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RESEARCH IN ENVIRONMENTAL PLANNING AND MANAGEMENT

Optical detection of microplastics in water

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Abstract
Unfortunately, the plastic pollution increases at an exponential rate and drastically endangers the marine ecosystem. According to World Health Organization (WHO), microplastics in drinking water have become a concern and may be a risk to human health. One of the major efforts to fight against this problem is developing easy-to-use, low-cost, portable microplastic detection systems. To address this issue, here, we present our prototype device based on an optical system that can help detect the microplastics in water. This system that costs less than $370 is essentially a low-cost Raman spectrometer. It includes a collimated laser (5 mW), a sample holder, a notch filter, a diffraction grating, and a CCD sensor all integrated in a 3D printed case. Our experiments show that our system is capable of detecting microplastics in water having a concentration less than 0.015% w/v. We believe that the designed portable device can find a widespread use all over the world to monitor the microplastic content in an easier and cost-effective manner.

Keywords Microplastic detection · Optical biosensor · Raman spectroscopy

Introduction

According to Lebreton et al. (Lebreton et al. 2019), production and use of plastics have been increasing at an exponential rate since the beginning of 1950s. In 2015, a record number of 300 million tons of plastics were produced on a global scale. Around 10,000 tons of the plastic waste end up in the surface waters or on the ocean floors. These plastics are non-biodegradable and break down to micro- and nano-structures (Ng et al. 2018) which can be consumed by animals and humans (Fig. 1).

It is predicted that by 2025, microplastic accumulation in the oceans will increase to hundreds of million tons (Jambeck et al. 2015) and the enormous amount of plastics on the world can cause harm to sea life and human health (Galloway 2015). The immunotoxicity of polyvinylchloride (PVC) and polyethylene (PE) to fish immune system was reported in (Espinosa et al. 2018). A recent review article overviews the potential risks of microplastics when these particles enter the human body (Campanale et al. 2020).

In order to easily and quickly assess the safety and quality of the water, there is a need for an equipment that is low-cost, light, and portable. To address these requirements, we turned our attention to the possibility of utilizing the Raman spectroscopy. Named after the Indian physicist C.V. Raman, the Raman spectroscopy is an optical technique that relies on the scattering of the light (Dietzek et al. 2010). Upon the interaction of the light with the matter, some portion of the light is scattered by the vibrating molecules. Therefore, this scattered light inherently carries the information of the molecular structure of the material. Portable Raman spectrometers have drawn considerable attention owing to their advantages (Moore and Scharff 2009). A handheld Raman spectrometer which was equipped with a 785-nm laser was evaluated in (Jehlička et al. 2011) to identify mineralogical specimens. In this work, we employed the physical mechanism of Raman scattering to detect the microplastic content in the water. After interacting with the laser light, the molecules scatter the light at frequencies shifted by their vibrational frequencies and thus, the scattering allows the detection of microplastics in water. To achieve this goal, we designed a low-cost Raman spectrometer employing a low-power laser, a sample holder, a notch filter, a diffraction grating, and a CCD sensor all

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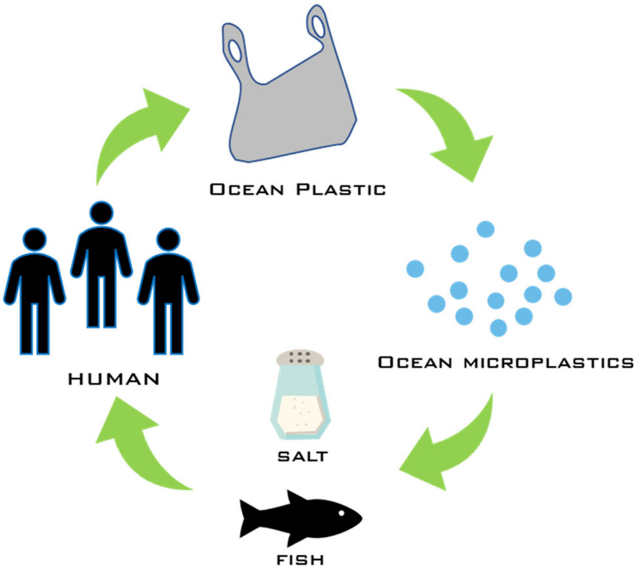


Fig. 1 Microplastics pollution cycle (Horton and Dixon 2018)

integrated within a 3D printed plastic case with dimensions of 5.6 cm × 5.6 cm × 3.1 cm. This system was then connected to a mobile phone via a dedicated application through Wi-Fi/ Bluetooth communication interface. We demonstrate that our system is capable of safely detecting microplastic particle content with concentrations less than 0.015% w/v while a saturation of the signals was observed at a concentration around 0.075% w/v.

Background

A Raman spectrometer utilizes a monochromatic light as an excitation source to be shined on to the sample (Aydogan and Tasal 2018). When this sample is hit with the monochromatic light source, while a major portion of the light is absorbed and transmitted, a very small portion undergoes scattering. This scattering can be of two distinctive types, namely elastic (Rayleigh or Mie depending on the particle size) and inelastic (Raman) scattering.

The concept of scattering involves photons from the light source interacting with the molecules in the sample. In doing so, the electrons in the molecules are excited and jump to a "Virtual Energy State". In this state, the electrons are unstable and they immediately tend to fall back to the ground level losing energy in the process. Subsequently, these electrons emit photons that may have the same or different energy levels as the incident photons. The energy change of these electrons determines the type of scattering the molecule undergoes.

When the electron falls down to the ground level with no change in its energy level, the photon emitted will have the same frequency as the incident light's frequency; hence, this type of scattering is called the elastic scattering (Mie or Rayleigh scattering).

In the case where these electrons fall down to a vibrational level instead of the ground level, a change occurs in the energy level (i.e., the electron absorbed a portion of the energy) by which the electron emits a photon that differs in frequency compared to the incident light's frequency. This type of scattering is referred to as the Raman scattering **(**inelastic scattering) (Lupoi et al. 2015).

Depending on the final energy of the electron upon return from the virtual state, Raman scattering can be distinguished into two different types namely Stokes and anti-Stokes scattering (Fig. 2) (Lupoi et al. 2015). Stokes scattering occurs when an electron falls to an energy level higher than its initial level, i.e., it absorbs energy (frequency of the scattered photon is lower than that of incident photon). Anti-Stokes scattering occurs when an electron emits energy, falling to an energy level lower than its initial level (frequency of the scattered photon is higher than of the incident photon).

In the literature, several handheld Raman spectrometers were reported for different applications such to identify minerals (Jehlička et al. 2011), to characterize the materials in artworks (Pozzi et al. 2019), to detect tuberculosis biomarker (Owens et al. 2018), to measure the hydrogen peroxide concentration (Stewart et al. 2012) to analyze the nutrient content of maize kernels (Krimmer et al. 2019), and to evaluate the clove oil to asses quality (Vargas Jentzsch et al. 2018). These reports demonstrate the potential on-site applications of handheld Raman spectrometers and in those reports, researchers used commercially available instruments. In another report (Zheng et al. 2014), researchers compared a handheld Raman spectrometer and a bench-top Raman spectrometer. They found that the bench-top Raman spectrometer was approximately 10 times more sensitive than the handheld one, but the handheld spectrometer was more consistent and allowed on-site analysis.

Experimental methods

Commercially available bench-top Raman spectrometers are very high-cost and bulky (Beganovic et al. 2019). They consist of a number of filters, with complex monochromators and complex lens configurations, and advanced detection systems. As an alternative to these systems, here, we propose designing a low-cost and mobile Raman spectroscopy system that is suitable for microplastic detection in water.

Our system design consists of five main components that are a collimated laser module (405 nm, 5 mW, Thorlabs CPS405) as our excitation light source; a quartz cuvette for holding our samples; a reject band notch filter (Omega Optical 450RB) is used in order to block the Rayleigh scattered light passing through a 0.6 mm slit. A 1000 lines/mm diffraction grating was used to disperse the scattered light into different wavelengths, and a CCD sensor (TSL1401CL) to capture the

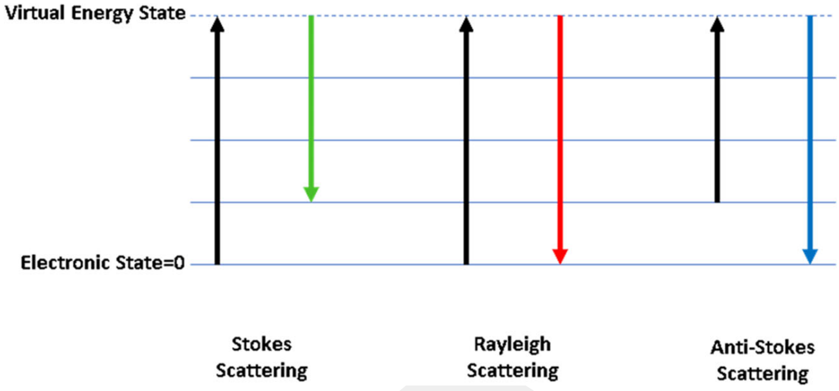


Fig. 2 Raman spectrum including Stokes, Rayleigh and anti-Stokes respectively (Lupoi et al. 2015)

scattered light for detection. A communication interface with a mobile phone was also included in our prototype system for accessing and communicating the data captured by the CCD. An illustration of the system is presented in Fig. 3 below.

An illustration of our measurement setup is presented in Fig. 3. In this design, we placed the sample on the light path at a normal angle. The light scattered by the sample reaches first the notch filter and blocks the light at 405 nm. Subsequently, the light is diffracted by a diffraction grating before it arrives the CCD. The diffraction occurs at angles $\theta = \sin^{-1}(n\lambda/d)$ where λ stands for the wavelength of the scattered light, d is the density of gratings that is 1000 lines/mm, n is the order of the diffraction, and θ is the angle of diffraction. The first-order and second-order diffraction angles for the excitation light at 405 nm were calculated to be 23.9° and 54.1°, respectively. To avoid any saturation effects due to the light source but also to minimize the overlap coming from anti-Stokes components of the second order diffraction, we placed our 8.1-mm-long CCD photodetector at a horizontal distance of 17.6 mm from the diffraction grating and a vertical distance of 7.8 mm above the light making an angle of 23.9°. By using a microcontroller, the CCD sensor was programmed to receive the data and thereafter the results were represented in a graphical format. An image of our system is presented in Fig. 4. Our system took 50 measurements for each concentration and average values were reported throughout the manuscript.

In our experiments, we employed 8.47-μm-sized plastic-coated ferromagnetic spherical particles at an initial concentration of 1% w/v bought from Spherotech. We diluted different volumes of particles using de-ionized water (2 mL) to vary the particle concentration up to 0.075% w/v. Before each measurement, the cuvette with microplastics was vortexed to have a uniform microplastic distribution in the water.

The open-source IoT platform ThingSpeak was used for communicating the microcontroller and a mobile phone via Wi-Fi/Bluetooth module. ThingSpeak uses data regression analytics in reading and storing data which then processes it to our mobile phones/laptops. For this system, a Wi-Fi setup and connection were established. With an in-built API, the system allows ThingSpeak to connect to the microcontroller and be able to send and store data into cloud computing. The stored data can be accessed via any mobile device having internet connection.

Results and discussion

In order to record the Raman-scattering intensity from the samples in water, we first recorded the signal received from the water sample (2 mL of water placed in a cuvette). This was recorded as a reference measurement and by adding tiny amounts of microplastics, output data were recorded and analyzed. The spectrum of pure water depicted in Fig. 5(a) possesses a peak at the wavenumber ~ 1600 cm^{-1} which we attribute to the signals received from the water molecules in agreement with Du et al. (2015). We would also expect to

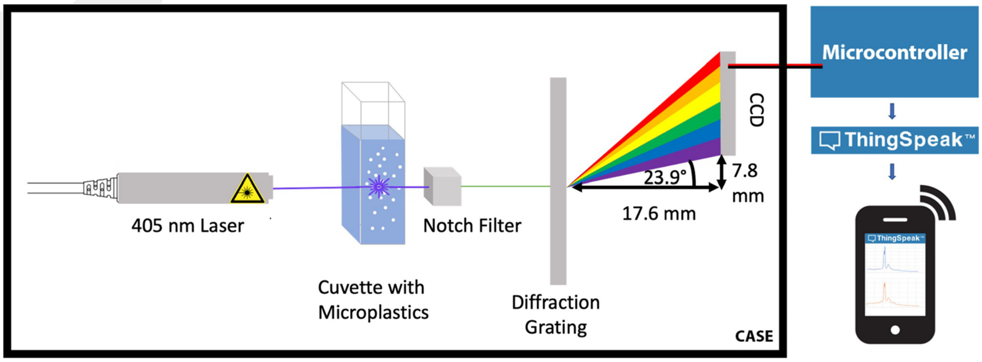


Fig. 3 The schematic of the design of optical detection system

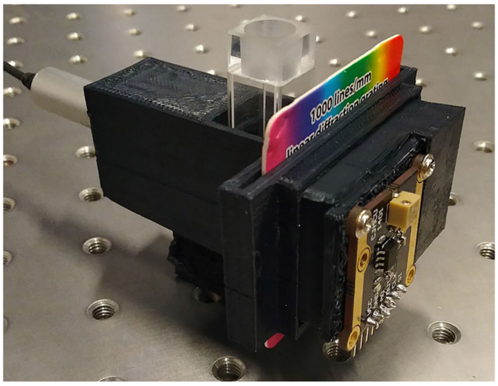
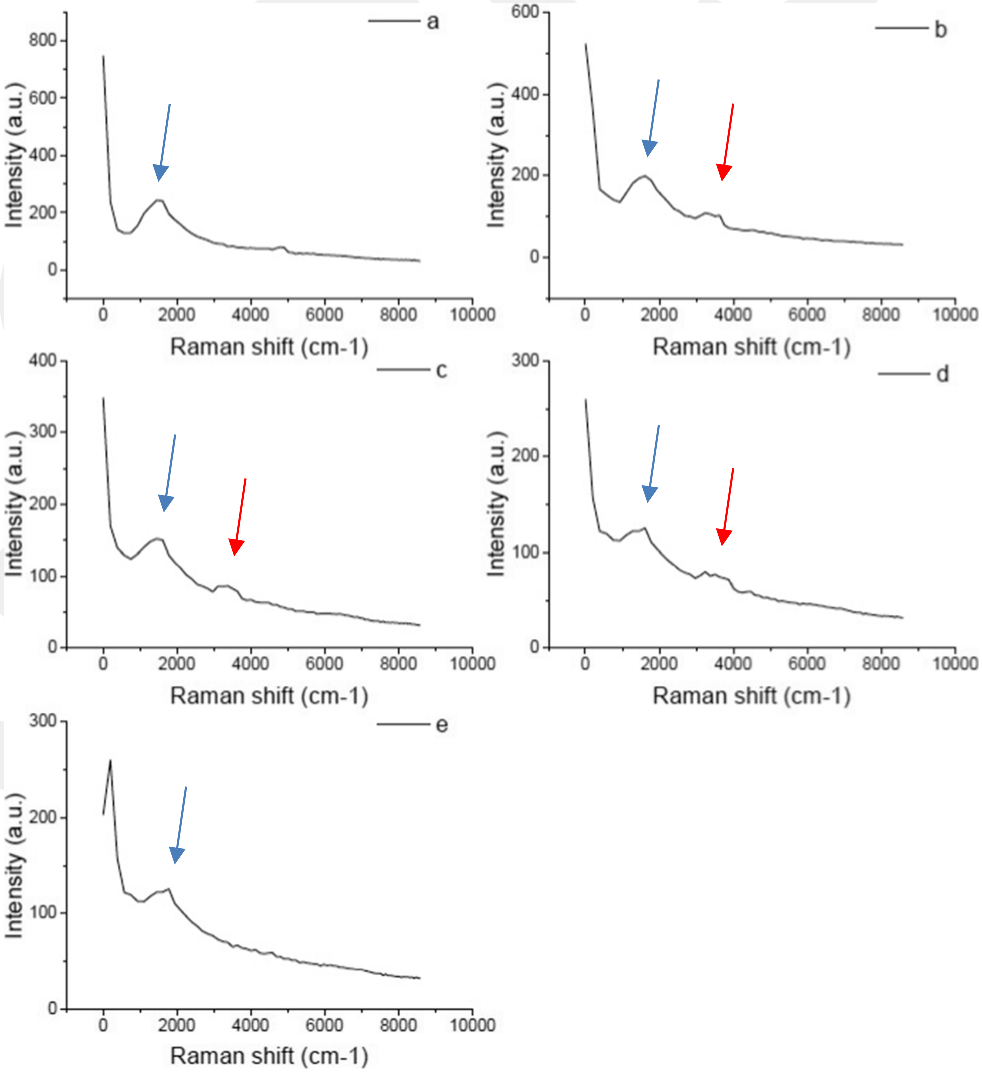


Fig. 4 Portable Raman spectrometer prototype with a 3D printed case

observe another peak at around 3400 cm^{-1}. We think that this peak does not strongly appear because we were not able to correct our data based on the responsivities of the individual photodetectors of the CCD. Although the relative responsivity of the whole CCD system was provided in the datasheet, there are differences in sizes of each pixel meaning that the responsivities of each pixel may be different relative to each other. Therefore, correcting the recorded signal based on the general responsivity information of the CCD would introduce an additional error. Furthermore, we considered that a relative change in the signals gives us enough information for the purposes of detecting the microplastics as we do not intend designing a Raman spectrometer in this work, but we aim at detecting the microplastics based on the signal variations.

After observing the Raman signal of water, we added 60 μL of the microparticles to 2 mL of water such that the final microplastic particle concentration is ~ 0.03% w/v. The collected Raman spectrum is shown in Fig. 5(b) and reveals new features emerging at wavenumbers between 3000 and 3500 cm^{-1}. Another observation is that the intensity of the collected signal dropped by about 25% upon addition of microplastics. The decrease in the intensity can be explained by the blocking of light that otherwise reaches the photodetector due to strong scattering of microplastic particles. On the

Fig. 5 Water measurement (**a**), 0.03% particle density measurement (**b**), 0.045% concentration measurement (**c**), 0.060% concentration measurement (**d**), and 0.075% concentration measurement (**e**). Blue arrows show the Raman signal of water, and red arrows show the Raman signal of microplastics



other hand, the recorded Raman shift indicated the presence of chemical groups which inelastically scatter the light. The magnetic particle we employed in this work were covered with polystyrene. This means the Raman signal we observe can either stem from the scattering of the inorganic magnetic part or the surrounding polymer. In the literature, the Raman signal belonging to inorganic components lies at smaller wavenumbers (Santillán et al. 2017); therefore, the observed Raman features should be due to the polystyrene surrounding particles. According to the literature (Serafim et al. 2014), the main Raman peaks of polystyrene are mainly located at ~ 1000 cm^{-1}, ~ 1600 cm^{-1}, and ~ 3000 cm^{-1}. When we check our results, we observe that the valley around 1000 cm^{-1} becomes flatter as the nanoparticle content increases in addition to the peaks emerging at wavenumbers > 3000 cm^{-1}. On the other hand, we do not observe features at ~ 1600 cm^{-1}, which—we think—happens due to the overwhelming signal coming from water.

As we further increased the density of these microparticles in water to 0.075% w/v, we observed the saturation of the signal (Fig. 5c). This was mainly due to the laser light being blocked by the particles. As also pointed above, the strong white appearance of the particle dispersion suggests that the Rayleigh scattering was very prominent at this concentration. Hence, we were not able to observe the microparticle peaks at the allocated wavenumber (3500 cm^{-1}) in our Raman spectrum. Following this observation, we recorded the Raman spectra of the microparticles at various concentrations to determine our working regime and recorded the Raman intensity at 3500 cm^{-1}. The graph presented in Fig. 6 indicates that our signal remains in the linear regime for concentrations between 0.015 and 0.035% w/v and then reaches saturation after this point due to strong scattering of the laser beam. This shows that despite the simple building blocks it was made of, our system is capable of detecting the Raman features of the microplastic at relatively low particle concentrations.

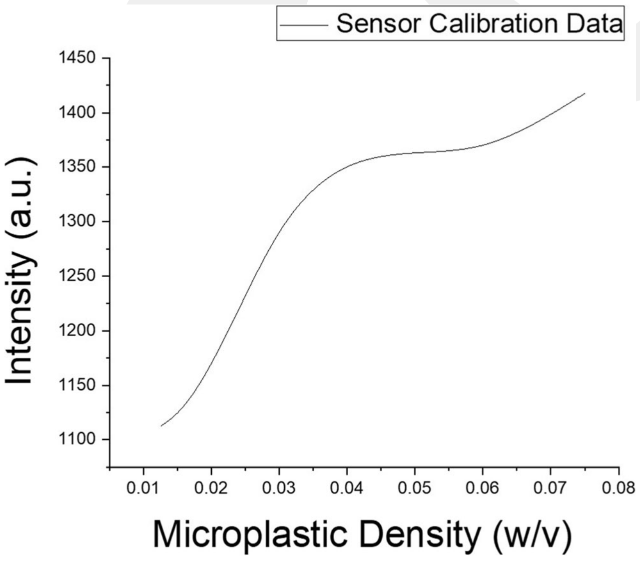


Fig. 6 Sensor calibration data for different density measurements between minimum and maximum measurement limits

In addition to the technical potential of our proposed system, our design is low cost which offers widespread use. In Table 1, the cost of the system is presented, the most expensive part in our system is the CCD sensor followed by the costs of the laser module and the notch filter. Overall, the cost of our setup is less than $370 which is around an order of magnitude less expensive than the cost of a more sophisticated commercial Raman spectroscopy system. An obvious drawback of the developed system is its low sensitivity due to the use of low-power laser source and less sensitive photodetectors. Nevertheless, the system is lighter, portable, and significantly cost-effective; thus, it enables the detection of microplastics easily at the site of test.

Previously bench top systems such as a Fourier transform infrared spectrometer (FTIR) (Mintenig et al. 2019) and a Raman spectroscopy (Kniggendorf et al. 2019) were reported to detect microplastics in water. On the other hand, portable systems that are able to quickly detect the presence of microparticles at a low cost are an important need. A portable system based on light reflection and transmission was also introduced for microplastic detection which is equipped with a 635-nm laser (Asamoah et al. 2019). The reported system did not include only a photodetector but also a charger-coupled device (CCD) camera to record the pattern of the forward scattered light. Combining CCD and photodetector enabled screening two types of microplastics. Compared to this system, our portable instrument has a lower cost. The conventional Raman spectroscopy systems for microplastic detection were reviewed in Anger et al. (2018). When compared to chromatography- and FTIR-based methods, conventional Raman spectroscopy (CRS) has the lowest detection limit for low-mass microplastics. The laser source that we used in our design has a numerical aperture (NA) of 0.8 which is comparable to sources used in CRSs (NA of 0.5–1). Some of the conventional systems include 50X or 20X objectives, but we did not include an objective for the sake of developing

Table 1 The costs of materials and equipment incurred in building our Raman spectrometer design

Components	Price
TSL1401CL CCD sensor	$88.7
Diffraction grating slides	$12.14
Microcontroller	$4.5
405RB Notch	$38.24
Case	$32
ESP8266 Wi-Fi Module	$2
LCD screen	$4
Laser module	$185
Total cost	$366.58

a low-cost system. The CRSs detected a Raman shift around 3000 cm^{-1} which is in good agreement with our measurements.

Conclusion

The production of plastics in today's world is increasing at a massive rate. This has a tremendous negative impact on the environment. When these plastics subsequently break down into micrometer-sized particles, drinking water and consuming the sea foods become a major health concern for the humans. To solve this issue, one of the important requirements is developing a low-cost system that would detect the presence of the microplastics. In this work, we address this problem and propose an optical detection system based on Raman spectroscopy having a cost less than $370. We showed that our system is able to detect the presence of microplastics at very low concentration with its linear detection regime lies between 0.015 and 0.035% w/v. We believe that our proposed system has the potential to be used ubiquitously against the microplastics problem in aqueous environments especially when a low-cost mobile setup is demanded.

Author contributions K.I. and T.E. conceptualized and designed the experiments. A.H.I., M.H.A.S., A.M.A, and S.A.Q. performed the experiments. I.O., T.E., and K.I. analyzed the data. A.H.I., M.H.A.S., A.M.A, and S.A.Q made the figures. K.I., A.H.I., and T.E. wrote the paper. All the authors read and contributed to the submitted version of the manuscript. K. I. acquired the funding.

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Data availability All relevant data are within the manuscript and available from the corresponding author upon request.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Ethical approval Not applicable.

Consent to participate All authors participated in this work.

Consent to publish All authors agree to publish.

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