

RESEARCH PAPER

Microwave Synthesis and Magnetic Investigation of CuFe_2O_4 Nanoparticles and Poly Styrene-Carbon Nanotubes Composites

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ABSTRACT

At the first step CuFe_2O_4 nanoparticles were synthesized by a fast and facile microwave method. The obtained nanoparticles and modified carbon nanotubes were added to poly styrene matrix. The products were characterized through Fourier transform infrared spectroscopy, X-ray diffraction, and scanning electron microscopy. Vibrating sample magnetometer shows nanoparticles exhibit ferromagnetic behavior. The influence of CuFe_2O_4 nanostructures on the flame retardancy of the polystyrene (PS) matrix was studied using UL-94 analysis. The enhancement of thermal stability and flame retardancy of nanocomposites is due to magnetic CuFe_2O_4 barrier against flame, oxygen and evaporation.

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INTRODUCTION

Spinel ferrite nanoparticles have attracted considerable interest and many efforts continue to investigate them for their technological applications in the microwave industries, magnetic recording, refrigeration systems, ferro-fluids, high frequency devices, biomedicine, catalysis, magnetic refrigerators, information storage, magnetic liquid, electrical insulation and biomedical field [1-3]. Ferrite structure generally allows the introduction of different metallic ions, which can change the magnetic and electrical properties considerably. Spinel, with the general formula of MFe_2O_4 , where M is a divalent cation, offer more interesting catalytic activities compared to the corresponding single component metal oxides. In a spinel structured the unit cell contains 32 oxygen atoms in cubic close packing with 8 tetrahedral (A) and 16 octahedral (B) occupied sites [1- 5]

CuFe_2O_4 has a normal spinel structure with tetrahedral A-sites occupied by Cu^{2+} ions and nanoparticles B-sites by Fe^{3+} ions. These properties are strongly dependent on the particles size,

shape, and dispersion, and therefore it is very important to carefully control the synthesis of particles of size distribution.

Metal oxide provides heat insulation by reflecting heat when it accumulates on the surface. Magnetic can be used as halogen-free flame-retardant for polymers. Magnetic nanoparticles can act as a reinforcing agent and flame retardant suppressant additive with low or zero emissions of toxic or hazardous substances. The main advantages of polymer materials over many metal compounds are high toughness, corrosion resistance, low density and thermal insulation. Improvement of the flame retardancy and thermal stability of polymers is a major challenge for extending their use for most applications. The use of halogen-free flame retardants is widespread due to the increasing concern about the health and environmental risks. One of the main disadvantages of traditional flame retardants is that for effective flame retardancy tests high loading levels are required to achieve the appropriate fire retardancy. Increasing the

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loading of inorganic metal hydroxides will result in a significant decrease in physical properties[6-12]. The higher level of flame retardancy of nanoparticles is due to their bigger surface to volume fractions which let them disperse into the polymeric matrix homogeneously, and hence leads to formation of a compact char during the combustion [13-21].

We report herein, the synthesis of CuFe_2O_4 nanoparticles with size about 30 nm were obtained by new microwave method at various powers. The obtained samples were characterized by scanning electron microscopy and X-ray diffraction pattern. The magnetic properties were investigated using a vibrating sample magnetometer.

MATERIALS AND METHODS

All chemicals were obtained from Merck and were used without further purifications. XRD patterns were recorded by a Philips, X-ray diffractometer using Ni-filtered Cu K_α radiation. For SEM images the samples were coated by a very thin layer of Au to make the sample surface conductor and prevent charge accumulation, and obtaining a better contrast. Room temperature magnetic properties were investigated using a vibrating sample magnetometer (VSM, made by Meghnatis Kavir Kashan Company, Iran) in an applied magnetic field sweeping between ± 10000 Oe, Infrared (IR) spectroscopy was taken on Nicolet.

Synthesis of CuFe_2O_4 nanoparticles

In a typical experiment, 0.002 mol of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 0.01 of $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were prepared separately and mixed together in 2:1 molar ratio. Then, NaOH solution (1M) was slowly added into the solution until the pH of the mixture

was 10 under microwave irradiation 15 min , 600W (30s On, 30s Off)

After cooling at room temperature, the resulting products were centrifuged for 15 min at 3,000 rpm, washed with distilled water and ethanol several times to remove the excess anions from the solution. Then precipitation was dried in an oven at 100°C for 3 h. The resulting red-brown powder was calcinated at 400°C for 3 h.

Synthesis of polymer- CuFe_2O_4 nanocomposite

4 g of PS was dissolved in 10 mL of dichloromethane and then CuFe_2O_4 (0.5 g) and modified-CNT (0.5 g) were dispersed in 5 mL of dichloromethane with ultrasonic waves (60W, 30 min). The dispersion of CuFe_2O_4 was then added slowly to the polymer solution. The solution was mixed under stirring for 6 h. For preparation of samples for UL-94 test after stirring, the product was casted on a template with dimension 130×13 mm and after about 48 h of solvent evaporation; the nanocomposite was placed in the vacuum oven for another 6 h for removal of residual traces of water. The final sheets for the test are $130 \times 13 \times 1.6$ mm in dimension (stay at oven 90°C for 48 h).

RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the CuFe_2O_4 nanoparticles prepared at 400°C for 3 h. The peak position and relative intensity of all diffraction peaks for the product match well with standard powder diffraction data. All the diffraction peaks in the XRD pattern can be indexed to those of the tetragonal structure of copper ferrite CuFe_2O_4 according to JCPDS No. 25-0283. It is indicated that pure CuFe_2O_4 can be obtained at 400°C for 3h.

Fig. 2 illustrates Scanning Electron Microscopy images of CuFe_2O_4 nanoparticles synthesized

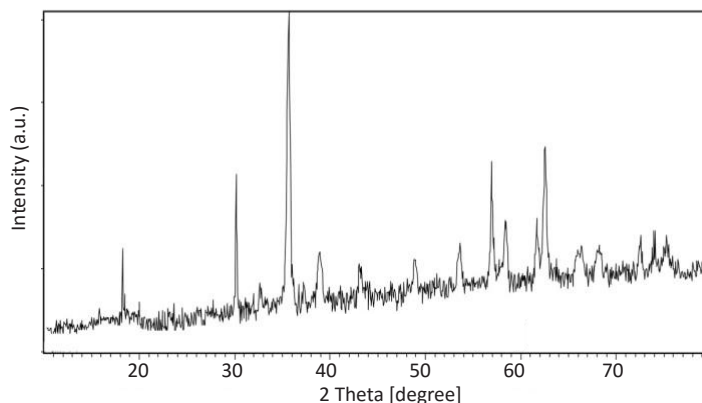


Fig. 1. XRD pattern of CuFe_2O_4 nanoparticles obtained at 300W

under microwave irradiation at 300W for 5min .

According to scanning electron microscopy average size of nanoparticles is about 30 nm.

Power effect on the morphology and particle size was investigated and various powers were used for synthesis of nanoparticles.

Fig. 3 shows SEM images of CuFe_2O_4 nanoparticles synthesized by microwave irradiation at 600W for 5min . Results confirm that mediocre size of nanostructures is around 35 nm.

SEM images of copper ferrite nanoparticles

prepared at 900 W and 5min are shown a Fig. 4 that outcomes approve average size is less than 40nm.

The experiment results indicated that CuFe_2O_4 nanoparticles can be obtained via microwave assisted microwave product, which were synthesis by reaction of Cu^{2+} and Fe^{3+} ions in alkaline condition. Subsequently, CuFe_2O_4 can be obtained from the reaction of $\text{Fe}(\text{OH})_3$ and $\text{Cu}(\text{OH})_2$.

The chemical reaction can be expressed as

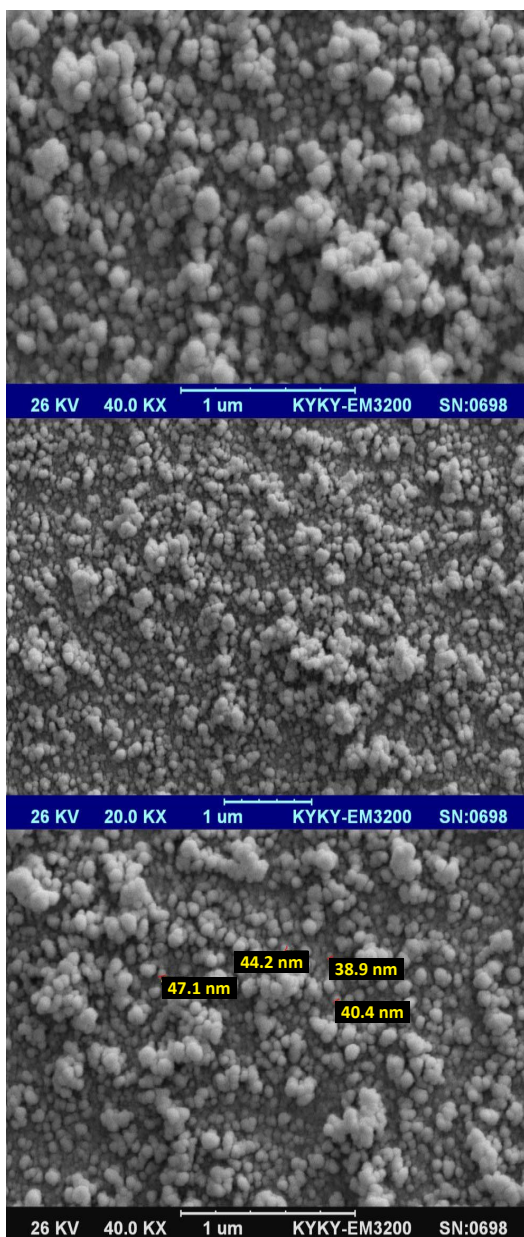


Fig. 2. SEM images of CuFe_2O_4 nanoparticles obtained at 300W.

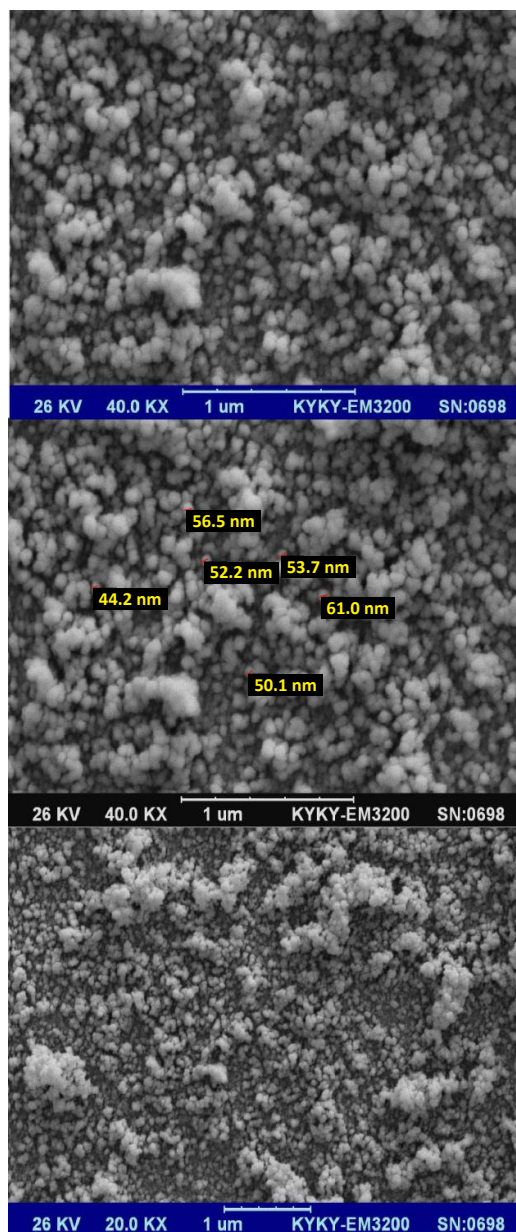


Fig. 3. SEM images of CuFe_2O_4 nanoparticles synthesized at 600W



Finally, CuFe₂O₄ nanoparticles were obtained via microwave-assisted microwaveproducts in a high temperature condition.

Figs 5 depict SEM images of poly styrene-carbon nanotube-CuFe₂O₄ nanocomposite which confirm presence of CNTs and ferrite nanoparticle in the polystyrene matrix.

The FT-IR spectrum of organic surfactant, the product after calcination in the frequency range from 4000 to 400 cm⁻¹ is depicted in Fig. 6. The very peak at 3500 to 3300 cm⁻¹ is due to O–H stretching mode.

In the FT-IR spectrum of the product after

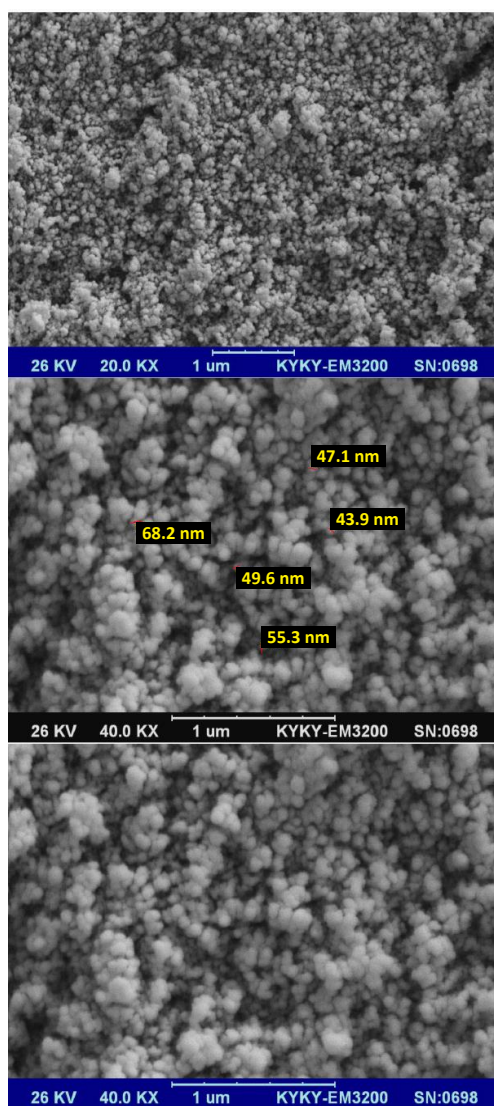


Fig. 4. SEM images of CuFe₂O₄ nanoparticles prepared at 900W

calcinations, there are two strong absorption bands at about 490 cm⁻¹ which correspond to M–O stretching vibration and O–M–O bending vibration of CuFe₂O₄, respectively.

Microwave method proposes easy manipulation in particle size and so magnetic properties by a simple change in power of pulsation and time of irradiation.

Fig. 7 shows the magnetic hysteresis curve of the ferrite prepared at 300W for the CuFe₂O₄ obtained at 400° C. The nanoparticles exhibited a weak ferromagnetic behavior with coercive force (Hc) value of 30 Oe, saturation magnetization (Ms) value of 24.7 emu/g [2]. These results are consistent with the reports that the magnetization is strongly dependent on their particle size.

Fig. 8 shows the magnetic hysteresis curves measured at 900W for the CuFe₂O₄ nanoparticles obtained at 400° C. The CuFe₂O₄ microcrystal exhibited a weak ferromagnetic behavior with coercive force about 50 Oe, saturation magnetization value of 31 emu/g.

Fig. 9 shows the magnetic hysteresis curves

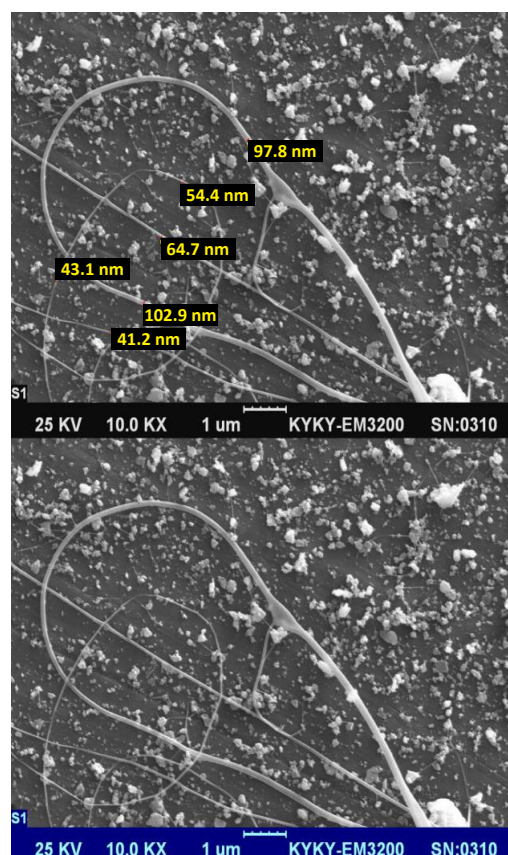
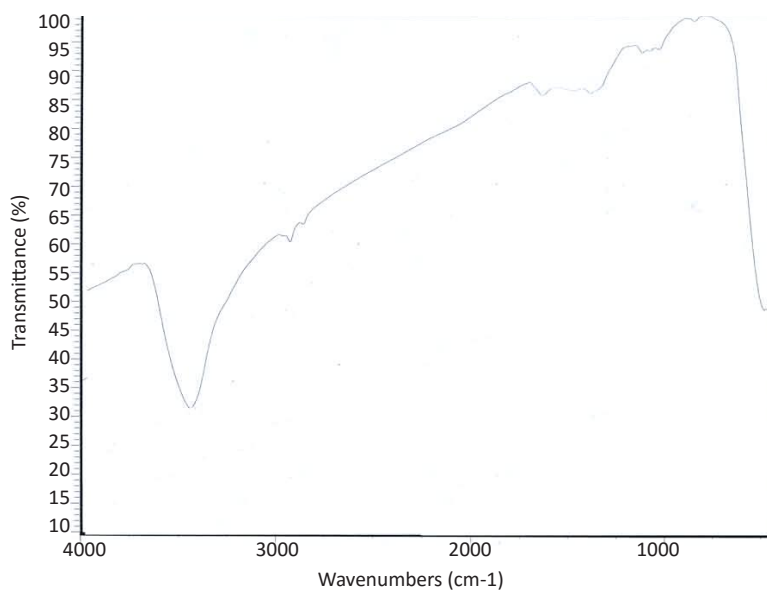


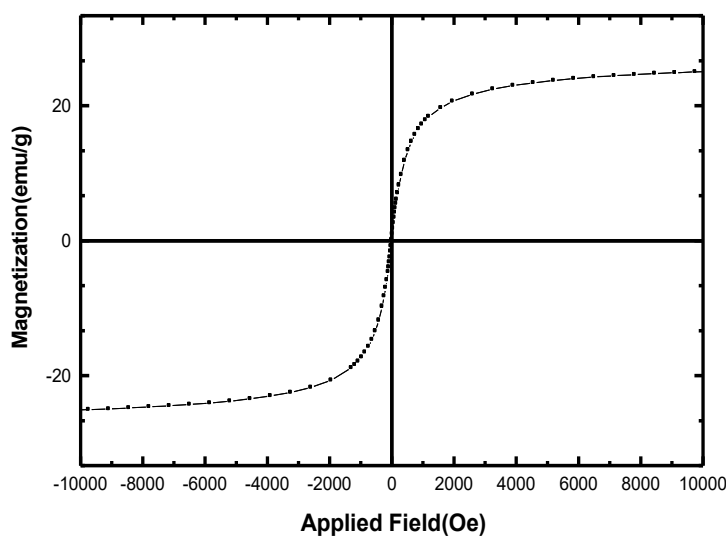
Fig.5. SEM images of PS-CNT-CuFe₂O₄ composite

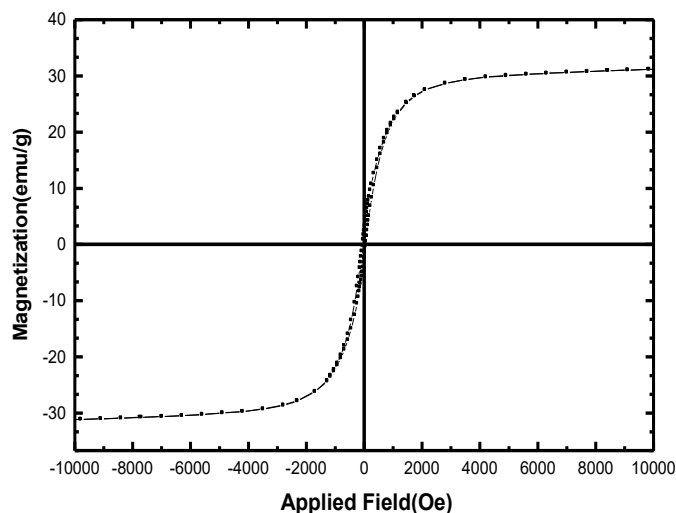
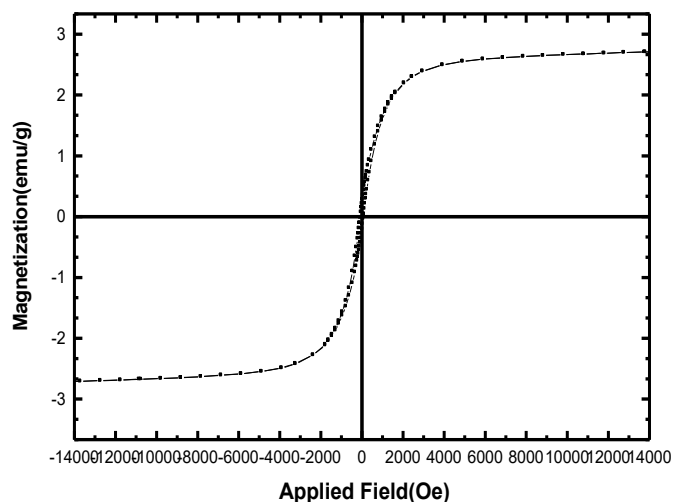
Fig.6. FT-IR spectrum of CuFe_2O_4 nanoparticles

of $\text{PS-CuFe}_2\text{O}_4$ nanocomposite. The CuFe_2O_4 microcrystal exhibited a weak ferromagnetic behavior with H_c around 120Oe, M_s value of 2.6 emu/g.

The effect of nanostructure on flame retardant properties has been considered using UL-94 test. In UL-94 a bar shape specimen of plastic $130 \times 13 \times 1.6$ mm is positioned vertically and held from the top. A Bunsen burner flame is applied to the specimen twice (10 s each). A V-0 classification is given to material that is extinguished in less than 10 s after any flame application, drips of particles allowed as

long as they are not inflamed. Materials are ranked as N.C. in UL-94 tests when the maximum total flaming time is above 50 s. The sample is classified HB when slow burning on a horizontal specimen; burning rate < 76 mm/min. A V-1 classification is received by a sample with maximum combustion time < 30 s, drips of particles allowed as long as they are not inflamed. The sample is classified V-2 if it satisfies the combustion time criteria of V-1, but flaming drips are allowed [6-10]. UL-94 tests for PS and PS-CuFe nanocomposites are HB and V-0 respectively. The results show that the CuFe_2O_4

Fig. 7. Hysteresis curve of CuFe_2O_4 nanoparticles at 300W.

Fig. 8. Hysteresis loop of CuFe_2O_4 nanoparticles at 900WFig. 9. Hysteresis loop of PS- CuFe_2O_4 nanocomposite

nanostructure can enhance the flame retardant property of the PS matrix.

The enhancement of flame retardancy of nanocomposites is due to that exfoliated CuFe_2O_4 have also a barrier effect to slow down the product volatilization and thermal transport during decomposition of the polymer. Adsorption of polymer chains onto the surface of CuFe_2O_4 nanoparticles results in a restriction of the segmental mobility and suppress chain-transfer reactions [9].

CONCLUSION

In summary, CuFe_2O_4 nanoparticles have been successfully prepared via a rapid microwave

method. The obtained nanoparticles and modified carbon nano tubes were added to poly styrene matrix. The products were characterized through Fourier transform infrared spectroscopy, X-ray diffraction, and scanning electron microscopy. Vibrating sample magnetometer shows nanoparticles exhibit ferromagnetic behavior. The influence of CuFe_2O_4 nanostructures on the flame retardancy of the polystyrene matrix was studied using UL-94 analysis. The enhancement of thermal stability and flame retardancy of nanocomposites is due to the magnetic insulator of CuFe_2O_4 against fire, oxygen and volatile components.

CONFLICT OF INTEREST

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

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