In Situ Self-Assembly of Ultrastable Gold Nanoparticles on Polyvinyl Alcohol Nanofibrous Mats for Use as Highly Reusable Catalysts

Lin Xu, Hongping Xiang, Zhengjian Chen, and Xu Zhang

ABSTRACT: Designing highly stable and reusable catalytic systems based on Au nanoparticles (NPs) is a significant challenge in nanocatalysis research. Here, we have fabricated polyvinyl alcohol (PVA) nanofibrous mat/Au NP composite catalysts with NPs in uniform size and good distribution by use of a developed in situ growth approach. In this method, Au seeds were first adsorbed on PVA nanofibrous mat surfaces rather than on relatively large Au NPs and then used to grow NPs in Au seed solution; thus, the steric hindrance effect was alleviated and a high loading was used for Au NPs up to 11 wt %. Strong interfacial interactions between the Au NPs and the PVA nanofibrous mats due to introducing a large number of hydrogen bonds provide high thermal stability for the PVA side chains, long-term catalytic stability, and excellent reusability. Consequently, the proposed in situ grown PVA/Au NP nanofibrous mats produce high catalytic activity for at least 15 cycles over a 30 d period. This work provides a potential approach for fabricating highly stable and reusable metal NPs on polymer nanofibrous mats to facilitate a wide variety of applications.

INTRODUCTION

Metal nanoparticles (NPs) have been the subject of increasing interest because of their importance in the field of nanoscience. Gold NPs, in particular, are one of the most widely studied NP systems because of their far-ranging potential applications, such as in catalysis, sensors, optical devices, energy, and biology.1−10 However, colloidal Au NPs have high surface energy, and not only readily aggregate but also are difficult to retrieve and reuse in aqueous or nonaqueous media. Therefore, stabilization is essential to immobilize Au NPs and prevent their aggregation in most applications, particularly in catalysis. Stabilization has been facilitated by the use of numerous carrier systems such as high surface area, high-porosity materials [e.g., zeolites and mesoporous silica (SBA)], two-dimensional nanomaterials (e.g., graphene oxide), and a variety of molecules (e.g., surfactants and dendrimers).11−32 Recently, environmentally benign polymer nanofibers have attracted considerable interest as Au NP stabilization carriers because of their high porosity, high surface area to volume ratios, and degradability in the environment.30−33 Compared to other high surface area and high-porosity materials employed as Au NP stabilization carriers for catalytic applications, electrospun polymer nanofibers can provide a larger number of active sites, for example, −SH, −COOH, and −NH3+ for stabilizing Au NPs and are much easier for fabrication.34−40 This results in a great variety of interactions for immobilizing Au NPs on nanofiber surfaces to form polymer/Au NP composite nanofibers, which have been prepared via the in situ reduction of HAuCl4 carried by polymer nanofibers. For example, Fang et al. demonstrated the immobilization of Au NPs on the surfaces of water-stable composite polyvinyl acetate and polyethyleneimine nanofibrous mats.35 However, this approach is unable to control the size of Au NPs; as a result, the NPs lack uniformity in size, which is unfavorable for their catalytic activity. Moreover, the distribution of Au NPs embedded in polymer nanofibers also tends to obstruct free contact between the reactants and the Au NPs during catalysis, reducing the catalytic performance. On the other hand, the composite polymer/Au NP nanofiber catalysts can be fabricated by directly adsorbing Au NPs on polymer nanofibers via active functional groups (e.g., −NH3+ and −COOH).36,37 This method can stabilize Au NPs in the controllable size and shape. However, the spatial steric hindrance effect tends to limit Au NP loading on the outer surfaces of matted nanofibers and thus leads to a very low loading percentage. Moreover, the composite polymer/Au NP nanofibers lack long-term catalytic stability because of a relatively small number of linkage points between the Au NPs and the polymer nanofibers, accordingly.

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the NPs readily aggregate over time. An ideal Au NP catalyst-carrier system allows for the fabrication of Au NPs with uniform sizes, uniform distribution on the carrier surface, and high loading mass percentage. Moreover, the fabricated polymer/Au NP catalyst should be stable over a long period of time and offer good reusability. In short, most routes to immobilize Au NPs on polymer nanofibers suffer from several drawbacks: (1) lacking of the long-term stability; (2) low loading amounts; (3) embedding in the polymer nanofibers which obstructs the reactants to contact with the Au NPs and thus inhibiting the catalytic properties; and (4) lacking the uniform size and distribution of Au NPs. Thus, designing highly effective Au NP catalytic systems with long-term catalytic stability and reusability is still a challenge and of significant interest in nanoscience research.

The present study addresses this challenge by proposing the application of an environmentally benign, degradable, and water-stable polyvinyl alcohol (PVA) nanofibrous mat carrier system to fabricate the composite PVA/Au NP nanofibrous mat catalysts. We have overcome these drawbacks and successfully fabricated the highly stable PVA/Au NP nanofibrous mats by in situ growing Au NPs from Au seeds adsorbed on the surfaces of PVA nanofibrous mats. The Au NPs, rather than relatively large Au NPs, adsorbed on PVA nanofibrous mat surfaces can alleviate the steric hindrance effect and thereby increase the Au NP loading up to 11 wt %.

The Au NPs in situ grown from Au seeds are in uniform size and distribution. Strong interfacial interactions between the Au NPs and the PVA nanofibrous mats stemmed from a large number of hydrogen bonds provide high thermal stability, long-term catalytic stability, and excellent reusability.

**RESULTS AND DISCUSSION**

Figure 1 presents a schematic diagram of the process of fabricating PVA/Au NP nanofibrous mat composites by the in situ growth of Au NPs. Water-stable PVA nanofibrous mats were prepared via an electrospinning process by adding glutaraldehyde (GA) into the PVA solution as a cross-linking agent. First, the water-stable PVA nanofibrous mats were placed in a diluted Au seed solution with hexadecyltrimethylammonium bromide (CTAB). The pH of the solution was adjusted to 3 to activate the hydroxyl groups of PVA for adsorbing the Au seeds it reached 200 ± 50 nm (II, Figure 2c). This is presumably because of the assembly of CTAB molecules on the PVA nanofibrous mat surfaces. With the PVA nanofibrous mats with Au seeds growing to NPs in situ, the mean diameter increased to 250 ± 50 nm (III, Figure 2d). We also note from Figure 2d that the Au NPs are uniformly distributed on the surfaces of the PVA nanofibrous mats with uniform size. The mean size of Au NPs was estimated to be 30 ± 2 nm, and a good size uniformity was observed on both the outermost and inner surfaces of the PVA nanofibrous mats, indicating that the Au seed adsorption step can alleviate the steric hindrance effect.

Figure 1. Schematic diagram of the proposed process for fabricating composites of PVA nanofibrous mats with Au NPs grown in situ from Au seeds.

The X-ray diffraction (XRD) pattern of the in situ grown PVA/Au NP nanofibrous mats shown in Figure S1 of Supporting Information presents that besides the peak at 19.4° observed for PVA nanofibrous mats, there are two other peaks located at 26.4 and 37.9°, indexed to CTAB and the (111) planes of fcc Au, respectively. The ultraviolet–visible (UV–vis) spectroscopy of the in situ grown PVA/Au NP nanofibrous mats in Figure S2 of Supporting Information displays a very prominent characteristic absorption peak at 540 nm, assigned to the localized surface plasmon resonance of Au NPs. The sharp peak indicates a narrow size distribution of Au NPs.

The thermal stability of PVA and other composite PVA/Au nanofibrous mats is examined by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) in a N₂ atmosphere as shown in Figure S3 of Supporting Information. The DTA results show that the maximum decomposition growth solution including CTAB, HAuCl₄, and ascorbic acid. Then the adsorbed Au seeds on the PVA nanofibrous mat surfaces grew to Au NPs in situ.

Figure 2a presents images of water-stable PVA nanofibrous mats (I), PVA nanofibrous mats with adsorbed Au seeds (II), and PVA nanofibrous mats with Au NPs grown in situ (III). (b–d) Corresponding SEM images of samples I, II, and III in (a), respectively. All the scale bars represent 1 μm.
temperatures $T_{\text{max}1}$ and $T_{\text{max}2}$ for the PVA nanofibrous mats are 332 ± 3 and 441 ± 3 °C, respectively, close to the previous results of 250–350 and 400–480 °C, which correspond to the thermal decomposition of the side and main chains of PVA, respectively. For the PVA/Au seed nanofibrous mats and in situ grown PVA/Au NP nanofibrous mats, their $T_{\text{max}1}$ increases to 366 ± 3 °C, about 34 °C greater than that of the PVA nanofibrous mats, while $T_{\text{max}2}$ increases very little, 443 ± 3 °C. This remarkable increase of $T_{\text{max}1}$ suggests the enhancement of the thermal stability of the side chains of PVA. Obviously, there exists a strong interaction among PVA and CTAB because of the assembly of the CTAB layer on the PVA nanofibrous mat surfaces, which impedes the elimination and oxidization of the side hydroxyl groups of PVA, and thus suppresses the thermal degradation process significantly. For the standard adsorbing PVA/Au NP nanofibrous mats, its $T_{\text{max}1}$ reduces to 318 °C. This is because first, the side hydroxyl groups of PVA are activated in weak acid solution during the adsorption of Au NPs. Second, CTAB molecules are cleaned up in the preparation of Au NPs; as a result, no free CTAB molecules can be adsorbed on the surface of PVA nanofibrous mats. The loading of Au NPs of the in situ grown PVA/Au NP nanofibrous mats is estimated to be 11 wt % from the TGA data, much higher than that of the PVA/Au seed nanofibrous mats (3.2 wt %) and standard adsorbed PVA/Au NP nanofibrous mats (3.9 wt %).

This high thermal stability and large Au loading of the in situ grown PVA/Au NP nanofibrous mats can be ascribed to the hydrogen bonds formed between the hydroxyl groups of PVA and the ammonium groups of CTAB (Figure 1). The Fourier-transform infrared (FTIR) spectra in Figure S4 of Supporting Information display an obvious red shift in the peak characteristic of O–H stretching vibrations from 3334 cm$^{-1}$ for PVA nanofibrous mats to 3315 cm$^{-1}$ for the PVA/Au NP nanofibrous mats. It suggests that there exists a strong interaction associated with a large number of hydrogen bonds between the hydroxyl groups of PVA and the ammonium groups of CTAB as shown in Figure 1 because the O–H stretching vibration peak is sensitive to the hydrogen bond. This is favorable for immobilizing the Au NPs on the PVA/CTAB composite nanofibrous mats, and thus facilitating the stability of the PVA/Au NP composite nanofibrous mats.

The potential catalytic applications of the composite PVA/Au NP nanofibrous mats were evaluated by conducting a series of catalytic experiments involving a reduction reaction transforming 4-nitrophenol to 4-aminophenol. The reaction was monitored using in situ UV–vis spectroscopy, and the intensity of the optical absorbance peak at 400 nm was employed to estimate the concentration of 4-nitrophenol in the aqueous solution. In order to give the control experiment of the size effect, the size of Au NPs of standard adsorbed PVA/Au NP nanofibrous mats was similar to that of the in situ grown PVA/Au NP nanofibrous mats. Figure 3a–d presents the UV–vis spectra over time of the PVA nanofibrous mats, PVA/Au seed nanofibrous mats, standard adsorbed PVA/Au NP nanofibrous mats, and in situ grown PVA/Au NP nanofibrous mats.
nanofibrous mats as catalysts. Figure 3a indicates that the characteristic optical absorbance peak intensity of 4-nitrophenol undergoes no significant change over a 30 min period when employing the PVA nanofibrous mats as catalysts, that is, PVA nanofibrous mats cannot catalyze the reaction. As shown in Figure 3b–d, the characteristic absorption peak intensities of 4-nitrophenol significantly decrease with increasing reaction time when employing the PVA/Au seed nanofibrous mats, standard adsorbed PVA/Au NP nanofibrous mats, and in situ grown PVA/Au NP nanofibrous mats as catalysts. Observably, the color of the reaction solution faded from yellow to transparent. The reaction kinetics are presented in terms of the ratio of the concentration of 4-nitrophenol with respect to time ($C_t$) to its initial concentration ($C_0$) as a function of time (Figure 3e). The results indicate that there is a linear relationship between $\ln(C_t/C_0)$ and reaction time, consistent with the pseudo-first-order kinetics of the reaction. A linear fitting presents that the slopes of $\ln(C_t/C_0)$ are $-0.00042$, $-0.056$, $-0.063$, and $-0.13$ for the catalytic reactions by the PVA nanofibrous mats, PVA/Au seed nanofibrous mats, standard adsorbed PVA/Au NP nanofibrous mats, and in situ grown PVA/Au NP nanofibrous mats, respectively. The slope stands for the reaction rate constant of catalytic reactions, $k$. It can be seen from Figure 3f that the in situ grown PVA/Au NP nanofibrous mats has the highest catalytic reaction activity, about two times larger than those of the PVA/Au seed nanofibrous mats and the standard adsorbed PVA/Au NP nanofibrous mats.

The long-term stability and reusability of the proposed PVA/Au NP nanofibrous mat catalyst were investigated using multiple cycles of the 4-nitrophenol to 4-aminophenol reduction reaction. After each catalytic reaction, the catalysts were stored in deionized ultrafiltered (DIUF) water for 2 days (d) with no subsequent treatment, and then the process was repeated. Figure 4a–c presents the plots of $\ln(C_t/C_0)$ as a function of time of the catalytic reactions for the PVA/Au seed nanofibrous mats for 1–5 cycles over a 10 d period, the standard adsorbed PVA/Au NP nanofibrous mats for 1–5 cycles over a 10 d period, and the in situ grown PVA/Au NP nanofibrous mats for 1–15 cycles over a 30 d period, respectively, with the corresponding reaction rate constants $k$ shown in Figure 4d–f, respectively. The $k$ value decreases continuously from 0.056 to 0.003 for the PVA/Au seed nanofibrous mat catalyst, while for the standard adsorbed PVA/Au NP nanofibrous mats keeps at a fairly uniform level up to the third cycle and then decreases substantially from 0.06 to 0.022. After 5 cycles, the $k$ value is reduced by 95% for the PVA/Au seed nanofibrous mats and 65% for the standard adsorbed PVA/Au NP nanofibrous mats, respectively. For the in situ grown PVA/Au NP nanofibrous mats, however, the $k$ value decreases from 0.13 to 0.088 over 15 cycles in the 30 d retention period (Figure 4f), just 32% reducing. Moreover, the smallest value of 0.088 is still greater than the initial one of 0.063 for the standard adsorbed PVA/Au NP nanofibrous mats. Obviously, the in situ grown PVA/Au NP nanofibrous mats provide better long-term catalytic stability and reusability.

Next, we analyze the mechanism behind the high catalytic activity and the long-term stability of the in situ grown PVA/Au NP nanofibrous mats. It is well known that the catalytic activity of Au NPs is primarily dependent on the total surface area, which facilitates efficient contact between the Au NPs and the substrate molecules. As shown in Figure 2d, the in situ grown Au NPs have a greater total surface area than Au seeds because of much larger size, and they are uniformly distributed on both the outermost and inner surfaces of the PVA nanofibrous mats. It is unlike the standard adsorbed PVA/Au NP nanofibrous mats in which Au NPs are only observed on the outermost surface of the PVA nanofibrous mats (Figure 4e) because of the steric hindrance effect. Estimated from the SEM data (Figures 2d and 4e), the particle number of in situ grown Au NPs on fiber is about 267/μm², while that of standard adsorbed Au NPs is about 36/μm². We assume that the particle number of Au seeds on fiber (PVA/Au seed nanofibrous mats) is the same as that of the in situ grown Au NPs. Therefore, considering their sizes of 3 nm for Au seed, 33 nm for the adsorbed Au NPs, and 30 nm for the in situ grown Au NPs, the surface area ratio of the three samples is 1:16.3:100. Clearly, a large surface area can indeed increase the

Figure 4. Kinetics of multiple cycles of 4-nitrophenol to 4-aminophenol reduction reactions with different nanofibrous mat catalysts: (a) PVA/Au seed nanofibrous mats (1–5 cycles over a 10 d period); (b) standard adsorbed PVA/Au NP nanofibrous mats (1–5 cycles over a 10 d period); and (c) in situ grown PVA/Au NP nanofibrous mats (1–15 cycles over a 30 d period). The reaction rate constant $k$ to the retention time obtained over multiple cycles for the different nanofibrous mat catalysts: (d) PVA/Au seed nanofibrous mats; (e) standard adsorbed PVA/Au NP nanofibrous mats (a SEM image inserted); and (f) in situ grown PVA/Au NP nanofibrous mats.
catalytic performance. However, the catalytic performance is not directly proportional to the surface area because the size of NPs also affects it. For long-term catalytic stability, the CTAB molecules as the protecting agent are retained as a double-layer on the Au NPs like a cell membrane.\textsuperscript{44,45} In the standard adsorbing process, the Au seeds and the Au NPs are typically adsorbed on the PVA nanofibrous mat surfaces via hydrogen bonds between the hydroxyl groups of PVA and the ammonium groups of CTAB. These hydrogen bonds are formed randomly and greatly influenced by the topological morphology of PVA nanofibrous mats. However, during the in situ growing process, Au atoms in situ grow on Au seeds along the PVA nanofibrous mats connected by the double-layer of CTAB (see Figure 1). A larger amount of hydrogen bonds is formed at the interface of Au NPs and PVA nanofibrous mats. Thus, ultrastable Au NPs are immobilized on PVA nanofibrous mats. In a word, the proposed in situ grown PVA/Au NP nanofibrous mats provide excellent long-term catalytic stability and reusability.

**CONCLUSIONS**

We have developed an in situ growth approach to fabricate composite PVA/Au NP nanofibrous mat catalysts by immobilizing Au NPs on the surface of PVA. Au NPs uniformly distribute on both the outermost and inner surfaces of PVA nanofibrous mats with a uniform size of 30 ± 2 nm and a high loading of 11 wt %. Compared to that of the naked PVA nanofibrous mats, the thermal stability of the side chains of PVA of in situ grown PVA/Au NP nanofibrous mats was remarkably enhanced, reflected by an increase of 34 °C of the decomposed temperature. It implies a strong interaction between PVA and Au NPs stabilized by CTAB, induced by a large number of hydrogen bonds between the hydroxyl groups of PVA and the ammonium groups of CTAB. Catalytic experiments demonstrate that the in situ grown PVA/Au NP nanofibrous mats have much higher catalytic reaction activity, about two times larger than that of the standard adsorbed PVA/Au NP nanofibrous mats, and display consistently high catalytic activity for at least 15 cycles over a 30 d period. Obviously, introducing numerous hydrogen bonds is favorable for immobilizing the Au NPs on PVA; as a result, the composite in situ grown PVA/Au NP nanofibrous mats achieve the long-term stability and reusability in catalysis. Our work provides a simple fabrication approach for stabilizing other metal NPs on polymer fibers to facilitate a wide variety of applications in catalysis, nano-optics devices, and sensing.

**EXPERIMENTAL SECTION**

Materials. PVA (88% hydrolyzed, $M_w = 89$–$98$ kg/mol), sodium borohydride (NaBH$_4$), ascorbic acid, and CTAB were obtained from Sigma-Aldrich. Chloroacetic acid (HAuCl$_4$ 3H$_2$O), GA (50% water solution), and hydrochloric acid (HCl, 36% water solution) were purchased from J & K Chemical Reagent Co., Ltd. (China).

Preparation of Water-Stable PVA Nanofibrous Mats. PVA was added into DIUF water at 80 °C followed by continuous stirring to dissolve PVA powder. The polymer concentrations of the solution were 14 wt %. 0.4 mL GA was added into 2 mL PVA solution and shaked into a uniform solution. The polymer/GA solutions were placed in a 5 mL syringe and electrospun using a high voltage dc power supply set to 23 kV, a 15 cm tip-to-substrate distance, and a 0.6 mL/h flow rate for 45 min. The PVA nanofibrous mats were deposited onto aluminum foil. These polymer nanofibers were then placed in an oven at 135 °C for 4 h to crosslink the PVA fibers.

Preparation of Au Seeds. The Au seed particles were prepared using a 7.75 mL aqueous growth solution containing 0.1 M CTAB and 3.23 × 10$^{-4}$ M HAuCl$_4$. To this growth solution, 600 μL of an ice-cold 0.01 M NaBH$_4$ was added.\textsuperscript{41} The resulting solution was stirred for 2 min and allowed to sit for 1 h before use.

Adsorption of Au Seeds on PVA Nanofibrous Mats. The above Au seeds solution was diluted by a factor of 4 using DIUF water and 0.5 mL of the diluted seeds solution was added to a 4 mL centrifugal tube. Next, added HCl solution to adjust the pH value of the diluted seed solution to 3, and then a piece of 2 cm × 2 cm water-stable PVA nanofibrous mat was placed in the diluted seeds solution for 4 h at 40 °C. Finally, the polymer nanofibrous mats were washed with DIUF water three times and stored in DIUF water in a centrifugal tube.

In Situ Growth of Au NPs on PVA Nanofibrous Mats. For the in situ growing of Au NPs on PVA nanofibrous mats, growth solutions were prepared that contained 4 mL of DIUF water, 800 μL of 0.2 M CTAB, and 100 μL of 0.02 M HAuCl$_4$. A 600 μL portion of 0.2 M ascorbic acid was then added to the growth solution and mixed thoroughly, turning the solution colorless. Next, a piece of 2 cm × 2 cm water-stable PVA nanofibrous mat with adsorbed Au seeds was added to the reaction vessel, and the solution was allowed to sit for 12 h at 40 °C, and then the polymer nanofibrous mats were washed with DIUF water three times and treated by the above reaction procedure again. Finally, the PVA nanofibrous mats with in situ growing Au NPs were stored in DIUF water in a centrifugal tube.

Preparation of Au NPs. Gold NPs were prepared according to a modified surfactant-directed seed-mediated approach. For Au NP synthesis, growth solutions were prepared that contained 4 mL of DIUF water, 800 μL of 0.1 M CTAB, and 100 μL of 0.01 M HAuCl$_4$. A 600 μL portion of 0.1 M ascorbic acid was then added to the growth solution and mixed thoroughly, turning the solution colorless. Next, the above seed solution was diluted by a factor of 10 using DIUF water, and 2.5 μL of the diluted seed solution was added to the reaction vessel, and the solution was allowed to sit for 12 h. The samples were washed with DIUF water three times by centrifugation (8000 rpm, 10 min). The precipitate was redispersed in DIUF water in a bottle.

Preparation of Standard Adsorbed PVA/Au NP Nanofibrous Mats. HCl solution was added into the above Au NP solution to adjust the pH value of the solution to 3, and then a piece of 2 cm × 2 cm water-stable PVA nanofibrous mat was placed in the Au NP solution for 4 h. Finally, the polymer composite nanofibrous mats were washed with DIUF water three times and stored in DIUF water in a centrifugal tube.

Catalytic Reduction of 4-Nitrophenol. The catalytic reduction of 4-nitrophenol was carried out in a quartz dish. 2 mL ice-cold 0.1 M NaBH$_4$ solution and 0.2 mL 0.02 M 4-nitrophenol were added into 17.8 mL DIUF water and stirred into a uniform solution. 2 cm × 2 cm PVA nanofibrous mats of Au seeds, in situ grown Au NPs, and adsorbed Au NPs were added into 2.5 mL of the above solution in a quartz dish. The catalytic reaction was in situ measured via an ultraviolet–visible spectrophotometer (UV2450, SHIMADZU) with the scanning wavelength ranging from 200 to 600 nm.
**Characterization.** The morphologies of polymer nanofibrous mats were observed by a XL-30 field-emission scanning electron microscope (Japanese, FEI). FTIR spectra were measured on a Nicolet NEXUS-470 infrared spectrophotometer. XRD patterns were measured by a Bruker D8 ADVANCE diffractometer at 40 kV and 40 mA with Cu Kα radiation. TGA was performed with a thermal analyzer, PerkinElmer TGA7 (ITK Co., Ltd.), at a heating rate of 10 °C·min⁻¹ and under nitrogen flow.

### ASSOCIATED CONTENT

#### Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b03436.

Experimental results of XRD, UV–vis spectra, TGA/DTG, FTIR spectra of water-stable PAN nanofibers and different composite PAN nanofibrous mats (PDF)

### AUTHOR INFORMATION

**Corresponding Authors**
*E-mail: xianghp@tongji.edu.cn (H.X.).
E-mail: chzhengjian@163.com (Z.C.).

**ORCID**
Hongping Xiang: 0000-0001-7255-5994
Xu Zhang: 0000-0002-6491-3234

**Notes**
The authors declare no competing financial interest.

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