Method screening for conjugation of the small molecules onto the vinyl-coated Fe$_3$O$_4$/silica nanoparticles: highlighting the efficiency of ultrasonication

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Abstract
Method development for surface functionalization of vinyl-coated iron oxide nanoparticles via [4 + 2] one-pot cycloaddition is presented in this work. Small molecules are loaded onto the surface of silica-coated magnetic nanoparticles (Fe$_3$O$_4$/SiO$_2$ NPs) by various methods. The main factors such as surface modification ratio, core/shell structure maintenance, spherical morphology preservation and particle size uniformity were precisely investigated by various analyses. In this regard, reflux, microwave and ultrasound wave irradiation have been well compared as three different effective methods for carrying out the cycloaddition (CA) reactions onto the surface of magnetic nanoparticles. Overall, it was concluded that the safer and faster method for this purpose is implemented by the ultrasound wave irradiation.

Abbreviations
NPs nanoparticles;
CA cycloaddition reaction.

1. Introduction
Ultrasound is an acoustic wave with a frequency above the human hearing threshold. Sonochemistry investigates the effect of high-frequency sound waves on the chemical and physical properties of materials. How it could be a great driving force for chemical reactions like forming or breaking covalent bonds also belongs to this field of study [1–5]. Several methods are used for the surface modification of iron oxide nanoparticles (Fe$_3$O$_4$ NPs) including reflux, ball milling, microwave radiation, autoclave at high temperatures and pressures, and ultrasonication [6–8]. Among all of them, ultrasonication is shown to be the most effective and economical method for the surface modification of Fe$_3$O$_4$ NPs. In addition, both morphology and particle size of the modified NPs are controlled well within the short period reaction times in comparison with other methods. Fe$_3$O$_4$ NPs are convenient conductible agent through their magnetic property [9–11]. Furthermore, they are also internalized into the alive cells with more convenience via endocytosis process through their nano scale [12–14]. In addition, their surfaces could be functionalized with various organic compounds to add special features like therapeutic or tracing capabilities. For instance, several magnetic systems from this category of heterogeneous nanosized materials have been designed and suitably applied for heavy metal removal from the aqueous resources [15]. Moreover, in medical sciences, they could be used for tracing and diagnosis via fluorescence detection in in vivo experiments [16]. Also, several catalytic systems have been designed and used for facilitating the chemical reactions via this method [17]. That is why, magnetic nanoparticles are considered as a useful and substantial tool for targeted drug delivery, therapeutic assisting and medicine detecting in the body’s internal
environment [18–22]. Since, the Fe$_3$O$_4$ NPs include hydroxyl groups, their surface could be easily modified by silica network or other organic compounds via covalent binding [23–25]. So far too much various strategies have been employed in this regard [25–29]. One of the well-known strategies is [4 + 2] cycloaddition (CA) approach with one-pot mechanism [30]. Protection of the Fe$_3$O$_4$ NPs against damaging to the core/shell structure, is the most important advantage of one-pot mechanisms such as CA and click chemistry rather than mechanism with successive reactions. They are considered as versatile tools for attaching organic molecules directly onto the surface of nanoscale particles such as silver, iron oxide and diamond [31–33].

This study focuses on the investigation of a faster and safer method for preparation of the nano-Fe$_3$O$_4$-supported organic compounds that could be utilized for different chemical and biological intentions. In this regard, various conditions for carrying out the CA reaction onto the NPs surfaces are experimented by using ultrasound wave irradiation and the obtained results are compared with microwave radiation and reflux methods. In this work, vinyl-modified Fe$_3$O$_4$ NPs have been prepared according to procedures introduced in literature and used as dienophile moiety of CA reaction [30]. For this purpose, thiophene (1), anthracene (2), 1,3-cyclohexadiene (3), 4-((1E,2E)-3-phenylallylidene aminophenol (4), and melamine (5) were used as diene moieties (scheme 1).

2. Results and discussion

2.1. Method development

One of the most important points for modification of the NPs is to provide the most suitable reaction conditions for them. It would be more sensitive if they have magnetic trait because they are absorbed to the magnet during the stirring. On the one hand, NPs are not dispersed very well and as a result their surfaces would not be finely functionalized with organic compounds. One the other hand, we have to apply more intense conditions or use auxiliaries like palladium to increase the reaction yields. So, the core/shell structure of silica coated-Fe$_3$O$_4$ NPs is
damaged in many cases. Therefore, in this study, we have made an effort to report resulted data as comparative values to show and prove the optimum method for the surface modification of the magnetic NPs via CA-conjugation. The CA strategy is one of the most substantial approaches of covalent binding in synthetic organic chemistry. This approach with one-pot mechanism would create six-membered rings by cycloaddition reaction. High temperature and pressure in autoclave, microwave irradiation, ball milling, and longtime reflux and ultrasound wave could provide the proper driving force for this reactions. In this work, ultrasound wave has been introduced as the best source for this purpose. Table 1 shows the details of the reaction conditions that have been investigated in our assessment. It can be deduced from table that the most suitable condition for Fe3O4/ SiO2 NPs surface modification via CA-conjugation is provided by the ultrasound waves. As it can be seen in the table, firstly, the optimization reactions were monitored for product 1 in various conditions, then other products were obtained in optimum conditions of each method and the resulted data were compared. It should also be noted that power values higher that 50% in microwave irradiation and temperatures higher than 100 °C and ultrasound wave higher than 80 KHz for long times caused NPs core/shell structure to be damaged. This happening was monitored by microscopic imaging. In the optimum conditions, a cleaner ultrasound wave bath was used with frequency 30 KHz and power density 150 Wl−1, and the temperature was maintained at around 25 °C by adding the ice pieces into the bath. As the main reason for choosing the solvents reported in table 1, suitable dissolution of diene moieties and also well dispersion of the nanoparticles are expressed. Moreover, since this report compares three different methods, we needed to investigate the effectiveness of high temperatures (above 100 °C) on the process. Therefore, methanol and ethanol could not be appropriate media for this purpose due to their low boiling points.

2.2. Method screening by analyses

2.2.1. FT-IR spectroscopy

In order to compare the resulted data from Fourier-transform infrared (FT-IR) spectra, we should consider preservation of silica network around the magnetic core, yield of CA-conjugation and lack of the physical adsorption as the main evaluation factors. The main peaks that are needed to be investigated belong to stretching vibrations of Fe—O, Si—OH, SiO—H, Si—O—Si, C=C, C—H sp3, C—H sp2 and O—H that appear about at 582, 800, 940, 1100, 1650, 2950, 3050 and 3100–3500 cm−1, respectively [30, 34]. As a sample for evaluation by FT-IR, product NO. 3 was chosen.

The FT-IR spectra related to the products k, l, and m (product codes, table 1), silica coated-Fe3O4 NPs and damaged core/shell structure are shown in figure 1 and the main factors of assessment were investigated. As it can be seen, the spectrum related to the product k shows that the structure of the silica network is damaged in reflux condition (spectrum b). It can be easily deduced from a significant reduction in Si—O—Si peak intensity at

| Table 1. The optimization reactions of the surface functionalization of iron oxide NPs with thiophene, via CA-conjunction. |
| --- |
| Entry | Product code | Product NO.b | Method | Reaction conditions | Reaction conditions | Time |
| 1 | a | 1 | Reflux | DMF/110 °C | DMF/110 °C | 24 h |
| 2 | b | 1 | Microwave irr. | DMF/Power: 40% | DMF/Power: 40% | 5 min |
| 3 | c | 1 | Microwave irr. | DMF/Power: 50% | DMF/Power: 50% | 5 min |
| 4 | d | 1 | Ultrasonication | DMF/50 KHz/25 °C | DMF/50 KHz/25 °C | 2 h |
| 5 | e | 1 | Ultrasonication | DMF/50 KHz/25 °C | DMF/50 KHz/25 °C | 4 h |
| 6 | f | 1 | Ultrasonication | DMF/50 KHz/50 °C | DMF/50 KHz/50 °C | 2 h |
| 7 | g | 1 | Ultrasonication | DMF/65 KHz/50 °C | DMF/65 KHz/50 °C | 2 h |
| 8 | h | 2 | Reflux | Xylene/100 °C | Xylene/100 °C | 24 h |
| 9 | i | 2 | Microwave irr. | Xylene/50% | Xylene/50% | 5 min |
| 10 | j | 2 | Ultrasonication | DMF/65 KHz/50 °C | DMF/65 KHz/50 °C | 2 h |
| 11 | k | 3 | Reflux | DMF/80 °C | DMF/80 °C | 24 h |
| 12 | l | 3 | Microwave irr. | DMF/50% | DMF/50% | 5 min |
| 13 | m | 3 | Ultrasonication | DMF/65 KHz/50 °C | DMF/65 KHz/50 °C | 2 h |
| 14 | n | 4 | Reflux | DMSO/70 °C | DMSO/70 °C | 12 |
| 15 | o | 4 | Microwave irr. | DMSO/50% | DMSO/50% | 5 min |
| 16 | p | 4 | Ultrasonication | DMSO/60 KHz/50 °C | DMSO/60 KHz/50 °C | 2 h |
| 17 | q | 5 | Reflux | DMF/100 °C | DMF/100 °C | 12 |
| 18 | r | 5 | Microwave irr. | DMF/50% | DMF/50% | 5 min |
| 19 | s | 5 | Ultrasonication | DMF/65 KHz/50 °C | DMF/65 KHz/50 °C | 2 h |

a The products are mentioned by these codes from here onwards;
b Considering scheme 1;
c Power = 40% means the microwave oven is producing microwaves 40 percent of the time and is off the other 60 percent of the time;
d A cleaner ultrasound bath was applied with 50 KHz frequency and 150 Wl−1 power density.
1010 cm$^{-1}$. But the peaks at 1635 cm$^{-1}$ and 2925 cm$^{-1}$ coming from C=C and C−H sp3, respectively, confirm the existence of 1,3-cyclohexadiene. Therefore, it can be concluded that the majority of 1,3-cyclohexadiene are adsorbed on the surface of NPs in the reflux condition. The spectrum (c) related to the product I shows that the core/shell structure has been properly preserved under microwave radiation but the CA reaction execution was not satisfying. Two sharp peaks at 1093 cm$^{-1}$ and 802 cm$^{-1}$, and a weak peak at 1656 cm$^{-1}$ prove this claim.

Ultimately, the clear spectrum related to the product m, carried out by ultrasound wave irradiation with 65 KHz at 50 °C in 2 h, shows great preservation of the core/shell structure and also considerable execution of the CA reaction onto the surface of NPs. The peak intensity reduction related to the appeared peak at 3000–3100 cm$^{-1}$ shows that the amount of C−H sp2 belong to the vinyl groups have been decreased after CA reaction. The existence of C−H sp3 has been confirmed by the peak appeared at 2974 cm$^{-1}$ as well. The peak at 1654 cm$^{-1}$ coming from C=C bond after CA reaction. Appearance of the sharp peaks at 1097, 802 and 488 cm$^{-1}$ prove the silica network preservation under ultrasound irradiations.

2.2.2. EDX elemental analysis

Figure 2 shows the results of the elemental analysis from energy-dispersive spectrophotometer (EDX) of Fe$_3$O$_4$/SiO$_2$ (a), Fe$_3$O$_4$/SiO$_2$/C=C (b), and product j (c), and also CHNS analysis results of Fe$_3$O$_4$/SiO$_2$/C=C NPs, product d, product j, and product m. These spectra revealed the existence of Fe, Si, O, C, N and S elements after carrying out the CA reactions. As it can be seen, the results from the EDX analysis confirm the obtained information from FT-IR spectroscopy about the implemented methods. In addition of the qualitative investigations, a quantitative assessment was also performed by the EDX and CHNS analyses. As can be seen in figure 2, the EDX tables revealed that the amount of the carbon element has been significantly increased after CA functionalization in the product j. The obtained results from CHNS analysis also disclosed that thiophene, anthracene, and 1.3-cyclohexadiene have been covalently loaded onto the NPs surfaces, because they were not separated after several times washing. As can be seen, the obtained results from CHNS analysis is in great correspondence with the EDX results.

2.2.3. Microscopic imaging

Morphology, size, core/shell structure and dispersion of the modified NPs are other important factors that highlight the quality of the modified NPs. Figure 3 illustrates the excellence of the ultrasound-assisted CA reaction onto the surface of the NPs for product h in comparison with other methods by field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). As illustrated in the images, the particle agglomeration was not observed for product j (image c) unlike products h and i (images a,b). Therefore, it can be concluded that the ultrasound wave irradiation has resulted in more uniform and monodispersed product in a limited range of size. In contrast, figures 3(a), (b), which are related to the reflux and microwave irradiation methods, show non-spherical morphology and uniform particles. Moreover, particle accumulation is also observed as a negative factor. In TEM image (d), it is clearly seen that there is no defined core/shell nanostructure after CA reaction via reflux method. Thus, it is concluded that the core/shell nanostructures have been extremely damaged under reflux conditions. In contrast, well conservation of the core/shell
Figure 2. EDX spectra of (a) Fe₃O₄/SiO₂ core/shell NPs, (b) vinyl-modified Fe₃O₄/SiO₂ NPs, (c) product j, and CHNS analysis of vinyl-modified Fe₃O₄/SiO₂ NPs, products d, j, and m.

| (d) Sample                  | %C  | %H  | %N  | %S |
|-----------------------------|-----|-----|-----|-----|
| Fe₃O₄/SiO₂/C=C              | 25.95 | 0.11 | 0.15 | -   |
| 1 after CA reaction         | 18.59 | 0.87 | 0.13 | 5.34 |
| 2 after CA reaction         | 57.63 | 1.81 | 0.17 | -   |
| 3 after CA reaction         | 32.63 | 1.24 | 0.21 | -   |

Figure 3. FESEM images of the products (a) h, (b) i, and (c) j, and TEM images of (d) h, and (e), (f) j.
nanostructures via ultrasound wave irradiation method is observed in the images (e) and (f). As can be seen, the dark areas are related to Fe₃O₄ magnetic core and light areas belong to the silica layer. The average size of the NPs was also obtained for product j by using Digimizer software, and size distribution diagram has been shown in the figure 4, as well. According to the graph, about 60% of the particles were in 30–35 nanometer.

2.2.4. Solid-state UV–visible spectroscopy

Figure 5(a) shows the UV–vis absorption spectra of anthracene and products h, i, and j, in solid state. According to the literature, the values of λ_max for anthracene and benzene are 386 and 222 nm, respectively [30]. In the UV–vis spectrum of the product h, since a sharp peak is observed at 389 nm which belongs to anthracene, it can be claimed that the microwave irradiation method has led NPs to adsorb anthracene onto their surfaces and CA reaction was not correctly performed. Most likely, microwave irradiation has heated up the NPs surfaces and physical adsorption has been occurred. It was previously confirmed by FT-IR and EDX analyses, as well. Figure 5 also shows that reflux method provides the required driving force for the execution of the CA reaction onto the surface of the NPs. As can be seen in the spectra, the optical activity of the NPs has been changed after reflux, although a partial UV–vis absorption is still seen. Ultimately, in the spectrum of the product j, the absorption peak at 222 nm and the lack of any peak at 389 nm shows that anthracene was not adsorbed onto the surface of NPs and CA-conjugation was implemented by ultrasound wave irradiation. To obtain more confirmation for anthracene consuming, the supernatant UV–vis absorption activity was also prepared before and after the functionalization of the NPs and CA reaction. As can be observed in figure 5(b), the UV–vis absorption activity of the anthracene solution was significantly decreased after CA execution. It means that a large amount of anthracene has been consumed for the CA reaction. For this purpose, the NPs of product j were magnetically collected and the supernatant was filtrated for two times before UV–vis activity monitoring.

Figure 4. Size distribution diagram of product j calculated for 20 NPs.

Figure 5. (a) Solid–state UV–vis spectra of anthracene and products h, i, and j, and (b) solution–phase UV–vis spectra of anthracene solution before CA reaction, and supernatant after CA reaction onto the vinyl-coated Fe₃O₄/SiO₂ core/shell NPs.
2.2.5. Fluorescence spectroscopy
Method efficiency was investigated by fluorescence absorption spectroscopy, as well. Figure 6 shows the graphs related to 4-(1E,2E)-3-phenylallylidene aminophenol (a) which had been prepared in our previous work, and the products n, o, and p (b-d) [30]. As the figure shows, product n has exhibited stronger fluorescence property after CA reaction in comparison with products o and p. But, according to the previous analyses, it seems that 4-(1E,2E)-3-phenylallylidene aminophenol has been adsorbed onto the surface and CA reaction was not performed. In fact, due to the destruction of the core/shell structure under reflux condition proven by FT-IR and EDX analyses, CA reaction could not be executed in the case of product n. The spectrum (d) shows that the CA-conjugation has not been implemented under microwave radiation. Finally, the absorption peak at 370 nm in the spectrum (c) proves that ultrasound-assisted CA reaction onto the surface of NPs would be a satisfactory method.

2.2.6. X-ray diffraction
Figure 7 shows the x-ray diffraction patterns of melamine (a) and the products q, r, and s (b-d). In the spectrum (b) which belongs to the product q, it can be observed that a broad peaks at 5° and 25° related to SiO2 network have been disappeared due to the destruction of the core/shell structure under reflux condition. Spectrum (b) also shows the weak peaks appeared 18.25°, 22.53° and 27.43° coming from adsorbed melamine molecules onto the surface. Spectrum (c) related to product r exhibits well preservation of the core/shell structure through the peaks appeared at 5° and 25°, but no considerable peak was seen for melamine and CA reaction. The most satisfying spectrum belongs to the product s, because all related peaks to the SiO2 network and melamine loaded by CA reaction are seen at 5°, 25°, 18.25°, 22.53° and 27.43°. The peaks related to melamine structure after CA reaction appeared at 29° and 31°, were covered by a broad peak at 30.72° coming from Fe3O4 in the spectrum (d). According to the database of JCPDS No. 19-0629, the peaks that are appeared at 18.73°, 30.72°, 36.22°, 43.83°, 54.00°, 57.73° and 63.43° in the spectra b–d, are corresponded with Fe3O4 NPs [30, 34].

2.2.7. Thermogravimetric & vibrating-sample magnetometer analyses
Differences in thermal behavior of Fe3O4/SiO2/C=NPs and product s is clearly observed in figure 8(a) that shows the obtained results from thermogravimetric analysis (TGA). As seen in the curves, the weight of the Fe3O4/SiO2/C=NPs is gradually decreased that is related to the both physically adsorbed and entrapped water molecules onto the surfaces and into the silica network [35]. Almost 8% of the weight loss was observed in a thermal range of 50 °C–580 °C. According to the literature, if there is any organic layer in the structure of the sample, it should be removed maximum until 300 °C [36]. Accordingly, it can be claimed that there is a melamine layer in the structure of the product s because a shoulder is seen in a range of 100 °C–250 °C. Almost 12% difference in the weight loss was observed between two samples in the thermal range 200 °C–580 °C that proves the presence of a new organic layer onto the product s surfaces. However, at ca. 620 °C the main collapse of the structure is started in both samples. As an additional confirmation for the core-coating process via CA
reaction, the magnetic behavior of the mentioned samples was studied by vibrating-sample magnetometer (VSM) analysis. As figure 8(b) shows, the magnetic property was decreased after core-coating by silica network, TMVS and melamine. This is an obvious fact that the magnetic behavior would be reduced proportional to more core coating by different layers.

3. Experimental

3.1. Materials and equipment
All solvents, chemicals, and reagents were purchased from Merck. FESEM images were prepared with MIRA3TESCAN-XMU, TEM was provided on a Philips CM200, EDX spectra were recorded on VEGA- TESCAN-XMU, FT-IR spectra were obtained through (Shimadzu) FT-IR-8400s, XRD measurements were carried out by using a DRON-8 x-ray diffractometer, fluorescence spectra were prepared with Shimadzu-RF- 6000, solid-state UV-visible spectroscopy was studied by using a Shimadzu-UV-2550/220v. Thermal analysis (TGA) was done by using of Bahr-STA 504 instrument under argon atmosphere, and the magnetic properties of sample were detected at room temperature using a VSM (Meghnatis Kavir Kashan Co., Kashan, Iran). An Eager 300 for EA1112 was applied for CHNS analysis, as well.

Figure 7. X-ray diffraction patterns of (a) melamine, and products (b) q, (c) r, and (d) s.
3.2. Practical section

3.2.1. Preparation of the vinyl modified Fe₃O₄/SiO₂ core/shell NPs
Initially, in a three-necked flask (100 ml) containing dry chloroform (70 ml), Fe₃O₄/SiO₂ NPs (10 g), that were prepared according to the literature, was charged. Then trimethoxy vinylsilane (3.54 g, 0.02 mol) was added to the reaction mixture drop-wise at room temperature. After completion of addition, the mixture was stirred for 12 h at the refluxing temperature of chloroform. Ultimately, the vinyl modified Fe₃O₄/SiO₂ NPs were collected by using an external magnet and also washed with ethanol several times. Relatively rough particles were dried in a vacuum at 50 °C.

3.2.2. General procedure for CA reaction under reflux condition
Firstly, vinyl modified Fe₃O₄/SiO₂ NPs (0.1 g) were dispersed in an appropriate solvent (as reported in the table 1) (6.0 ml), by using ultrasonic for about 5 min. Next, diene moiety (scheme 1, 1—5) (0.05 mol) was added into the flask. Then, the mixture was stirred under specified conditions for appropriate times, as reported in the table 1. After completion of the reaction, the magnetic NPs were simply separated from the reaction mixture by using an external magnet, washed with ethanol and then dried in an oven at 60 °C.

3.2.3. General procedure for microwave-assisted CA reaction
Vinyl modified Fe₃O₄/SiO₂ NPs (0.05 g) were put into a test tube and dispersed in an appropriate solvent (as reported in the table 1) (3.0 ml), by using an ultrasonic bath for about 5 min. Then, diene moiety (Scheme 1, 1 — 5) (0.03 mol) was added into the tube. Next, the tube was put into the microwave apparatus. The experiment was initiated from 5 min—10% and was continued by increasing in the power of microwave radiation. The optimization reactions were carried out for 1 and the optimum condition was obtained in 50%, as reported in the table 1. After completion of the reaction, magnetic NPs were separated from the reaction mixture by using an external magnet, washed with ethanol and then dried in an oven at 60 °C.

3.2.4. General procedure for ultrasound-assisted CA reaction
Vinyl modified Fe₃O₄/SiO₂ NPs (0.05 g) were put into a test tube (Threaded Test Tube with Phenolic Cap, 13 × 100 mm), with an appropriate solvent (as reported in the table 1) (3.0 ml). We tried to provide the same reaction conditions with the microwave radiation method. Then, diene moiety (1 — 5) (0.03 mol) was added into the tube. Next, the tube was put into the ultrasound bath (50 KHz, 150 W l⁻¹), and the temperature was maintained at around 25 °C by adding ice pieces into the ultrasound wave bath. After completion the reaction, magnetic NPs were separated from the reaction mixture by using an external magnet, washed with ethanol and then dried in an oven at 60 °C.
4. Conclusions

Surface functionalized magnetic iron oxide NPs with fluorescence active compounds like anthracene, would be so useful in biological studies. On the one hand, they are equipped with small molecules which are used as antimicrobial agents and also are traceable in the body’s internal environment. On the other hand, they are conductible through their magnetic feature by applying an external magnetic field. Functionalized magnetic iron oxide NPs could also be used as easily separable and in many cases recyclable nano-organocatalyst in chemical reactions [37]. Therefore, construction of the magnetic core/shell NPs by execution of the most safe and efficient synthetic route would find more importance. Reduction of the reaction time for CA reactions onto the surface of NPs and also maintenance of core/shell structure of products 1—5 during the reaction (Scheme 1), were investigated for ultrasound-assisting method by analyses. The silica network destruction under reflux condition was observed in the FT-IR spectrum of product k. The FT-IR spectra have also elucidated that microwave radiation would not be a proper method for surface modifications (figure 1). The EXD spectra and the peak intensity of the present elements have proven the advantages of ultrasound-assisting method (figure 2). The core/shell structure, spherical morphology and uniformity of the product f were compared with product h and product i by FESEM and TEM images (figure 3). It was proven that monodispersed product with preserved core/shell structure were obtained by ultrasound wave. The mean size of the uniform NPs that were obtained by ultrasound wave, was also calculated for 20 NPs (figure 4). The surface modification ratio was also monitored by solid-state UV spectroscopy, fluorescence absorption spectroscopy and XRD, and the efficiency of ultrasound-assisting method was well proven (figures 5—7). Overall, by this study, it was well proven that we could obtain high quality product by using ultrasound wave as the reaction driving force by great saving the time.

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Conflict of interest

The authors declare no conflict of interest.

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