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Influence of Zr-metal-organic framework coupling on the morphology and photoelectrochemical properties of SnO₂

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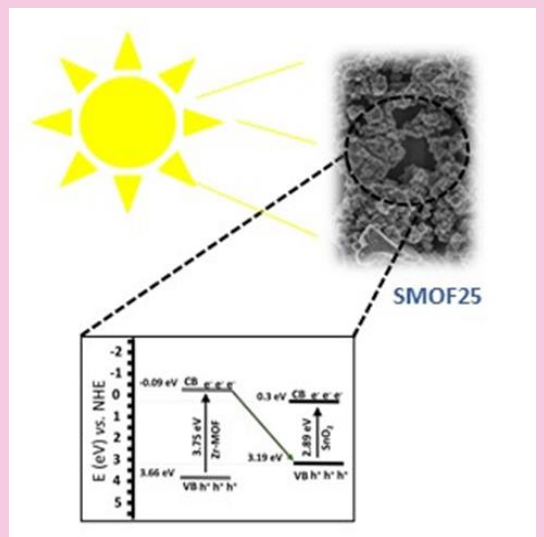
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ABSTRACT: In this work, we investigated the effect of the coupling of the Zr-metal-organic framework (MOF) and SnO₂ and its potential for application as photoelectrode in solar cells. Coupling was performed by mechanical mixture followed by heat treatment. The effect of adding two amounts of Zr-MOF (25 and 50 wt%) on morphology and photoelectrochemical properties was investigated. The results of the J-V curves show that the coupling of 25 wt% Zr-MOF with SnO₂ improved the charge transfer characteristics under light irradiated in 1.6 times compared to the pure SnO₂.



1. Introduction

Due to the scarcity of natural resources, the current technological society faces great challenges in relation to its own sustainability (Zhang and Sun, 2019). As a result, the demand for new clean and efficient technologies with lower environmental costs is growing. In this context, solar energy technology stands out, which can be easily found on almost the entire planet.

Research involving solar energy conversion into electricity has drawn a lot of attention, especially in photovoltaic devices such as solar cells (Kojima *et al.*, 2009). Among them, dye-sensitized solar cells (DSSCs) stand out for their low cost and simple fabrication method (Bora *et al.*, 2018; Chen *et al.*, 2018). However, such devices have low power conversion efficiency (PCE), which represents a barrier to the use of these devices in the photovoltaic market (Bashar *et al.*, 2019; Selvaraj *et al.*, 2018). Low PCE is related to the electronic, morphological and optical properties of materials used as photoanodes.

Currently, the most used n-type metal oxide as photoanode in DSSC is TiO_2 (Agbo *et al.*, 2016; Bhogaita *et al.*, 2016). Nevertheless, its material displays some deficiencies, such as low electron mobility and photic instability (W. Yang *et al.*, 2017). In addition, to removing organic compounds of the TiO_2 synthesis of it, it is necessary to use high temperatures, which results in higher production costs (W. Yang *et al.*, 2017). A great candidate to replace the conventional TiO_2 layer is the SnO_2 (Jiang *et al.*, 2017; Ke *et al.*, 2015) due to its wide bandgap, high optical transmittance in the visible, high mobility ($240 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), excellent optical and chemical stability, and low-cost preparation at low temperature (Mathiazhagan *et al.*, 2020). However, as the SnO_2 conduction band-edge is more positive than TiO_2 ($\sim 400 \text{ mV}$), under 1 Sun simulated light (AM 1.5 G) using a solar simulator, the Fermi quasi-equilibrium level will shift down to the redox potential of the liquid electrolyte, resulting in a lower open-circuit voltage compared to TiO_2 (Suresh *et al.*, 2018). These characteristics may make the DSSCs that use SnO_2 as photoanode achieve PCE of only 1.2% while DSSCs working with TiO_2 have a PCE of 5.9% (Concina and Vomiero, 2014). In order to overcome these limitations presented by SnO_2 , an alternative found is the modification of its surface (Qian *et al.*, 2009).

The unique characteristics of the metal-organic frameworks (MOFs) such as high porosity, high surface area, accessible active internal energy migration pathways that can increase the electron

transfer and reduce the charge recombination, have motivated research about their photocatalytic and photovoltaic applications (Zhang *et al.*, 2020). MOFs are hybrid materials built by combining the organic ligands and metal nodes through coordinate bonds (Bao *et al.*, 2016; H. Liu *et al.*, 2016; Li *et al.*, 2016).

Recently, our group investigated the coupling of ZnO and Zr-MOF to develop a photoanode to be applied in DSSCs. In this research, the results showed that the ZnO electrode with 25 wt% Zr-MOF has the ability to potentiate charge transport and inhibit charge recombination, making it a promising photoelectrode for solar cells (da Trindade *et al.*, 2021).

Based on our previous results, in this present work, we seek to report the investigation of the Zr-MOF/ SnO_2 coupling in the SnO_2 morphology and its photoelectrochemical properties for future application in photoanodes for DSSCs.

2. Experimental

2.1 SnO_2 synthesis

The coprecipitation method in aqueous media was used to prepare the SnO_2 particles. In this method, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (6.77 g, Vetec) was mixed with deionized H_2O (30 mL) under constant stirring at room temperature. After dissolution, H_2O_2 (35 mL, Synth) and KOH solution (35 mL/2 mol L^{-1} , Synth) were added. The precipitate was washed with deionized water until pH = 7. The obtained material was oven-dried at 60 °C for 8 h.

2.2 Zr-MOF synthesis

The metal-organic framework synthesis (Zr-MOF) was performed by a solvothermal method as related in our previous work (da Trindade *et al.*, 2019). The ZrCl_4 (1.4 mmol, Aldrich) and terephthalic acid (1.4 mmol, Aldrich) were previously dissolved in N, N-dimethylformamide (DMF, 99.8%, Aldrich) and the solution was put in an autoclave. The reaction was kept in a greenhouse at 125 °C for 24 h. After this time the obtained precipitate was washed with methanol and dried at 60 °C.

2.3 Electrode preparation

The electrodes were prepared with SnO_2 and Zr-MOF using two mass ratios of Zr-MOF, according to Tab. 1. The electrode preparation procedure was performed according to the literature (da Trindade *et*

al., 2018; 2020a). Viscous pastes were prepared by mixing the desired particles with ethanol (200 μL) and sonicated for 30 min. After this, deionized water (60 μL) was added, and the mixture was sonicated again for 30 min. The obtained suspensions were applied onto fluorine-doped tin oxide (FTO) substrates in an area of 1 cm^2 using a micropipette. The films were allowed to dry at 25 $^{\circ}\text{C}$ for 1 h, and then calcined at 400 $^{\circ}\text{C}$ for 1 h, at heating and cooling rates of 0.1 $^{\circ}\text{C min}^{-1}$.

Table 1. Samples designation and composition.

Sample designation	SnO ₂ (g)	Zr-MOF (g)
SnO ₂	0.0125	-
Zr-MOF	0.0125	-
SMOF25	0.0094	0.0031
SMOF50	0.0062	0.0062

2.4 Samples characterization

All samples were characterized by X-ray diffraction (XRD, Rigaku detector ($\text{CuK}\alpha$, $\lambda = 0.15406 \text{ nm}$), Fourier-transform infrared spectroscopy (FTIR, Bruker EQUINOX 55 spectrometer), thermogravimetry (TG) analysis (TA Instruments Q-50 apparatus), field emission gun-scanning electron microscope (FEG-SEM, ZEISS model 105 DSM940A instrument, 10 keV), UV-Vis spectra (Cary 5 G [Varian] apparatus) and Brunauer-Emmett-Teller (BET) surface area measurements (Micromeritics TriStar II 3020).

The photoelectrochemical measurements were performed in a three-electrode cell where the prepared electrode, Pt wire and Ag/AgCl electrode have been used as working, counter and reference electrodes, respectively. This cell had a quartz glass window, and the electrolyte was acetonitrile solution with LiI (10 mmol L^{-1}), I₂ (1 mmol L^{-1}), and LiClO₄ (0.1 mol L^{-1}). The current density-voltage (J-V) curves of the samples have been analyzed for both illuminated and dark conditions using an Autolab PGSTAT302 N potentiostat and a Newport Sol3A Class AAA solar simulator with a 100 W Xenon lamp.

3. Results and discussion

Figure 1 shows the XRD patterns of all samples. The SnO₂ presents 2θ diffraction angles at 26.4, 33.7, 37.8, 51.6, 54.2, 62.1, 65.5 and 78.6 degrees and (110), (101), (200), (211), (220), (310), (301) and (321) diffraction planes, respectively, corresponding to rutile structure (JCPDS n^o: 41-1445) (Debataraja *et al.*, 2017). The Zr-MOF presents the XRD patterns that

correspond with the Zr-MOF (UiO-66) reported previously (Luan *et al.*, 2015; da Trindade *et al.*, 2020b). When the SnO₂ sample is modified with 25 or 50 wt% of Zr-MOF, it can be observed that the referring to SnO₂ and an absorption peak appears between 5 and 10 $^{\circ}$, which confirms the presence of Zr-MOF in both samples. It is also possible to observe that in the 50 wt% sample the presence of other diffraction peaks referring to Zr-MOF. This result was expected since there was a significant increase in the Zr-MOF mass amount compared to the 25 wt% sample.

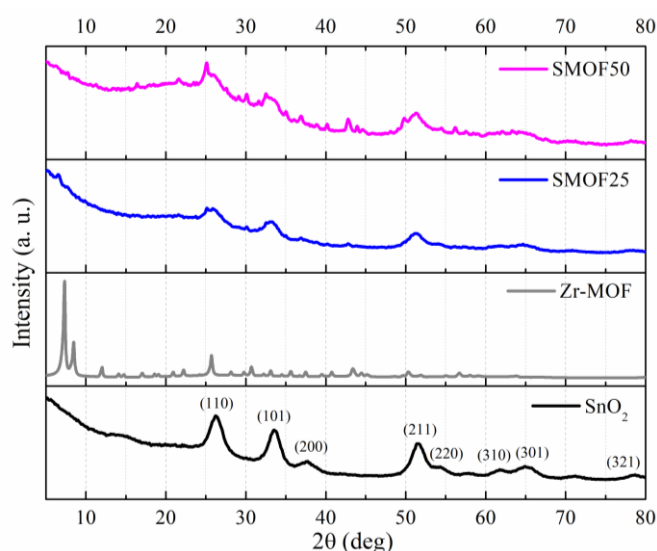


Figure 1. XRD patterns of SnO₂, Zr-MOF, SMOF25 and SMOF50 samples.

Figure 2 shows the FTIR and TG analyzes of SnO₂, Zr-MOF and modified samples. At the SnO₂ FTIR spectrum (Fig. 2a) we observed bands in 3300 and 1640 cm^{-1} that can be attributed to the O-H stretching of adsorbed water molecules. In addition, the band at 640 cm^{-1} refers to framework vibrations of SnO₂ (Zhan *et al.*, 2013). The Zr-MOF spectrum presents broadband at 3300 cm^{-1} that is due to the O-H stretching from water molecules in the MOFs (Zango *et al.*, 2020). The well-defined bands at 1570 and 1387 cm^{-1} refer to the C=O and C-N stretching modes, respectively. The C_{Ar}, δ -H stretching modes and the Zr₆(OH)₄O₄ cluster appears at 750 and 666 cm^{-1} , respectively (Butova *et al.*, 2020; da Trindade *et al.*, 2020b). For the modified samples, SMOF25 and SMOF50, similar spectra can be noted. Characteristic peaks of the SnO₂ and Zr-MOF were observed at both modified samples. However, the intensity of the bands increases with increasing the MOF amount in the sample. These results affirm that the Zr-MOF was successfully coupling into the SnO₂ corroborating the

data observed by XRD. TG measurements were carried out to verify the thermal stability of SnO_2 , Zr-MOF and modified samples (Fig. 2b). The pure SnO_2 sample presents only one stage of weight loss of 7% from 25 to 80 °C due to the removal of adsorbed water molecules. Zr-MOF has three stages of mass loss with first up to 125 °C which is attributed to desorption of physisorbed water, the second between 125–550 °C which may be due to the removal of the solvent (DMF) and the dehydroxylation of the zirconium oxo-clusters (X. Liu *et al.*, 2016) and the last stage (550–700 °C) is due to the Zr-MOF decomposition (Q. Yang *et al.*, 2018). When 25 wt % Zr-MOF is coupled to SnO_2 (SMOF25), it can be observed that there is an increase in thermal stability in relation to the pure SnO_2 sample. In the SMOF25 sample, there is an initial weight loss of approximately 3% that can be attributed to the removal of adsorbed water molecules. The increase in the initial thermal stability also is observed for the SMOF50 sample with a mass loss of 6%. However, at 500 °C the beginning of the Zr-MOF decomposition is observed. These data show that adding 25 wt % Zr-MOF to the SnO_2 sample works as a thermal stabilizer.

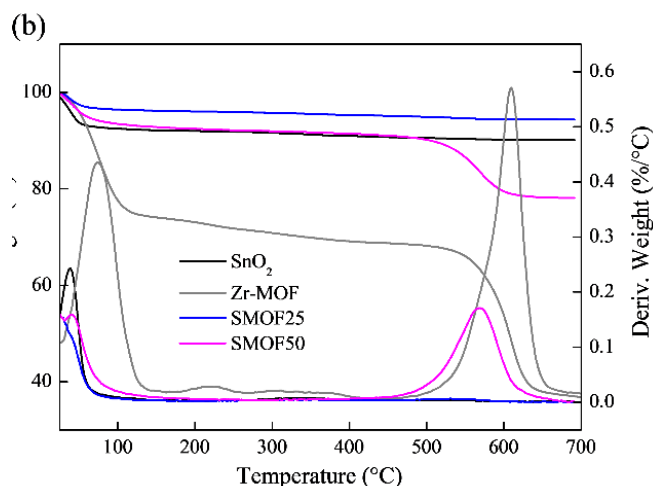
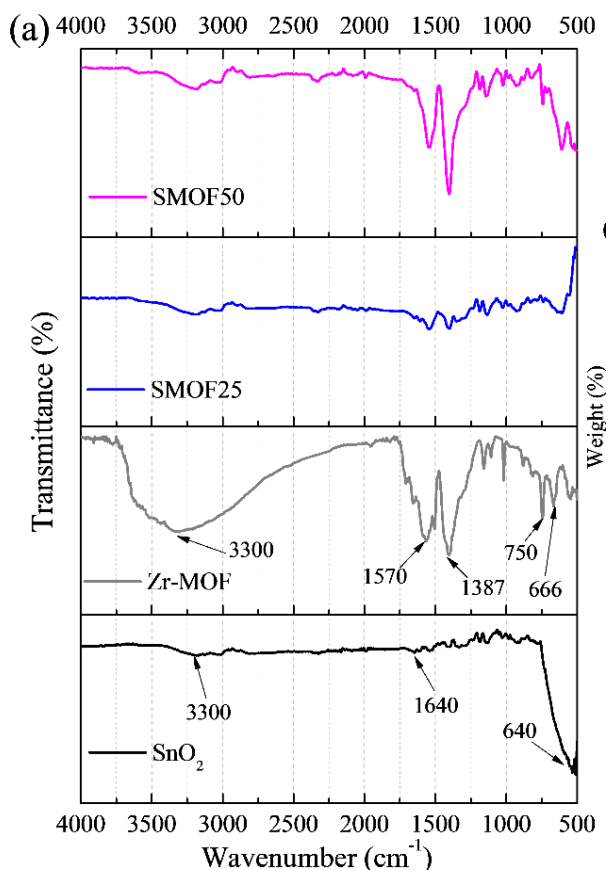
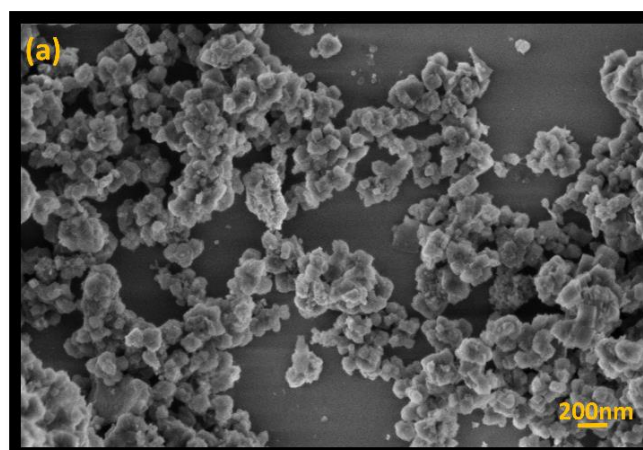


Figure 2. FTIR spectra (a) and TG curves (b) of SnO_2 , Zr-MOF, SMOF25 and SMOF50 samples.

FE-SEM images for all samples are shown in Fig. 3. SnO_2 particles (Fig. 3a) tend to form agglomerates with irregular shapes. The Zr-MOF sample has an octahedral shape with different sizes as reported in the literature (Waitschat *et al.*, 2018). When 25 wt% Zr-MOF is coupled to the SnO_2 (Fig. 3c), there is a tendency to form clustered structures which are potentiated by increasing the Zr-MOF mass ratio (Fig. 3d). In the SMOF50 sample, the formation of agglomerates of smaller and fewer uniform particles is observed.



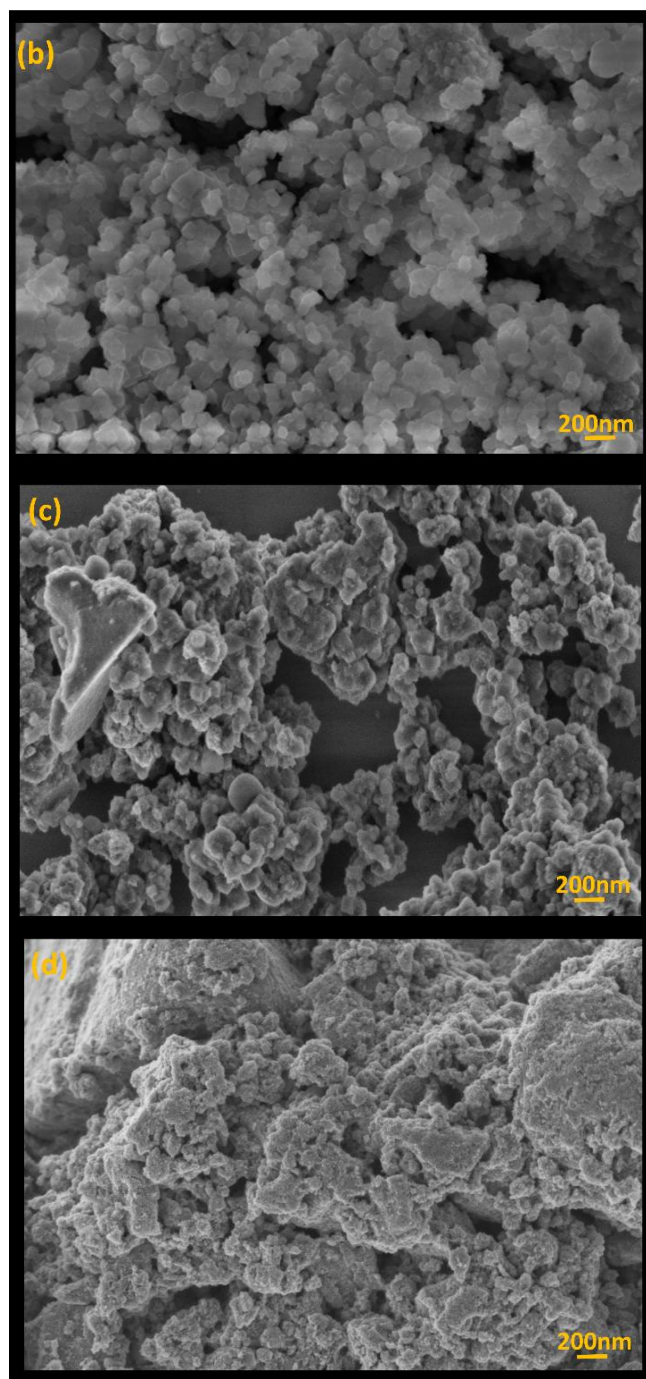
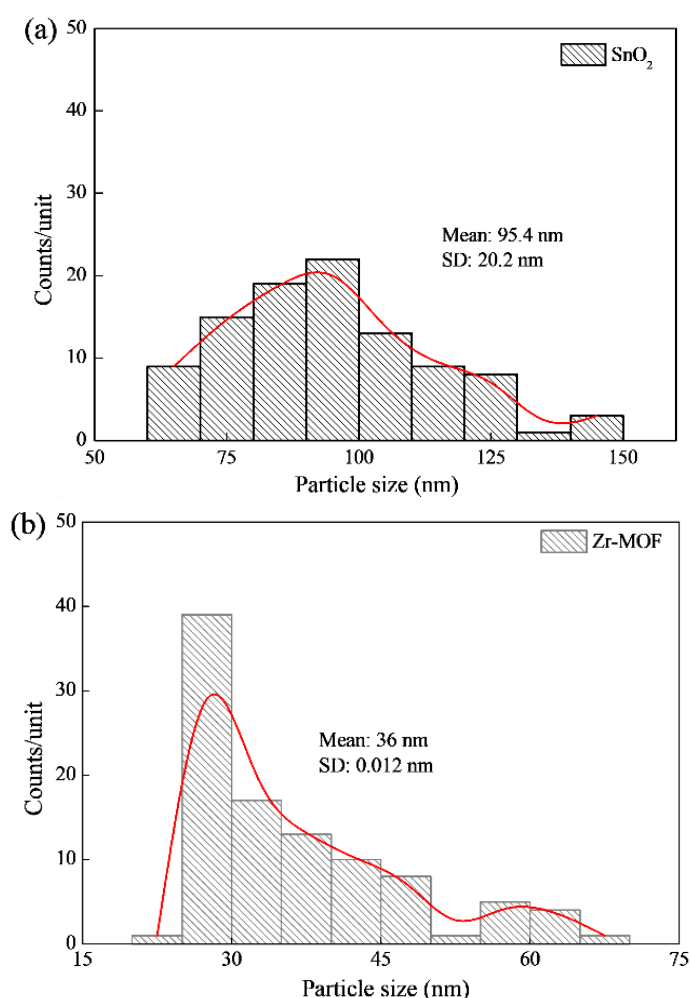


Figure 3. FE-SEM images of SnO₂ (a), Zr-MOF (b), SMOF25 (c), and SMOF50 (d) samples.

Through the FE-SEM images, the particle size was estimated, Fig. 4a–d. The SnO₂ and the Zr-MOF samples present approximately 95.4 and 36 nm particle sizes, respectively. When these two samples are coupled, the particle sizes obtained are approximately 99.6 and 148.7 nm for SMOF25 and SMOF50 samples, respectively. These results reveal that the coupling of SnO₂ with Zr-MOF provokes an increase in particle size. The N₂ adsorption-desorption isotherms of SnO₂,

Zr-MOF, SMOF25 and SMOF50 particles are shown in Fig. 4e. The SnO₂ and SMOF25 samples show typical type IV isotherms with a hysteresis loop and, the Zr-MOF and SMOF50 samples present typical type I isotherms. Type IV isotherms are characteristic of mesoporous nature and the hysteresis loop commonly suggests improved pore size and pore connectivity of the synthesized samples (Mallesham *et al.*, 2020). While type I isotherms indicate the microporous nature of the synthesized samples (Q. Yang *et al.*, 2018). It can be hypothesized that the reduction of the specific surface area with the addition of the Zr-MOF implies that the SnO₂/Zr-MOF coupling results in the reduction of the vacancies in the Zr-MOF (Fu *et al.*, 2019).



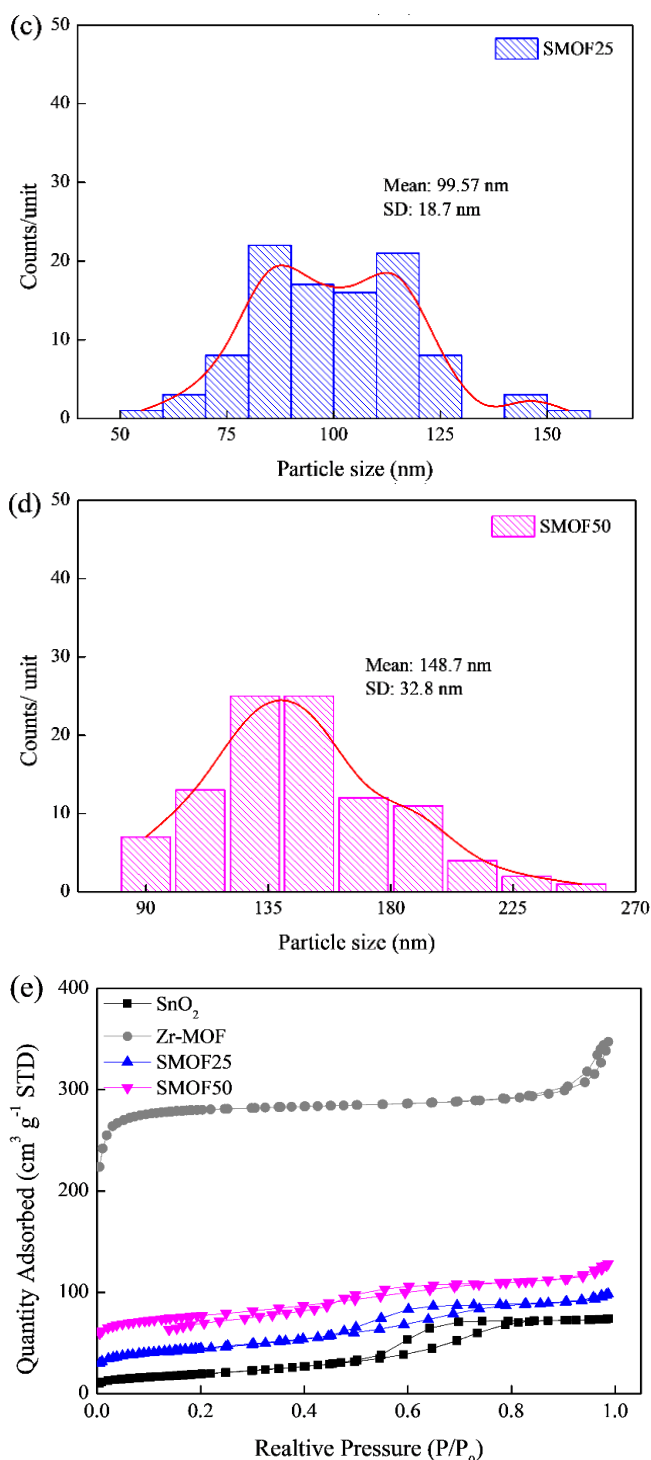


Figure 4. Particle sizes of SnO₂ (a), Zr-MOF (b), SMOF25 (c), and SMOF50 (d), and typical N₂ adsorption-desorption isotherm (e) of the samples.

The BET surface area and pore diameter are presented in Tab. 2. These results show that when SnO₂ is coupling with Zr-MOF the surface area increases from 68.44 m² g⁻¹ to 158 and 270.3 m² g⁻¹ with the addition of 25 and 50 wt% of Zr-MOF (SMOF25 and

SMOF50), respectively. In contrast, the pore diameter decreases with coupling. These changes observed in the surface area and pore diameter can be caused by the increase of clusters formation as a result of the increase of the particles sizes.

Table 2. BET surface area and pore diameter, and FE-SEM average particle size of the samples.

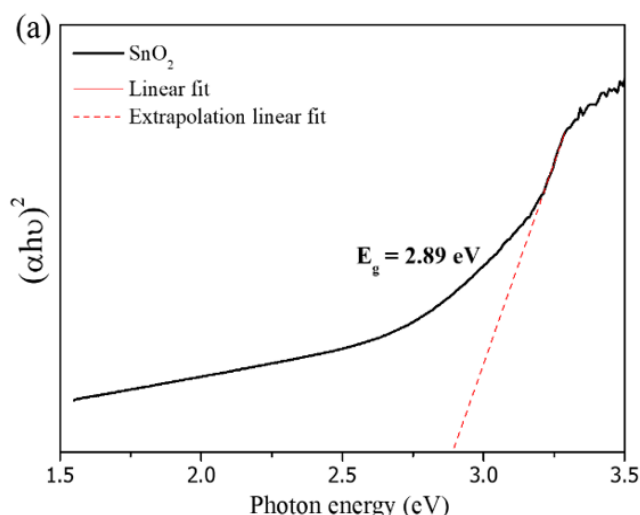
Sample	BET		FE-SEM
	Surface area (m ² g ⁻¹)	Pore diameter (nm)	Average particle size (nm)
SnO ₂	68.44	4.5	95.4
Zr-MOF	985.2	10.0	36.0
SMOF25	158.0	4.3	99.6
SMOF50	270.3	3.4	148.7

The Tauc method was used to determining the bandgap (Coulter *et al.*, 2017), Eq. 1:

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \quad (1)$$

where h is Planck's constant, ν is the photon's frequency, α is the absorption coefficient, E_g is the bandgap, and A is the slope of the Tauc plot in the linear region.

The SnO₂ and Zr-MOF are direct bandgap semiconductors with n equal to 1/2 (Ganose and Scanlon, 2016; Hendrickx *et al.*, 2018). The E_g values for all samples are shown in Fig. 5. The bandgap values are 2.89, 3.75, 2.27 and 2.12 eV for SnO₂, Zr-MOF, SMOF25 and SMOF50 samples, respectively. It can be seen that the bandgap is reduced with increasing in Zr-MOF concentration coupled to SnO₂. This behavior can be explained by factors like particle size, optical properties and surface morphology, which influence the penetration of light photons (da Trindade *et al.*, 2021).



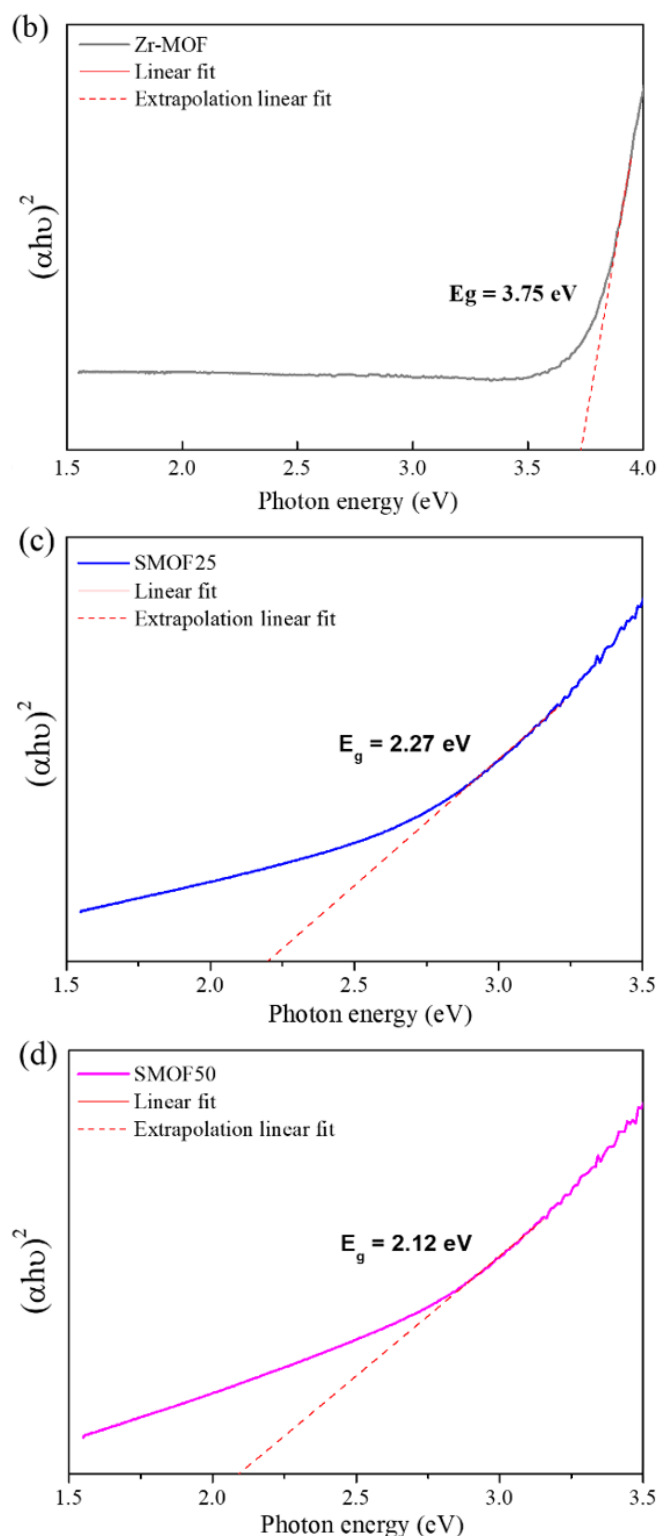


Figure 5. Tauc plot from UV-Vis analysis of SnO₂ (a), Zr-MOF (b), SMOF25 (c) and SMOF50 (d) samples.

The J-V curves of SnO₂, SMOF25 and SMOF50 photoanodes were analyzed in the potential range of 0–1.3 V at 20 mV s⁻¹ in an I₃⁻/I⁻ solution, Fig. 6. Current densities at 1.0 V in the presence of

light are 2.77, 4.5 and 2.23 mA cm⁻² for SnO₂, SMOF25 and SMOF 50, respectively. The results show that the coupling of 25 wt% Zr-MOF with SnO₂ improved the charge transfer characteristics under light irradiated compared to the pure SnO₂ and SMOF50 samples. The SMOF50 sample presented a current density lower than the other samples, indicating that 50 wt% Zr-MOF can reduce the active sites and delay the diffusion process for the electrolyte. This result demonstrates that the coupling of 25 wt% Zr-MOF with SnO₂ is promising for the development of photoanodes for DSSCs considering that the values of short-circuit density (J_{sc}), found in the literature, for the pure TiO₂ can range from 2.51 to 12.9 mA cm⁻² (Concina and Vomiero, 2014; Khannam *et al.*, 2016). In the present work, the DSSC device was not assembled, we only tested the photoanode in I₃⁻/I⁻ solution and without sensitized it by immersing in a dye solution. Therefore, by the obtained results, it is expected that when tested in the DSSC it will reach values similar or superior to cells with TiO₂.

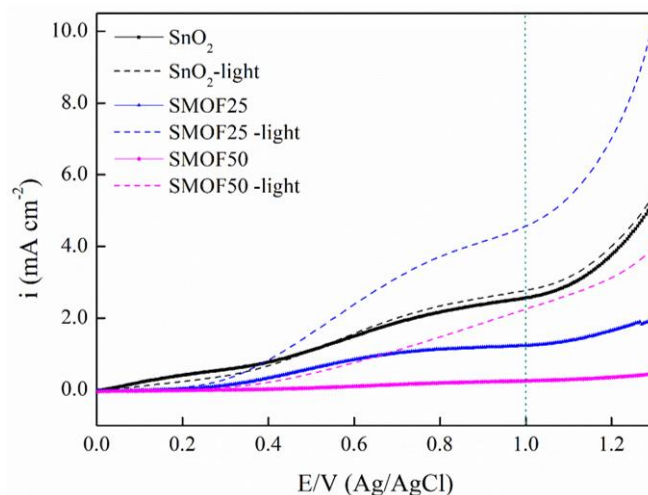


Figure 6. J-V curves of the SnO₂, Zr-MOF, SMOF25 and SMOF50 samples at 20 mV s⁻¹.

The valence band (E_{VB}) and conduction band (E_{CB}) potentials can be calculated by the Mulliken method, Eqs. 2 and 3, respectively (Kandasamy *et al.*, 2018):

$$E_{VB} = \chi - E_e + 0.5E_g \quad (2)$$

$$E_{CB} = E_{VB} - E_g \quad (3)$$

where χ is the electronegativity of the semiconductor and E_e is the energy of the free electrons on the hydrogen scale (4.5 eV) and E_g is the bandgap energy of the material.

The SnO_2 electronegativity is 6.25 eV and the E_{CB} of Zr-MOF is -0.09 eV (vs. NHE); so, we can propose an energy band diagram for Zr-MOF coupling with SnO_2 , Fig. 7 (Abdelkader *et al.*, 2015; Wang *et al.*, 2016). In the proposed energy band diagram when the SnO_2 /Zr-MOF sample is exposed to visible light, the photogenerated electrons (e^-) in the Zr-MOF conduction band (CB) migrated to SnO_2 , while the holes (h^+) remained in the Zr-MOF valence band (VB), resulting in the separation of the charge carriers.

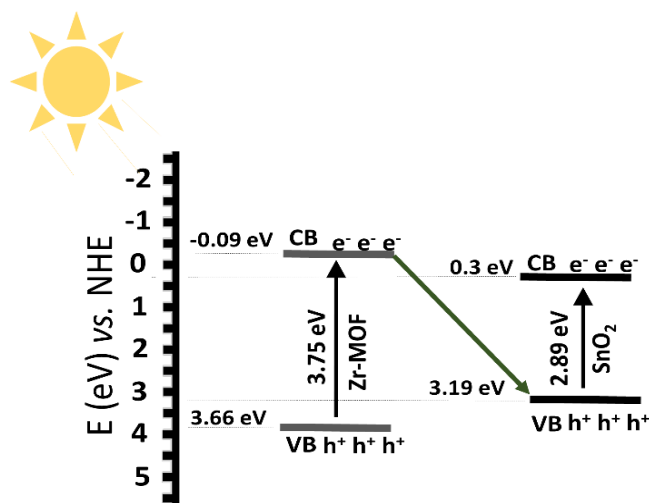


Figure 7. Proposed energy band diagram of the SnO_2 /Zr-MOF composite.

4. Conclusions

The Zr-MOF coupling in the SnO_2 was prepared by mechanical mixture followed by heat treatment. The effect of the coupling has been investigated using structural, optical and photoelectrochemical analysis. The XRD and the FTIR reveals the incorporation of Zr-MOF into the SnO_2 lattice. The FE-SEM characterization shows an increase in the tendency to form clusters with an increase in the Zr-MOF concentration. The J-V data show that the coupling of 25 wt% Zr-MOF with SnO_2 improved 1.6 times the charge transfer characteristics under light irradiated compared to the pure SnO_2 and 2 times when compared to the SMOF50 sample. This result demonstrates that the coupling of 25 wt% Zr-MOF with SnO_2 is promising for the development of photoanodes for DSSCs.

Authors' contribution

Conceptualization: da Trindade, L. G.

Data curation: Silva, B. L. Z.; da Trindade, L. G.

Formal Analysis: Silva, B. L. Z.; da Trindade, L. G.; Zanchet, L.

Funding acquisition: Not applicable.

Investigation: da Trindade, L. G.

Methodology: da Trindade, L. G.; Mazzo, T. M.

Project administration: Mazzo, T. M.; da Trindade, L. G.

Resources: Longo, E.

Software: Not applicable.

Supervision: Mazzo, T. M.

Validation: da Trindade, L. G.

Visualization: da Trindade, L. G.

Writing – original draft: da Trindade, L. G.; Zanchet, L.

Writing – review & editing: Mazzo, T. M.; Longo, E.; da Trindade, L. G.

Data availability statement

The data will be available upon request.

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