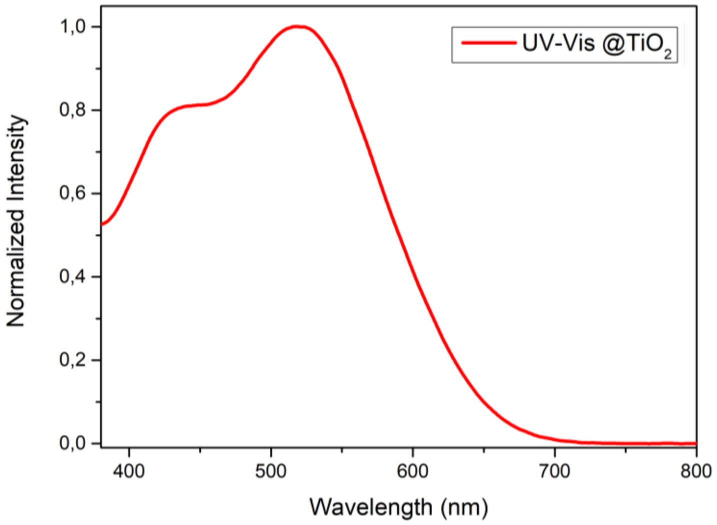
HRMS (ESI) for $C_{42}H_{33}N_5O_2S_3$ [M]$^+$: calcd. 735.17909, found: 735.17888 *m/z*.

PHOTOPHYSICS

Absorption spectrum (THF)



Absorption spectrum (@TiO_2)

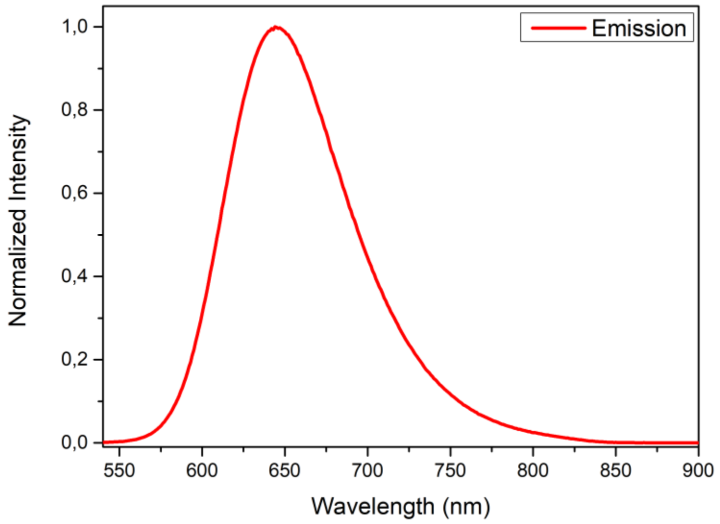


Absorption parameters

λ_{max} (THF) = 532 nm (ε_{max} = 6.43 × 10^4 M^{-1} cm^{-1})

λ_{max} (@TiO_2) = 523 nm

Emission spectrum (THF, λ_{exc} = 525 nm, 25 °C)



Emission parameters

λ_{max} (THF) = 644 nm.

ELECTROCHEMISTRY

Cyclic Voltammetry (Working electrode: glassy carbon; counter-electrode: platinum; reference electrode: Ag/$AgNO_3$ in MeCN; supporting electrolyte: $C_{16}H_{36}NPF_6$ 0.1 M in THF; ferrocene as an external standard)

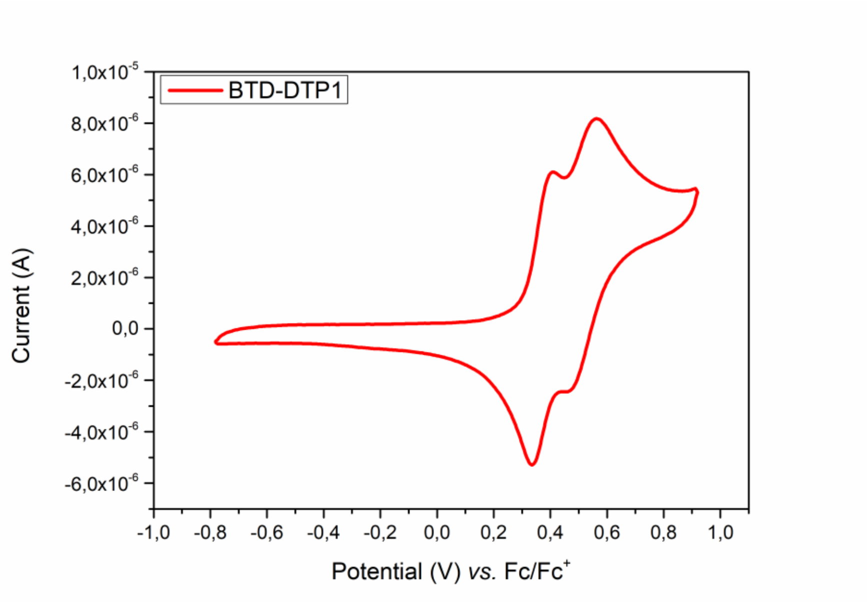
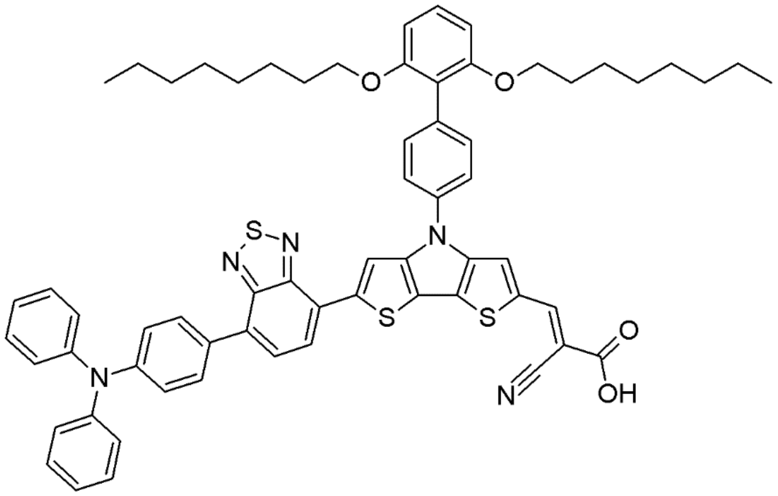


Photo-electrochemical parameters

- $E_{S+/S}$ = + 1.00 V *vs.* NHE (Values obtained using ferrocene as an external standard and assuming a reduction potential of +0.63 V for the Fc^+/Fc couple *vs.* NHE)
- $E_{0\text{–}0}$ = + 2.09 eV (Calculated from the intersection of the absorption and emission spectra in THF solution)
- E_{S+/S^*} = – 1.09 V *vs.* NHE (Calculated using the equation $E_{S+/S^*} = E_{S+/S} - E_{0\text{–}0}$)

5 Colorante BTD-DTP2

BTD-DTP2



Chemical Formula: $C_{64}H_{61}N_5O_4S_3$
Molecular Weight: 1060.40

SUMMARY

^{1}H-NMR	✓	XRD	☐	Abs. spectra	✓
^{13}C-NMR	✓	TG	☐	Abs. coeff.	✓
other nuclei	☐	DTA	☐	Ems. spectra	✓
FT-IR	✓	Redox	✓	QY	☐
MS	✓	Mol. Model.	☐	LT	☐
H, C, N	☐				

SYNTHESIS

Reagents	MW	d (g/mL)	mmol / eq	m (mg)	V (mL)
4-(2',6'-bis(octyloxy)-[1,1'-biphenyl]-4-yl)-6-(7-(4-(diphenylamino)phenyl)benzo[*c*][1,2,5] thiadiazol-4-yl)-4*H*-dithieno[3,2-*b*:2',3'-*d*]pyrrole-2-carbaldehyde	993.35	-	0.121 / 1.0	120	-
Cyanoacetic acid	85.06	-	0.604 / 5.0	51	-
Ammonium acetate	77.08	-	0.181 / 1.5	14	-
Toluene	92.14	0.867	-	-	3.0
Acetic acid	60.05	1.05	-	-	1.5

Procedure

Under inert atmosphere, the aldehyde was dissolved in toluene and glacial acetic acid (2:1 v/v), then cyanoacetic acid and ammonium acetate were added. The resulting mixture was stirred at 110 °C for 4 hours, then cooled down to room temperature. After dilution with additional toluene, the organic phase was washed twice with $HCl_{(aq.)}$ 0.3 M and the solvent evaporated.

Purification

The resulting solid was purified by washing with several portions of n-pentane, ethyl acetate, and methanol, and dried under vacuum.

Yield: 98% (126 mg, 0.119 mmol)

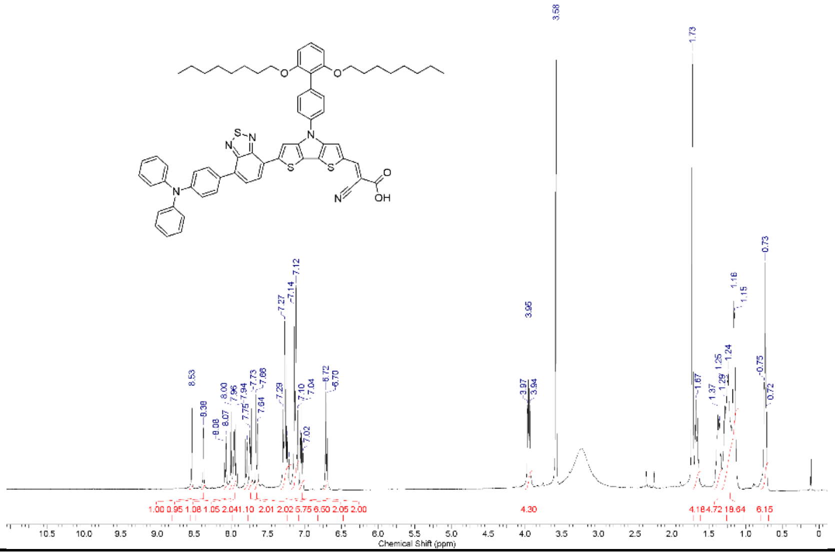
Biblio

Sustainable Energy Fuels, **2021**, *5*, 1171

CHARACTERIZATION

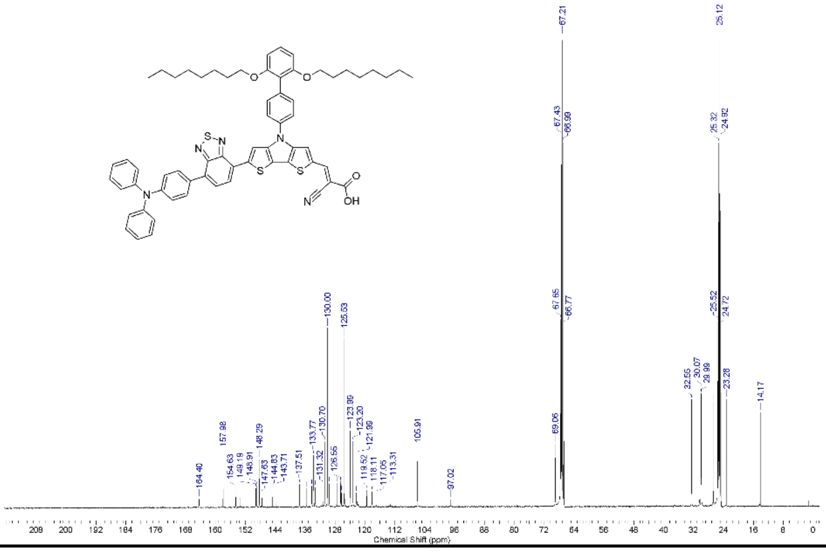
^{1}H NMR (THF-d_8, 400 MHz)

δ (ppm) = 8.53 (s, 1H), 8.38 (s, 1H), 8.08 (d, *J* = 7.6 Hz, 1H), 8.00 (s, 1H), 7.95 (d, *J* = 8.6 Hz, 2H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.20–7.32 (m, 5H), 7.08–7.19 (m, 6H), 7.04 (t, *J* = 8.4 Hz, 2H), 6.71 (d, *J* = 8.4 Hz, 2H), 3.95 (t, *J* = 6.4 Hz, 4H), 1.67 (q, *J* = 6.8 Hz, 4H), 1.32–1.42 (m, 4H), 1.10–1.31 (m, 16H), 0.69–0.80 (m, 6H).



^{13}C-NMR (THF-d_8, 100 MHz)

δ (ppm) = 164.4, 158.0, 154.6, 153.3, 149.2, 148.9, 148.3, 147.6, 144.8, 143.7, 137.5, 135.6, 134.2, 133.8, 133.3, 131.3, 130.7, 130.0, 129.5, 127.5, 126.6, 126.5, 126.3, 125.5, 124.0, 123.2, 122.4, 122.0, 119.5, 118.1, 117.1, 113.3, 105.9, 97.0, 69.1, 32.6, 30.1, 30.0, 29.9, 26.8, 23.3, 14.2.

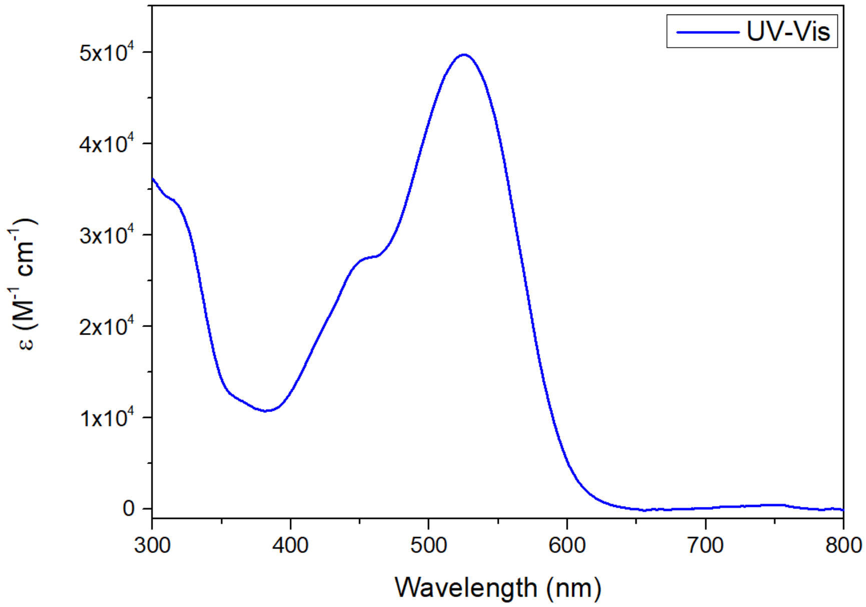


FT-IR (KBr): $\tilde{\nu}$ = 3453, 3033, 2922, 2856, 2206, 1664, 1572, 1487, 1380, 1251, 1159, 1096, 816, 698 cm^{-1}

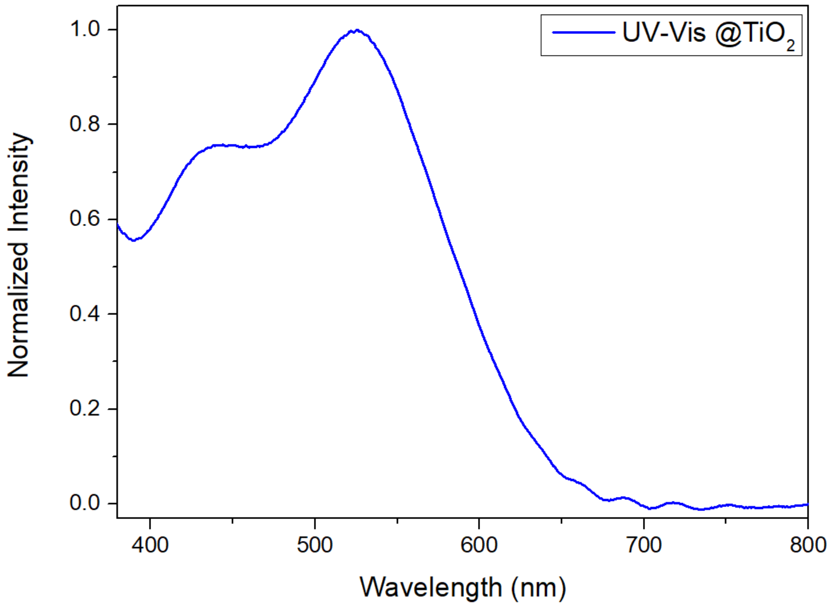
HRMS (ESI) for $C_{64}H_{61}N_5O_4S_3$ [M]$^+$: calcd. 1059.38802, found: 1059.38610 *m/z*.

PHOTOPHYSICS

Absorption spectrum (THF)



Absorption spectrum (@TiO_2)

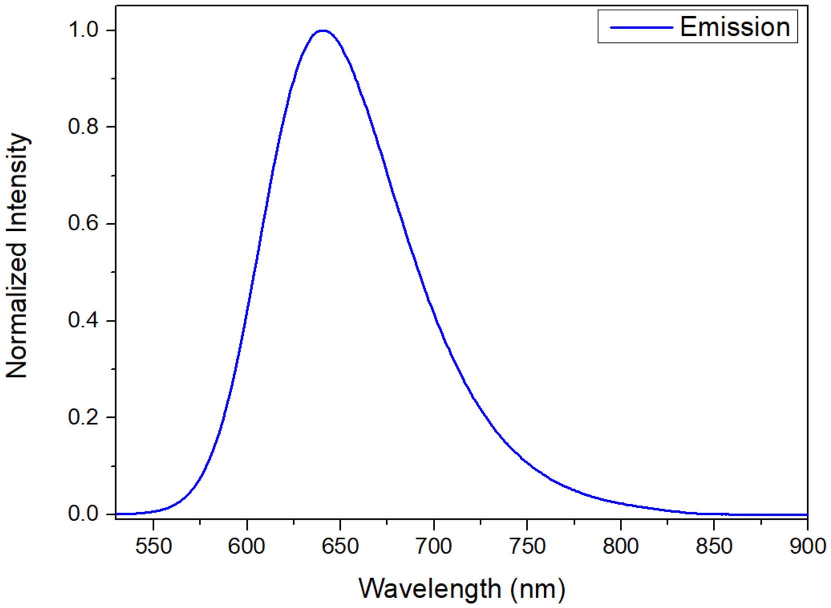


Absorption parameters

λ_{max} (THF) = 525 nm (ε_{max} = 4.95 × 10^4 M^{-1} cm^{-1})

λ_{max} (@TiO_2) = 526 nm

Emission spectrum (THF, λ_{exc} = 525 nm, 25 °C)



Emission parameters

λ_{max} (THF) = 639 nm.

ELECTROCHEMISTRY

Cyclic Voltammetry (Working electrode: glassy carbon; counter-electrode: platinum; reference electrode: Ag/AgNO$_3$ in MeCN; supporting electrolyte: $C_{16}H_{36}NPF_6$ 0.1 M in THF; ferrocene as an external standard)

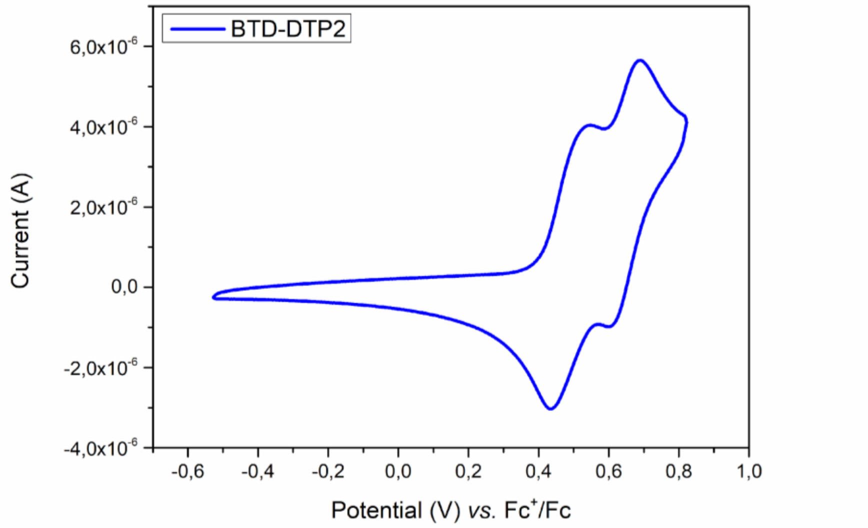
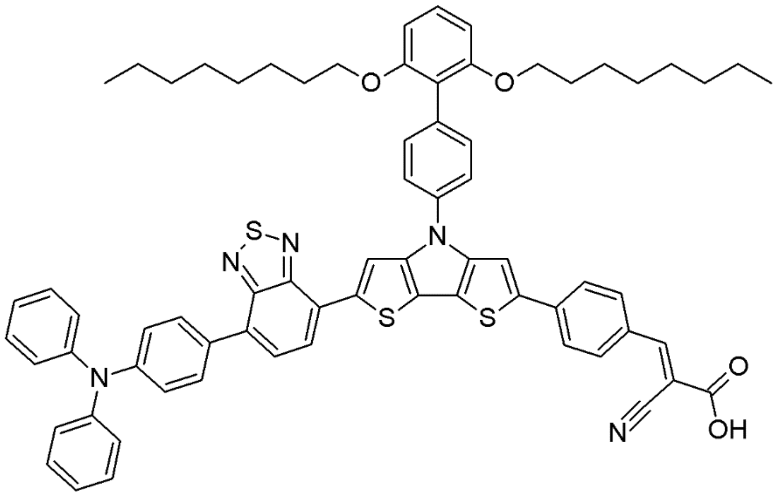


Photo-electrochemical parameters

- $E_{S+/S}$ = + 1.12 V *vs.* NHE (Values obtained using ferrocene as an external standard and assuming a reduction potential of +0.63 V for the Fc^{+}/Fc couple *vs.* NHE)
- $E_{0–0}$ = + 2.11 eV (Calculated from the intersection of the absorption and emission spectra in THF solution)
- $E_{S+/S*}$ = – 0.99 V *vs.* NHE (Calculated using the equation $E_{S+/S*} = E_{S+/S} – E_{0–0}$)

6 Colorante BTD-DTP3

BTD-DTP3



Chemical Formula: $C_{70}H_{65}N_5O_4S_3$
Molecular Weight: 1136.49

SUMMARY

^{1}H-NMR	☒	XRD	☐	Abs. spectra	☒
^{13}C-NMR	☒	TG	☐	Abs. coeff.	☒
other nuclei	☐	DTA	☐	Ems. spectra	☒
FT-IR	☒	Redox	☒	QY	☐
MS	☒	Mol. Model.	☐	LT	☐
H, C, N	☐				

SYNTHESIS

Reagents	MW	d (g/mL)	mmol / eq	m (mg)	V (mL)
4-(4-(2',6'-bis(octyloxy)-[1,1'-biphenyl]-4-yl)-6-(7-(4-(diphenylamino)phenyl)benzo[*c*][1,2,5]thiadiazol-4-yl)-4*H*-dithieno[3,2-*b*:2',3'-*d*]pyrrol-2-yl)benzaldehyde	1069.45	-	0.047 / 1.0	50	-
Cyanoacetic acid	85.06	-	0.234 / 5.0	20	-
Ammonium acetate	77.08	-	0.070 / 1.5	5.4	-
Toluene	92.14	0.867	-	-	2.0
Acetic acid	60.05	1.05	-	-	1.0

Procedure

Under inert atmosphere, the aldehyde was dissolved in toluene and glacial acetic acid (2:1 v/v), then cyanoacetic acid and ammonium acetate were added. The resulting mixture was stirred at 110 °C for 4 hours, then cooled down to room temperature. After dilution with additional toluene, the organic phase was washed twice with $HCl_{(aq.)}$ 0.3 M and the solvent evaporated.

Purification

The resulting solid was purified by washing with several portions of n-pentane, ethyl acetate, and methanol, and dried under vacuum.

Yield: 77% (41 mg, 0.036 mmol)

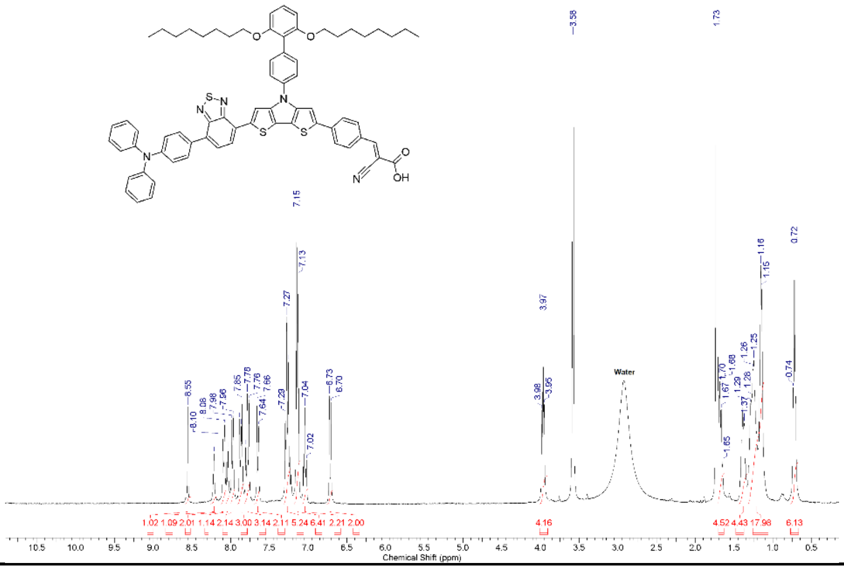
Biblio

Sustainable Energy Fuels, **2021**, *5*, 1171

CHARACTERIZATION

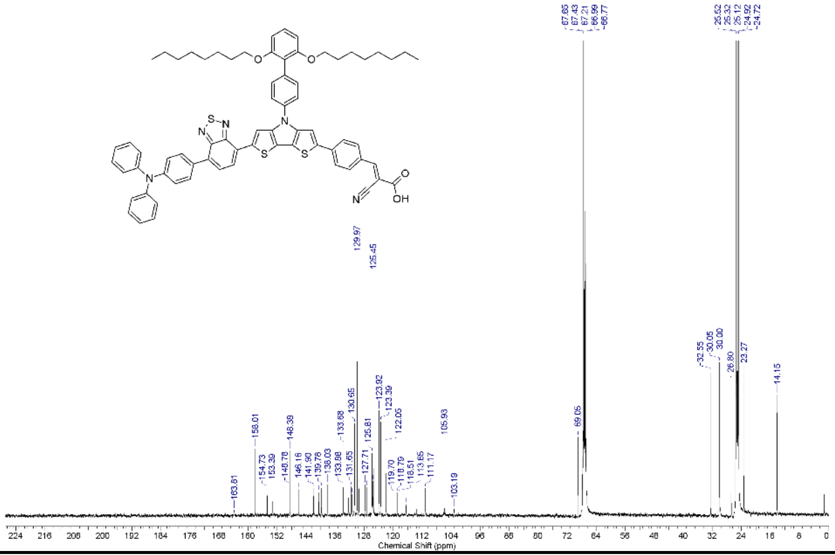
^{1}H NMR (THF-d_8, 400 MHz)

δ (ppm) = 8.55 (s, 1H); 8.22 (s, 1H); 8.09 (d, *J* = 8.4 Hz, 2H); 8.04 (d, *J* = 7.6 Hz, 1H); 7.97 (d, *J* = 8.4 Hz, 2H); 7.83–7.91 (m, 3H); 7.74–7.82 (m, 3H); 7.65 (d, *J* = 8.4 Hz, 2H); 7.22–7.32 (m, 5H); 7.09–7.19 (m, 6H); 7.00–7.08 (m, 2H); 6.71 (d, *J* = 8.4 Hz, 2H); 3.92 (t, *J* = 6.2 Hz, 4H); 1.63–1.72 (m, 4H); 1.33–1.44 (m, 4H); 1.12–1.32 (m, 16H); 0.67–0.78 (m, 6H).



^{13}C-NMR (THF-d_8, 100 MHz)

δ (ppm) = 163.8, 158.0, 154.7, 153.4, 153.3, 148.8, 148.4, 146.2, 146.0, 141.9, 140.5, 139.8, 138.0, 133.9, 133.7, 132.5, 132.4, 131.7, 131.3, 130.7, 130.0, 129.5, 127.7, 127.2, 125.8, 125.6, 125.5, 123.9, 123.4, 122.1, 119.7, 118.8, 118.5, 116.4, 113.7, 111.2, 105.9, 103.2, 69.1, 32.6, 30.1, 30.0, 29.9, 26.8, 23.3, 14.2.

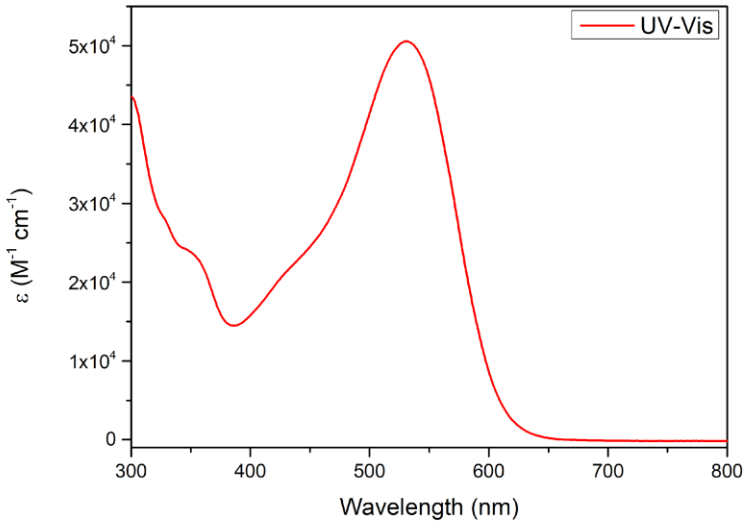


FT-IR (KBr): $\tilde{\nu}$ = 3431, 3018, 2922, 2848, 2214, 1690, 1579, 1491, 1395, 1273, 1181, 1096, 816, 698 cm^{-1}

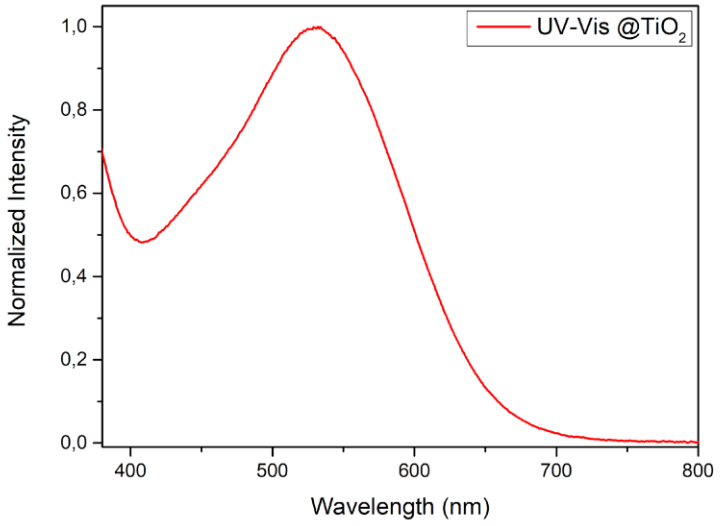
HRMS (ESI) for $C_{70}H_{65}N_5O_4S_3$ [M]$^+$: calcd. 1135.41932, found: 1135.42119 *m/z*.

PHOTOPHYSICS

Absorption spectrum (THF)



Absorption spectrum (@TiO_2)

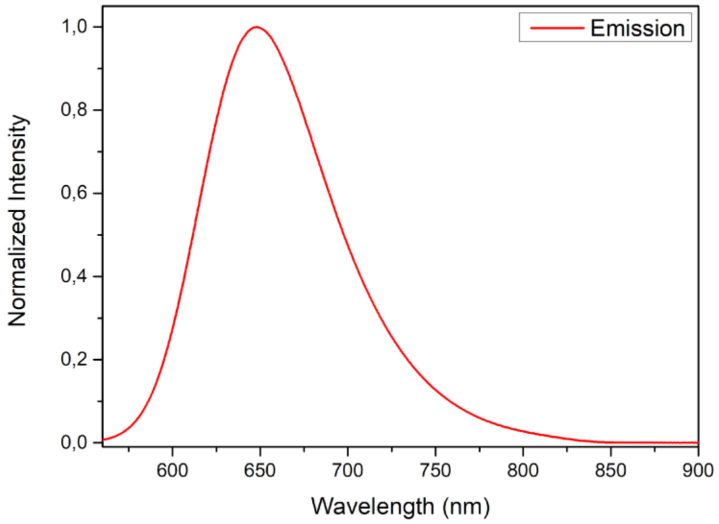


Absorption parameters

λ_{max} (THF) = 531 nm (ε_{max} = 5.08 × 10^4 M^{-1} cm^{-1})

λ_{max} (@TiO_2) = 532 nm

Emission spectrum (THF, λ_{exc} = 531 nm, 25 °C)



Emission parameters

λ_{max} (THF) = 648 nm.

ELECTROCHEMISTRY

Cyclic Voltammetry (Working electrode: glassy carbon; counter-electrode: platinum; reference electrode: Ag/AgNO$_3$ in MeCN; supporting electrolyte: $C_{16}H_{36}NPF_6$ 0.1 M in THF; ferrocene as an external standard)

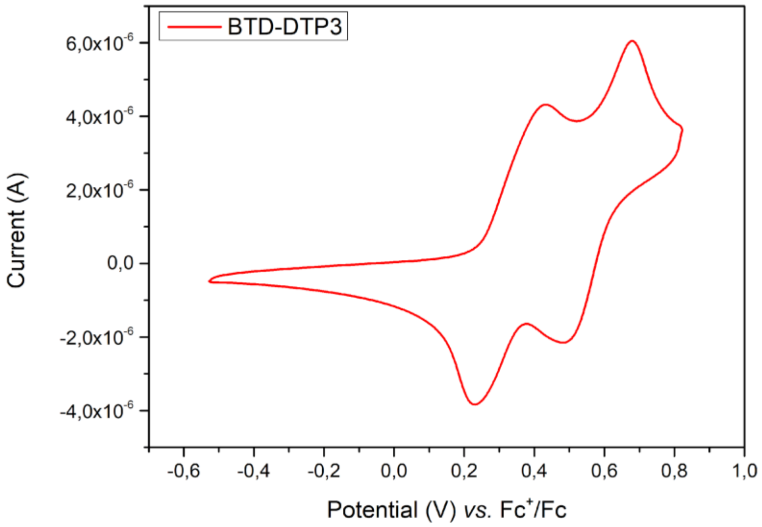


Photo-electrochemical parameters

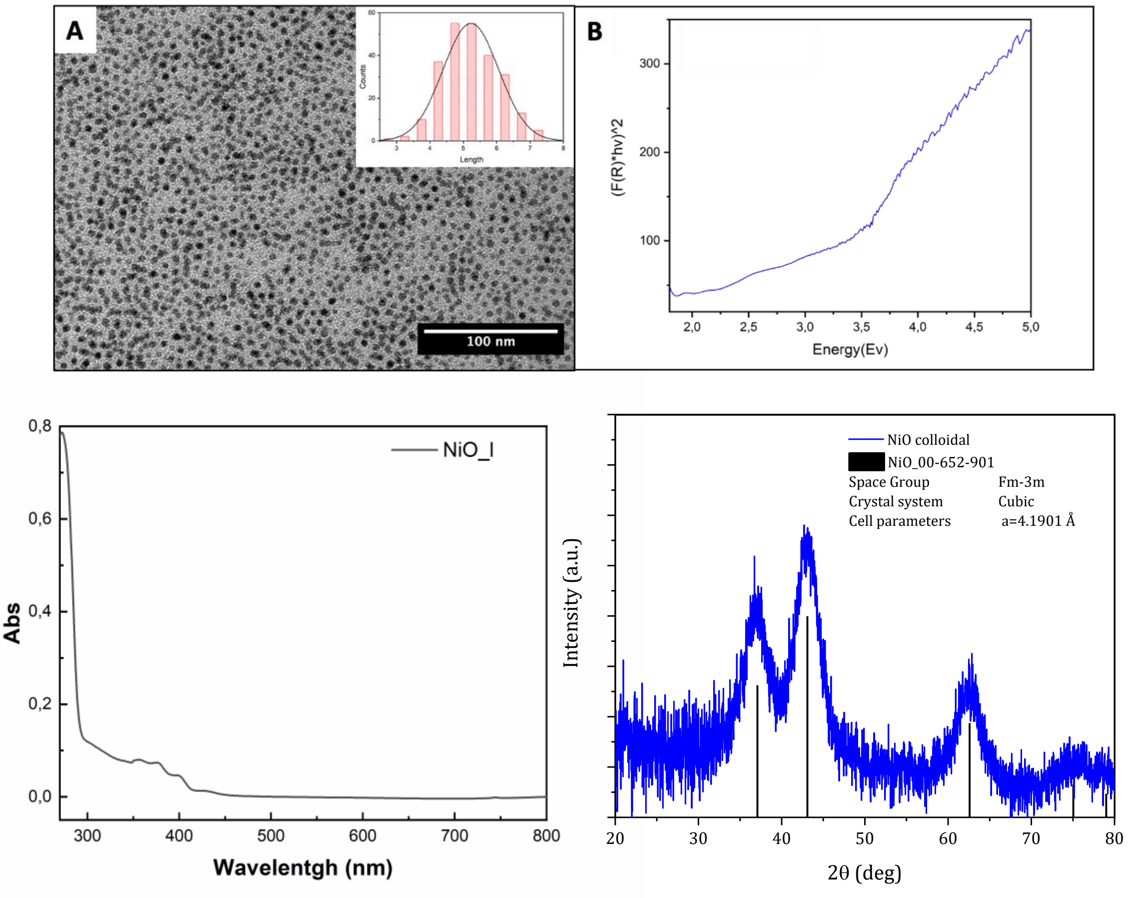
- $E_{S+/S}$ = + 0.96 V *vs.* NHE (Values obtained using ferrocene as an external standard and assuming a reduction potential of +0.63 V for the Fc$^+$/Fc couple *vs.* NHE)
- E_{0-0} = + 2.08 eV (Calculated from the intersection of the absorption and emission spectra in THF solution)
- E_{S+/S^*} = – 1.12 V *vs.* NHE (Calculated using the equation $E_{S+/S^*} = E_{S+/S} - E_{0-0}$)

7 NiO

7.1 NiO Colloidale

<table>
<tr><th colspan="4">Colloidal NiO Nanoparticles</th></tr>
<tr><td>Reagents</td><td>MW (g/mol)</td><td>M</td><td>V(mL)</td></tr>
<tr><td>Nickel(II) acetylacetonate ($C_{10}H_{14}NiO_4$)</td><td>256,91</td><td>1 mmol</td><td></td></tr>
<tr><td>borane-triethylamine complex $[(C_2H_5)_3N{\cdot}BH_3]$</td><td>115.02</td><td>1.4 mmol</td><td>0.350</td></tr>
<tr><td colspan="4">Volume obtained for reactions batch:
colloidal dispersion 0.3 M</td></tr>
<tr><td colspan="4">Ni(II) acetylacetonate ($C_{10}H_{14}NiO_4$) (1 mmol) was dissolved in 15 ml of oleylamine ($C_{18}H_{37}N$) with 1 mmol of oleic acid ($C_{18}H_{34}O_2$). The solution was heated to 110 °C for more than 30 min, stirring vigorously to degas the dissolved oxygen and evaporate moisture, and then cooled and kept at 90 °C. Next, 2.4 mmol of borane-triethylamine complex $[(C_2H_5)_3N{\cdot}BH_3]$ mixed with 2 ml of oleylamine was rapidly injected into the solution. The resulting solution was kept at 90 °C for 1 h under vigorous stirring and then cooled to room temperature. Ethanol (C_2H_6O) (30 ml) was added to the solution, and the mixture was centrifuged at 10000 for 15 min to collect NiO NPs</td></tr>
<tr><td colspan="4">Good dispersive solvents
• chloroform
• dicholoromethane
• hexane</td></tr>
<tr><td colspan="4">Characterization
o XRD
o Abs spectra</td></tr>
</table>

- ☒ Diffuse reflectance spectroscopy
- ○ SEM
- ☒ TEM
- ○ Specific surface area (BET)



Panel A: TEM micrograph of synthesized NiO nanoparticles, inset shows the size distribution. Panel B: Tauc diagram measured from the spectrum in diffuse reflectance. Absorption spectrum and XRD characterization are also reported.

Eg: 3,43 eV
Size: **(5,2 ± 0,8) nm**

Biblio

Usik Kwon et al. Solution-Processible Crystalline NiO Nanoparticles for High-Performance Planar Perovskite Photovoltaic Cells. *Sci Rep* 6**,** 30759 (**2016**).

7.2 NiO Sol-Gel

Sol Gel NiO Nanoparticles

Reagents	MW	M(mol/L)	V(mL)
$Ni(NO_3)_2$-$6H_2O$	290.79	0.25	50
NaOH	39,997	10 M	

Grams for reactions batch

2.5 g

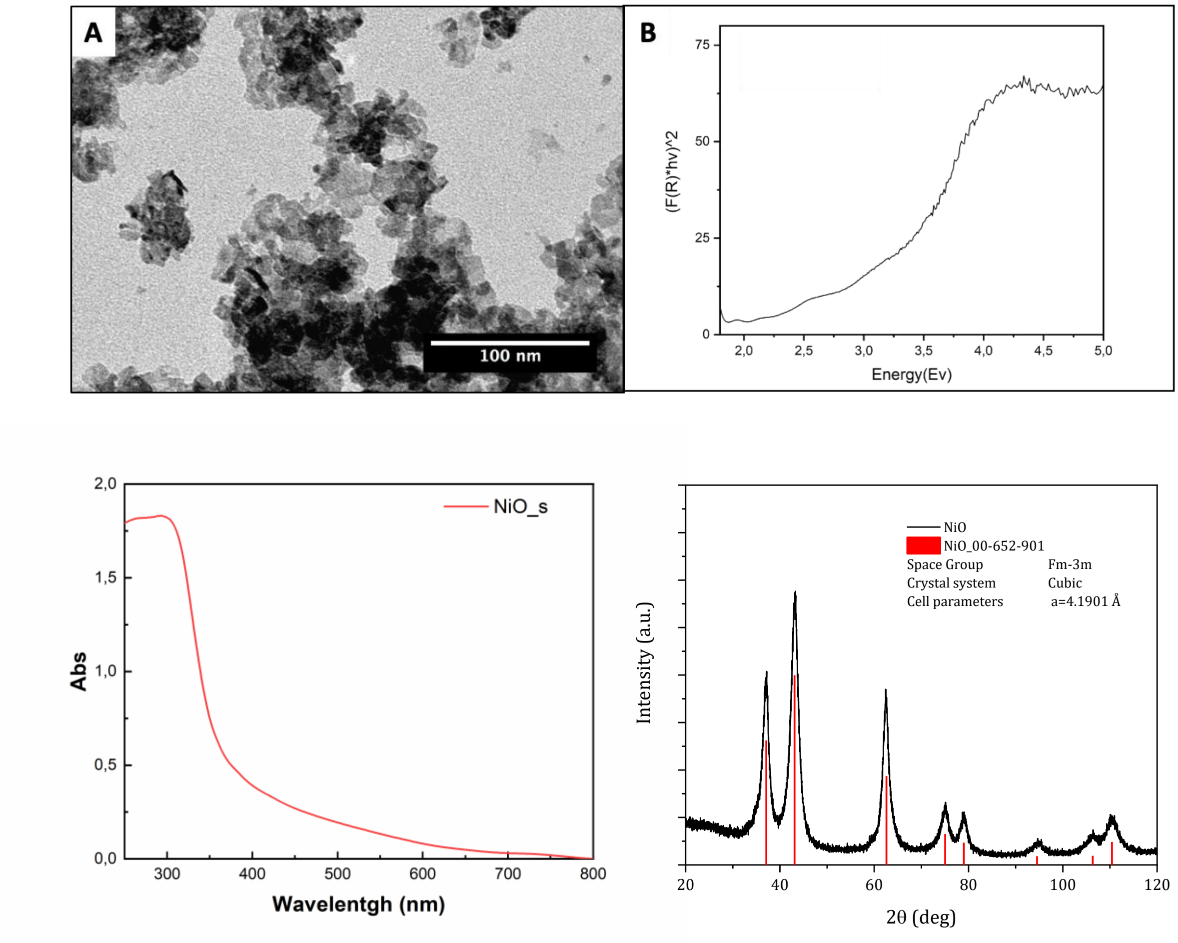
$Ni(NO_3)_2$-$6H_2O$ (0.25 mol), was dissolved in 50 mL of deionized H_2O to obtain a dark green solution. Next, the pH of the solution was adjusted to 10 by adding 10 M NaOH aqueous solution drop by drop. After stirring for 1 h, the green colloidal precipitate was collected by centrifugation at 6000 rpm for 10 min, washed twice with deionized water and dried at 80 °C for 6 h. The green solid obtained was calcined at 270 °C for 2 h to obtain a black powder.

Good dispersive solvent

- Isopropanol
- Butanol

Characterization

✓ XRD
✓ Abs spectra
✓ Diffuse reflectance spectroscopy
✓ UPS
○ SEM
✓ TEM
○ Specific surface area (BET)



Panel A: TEM micrograph of synthesized NiO nanoparticles. Panel B: Tauc plot measured from the spectrum in diffuse reflectance spectroscopy. Absorption spectrum and XRD characterization are also reported.

NiO **Eg: 3,54 eV**

UPS data: **work function = 4.6 eV**, **VBM (vs vacuum) = -5.33 eV**

Biblio:

Ryuji Kaneko et al., Cobalt-doped nickel oxide nanoparticles as efficient hole transport materials for low-temperature processed perovskite solar cells, Solar Energy, 181(**2019**) Pages 243-250,

8 SnO_2

8.1 SnO_2 sintesi idrotermale

SnO_2 Nanoparticles by hydrothermal method

Reagents	MW	M(mol/L)	V(mL)
$SnCl_4*5H_2O$	350.60	0.09	15
NaOH	39.99	pH 6	1
NH_4OH	35.04	pH 6	0.2

Grams for reactions batch

2 g

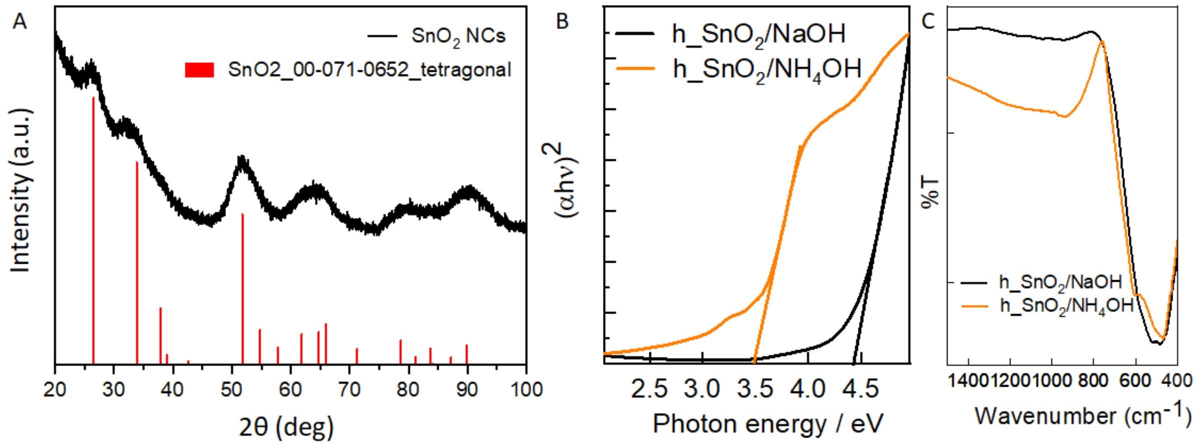
A $SnCl_4·5H_2O$ solution (0.09 M) was prepared by dissolving $SnCl_4·5H_2O$ in a H_2O and ethanol (EtOH) mixture 3:1 (volume ratio) at pH 6 using either NaOH or NH_4OH as base to catalyse the sol-gel reaction, and then was transferred to a Teflon-lined stainless autoclave (15 mL) and kept at 180 °C for 6 h. The products were collected by centrifugation at 10 000 rpm and washed with ethanol and deionized water. After oven-drying, the hydrothermal SnO_2 NCs can be obtained.

Good dispersive solvents

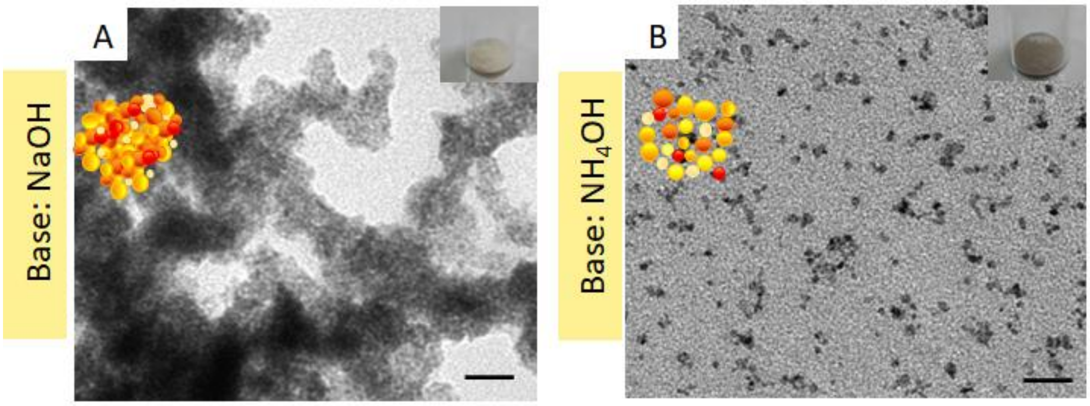
- Isopropanol
- Butanol

Characterization

- ✓ XRD
- ✓ Diffuse reflectance spectroscopy
- ✓ FTIR
- ✓ TEM
- ✓ Specific surface area (BET)



Panel A: XRD diffraction patterns of the SnO$_2$ NCs synthesized using NaOH with reference pattern for tetragonal SnO$_2$ #00-071-0652, Panel B: Tauc diagrams measured from the spectra in diffuse reflectance, Panel C: ATR-FTIR spectra in the 1500-400 cm-^{1} spectral region



Panel A,B: TEM micrographs (Scale bar 20 nm) of the SnO$_2$ NCs synthesized using NaOH (Panel A) and NH$_4$OH (Panel B)

h_SnO$_2$/NaOH **Eg:** 4.41 eV UPS Data: **Work Function=7.0 eV; VBM (Vacuum) = -9.7eV**

h_SnO$_2$/NH$_4$OH **Eg:** 3.50 eV

Sample	**SSA (m^2/g)**	**Total pore volume at 0.995 p/p^0**
SnO$_2$	81	0.6711

Biblio

Zhu Zonglong, et al., Enhanced Efficiency and Stability of Inverted Perovskite Solar Cells Using Highly Crystalline SnO$_2$ Nanocrystals as the Robust Electron-Transporting Layer, Adv. Mater. 2016, 28, 6478-6484, https://doi.org/10.1002/adma.201600619

8.2 SnO_2 sintesi per precipitazione

SnO_2 Nanoparticles by precipitation approach

Reagents	MW	M(mol/L)	V(mL)
$SnCl_4*5H_2O$	350.60	0.09	22
NaOH	39.99	pH 9	1
NH_4OH	35.04	pH 9	0.9

Grams for reactions batch

2 g

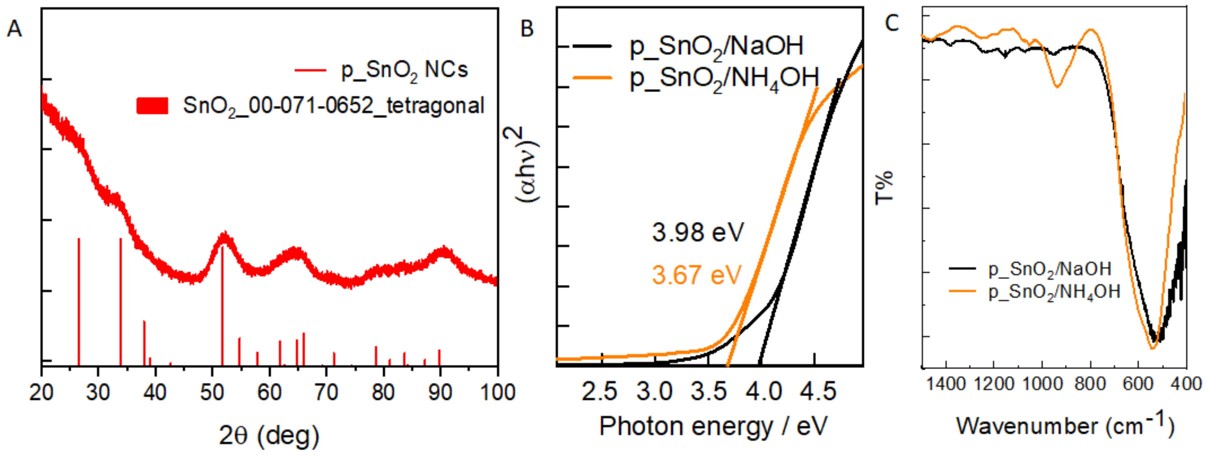
For the sol-precipitation synthesis, a $SnCl_4·5H_2O$ solution (0.09 M) in a H_2O/EtOH mixture 3:1 (volume ratio) was prepared and the pH was adjusted to 9 by adding either NaOH or NH_4OH as base to catalyse the sol-gel reaction. Then, the solution was heated from T_{room} to 80°C in 30 minutes in a silicon oil bath and stirred for 6 h. The products were collected by centrifugation at 10 000 rpm and washed with ethanol and deionized water. After oven-drying, the SnO_2 NCs can be obtained.

Good dispersive solvents

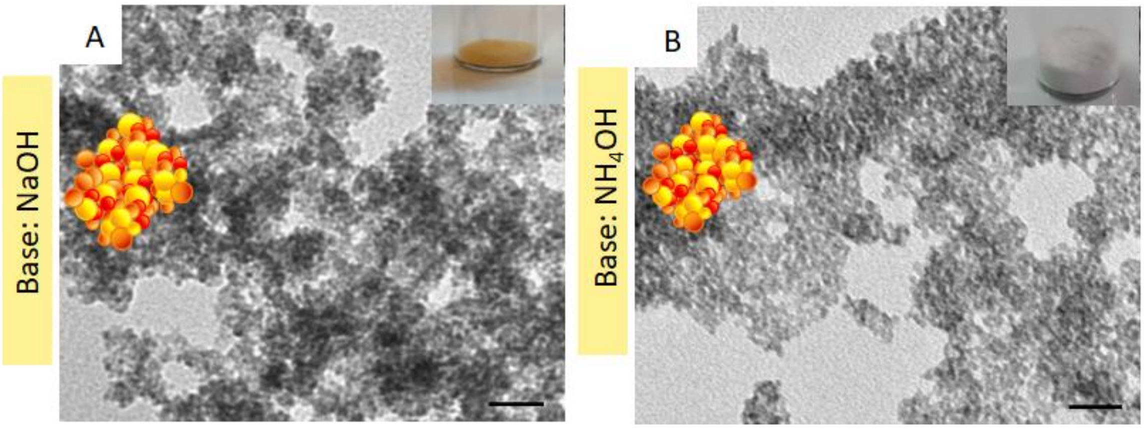
- Isopropanol
- Butanol

Characterization

- ☒ XRD
- ☒ Diffuse reflectance spectroscopy
- ☒ FTIR
- ☒ TEM
- ☒ Specific surface area (BET)



Panel A: XRD diffraction patterns of the SnO_2 NCs synthesized using NH_4OH with reference pattern for tetragonal SnO_2 #00-071-0652, Panel B: Tauc diagrams measured from the spectra in diffuse reflectance, Panel C: ATR-FTIR spectra in the 1500-400 cm^{-1}spectral region



Panel A,B: TEM micrographs (Scale bar 20 nm) of the SnO_2 NCs synthesized using NaOH (Panel A) and NH_4OH (Panel B)

p_SnO_2/NaOH **Eg:** 3.98 eV

p_SnO_2/NH_4OH **Eg:** 3.67 eV UPS Data: **Work Function=6.9eV; VBM (Vacuum)=-9.5eV**

Sample	**SSA (m^2/g)**	**Total pore volume at 0.995 p/p^0**
p_SnO_2/NaOH	104	0.065
p_SnO_2/NH_4OH	222	0.391

Biblio

A. Bouaine, et al., Structural, Optical, and Magnetic Properties of Co-doped SnO_2 Powders Synthesized by the Coprecipitation Technique, J. Phys. Chem. C 2007, 111, 7, 2924–2928, https://doi.org/10.1021/jp066897p

8.3 SnO_2 sintesi per riflusso

Colloidal SnO_2 Nanoparticles by reflux process

Reagents	MW (g/mol)	M(mol/L)	V(mL)
$SnCl_2*2H_2O$	225.64	0.1	25

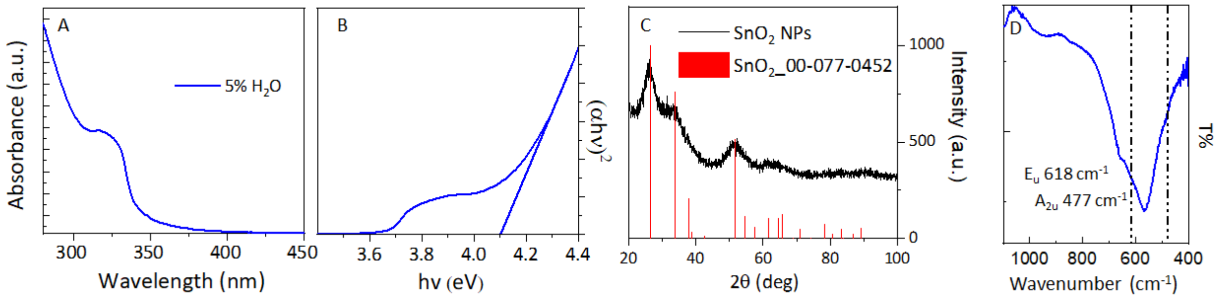
SnO_2 colloidal nanocrystals (NCs) have been synthesized by reflux process. $SnCl_2·2H_2O$ solution (0.1 M) was prepared by dissolving $SnCl_2·2H_2O$ in a solvent mixture based on butanol/ 5% water under constant magnetic stirring, keeping the temperature at 30°C for 10 minutes. To obtain SnO_2 organic sol, the just dissolved $SnCl_2·2H_2O$ solution was heated at 100°C under refluxing for 6h. First, the intermediate product, $Sn(OH)_2$, forms by the hydrolysis of the tin alkoxide and subsequently, during the refluxing step in aqueous-butanol mixture, $Sn(OH)_2$ transforms into SnO_2 nuclei which undergo a growth process. After the solution was cooled to room temperature, the SnO_2 NCs was collected.

Dispersive solvent

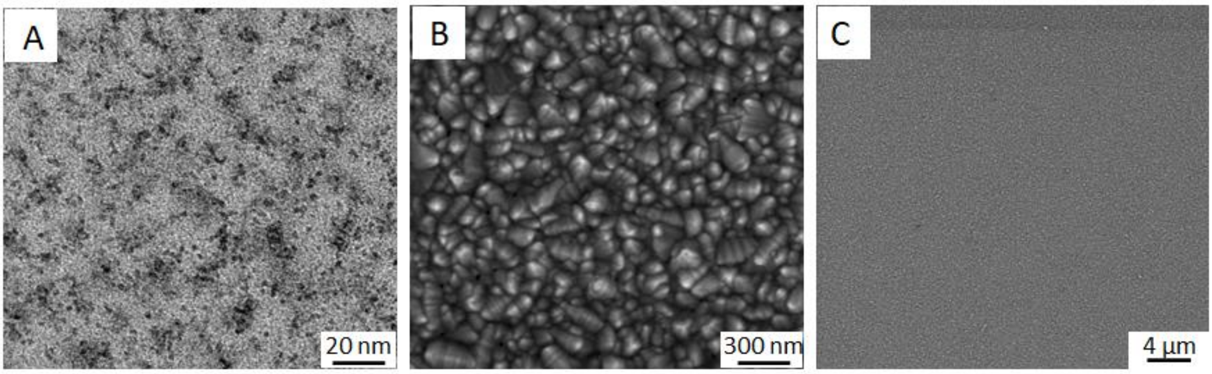
- Butanol/ 5% water

Characterization

☑ XRD
☑ Abs spectra
☑ FTIR
☑ SEM
☑ TEM



Panel A: UV-Vis absorption; Panel B: Tauc plot of the SnO_2 NCs; Panel C: XRD diffraction pattern of SnO_2 NCs in BuOH/H_2O 5% and reference pattern for tetragonal SnO_2 PDF # 00-077-0452; Panel D: ATR-FTIR spectra in the 1500-400 cm^{-1}spectral region



Panel A: TEM micrograph of synthesized SnO_2 NCs. Panel B, C: SEM micrographs at different magnification of SnO_2 NC film.

SnO_2 **Eg: 4.10** eV

Biblio

Chen, C.; Jiang, Y.; Juo, J.; Wu, X.; Zhang, W.; Wu, S.; Gao, X.; Hu, X.; Wang, Q.; Zhou, G.; Chen, Y.; Liu, J-M.; Kempa, K.; Gao, J., Solvent-Assisted Low-Temperature Crystallization of SnO_2 Electron-Transfer Layer for High-Efficiency Planar Perovskite Solar Cells, Adv. Funct. Mater. 2019, 1900557. https://doi.org/10.1002/adfm.201900557

9 TiO_2

Mesoporous TiO_2 Nanoparticles

Reagents	MW (g/mol)	M(mol/L)	V(mL)
$TiOSO_4$	193.93	2.15	50
NH_4HCO_3	79.056	2.00	76

Grams for reactions batch

5 g

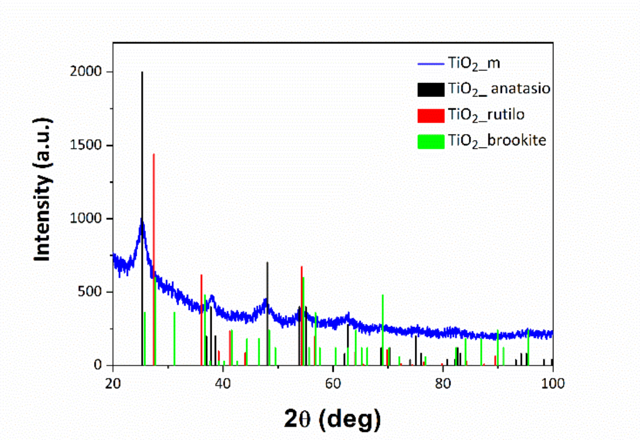
The synthesis of TiO_2 nanoparticles (NPs) involves $TiOSO_4$ as cost effective Ti^{4+} precursor and exploits a precipitation method in alkaline solution by dropwise addition of the $TiOSO_4$ solution to NH_4HCO_3 (Figure 3A) under constant magnetic stirring. Upon mixing, $TiOSO_4$ suddenly reacts promoting the formation and precipitation of Ti-hydroxide species resulting in a coalescence of the reaction mixture that turn in a milky slurry at the end of the reaction. The obtained nanocrystals were collected by centrifugation at 3000 rpm. The collected paste was repeatedly washed by subsequent cycles of dispersion in water and centrifugation. The obtained white precipitate was thermally treated at 110°C in oven for 16 hours (h)

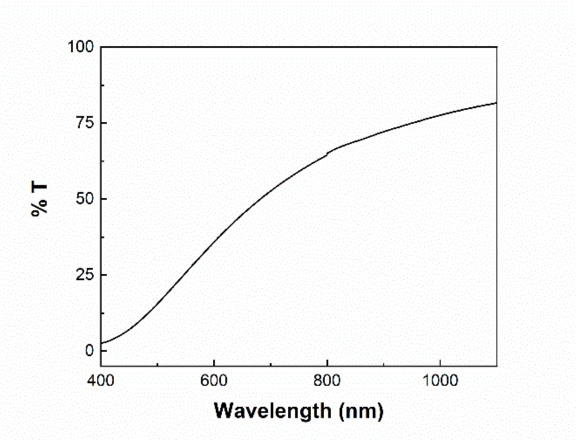
Good dispersive solvent

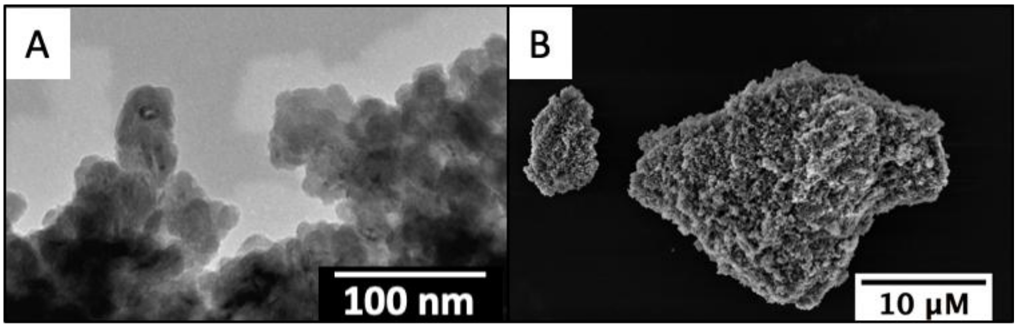
- Isopropanol
- Butanol

Characterization

- XRD
- Abs spectra
- Diffuse reflectance spectroscopy
- SEM
- TEM
- Specific surface area (BET)







Panel A: TEM micrograph of synthesized TiO2 nanoparticles. Panel B: SEM micrograph of TiO2 NC aggregates.

TiO_2 **Eg:** 3,65 eV

UPS data: **work function =6.2 eV, VBM (vs vacuum) = -9.0 eV**

Sample	**SSA (m^2/g)**	**d_{BET} (nm)**	**BJH desorption average pore width (nm)**	**BJH cumulative pore volume (cm^3/g)**	**Total pore volume (cm^3/g) at p/p0 0.98**
TiO_2_m	336,5	4,57	3,7	0,304	0,308

Biblio

Dell’Edera, M.; Petronella, F.; Truppi, A.; Liotta, L.F.; Gallì, N.; Sibillano, T.; Giannini, C.; Brescia, R.; Milano, F.; Striccoli, M.; Agostiano, A.; Curri, M.L.; Comparelli, R. Low Temperature Synthesis of Photocatalytic Mesoporous TiO_2 Nanomaterials. *Catalysts* **2020**, *10*, 893. https://doi.org/10.3390/catal10080893

10 WO_3

WO_3 Nanoparticles by Sol Gel – Orthorhombic phase

Reagents	MW	M(mol/L)	V(mL)
Sodium tungstate dihydrate	329.85	0,1	200
HCl	36,458	12.18	1.7

Grams for reactions batch

1.7 gr

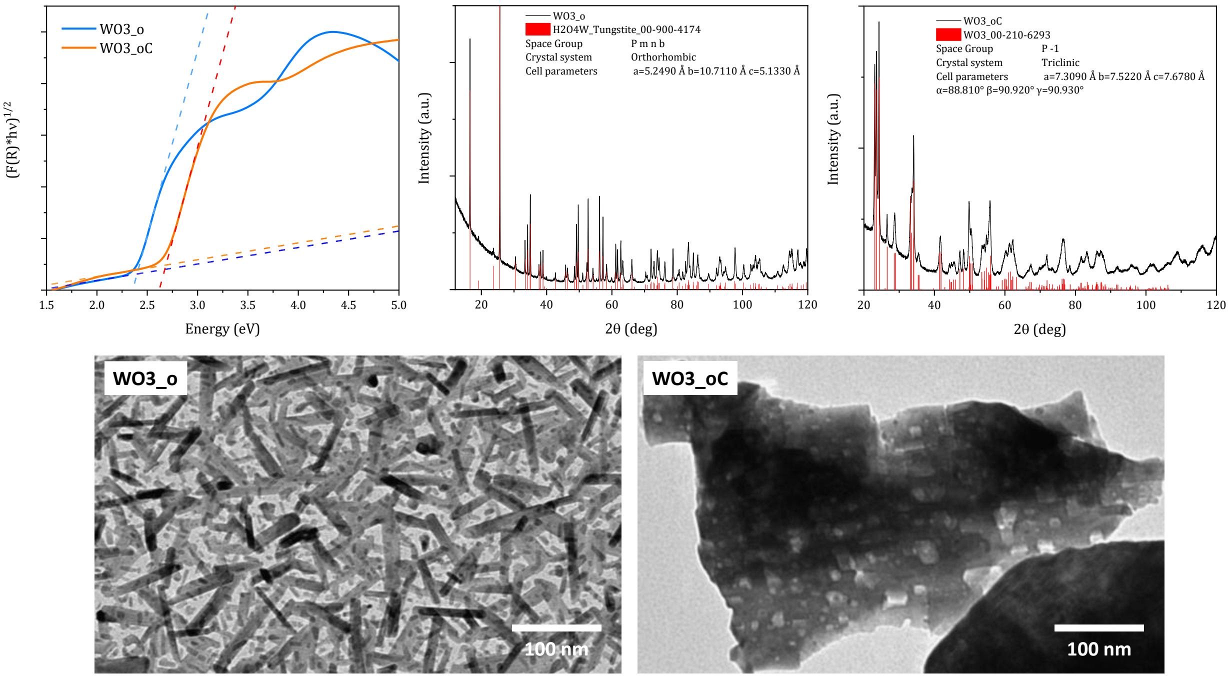
Nanoparticles of orthorhombic WO3 (WO3_o) have been synthesized through a sol gel process. For synthesis, 3.3g of sodium tungstate dihydrate ($Na_2WO_4\times 2H_2O$) are dissolved in 200 ml of deionized water; then, 1.7mL of HCl 37% w/w (12.18 M) are added dropwise. The solution is stirred for 24 h at 50°C, after which the yellow precipitate is washed by 4 cycles with deionized water. The washed precipitate is transferred to an oven at a temperature of 70°C for 16 hours to obtain a yellow powder (WO3_o). The product is then calcined at 450°C for 2 hours (WO3_oC) in air.

Good dispersive solvents

- Isopropanol
- Butanol

Characterization

- ☑ XRD
- ☑ Abs spectra
- ☑ Diffuse reflectance spectroscopy
- ○ SEM
- ☑ TEM
- ○ Specific surface area (BET)



Tauc plot of the synthetized WO3_o and WO3_oC, and their XRD spectra and TEM micrographs

WO3_o **Eg: 2.40** eV

WO3_oC **Eg: 2.69** eV.

Biblio

M. Abbaspoor, M. Aliannezhadi, F. S. Tehrani, ''Effect of solution pH on as-synthesized and calcined WO3 nanoparticles synthesized using sol-gel method, Optical Materials'', 121, **2021**, 111552, https://doi.org/10.1016/j.optmat.2021.111552.

WO_3 Nanoparticles by Sol Gel – Orthorhombic & hexagonal phase

Reagents	MW	M(mol/L)	V(mL)
Sodium tungstate dihydrate	329.85	0,1	200
HCl	36,458	12.18	2.1

Grams for reactions batch

1.8 gr

Nanoparticles of mixed 80% orthorhombic – 20% hexagonal WO3 (WO3_(o+h)) have been synthesized using the same procedure described for WO3_o sample. The only difference consists in the amount of HCl 37% w/w added to the tungsten salt precursor, that is now of 2.1mL instead 1.7mL. The reaction time and temperature are the same and the precipitate is collected and washed in the same way. Also, this sample is calcinated at 450°C for 2h (WO3_(o+h)).

Good dispersive solvent

- Isopropanol
- Butanol

Characterization

☑ XRD

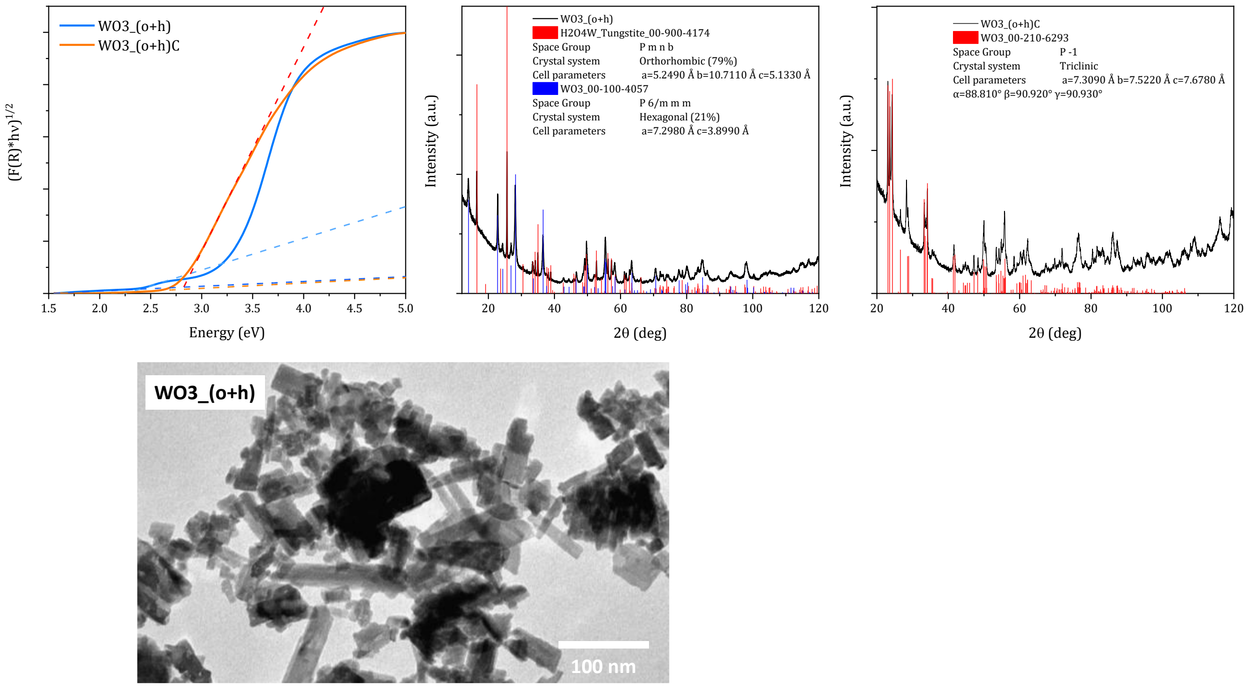
☑ Abs spectra

☑ Diffuse reflectance spectroscopy

○ SEM

☑ TEM

○ Specific surface area (BET)



Tauc plot of the synthetized WO3_(o+h) and WO3_(o+h)C, and their XRD spectra and TEM micrograph

WO3_(o+h) **Eg: 2.41** eV

WO3_(o+h)C **Eg: 2.80** eV.

Biblio

M. Abbaspoor, M. Aliannezhadi, F. S. Tehrani, ‘’Effect of solution pH on as-synthesized and calcined WO3 nanoparticles synthesized using sol-gel method, Optical Materials’’, 121, **2021**, 111552, https://doi.org/10.1016/j.optmat.2021.111552.

11 Composito TiO_2/WO_3

TiO_2/WO_3 Nano-heterostructures

Reagents	MW	M(mol/L)	V(mL)
Sodium tungstate dihydrate	329.85	0,05	100
HCl	36,458	2	10
TiO_2_m	presyntesized		5gr

Grams for reactions batch

6 g

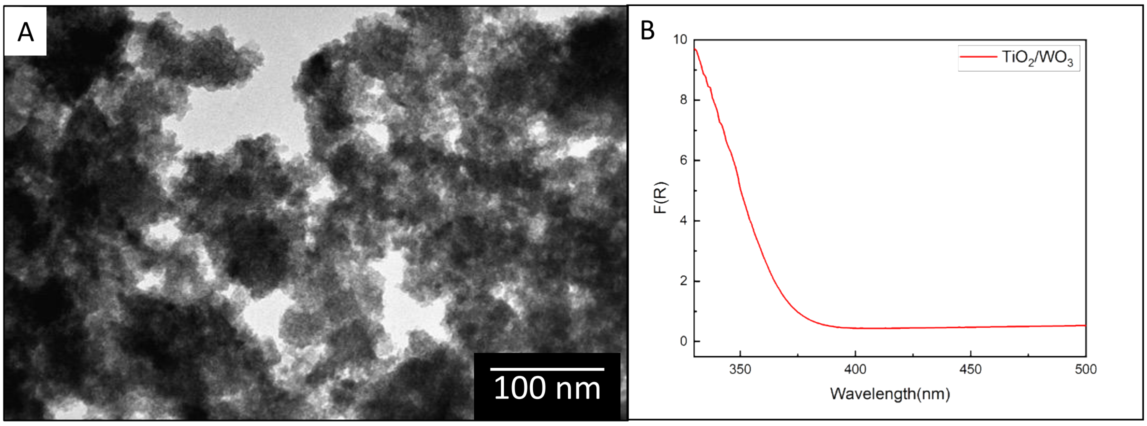
Nanostructure TiO_2/WO_3 was synthesized using sol gel approach. 1.6 g of sodium tungstate dihydrate was dissolved in 100 ml of deionized water and 5 g of previously synthesized mesoporous TiO_2; then, HCl (2 M) was added dropwise until a pH value of 1.5 was reached. The solution was stirred for 1 h, after which the impurities were removed by washing cycles with deionized water and ethanol three times. The washed precipitate was transferred to an oven at a temperature of 70°C for 16 hours to obtain a yellow powder (TiO_2/WO3).

Good dispersive solvents

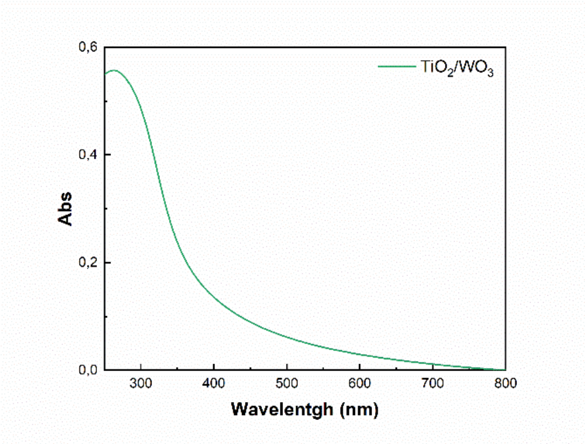
- Isopropanol
- Butanol

Characterization

○ XRD
☒ Abs spectra
☒ Diffuse reflectance spectroscopy
☒ SEM
☒ TEM
☒ Spacific surface area (BET)



Panel A: TEM micrograph of synthesized TiO_2/WO_3 nanoparticles,. Panel B: Tauc diagram measured from the spectrum in diffuse reflectance.



TiO_2/WO_3 **Eg:** 3,65 eV

Sample	SSA (m^2/g)	d_{BET} (nm)	BJH desorption average pore width (nm)	BJH cumulative pore volume (cm^3/g)
TiO_2/WO_3	337.0	5.5	0.37	337.0

Biblio

Mohaddeseh Jamali et al. Effect of synthesis route on the structural and morphological properties of WO_3 nanostructures Materials Science in Semiconductor Processing 107 (**2020**) 104829

12 MnO_2

[MnO_2]
Obtained from industrial wastes

Chemical Formula: MnO_2
Molecular Weight: 86.94 g/mol

SUMMARY

XRD	✓
Raman	✓
FTIR-ATR	✓
TGA	✓
XPS	✓
BET analysis	✓
Electrochemical characterization	✓

SYNTHESIS

Reducing agents	MW (g/mol)	d (g/mL)	mol / eq	m (mg)	V (mL)
K_2MnO_4	197,132	2.78	≈ 0.1 M	---	100 mL solution
H_2O_2 (30%)	34.016	1.11-1.12	---	9 g (H_2O_2 solution, 30% w/w in H_2O); ≈3 g H_2O_2	≈ 8 mL (H_2O_2 solution, 30% w/w in H_2O)

Procedure: Alkaline fusion with KOH was used to extract manganese as K_2MnO_4 from Mn-based industrial waste. The procedure was carried out to separate iron from manganese in the residue. Alkaline fusion was performed on a 10 g of industrial residue sample (KOH concentration: 20 g in 40 mL deionized water) at 280°C. The extraction was repeated three times (35 min each) and water (10 mL) was added in the second and third step of the cycle. The resulting solid was leached with a 1 M KOH solution to attain an iron-free solution containing manganate, aluminate, and silicate. The potassium manganate solution (approximately 0.1 M, measured by UV-Vis spectroscopy) was reduced through H_2O_2 (30% w/w in H_2O) leading to a brownish MnO_2 precipitate.

Purification

The precipitate was filtered and washed with a diluted KOH solution and deionized water up to neutrality. Purification procedure involved no further steps. The solid was dried overnight in an oven at 110 °C.

Yield: about 60% of manganese was recovered from Mn-based industrial waste (based on gravimetric, quantitative precipitation of $BaMnO_4$). About 2 g of δ-MnO_2 are produced from 10 g of industrial waste.

Bibliography

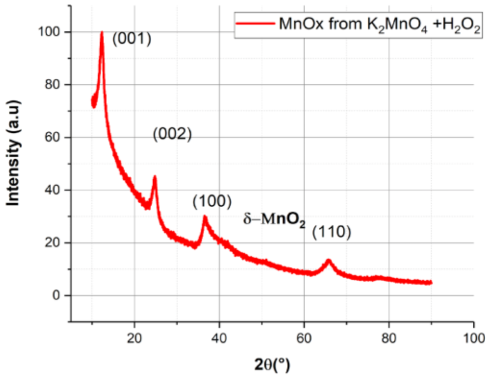
1. R.A. da Rocha, C.L. Quintanilha, T.V. Lanxin et al., Production of potassium manganate and barium manganate from spent zinc–MnO_2 dry cells via fusion with potassium hydroxide, *J. Power Sources* **268** (2014) 831.

2. B.A.M. Figueria, R.S. Angélica, M.L. da Costa et al., Conversion of different Brazilian manganese ores and residues into birnessite-like phyllomanganate, *Appl. Clay Sci.* **86** (2013) 54.
3. Y. Ma, J. Luo, S. Suib, Syntheses of birnessites using alcohols as reducing reagents: Effects of synthesis parameters on the formation of birnessites, *Chem. Mater.* **11** (1999) 1972.
4. E. Narita, T. Okabe, The formation and some properties of hydrous manganese (IV) oxide, *Bull. Chem. Soc. Jpn.* **53** (1980) 525.

CHARACTERIZATION

XRD

The X-ray diffraction (XRD) patterns were collected with an X-Pert (Panalytical) diffractometer in the 10-90° 2θ range.



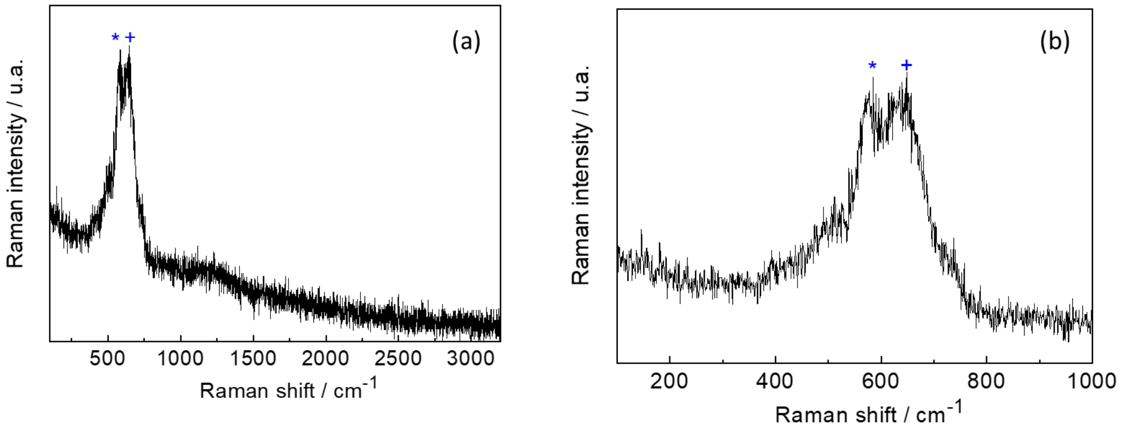
The compound turned out to be a poorly crystalline form of δ-MnO_2. Therefore, the synthesized material is a non-stoichiometric, quasi-amorphous, hydrated manganese oxide possessing a “birnessite-like” (i.e., layered) structure. Thus, the prepared material can be considered as a potassium “manganite”. Manganites should be regarded as a hydrated (generally non-crystalline), salt-like combination of manganese dioxide and the cation of the base forming metal (general formula: $A_xMnO_{2\pm\delta}\cdot yH_2O$, where A is a base metal cation). Manganites have been obtained over the years by reducing permanganates (usually $KMnO_4$) in alkaline aqueous solutions with practically any oxidable material such as H_2O_2, alcohols, sugars. An industrial relevant manganite prepared from an industrial by-product/waste, similar to the present material, is “permanox”. Such an oxide stems from the industrial synthesis of saccharine by means of potassium permanganate and is a δ-MnO_2 containing approximately 79% MnO_2, 5-18% water and 4-10% potassium as KOH. Before being phased out because of electrolytic manganese dioxide introduction permanox was a standard depolarizer for alkaline and zinc-carbon batteries.

Bibliography

1. D. Othmer, R.E. Kirk-Othmer, *Encyclopedia of Chemical Technology* **15** (2004) 500.
2. A.H. Reidies Ullmann’s, *Encyclopedia of Industrial Chemistry* **16** (2000) 123.
3. P. Strobel, H. M. Helsa, Extended X-ray absorption fine structure study of potassium and caesium phyllomanganates, *J. Mater. Chem.* **3** (1993) 77.
4. K. J. Euler, H. M. Helsa, Electrical characteristics of a highly hydrated battery grade manganese dioxide powder, *J. Power Sources* **4** (1979) 77.

Raman

The Raman spectra of MnO_2 powder were recorded with a Renishaw micro-Raman 1000 system exciting at 632.8 nm (HeNe laser) from 100.00 to 3200.00 cm^{-1} (a) and from 100.00 – 1000.00 cm^{-1} (b) at RT.



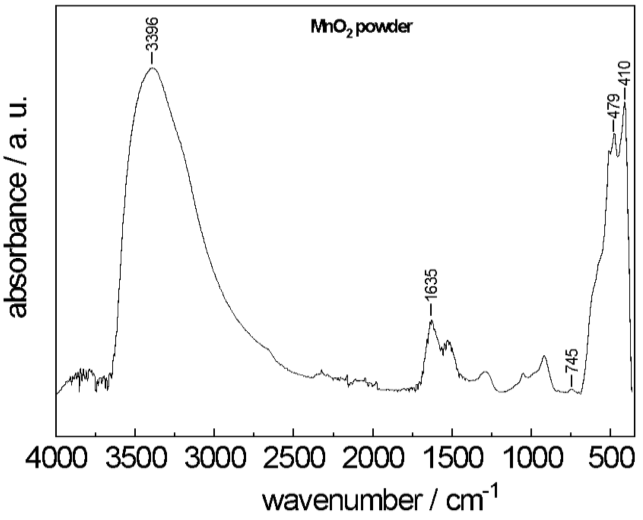
(*) 578 cm^{-1}: stretching vibration ν_3(Mn –O) in the basal plane of [MnO_6] sheets; (+) 637 cm^{-1}: symmetric stretching vibration ν_2(Mn –O) of MnO_6 groups.

Bibliography

1. C. Julien, M. Massot, R. Baddour-Hadjean et al., Raman spectra of birnessite manganese dioxides, *Solid State Ion.* **159** (2003) 345.

ATR-FTIR

The Attenuated Total Reflectance Fourier Transform (ATR-FTIR) measurements were performed with a N_2 purged Bruker Vertex 70 interferometer using a single reflection Platinum-ATR accessory (diamond crystal), a DLaTGS detector and a KBr beamsplitter. The spectra were recorded from 4000 to 370 cm^{-1} with 4 cm^{-1} resolution at RT. The ATR-FTIR spectra correction was carried out.



3396 cm^{-1}: O-H stretching vibrational mode of adsorbed water by the MnO_2.
1635 cm^{-1}: bending mode of hydroxyl groups.
745, 479, 410 cm^{-1}: vibration modes of Mn-O, Mn-O-Mn, and O-Mn-O bonds.

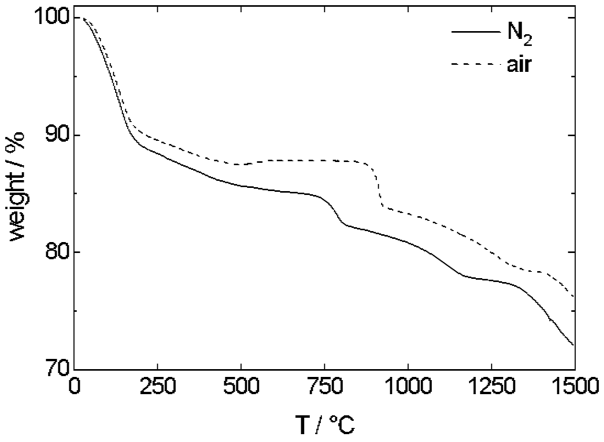
Bibliography

1. P. Yadav, A. Bhaduri, Chemically synthesized manganese oxide nanorods for effectual organic dye removal and energy storage application, *Mater. Chem. Phys.* **299** (2023) 127495.

TGA

The thermogravimetric analysis (TGA) was carried out by means of SDT Q600 apparatus from 30°C up to 1500 °C at a scan rate of 10°C/min under N_2 flow and in air.

The weight loss up to 250°C (11.52% in N_2 and 10.26% in air) is due to the removal of physically adsorbed, crystalline water, hydroxyl groups, and of other adsorbed species from the K-birnessite structure, in agreement with ATR-FTIR and XPS results. The smaller weight loss up to 500°C corresponds to the removal of residual water molecules in the interlayer space in order to accomplish the phase transition of layered δ-MnO_2 to α-MnO_2 with a tunnel-like crystal structure [1]. The decomposition of α-MnO_2 to Mn_2O_3 and Mn_3O_4 occurs up to 800°C and 1300°C, respectively [2-4]. The weight loss occurring above 1300°C to 1500°C is presumably related to the formation of MnO [5].



	T start (°C)	T stop (°C)	Weight loss (%) in N_2	Weight loss (%) in air
	30	250	11.52	10.26
	250	500	2.78	2.076
	30	500	14.30	12.33
	500	800	3.00	-0.33
	500	950	4.35	3.735
	650	850	3.05	0.1302
	800	950	1.35	4.065
	850	1215	4.29	6.931
	950	1015	0.64	0.4889
	950	1100	2.00	1.345
	950	1300	3.93	4.572
	950	1390	5.65	5.283
	1215	1500	5.58	4.38
	1300	1500	5.19	2.761
	1390	1500	3.47	2.052
Tot.	30	1500	27.77	23.40

Bibliography

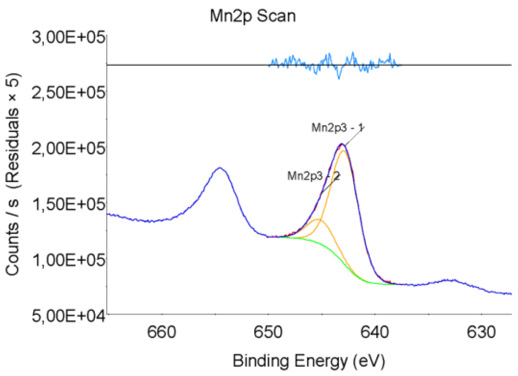
1. B.A.M. Figueira, R.S. Angélica, M.L. da Costa et al., *Appl. Clay Sci.* **86** (2013) 54.
2. G. Sun, C. Jia, J. Zhang, et al. Core-shell structure $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$@ ultrathin δ-$MnO_2$ nanoflakes cathode material with high electrochemical performance for lithium-ion batteries, *Ionics* **25** (2019) 5249.
3. Y. Munaiah, B. G. S. Raj, T. P. Kumar, Facile synthesis of hollow sphere amorphous MnO_2: the formation mechanism, morphology and effect of a bivalent cation-containing electrolyte on its supercapacitive behavior, *J. Mater. Chem. A* **1** (2013) 4300.

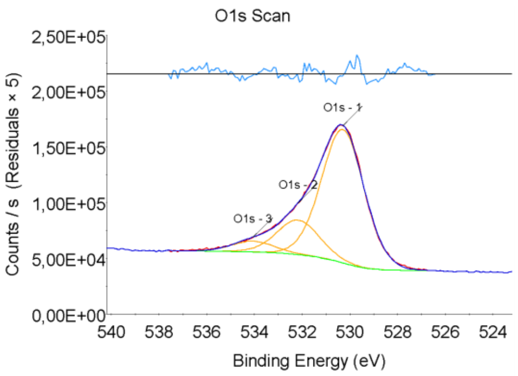
4. J. A. Lee, C. E. Newnham, F. L. Tye, Energetics of water desorption from a γ-manganese dioxide, *J. Colloid Interface Sci.* **42** (1973) 372.
5. D. M. Tinsley, J. H. Sharp, Thermal analysis of manganese dioxide in controlled atmospheres, *J. Therm. Anal.* **3** (1971) 43.

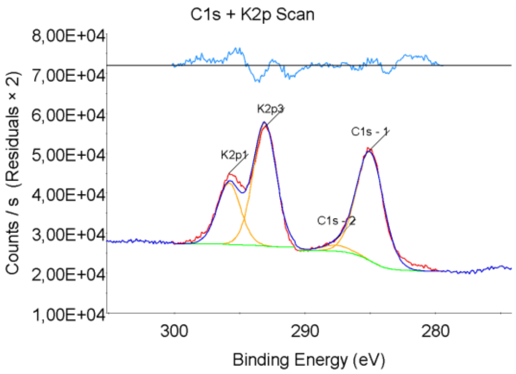
XPS

The X-Ray Photoelectron Spectroscopy (XPS) experiments were carried out by an ESCALAB 250 Xi, equipped with a monochromatic X-ray source (Al K_α – 1486.6 eV), and six channeltrons detection system. The spectra were acquired operating at 50 eV pass energy (CAE), while the binding energy (BE) scale was aligned using an electron flux at low energy (flood gun).

Name	Peak BE	FWHM eV	Area (P) CPS.eV	Atomic %	Assignment
C1s - 1	285.0	2.45	72608.65	26.4	Aliphatic carbon
C1s - 2	287.6	2.45	4130.79	1.5	C = O
K2p3	293.1	2.10	70739.51	9.8	K(+1)
Mn2p3 - 1	642.8	3.03	332929.56	16.6	MnO_2
Mn2p3 - 2	645.1	3.03	70687.70		MnO_2 – satellite peak
O1s - 1	530.3	2.09	271687.73	34.4	MnO_2
O1s - 2	532.2	2.09	68514.88	8.7	C = O
O1s - 3	534.1	2.09	21142.22	2.7	Adsorbed water

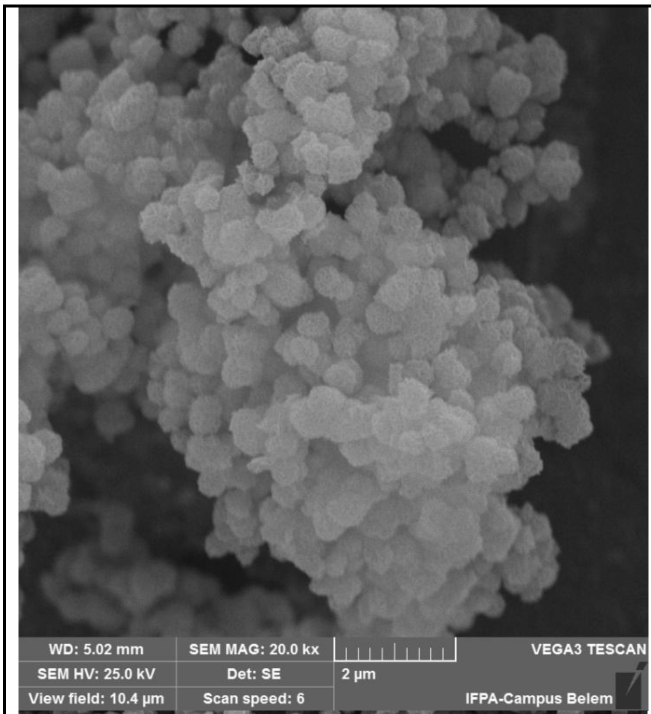


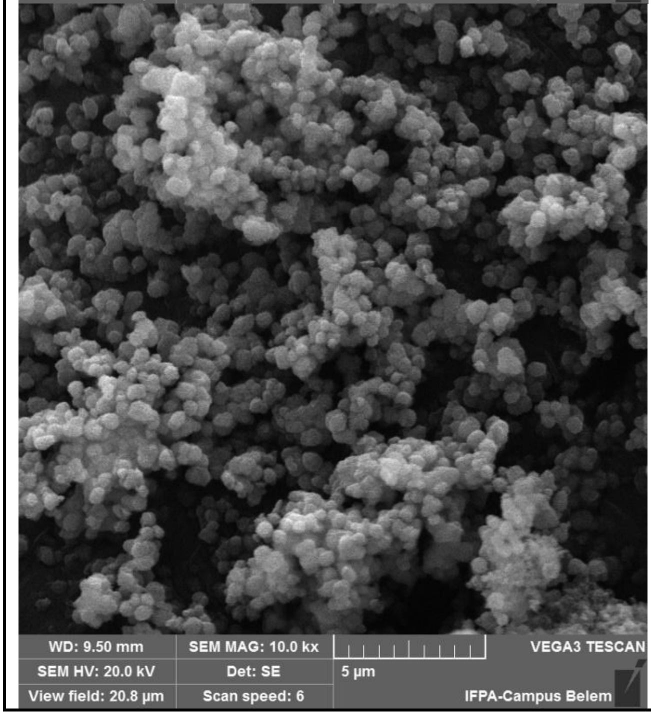


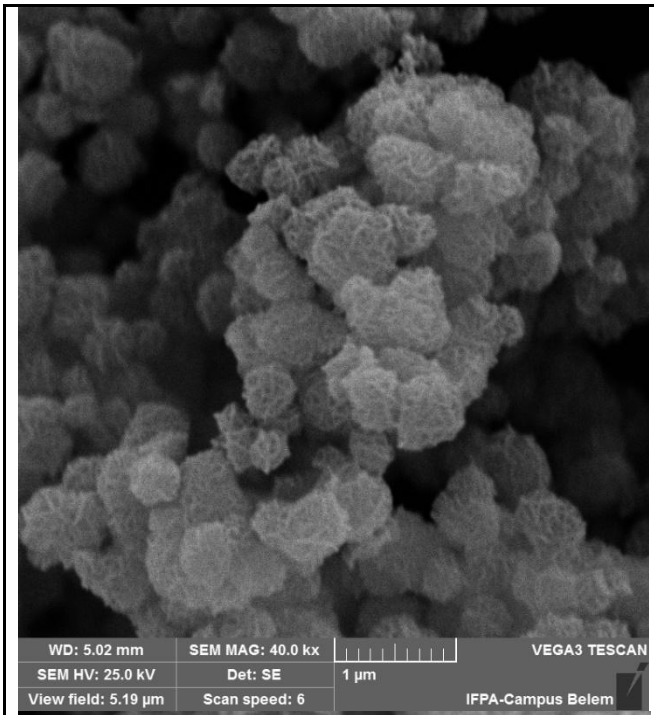


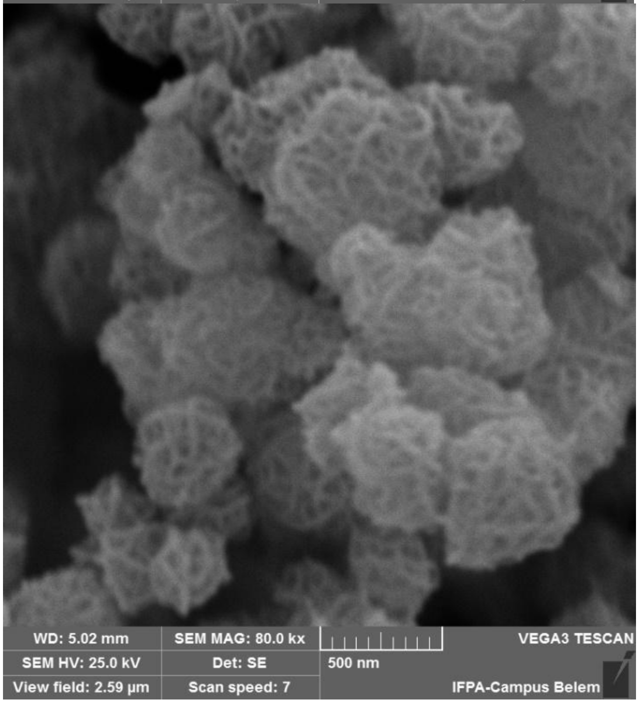
SEM

SEM images were collected with a JEOL JSM-6300 scanning electron microscope equipped with a field-emission electron source. The samples were coated with gold on JEOL JFC-1600 auto fine coater.


WD: 5.02 mm
SEM MAG: 20.0 kx
VEGA3 TESCAN
SEM HV: 25.0 kV
Det: SE
2 µm
View field: 10.4 µm
Scan speed: 6
IFPA-Campus Belem


WD: 9.50 mm
SEM MAG: 10.0 kx
VEGA3 TESCAN
SEM HV: 20.0 kV
Det: SE
5 µm
View field: 20.8 µm
Scan speed: 6
IFPA-Campus Belem

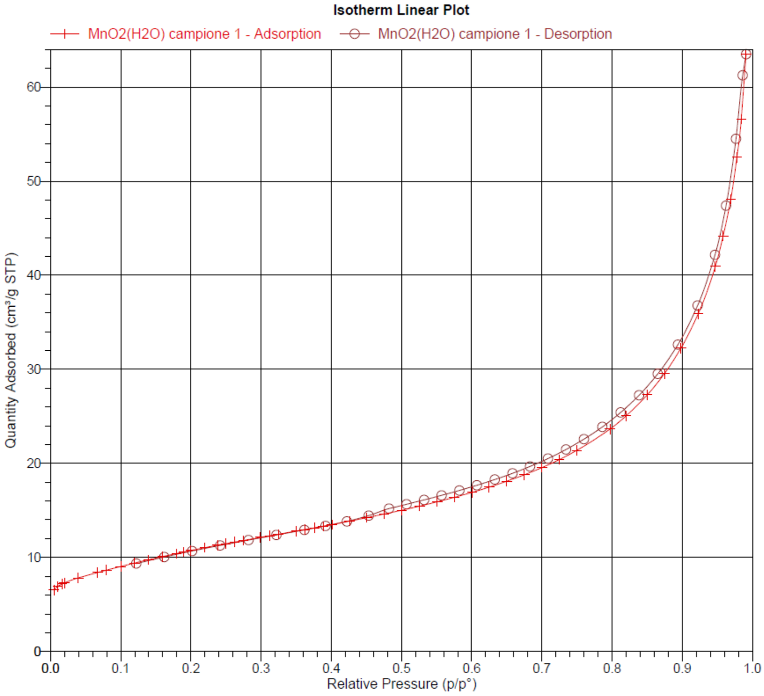




The powder has cauliflower-like grains that in turn are composed of almost hierarchical sub-micrometric (about 500-600 nm) particles.

BET ANALYSIS

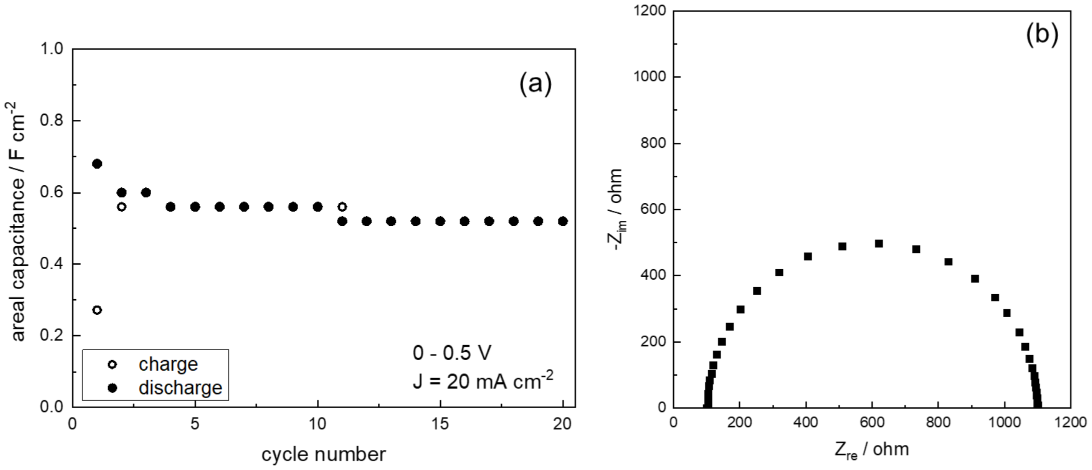
The N_2 adsorption/desorption isotherms were carried out at 77 K by means of a 3-Flex 3500 analyzer (Micromeritics, Norcross, GA, USA).



BET = 38 ± 1 m^2/g (7 m^2/g due to micropores); pores total volume = 0.0984 cm^3/g. Pore distribution with diameter in the range 0 – 1000 Å, with two maximum at > 17 Å (due to micropores) and at ca. 34 Å.

ELECTROCHEMICAL CHARACTERIZATION

Symmetric supercapacitors were assembled by using the as-prepared MnO_2 as active material (70 wt.%), carbon black as conductive additive (20 wt.%) and polyvinylidene difluoride (PVdF) as binder (10 wt.%). Charge/discharge cycles featuring an areal capacitance of ca. 0.6 F g^{-1} (a) at room temperature and 20 mA cm^{-2} between 0.0 and 0.5 V in 6 M KOH were carried out by means of a Battery tester Maccor model 4000. Electrochemical impedance spectroscopy measurements (b) were performed in 2-electrode mode in the range 1 MHz – 0.1 Hz, ac 10 mV, by using Ivion Technologies impedance analyzer model IviumStat (electrochemical interface).



13 Fotoelettrodo di TiO_2 sensibilizzato con il colorante **N3**

PHOTO-ELECTRODE BASED ON TiO_2 SENSITIZED WITH N3 DYE

SUMMARY

SEM	☒
Optical properties	☒
Electrochemistry	☒
Photo-electrochemistry	☒

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 TiO_2-based ink 18NR-T (Greatcell Solar Materials), with viscosity between 40-55 Pa*s.

Dye N3 (cis-Bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II), Sigma Aldrich) with chemical formula $C_{26}H_{16}N_6O_8RuS_2$ 0.3 mM in Absolute Ethanol.

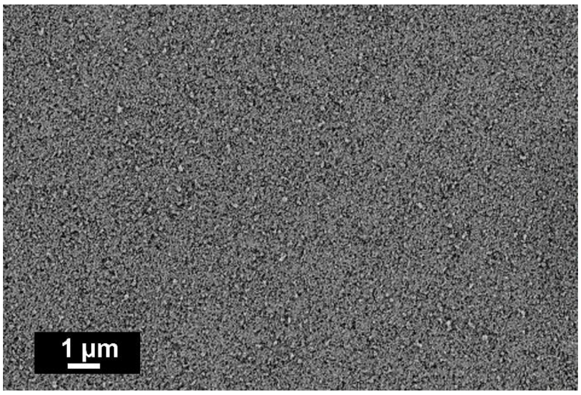
Procedure

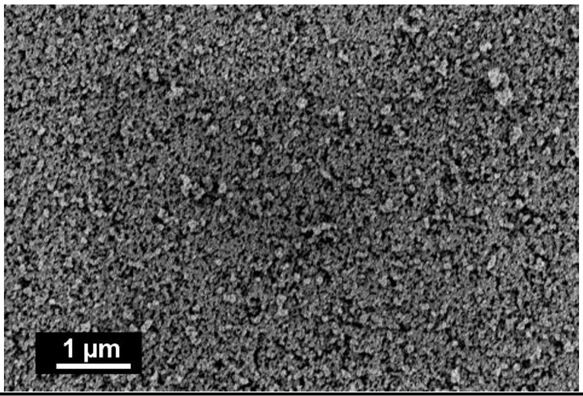
Thin film based on TiO_2 was prepared by semi-automatic screen-printed machine AUREL 900 (Aurel Automation S.p.A., Italia) with speed of 90 mm/s and 3 depositions. A thickness of 11.84 µm and active area of 0.25 cm^2 were achieved. Between each deposition a drying treatment of 80°C in IR oven was used. Finally, a thermal treatment at 500°C for 30’ was done to consolidate the film. The as obtained film was sensitized overnight in 0.3 mM N3 dye solution and the excess of dye was removed by absolute ethanol.

CHARACTERIZATION

SEM

SEM images were collected with a ZEISS SIGMA, Carl Zeiss Microscopy GmbH scanning electron microscope equipped with a field-emission electron source.



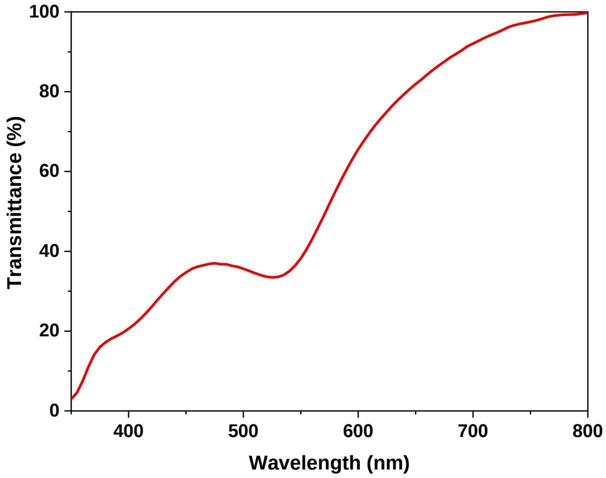


Homogenous microstructure with nanoparticles with regular porous (diameter between 100 e 120 nm).

OPTICAL PROPERTIES

Transmittance spectra

Acquire in the range between 350 and 800 nm with an integrating sphere.



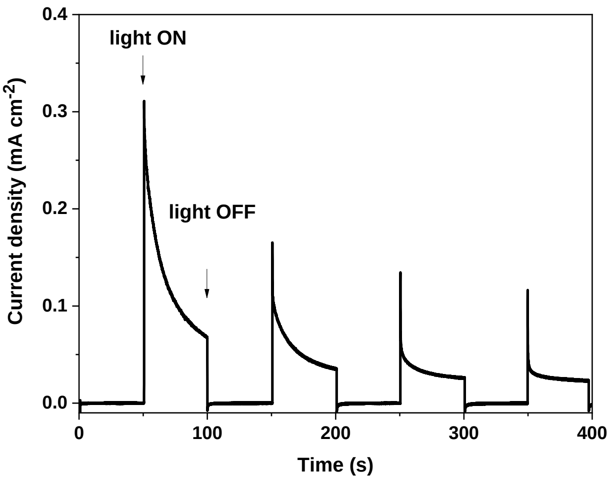
Optical parameters

Ability to harvest light in the Visible region.

Transparency at 700 nm of 92%.

PHOTO-ELECTROCHEMISTRY

Cronoamperometry in a photoelectrochemical cell with working electrode: FTO+film; counter-electrode: platinum wire; reference electrode: aqueous Ag/AgCl (sat. KCl); electrolyte: $LiClO_4$ 0.2 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).



Electrochemical Impedance Spectroscopy in a photoelectrochemical cell with working electrode: FTO+film; counter-electrode: platinum wire; reference electrode: aqueous Ag/AgCl (sat. KCl); electrolyte: $LiClO_4$ 0.2 M in H_2O MQ. Frequency range between $1x10^5$ Hz e 0.05 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).

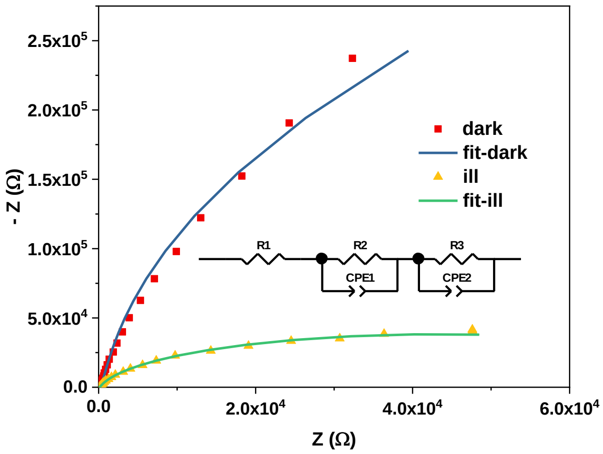


Photo-electrochemical parameters

- Photo-current equal to 0.6 mA cm^{-2}.
- Electrical resistance of 118 Ω.
- Charge transfer resistance electrode/electrolyte interface under illumination equal to $8.6x10^4$ Ω.

14 Fotoelettrodo di TiO_2 sensibilizzato con il colorante **AD418**

PHOTO-ELECTRODE BASED ON TiO_2 SENSITIZED WITH AD418 DYE

SUMMARY

SEM	☒
Optical properties	☒
Electrochemistry	☒
Photo-electrochemistry	☒

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 TiO_2-based ink 18NR-T (Greatcell Solar Materials), with viscosity between 40-55 Pa*s.

Dye AD418 (chemical formula $C_{43}H_{44}N_2O_4S_2$) 0.3 mM in ethanol:THF.

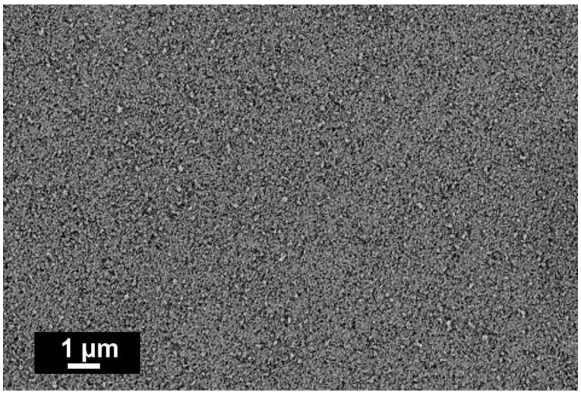
Procedure

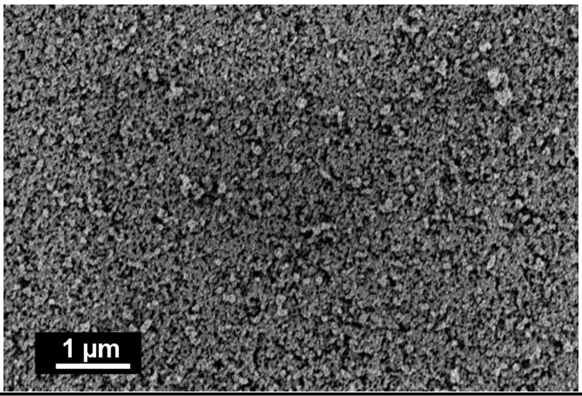
Thin film based on TiO_2 was prepared by semi-automatic screen-printed machine AUREL 900 (Aurel Automation S.p.A., Italia) with speed of 90 mm/s and 3 depositions. A thickness of 11.84 µm and active area of 0.25 cm^2 were achieved. Between each deposition a drying treatment of 80°C in IR oven was used. Finally, a thermal treatment at 500°C for 30’ was done to consolidate the film. The as obtained film was sensitized overnight in 0.3 mM AD418 dye solution and the excess of dye was removed by absolute ethanol.

CHARACTERIZATION

SEM

SEM images were collected with a ZEISS SIGMA, Carl Zeiss Microscopy GmbH scanning electron microscope equipped with a field-emission electron source.



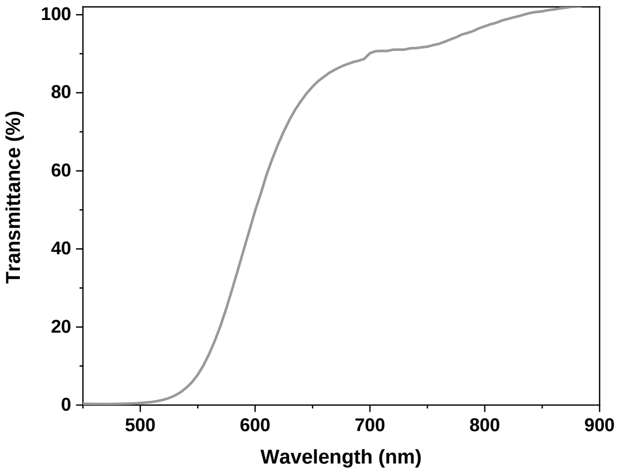


Homogenous microstructure with nanoparticles with regular porous (diameter between 100 e 120 nm).

OPTICAL PROPERTIES

Transmittance spectra

Acquire in the range between 400 and 900 nm with an integrating sphere.



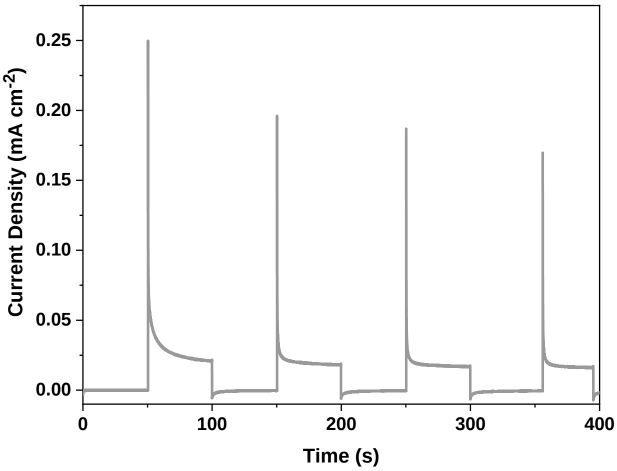
Optical parameters

Ability to harvest light in the Visible region.

Transparency at 700 nm of 90%.

PHOTO-ELECTROCHEMISTRY

Cronoamperometry in a photoelectrochemical cell with working electrode: FTO+film; counter-electrode: platinum wire; reference electrode: aqueous Ag/AgCl (sat. KCl); electrolyte: $LiClO_4$ 0.2 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).



Electrochemical Impedance Spectroscopy in a photoelectrochemical cell with working electrode: FTO+film; counter-electrode: platinum wire; reference electrode: aqueous Ag/AgCl (sat. KCl); electrolyte: $LiClO_4$ 0.2 M in H_2O MQ. Frequency range between $1x10^5$ Hz e 0.05 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).

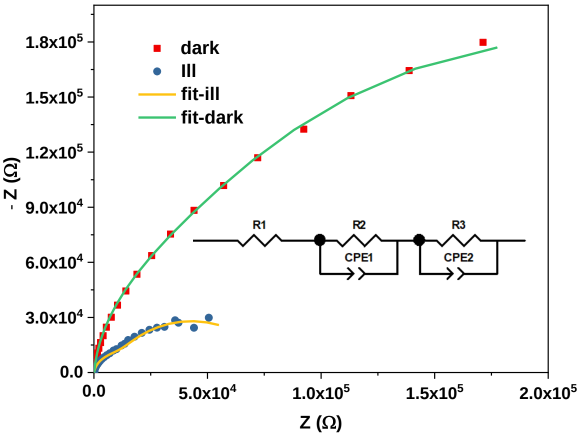


Photo-electrochemical parameters

- Photo-current equal to 0.019 mA cm^{-2}.
- Electrical resistance of 116 Ω.
- Charge transfer resistance electrode/electrolyte interface under illumination equal to $6.67x10^4$ Ω.

15 Fotoelettrodo di TiO_2 sensibilizzato con il colorante **TTZ5**

PHOTO-ELECTRODE BASED ON TiO_2 SENSITIZED WITH TTZ5 DYE

SUMMARY

SEM	☒
Optical properties	☒
Electrochemistry	☒
Photo-electrochemistry	☒

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 TiO_2-based ink 18NR-T (Greatcell Solar Materials), with viscosity between 40-55 Pa*s.

Dye TTZ5 (molecular formula $C_{76}H_{94}N_4O_6S_7$) 0.3 mM in ethanol:THF.

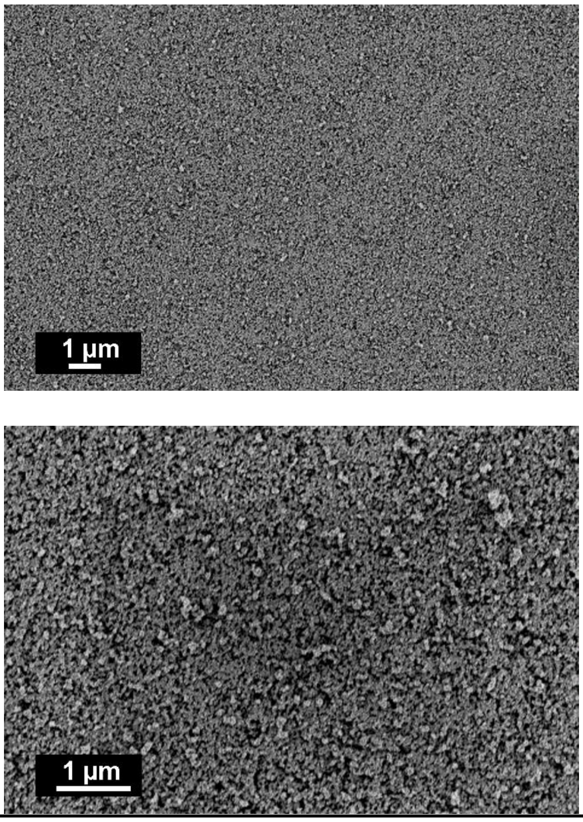
Procedure

Thin film based on TiO_2 was prepared by semi-automatic screen-printed machine AUREL 900 (Aurel Automation S.p.A., Italia) with speed of 90 mm/s and 3 depositions. A thickness of 11.84 µm and active area of 0.25 cm^2 were achieved. Between each deposition a drying treatment of 80°C in IR oven was used. Finally, a thermal treatment at 500°C for 30’ was done to consolidate the film. The as obtained film was sensitized overnight in 0.3 mM TTZ5 dye solution and the excess of dye was removed by absolute ethanol.

CHARACTERIZATION

SEM

SEM images were collected with a ZEISS SIGMA, Carl Zeiss Microscopy GmbH scanning electron microscope equipped with a field-emission electron source.

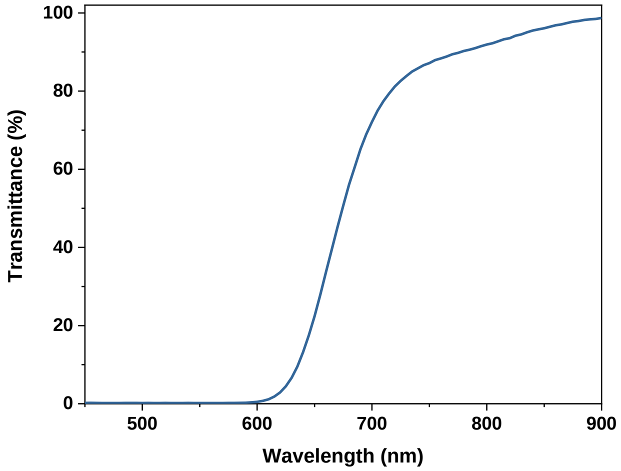


Homogenous microstructure with nanoparticles with regular porous (diameter between 100 e 120 nm).

OPTICAL PROPERTIES

Transmittance spectra

Acquire in the range between 400 and 900 nm with an integrating sphere.



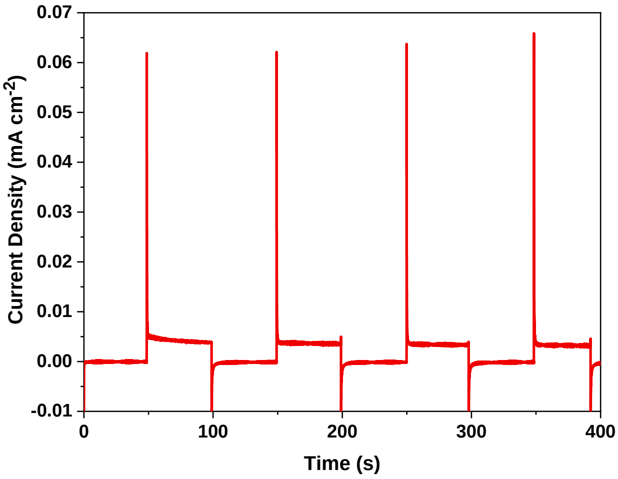
Optical parameters

Ability to harvest light in the Visible region.

Transparency at 700 nm of 72%.

PHOTO-ELECTROCHEMISTRY

Cronoamperometry in a photoelectrochemical cell with working electrode: FTO+film; counter-electrode: platinum wire; reference electrode: aqueous Ag/AgCl (sat. KCl); electrolyte: $LiClO_4$ 0.2 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).



Electrochemical Impedance Spectroscopy in a photoelectrochemical cell with working electrode: FTO+film; counter-electrode: platinum wire; reference electrode: aqueous Ag/AgCl (sat. KCl); electrolyte: $LiClO_4$ 0.2 M in H_2O MQ. Frequency range between $1x10^5$ Hz e 0.05 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).

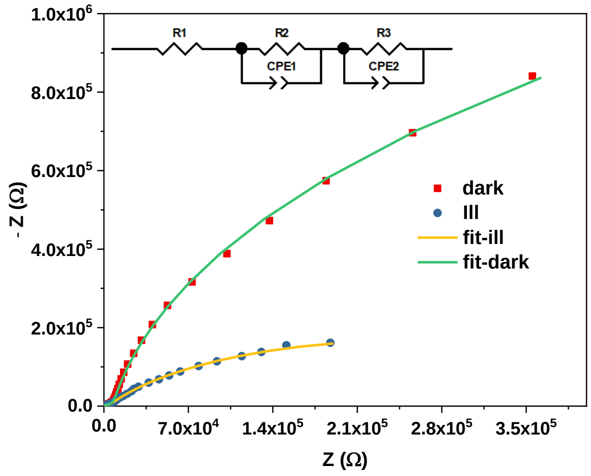


Photo-electrochemical parameters

- Photo-current equal to 0.0037 mA cm^{-2}.
- Electrical resistance of 172 Ω.
- Charge transfer resistance electrode/electrolyte interface under illumination equal to 4.98×10^5 Ω.

16 Fotoelettrodo di TiO_2 sensibilizzato con il colorante **TTZ9**

PHOTO-ELECTRODE BASED ON TiO_2 SENSITIZED WITH TTZ9 DYE

SUMMARY	
SEM	☒
Optical properties	☒
Electrochemistry	☒
Photo-electrochemistry	☒

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 TiO_2-based ink 18NR-T (Greatcell Solar Materials), with viscosity between 40-55 Pa*s.
Dye TTZ9 (molecular formula $C_{82}H_{96}N_6O_6S_8$) 0.3 mM in ethanol:THF.

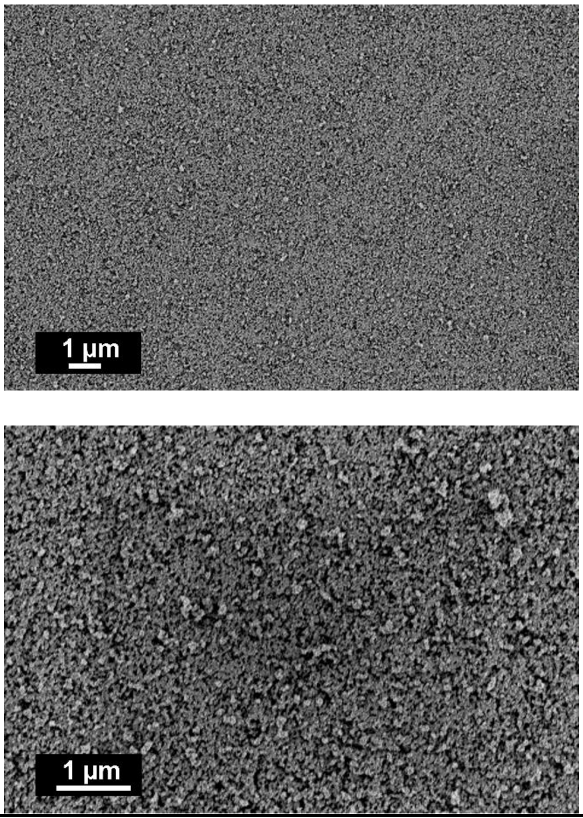
Procedure

Thin film based on TiO_2 was prepared by semi-automatic screen-printed machine AUREL 900 (Aurel Automation S.p.A., Italia) with speed of 90 mm/s and 3 depositions. A thickness of 11.84 µm and active area of 0.25 cm^2 were achieved. Between each deposition a drying treatment of 80°C in IR oven was used. Finally, a thermal treatment at 500°C for 30' was done to consolidate the film. The as obtained film was sensitized overnight in 0.3 mM TTZ9 dye solution and the excess of dye was removed by absolute ethanol.

CHARACTERIZATION

SEM

SEM images were collected with a ZEISS SIGMA, Carl Zeiss Microscopy GmbH scanning electron microscope equipped with a field-emission electron source.

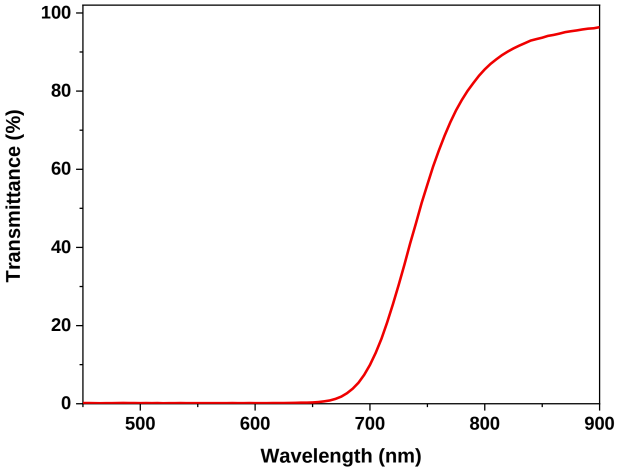


Homogenous microstructure with nanoparticles with regular porous (diameter between 100 e 120 nm).

OPTICAL PROPERTIES

Transmittance spectra

Acquire in the range between 400 and 900 nm with an integrating sphere.



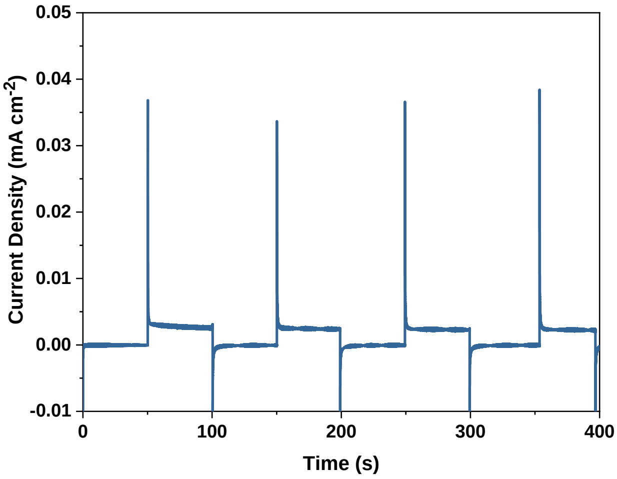
Optical parameters

Ability to harvest light in the Visible region.

Transparency at 700 nm of 10%.

PHOTO-ELECTROCHEMISTRY

Cronoamperometry in a photoelectrochemical cell with working electrode: FTO+film; counter-electrode: platinum wire; reference electrode: aqueous Ag/AgCl (sat. KCl); electrolyte: $LiClO_4$ 0.2 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).



Electrochemical Impedance Spectroscopy in a photoelectrochemical cell with working electrode: FTO+film; counter-electrode: platinum wire; reference electrode: aqueous Ag/AgCl (sat. KCl); electrolyte: $LiClO_4$ 0.2 M in H_2O MQ. Frequency range between $1x10^5$ Hz e 0.05 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).

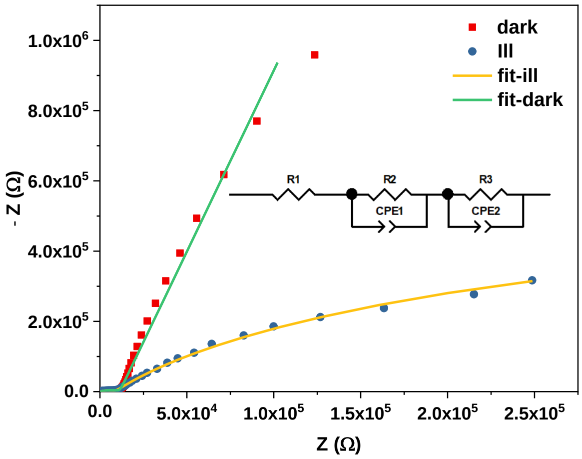


Photo-electrochemical parameters

- Photo-current equal to 0.0026 mA cm^{-2}.
- Electrical resistance of 273 Ω.
- Charge transfer resistance electrode/electrolyte interface under illumination equal to 1.07 $x10^6$ Ω.

17 Fotoelettrodo di TiO_2 sensibilizzato con il colorante **BTD-DTP1**

PHOTO-ELECTRODE BASED ON TiO_2 SENSITIZED WITH BTD-DTP1 DYE

SUMMARY

SEM	☒
Optical properties	☒
Electrochemistry	☒
Photo-electrochemistry	☒

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 TiO_2-based ink 18NR-T (Greatcell Solar Materials), with viscosity between 40-55 Pa*s.
Dye BTD-DTP1 (molecular formula $C_{42}H_{33}N_5O_2S_3$) 0.3 mM in ethanol:THF.

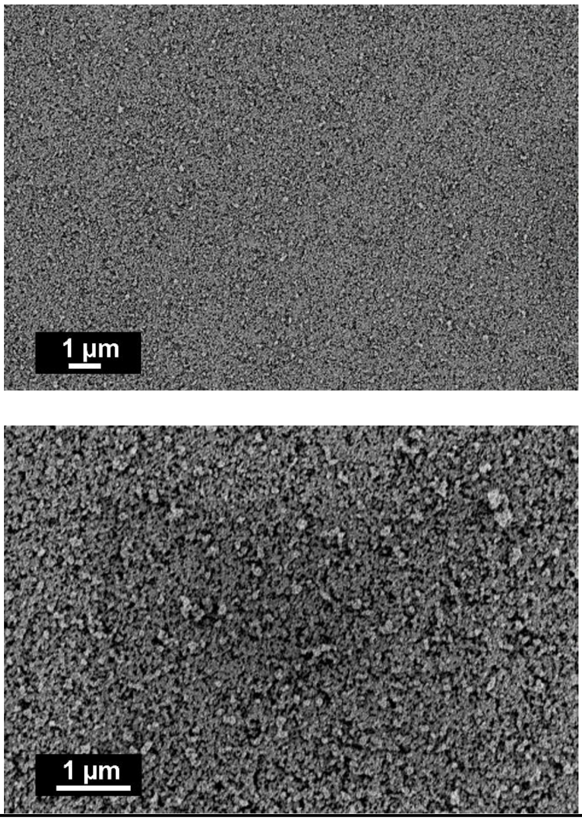
Procedure

Thin film based on TiO_2 was prepared by semi-automatic screen-printed machine AUREL 900 (Aurel Automation S.p.A., Italia) with speed of 90 mm/s and 3 depositions. A thickness of 11.84 μm and active area of 0.25 cm^2 were achieved. Between each deposition a drying treatment of 80°C in IR oven was used. Finally, a thermal treatment at 500°C for 30’ was done to consolidate the film. The as obtained film was sensitized overnight in 0.3 mM BTD-DTP1 dye solution and the excess of dye was removed by absolute ethanol.

CHARACTERIZATION

SEM

SEM images were collected with a ZEISS SIGMA, Carl Zeiss Microscopy GmbH scanning electron microscope equipped with a field-emission electron source.

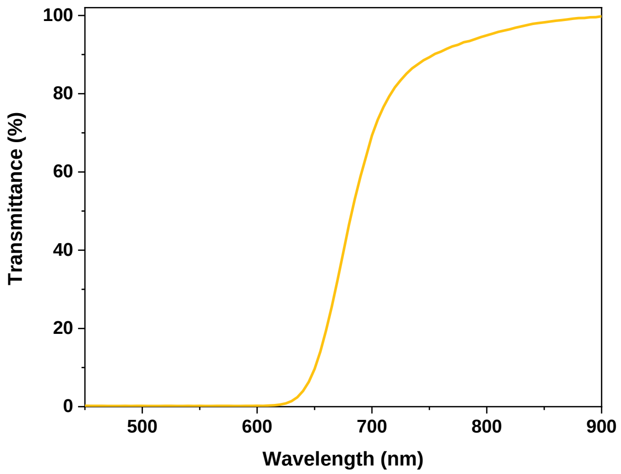


Homogenous microstructure with nanoparticles with regular porous (diameter between 100 e 120 nm).

OPTICAL PROPERTIES

Transmittance spectra

Acquire in the range between 400 and 900 nm with an integrating sphere.



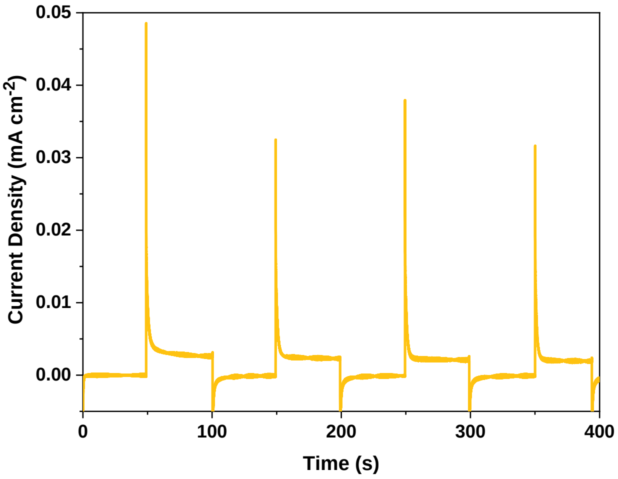
Optical parameters

Ability to harvest light in the Visible region.

Transparency at 700 nm of 69%.

PHOTO-ELECTROCHEMISTRY

Cronoamperometry in a photoelectrochemical cell with working electrode: FTO+film; counter-electrode: platinum wire; reference electrode: aqueous Ag/AgCl (sat. KCl); electrolyte: $LiClO_4$ 0.2 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).



Electrochemical Impedance Spectroscopy in a photoelectrochemical cell with working electrode: FTO+film; counter-electrode: platinum wire; reference electrode: aqueous Ag/AgCl (sat. KCl); electrolyte: $LiClO_4$ 0.2 M in H_2O MQ. Frequency range between 1x10^5 Hz e 0.05 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).

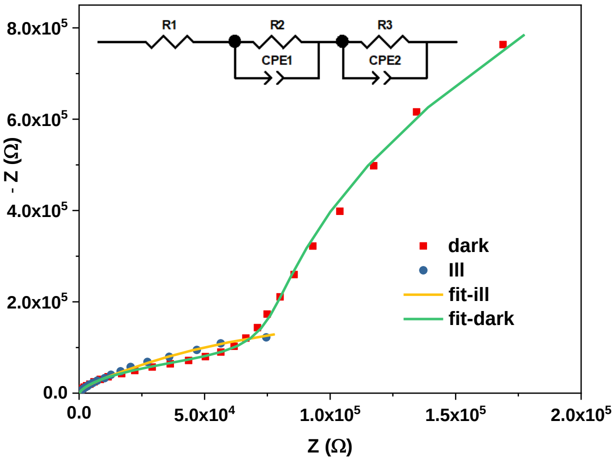


Photo-electrochemical parameters

- Photo-current equal to 0.0024 mA cm^{-2}.
- Electrical resistance of 111 Ω.
- Charge transfer resistance electrode/electrolyte interface under illumination equal to 3.67 x10^5 Ω.

18 Fotoelettrodo di TiO_2 sensibilizzato con il colorante **BTD-DTP2**

PHOTO-ELECTRODE BASED ON TiO_2 SENSITIZED WITH BTD-DTP2 DYE

SUMMARY

SEM	☒
Optical properties	☒
Electrochemistry	☒
Photo-electrochemistry	☒

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 TiO_2-based ink 18NR-T (Greatcell Solar Materials), with viscosity between 40-55 Pa*s.
Dye BTD-DTP2 (molecular formula $C_{64}H_{61}N_5O_4S_3$) 0.3 mM in ethanol:THF.

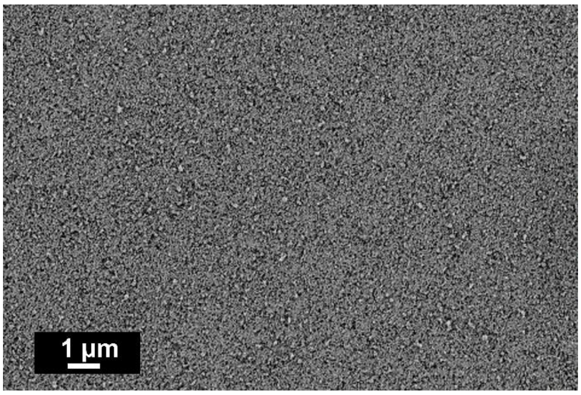
Procedure

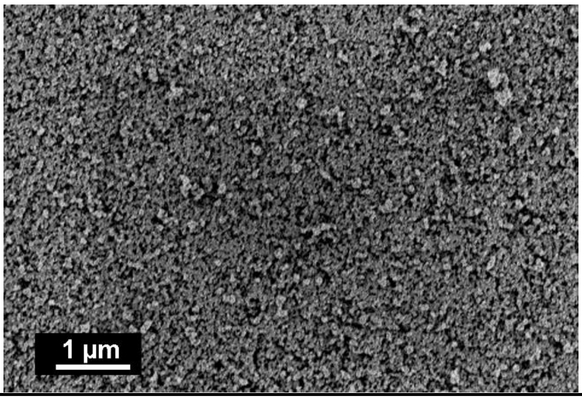
Thin film based on TiO_2 was prepared by semi-automatic screen-printed machine AUREL 900 (Aurel Automation S.p.A., Italia) with speed of 90 mm/s and 3 depositions. A thickness of 11.84 µm and active area of 0.25 cm^2 were achieved. Between each deposition a drying treatment of 80°C in IR oven was used. Finally, a thermal treatment at 500°C for 30’ was done to consolidate the film. 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.

CHARACTERIZATION

SEM

SEM images were collected with a ZEISS SIGMA, Carl Zeiss Microscopy GmbH scanning electron microscope equipped with a field-emission electron source.



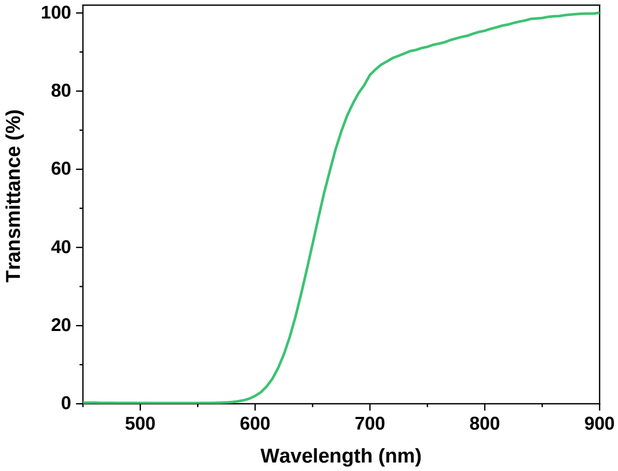


Homogenous microstructure with nanoparticles with regular porous (diameter between 100 e 120 nm).

OPTICAL PROPERTIES

Transmittance spectra

Acquire in the range between 400 and 900 nm with an integrating sphere.

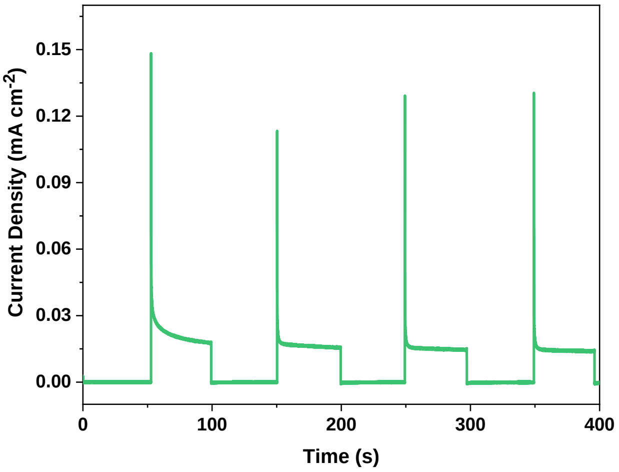


Optical parameters

Ability to harvest light in the Visible region.
Transparency at 700 nm of 84%.

PHOTO-ELECTROCHEMISTRY

Cronoamperometry in a photoelectrochemical cell with working electrode: FTO+film; counter-electrode: platinum wire; reference electrode: aqueous Ag/AgCl (sat. KCl); electrolyte: $LiClO_4$ 0.2 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).



Electrochemical Impedance Spectroscopy in a photoelectrochemical cell with working electrode: FTO+film; counter-electrode: platinum wire; reference electrode: aqueous Ag/AgCl (sat. KCl); electrolyte: $LiClO_4$ 0.2 M in H_2O MQ. Frequency range between 1x10^5 Hz e 0.05 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).

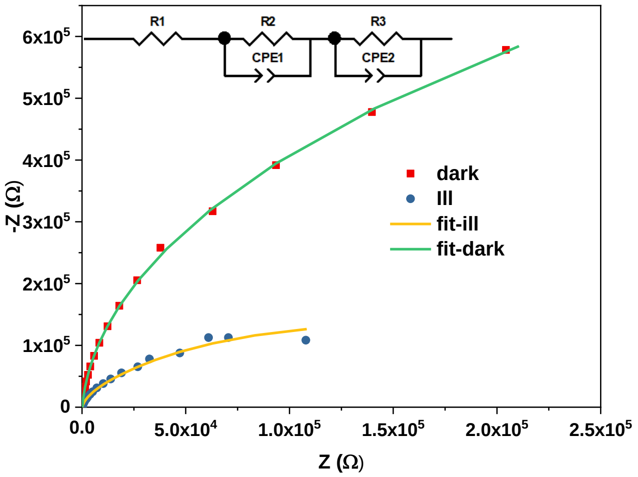


Photo-electrochemical parameters

- Photo-current equal to 0.016 mA cm^{-2}.
- Electrical resistance of 116 Ω.
- Charge transfer resistance electrode/electrolyte interface under illumination equal to 2.61 x10^5 Ω.

19 Fotoelettrodo di TiO_2 sensibilizzato con il colorante **BTD-DTP3**

PHOTO-ELECTRODE BASED ON TiO_2 SENSITIZED WITH BTD-DTP3 DYE

SUMMARY	
SEM	☒
Optical properties	☒
Electrochemistry	☒
Photo-electrochemistry	☒

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 TiO_2-based ink 18NR-T (Greatcell Solar Materials), with viscosity between 40-55 Pa*s.
Dye BTD-DTP3 (molecular formula $C_{70}H_{65}N_5O_4S_3$) 0.3 mM in ethanol:THF.

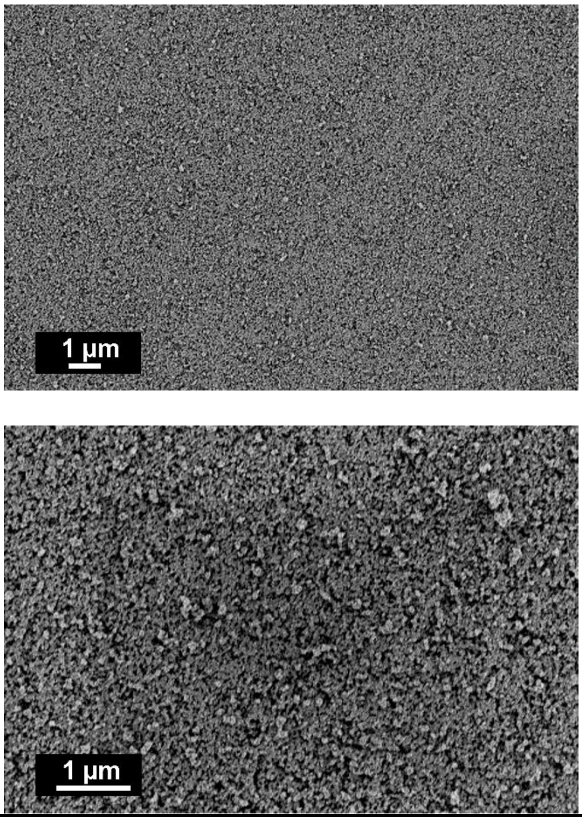
Procedure

Thin film based on TiO_2 was prepared by semi-automatic screen-printed machine AUREL 900 (Aurel Automation S.p.A., Italia) with speed of 90 mm/s and 3 depositions. A thickness of 11.84 µm and active area of 0.25 cm^2 were achieved. Between each deposition a drying treatment of 80°C in IR oven was used. Finally, a thermal treatment at 500°C for 30' was done to consolidate the film. The as obtained film was sensitized overnight in 0.3 mM BTD-DTP3 dye solution and the excess of dye was removed by absolute ethanol.

CHARACTERIZATION

SEM

SEM images were collected with a ZEISS SIGMA, Carl Zeiss Microscopy GmbH scanning electron microscope equipped with a field-emission electron source.

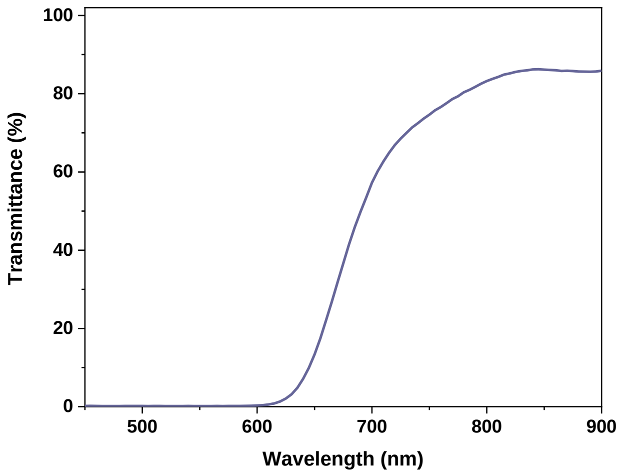


Homogenous microstructure with nanoparticles with regular porous (diameter between 100 e 120 nm).

OPTICAL PROPERTIES

Transmittance spectra

Acquire in the range between 400 and 900 nm with an integrating sphere.



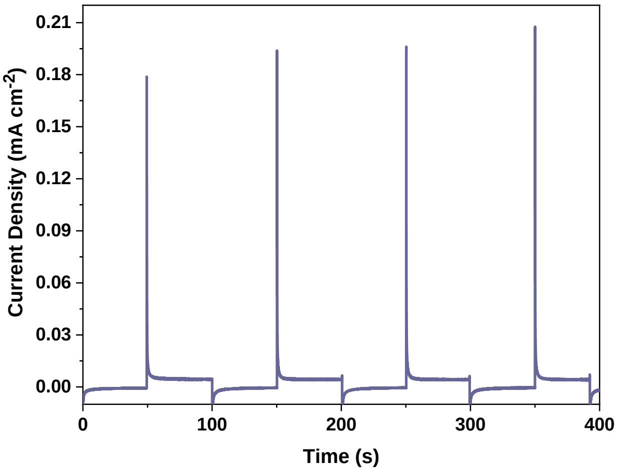
Optical parameters

Ability to harvest light in the Visible region.

Transparency at 700 nm of 57%.

PHOTO-ELECTROCHEMISTRY

Cronoamperometry in a photoelectrochemical cell with working electrode: FTO+film; counter-electrode: platinum wire; reference electrode: aqueous Ag/AgCl (sat. KCl); electrolyte: $LiClO_4$ 0.2 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).



Electrochemical Impedance Spectroscopy in a photoelectrochemical cell with working electrode: FTO+film; counter-electrode: platinum wire; reference electrode: aqueous Ag/AgCl (sat. KCl); electrolyte: $LiClO_4$ 0.2 M in H_2O MQ. Frequency range between $1x10^5$ Hz e 0.05 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).

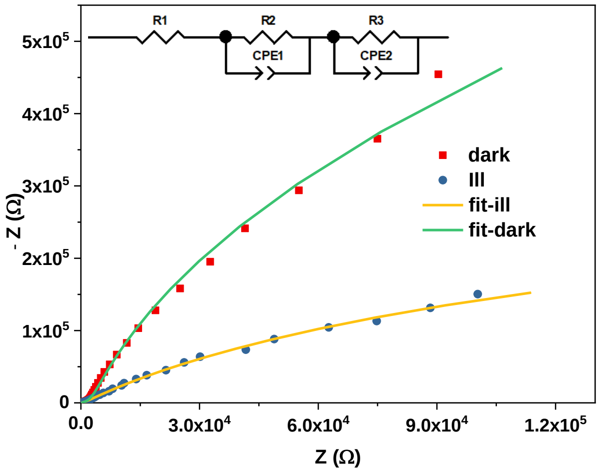


Photo-electrochemical parameters

- Photo-current equal to 0.0045 mA cm^{-2}.
- Electrical resistance of 143 Ω.
- Charge transfer resistance electrode/electrolyte interface under illumination equal to $6.13 x10^5$ Ω.

20 Fotoelettrodo ricaricabile con TiO_2/**N3**/GO

PHOTO-RECHARGEABLE ELECTRODE BASED ON TiO_2 SENSITIZED WITH N3 DYE AND GRAPHENE OXIDE

SUMMARY

SEM	☒
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 2.5x2.5 cm^2.
Screen printing TiO_2-based ink 18NR-T (Greatcell Solar Materials), with viscosity between 40-55 Pa*s.
Dye N3 (cis-Bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II), Sigma Aldrich) 0.3 mM in Absolute Ethanol.
Graphene oxide (GO, 4 mg/mL in water, Sigma Aldrich), Nafion (Nafion ® 5 wt % in alchol and water)

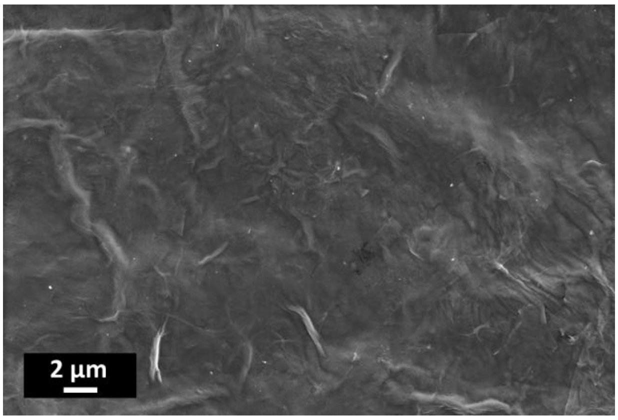
Procedure

Thin film based on TiO_2 was prepared by semi-automatic screen-printed machine AUREL 900 (Aurel Automation S.p.A., Italia) with speed of 90 mm/s and 3 depositions. A thickness of 11.84 μm and active area of 0.25 cm^2 were achieved. Between each deposition a drying treatment of 80°C in IR oven was used. Finally, a thermal treatment at 500°C for 30' was done to consolidate the film. 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, a graphene oxide-based ink was deposited by drop-by-drop deposition (150 μL) and dried overnight. In particular, GO 83% vol. 17 % vol. Nafion composition was used, and the final amount of ink deposited was 0.0024 g.

CHARACTERIZATION

SEM

SEM images were collected with a ZEISS SIGMA, Carl Zeiss Microscopy GmbH scanning electron microscope equipped with a field-emission electron source.

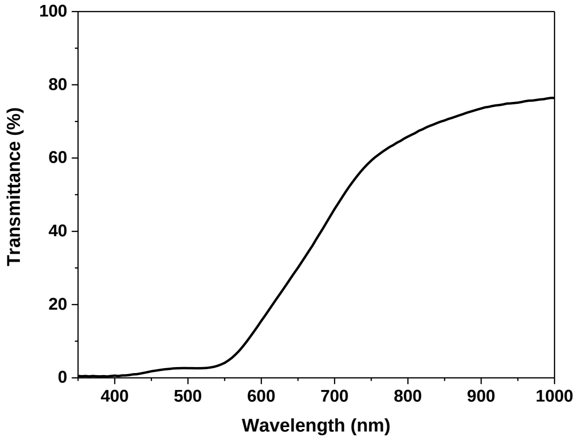


A typical graphene oxide microstructure was observed on TiO_2 sensitized film.

OPTICAL PROPERTIES

Transmittance spectra

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

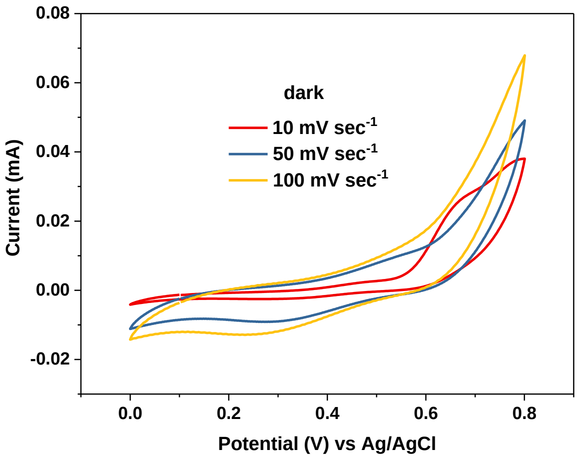


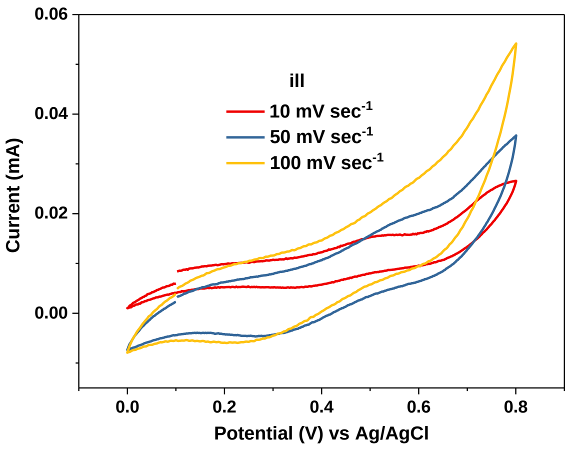
Optical parameters

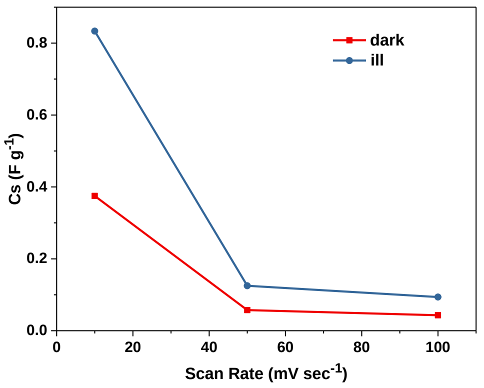
Ability to harvest light in the Visible region.
Transparency at 700 nm of 43%.

PHOTO-ELECTROCHEMISTRY

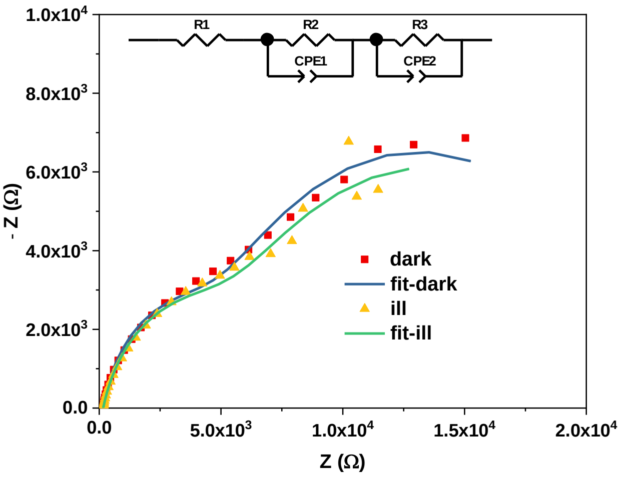
Cyclic Voltammetry in a photoelectrochemical cell with working electrode: FTO+film; counter-electrode: platinum wire; reference electrode: aqueous Ag/AgCl (sat. KCl); electrolyte: $LiClO_4$ 0.1 M in H_2O MQ. Potential applied between 0.8 V and 0 V vs Ag/AgCl and scan rate of 10, 50, 100 mV sec^{-1}.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







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).



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 0V and 0.8 V vs Ag/AgCl with current density of 0.12 A g^{-1}. Dark and illumination conditions with 1000 W m^{-2} as irradiance (calibrated with a reference cell).

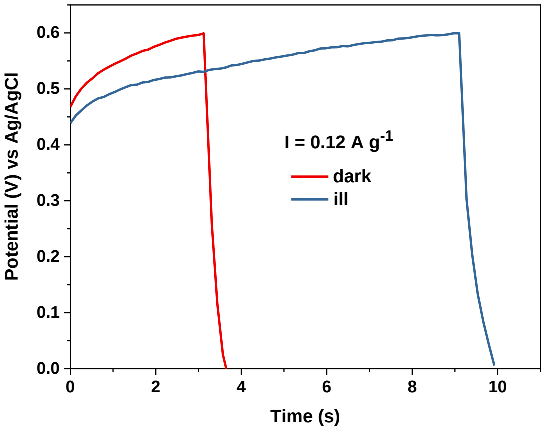


Photo-electrochemical parameters

- Specific capacitance under illumination 0.27 F g^{-1} at 0.12 A g^{-1}.
- Electrical resistance under illumination of 163 Ω.
- Charge transfer resistance electrode/electrolyte interface under illumination equal to 17403 Ω.

21 Fotoelettrodo ricaricabile con TiO_2/**N3**/PEDOT

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

SUMMARY

SEM	☒
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 2.5x2.5 cm^2.

Screen printing TiO_2-based ink 18NR-T (Greatcell Solar Materials), with viscosity between 40-55 Pa*s.

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)

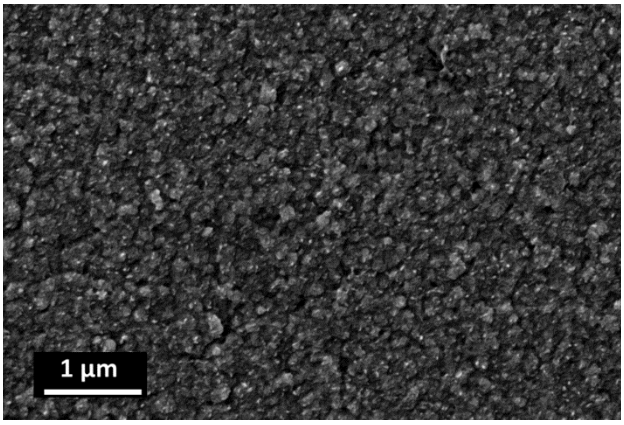
Procedure

Thin film based on TiO_2 was prepared by semi-automatic screen-printed machine AUREL 900 (Aurel Automation S.p.A., Italia) with speed of 90 mm/s and 3 depositions. A thickness of 11.84 µm and active area of 0.25 cm^2 were achieved. Between each deposition a drying treatment of 80°C in IR oven was used. Finally, a thermal treatment at 500°C for 30′ was done to consolidate the film. 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. Controlling the amount of charge (0.1 C) the final amount of PEDOT deposited was 0.00049 g.

CHARACTERIZATION

SEM

SEM images were collected with a ZEISS SIGMA, Carl Zeiss Microscopy GmbH scanning electron microscope equipped with a field-emission electron source.

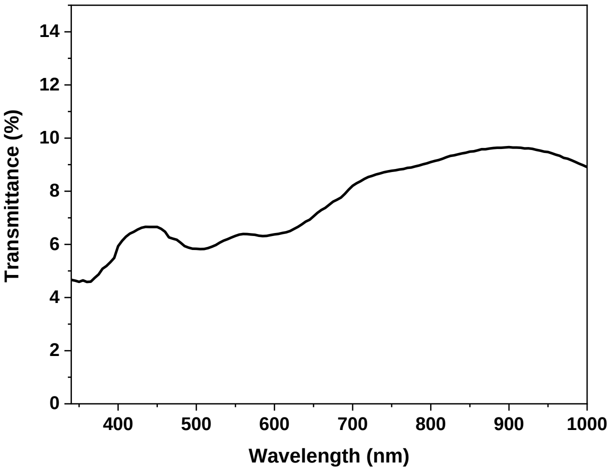


A regular morphology with small particles was observed for PEDOT layer electro-deposited on sensitized TiO_2 film.

OPTICAL PROPERTIES

Transmittance spectra

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



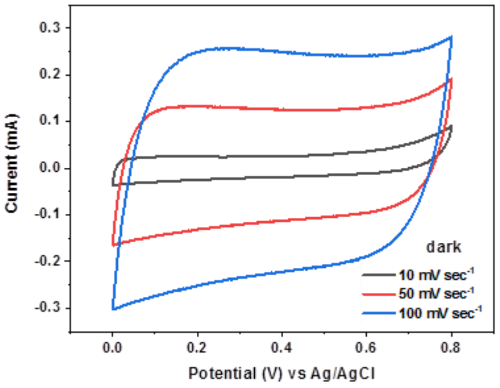
Optical parameters

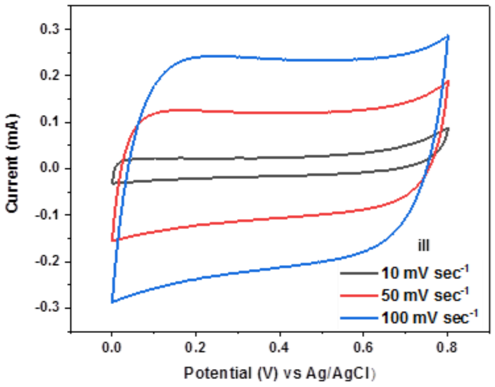
Ability to harvest light in the Visible region.

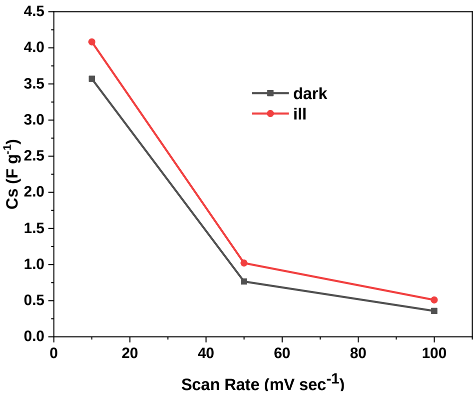
Transparency at 700 nm of 8%.

PHOTO-ELECTROCHEMISTRY

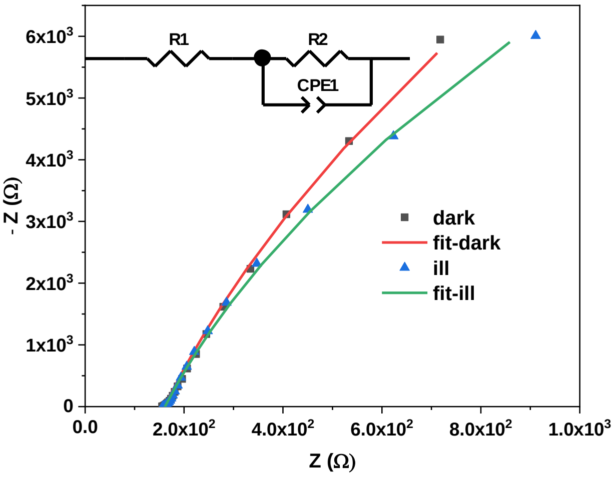
Cyclic Voltammetry in a photoelectrochemical cell with working electrode: FTO+film; counter-electrode: platinum wire; reference electrode: aqueous Ag/AgCl (sat. KCl); electrolyte: $LiClO_4$ 0.1 M in H_2O MQ. Potential applied between 0.8 V and 0 V vs Ag/AgCl and scan rate of 10, 50, 100 mV sec^{-1}.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







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).



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 0V and 0.8 V vs Ag/AgCl with current density of 0.12 A g^{-1}. Dark and illumination conditions with 1000 W m^{-2} as irradiance (calibrated with a reference cell).

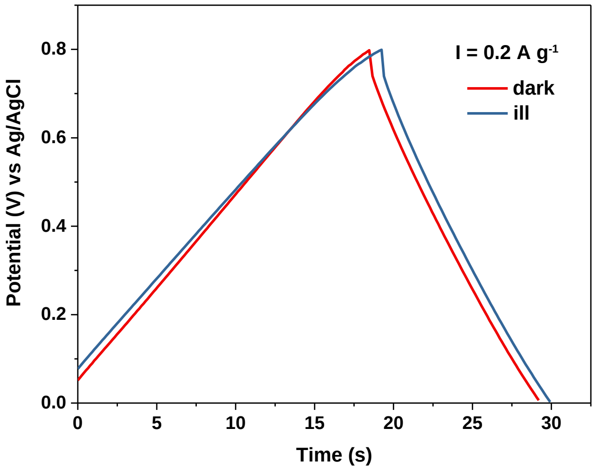


Photo-electrochemical parameters

- Specific capacitance under illumination 2.8 F g^{-1} at 0.2 A g^{-1}.
- Electrical resistance under illumination of 161 Ω.
- Charge transfer resistance electrode/electrolyte interface under illumination equal to 1.1×10^5 Ω.

22 Fotoelettrodo ricaricabile con TiO_2/**AD418**/PEDOT

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

SUMMARY

SEM	☒
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 2.5x2.5 cm^2.
Screen printing TiO_2-based ink 18NR-T (Greatcell Solar Materials), with viscosity between 40-55 Pa*s.
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)

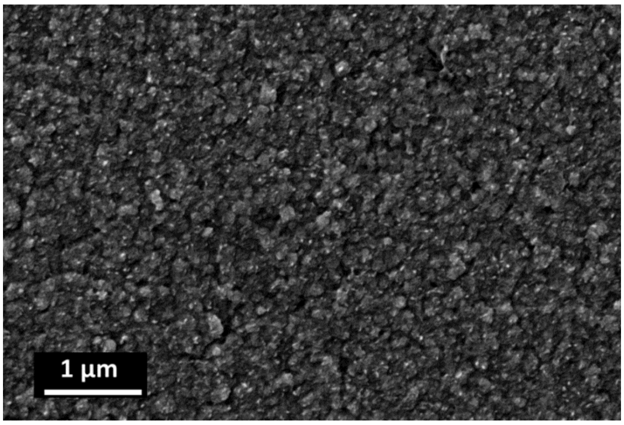
Procedure

Thin film based on TiO_2 was prepared by semi-automatic screen-printed machine AUREL 900 (Aurel Automation S.p.A., Italia) with speed of 90 mm/s and 3 depositions. A thickness of 11.84 µm and active area of 0.25 cm^2 were achieved. Between each deposition a drying treatment of 80°C in IR oven was used. Finally, a thermal treatment at 500°C for 30’ was done to consolidate the film. 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. Controlling the amount of charge (0.1 C) the final amount of PEDOT deposited was 0.00049 g.

CHARACTERIZATION

SEM

SEM images were collected with a ZEISS SIGMA, Carl Zeiss Microscopy GmbH scanning electron microscope equipped with a field-emission electron source.

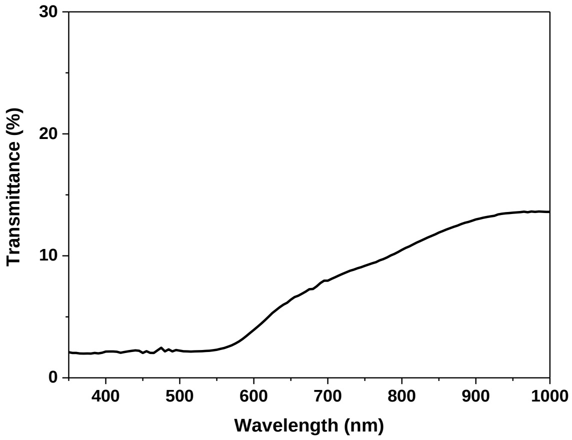


A regular morphology with small particles was observed for PEDOT layer electro-deposited on sensitized TiO_2 film.

OPTICAL PROPERTIES

Transmittance spectra

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



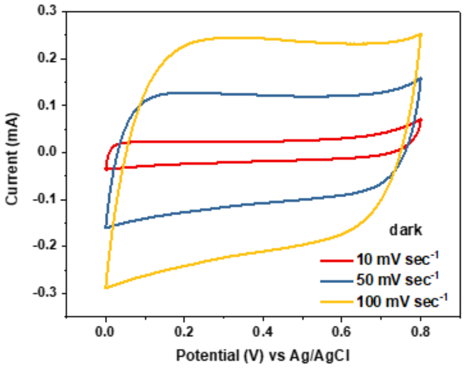
Optical parameters

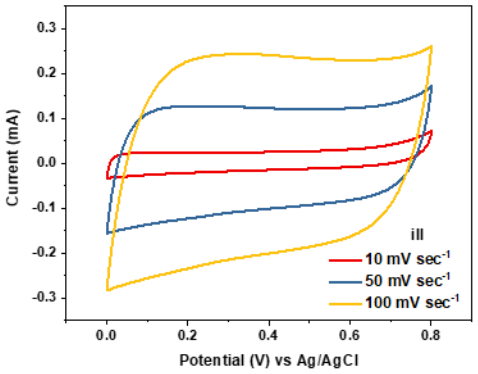
Ability to harvest light in the Visible region.

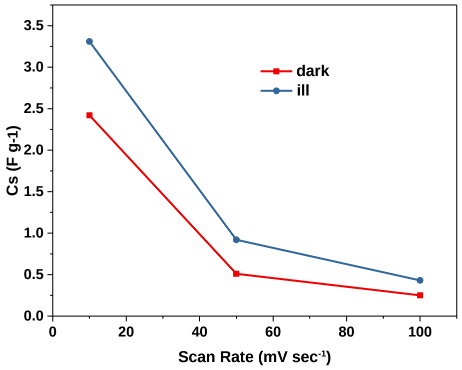
Transparency at 700 nm of 8%.

PHOTO-ELECTROCHEMISTRY

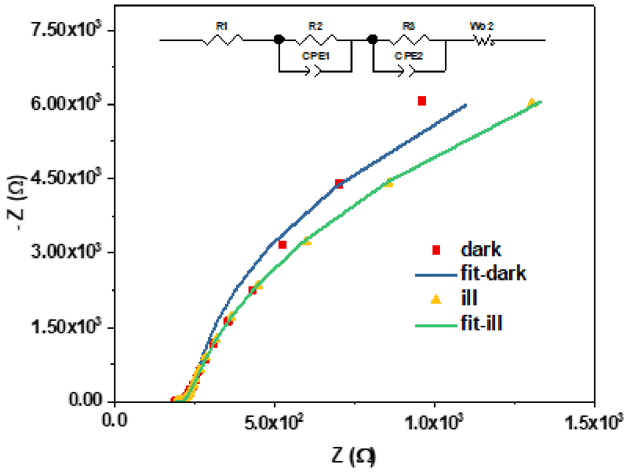
Cyclic Voltammetry in a photoelectrochemical cell with working electrode: FTO+film; counter-electrode: platinum wire; reference electrode: aqueous Ag/AgCl (sat. KCl); electrolyte: $LiClO_4$ 0.1 M in H_2O MQ. Potential applied between 0.8 V and 0 V vs Ag/AgCl and scan rate of 10, 50, 100 mV sec^{-1}.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







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).



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 0V and 0.8 V vs Ag/AgCl with current density of 0.12 A g^{-1}. Dark and illumination conditions with 1000 W m^{-2} as irradiance (calibrated with a reference cell).

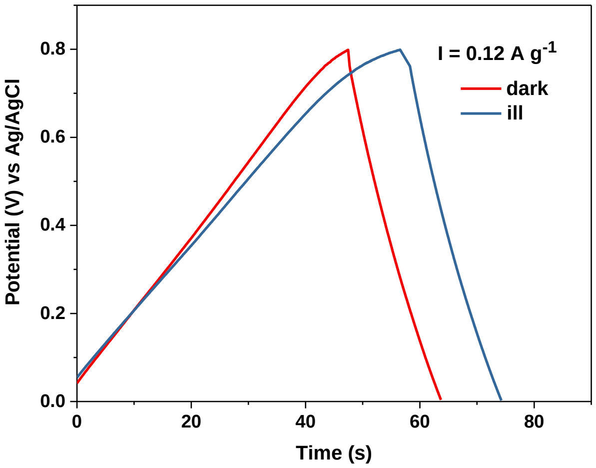


Photo-electrochemical parameters

- Specific capacitance under illumination 2.83 F g^{-1} at 0.12 A g^{-1}.
- Electrical resistance under illumination of 190 Ω.
- Charge transfer resistance electrode/electrolyte interface under illumination equal to 38154 Ω.

23 Fotoelettrodo ricaricabile con TiO_2/**BTD-DTP2**/PEDOT

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

SUMMARY

SEM ☒
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 2.5x2.5 cm^2.
Screen printing TiO_2-based ink 18NR-T (Greatcell Solar Materials), with viscosity between 40-55 Pa*s.
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)

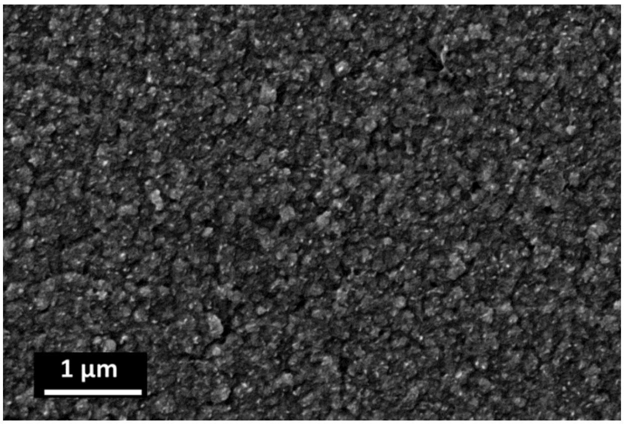
Procedure

Thin film based on TiO_2 was prepared by semi-automatic screen-printed machine AUREL 900 (Aurel Automation S.p.A., Italia) with speed of 90 mm/s and 3 depositions. A thickness of 11.84 µm and active area of 0.25 cm^2 were achieved. Between each deposition a drying treatment of 80°C in IR oven was used. Finally, a thermal treatment at 500°C for 30' was done to consolidate the film. 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. Controlling the amount of charge (0.1 C) the final amount of PEDOT deposited was 0.00049 g.

CHARACTERIZATION

SEM

SEM images were collected with a ZEISS SIGMA, Carl Zeiss Microscopy GmbH scanning electron microscope equipped with a field-emission electron source.

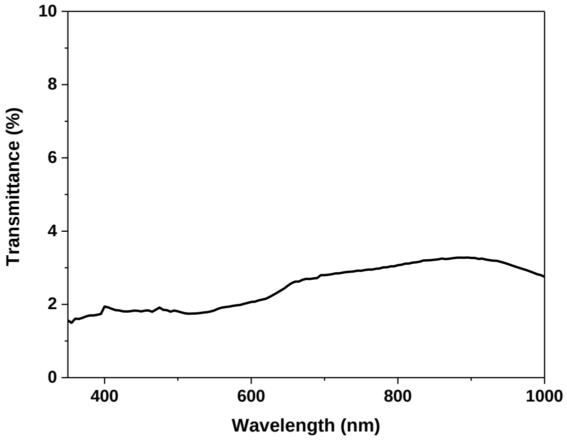


A regular morphology with small particles was observed for PEDOT layer electro-deposited on sensitized TiO_2 film.

OPTICAL PROPERTIES

Transmittance spectra

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



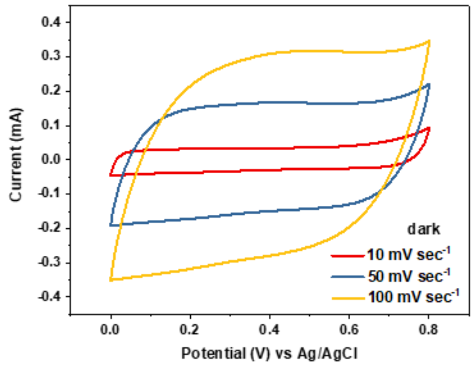
Optical parameters

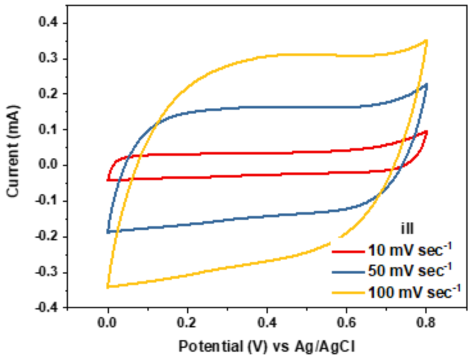
Ability to harvest light in the Visible region.

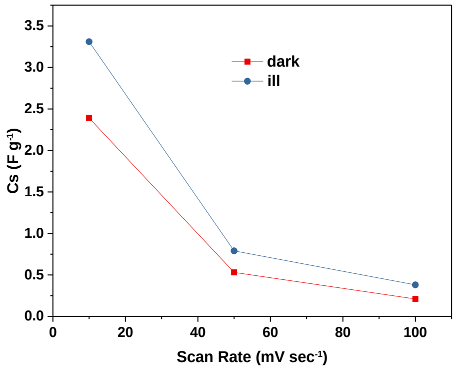
Transparency at 700 nm of 3%.

PHOTO-ELECTROCHEMISTRY

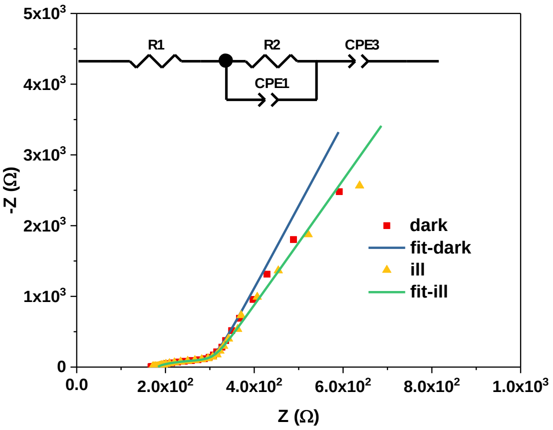
Cyclic Voltammetry in a photoelectrochemical cell with working electrode: FTO+film; counter-electrode: platinum wire; reference electrode: aqueous Ag/AgCl (sat. KCl); electrolyte: $LiClO_4$ 0.1 M in H_2O MQ. Potential applied between 0.8 V and 0 V vs Ag/AgCl and scan rate of 10, 50, 100 mV sec^{-1}.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







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).



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 0V and 0.8 V vs Ag/AgCl with current density of 0.12 A g^{-1}. Dark and illumination conditions with 1000 W m^{-2} as irradiance (calibrated with a reference cell).

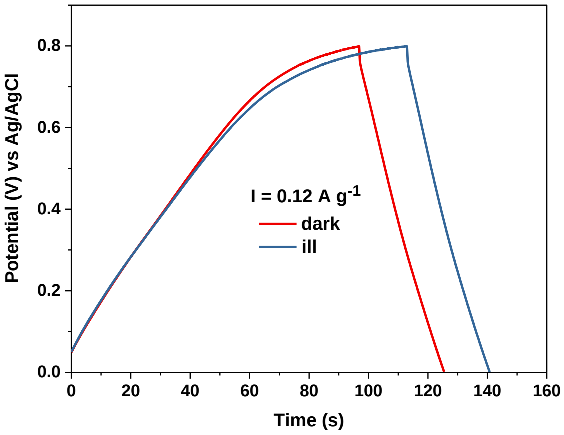


Photo-electrochemical parameters

- Specific capacitance under illumination 4.58 F g^{-1} at 0.12 A g^{-1}.
- Electrical resistance under illumination of 183 Ω.
- Charge transfer resistance electrode/electrolyte interface under illumination equal to 119 Ω.

24 Fotoelettrodo di WO_3

PHOTO-RECHARGEABLE ELECTRODE BASED ON WO_3

SUMMARY

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

WO_3 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 was developed using (active material content between 15 ed il 20 wt.%), α-terpineol and cellulose (Sigma Aldrich).

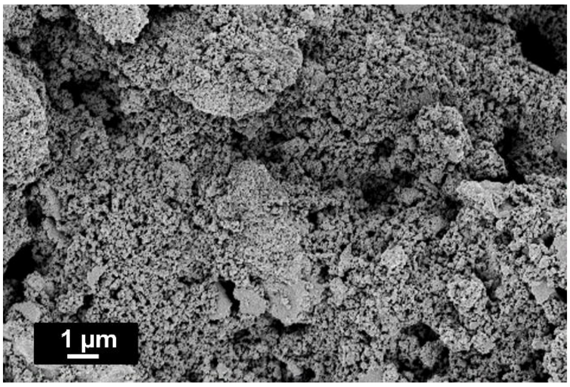
Procedure

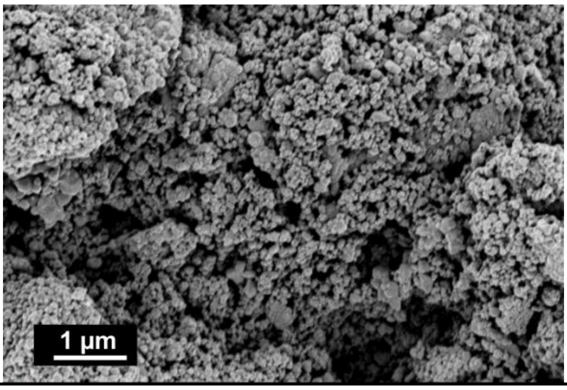
Thin film based on WO_3 was prepared by semi-automatic screen-printed machine AUREL 900 (Aurel Automation S.p.A., Italia) with speed of 45 mm/s and 10 depositions. A thickness of 22 µm and active area of 0.25 cm^2 were achieved. Between each deposition a drying treatment of 80°C in IR oven was used. Finally, a thermal treatment at 500°C for 30’ was done to consolidate the film.

CHARACTERIZATION

SEM

SEM images were collected with a ZEISS SIGMA, Carl Zeiss Microscopy GmbH scanning electron microscope equipped with a field-emission electron source.





Microstructure with aggregates covered with small WO_3 nanoparticles with distributed porosity with dimension in the range of few nanometres until to over 1 µm.

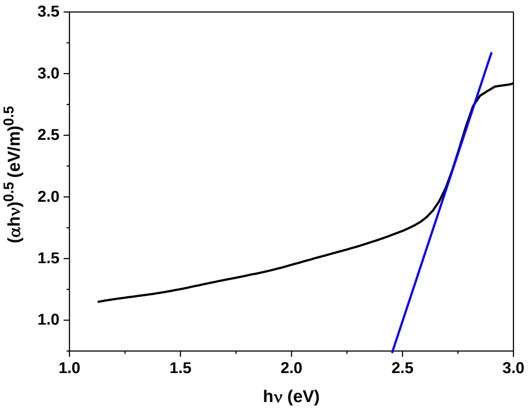
OPTICAL PROPERTIES

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.

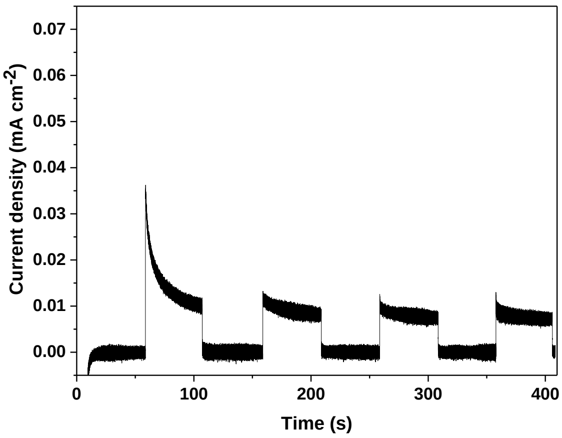


Optical parameters

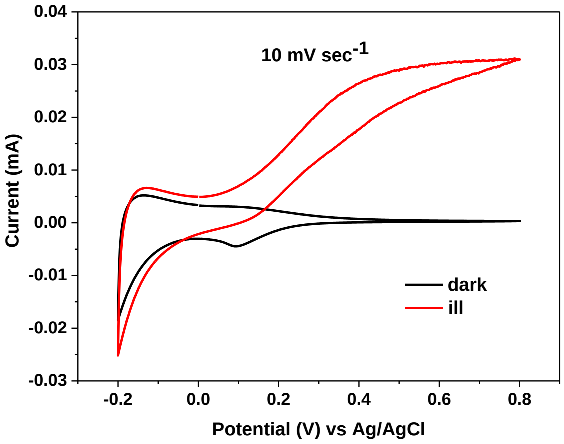
E_g= 2.45 eV

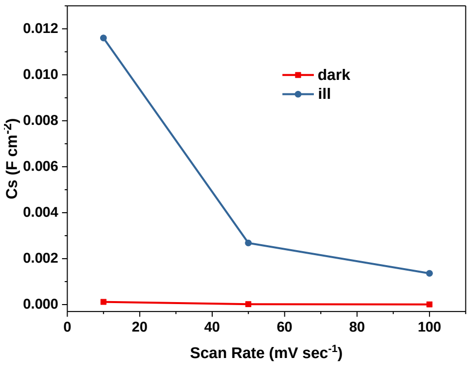
PHOTO-ELECTROCHEMISTRY

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).

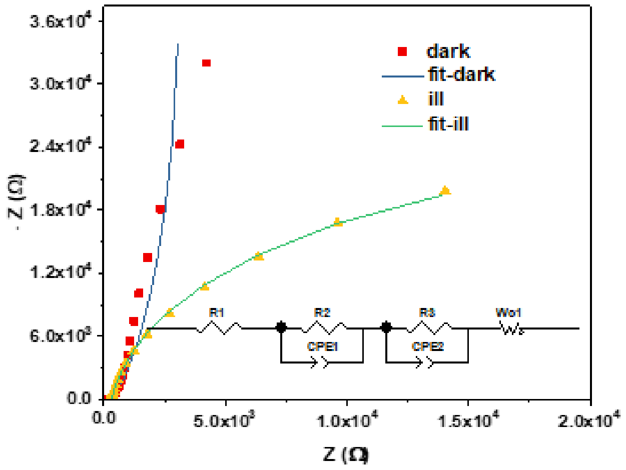


Cyclic Voltammetry in a photoelectrochemical cell with working electrode: FTO+film; counter-electrode: platinum wire; reference electrode: aqueous Ag/AgCl (sat. KCl); electrolyte: $LiClO_4$ 0.1 M in H_2O MQ. Potential applied between 0.8 V and 0 V vs Ag/AgCl and scan rate of 10, 50, 100 mV sec^{-1}.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





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).



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 0V and 0.8 V vs Ag/AgCl with current density of 0.0002 A g^{-1}. Dark and illumination conditions with 1000 W m^{-2} as irradiance (calibrated with a reference cell).

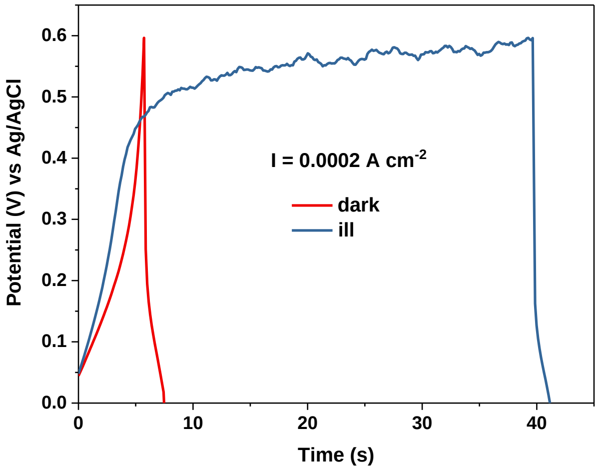


Photo-electrochemical parameters

- Photo-current equal to 0.01 mA cm^{-2}
- Areal capacitance under illumination 1.6 mF cm^{-2} at 0.0002 A cm^{-2}.
- Electrical resistance under illumination of 173 Ω.
- Charge transfer resistance electrode/electrolyte interface under illumination equal to 28992 Ω.