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Improved Silicon surface passivation by hybrid composites formed by PEDOT:PSS with anatase TiO_2 nanoparticles

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Abstract

In this work, hybrid composites formed by PEDOT:PSS (poly(3,4-ethylene dioxythiophene):-polystyrene sulfonate) and anatase TiO_2 nanoparticles synthesized by hydrolysis were spin-coated on Si substrates in order to evaluate their potential implementation in Si-hybrid solar cells, based on their passivation behaviour. X-ray diffraction (XRD), photoluminescence (PL), Raman spectroscopy, quasi-steady state photoconductance (QSS-PC) based on PL imaging, and Hall effect measurements were carried out for the structural, optical and electrical characterization. Enhanced carrier lifetime values of $\tau \sim 0.5$ ms were obtained by adding a controlled amount of TiO_2 nanoparticles (0.5 % wt.) to the PEDOT:PSS matrix.

Keywords: Hybrid composite ; TiO_2 ; nanoparticles ; PEDOT:PSS ; Si-passivation

1. Introduction

Despite the efficiency increases achieved within a very short time in organic solar cells, [1,2] there are still unresolved challenges limiting their production in commercial scale, such as their low stability and conductivity. Some of these aspects can be overcome by the combination of organic and inorganic materials in the form of hybrid composites, [3–6] which can lead to enhanced performance and advantages due to the synergy between the counterparts. Actually, silicon-organic hybrid composites represent a very promising candidate for clean and low-cost photovoltaic technologies. However, one of the most challenging problems is ensuring the required Si surface passivation in order to achieve a competitive solar cell performance.

In this work, an efficient method to passivate the Si surface without additional costs, based on hybrid composites formed by anatase TiO_2 nanoparticles embedded in PEDOT:PSS, has been evaluated. The hybrid layers were deposited by spin-coating, avoiding high-temperature, vacuum, and expensive processing, as well as pre-treatments of the Si surface. Promising results have been achieved in the enhancement of the carrier lifetime and the conducivity by the controlled addition of solvents and TiO_2 nanoparticles in the polymer, as compared with previous works.

2. Experimental method

A soft chemistry route based on hydrolysis was used for the synthesis of TiO_2 nanoparticles. Firstly, the selected precursor $Ti(OBu)_4$ (Sigma Aldrich purity 97%) was mixed in a controlled ratio with 1-butanol. Distilled water was added at continuous stirring and room temperature to induce hydrolysis. After rinsing to obtain neutral pH, the obtained powder was treated at 250 ° C during 24 h to obtain crystalline anatase TiO_2 phase.

Hybrid composites were prepared by adding a controlled amount of TiO_2 nanoparticles (0.5, 1, or 2 % wt.) to the PEDOT: PSS (Clevios, PH1000, 1.0-1,3 wt% in water), mixed with an ultrasonic bath for 15 minutes and with an ultrasonic probe during 30 s. The mixture was spin-coated on silicon n-type substrates (FZ, TOPSIL, thickness 280 ± 20 nm) and over glass substrates and finally dried at 120 ºC for 15 min to evaporate the remaining water.

Prior to the addition of nanoparticles, dimethyl sulfoxide (DMSO) was added in 5 wt% [7–9] to the polymer to avoid agglomeration and enhance both dispersion and conductivity, while for the achievement of better surface wettability Triton X-100 was added in 0.1 wt% to the mixture [10]. The obtained solution was magnetically stirred and filtered with a Polyethersulfone (PES) membrane (0.45 µm porosity).

The structural characterization of the nanoparticles was carried out by X-ray diffraction (XRD) in a PANanalytical X'Pert Powder equipment, using the copper Kα line λ_{Cu} = 1.5404 Å. Raman measurements were performed on a confocal microscope Horiba Jobin Yvon LabRam HR 800 using a He-Ne laser (λ = 633nm). Photoluminescence (PL) was studied at room temperature using the same confocal microscope equipped with a He-Cd UV laser (λ = 325 nm) as excitation source and using neutral filters to diminish the laser power density. Quasi-steady state photoconductance (QSS-PC) measurements were carried out using a BT Imaging LIS-R1 with a laser (λ = 808 nm) at constant illumination intensity of 4.2 10^{-2} Wcm^{-2}. Electric measurements were carried out at room temperature in a 4-probe Hall effect Ecopia AMP55T HMS-7000 system equipped with 4 Au probes.

3. Results and discussion

Figure 1a shows the XRD pattern from TiO_2 nanoparticles. The broad peaks indicate the reduced dimensions of the synthesized particles. The peaks can be indexed to the TiO_2 anatase-type structure (ICDS 01-071-1166). Due to the low temperature used during the synthesis, a weak peak corresponding to the (121) planes from brookite TiO_2 (ICSD 00-015-0875) can be also appreciated at around 30.8°, which disappears by increasing the temperature of annealing. Based on the Scherrer formula, an average crystallite size around 6.8 ± 0.1 nm was calculated for the nanoparticles, with lattice parameters of $a = b = 3.759$ Å and $c = 9.195$ Å. Energy dispersive measurements (not shown here) confirm the only presence of Ti and O, within the resolution of the technique.

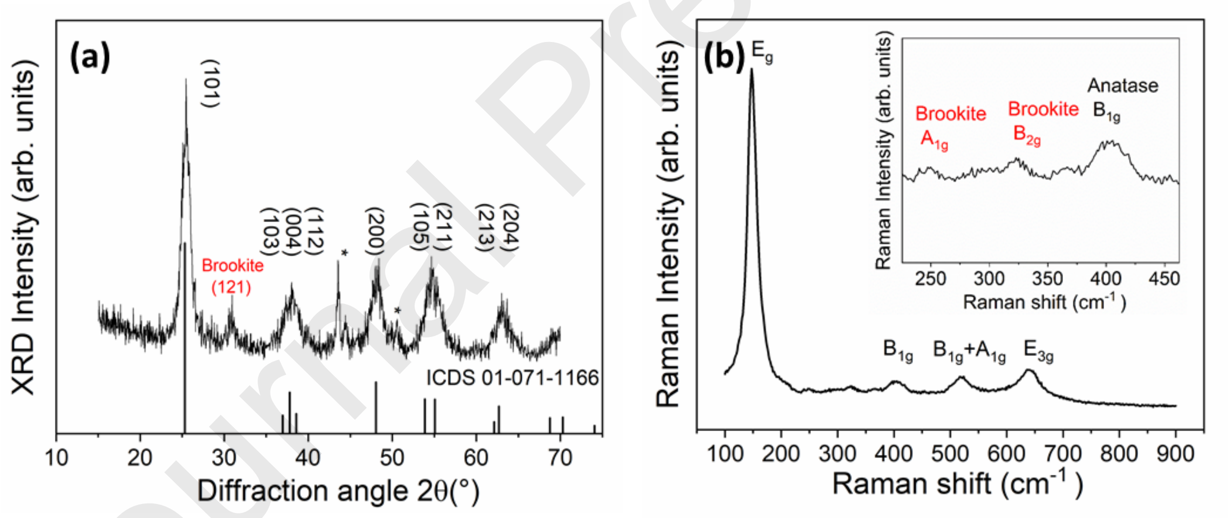

Fig.1. (a) XRD pattern and (b) Raman spectrum from TiO_2 nanoparticles. The peak marked with * around 43.5-44.5°and 50° in (a) corresponds to the sample holder.

The Raman spectrum from the nanoparticles (Fig. 1b) shows the usual active vibrational modes for anatase TiO_2, centered at 147 cm^{-1} (E_g), 197 cm^{-1} (E_g) , 399 cm^{-1} (B_{1g}) , 517 cm^{-1} (B_{1g}+A_{1g}), and 640 cm^{-1} (E_g) [11]. The E_g vibrational mode at 147 cm^{-1}, associated with symmetrical stretching of O-Ti-O groups, clearly dominates the Raman signal. Weak peaks from brookite can be also detected in this case [12](inset in Figure 1b), while peaks from the precursors or other Ti-O compounds were not observed.

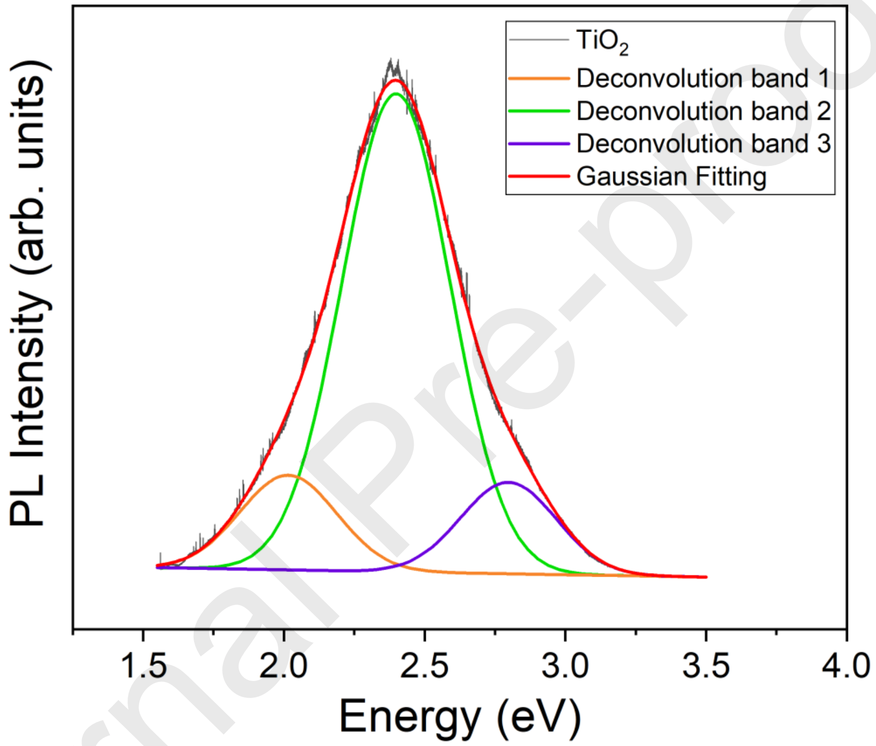

Fig. 2. Photoluminescence spectrum of TiO_2 nanoparticles including the corresponding Gaussian deconvolution to 3 bands.

Figure 2 shows the PL spectrum from anatase TiO_2 nanoparticles acquired at room temperature using a He-Cd laser (λ = 325 nm) as excitation source and neutral filters in order to decrease the laser intensity and avoid the formation of rutile. The corresponding luminescent signal is dominated by a broad emission centered around 2.38 eV. This feature is usually related to surface defects associated with oxygen deficiency [11]. Besides, emissions with lower intensity are observed at around 2 eV (due to oxygen deficiency and undercoordinated Ti atoms) and 2.8 eV (related to self- trapped excitons) [11], as shown in the deconvolution of the PL spectrum in Gaussian bands included in Figure 2.

Table 1. Hall effect measurements from bare PEDOT:PSS mixture and hybrid composites measured at I=0.1mA.

Sample	**Charge carrier concentration (cm^{-3})**	**Conductivity σ (Ω^{-1} cm^{-1})**
PEDOT:PSS	$(7.37\pm1.38)\cdot10^{21}$	$(1.89\pm0.01)\cdot10^{2}$
PEDOT:PSS + 0.5 %wt TiO_2	$(2.99\pm0.71)\cdot10^{21}$	$(2.33\pm0.03)\cdot10^{2}$
PEDOT:PSS + 1 %wt TiO_2	$(1.24\pm0.38)\cdot10^{21}$	$(1.92\pm0.05)\cdot10^{2}$
PEDOT:PSS + 2 %wt TiO_2	$(1.30\pm0.49)\cdot10^{22}$	$(4.39\pm0.03)\cdot10^{2}$

Bare PEDOT:PSS mixture, as well as hybrid composites of PEDOT:PSS with variable concentration of TiO_2 nanoparticles were spin-coated on Si and glass substrates in form of layers with a thickness around 100 nm. All the samples show good transparency in the visible range. Hall-effect measurements were carried out at room temperature on the hybrid composites with variable concentration of nanoparticles spin-coated on glass substrates, as well as on bare PEDOT:PSS mixture as a reference. The corresponding conductivity and charge carrier concentration values are indicated in Table 1. Enhanced conductivity is achieved for the hybrid composites when the concentration of nanoparticles is increased, obtaining the highest conductivity and carrier concentration values around 4.4 10^2 $\Omega^{-1}cm^{-1}$ and 1.3 10^{22} cm^{-3}, respectively, for the 2 wt. % of TiO_2 nanoparticles. Diverse authors reported improved PEDOT:PSS conductivity due to the rearrangement of the PEDOT:PSS chains configuration induced by the presence of nanoparticles with charged surfaces [13]. Percolation effects could be also considered for the samples with the highest amount of nanoparticles.

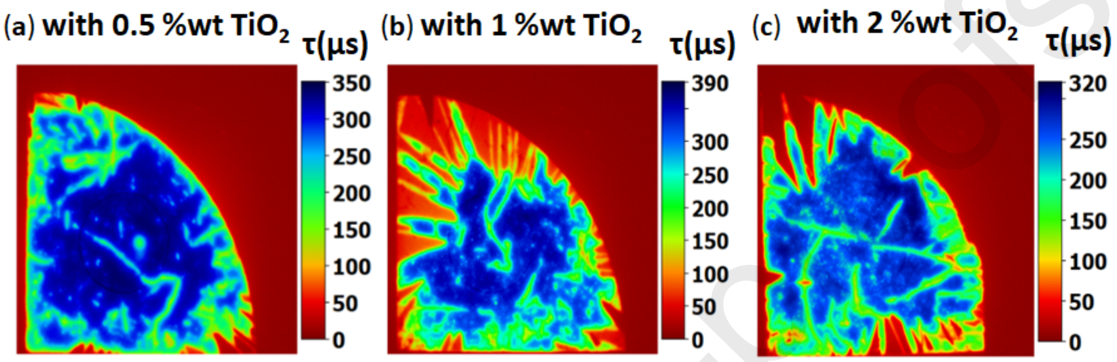

Fig. 3. PL images from composites with TiO_2 nanoparticles in (a) 0.5% wt., (b) 1 % wt., and (c) 2 % wt.

The passivation behavior of the hybrid layers over silicon was analyzed based on the QSSPC-calibrated PL imaging, as shown in Figure 3. Color bars besides the PL images indicate the charge carrier lifetime values, which were calculated from the corresponding QSS-PC curves as a function of the injection level (not shown here). High carrier lifetimes around 0.5 ms were obtained with the addition of DMSO and Triton X-100 to the PEDOT:PSS [13]. This lifetime value can be slightly increased ($\tau \sim 520$ μs) for the composites with TiO_2 nanoparticles in 0.5 wt %, which also improves the conductivity. However, higher concentrations of nanoparticles decreases the lifetime values ($\tau \sim 400$ μs). A charge-assisted passivation mechanism due to the presence of nanoparticles with positively charged surfaces, mainly due to hydroxyl groups, can be considered in the understanding of the observed passivation behaviour [5]. The lifetime values obtained in this work are competitive as compared with classical lifetime values reported for SiN_x:H or a-Si deposited with high temperature and expensive techniques [14].

4. Conclusion

Hybrid composites formed by PEDOT:PSS and TiO_2 nanoparticles in a variable ratio (0.5 , 1, 2 % wt.) were obtained and spin-coated on Si-substrates. The anatase TiO_2 nanoparticles synthesized by a hydrolysis method show averaged dimensions of 7 nm and PL emission mainly due to oxygen deficiency. A weak amount of brookite TiO_2 was also detected by XRD and Raman spectroscopy. Changes in the conductivity and carrier concentration were induced by a variable incorporation of TiO_2 nanoparticles in the polymeric matrix. Enhanced carrier lifetime values were achieved by addition of 0.5 % wt of TiO_2 in the composite.

CRediT authorship contribution statement

Conceptualization, D.M., J.R.-C., S.Z.K, E.S.M, and A.C. ; data curation, A.V.-L and A.Y; formal analysis A.V.-L; funding acquisition, S.Z.K, E.S.M, and A.C, investigation, A.V.-L ; methodology, A.V.-L, D.M., J.R.-C., S.Z.K and A.C.; project administration, S.Z.K, E.S.M, and A.C.; supervision, D.M., S.Z.K and A.C; validation, A.V.-L, A.Y., D.M., J.R.-C., S.Z.K, and A.C.; visualization, A.V.-L.; Roles/Writing - original draft A.V.-L.; Writing - review & editing, A.V.-L, D.M., J.R.-C., S.Z.K and A.C.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

1. Hu L, Song J, Yin X, Su Z and Li Z. *Polymers (Basel).* 2020; **12**: 145.
2. Hsu HC, Lai Y, Hsieh WC and Lin CF. *IEEE J. Photovoltaics* 2019; **9**: 688-693.
3. Bhowal AC, Talukdar H and Kundu S. *Polym. Bull.* 2019; **76**: 5233-5251.
4. Maiaugree W, Pimanpang S, Towannang M, Saekow S, Jarernboon W and Amornkitbamrung V. *J. Non. Cryst. Solids* 2012; **358**: 2489-2495.
5. García-Tecedor M, Karazhanov SZ, Vásquez GC, Haug H, Maestre D, Cremades A, Taeño M, Ramírez-Castellanos J, González-Calbet JM, Piqueras J, You CC and Marstein ES. *Nanotechnology* 2018; **29**: 035401.
6. García-Carrión M, Ramírez-Castellanos J, Nogales E, Méndez B, You CC, Karazhanov S and Marstein ES. *Mater. Lett.* 2020; **261**: 127088.
7. Nagata R, Yanagi Y, Fujii S, Kataura H and Nishioka Y. *IEICE Trans. Electron.* 2015; **E98.C**: 411-421.
8. Pathak CS, Singh JP and Singh R. *Curr. Appl. Phys.* 2015; **15**: 528-534.

9. Mahato S, Puigdollers J, Voz C, Mukhopadhyay M, Mukherjee M and Hazra S. *Appl. Surf. Sci.* 2020; **499**: 143967.

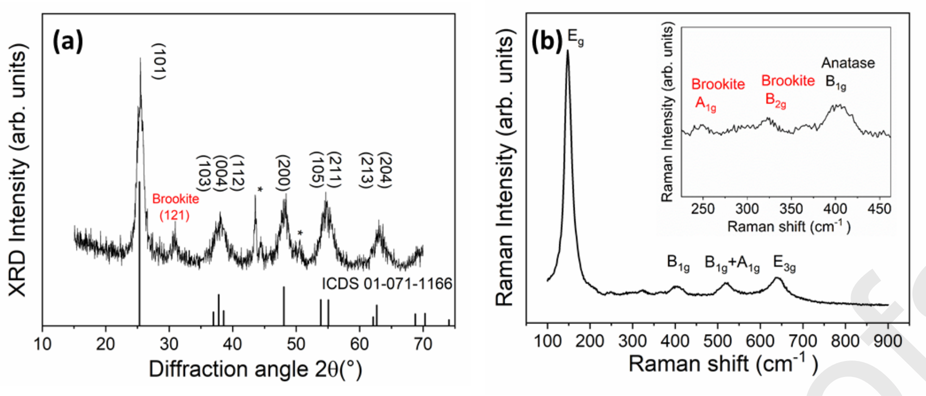
10. Yoon S-S and Khang D-Y. *J. Phys. Chem. C* 2016; **120**: 29525-29532.

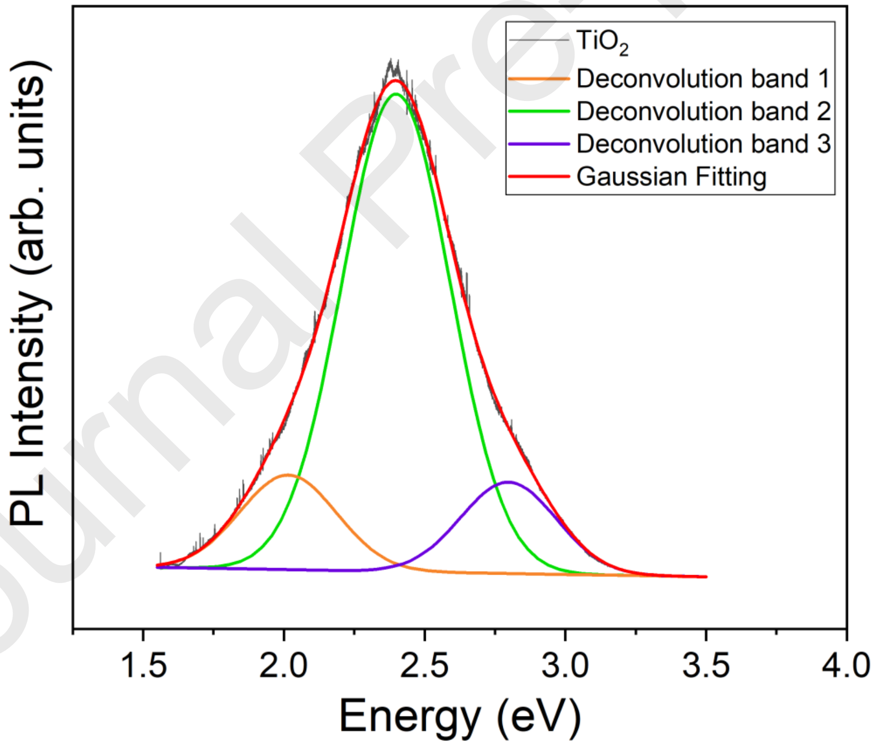
11. Vásquez GC, Maestre D, Cremades A, Piqueras J, Peche-Herrero MA, Ramírez-Castellanos J, González-Calbet JM and Alemán B. *J. Mater. Chem. C* 2014; **2**: 10377-10385.

12. Iliev MN, Hadjiev VG and Litvinchuk AP. *Vib. Spectrosc.* 2013; **64**: 148-152.

13. Vázquez-López A, Yaseen A, Maestre D, Ramírez-Castellanos J, Marstein ES, Karazhanov SZ and Cremades A. *Molecules* 2020; **25**: 695.

14. Cheng X, Haug H, Sabatino M Di, Zhu J and Marstein ES. *IEEE J. Photovoltaics* 2016; **6**: 1103-1108.


(a)
XRD Intensity (arb. units)
(101)
Brookite
(121)
(103)
(004)
(112)
*
(200)
*
(105)
(211)
(213)
(204)
ICDS 01-071-1166
10
20
30
40
50
60
70
Diffraction angle 2θ(°)
(b)
E_g
Raman Intensity (arb. units)
Raman Intensity (arb. units)
Brookite
A_{1g}
Brookite
B_{2g}
Anatase
B_{1g}
250
300
350
400
450
Raman shift (cm^{-1})
B_{1g}
$B_{1g}+A_{1g}$
E_{3g}
100
200
300
400
500
600
700
800
900
Raman shift (cm^{-1})


PL Intensity (arb. units)
TiO_2
Deconvolution band 1
Deconvolution band 2
Deconvolution band 3
Gaussian Fitting
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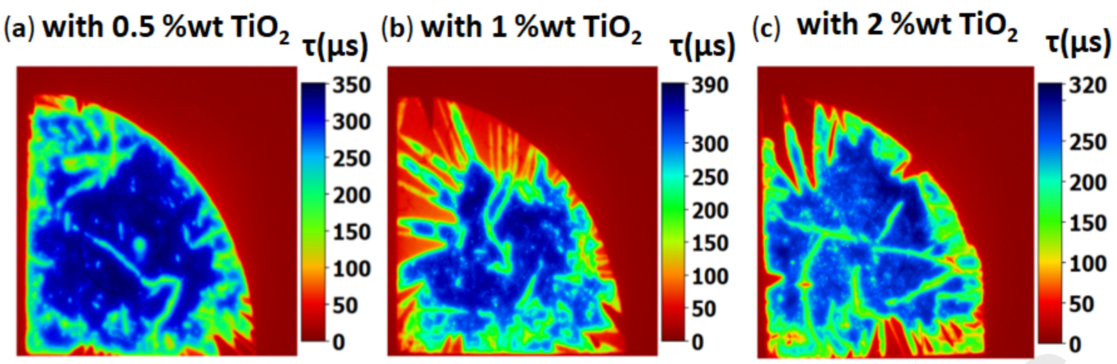
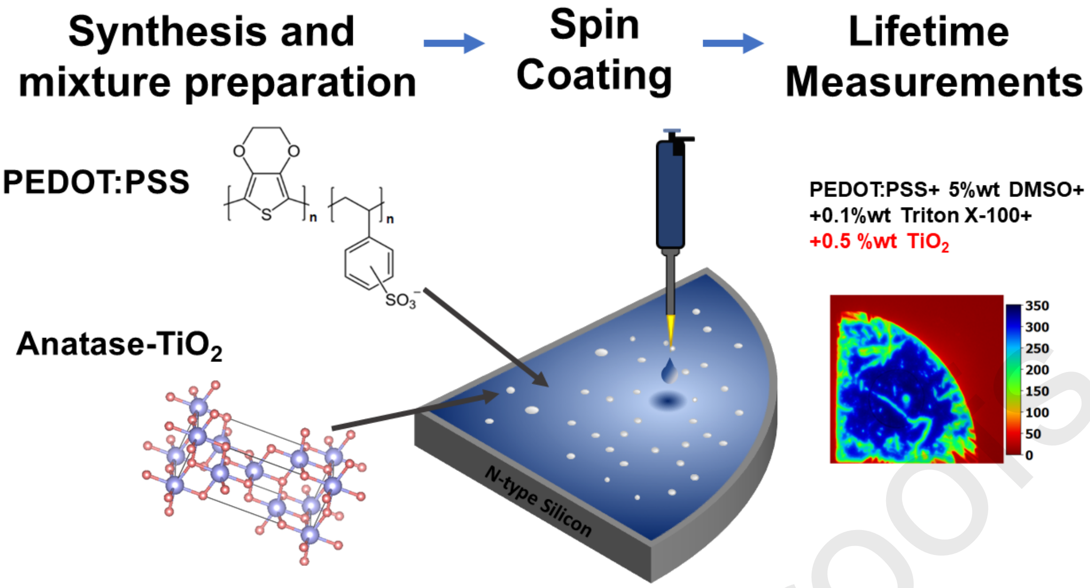
2.0
2.5
3.0
3.5
4.0
Energy (eV)



Highlights

- Synthesis and characterization of hybrid composites formed by TiO_2 nanoparticles and PEDOT:PSS
- Deposition of the hybrid composites on Si-substrates by spin coating and study of their passivation behaviour
- Improvement of the conductivity and the carrier lifetime values by controlled addition of TiO_2 and solvents to the PEDOT:PSS.



CRediT authorship contribution statement

Conceptualization, D.M., J.R.-C., S.Z.K, E.S.M, and A.C. ; data curation, A.V.-L and A.Y; formal analysis A.V.-L; funding acquisition, S.Z.K, E.S.M, and A.C, investigation, A.V.-L ; methodology, A.V.-L, D.M., J.R.-C., S.Z.K and A.C.; project administration, S.Z.K, E.S.M, and A.C.; supervision, D.M., S.Z.K and A.C; validation, A.V.-L, A.Y., D.M., J.R.-C., S.Z.K, and A.C.; visualization, A.V.-L.; Roles/Writing - original draft A.V.-L.; Writing - review & editing, A.V.-L, D.M., J.R.-C., S.Z.K and A.C.

Declaration of interests

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