J Nanostruct 16(4): 5631-5638, Autumn 2026

RESEARCH PAPER

Green Hydrothermal Preparation of $Bi_2Ca_3Co_2O_9$ Nanoparticles Mediated by Trifolium repens Leaf Extract

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ARTICLE INFO

Article History:
Received 29 June 2026
Accepted 05 September 2026
Published 01 October 2026

Keywords:
$Bi_2Ca_3Co_2O_9$
Green synthesis
Hydrothermal
Nanoparticles
Trifolium repens

ABSTRACT

A green hydrothermal route was used for the preparation of $Bi_2Ca_3Co_2O_9$ nanoparticles (BCCO) in the presence of *trifolium repens* leaf extract as a natural capping agent. Crystallite size determination using the Scherrer method showed that the BCCO prepared with the natural capping agent exhibited finer crystallites (17.42 nm) compared to the sample synthesized in a pure water medium (22.15 nm), demonstrating the efficacy of *trifolium repens* extract in controlling crystallite growth. Additionally, field emission scanning electron microscopy (FESEM) confirmed the restricted particle growth, leading to formation of nanoparticles with average sizes ranging from 50 to 100 nm. Fourier transform infrared (FT-IR) spectroscopy verified the presence of organic functional groups derived from the compounds within the used extract, which effectively stabilized the BCCO nanoparticles during the hydrothermal process. Moreover, the prepared samples were utilized in photocatalytic degradation of methyl orange under LED light. The results showed that the BCCO nanoparticles acted as a highly efficient photocatalyst, achieving a 97% degradation efficiency.

How to cite this article
Mohammed Taib A., Toma Al-Bakzo D., Saeed N., Saied S. Green Hydrothermal Preparation of $Bi_2Ca_3Co_2O_9$ Nanoparticles Mediated by Trifolium repens Leaf Extract. J Nanostruct, 2026; 16(4):5631-5638. DOI: 10.22052/JNS.2026.04.093

INTRODUCTION

Nowadays, nanotechnology has attracted widespread attention across scientific literature, facilitating the fabrication of advanced devices and products with exceptional properties. The automotive, aerospace, biomedical, and materials engineering sectors represent leading fields that have substantially benefited from nanomaterials [1-3]. For example, recently, the diagnosis of chronic diseases has become significantly faster than in the past, largely due to nanomaterial-based diagnostic tools incorporating metal-based quantum dots, carbon quantum dots, and other functional nanoparticles [4-6]. Furthermore, nanocomposites that are lighter yet stronger than conventional steels have been increasingly integrated into aerospace and automotive industries [7, 8].

Despite the appreciated benefits of nanomaterials, environmental risks associated with their uncontrolled release have raised significant concerns with scientific communities [9, 10]. Furthermore, a second source of contamination originates from the hazardous chemicals used during conventional nanomaterial synthesis [11-14]. In this context, green chemistry offers

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a promising solution to mitigate this emerging environmental crisis [15, 16]. Plant extracts have drawn considerable interest for the green synthesis of nanomaterials [17]. They contain diverse organic compounds—such as polyphenols, protein, glycerides, glucose, and esters—which provide steric hindrance, thereby restricting particle growth during synthetic reaction [18, 19].

In recent years, hundreds of works have been published for the green synthesizing nanomaterials. For instance, Rathod et al. reported the green synthesis of $CoFe_2O_4$ nanoparticles using *Coriandrum sativum* extract [20]. Shaibu et al. studied photocatalytic degradation of polyethylene films using green synthesized ZnO and Fe_3O_4 nanoparticles from *Acacia nilotica* [21]. Also, *Garcinia cowa* leaf extract has been used for synthesizing of ZnO nanoparticles [22].

Trifolium repens, commonly known as white clover, is a plant native to Europe and Asia that typically grows in lawns and pastures [23, 24]. It contains a variety important organic compounds, including flavonoids, iso-flavonoids, phenolic acids, terpenoids, fatty acids, providing significant antioxidant, anti-inflammatory, and phytoestrogenic activities [25, 26]. Historically, it has been used as an herbal medicine for curing respiratory infections and coughs, fever, and stomach disorders [27, 28]. Besides, trifolium repens has the great potential for wound-healing and treatment of eczema [29]. Moreover, owing to the aforementioned organic ingredients within the *trifolium repens*, its extract can serve as the green capping agent for synthesizing nanoparticles [30, 31].

Herein, we synthesized $Bi_2Ca_3Co_2O_9$ nanoparticles (BCCO) through a hydrothermal method using the green capping agent. Extract from *trifolium repens* leaves was used for this purpose. As mentioned above, these herbal extracts contain valuable organic compounds, which are useful for stabilizing nanoparticles. The synthesized nanoparticles were carefully studied using X-ray diffraction (XRD), field emission electron microscope (FESEM), and Furrier transform infrared spectroscopy (FT-IR).

MATERIALS AND METHODS

Nitrate precursors, including $Bi(NO_3)_3.5H_2O$, $Ca(NO_3)_2.4H_2O$, and $Co(NO_3)_2.6H_2O$, were supplied and used without additional purification. Fresh *trifolium repens* leaves were used to prepare extract solution.

Preparation of green capping agent

Fresh *Trifolium repens* leaves were chopped and immersed in 100 mL of warm distilled water. Subsequently, the mixture was stirred for 5 h upon heating at 60 °C. The resulting mixture was filtered using Whatman filter paper to obtain a clear and transparent solution, schematically presented in Fig. 1.

Green hydrothermal preparation of $Bi_2Ca_3Co_2O_9$ nanoparticles[32]

The green $Bi_2Ca_3Co_2O_9$ nanoparticles (abbreviated as *g*-BCCO) were prepared using the *trifolium repens* leaf extract. 2.0 mmol of

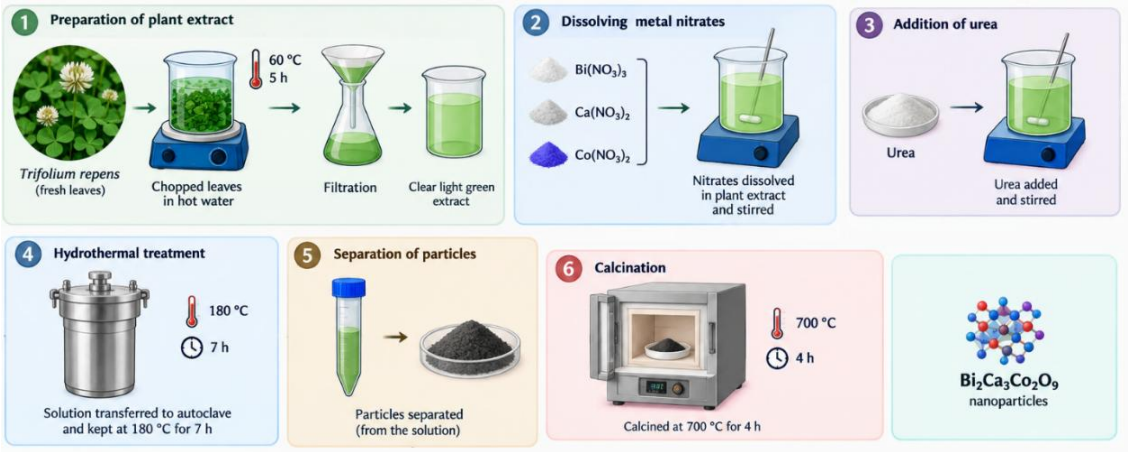


Fig. 1. BCCO synthetic route using *trifolium repens* leaf extract.

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$Bi(NO_3)_3.5H_2O$, 3.0 mmol of $Ca(NO_3)_2.4H_2O$, and 2.0 mmol of $Co(NO_3)_2.6H_2O$ were dissolved in 30 mL of the as-prepared green capping agent solution. The mixture was stirred for 15 min followed by addition of 0.5 g urea. Then, the solution was poured into a 100 mL autoclave and maintained at 180 °C for 7 h. After the completion of the hydrothermal reaction, the resulting precipitate was collected by filtration, rinsed by distilled water, dried and finally calcined at 700 °C for 4 h. The BCCO synthetic route is schematically represented in Fig. 1. The BCCO was also prepared in pure water medium without addition of the green capping agent, abbreviated as *w*-BCCO.

Characterization

The BCCO nanoparticles were carefully investigated to identify the crystal system, surface functional groups, morphology and composition of the nanoparticles using XRD (X'pert Pro MPD Philips), FT-IR (Bruker Tensor), and FESEM (TESCAN mira 3) analyses.

RESULTS AND DISCUSSION

Fig. 2 shows the XRD pattern for the *g*-BCCO nanoparticles prepared using the green capping agent. The diffraction peaks correspond well to the reference code of 052-0125 for bismuth calcium cobalt oxide. For comparison, the XRD result for the BCCO prepared in the absence of capping agent (*w*-BCCO) is also provided in Fig. 2, revealing the similar pattern with the sample synthesized using the *trifolium repens* extract. As seen in Fig. 2, the *g*-BCCO shows the slightly broader and less intense peaks compared to that of the *w*-BCCO. This slight peak broadening is primarily attributed to the restricted crystal growth resulting from the steric hindrance imparted by the functional organic groups in the *trifolium repens* extract. To quantify this effect, the average crystallite size was determined by the Scherrer method [33], yielding values of 22.15 nm for the w-BCCO and 17.42 nm for the g-BCCO. These results confirm that the used green capping agent effectively controlled crystallite growth during the hydrothermal process without altering the crystal phase purity.

FT-IR spectroscopy was used to characterize the functional groups for the *g*-BCCO nanoparticles. Fig. 3 shows the absorption bands corresponding to the organic compounds within the used capping agents for the synthesis of *g*-BCCO nanoparticles. Obviously, the presence of C-O (1252 cm^{-1}), C=O

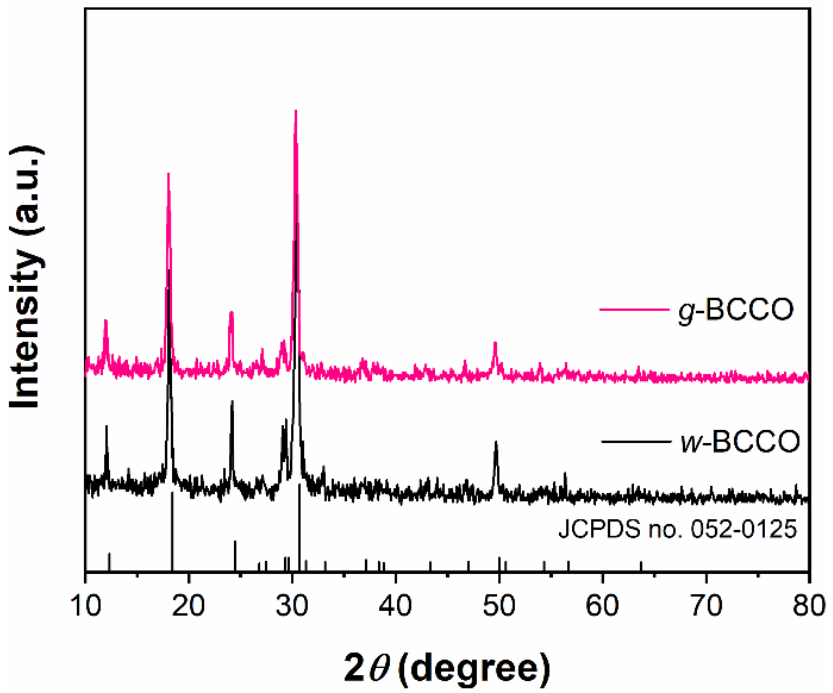


Fig. 2. XRD patterns for the BCCO prepared in the absence and presence of *trifolium repens* leaf extract.

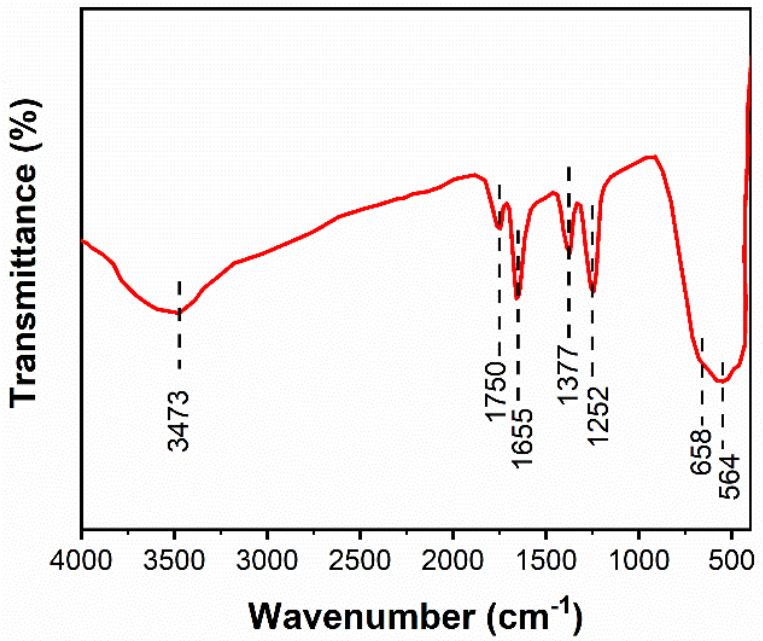


Fig. 3. FT-IR spectroscopy result for the prepared BCCO nanoparticles using *trifolium repens* leaf extract.

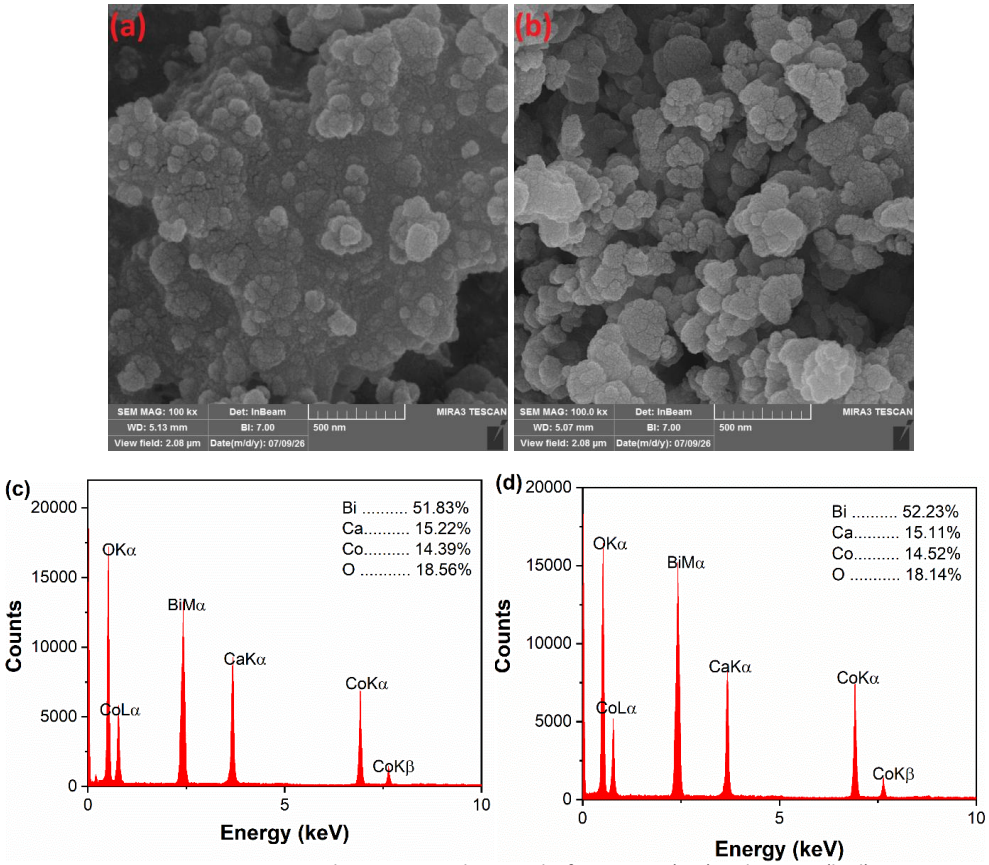


Fig. 4. FESEM images and EDX microanalysis results for w-BCCO (a, c) and g-BCCO (b, d).

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(1750 cm^{-1}), C=C (1655 cm^{-1}), and C-N (1377 cm^{-1}) confirmed the successful interaction of the used green capping agent to restrain the particle growth [34, 35]. Additionally, there is the broad band centered at around 3473 cm^{-1}, which is assigned to the vibrational mode of O-H groups [36]. The metal-oxygen bands are observed as the strong absorption at the range of 600-400 cm^{-1}. The absorption peaks at 658 and 564 cm^{-1} belong to the Bi-O and Ca-O/Co-O bonds, respectively [37, 38].

Fig. 4 displays FESEM images for *w*-BCCO (a) and *g*-BCCO (b). The *w*-BCCO (Fig. 4a) sample shows the micro-size particles with the uneven surface. However, Fig. 4b obviously represents the irregular shape of the nanoparticles in the size range of 50-100 nm. In addition, the agglomerated particles are also observed for the *g*-BCCO sample. This difference in the morphology is attributed to the use of the *trifolium repens* extract for the BCCO. Clearly, the used green capping agent stabilized the nanoparticles during the hydrothermal reaction. As can be seen in Fig. 4a, in the absence of the *trifolium repens* extract, the uncontrolled particle growth led to the formation of micro scale BCCO particles. The composition of the prepared samples were investigated using EDX analysis, showing in Fig. 4c and 4d. Both *w*-BCCO and *g*-BCCO have approximately similar composition comprising bismuth, calcium, cobalt, and oxygen with relative amounts provided in the inset to the EDX spectra.

Fig. 5 provides a proposed illustration for the surrounded BCCO nanoparticles with organic compounds present in the green capping agents. It can be truly concluded that the absorbed organic ingredients within the trifolium repens extract such as phenolic acids and flavonoids lead to the strong steric effect around the individual particles hindering them from aggregating [39, 40].

The prepared BCCO was tested to investigate its photocatalytic potential for degrading organic pollutants. In this regard, the BCCO was utilized for visible-light removal of methyl orange in an aqueous solution. 50 mL of 30 mg/L of methyl orange was exposed to a visible light beam from an LED lamp (50 W), and different type of BCCO was added. The degradation results were checked every 30 min using UV/Vis spectroscopy at maximum absorption wavelength of methyl

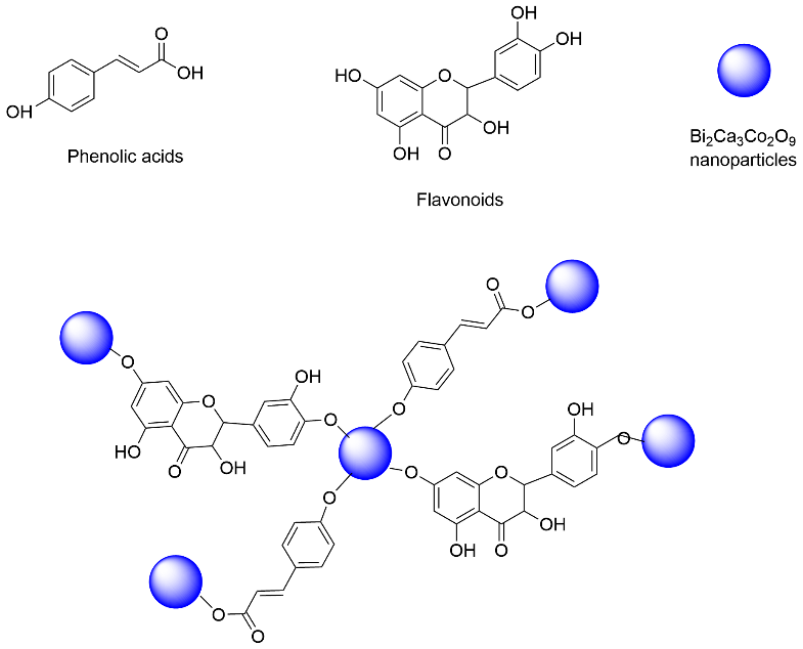


Fig. 5. Schematic illustration for restriction growth of BCCO nanoparticles using typical organic compounds within *trifolium repens* leaf extract.

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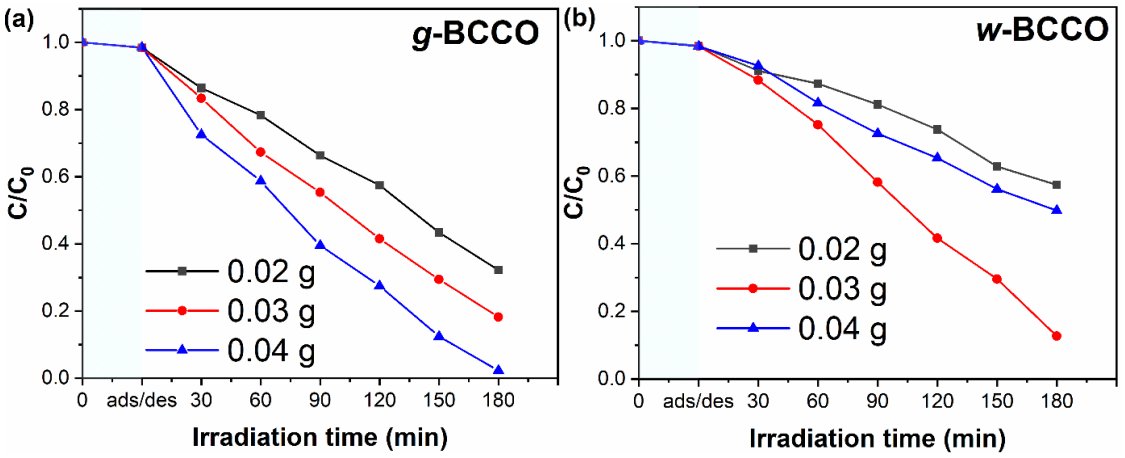


Fig. 6. Photocatalytic potential of BCCO for degradation of methyl orange.

orange at 510 nm.

Fig. 6a clearly represents the *g*-BCCO provides higher photo-activity toward degradation of methyl orange. After completion of the photocatalytic reaction (180 min), the results showed that the *g*-BCCO degraded the methyl orange by 97.72%, which is higher than that of *w*-BCCO (87.31%), as shown in Fig. 6b. The significant photocatalytic capability of the *g*-BCCO is attributed to its finer particle size. As shown in FESEM images (Fig. 4b), the *g*-BCCO possesses the nano-scaled particles, which impart the higher surface area and, in turn, the higher concentration of the photocatalytic active sites. The higher photocatalytic active sites imply that many more surface spots are available to advance the degradation reaction.

Moreover, the Fig. 6 exhibits the degradation reactions using different amounts (0.02, 0.03, 0.04 g) of *g*-BCCO and *w*-BCCO. For *g*-BCCO (Fig. 6a), there is an increasing trend from 0.02 to 0.04 g, whereas the methyl orange degradation reached the highest yield using 0.03 g of *w*-BCCO (Fig. 6b) and its increased amount (0.04 g) led to degradation decline to 50.17%.

CONCLUSION

In summary, nanoscale $Bi_2Ca_3Co_2O_9$ (BCCO) nanoparticles were successfully synthesized via a facile and green hydrothermal route utilizing *trifolium repens* leaf extract as a natural capping and stabilizing agent. Structural and morphological characterizations confirmed that the bioactive compounds present in the plant extract—such as polyphenols and flavonoids—exert the pronounced steric hindrance, effectively suppressing particle agglomeration and crystal growth. Consequently, the BCCO nanoparticles exhibited the crystallite size of 17.42 nm and nanoscale morphology (50-100 nm) compared to the water-mediated reference sample. FT-IR spectroscopy further validated the successful adsorption of organic functional groups onto the nanoparticle surface. Furthermore, photocatalytic evaluation under visible LED irradiation demonstrated that the green-synthesized BCCO achieved an outstanding methyl orange degradation efficiency of 97%. In contrast, the water-mediated BCCO sample showed an 87% degradation efficiency. These findings highlight that the green-assisted hydrothermal approach provides an effective strategy for tailoring the microstructural properties of mixed-metal oxides, rendering them highly promising candidates for environmental remediation and the photocatalytic applications.

ACKNOWLEDGMENT

The researchers thank the College of Education for Pure Sciences at the University of Mosul for supporting this research by providing the laboratories and materials necessary for the study. They also thank Al-Noor University for supporting the work under the project (Grant No. ANUI2026SCI24) and for covering the costs of laboratory analyses.

CONFLICT OF INTEREST

The authors declare that there is no conflict

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of interests regarding the publication of this manuscript.

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