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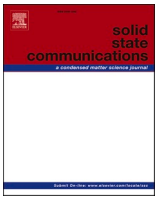

Electronic and optical properties of the recently synthesized 2D Vivianites (Vivianenes): Insights from first-principles calculations

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ABSTRACT

Vivianite ($Fe_3(PO_4)_2{\cdot}8H_2O$) is a naturally occurring layered material. In this work, we have investigated its 2D monolayer form, Vivianene, through DFT and ab initio molecular dynamics simulations. Vivianene retains the main structural features of the bulk structure and shows thermal stability at room temperature. It presents an indirect bandgap of 3.03 eV, slightly lower than bulk Vivianite (3.21 eV), with Fe *d* orbitals dominating the electronic states. Optical results reveal a higher optical bandgap (3.6 eV) and strong absorption in the ultraviolet region. The refractive index and reflectivity indicate efficient light absorption. These results pose Vivianene as a promising 2D material for optoelectronics, sensing, and energy-related technologies applications.

1. Introduction

Graphene has created a revolution in materials science since its synthesis in 2004. Since then, extensive investigations have been carried out into new two-dimensional (2D) materials, revealing a range of emergent properties when materials are reduced to a single or a few atomic layers. These properties, including a high surface-area-to-volume ratio, tunable electronic structures, and enhanced mechanical flexibility, make 2D materials promising candidates for various technological applications, from sensors and energy storage to optoelectronic devices [1–3]. Given the growing interest in expanding the library of 2D materials beyond graphene, significant attention has been directed toward layered materials that can be exfoliated into their monolayer forms [1,2].

Due to their abundance and environmental significance, Vivianites ($Fe_3(PO_4)_2{\cdot}8H_2O$) are an important family among naturally occurring layered materials. These ferrous phosphate minerals are commonly found in anoxic environments, where they play a fundamental role in the phosphorus cycle and contaminant immobilization [4,5]. Similar to other layered materials, such as hematene (2D α-Fe_2O_3) [6], ilmenene (2D $FeTiO_3$) [7], and chromiteen (2D $FeCr_2O_4$) [8], Vivianites possess a crystalline structure that allows for exfoliation into its 2D form, generically referred to as Vivianenes. The exfoliation process exploits weak interlayer interactions, facilitating perfect basal cleavage and isolating stable monolayers with potentially novel properties [1,5].

The electronic properties of Vivianites have been previously studied using density functional theory (DFT) calculations, which have estimated their electronic bandgap to range from 3.3 eV [9] to 4.6 eV [10]. This variation highlights the sensitivity of the bandgap to the methodological approaches employed and underscores the need for further investigations, particularly under reduced dimensionality. A reliable estimation of their electronic bandgap values is fundamental, as this parameter determines the photon energy required for electron-hole pair separation, a key factor for optoelectronic and catalytic applications [4].

Although Vivianites have been extensively investigated in their bulk form, their corresponding 2D structures, Vivianenes, remain largely unexplored in the literature [5]. The 2D exfoliated structures enable access to intrinsic properties that facilitate innovative applications in

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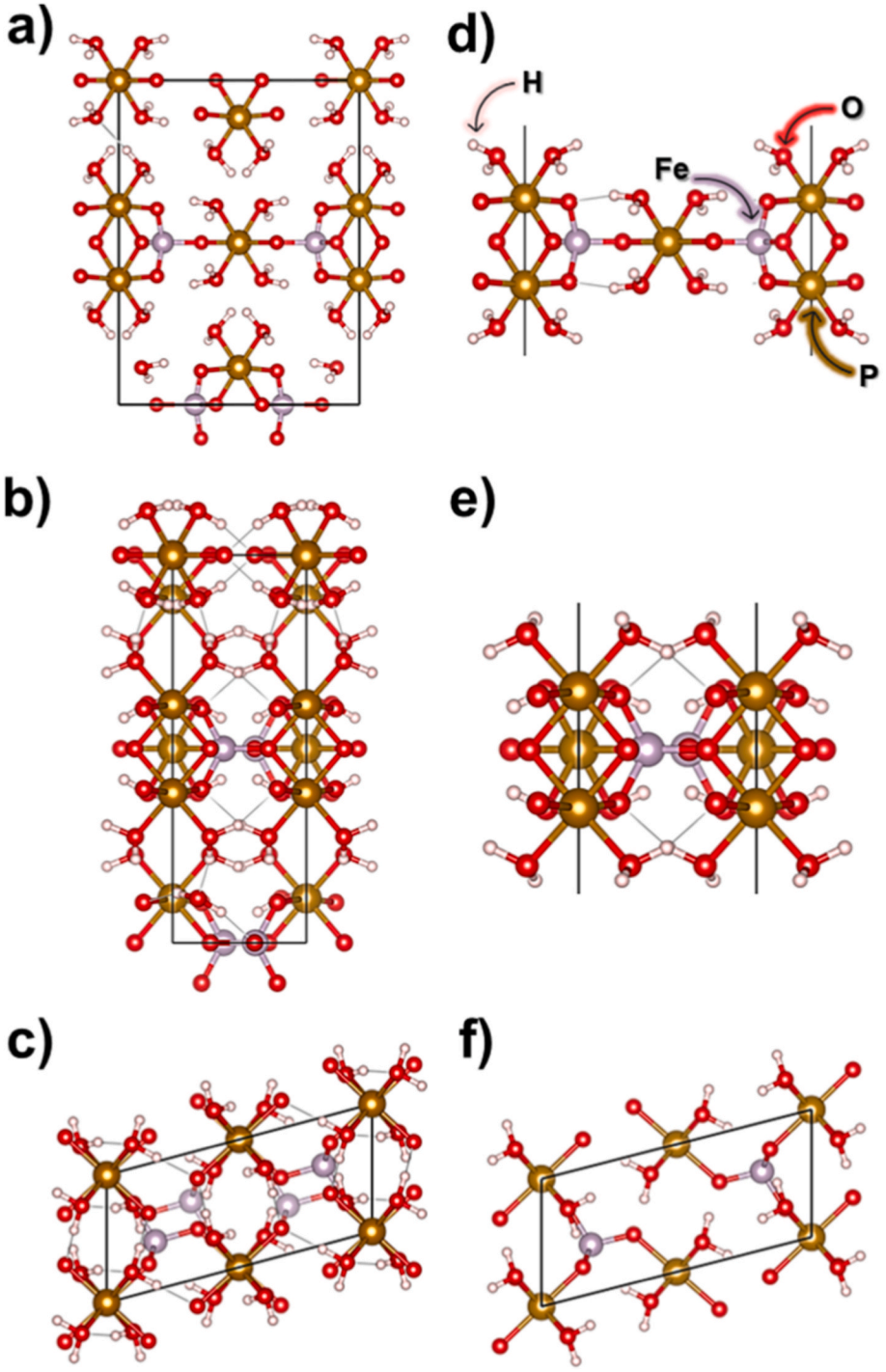

Fig. 1. Optimized structures of Vivianite and its corresponding two-dimensional (2D) form, Vivianene. Different crystallographic planes are presented: (a)–(c) for Vivianite and (d)–(f) for Vivianene. Panels (a), (b), and (c) show the structures along the xy, yz, and xz planes, respectively, for Vivianite, while panels (d), (e), and (f) display the corresponding planes for Vivianene. **Hydrogen (H), oxygen (O), iron (Fe), and phosphorus (P) atoms are depicted in white, red, gray, and gold, respectively.** (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

advanced technologies, such as pesticide sensing [5]. However, fundamental aspects of the electronic and optical properties of Vivianenes remain to be further investigated.

In this work, we present comprehensive theoretical analyses of vivianenes, focusing on their structural stability, electronic properties, and, mainly, on their optical behavior. Using DFT-based and ab initio molecular dynamics (AIMD) simulations, we compare bulk vivianite with its two-dimensional counterpart, highlighting the influence of reduced dimensionality. While previous studies have addressed the structural and electronic aspects of vivianenes, their optical properties remain largely unexplored. Our study provides a detailed theoretical investigation of the optical response of vivianenes, revealing key features relevant to optoelectronic and sensing applications. These findings advance the current understanding of 2D phosphate materials and offer a foundation for future research and technological development in this class of materials.

Table 1
Experimental (Exp.) and DFT results for the structural, electronic, and optical properties of Vivianite and Vivianene. Lattice parameters a, b, and c are given in Å. Electronic (E_g) and optical (E_g^{opt}) bandgap values are in eV.

System	Vivianite (Exp.)	Vivianite [9]	Vivianite (This work)	Vivianene [10]	Vivianene (This work)
a	10.09 [5]	9.884	9.91	10.021	9.98
b	13.44 [5]	13.146	12.87	–	–
c	4.73 [5]	4.568	4.59	4.625	4.58
γ	104.3 [4]	104.97	105.0	101.88	104.5
E_g	–	3.30	3.21	3.29	3.03
E_g^{opt}	3.5 [4]	–	3.2	–	3.5–3.7

2. Computational details

To investigate the properties of bulk Vivianite and its monolayer (010 plane, referred to here as Vivianene), we carried out ab initio simulations using the Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA) code [11,12]. SIESTA is based on the DFT formalism [13]. We have used the Perdew-Burke-Ernzerhof (PBE) [14] exchange-correlation functional within the Generalized Gradient Approximation (GGA), along with a polarized double-ζ (DZP) basis set composed of numerical orbitals. A mesh cutoff of 300 Ry was adopted, and the Brillouin zone was sampled using a Γ-centered Monkhorst-Pack grid with 3 × 3 × 5 and 3 × 1 × 5 **k**-points sampling [15] for the bulk and monolayer structures, respectively. For Vivianene, a vacuum buffer region of 25 Å was set along the *y*-direction to prevent spurious interactions with mirror images. Here, the 2D system is oriented along the *xz* plane. The Seek-Path [16] methodology was employed to determine the k-point paths based on crystal symmetry for computing the band structures of vivianite and vivianene. For vivianite, the high-symmetry path includes: Γ (0.0, 0.0, 0.0), Z (0.0, 0.5, 0.0), Q (0.0, 0.5, 0.5), F (0.0, 0.0, 0.5), Γ (0.0, 0.0, 0.0), A (0.5, 0.0, 0.0), L (0.5, 0.5, 0.0), and Z (0.0, 0.5, 0.0). For Vivianene, the selected path comprises F (0.0, 0.0, 0.5), Γ (0.0, 0.0, 0.0), and A (0.5, 0.0, 0.0). Convergence tests were thoroughly carried out for both the real-space mesh cutoff and the k-point grid, ensuring that the selected parameters yielded total energy differences smaller than 2×10^{-5} eV.

Regarding the self-consistency iteration convergence, we have considered it converged when the difference between the input and output elements of the density matrix was smaller than 10^{-4} and when the residual forces were below 0.05 eV/Å. Initially, all calculations were performed at 0 K.

We have also carried out AIMD simulations to assess Vivianene's structural thermal stability and investigated the dynamics of its intrinsic water-like structures. These AIMD runs were performed for approximately 3.5 ps with a time step of 1 fs in an NVT ensemble at 300 K, employing a Nosé-Hoover thermostat [11,12]. The simulations were performed using a mesh cutoff of 250 Ry, and the Brillouin zone was sampled using a 2 × 1 × 2 Monkhorst-Pack **k**-point grid [15].

For the optical properties analyses, we have calculated the absorption coefficient (α), reflectivity (R), and refractive index (η) as functions of the photon energy frequency (ω) using the method described in Ref. [17] and the following equations:

$$\alpha(\omega) = \sqrt{2}\omega \cdot \left[\left(\epsilon_1^2(\omega) + \epsilon_2^2(\omega)\right)^{1/2} - \epsilon_1(\omega) \right]^{1/2},$$

$$R(\omega) = \left[\frac{\left(\epsilon_1(\omega) + i\epsilon_2(\omega)\right)^{1/2} - 1}{\left(\epsilon_1(\omega) + i\epsilon_2(\omega)\right)^{1/2} + 1} \right]^2,$$

and

$$\eta(\omega) = \frac{1}{\sqrt{2}} \left[\left(\epsilon_1^2(\omega) + \epsilon_2^2(\omega)\right)^{1/2} + \epsilon_1(\omega) \right]^2.$$

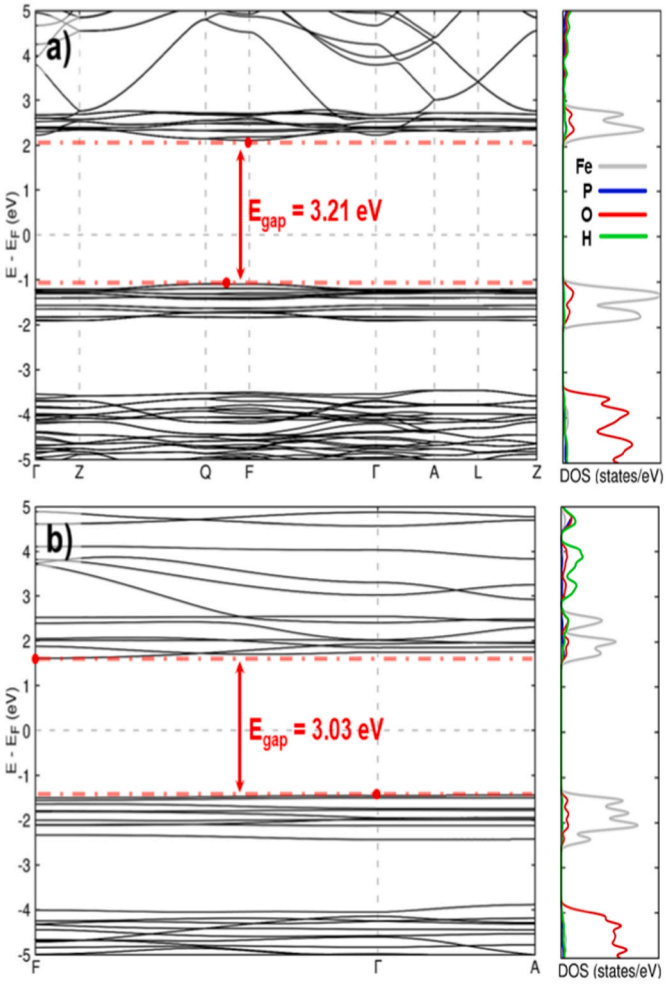

Fig. 2. Electronic band structure and the corresponding projected density of states of (a) Vivianite and (b) Vivianene.

3. Results and discussions

To assess the influence of dimensional reduction on Vivianite, we first investigate its structural and electronic properties in the bulk form as a reference for comparison with its two-dimensional counterpart. Fig. 1(a)–(c) presents the bulk form of Vivianite. The results of its structural characteristics are summarized in Table 1, where DFT-based calculations yielded lattice parameters of a = 9.91 Å, b = 12.87 Å, c = 4.59 Å, along with an angle $\gamma = 105.0^\circ$. Additionally, the electronic bandgap was calculated to be approximately 3.2 eV. These values are in good agreement with previous experimental findings [5], with deviations of less than 4 % for all discussed features, indicating that the computational model employed here provides a reliable description of the Vivianite crystalline structure. Furthermore, the results are also in good agreement with recent crystallographic data for synthetic Vivianite, which reported a = 10.101 Å, b = 13.452 Å, c = 4.711 Å, and $\gamma = 104.30^\circ$ [4].

Vivianene, the monolayer structure shown in Fig. 1(d)–(f), was experimentally obtained by cleaving bulk Vivianite along the (010) direction [5]. In this configuration, the central Fe atom interacts with four water-like molecules, and the unit cell is composed of 37 atoms, corresponding to half the number of atoms in the bulk Vivianite unit cell. In the 2D form, the optimized lattice parameters are a = 9.98 Å, c = 4.59 Å, and $\gamma = 104.5^\circ$. These values are comparable to those obtained for bulk Vivianite, with deviations below 1 %, indicating that Vivianene retains the main structural features of its bulk form. Vivianene consists mainly of $[PO_4]$ and $[FeO_6]$ clusters, with average P–O bond lengths of 1.57 Å

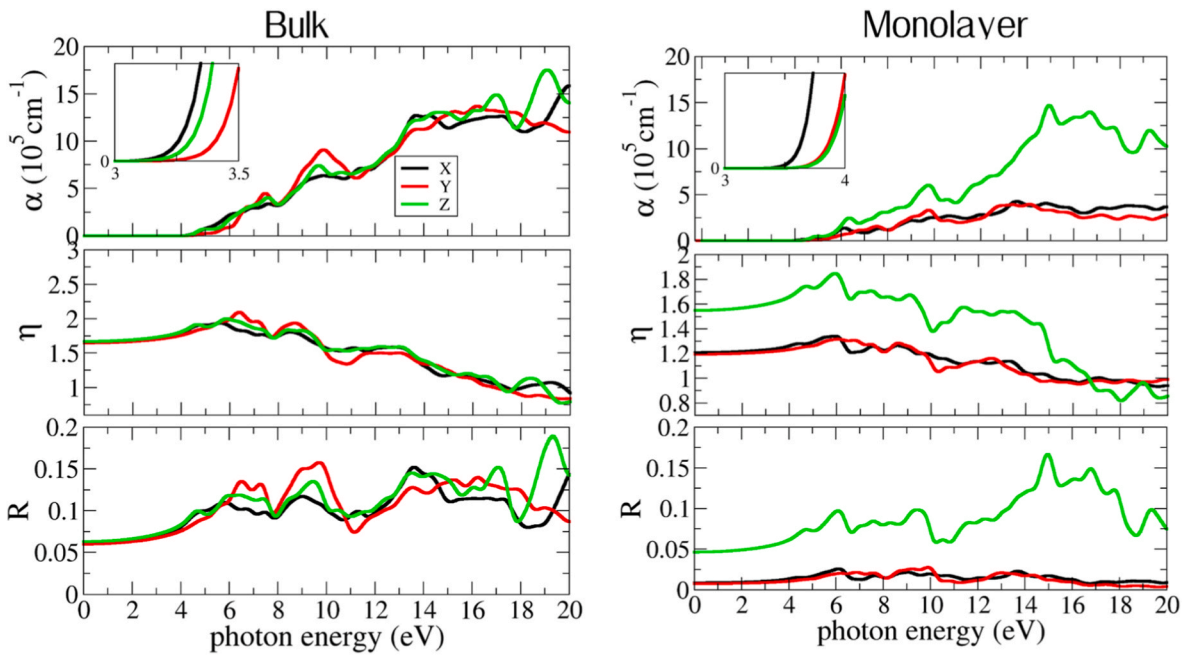

Fig. 3. The simulated absorption coefficient α, refractive index η, and reflectivity R as a function of the photon energy value.

and Fe–O bond lengths of 2.03 Å. Additionally, the free water molecules are, on average, located 3.64 Å from the [PO_4] clusters, and the mean O–H bond length is approximately 1.0 Å, consistent with values previously reported in the literature [4].

To further assess the thermodynamic stability of Vivianene and analyze the behavior of the water-like structures, we performed AIMD simulations. The results revealed no significant variation in the total energy over 3.5 ps at 300 K, indicating that the system maintains its structural integrity under these conditions. Furthermore, the water-like molecules did not exhibit significant displacement relative to the monolayer. The initial distance between the water molecule and the phosphorus atom in Vivianene was 3.64 Å, fluctuating within the range of 3.40–4.15 Å around the original position throughout the simulation time.

Regarding the electronic properties of Vivianite and Vivianene, we have calculated the electronic band structure and the corresponding projected density of states (PDOS). The results are presented in Fig. 2. Both structures exhibit indirect electronic band gaps, with values of 3.21 eV for the bulk structure and 3.03 eV for the monolayer. These results are not typical for the transition from 3D to 2D materials. Generally, quantum confinement effects tend to increase the band gap in 2D structures due to reduced dimensionality. However, similar behavior has also been reported for other materials [10].

Furthermore, Fig. 2 shows that the 2D structure exhibits flatter bands compared to the bulk structure, suggesting a decrease in electron mobility. The PDOS displays a similar pattern for both the bulk and monolayer forms. The top and bottom of the valence and conduction bands are primarily composed of *d* orbitals from Fe atoms, with minor contributions from oxygen atoms. The contribution of Fe to the valence bands decreases at higher negative energy values, while the contributions of oxygen become more significant.

Additionally, to assess the influence of thickness, we performed calculations for up to five-layer Vivianene structures. The results show a slight but consistent increase in the band gap values with additional layers, indicating a gradual convergence toward bulk-like electronic behavior. This trend is consistent with other 2D material systems and reinforces the monolayer as a valid reference basis for understanding few-layer counterparts [18–20].

Finally, we discuss the optical properties of the systems investigated in this study. We present the absorption coefficient (α), the refractive index (η), and the reflectivity (R) of Vivianite (Fig. 3, left) and Vivianene (Fig. 3, right) as a function of photon energy, ranging from 0 to 20 eV. In the case of the monolayer, the dielectric response has been properly normalized to exclude vacuum contributions in the out-of-plane direction, following best practices for 2D materials. This correction ensures that the absorption spectra are independent of vacuum thickness and can be meaningfully compared with the bulk counterpart.

After the correction, the monolayer exhibits a lower overall absorption intensity than the bulk, but the difference is more moderate than initially observed. In both systems, absorption is nearly isotropic below 13 eV, with polarization-dependent features becoming more pronounced only in the deep ultraviolet region. As shown in the insets, the onset of absorption occurs at approximately 3.2 eV for bulk Vivianite and 3.6 eV for Vivianene, consistent with the expected quantum confinement effect. No significant absorption features appear in the infrared or visible ranges, indicating significant UV activity. The refractive index remains significantly larger than the reflectivity throughout the spectrum, confirming that most of the incident light is absorbed. Notably, the corrected spectra now provide a more realistic estimate of the monolayer's optical response and reinforce the reliability of the trends observed across both dimensionalities.

Overall, to assess the influence of temperature, we performed ab initio molecular dynamics simulations at 300 K. The Vivianene structure remained stable throughout the simulation, and the water-like molecules exhibited localized and constrained motion. Although the electronic and optical properties were calculated from the relaxed structure at 0 K, this approach is supported by our results for bulk Vivianite, where the same methodology yielded lattice parameters and optical bandgap values in close agreement with experimental data. The thermal stability observed in AIMD further indicates that no significant structural distortions are expected at room temperature. Therefore, we consider that the electronic and optical properties obtained at 0 K remain a valid representation of the system under ambient conditions.

4. Conclusions

In this work, we have carried out a comprehensive theoretical investigation of Vivianene, the 2D counterpart of bulk Vivianite,

focusing on its structural, electronic, and optical properties. Our results show that Vivianene retains the main structural characteristics of its bulk precursor, with minimal deviations in lattice parameters and high thermal stability at room temperature, as confirmed by AIMD simulations. Electronic structure calculations revealed that both materials exhibit indirect band gaps, with values of 3.21 eV for Vivianite and 3.03 eV for Vivianene. These results indicate a deviation from the typical quantum confinement trend in 2D materials. The PDOS analysis showed that Fe *d* orbitals dominate the valence and conduction bands. The optical response of Vivianene revealed an increased optical band gap (3.6 eV) compared to bulk Vivianite (3.2 eV), with absorption primarily in the ultraviolet region. The refractive index and reflectivity analysis suggest intense optical activity, making Vivianene a promising material for optoelectronic applications.

CRediT authorship contribution statement

Raphael Benjamim de Oliveira: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation. **Bruno Ipaves:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Guilherme da Silva Lopes Fabris:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Surbhi Slathia:** Writing – original draft, Investigation, Formal analysis, Data curation. **Marcelo Lopes Pereira Júnior:** Writing – review & editing, Methodology, Investigation, Funding acquisition, Formal analysis. **Raphael Matozo Tromer:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Chandra Sekhar Tiwary:** Writing – review & editing, Supervision, Resources, Investigation, Funding acquisition, Conceptualization. **Douglas Soares Galvão:** Writing – review & editing, Validation, Supervision, Project administration, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Bruno Ipaves reports financial support was provided by State of Sao Paulo Research Foundation. Raphael Benjamim de Oliveira reports was provided by State of Sao Paulo Research Foundation. Douglas Soares Galvao reports was provided by State of Sao Paulo Research Foundation. Marcelo Lopes Pereira Junior reports was provided by Foundation for Research Support of the Federal District. Marcelo Lopes Pereira Junior reports was provided by National Council for Scientific and Technological Development. Marcelo Lopes Pereira Junior reports was provided by Coordination of Higher Education Personnel Improvement. If there are other authors, they 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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Data availability

Data will be made available on request.

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