

CHARACTERIZATION AND EFFICACY OF FLUORIDE ELUSION OF A NOVEL GLASS IONOMER NANO ZIRCONIA SILICA HYDROXYAPATITE HYBRID MATERIAL

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ABSTRACT: In restorative dentistry, there has been a growing shift towards using nanoparticles dispersed in the polymer matrix to improve properties of dental restorative materials. A new nano zirconia-silica-hydroxyapatite (nanoZrO₂-SiO₂-HA) was synthesized by one-pot synthesis. The nanopowder was then incorporated into conventional glass ionomer cement (cGIC) (Fuji IX[®]) and characterized using Fourier transform infrared spectroscopy (FTIR). The effect of addition of nanoZrO₂-SiO₂-HA to cGIC on its fluoride ion (F⁻) elusion ability was also evaluated. The characterization studies confirmed that all particles were in the nanoscale range and were evenly and homogeneously dispersed throughout the sample with high density patterns visible for zirconia, calcium, and phosphorus. The incorporation of 5% nanoZrO₂-SiO₂-HA into cGIC did not impede its F⁻ ion releasing ability in any way. It, in fact, resulted in an overall higher F⁻ ion elusion from the GIC nano ZrO₂-SiO₂-HA when compared to the control group throughout the duration of the study ($p \leq 0.05$). Therefore, the nanoZrO₂-SiO₂-HA can be a promising filler for GIC to be used as restorative dental material in high stress bearing areas.

Keywords: Characterization; Fluoride elusion; Glass ionomer; Nano zirconia-silica-hydroxyapatite; Sol-gel processes; Spectroscopy; Zirconia hydroxyapatite.

INTRODUCTION

Many restorative materials have been used in dentistry over the decades. The use of amalgam has seen a negative shift in the past decade partly attributed to the concern of health professionals regarding its poor safety.¹ The trend now is to encourage the use of tooth-colored restorative materials such as glass ionomer cement (GIC) and composite resins (CR). Glass ionomer cements were first introduced in dentistry in 1969 by Wilson and Kent at the Laboratory of the Government Chemist, Department of Trade and Industry, London.²

GIC is the generic name designated to identify a group of materials comprising of alumino-silicate polyacrylates.^{3,4} As aqueous polyelectrolyte systems, GICs are known for their easy handling, chemical bonding to tooth substrate, fluoride ion (F⁻) release ability, coefficient of thermal expansion similar to dentine, and acceptable aesthetic quality.⁵ In the clinic, however, the use of GIC is limited due to its relatively inferior mechanical properties and sensitivity to initial desiccation and moisture⁵⁻⁷.

To expand the usage of conventional GIC (cGIC), especially for restoration of adult teeth and for anterior teeth restorations, the physical, mechanical, and aesthetic

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properties must improve.⁸ Metal powders,⁹ reactive glass fibres,¹⁰ and other micron size filler particles have been evaluated as means to improve the mechanical properties of GICs. However, it was observed that these fillers adversely affected the adhesive and fluoride release properties. In restorative dentistry, there has also been a growing shift towards using nanoparticles to improve properties of cGICs.¹¹ In the last decade, nanoscale hydroxyapatite (HA: $\text{Ca}_{10}(\text{PO}_4)_6\text{OH}_2$)¹² in combination with HA-silica (SiO_2)¹³ has been successfully used to improve GICs. Recently, nanophases of zirconia (ZrO_2) or a combination of HA- ZrO_2 ^{14,15} have been incorporated in attempts to strengthen GIC with enhanced outcomes. Zirconium and its oxide have been used widely for the toughening and strengthening of brittle HA bio glasses in biomedical applications owing to their excellent dimensional stability and toughness similar to stainless-steel.¹⁶ Another more recent study was done by our research group to evaluate the microhardness of a HA- SiO_2 - ZrO_2 -incorporated GIC with some encouraging results.¹⁷ However, there is still a dearth of information on the assessment of fluoride release property of nano zirconia-silica-hydroxyapatite (nano ZrO_2 - SiO_2 -HA) GIC hybrid.

Fluoride has been shown to have an effect on the development of caries.¹⁸ It has a positive effect on the reduction of mineral loss and enhancing mineral precipitation back on teeth. On the other hand, excessive F^- ion can result in enamel fluorosis during the formative stages of the permanent dentition.¹⁸⁻²⁰ As such, F^- ion will physico-chemically induce mineral precipitation on the tooth structure in the form of fluorapatite, inhibit the growth and attachment of bacteria on tooth surfaces, and impede the formation of a complex bacteria biofilm.²¹ Hence, the ability to release F^- ion is an important factor for a successful dental material.

Fluoride is released from cGIC primarily as sodium fluoride (NaF). NaF is not a matrix forming species so the cement is not weakened by loss of fluoride ions. The mechanism of fluoride release is complex and is dominated by diffusion mechanisms where the rate of fluoride release is reduced as the time passes according to concentration gradient.^{22,23}

The aim of this study was to evaluate the effect of a novel nano zirconia-silica-hydroxyapatite reinforcement phase on the efficacy of F^- ion release from cGIC. The nano powder was synthesized and characterized qualitatively prior to the evaluation of F^- ion release ability of the GIC nano ZrO_2 - SiO_2 -HA hybrid material. The hypothesis tested was that addition of nano ZrO_2 - SiO_2 -HA to the cGIC does not impede and significantly improves its F^- ion release property.

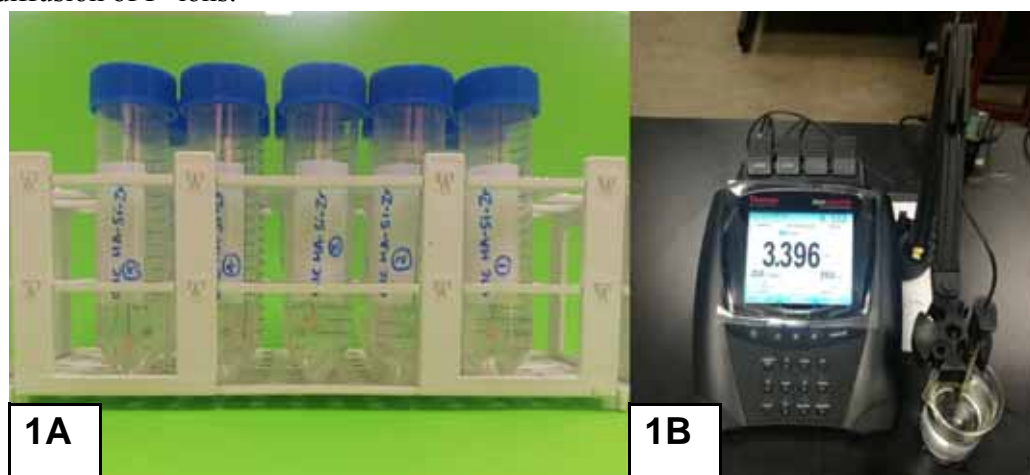
MATERIALS AND METHODS

Synthesis of nano zirconia-silica-hydroxyapatite (nano ZrO_2 - SiO_2 -HA): The alumino-silicate glasses and the polyacids used in the research study were from commercially available Fuji IX[®] (GC Corp., Tokyo; Japan). All the other chemicals and materials were of analytical grade and used as received from the manufacturer. Tetraethyl orthosilicate (TEOS; >99%), ammonia (NH_3 ; 25%), and calcium hydroxide [$\text{Ca}(\text{OH})_2$; >98%] were obtained from Merck Serono Pvt. NSW; Australia. Phosphoric acid (H_3PO_4 ; >99%), ethanol ($\text{C}_2\text{H}_5\text{OH}$; >99%) were procured from Sigma-Aldrich Co. LLC, MO; USA, and Zr nanopowder (ZrO_2 ; >99%) from US Research Nanomaterials Inc., TX; USA. The nano ZrO_2 - SiO_2 -HA was synthesized using a modification of the sol-gel technique²⁴ described by Ab Rahman et al.¹⁷

Fabrication of GIC nano ZrO_2 - SiO_2 -HA hybrid samples: Conventional GIC, Fuji IX[®], was used as control and base material. The nano ZrO_2 - SiO_2 -HA powder was added at 5% by weight, into the cGIC. The mixture was then ground manually using a pestle and mortar in a control grinding process for about 10 min. All the samples (cGIC and GIC nano ZrO_2 - SiO_2 -HA) were prepared by mixing with Fuji IX[®]-liquid at the recommended powder/liquid ratio (P/L) of 3:6. The F^- ion release evaluation experiment was performed after 24 hr of setting.

Characterization of GIC nano ZrO_2 - SiO_2 -HA hybrid: Fourier transform infrared spectra (Spectrum Two[™] FTIR, PerkinElmer; MA, USA) of the nano ZrO_2 - SiO_2 -HA powder was measured in the spectral range of 400–4000 cm^{-1} . The spectral resolution for the EDX was between 0.16 cm^{-1} and 0.5 cm^{-1} which is universal for most applications.

Fluoride release, sample preparation, and testing: For the F^- ion release measurements, a total of 20 samples ($n=10$ /group) measuring 5 mm × 2 mm in thickness were prepared in a stainless-steel split mold. Samples were covered with celluloid strips and pressed with a glass plate. After 15 min, all the samples (experimental and control) were removed from the mold and stored at 37°C and 100% relative humidity for 50 min. The samples were individually suspended by nylon thread in 10 mL of deionized water in sealed containers and then stored at 37°C (Figure 1A). For the measurements, each disk was removed from the storage water, dried on filter paper, and immediately immersed in 10 mL of fresh deionized water for further equilibration. To the previous storage water 1 mL total ionic strength adjustment buffer solution (TISAB III, Thermo Fisher Scientific, USA) was added to decomplex the F^- ions. The F^- concentration was measured every day for 7 days and then every 7 days for 30 days using an ion selective fluoride electrode (ISE) connected to an ion analyzer (Figure 1B) (OrionStar[™] A214, Thermo Scientific, USA). This time period was chosen because the fluoride release from GICs involves two processes, one a rapid surface elusion and the other a slower, continuous bulk diffusion of F^- ions.²⁵⁻²⁸



Figures 1A and 1B. 1A: Samples suspended in 10 mL deionized water; 1B: F^- ion release measured using an ion selective electrode and an ion analyser.

Statistical analysis: The data was analysed using SPSS version 22.0 (SPSS Inc., Chicago, IL, USA). Numerical data was tabulated and presented as mean ± SD based

on their normality distribution. A p -value ≤ 0.05 was considered as statistically significant. The data thus obtained from the F^- ion specific electrode (ISE) potentiometric analysis was tabulated and statistically analysed using repeated measures ANOVA and multiple comparisons.

RESULTS

Characterization of GIC nanoZrO₂-SiO₂-HA hybrid: FTIR analysis shows some variations in adsorption peaks of the GIC 5% nanoZrO₂-SiO₂-HA in the hybrid material (Figure 2).

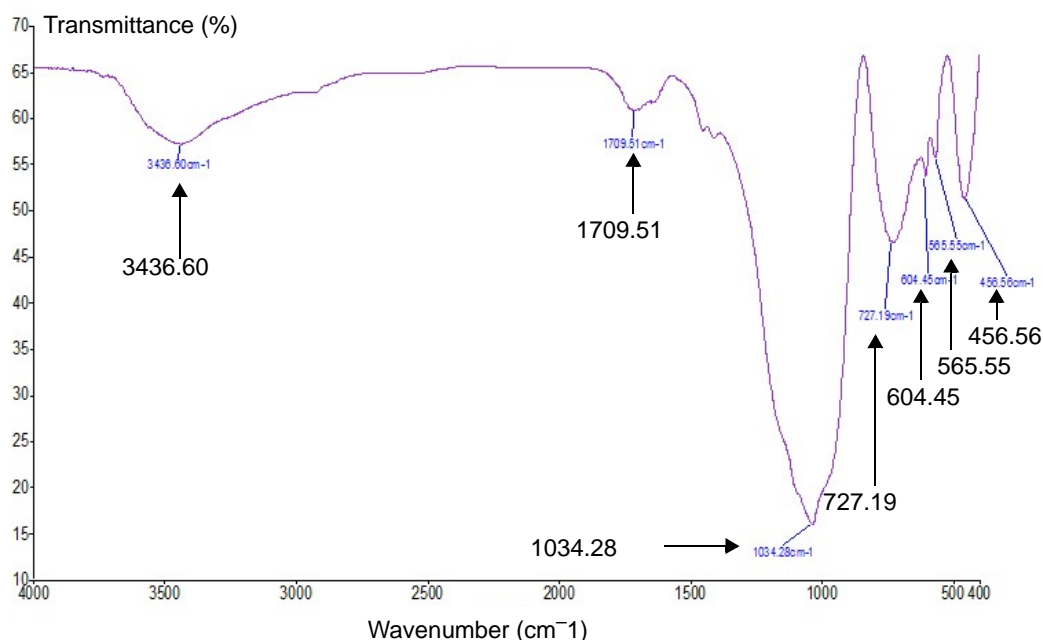


Figure 2. Fourier transform infrared (FTIR) spectra of GIC nanoZrO₂-SiO₂-HA hybrid.

The band at 3436.60 cm^{-1} is due to ν_2 bending mode of absorbed water OH stretching vibration confirming the presence of alcohols and phenols.^{17,29,30} This might also be due to O-H stretching vibration of incomplete silanol group also. The band at 1635 cm^{-1} in the FTIR spectra of nanoZr-Si-HA shifts to 1709.51 cm^{-1} here and is due to stretching vibration of carboxyl group of ketones or quinone. This confirms these units are present in humic acids. This confirms ν_3 stretching vibration of PO_4^{3-} . The prominent peak at 1034.28 cm^{-1} becomes a bit broad in the GIC 5% nanoZrO₂-SiO₂-HA hybrid but is otherwise stable in position same as in the spectra of the nanoZr-Si-HA. It arises due to symmetric and asymmetric stretching of Si-O-Si, i.e., with the addition of Zr it increases the distance of Si-O.^{17,29,31} It specifies the Zr-O-Si bond formation and is because of the large ionic radius of Zr.^{15,32} It might also be due to the asymmetric stretching in random network with lower symmetry. It is also due to the presence of AlPO_4 .

The peak at 727.19 cm^{-1} arises due to CaF_2 ; this peak might also be due the presence of $\theta\text{-Al}_2\text{O}_3$ at 604.45 cm^{-1} . This is also assigned to OH^- deformation mode; this peak is due to the presence of $\alpha\text{-Al}_2\text{O}_3$. A new peak 456.56 cm^{-1} appears due to the bending vibration of Si-O-Si , AlPO_4 , and $\alpha\text{-Al}_2\text{O}_3$. These results indicate some molecular interaction present between the nano $\text{ZrO}_2\text{-SiO}_2\text{-HA}$ and GIC in the composite and thus provide a conformation for a good bond between GIC and nano $\text{ZrO}_2\text{-SiO}_2\text{-HA}$.

Fluoride release results: The results of the F^- ion release for control (Fuji IX[®]) and GIC nano $\text{ZrO}_2\text{-SiO}_2\text{-HA}$ experimental group after 1 month of storage in deionized water and at 37°C were recorded. Table 1 shows the descriptive statistics of mean F release from the control and GIC nano $\text{ZrO}_2\text{-SiO}_2\text{-HA}$ groups.

Table 1. Descriptive statistics of the mean fluoride release at the various time intervals

Group	Day	Mean F release	Std. error	95% Confidence interval	
				Lower bound	Upper bound
Control (Fuji IX)	1	3.68	0.216	3.228	4.137
	2	0.94	0.073	0.795	1.100
	3	0.51	0.065	0.375	0.649
	4	0.41	0.141	0.123	0.714
	5	0.39	0.046	0.298	0.492
	6	0.28	0.021	0.235	0.325
	14	0.20	0.036	0.128	0.278
	21	0.13	0.025	0.080	0.184
	28	0.09	0.029	0.036	0.157
GIC nano $\text{ZrO}_2\text{-SiO}_2\text{-HA}$	1	5.25	0.216	4.805	5.714
	2	1.16	0.073	1.012	1.318
	3	1.07	0.065	0.933	1.207
	4	0.97	0.141	0.677	1.267
	5	0.80	0.046	0.712	0.907
	6	0.53	0.021	0.487	0.577
	14	0.48	0.036	0.407	0.557
	21	0.26	0.025	0.214	0.318
	28	0.19	0.029	0.132	0.252

Table 2 shows mean \pm SD of F⁻ release from day 1 to day 6 and weekly thereafter till 28 days. Highly significant difference ($p \leq 0.01$) in amount of mean F release was observed from both the groups for all the time intervals with the exception of day 2, day 4, and day 28 which were significant ($p \leq 0.05$). Both the control (Fuji IX[®]) and GIC nanoZrO₂-SiO₂-HA showed similar pattern of F⁻ release during the course of the study. The highest F elusion was measured on day 1 ($p = 0.000$) for both control (3.68 ppm \pm 0.69) and GIC nanoZrO₂-SiO₂-HA (5.25 ppm \pm 0.67) groups. For both the control and GIC nanoZrO₂-SiO₂-HA groups, greatest increase in F ion release was observed from day 1 to day 3 ($p = 0.000$). Repeated measures ANOVA showed statistically significant difference between the two groups demonstrating similar patterns of F⁻ ion release for all the time intervals (Table 2).

Table 2. Evaluation of the fluoride release (ppm, mean \pm SD) from the control and the GIC 5% nano ZrO₂-SiO₂-HA groups over one month

Group and p value	Fluoride release (ppm)								
	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 14	Day 21	Day 28
	(mean \pm SD)	(mean \pm SD)	(mean \pm SD)	(mean \pm SD)	(mean \pm SD)	(mean \pm SD)	(mean \pm SD)	(mean \pm SD)	(mean \pm SD)
Control (Fuji IX)	3.68 \pm 0.69	0.94 \pm 0.13	0.51 \pm 0.07	0.41 \pm 0.15	0.39 \pm 0.11	0.28 \pm 0.03	0.20 \pm 0.08	0.13 \pm 0.05	0.09 \pm 0.04
GIC nanoZrO ₂ -SiO ₂ -HA	5.25 \pm 0.67 [†]	1.16 \pm 0.29*	1.07 \pm 0.28 [†]	0.97 \pm 0.60*	0.80 \pm 0.17 [†]	0.53 \pm 0.09 [†]	0.48 \pm 0.13 [†]	0.26 \pm 0.09 [†]	0.19 \pm 0.12*
p value	0.000	0.048	0.000	0.012	0.000	0.000	0.000	0.001	0.030

Repeated measures of ANOVA compared to the control group: *Significant difference, p value \leq 0.05; [†]Highly significant difference, p value \leq 0.01.

DISCUSSION

Fluoride ion release from GICs is an exceptional property and plays a major role in their selection for restorative dental application.³³ It seems that F⁻ ions released from GICs act in a dose-dependant manner. The present *in vitro* study evaluated the quantity of F⁻ ions released from the control and GIC nanoZrO₂-SiO₂-HA groups over a one-month period. Deionized water was chosen as the immersion medium as it does not contain traces of any ions including F⁻. Thus, it helped in an accurate assessment of F⁻ ion release from the GIC.³⁴

Figure 3, reveals a similar pattern of F⁻ ion release, this implies that the nanoZrO₂-SiO₂-HA particles when added to GIC do not interfere with its ability to release F⁻. It has been shown in our study, that the highest F⁻ elution was seen on the day 1 of immersion in deionized water for both GIC nanoZrO₂-SiO₂-HA (5.25ppm) and control (3.68 ppm) groups and after that, F⁻ ion release from the samples decreased

gradually (Table 2). The same F^- release pattern has been previously reported by the other researchers.³⁵⁻³⁷

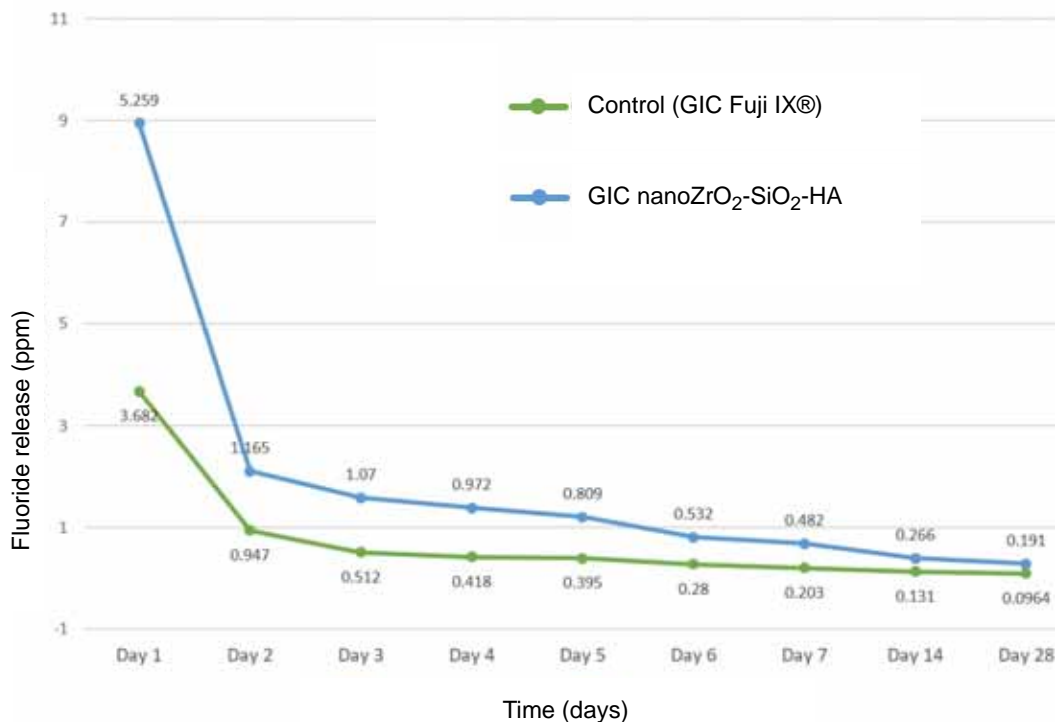


Figure 3. Fluoride release measurement of GIC nanoZrO₂-SiO₂-HA hybrid and control over a one-month period.

However, in a study on Zr-reinforced GIC, the authors reported an initial low F^- release on day 1 and a later higher F^- elusion on day 7.²⁶ It is a well-known fact that F^- release from GIC is in the form of NaF and CaF₂ and as such, F^- ion release from GIC is governed by the NaF and CaF₂ content of the cement,³⁸ which may explain the initial low F^- release.

In our study, for both the control and GIC nanoZrO₂-SiO₂-HA groups, greatest F^- elution was observed from day 1 to day 3 ($p=0.000$). These findings were in agreement with similar observations made by other studies on HA-reinforced GIC²⁷ and forsterite-reinforced GIC,³⁷ respectively.

An initial fluoride burst effect is desirable, as it will reduce the viable bacteria that may be left in the cavity preparation and induce dentin remineralization. The reason for the initial burst of fluoride is due to the F^- ions released from the glass particles as they dissolve in polyacid during the setting reaction.³⁹

In this study, F^- release of GIC nanoZrO₂-SiO₂-HA group was significantly higher than the control group for all the timelines ($p<0.05$) and these findings were corroborated by other studies.^{27,40,41} Even though, the GIC glass powder is the only source of F^- , still higher F^- ion release was measured from the GIC nanoZrO₂-SiO₂-HA than from the control group despite the lower F^- content in the HA-added GICs. It has been suggested that there is a possibility that Ca ions in the HA of the

nanoZrO₂-SiO₂-HA powder influences the F⁻ release.⁴⁰ SEM studies have shown that the HA, glass core, and GIC matrix may react with each other resulting in dissolution of HA particles and its infiltration by F⁻, Si, Al, and Sr.⁴¹ These findings suggest that the release and recharge of F⁻ ion occurs in both the matrix and nanoZrO₂-SiO₂-HA reinforced GICs.

CONCLUSION

Within the limitations of this *in vitro* study, it can be concluded that the addition of nanoZrO₂-SiO₂-HA to the cGIC did not impede its F⁻ releasing ability in any way. It, in fact, resulted in an overall higher F⁻ elusion from the GIC nanoZrO₂-SiO₂-HA when compared to the control group throughout the duration of the study. Therefore, these nanoceramics can be considered as promising fillers for GIC to be used as a restorative dental material in high stress areas.

ACKNOWLEDGEMENT

The authors would like to acknowledge the expertise rendered by Professor Ismail Ab Rahman, toward the research experiment design. This research study was financially supported by Universiti Sains Malaysia under Research University Grant Scheme No. RUI 1001/PPSG/812164.

CONFLICT OF INTEREST

The authors declare no competing financial interests.

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