

Proceedings

# Microwave-Assisted Hydrothermal Synthesis of Zn<sub>2</sub>SnO<sub>4</sub> Nanostructures for Photocatalytic dye Degradation <sup>†</sup>

Ana Rovisco <sup>\*</sup>, Rita Branquinho, Rodrigo Martins, Elvira Fortunato and Pedro Barquinha <sup>\*</sup>

CENIMAT/i3N, Department of Materials Science, NOVA School of Science and Technology (FCT-NOVA) and CEMOP/UNINOVA, NOVA University Lisbon, Campus de Caparica, 2829-516 Caparica, Portugal; ritasba@fct.unl.pt (R.B.); rfp@fct.unl.pt (R.M.); emf@fct.unl.pt (E.F.)

<sup>\*</sup> Correspondence: a.rovisco@campus.fct.unl.pt (A.R.); pmcb@fct.unl.pt (P.B.)

<sup>†</sup> Presented at the 2nd International Online-Conference on Nanomaterials, 15–30 November 2020; Available online: <https://iocn2020.sciforum.net/>.

Published: 15 November 2020

**Abstract:** Zinc-tin oxide (ZTO) nanostructures appear as one of the most promising material systems for a new generation of nanodevices. In this work, a microwave-assisted hydrothermal synthesis to produce different shapes of Zn<sub>2</sub>SnO<sub>4</sub> nanostructures (nanoparticles, octahedrons and nanoplates) is presented. Reproducible and homogeneous results were obtained with the advantage of reducing up to 20 h the synthesis time when compared to using conventional oven. Furthermore, the photocatalytic activity of the Zn<sub>2</sub>SnO<sub>4</sub> nanostructures in the degradation of rhodamine B under UV light was studied. Zn<sub>2</sub>SnO<sub>4</sub> nanoparticles demonstrated better performance with >90 % of degradation being achieved in 2.5 h.

**Keywords:** Zn<sub>2</sub>SnO<sub>4</sub>; ZTO; octahedrons; nanoparticles; nanoplates; microwave-assisted hydrothermal synthesis; photocatalysis; rhodamine B

## 1. Introduction

Zinc-tin oxide (ZTO) material system possesses a wide range of attractive properties for a new generation of multifunctional nanodevices. It can crystallize in Zn<sub>2</sub>SnO<sub>4</sub> and ZnSnO<sub>3</sub> phases, with different types of nanostructures possible for each phase. Each has unique properties suitable for applications in catalysis, sensors, transistors, memories, or energy harvesting devices [1–5].

Hydrothermal synthesis is one of the best methods to obtain complex oxides due to its characteristic pressure and temperature conditions. These processes are commonly performed using conventional ovens, nevertheless, the microwave-assisted synthesis is an interesting alternative for the inorganic nanostructures' fabrication, due to its faster reactions, consequence of its heating process. This contributes to an enhancement of the product purity and yield [6–10]. Several ZnO and SnO<sub>2</sub> nanostructures have been reported by microwave-assisted synthesis [7,11–16], however the advantageous multicomponent ZTO is significantly more difficult to obtain. Nevertheless, ZTO nanostructures synthesized in microwave systems have already been reported [8,17–19]. A simple method to produce quantum dots using a conventional microwave was demonstrated by Lehnen et al. [8], while Nehru et al. produced Zn<sub>2</sub>SnO<sub>4</sub> nanostructures in a microwave system by using an urea-based combustion process [17]. Recently, Jain et al. reported a microwave-assisted hydrothermal synthesis of Zn<sub>2</sub>SnO<sub>4</sub> nanorods using a power of 600 W for 15 min, and an annealing treatment at 700 °C for 5 h [19]. In this work a seed-layer free microwave-assisted hydrothermal synthesis of Zn<sub>2</sub>SnO<sub>4</sub> nanostructures with different morphologies (nanoparticles, octahedrons and nanoplates) is presented. The Zn<sub>2</sub>SnO<sub>4</sub> nanostructures were obtained in ≤ 60 min without employing any annealing treatment. The photocatalytic performance of these nanostructures in degradation of rhodamine B

(RhB) under UV light is also shown, with a better performance being observed when using the  $Zn_2SnO_4$  nanoparticles.

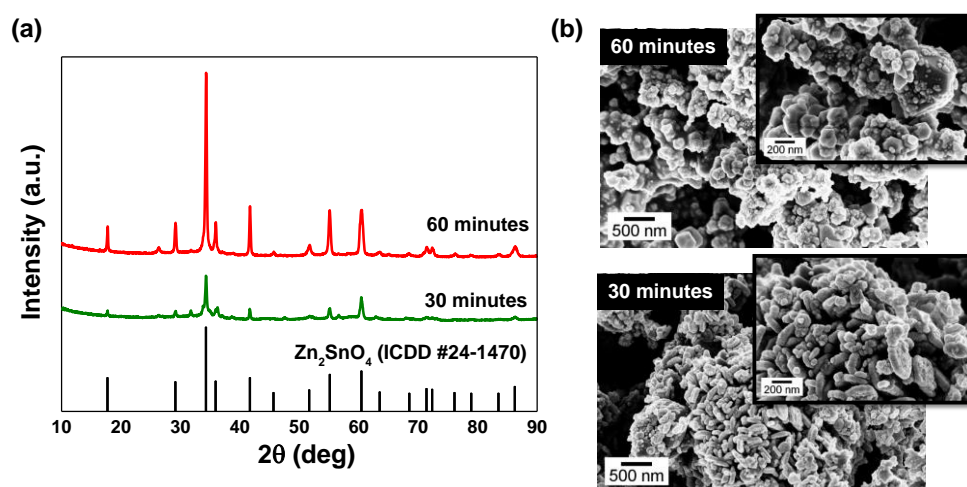
## 2. Materials and Methods

The  $Zn_2SnO_4$  octahedrons and nanoplates were synthesized through the hydrothermal process described in reference [20]. The  $Zn_2SnO_4$  nanoparticles were synthesized based on the synthesis of Annamalai et al. [21]. After its preparation, the solutions were kept in the microwave (CEM Focused Microwave Synthesis System Discover SP), in a dynamic mode at 200 °C, establishing a maximum pressure of 270 PSI and a maximum power of 100 W for the nanoparticles and 80 W for the octahedrons and the nanoplates. The nanostructures were washed several times alternately with IPA and  $H_2O$ , and then dried at 60 °C for 2h in vacuum [22]. A PANalytical's X'Pert PRO MRD diffractometer (with Cu K $\alpha$  radiation) was used to determine the crystalline structure of the  $Zn_2SnO_4$  nanostructures. The data was acquired in the 10–90° 2 $\theta$  range with a step size of 0.033°. The morphology of the nanostructures was carried out by a Carl Zeiss AURIGA CrossBeam (FIB-SEM) workstation. The photocatalytic performance of the ZTO nanostructures in the degradation of rhodamine B (RhB) was evaluated at room temperature. For each experiment, 40 mg of each powder containing the different nanostructures was dispersed in 50 mL of the RhB solution (5 mg/L). The RhB used is from Sigma Aldrich. The photocatalysis tests were performed under UV light using 3 lamps (Osram, HNS L 95 W 2G11) with an emission wavelength range of 200–280 nm (ozone free), aligned in parallel at a distance of 10 cm from the solutions with the nanostructures.

## 3. Results and Discussion

### 3.1. Microwave-Assisted Synthesis of $Zn_2SnO_4$ Nanostructures

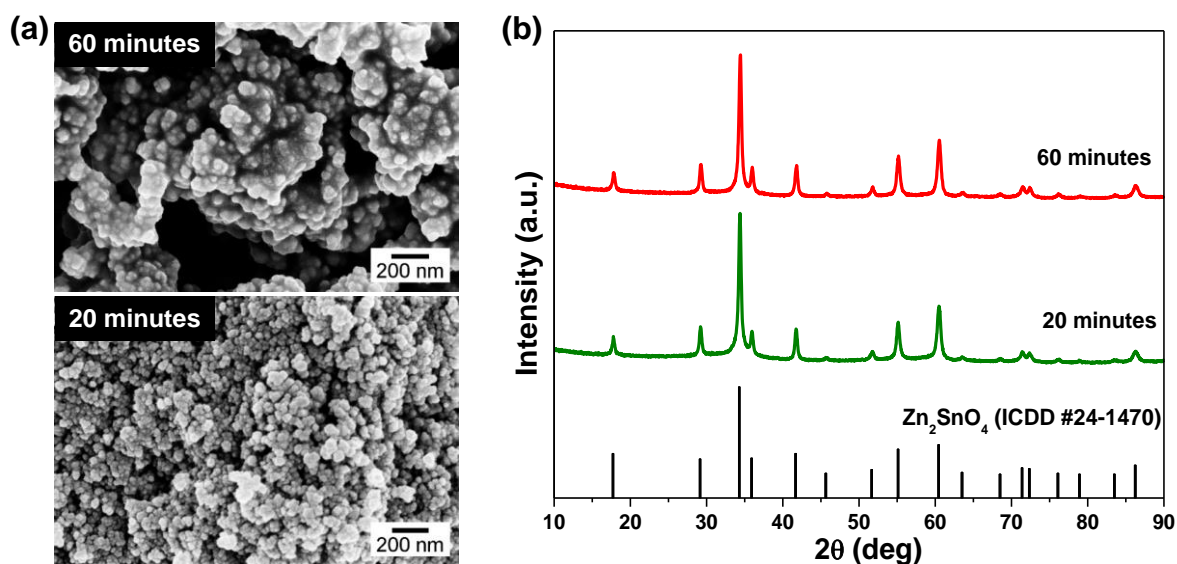
In a previous work,  $Zn_2SnO_4$  octahedrons were synthesized by a hydrothermal method in a conventional oven at 200 °C for 24 h [20]. A posteriori, a shorter duration of 12 h was also studied and it was found that this is not enough time to produce purely the  $Zn_2SnO_4$  phase, leading instead to a predominance of  $Zn_2SnO_4$  nanoplates, which are an intermediate structure in the formation of the  $Zn_2SnO_4$  octahedrons [23]. Following these results,  $Zn_2SnO_4$  octahedrons and nanoplates were synthesized replacing the conventional oven by a microwave system. Figure 1 shows the XRD patterns and the SEM images for the ZTO nanostructures obtained with these microwave-assisted syntheses. The same trend observed for the oven syntheses is verified for microwave syntheses even if employing significantly shorter times, i.e., longer synthesis lead to the achievement of pure phase  $Zn_2SnO_4$  octahedrons, while some mixture of phases is achieved for shorter syntheses, producing mainly  $Zn_2SnO_4$  nanoplates [23].



**Figure 1.** (a) XRD pattern and (b) SEM images of the  $Zn_2SnO_4$  nanoplates and octahedrons synthesized in the microwave system (for 30' and 60').

Based on the synthesis described by Annamalai et al. [21] in a conventional oven, and aiming to reduce the synthesis time,  $Zn_2SnO_4$  nanoparticles were also synthesized using the microwave system. This synthesis was performed at 200 °C, establishing a maximum power of 100 W and a maximum pressure of 270 PSI. Two synthesis durations were considered, 20 min and 60 min.

In Figure 2 the SEM images and the XRD patterns are presented, showing that in both cases small nanoparticles with a pure  $Zn_2SnO_4$  phase were obtained. This shows that it is possible to reduce at least 5 h of synthesis time, compared to the synthesis reported by Annamalai et al. [21], and still produce  $Zn_2SnO_4$  nanoparticles with a good quality.

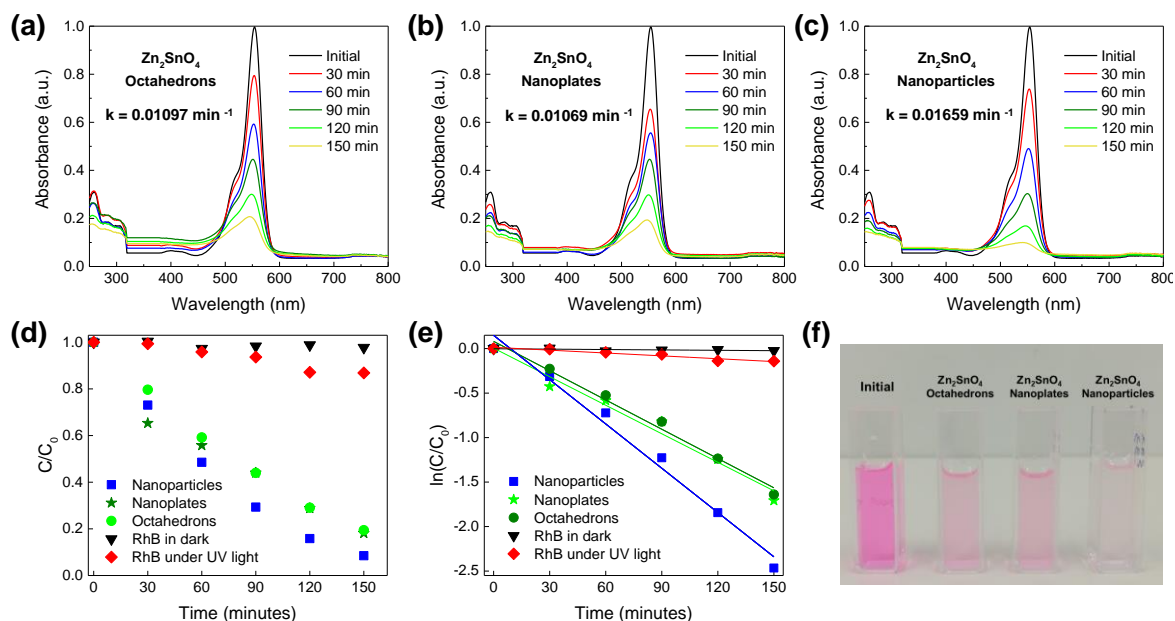


**Figure 2.** (a) XRD patterns and (b) SEM images of the  $Zn_2SnO_4$  nanoparticles synthesized by microwave-assisted synthesis for 20 min and 60 min.

In general, these studies showed the efficiency of the microwave heating method to produce high quality  $Zn_2SnO_4$  nanoplates, octahedrons and nanoparticles, without post-processing annealing treatment and with the advantage of allowing for much shorter syntheses than usually needed when using conventional ovens.

### 3.2. Photocatalytic Activity of $Zn_2SnO_4$ Nanostructures

The photocatalytic activity of the  $Zn_2SnO_4$  octahedrons, nanoplates and nanoparticles produced by microwave-assisted hydrothermal synthesis in only 60 min. was studied in the degradation of RhB under UV light. Figure 3 shows the absorbance spectra variation of the RhB solution with the UV light exposure time in the presence of each ZTO nanostructure. It is possible to observe that the nanoparticles have a much higher degradation rate ( $0.01659 \text{ min}^{-1}$ ), than the octahedrons ( $0.01069 \text{ min}^{-1}$ ) and the nanoplates ( $0.01097 \text{ min}^{-1}$ ). This can be due to the higher surface area of the nanoparticles compared with the other two nanostructures, which also can explain the smaller degradation rate of the octahedrons compared with the nanoparticles and the nanoplates. The degradation rate was obtained through the pseudo-first order reaction kinetic model, which is represented by  $\ln(C_0/C) = kt$ , where  $C_0$  is the initial concentration ( $\text{mg}\cdot\text{L}^{-1}$ ) [19,24,25].



**Figure 3.** Absorbance spectra of the photocatalytic degradation of RhB under UV light using as photocatalyst  $Zn_2SnO_4$  (a) octahedrons, (b) nanoplates and (c) nanoparticles. (d)  $C/C_0$  comparison of the photocatalytic degradation between ZTO nanostructures. (e) Kinetic parameters of the RhB degradation under UV of each  $Zn_2SnO_4$  nanostructure. (f) Photograph image of the initial RhB solution and after its degradation under UV light during 150 min using each of the  $Zn_2SnO_4$  nanostructures as photocatalyst.

#### 4. Conclusions

While  $Zn_2SnO_4$  nanostructures such as octahedrons, nanoplates and nanoparticles present great interest for different applications, sometimes the reaction times and/or yield are not practical, especially when considering devices which require a high volume of particles. Thus, microwave-assisted synthesis was explored in this work due to its faster and more uniform heating rate. This method has shown to be able to result in different ZTO nanostructures ( $Zn_2SnO_4$  octahedrons, nanoplates and nanoparticles), allowing to decrease the synthesis time up to 20 h, when comparing with the conventional oven. Furthermore, the photocatalytic activity of the ZTO nanostructures synthesized in only 60 min was studied in the degradation of rhodamine B under UV light, revealing a higher degradation rate using the nanoparticles ( $0.01659 \text{ min}^{-1}$ ) as photocatalyst then using the nanoplates ( $0.01097 \text{ min}^{-1}$ ) and the octahedrons ( $0.01069 \text{ min}^{-1}$ ).

**Funding:** This work is funded by National Funds through FCT—Portuguese Foundation for Science and Technology, Reference UID/CTM/50025/2019 and FCT/MCTES, as well as PTDC/NAN-MAT/30812/2017 (project NeurOxide), and the doctoral grant research number SFRH/BD/131836/2017. This work also received funding from the European Community’s H2020 program under grant agreement No. 716510 (ERC-2016-StG TREND), No. 787410 (ERC-2018-AdG DIGISMART) and No. 685758 (1D-Neon).

**Conflicts of Interest:** The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

#### References

- Baruah, S.; Dutta, J. Zinc stannate nanostructures: Hydrothermal synthesis. *Sci. Technol. Adv. Mater.* **2011**, *12*.
- Sun, S.; Liang, S. Morphological zinc stannate: synthesis, fundamental properties and applications. *J. Mater. Chem. A* **2017**, *5*, 20534–20560.

3. Dong, H.; Zhang, X.; Zhao, D.; Niu, Z.; Zeng, Q.; Li, J.; Cai, L.; Wang, Y.; Zhou, W.; Gao, M.; et al. High performance bipolar resistive switching memory devices based on Zn<sub>2</sub>SnO<sub>4</sub> nanowires. *Nanoscale* **2012**, *4*, 2571–2574.
4. Lim, T.; Kim, H.; Meyyappan, M.; Ju, S. Photostable Zn<sub>2</sub>SnO<sub>4</sub> Nanowire Transistors for Transparent Displays. *ACS Nano* **2012**, *6*, 4912–4920.
5. Rovisco, A.; dos Santos, A.; Cramer, T.; Martins, J.; Branquinho, R.; Águas, H.; Fraboni, B.; Fortunato, E.; Martins, R.; Igreja, R.; et al. Piezoelectricity Enhancement of Nanogenerators Based on PDMS and ZnSnO<sub>3</sub> Nanowires through Microstructuring. *ACS Appl. Mater. Interfaces* **2020**, *12*, 18421–18430.
6. Chen, D.; Wang, Q.; Shen, G.; Wang, R.; Shen, G. Ternary oxide nanostructured materials for supercapacitors : a review. *J. Mater. Chem. A Mater. Energy Sustain.* **2015**, *3*, 10158–10173.
7. Wojnarowicz, J.; Chudoba, T.; Gierlotka, S.; Lojkowski, W. Effect of Microwave Radiation Power on the Size of Aggregates of ZnO NPs Prepared Using Microwave Solvothermal Synthesis. *Nanomaterials* **2018**, *8*, 343.
8. Lehnen, T.; Zopes, D.; Mathur, S. Phase-selective microwave synthesis and inkjet printing applications of Zn<sub>2</sub>SnO<sub>4</sub> (ZTO) quantum dots. *J. Mater. Chem.* **2012**, *22*, 17732.
9. Bilecka, I.; Niederberger, M. Microwave chemistry for inorganic nanomaterials synthesis. *Nanoscale* **2010**, *2*, 1358–1374.
10. Chen, D.; Wang, Q.; Shen, G. Ternary oxide nanostructured materials for supercapacitors : A review. *J. Mater. Chem. A Mater. Energy Sustain.* **2015**, *3*, 10158–10173.
11. Pimentel, A.; Ferreira, S.; Nunes, D.; Calmeiro, T.; Martins, R.; Fortunato, E. Microwave Synthesized ZnO Nanorod Arrays for UV Sensors: A Seed Layer Annealing Temperature Study. *Materials (Basel)*. **2016**, *9*, 299.
12. Pimentel, A.; Nunes, D.; Duarte, P.; Rodrigues, J.; Costa, F.M.; Monteiro, T.; Martins, R.; Fortunato, E. Synthesis of Long ZnO Nanorods under Microwave Irradiation or Conventional Heating. *J. Phys. Chem. C* **2014**, *118*, 14629–14639.
13. Pimentel, A.; Rodrigues, J.; Duarte, P.; Nunes, D.; Costa, F.M.; Monteiro, T.; Martins, R.; Fortunato, E. Effect of solvents on ZnO nanostructures synthesized by solvothermal method assisted by microwave radiation: a photocatalytic study. *J. Mater. Sci.* **2015**, *50*, 5777–5787.
14. Nunes, D.; Pimentel, A.; Pinto, J.V.; Calmeiro, T.R.; Nandy, S.; Barquinha, P.; Pereira, L.; Carvalho, P.A.; Fortunato, E.; Martins, R. Photocatalytic behavior of TiO<sub>2</sub> films synthesized by microwave irradiation. *Catal. Today* **2016**, *278*, 262–270.
15. Nunes, D.; Pimentel, A.; Barquinha, P.; Carvalho, P.A.; Fortunato, E.; Martins, R. Cu<sub>2</sub>O polyhedral nanowires produced by microwave irradiation. *J. Mater. Chem. C* **2014**, *2*, 6097.
16. Xiao, L.; Shen, H.; Von Hagen, R.; Pan, J.; Belkoura, L.; Mathur, S. Microwave assisted fast and facile synthesis of SnO<sub>2</sub> quantum dots and their printing applications. *Chem. Commun.* **2010**, *46*, 6509–6511.
17. Nehru, L.C.; Sanjeeviraja, C. Processing Research Controllable growth of Zn<sub>2</sub>SnO<sub>4</sub> nanostructures by urea assisted microwave-assisted solution combustion process. **2013**, *14*, 606–609.
18. Reyes, O.; Pal, M.; Escorcia-García, J.; Sánchez-Albores, R.; Sebastian, P.J. Microwave-assisted chemical synthesis of Zn<sub>2</sub>SnO<sub>4</sub> nanoparticles. *Mater. Sci. Semicond. Process.* **2020**, *108*, 104878.
19. Jain, S.; Shah, A.P.; Shimpi, N.G. An efficient photocatalytic degradation of organic dyes under visible light using zinc stannate (Zn<sub>2</sub>SnO<sub>4</sub>) nanorods prepared by microwave irradiation. *Nano Struct. Nano Objects* **2020**, *21*, 100410.
20. Rovisco, A.; Branquinho, R.; Martins, J.; Oliveira, M.J.; Nunes, D.; Fortunato, E.; Martins, R.; Barquinha, P. Seed-Layer Free Zinc Tin Oxide Tailored Nanostructures for Nanoelectronic Applications: Effect of Chemical Parameters. *ACS Appl. Nano Mater.* **2018**, *1*, 3986–3997.
21. Annamalai, A.; Carvalho, D.; Wilson, K.C.; Lee, M.-J. Properties of hydrothermally synthesized Zn<sub>2</sub>SnO<sub>4</sub> nanoparticles using Na<sub>2</sub>CO<sub>3</sub> as a novel mineralizer. *Mater. Charact.* **2010**, *61*, 873–881.
22. Rovisco, A.; Branquinho, R.; Martins, J.; Fortunato, E.; Martins, R.; Barquinha, P. Growth Mechanism of Seed-Layer Free ZnSnO<sub>3</sub> Nanowires: Effect of Physical Parameters. *Nanomaterials* **2019**, *9*, 1002.
23. Rovisco, A. Solution-based Zinc-Tin Oxide nanostructures : from synthesis to applications, Ph.D. Thesis, Universidade NOVA de Lisboa, Lisboa, Portugal, 2019.
24. Barrocas, B.; Sérgio, S.; Rovisco, A.; Melo Jorge, M.E. Visible-Light Photocatalysis in Ca<sub>0.6</sub>Ho<sub>0.4</sub>MnO<sub>3</sub> Films Deposited by RF-Magnetron Sputtering Using Nanosized Powder Compacted Target. *J. Phys. Chem. C* **2014**, *118*, 590–597.

25. Zhao, Q.; Deng, X.; Ding, M.; Huang, J.; Ju, D.; Xu, X. Synthesis of hollow cubic  $Zn_2SnO_4$  sub-microstructures with enhanced photocatalytic performance. *J. Alloys Compd.* **2016**, *671*, 328–333.

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).