Correlating Light Absorption with Various Nanostructure Geometries in Vertically Aligned Si Nanowire Arrays

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Supporting Information

ABSTRACT: Exploring the interactions between light and nanostructures contributes greatly to understanding and engineering nanoscale optical phenomena related to device performance. However, this often involves a compromise between uniformity and scalability. Given that optical properties, and especially light absorption, are governed by the geometries of nanostructures, this study investigated the correlation between light absorption and vertically aligned silicon nanowire (v-SiNW) arrays synthesized using KrF stepper lithography. Controlled growth experiments of the v-SiNW arrays indicated that their geometrical parameters strongly influence their corresponding light absorption properties, as confirmed by reflection measurements and finite difference time domain (FDTD) simulations, which showed specific wavelength-dependent absorption. Moreover, the extent of tapering the v-SiNW arrays was modulating to achieve broad absorption of visible light resulting from the gradual change in diameter and to optimize their optical characteristics, based on diameter-dependent nanophotonic resonance, for use in various applications.

KEYWORDS: light adsorption, vertically aligned silicon nanowire, KrF stepper lithography, selective wavelength-dependent absorption, tapering degree

Biological nanostructures have attracted the attention of many researchers owing to their distinct properties, including the antireflective property of moth eyes, photonic crystals of butterfly wings, the hydrophobicity-based self-cleaning ability of lotus leaves, and the fibrous geometry-based adhesion of gecko toes. With a view to mimic such phenomena, bioinspired fabrication allows us to better understand and imitate biological morphogenesis facilitating the development of various innovative industrial applications. For example, compared to conventional antireflective chemical coatings, black silicon, which has been inspired by the corneal surface of the moth eye and composed of silicon nanopillars smaller than the wavelength of visible light, has been found to be an effective broadband antireflection material over the visible wavelength range. The development of bioinspired fabrication techniques for enhancing the antireflection property is important to improve the performance of optoelectronic devices such as solar cells, displays, and photodetectors. Recently, many researchers have been interested in enhancing absorption to achieve competitive conversion efficiencies by means of nanostructures for photovoltaic cells with improving performance. However, such development often involves a compromise between theoretical and experimental data because of poor uniformity and scalability of the produced nanostructures. Thus, it has been difficult to precisely investigate the correlation between light absorption and nanostructure geometries due to randomized absorption resulting from structural heterogeneity.

Various nanostructured surfaces have been investigated to increase light absorption and decrease reflection of normally incident light, such as diffraction gratings, photonic crystals, and textured surfaces. These studies have shown that their antireflection behavior can be controlled by adjusting their geometrical parameters like periodicity, height, and shape, which change the refractive indices in the nanostructures. As an antireflective nanostructure, well-defined and vertically aligned Si nanowire (v-SiNW) arrays can be fabricated uniformly by means of a top-down approach using lithographic patterning followed by anisotropic etching. E-beam lithography can precisely control the surface topography on the order of nanometers. However, the resultant low quality of its physical properties, such as rough v-SiNW sidewall surfaces and the existence of small debris on the substrate caused by the etching process, render them unsuitable for effective light absorption.

In contrast, v-SiNW arrays with high aspect ratios and smooth surfaces can be grown by a bottom-up approach using chemical vapor deposition (CVD), which also allows control over key parameters such as the diameter, length, pitch,
growth direction, \(^26\) and shape. In addition, it is possible to obtain more complicated nanostructures, including those that are tapered, \(^27\) branched, \(^28\) or kinked \(^29\) nanowire superstructures. During the synthesis of SiNWs by CVD, growth follows a vapor−liquid−solid (VLS) mechanism assisted by a metal catalyst. \(^30\) The size and position of the metal catalyst directly influence the diameter and position of the SiNWs, respectively, \(^31\) and vertical growth of SiNWs is achieved by maintaining epitaxial interfaces between the SiNWs and the Si substrate.

Here, we investigated the correlation between light absorption and \(v\)-SiNW arrays with various types of geometries, which were grown by a Au catalyzed-VLS process using the CVD method, and their optical properties were characterized by reflection measurements. To precisely control their structural parameters (e.g., length, pitch, and diameter) over a large area, the Au catalyst was patterned as an array of Au nanodisks (AuNDs) with different pitches and heights using krypton fluoride (KrF) stepper lithography, which in turn caused variations in the pitch and volume of catalytic Au nanoparticles (AuNPs) during the VLS process, respectively. Furthermore, the optical properties of the highly tapered \(v\)-SiNW arrays for light absorption in a broad wavelength range were verified on the basis of diameter-dependent nanophotonic resonance. Finally, the correlation between light absorption and the \(v\)-SiNW arrays was predicted by performing finite-difference time-domain (FDTD) simulations.

**EXPERIMENTAL SECTION**

**Chemicals.** Silicon tetrachloride (SiCl\(_4\), 99.998%) and ammonium fluoride (NH\(_4\)F, \(~40\% \) in water) were purchased from Aldrich (St. Louis, MO, U.S.A.). Hydrofluoric acid (HF, 48–51% solution in water) was purchased from Acros (Pittsburgh, PA, U.S.A.). Acetone and isopropyl alcohol were purchased from Samchun (Seoul, South Korea). Si(111) wafers were purchased from LG Siltron (Seoul, South Korea).

**Preparation of the AuNP Pattern on the Substrate.** The procedure to create the AuND pattern on the Si(111) substrate is described below (and depicted in the Supporting Information, Figure S1a). The Si(111) wafer used as the substrate for growth of the \(v\)-SiNW arrays was first cleaned by washing with acetone and isopropyl alcohol several times. Then, a native oxide layer was deposited on the substrate by thermal annealing at 600 °C for 1 h in air. Subsequently, the prepared substrate was coated with a positive-type krypton fluoride (KrF) photoresist (PR, TDUR-P905) and mixed with a thinner (1-methoxy-2-propanol acetate) at a thickness of 400 nm by spin coating. The patterning process proceeded via KrF stepper lithography, and the exposed PR was removed through the developing process. A gold (Au) film (30 nm in thickness) was deposited by e-beam evaporation on the PR patterning substrate. By dipping the substrate in the PR removal reagent, the AuND pattern was left behind with a morphology similar to that of a disk. The AuND pattern shows a hole size of 400 nm and pitch size ranges from 2 to 8 \(\mu\)m. The reaction used to grow the \(v\)-SiNW arrays using the AuND pattern as the catalyst consisted of two steps (Figure S1b). First, the AuND pattern was annealed under 100 sccm Ar at 1000 °C for 2 h to assist the agglomeration of a single large Au nanoparticle (AuNP) for \(v\)-SiNW growth. After annealing, the morphology of the Au patterns changed from disks to spheres, resulting in the formation of AuNPs. Before the growth of the SiNWs, the native oxide layer underneath the AuNPs was removed by dipping the substrate in a buffered HF solution (9% of a 48–51% HF solution in water, 32% of a \(~40\%\) NH\(_4\)F solution in water) for 4 min. Finally, the \(v\)-SiNW arrays were synthesized from the AuNP pattern via the VLS mechanism.
Figure 2. Controlled growth of \( \nu \)-SiNW arrays. Tilt-view (20°) SEM images of \( \nu \)-SiNW arrays after VLS growth with growth times of (a) 5, (b) 7.5, and (c) 10 min; with pitches of (e) 4, (f) 6, and (g) 8 \( \mu \)m for 6 min, and with diameters of (i) 217, (j) 302, and (k) 443 \( \mu \)m for 9 min at 850 °C. The scale bars are 2 \( \mu \)m and the scale bars of the insets are 200 nm. Plots of the SiNW diameters and lengths as a function of (d) growth time, (h) pitch, and (l) AuND height. The uncertainty has been calculated as the standard deviation of the measured values.

**Synthesis of the SiNWs.** The \( \nu \)-SiNW arrays were synthesized by CVD in a 12 in. horizontal tube furnace (Lindberg/Blue M) equipped with a 1 in. diameter quartz tube (Figure S1c). The substrate covered with the AuNP pattern was placed at the center of the heating zone in the tube furnace. Before the experiment, the quartz tube was evacuated and flushed several times with \( \text{H}_2 \) gas (high purity, 99.999%) to minimize oxygen contamination. The second step for SiNW growth is shown in the reaction diagram of Supporting Information, Figure 1b. After loading the Si(111) substrate (covered with the AuNP pattern) in the center of the tube furnace, the temperature was increased to 850 °C at a rate of 10 °C/min. The \( \text{H}_2 \) gas used in the reaction played a dual role. First, \( \text{H}_2 \) gas is the carrier gas (C) that passes through the bubbler containing the SiCl\(_4\) solution, which is used as the Si precursor, and carries the precursor into the reactor. The other role of \( \text{H}_2 \) is as a diluent gas (D), which directly enters the reactor and adjusts the concentration of the Si precursor. Before SiNW growth, the diluent gas flow is set at 100 sccm during the ramping period; then, the carrier and diluent gas flows are set at 100 and 200 sccm, respectively, during the growth period. After a growth reaction duration of 10 min, the reactor was cooled until room temperature was reached.

**Characterization.** The surface morphologies of the synthesized \( \nu \)-SiNWs were characterized using field-emission scanning electron microscopy (FE-SEM, JEOL JSM-7600F) at an acceleration voltage of 15 kV. The monocristalline structure of SiNW was analyzed with a JEOL 2010 transmission electron microscope (TEM). The samples for TEM imaging were obtained by depositing a solution of SiNWs in ethanol (prepared by sonicating the as-synthesized substrate in ethanol) onto holey carbon 300 mesh copper grids (Structure Probe, Inc.).

**Reflection Measurements.** The experimental apparatus used for the reflection measurements of the \( \nu \)-SiNW array samples with white LED is described in Figure S5. The incident light was focused using an objective lens, and an iris controlled the intensity. The reflected light was also collected into a spectrometer through a beam splitter. The reflection spectra were acquired with a Si(111) wafer as the background.

**Optical Simulations.** The optical properties of the \( \nu \)-SiNW arrays were simulated by FDTD solvers supplied by Lumerical Solutions, Inc. Two-dimensional (yz-plane) models were designed by inputting the diameter, length, and shape of the SiNWs. Perfectly matched layer boundary conditions were imposed in the xy-plane and along the z-axis. A plane wave pulse source was introduced along the z-axis, and monitors were set to compute the electric field distributions in the SiNWs.

**RESULTS AND DISCUSSION**

**Geometry Controlled Growth of \( \nu \)-SiNW Arrays.** In order to investigate the optical properties of various types of nanostructures, we synthesized patterned \( \nu \)-SiNW arrays by CVD using AuNPs patterned by KrF stepper lithography, as described in Figure 1a. The AuND pattern size was reduced 4-fold compared with the original mask pattern (see Section S1 in the Supporting Information). The SiNW growth process using the AuND patterns as the metal catalyst is shown in Figure 1b, in which the diameter, height, and pitch of the AuND are represented as \( d \), \( h \), and \( P \), respectively. Before synthesis of the SiNWs, it was necessary to anneal the AuNDS, which consisted of several small particles (Figure 1c), to obtain one large AuNP (Figure 1d). By this annealing procedure, AuNPs with diameter \( D' \) were formed by the migration of Au atoms at high temperature. By introducing gas-phase Si precursors, \( \nu \)-SiNWs were obtained via the VLS mechanism (Figure 1e). The diameter and length of the \( \nu \)-SiNWs are denoted as \( D \) and \( L \), respectively (see Figure S1 in the Supporting Information for details of the SiNW growth). Since the SiNWs are formed by precipitation at the interface between the AuNP and the Si(111) substrate, the diameter (D) of the SiNWs can be controlled by the AuNP diameter (\( D' \)), which is influenced by the AuNP volume. The AuNP volume can in
turn be regulated by the height of the AuNPs when their diameter is uniform. Furthermore, the pitch of the SiNWs can be controlled by the AuND pitch as dictated by the mask pattern, and their length can be increased by increasing the growth time (Figure 1f).

The synthesized ν-SiNW arrays were characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) to evaluate their length, pitch, and diameter, as shown in Figures 2 and S2. TEM analysis shows that the SiNWs are monocrystalline and grow along the [111] direction, which proves epitaxial growth on the Si(111) substrate.34 Moreover, it is possible to achieve ν-SiNWs with hexagonal arrays over 1 cm × 1 cm area (Figure S3).

ν-SiNW arrays with growth times of 5, 7.5, and 10 min (Figure 2a–c) showed increases in both the diameter and length as the growth time increased (Figure 2d) because of the vapor–solid (VS)35 and VLS growth mechanisms,36 which affect their radial and axial growth, respectively. In addition, the pitch of the ν-SiNW arrays could be controlled by positioning the AuNDS with different pitches of 4, 6, and 8 μm consisting of 6.25 × 106, 2.78 × 106, and 1.56 × 106 AuNDS, respectively, in an area of 1 cm × 1 cm (Figure 2e–g). The ν-SiNWs are seen to have a nearly constant diameter but increase in length with increasing pitch (Figure 2h). Given that the same amount of Si precursor was used to grow the SiNWs at the same growth time regardless of their pitch, we attribute the aforementioned increase in length to the increased axial growth of the SiNWs, which was caused by the decreased density of the AuNDS with increasing pitch.

ν-SiNW arrays with diameters of 217, 302, and 443 nm (Figure 2i–k) can be obtained by controlling the height of the AuNDS (see Section S2 and Figure S4 in the Supporting Information). The experimental diameters of the SiNWs agreed well with the calculated values; however, the lengths of the SiNWs decreased with increasing SiNW diameter. Given that the required volumes of Si crystal are 3.70 × 1010, 6.70 × 1010, and 1.54 × 1010 nm3/μm for the unit growth of SiNWs with diameters of 217, 302, and 443 nm, respectively, the above decrease in length is quite reasonable, since a large amount of Si precursor is necessary for the unit growth of thick SiNWs.

Light absorption of ν-SiNW arrays with various geometries. The correlation between light absorption and ν-SiNW arrays with different lengths, pitches, and diameters was investigated using reflection measurements in the visible wavelength range (Figure S5).35 To ensure an appropriate comparison of the optical properties, ν-SiNWs with similar dimensions were used (Figure S6). The unique optical properties are demonstrated through reflection spectra showing the absorption resonance, whose position and intensity depend on the SiNW arrays geometrical parameters such as the length, pitch, and diameter.36 The pathway of the normally incident light is illustrated in Figure 3a.35 Light that does not interact with the NWs is reflected or transmitted at the bottom of the silicon/air interface, whereas light with specific wavelengths is absorbed along the NW. To evaluate the absorption resonance only from the perspective of the v-SiNW array geometries, total reflection was defined from the baseline using a bare Si wafer, which provide a measure of the absorption and transmission from the Si wafer that can be disregarded. The reflection spectra in Figure 3b show the absorption properties of ν-SiNW arrays with different lengths (P = 4 μm) shown in Figure 2a–c. The maximum absorption wavelengths (λmax) in the spectra were slightly red-shifted and the degree of absorption resonance increased with increasing SiNW length. In the case of L = 0 μm, the incident light was almost completely reflected and there was a small absorption resonance (~4%) caused by surface plasmon resonances (Figure S4a in the Supporting Information),37 which indicates that the AuNPs (including Au
Figure 4. Broad absorption resonance of tapered v-SiNW arrays. Tilt-view (20°) SEM images of v-SiNW arrays after VLS growth with different tapering degrees (rs) of (a) 0.9375 × 10⁻³, (b) 1.357 × 10⁻³, and (c) 1.882 × 10⁻³. The scale bars are 2 μm and the scale bars of the insets are 1 cm. Insets of (a–c) clearly show different colors of the as-grown v-SiNW arrays on the substrate with different SiNW shapes. (d) Reflection spectra of the v-SiNWs with (a) straight, (b) slightly tapered, and (c) highly tapered shapes. (e) Schematic illustration of diameter-dependent wavelength selective waveguiding systems with different shapes. Two-dimensional electric field distributions of various SiNWs with (f) straight, (g) slightly tapered, and (h) highly tapered shapes in the visible wavelength range (450–750 nm) showing diameter selectivity for wavelengths of (i) 475, (j) 576, and (k) 725 nm for the highly tapered SiNWs obtained by FDTD simulations.

alloys at the top of the SiNWs) had a small effect on the reflection measurements. Therefore, based on the diameter-dependence of the nanophotonic resonances, we attribute the aforementioned red-shift of λ_eff to the slight increase in the SiNW diameter from 200 to 220 nm owing to VS growth (Figure 2d). In addition, the above increase in absorption resonance with increasing SiNW length can be elucidated by the equation R = R_eff exp(2α_{eff}L). In this equation, R_eff and α_eff represent the reflection at the Si substrate interface and the effective absorption coefficient of the SiNW array, respectively, and L is the length of the NW. Given that the incident light is more likely absorbed along the NWs, we believe that the degree of absorption resonance increases with increasing SiNW length.

The reflection spectra for the v-SiNW arrays with different pitches (D = 200 nm and L = 10 μm; Figure S6a–c) are shown in Figure 3c. The fill fractions, defined as the cross sectional area of a single SiNW divided by the area of the unit cell, are 0.20, 0.09, and 0.05% for the v-SiNW arrays with pitches of 4, 6, and 8 μm, respectively. These values are less than 5%, which suggests that the v-SiNW arrays in our geometrical model are sparse, resulting in very minimal coupling between the SiNWs. The λ_max for the v-SiNW arrays with different pitches remained constant and hence are not strongly dependent on the pitch due to the sparse v-SiNW arrays. The extent of absorption resonance decreased with decreasing SiNW density, which were 6.25 × 10⁶, 2.78 × 10⁶, and 1.56 × 10⁶ NWs/cm² for the v-SiNW arrays with pitches of 4, 6, and 8 μm, respectively. Therefore, light coupling predominantly occurs in the localized radial resonant modes inside the v-SiNWs rather than as an absorption resonance from the v-SiNW array periodicity.

As shown in Figure 3d, unique optical properties were observed in the reflection spectra of the SiNWs with diameters of 217, 302, and 443 nm (P = 4 μm and L = 12 μm; Figure S6d–f), which demonstrated multiple absorption resonance for SiNWs with large diameters. These samples show at least one strong absorption resonance, with the absorption resonances increasing as the diameter increase. In addition, the corresponding fill fractions of the v-SiNW arrays are 0.20, 0.44, and 0.79% for arrays with diameters of 217, 302, and 443 nm, respectively, and the SiNWs in these sparse v-SiNW arrays rarely interact with each other. For thick SiNWs, oscillatory behavior in the reflection spectra was observed when higher order modes in the NW structure are considered (Figure 3a).

Therefore, we attribute these multiple absorption features of thick SiNWs to an increase in the radial resonant modes with a transverse component. In addition, we simulated the electric field distributions in v-SiNWs with diameters 200 nm (Figures 3e–g and S7), 300 nm (Figure S7), and 400 nm (Figure 3h–i) at specific wavelengths. To investigate the axial and radial waveguide modes, electrical field distributions in the v-SiNWs were calculated by FDTD simulations, including vertical (Figure 3) and horizontal cross-section views (Figure S8). The results show a specific absorption resonance of one strong absorption with higher electric field intensity along the v-SiNW axis for D = 200 nm, which suggests a diameter-dependent absorption resonance at specific wavelengths. Additionally, we calculated absorption
resonances for \( D = 300 \) and 400 nm, which correspond to the experimental results shown in Figure 3d and verify the diameter-dependence observed in the absorption resonance.

To achieve broad absorption resonance by controlling the SiNWs shape,\(^{14}\) we designed a tapered geometry of v-SiNWs containing various resonant wavelengths within a single NW\(^{40}\) and synthesized cylindrically tapered v-SiNW arrays with different tapering degrees (\( \sigma \)) by chemical vapor deposition. The tapering degrees of the v-SiNW arrays can be defined as \( \sigma = (D_B - D_T) / 2L \), where \( D_B \) and \( D_T \) represent the bottom and top diameters of the SiNW, respectively.\(^{77}\) According to this equation, the v-SiNWs \( \sigma \) values of (shown in Figure 4a–c) are 0.9375 \( \times \) 10\(^{-3} \), 13.57 \( \times \) 10\(^{-3} \), and 18.82 \( \times \) 10\(^{-3} \), respectively (see Section S3 in the Supporting Information for details on the synthesis of the tapered SiNWs). There is a distinct color difference of the tapered v-SiNW arrays with different \( \sigma \) values (inset of Figure 4a–c), with the highly tapered array being black in color.\(^{14}\)

Absorption Resonances in Tapered v-SiNW Arrays.

We investigated the light absorption of the v-SiNW arrays with different tapering degrees (\( P = 4 \) \( \mu \)m and \( L = 16 \) \( \mu \)m) by measuring their reflection spectra (Figures 4d and S9). As seen, the straight v-SiNW array shows a diameter-dependent absorption resonance,\(^{35}\) whereas the highly tapered v-SiNW arrays show broad absorption over the entire wavelength range.\(^{43}\) The tapered v-SiNWs consist of a continuous range of diameters along to the NW; hence, it is possible to absorb almost the entire wavelength range in the visible spectrum (Figure 4e).\(^{34}\) In addition, a gradual change in the v-SiNW morphology (e.g., to a tapered shape) can induce a gradual change in the refractive indexes across the air-to-NW axis, leading to a small mismatch in the refractive index between the substrate and NW.\(^{35}\) If the incident light is not normal, the v-SiNW arrays showed nearly perfect broad absorption up to 60\(^{\circ}\), which is higher than straight v-SiNW arrays (70\%).\(^{11}\) Therefore, we believe that the broadband light absorption resonance of the v-SiNW arrays can be enhanced by increasing the extent of SiNW tapering.

The two-dimensional electric field distributions inside the v-SiNWs with various tapering degrees (\( \sigma \)) and, hence, geometries, including straight (\( D_T = 200 \) nm and \( D_B = 200 \) nm), slightly tapered (\( D_T = 200 \) nm and \( D_B = 500 \) nm), and highly tapered (\( D_T = 200 \) nm and \( D_B = 800 \) nm), were calculated in the visible wavelength range from 450 to 750 nm by FDTD simulations (Figure 4f–h). The electric field intensity distributed inside the tapered SiNWs is higher than that inside the straight SiNWs because the variable diameter of the tapered SiNWs absorbs several wavelengths according to diameter-dependent light absorption resonance.\(^{34}\) In addition, the incident light propagated deeply and distributed close to the base of the tapered SiNWs, suggesting stronger penetration and higher resonance of absorbed light than that observed for the straight NWs.\(^{34}\)

We also investigated the absorption resonances of highly tapered SiNWs at three different wavelengths (475, 576, and 725 nm) using the FDTD simulations (Figure 4i–k). Careful comparison of their electric field distributions reveals that the absorption resonance in the tapered SiNWs occurs via light focusing in a certain area, the position of which is wavelength-dependent.\(^{40}\) In this way, shorter wavelengths (\( \lambda = 475 \) nm) are absorbed closer to the top of tapered SiNWs with small diameters (Figure 4i), whereas longer wavelengths (\( \lambda = 725 \) nm) are absorbed closer to their bottom with larger diameters (Figures 4k and S10 in the Supporting Information shows a comparison of straight SiNWs).

## CONCLUSION

In conclusion, understanding the correlation between light absorption and nanostructures is crucial to take advantage of desirable optical phenomena in nanophotonics, which is related to both device function and performance. We demonstrated that v-SiNW arrays with various geometries, such as length, pitch, and diameter, facilitate such an understanding by combining experimental reflection measurements and theoretical FDTD simulations. The v-SiNW arrays showed specific absorption resonances that were dependent on their geometrical parameters, especially diameter-dependent selectivity of the absorption resonance, which matched well with the FDTD simulations. Specifically, broad absorption in the visible light region can be achieved with tapered v-SiNW arrays. The diameters of the highly tapered v-SiNW arrays change gradually along the NW length; therefore, they can absorb light over the entire visible wavelength range. We believe that this research can greatly improve existing and future nanoscale optical applications, in addition to providing valuable insight into producing high-quality optoelectronic devices such as solar cells, displays, and photodetectors. Furthermore, the enhanced absorption of tapered v-SiNW arrays will be promising candidates for improving the efficiency of the photovoltaic technologies.

## ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsphotonics.7b01018.

Additional TEM and SEM images, correlation between the AuND height and AuNP diameter, FDTD simulations (PDF).

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**Author Contributions**

Y.-S.P. and J.S.L. designed the experiments and Y.-S.P. performed all experiments. Y.-S.P. and J.S.L wrote the paper. All authors analyzed the data, discussed the results, and commented on the manuscript.

**Notes**

The authors declare no competing financial interest.

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