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Synthesis, Structural and Antibacterial Activity of $Zn_{1-x}Ni_xFe_2O_4$ Nanoparticles

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In present work, nickel doped zinc ferrite nanoparticles were prepared *via* hydrothermal technique. The prepared nanopowders were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), Fourier-transform infrared spectroscope (FTIR), vibrating sample magnetometer (VSM) and antimicrobial activity. The XRD analysis revealed that the presence of sharp diffraction peaks and cubic-structure of the prepared samples. SEM analysis revealed that there is a significant degree of agglomeration in the samples, whereas VSM studies revealed the magnetic behaviour and cation distribution in the prepared samples. The prepared nanopowder has also been evaluated for its antimicrobial properties against Gram-negative bacteria (*Enterobacter aerogenes*) and Gram-positive bacteria (*Enterococcus faecalis*). An increasing in the ratio of nickel to zinc in ferrite nanoparticles led to an evident rise in their activity. These nanoparticles with enhanced structure and antimicrobial properties could find applications in hygiene, therapeutic and textile fields.

Keywords: Zinc ferrite, X-ray diffraction, Crystallite size, Magnetic properties, Antibacterial activity.

INTRODUCTION

In recent years, zinc ferrite nanoparticles incorporated with nickel have gained much attraction owing to their versatile magnetic and antimicrobial properties [1]. Specifically, based on their low dielectric loss and high resistivity these materials are useful for radio frequency applications, rod antennas also capable catalytic agent in organic/inorganic processes [2], transformer cores [3], as well as radar-absorbing materials [4]. The operationalization of the nickel based zinc ferrite nanoparticles tenders a new way to introduce magnetically spotted remedies in biomedicine, antimicrobial activity or biological compatibility [5,6] by using their appropriate properties.

Naturally, to exhibit antimicrobial behaviour the particles in nano-region have to explore the following characteristics like precise shape control and size of the particle and dispersion [7]. Especially, it is mandate to stabilization of dispersion of the nanoparticles in aqueous medium. Hence, coating of the nanoparticles with organic/inorganic substances and polymer-shells is commonly being the initial step which leads to induce the nanoparticles with good dispersion and excellent biocompatibility [8]. Velmurugan *et al.* [9] synthesized nickel zinc ferrites through self-combustion method to enhance the colloidal dispersion and controlled particle size. It is found that the bacteriostatic/bactericidal effect were dependent on the size and dose dependen. Ansari *et al*. [10] prepared thin magnetic nanoparticles using sol-gel synthesis method, which exhibit improved the bacterial activity by different coating agents. Furthermore, through recycling and recovery, the magnetic behaviour of the nanostructures can be modified at the site of action by the impact of external fields. The synthetic method *i.e.* hydrothermal method enhances the properties of the nanoparticles by controlling the elemental-composition, morphology, homogeneity *via* uniform distribution of metal clusters during the reaction. In this concern, the hydrothermal technique is considered as better choice over traditional techniques for synthesizing metal-oxide nanoparticles [11].

The zinc ferrite nanoparticles exhibit an inverted spinel structure with octahedral sites distributed evenly by Zn^{2+} and Fe^{3+}. Furthermore, $ZnFe_2O_4$ exhibited spinel-structure with Zn^{2+} and Fe^{3+} in tetrahedral and octahedral position [12]. Therefore, nickel substitution in $ZnFe_2O_4$ may exhibit vague spinel-structure which depends on the precursor concentration [13]. Literature suggests that the magnetic behaviour of spinel is susceptible to the cation type distribution in the interstitial sites [14]. Furthermore, one study reported that nickel substitution lead to decrement of curie temperature in the ferrites [15]. Nevertheless, few literature is available on the usage of magnetic particles in nano-region for applications in biomedicines [16]. Therefore, the aim of present study is to prepare novel nickel doped zinc-nanoparticles $Zn_{1-x}Ni_xFe_2O_4$ (x = 0.2, 0.4, 0.6 and 0.8) *via* inexpensive hydrothermal technique as antimicrobial agents. In this concern, the effect of the nickel-concentration microstructure, morphology and antimicrobial properties of prepared nanoparticles were systematically investigated.

EXPERIMENTAL

The metallic nitrate solutions $Fe(NO_3)_3·9H_2O$, $Zn(NO_3)_2·6H_2O$ and $Ni(NO_3)_2·6H_2O$ (Sigma-Aldrich with ≤ 99% purity) were blended vigorously in stoichiometric ratios in double distilled water.

Synthesis: The precursor mixture was stirred vigorously for about 2 h then obtained an homogenous solution. After that the solution was transferred to a Teflon container followed by autoclave reactor. For the purpose of hydrothermal reaction the reactor was heated in oven at 150 ºC for about 8 h. Later on, it was the reactor to reach room temperature naturally. The obtained precipitate was washed several times with ethanol and water. Finally, the solid content was heated at 60 ºC for 1 h and then grinded to attain fine powder particles [17-23]. The general equation for the $Zn_{1-x}Ni_xFe_2O_4$ synthesis is represented as follows:

$$Zn(NO_3)_2·6H_2O + Ni(NO_3)_2·6H_2O + Fe(NO_3)_3·9H_2O \longrightarrow ZnNiFe_2O_4 + 10HNO_3 + 25H_2O + 1/2O_2$$

The nanoparticles with general formula $Zn_{1-x}Ni_xFe_2O_4$ (x = 0.2, 0.4, 0.6 and 0.8), here in after denoted as $ZNiF_{0.2}$, $ZNiF_{0.4}$, $ZNiF_{0.6}$ and $ZNiF_{0.8}$ were synthesized by hydrothermal technique. The structural investigation was done by Seifert diffractometer (XRD-3003) with Ni-*K*α radiation (λ = 1.5406 Å), for 2θ in range of 10º and 90º. The existence of metal-oxide bonds was revealed by JASCO-660+ spectrophotometer with KBr-pellet method. The morphological analysis was done by scanning electron microscope, whereas the magnetic behaviour was elucidated by VSM-3900 Princeton.

Antibacterial activity: By using disc diffusion method antibacterial activity of $Zn_{1-x}Ni_xFe_2O_4$ (x = 0.2, 0.4, 0.6 and 0.8) nanoparticles was evaluated against *Enterobacter aerogenes* (Gram-negative) and *Enterococcus faecalis* (Gram-positive). Besides in a Nutrient medium, the standard bacteria strains were cultured and incubated at room temperature for 24 h. Afterwards, from the culture of bacterial colonies the suspensions of bacterial strains was prepared with 10^6 CFU/mL using a haemocytometer. Later, the suspension were splashed on the surface of agar plated with different nickel concentration to get uniform growth [24]. After incubation at 37 ºC, the number of grown colonies was counted after 24 and 48 h.

RESULTS AND DISCUSSION

XRD studies: Fig. 1 exhibits the X-ray diffraction patterns of nickel doped zinc ferrite nanoparticles. It is observed that the peak at 36.65° is the strongest reflection peak for all the samples. Also, the Miller indices (311) confirmed the spinel phase of the prepared samples. Therefore, the XRD analysis confirms the existence of a single-phase spinel-structure. Further, all the observed peaks are in good agreement with JCPDS card no. 73-1963 [25]. In addition, with the help of Scherrer's equation, the size of the crystallite was elucidated:

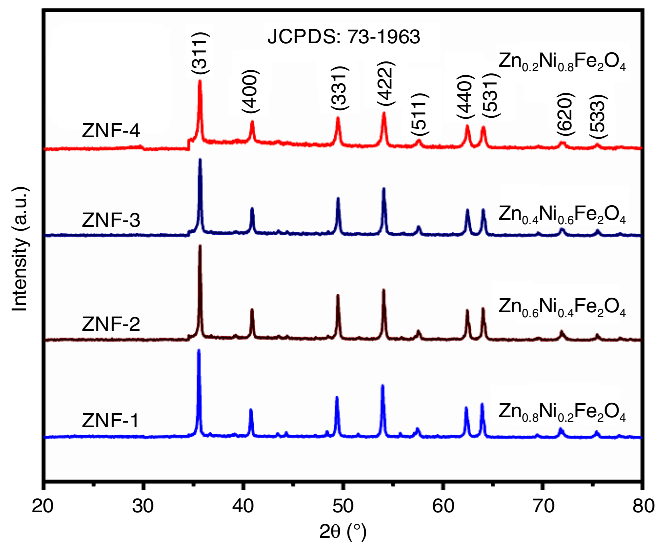

Fig. 1. X-ray diffraction pattern of $Zn_{1-x}Ni_xFe_2O_4$ (x = 0.2-0.8) (ZNF) nanoparticles

$$D_{hkl} = \frac{k\lambda}{\beta(2\theta)\cos\theta} \quad (1)$$

where D = size of the crystallite, λ = wavelength of the X-ray source, β = full-width at half-maxima and θ = angle of diffraction. The crystallites size of the samples were found to be 41.42, 45.18, 45.61 and 47.68 nm for $ZNiF_{0.2}$, $ZNiF_{0.4}$, $ZNiF_{0.6}$ and $ZNiF_{0.8}$, respectively.

SEM studies: The surface morphology and size of the prepared ZNF-nanoparticles was revealed by SEM-analysis. The micrographs of the prepared samples annealed at 600 °C are displayed in Fig. 2. The ZNF nanoparticles exhibited the spherical morphology with homogenous distribution with average grain size of ~ 60 µm [26-29]. The broadened spheres and tiny spheres could be fine-grains. The magnetic attraction of nanoparticles causes the synthesized samples to have anomalous sizes, shapes and cohesion of grains, which in turn affects the biological activity and integration of the samples, including their antibacterial effect. Due to the smooth surface of synthesized nanoparticles have capable to interact with the wall of bacterial cell [30]. Similarly, smaller spherical nanoparticles have better antibacterial efficacy than the larger spherical nanoparticles since they have a larger surface area.

FTIR studies: At room temperature, the presence of functional groups and metal-oxide bonds in the synthesized nanoparticles were confirmed by FTIR-spectra as shown in Fig. 3. The FTIR spectra of $Zn_{1-x}Ni_xFe_2O_4$ (x = 0.2, 0.4, 0.6 and 0.8) samples were studied in the wavenumber ranging from 4000-400 cm^{-1}. All the samples consists of six absorption bands and were observed around at 420, 509, 1330, 1644, 2342 and 3364

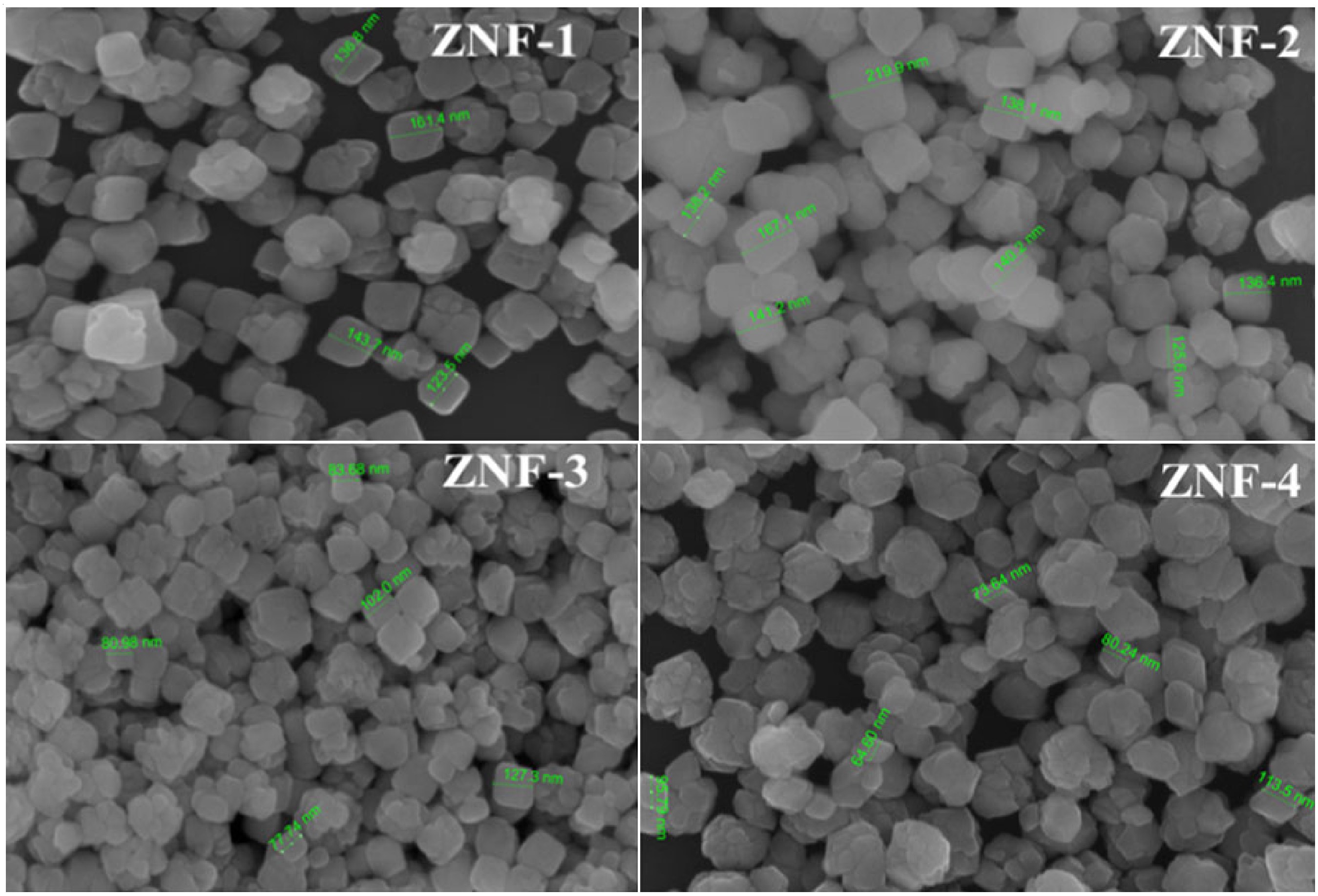

Fig. 2. SEM-images of $Zn_{1-x}Ni_xFe_2O_4$ (x = 0.2-0.8) nanoparticles

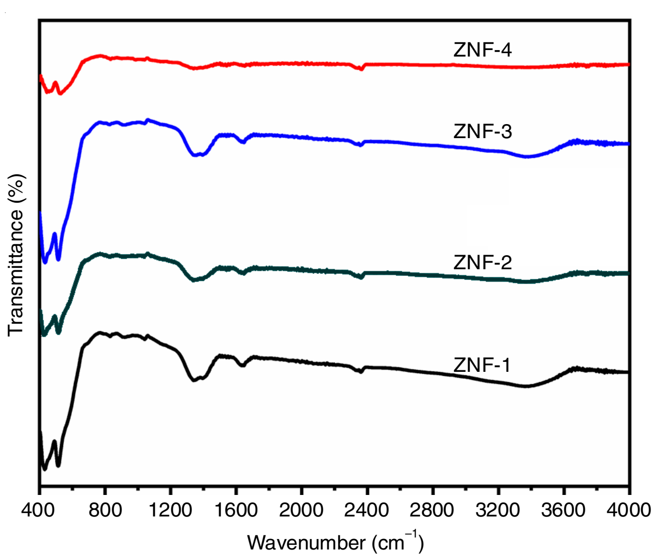

Fig. 3. FTIR spectra of $Zn_{1-x}Ni_xFe_2O_4$ (x = 0.2-0.8) (ZNF) nanoparticles

cm^{-1}. Moreover, the key peaks related to spinel structure were observed *i.e.* a peak corresponds to 420 cm^{-1} accredited to the stretching vibration of Fe-O in the octahedral-sites. Besides, a band at 509 cm^{-1} is ascribed to intrinsic stretching vibration of Zn-O in tetrahedral-site, which is in agreement with the reported literature [31]. The strongest absorption peak observed in range of 600-400 cm^{-1} is endorsed usually to the intrinsic stretching vibrations tetrahedral oxygen and metal ion bonds [32], while the weakest absorption peak is related to stretching vibration of oxygen and octahedral metal ionic bonds. The bands at 1330 and 1644 cm^{-1} resemble to the stretching vibration of C-H bond [33]. The bending and stretching vibrations of H-O-H bonds on the surface are responsible for the other reasonable absorption peaks at 2342 and 3363 cm^{-1}, respectively.

Magnetic studies: Magnetic properties of as-synthesized ZNF nanoparticles were investigated using vibrating sample magnetometer (VSM) as shown in Fig. 4. Zinc ferrite displays normal spinel-structure in which A-site is allocated by Zn and B-site is accompanied by Fe-cations. The induced magnetic moment between cations is accountable for the generation of magnetization. Generally, the magnetic behaviour is affected by some factors like method of preparation, size of the crystallite, distribution of cations, *etc.* [34-36]. Saturation magnetization also varies with the nickel concentration as shown in Fig. 4. The sample with high nickel content displays a large value of saturation magnetization. Therefore, according to the literature [37], these various samples can consistently react with micro-organisms. Hence, prepared materials, specifically, ZNF4 may be suitable for antimicrobial applications.

Antimicrobial activity: The bactericidal effect of the synthesized ZNF-nanoparticles was studied by performing disc-diffusion test technique against *E. aerogenes* (Gram-negative) and *E. faecalis* (Gram-positive) bacterial strains. The absence

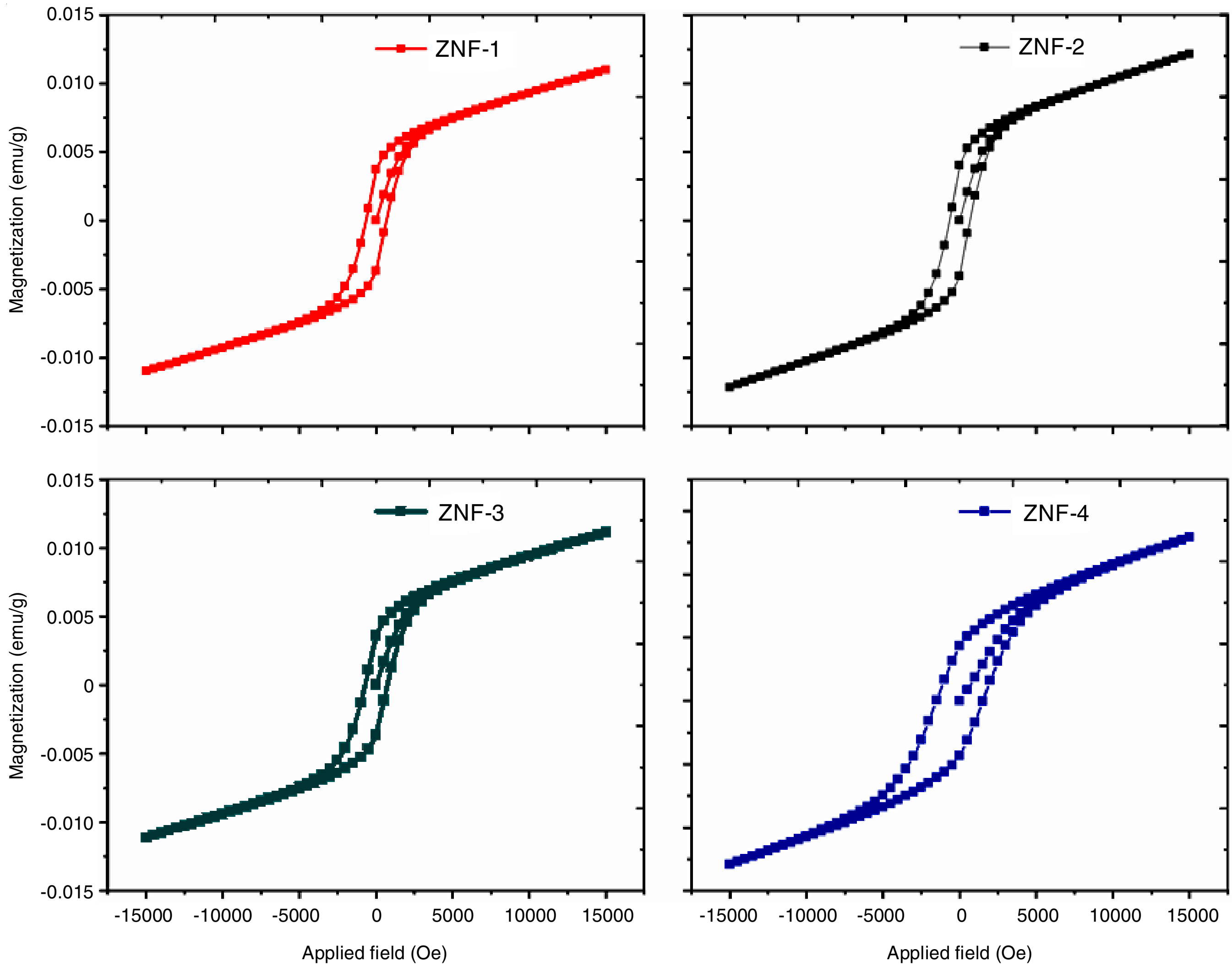

Fig. 4. M-H loops of $Zn_{1-x}Ni_xFe_2O_4$ (x = 0.2-0.8) (ZNF) nanoparticles

of growth surrounding the nanoparticle is an indirect measure of the ability of ferrites to inhibit the growth of bacteria. Based on results in Table-1, *E. aerogenes* and *E. faecalis* could be killed by synthesized ZNF nanoparticles, in addition, the synthesized nanoparticles exhibit their antibacterial effects to a greater extent in the studied bacterial strains. *E. aerogenes* was found to have unusual arrangements of lipids consisting of lipopolysaccharides and peptidoglycans. *E. faecalis*, on the other hand, has a structure predominated by thick peptidoglycans with cell walls that serve as a boundary to protect proteins and allow them to leak out easily when the cell membrane is damaged [38]. Present experimental results showed that the prepared nanoparticles can disruption of cell membrane in both *E. aerogenes* and *E. faecalis* strains and may leads to the damage of the cell membrane followed by bacterial death.

TABLE-1
ANTIBACTERIAL ACTIVITIES OF ZINC COPPER FERRITE NANOPARTICLES *via* KIRBY-BAUER DISK DIFFUSION TECHNIQUE

Nanoparticles	Inhibition zone (cm)	
	Enterococcus faecalis (Gram-positive)	*Enterobacter aerogenes* (Gram-negative)
ZNF-1	1.2 ± 0.2	1.4 ± 0.1
ZNF-2	1.7 ± 0.1	1.9 ± 0.3
ZNF-3	1.9 ± 0.2	2.0 ± 0.3
ZNF-4	2.1 ± 0.2	2.2 ± 0.2

Conclusion

Nickel substituted zinc ferrite nanoparticles $Zn_{1-x}Ni_xFe_2O_4$ (x = 0.2, 0.4, 0.6 and 0.8) were synthesized using hydrothermal technique. The X-ray diffraction studies confirmed that all the prepared nanoparticles show good crystallanity. Besides, a scanning electron microscopy images revealed the spherical shape of the prepared nanoparticles. Further, the substitution of nickel strongly influenced the microstructure, also enhances the antimicrobial behaviour. Later, it was observed that size of the crystallites enhances from 41.42 to 47.68 nm with Ni content. The M-H loops evinced that the sample with large Ni-content shows good magnetic properties which inturn suitable for antimicrobial applications. Also, the ZNF nanoparticles revealed the good antimicrobial behaviour and triggered bacterial cell-death through protein leakage and membranes disruption of *Enterobacter aerogenes* and Gram-positive *Enterococcus faecalis* strains. Hence, the prepared nickel substituted zinc ferrite nanoparticles exhibit good antimicrobial behaviour and may be suitable for the antimicrobial applications.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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