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Introduction

Biopolymers hold great potential as key components in fabricating advanced hybrid materials owing to their sustainability and ubiquitous availability. Within this framework, nanocelluloses, a general term used for cellulose nanocrystals (CNCs) and cellulose nanofibers (CNFs), stand out as leading candidates due to their exceptional mechanical properties, distinctive physical properties, high crystalline order and chirality, along with their remarkable attributes such as cost-effectiveness and ease of processing into larger-scale materials. In addition, CNCs and CNFs enable the design of nanomaterials where high aspect ratio and interconnectedness play important roles.^{1–6} They have a multitude of applications, including

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Nanostructuring niobium oxides using polymer-grafted cellulose nanocrystals and nanofibers as sacrificial scaffolds[†]

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The unique one-dimensional structure and surface functionality of cellulose nanocrystals (CNCs) and cellulose nanofibers (CNFs) render them promising candidates for renewable nanomaterials. Here, we report the template-directed synthesis of highly polycrystalline Nb₂O₅ polymorphs using polymer brush-grafted CNCs and CNFs as sacrificial scaffolds. The scaffolds consisted of a CNC or CNF core, from which poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) brushes were grafted using surface-initiated atom transfer radical polymerization (SI-ATRP). The nanocellulose-*g*-PDMAEMA nanoreactors were complexed with a water-soluble Nb₂O₅ precursor, ammonium niobate(v) oxalate hydrate (NbOxA), *via* electrostatic interaction before they were heated to different temperatures to fabricate one-dimensional polycrystalline niobium pentoxides (*nc*-Nb₂O₅), orthorhombic Nb₂O₅ (T-Nb₂O₅) and *monoclinic* Nb₂O₅ (H-Nb₂O₅) were synthesized. Finally, we show that the polycrystalline *nc*-Nb₂O₅ and *nf*-Nb₂O₅ can function as photocatalysts for decomposing rhodamine B.

strengthening the mechanical properties of polymer films^{7,8} and developing advanced functional materials such as viscosity modifiers,⁹ stabilizers for Pickering emulsions,^{10–12} heterogeneous catalyst supports,¹³ antibacterial agents¹⁴ and antifouling/separation membranes.^{15,16}

The intrinsic high aspect ratios of CNCs and CNFs, with lateral dimensions at the nanoscale, spanning from nanometers to micrometers in length, along with tunable surface functionalities render them well suited for preparing 1D anisotropic hybrid nanomaterials. Specifically, nanocellulose surface modification with polymer brushes has proved to be a robust approach for preparing 1D core–shell particles that can function as nanoreactors to fabricate energy-storing, opto-electronic and catalytic nanomaterials.^{17–19}

Nanostructured metal oxides have been extensively researched as they hold great promises for a plethora of applications including, but not limited to, catalysis, sensing and energy storage.^{17,20,21} Among these, niobium pentoxide (Nb₂O₅) has garnered great attention due to its non-toxic nature and strong redox ability.^{22–24} Nb₂O₅ can be synthesized in several structural forms, including amorphous and crystalline pseudohexagonal phases (TT-Nb₂O₅), an orthorhombic phase (T-Nb₂O₅), and a monoclinic phase (H-Nb₂O₅), depending on factors such as temperature and processing time. This polymorphism underlies the versatility of Nb₂O₅ for

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applications, particularly as photocatalysts^{23,25,26} and energystoring materials.²⁷ While various morphologies have been reported for Nb₂O₅, such as nanobelts,²⁸ nanosheets^{29,30} and nanowires,³¹ the nanostructuring of Nb₂O₅ remains largely unexplored.

In this work, a series of one-dimensional, polycrystalline Nb₂O₅ samples with different crystalline phases were synthesized using soft-templating polymer-grafted nanocelluloses (Scheme 1). CNC-g-PDMAEMA and CNF-g-PDMAEMA were prepared through surface-initiated atom transfer radical polymerisation (SI-ATRP) of DMAEMA from their corresponding nanocellulose-based polyinitiator, CNC-Br or CNF-Br. A water-soluble niobium salt, ammonium niobate(v) oxalate dihydrate (NbOxA), was loaded into the polyelectrolyte PDMAEMA shell of CNC-g-PDMAEMA and CNF-g-PDMAEMA. By calcining the NbOxA-loaded nanocellulose polymer brushes at different temperatures, phase-pure pseudohexagonal, orthorhombic, and monoclinic Nb₂O₅ samples were fabricated. Subsequently, the photocatalytic activities of the various nanostructured oxides were tested.

Experimental section

Preparation of pristine CNFs

Purified sugarcane trash pulp was first produced using the method reported before.¹⁰ Washed and ground fibres were treated with a 2% (w/v) sodium hydroxide solution using a 10:1 solvent to trash ratio at 80 °C for two hours, followed by rinsing with 60 °C water. The alkali-treated fibres were then bleached twice using an acidic solution of 1% (w/v) sodium chlorite (pH = 4, the pH was decreased using glacial acetic acid) at 70 °C for one hour at a 30:1 solvent to fibre ratio. Cellulose nanofibers (CNFs) were prepared by passing a 0.7% (w/v) dispersion of bleached pulp through a high-pressure homogenizer (GEA Niro-Soavi Panda NS1001 L 2 K Homogenizer), for one pass at 400 bar, one pass at 800 bar and three passes at 1100 bar. For the production of H₂SO₄treated fibres, the bleached pulp was treated with a 40% (v/v) H₂SO₄ solution at 45 °C for 3 hours. After hydrolysis, the fibre dispersion was centrifuged for 15 minutes at 10000 rpm 4 times to remove the excess acid and dissolved extractables.



 $Scheme \ 1 \quad \text{Template-directed fabrication of Nb_2O_5 polymorphs using nanocellulose-based polymer brush templates.}$

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Subsequently, the resulting precipitate was dialysed in deionised water for one week until a pH value of 7 was achieved, and then re-suspended in deionised water using an ultrasonic probe (Q500 Sonicator, QSonica Newtown, United States) set at 25% amplitude, with a frequency of 20 kHz and an output energy of 500 W for 5 minutes.

Preparation of CNC-Br and CNF-Br polyinitiators

Pristine CNCs or CNFs (0.300 g, 1.85 mmol) were dispersed in DMF (300 mL) to achieve a homogeneous suspension, facilitated by sonication using a Soniclean 120T sonicator (240 V, 50/60 Hz) for 10 min. To the nanocellulose suspension, triethylamine (TEA, 0.562 g, 5.55 mol) and 4-dimethylaminopyridine (DMAP, 22.6 mg, 1.85×10^{-1} mmol) were added. The nanocellulose suspension was later cooled to 0 °C in an ice bath. After stirring for 30 minutes, α -bromoisobutyryl bromide (α -BiBB, 1.28 g, 5.55 mmol) was introduced dropwise into the cold nanocellulose suspension. The esterification reaction was allowed to proceed overnight. The resulting polvinitiator was purified through multiple cycles of centrifugation and redispersion in DMF (3×45 mL) and water (1×45 mL). The CNC-Br and CNF-Br polyinitiators were freeze-dried from milliQ water. The mass percentage of bromine (Br wt%) was determined using elemental analysis.

Preparation of CNC-g-PDMAEMA and CNF-g-PDMAEMA nanoreactors

The general procedure for the grafting-from SI-ATRP of the polymer brush-grafted nanocellulose is as follows. The CNC-Br polyinitiator (100 mg, $n(Br) = 2.5 \times 10^{-2}$ mmol), DMAEMA (1.05 mL, 6.2 mmol), PMDETA (13 mg, 7.5×10^{-2} mmol) and DMF (20 mL) were mixed. The reaction mixture was degassed by four freeze-pump-thaw cycles with N2. Subsequently, CuCl $(2.5 \text{ mg}, 2.5 \times 10^{-2} \text{ mmol})$ was introduced into the frozen reaction mixture under a gentle N2 flow. The SI-ATRP reaction was initiated at 65 °C after the final freeze-pump-thaw cycle. The polymerisation was terminated after 2 h by exposure to atmospheric air and cooling to room temperature. CNF-g-PDMAEMA was synthesized following the same procedure by substituting CNC-Br with CNF-Br. The resulting polymer-grafted nanocellulose was purified by several cycles of centrifugation and redispersion in DMF $(3 \times 45 \text{ mL})$ and water $(1 \times 45 \text{ mL})$ before they were freeze-dried from water. Monomer conversions for CNC-g-PDMAEMA and CNF-g-PDMAEMA were 10% and 8%, respectively, as determined from changes in the characteristic ¹H NMR integrals. The degrees of polymerisation (DP) were calculated to be PDMAEMA25 and PDMAEMA21, respectively, assuming all initiation sites were initiated during polymerisation. The same reaction was conducted using a sacrificial initiator, ethyl α -bromoisobutyrate (EBiB, 8.0 mg, 4.1 × 10⁻² mmol), to evaluate the control of polymerisation.

Synthesis of nanostructured Nb_2O_5 using polymer-grafted nanocelluloses

In a typical hybrid synthesis, the polymer-grafted nanocellulose, CNC-g-PDMAEMA (0.300 g, 1.45 mmol DMAEMA) or CNF-g-PDMAEMA (0.300 g, 0.94 mmol DMAEMA), was dispersed in water to obtain a homogeneous suspension (0.5 mg mL⁻¹) by sonication for 10 min. To facilitate NbOxA complexation with the PDMAEMA brush, the pH of the suspension was adjusted to pH 2 using 1.0 M HCl to increase the degree of DMAEMA protonation. The nanocellulose polymer brush suspensions were added dropwise to the NbOxA solution (2.2 g, 7.3×10^{-2} mmol/2.1 g, 7.1×10^{-2} mmol, 5 eq.). The infiltration process was allowed to proceed overnight. The as-synthesised nc-NbOxA and nf-NbOxA hybrids were purified by several cycles of centrifugation and redispersion in water $(3 \times 45 \text{ mL})$, in which the free NbOxA in the supernatant layer in each cycle was removed after centrifugation. The purified hybrids were subsequently freeze-dried from water before they were calcined in air at different controlled temperatures for either 2 hours (Nb₂O₅-550, Nb₂O₅-700, and Nb₂O₅-800) or 10 hours (Nb₂O₅-1100).

Synthesis of bulk pseudohexagonal Nb₂O₅

The NbOxA powder (100 mg, 3.3×10^{-1} mmol) was calcined at 550 °C for 2 hours.

Photocatalytic activity measurements

The photocatalytic activities of the nc-Nb₂O₅ and nf-Nb₂O₅ samples were assessed by degrading rhodamine B. The photocatalytic reactions were performed in a vial at room temperature. For each run, the Nb₂O₅ photocatalyst (15 mg) was added to the rhodamine B solution (30 mg L⁻¹, 20 mL) in milliQ water. The slurry was then placed in a Rayonet RPR-100 photochemical reactor under illumination with 16 UV-C lamps (maximum intensity at 254 nm). To obtain the adsorption–desorption equilibrium, the samples were stirred continuously in the dark for 15 minutes. Aliquots of the slurry (1.5 mL) were taken every 30 minutes and centrifuged to remove the catalyst prior to spectrometric analysis.

Results and discussion

SI-ATRP as a means to graft polymer chains from surfaces and particles is well established^{4,32,33} and has been successfully extended to nanocelluloses.^{6,34,35} The synthesis of CNC-g-PDMAEMA and CNF-g-PDMAEMA is illustrated in Scheme 1. Pristine CNCs and CNFs were prepared following a previously reported protocol (ESI, Fig. S1[†]).¹² It should be noted that nanocelluloses with a low aspect ratio (<100), typically obtained via an acid hydrolysis process, are commonly called "cellulose nanocrystals" (CNCs). In order to avoid confusion, the wood-derived commercial nanocellulose is called CNC and the high aspect ratio sugarcane acid hydrolyzed fibre is called CNF in this study. The hydroxyl groups on the surfaces of pristine CNCs and CNFs were esterified to ATRP initiator sites using α-BiBB, effectively functioning as 1D polyinitiators (CNC-Br and CNF-Br). The successful introduction of ATRP initiators onto the surfaces of pristine CNCs and CNFs was verified using FTIR, where the appearance of new stretching bands at 1723 cm⁻¹ (CNC-Br) and 1716 cm⁻¹ (CNF-Br) revealed the presence of carbonyl functionalities of the initiators. Elemental analysis of CNC-Br and CNF-Br elucidated bromine contents of 2% by mass, respectively, corresponding to a degree of substitution of approximately 12% on the nanocellulose surface (Fig. 2a).

Subsequently, PDMAEMA polymer side chains were grafted via SI-ATRP using the "grafting-from" approach. Using the sacrificial initiator approach,³⁶ the controlled character of the polymerisations were demonstrated by linear first-order kinetic plots $(\ln[M_0]/[M])$ against time (ESI, Fig. S2[†]). The corresponding monomer conversions progressed in a linear fashion from 0 to 4 hours. The resulting sacrificial PDMAEMAfree polymers also showed dispersities (D) of 1.12 and 1.13 (ESI, Fig. S3[†]). The ¹H NMR spectra of CNC-g-PDMAEMA and CNF-g-PDMAEMA with peak assignments are shown in Fig. 1b. Qualitative examination via FTIR confirmed the presence of PDMAEMA side chains in both nanocellulose-based polymer brushes (Fig. 1a). This confirmation was highlighted by a more prominent C=O stretching band and an additional band at 1440 cm⁻¹, suggestive of carbonyl and *N*-methyl functionalities of the PDMAEMA side chains.

In an acidic aqueous environment, the PDMAEMA side chain-enriched shell enveloping the nanocelluloses is positively charged, thereby orchestrating the complexation of negatively charged niobate precursors to yield their corresponding hybrids, nc-NbOxA (CNC-g-PDMAEMA@NbOxA) and nf-NbOxA (CNF-g-PDMAEMA@NbOxA). The selection preference for the water-soluble NbOxA stems from its superior stability in water relative to its alternative water-insoluble precursor, niobium pentachloride (NbCl₅), which undergoes rapid hydrolysis under aqueous conditions, leading to premature decomposition that forms Nb₂O₅.³⁷ Scanning electron microscopy (SEM) images of nc-NbOxA and nf-NbOxA are shown in Fig. S4.† Thermogravimetric analysis (TGA) was used to determine the weight content of Nb₂O₅ in both the nc-NbOxA and nf-NbOxA hybrids, indicating substantial incorporation of Nb_2O_5 within the nanocellulose brush templates (Fig. 1c), specifically, 44 wt% for nc-NbOxA and 42 wt% for nf-NbOxA. These weight contents are in line with their comparable side chain lengths, highlighting consistency among the samples.

Next, to generate nc-Nb₂O₅ and nf-Nb₂O₅ and study their crystalline phases as a function of calcination temperature, the nc-NbOxA and nf-NbOxA hybrids were subjected to controlled



Fig. 1 (a) FTIR spectra of pristine, ATRP initiator-functionalised and PDMAEMA-grafted CNFs and CNFs. The emergence of a carbonyl peak at 1728 cm⁻¹ validates the incorporation of ATRP initiators on CNC-Br and CNF-Br. The more pronounced peaks at 1728 cm⁻¹ and 1442 cm⁻¹ indicate the presence of PDMAEMA polymer side chains. (b) ¹H NMR spectral assignments for CNC-*g*-PDMAEMA₂₅ and CNF-*g*-PDMAEMA₂₁ recorded in CDCl₃. (c) TGA profiles of the hybrids of CNC-*g*-PDMAEMA₂₅ and CNF-*g*-PDMAEMA₂₁ in air.

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heating at temperatures of 550 °C, 700 °C, 800 °C and 1100 °C with the dual purpose of removing all organic materials (ESI, Fig. S5†) and inducing crystallisation towards metal oxides. Morphological changes among the samples were observed using SEM and TEM (Fig. 2). In addition, powder X-ray diffraction (PXRD) was employed to evaluate changes in the crystalline phases (Fig. 3), and their average crystallite sizes were estimated using the Scherrer equation.³⁸

At 550 °C, both *nc*-Nb₂O₅-550 and *nf*-Nb₂O₅-550 display a phase-pure pseudohexagonal Nb₂O₅ structure (Fig. 3a and b),

with an average particle diameter of 20 nm (Fig. 2a and b). Their crystallite sizes were estimated to be 25 nm and 23 nm, respectively, using the Scherrer equation. In the case of *nc*-Nb₂O₅-550, the particles show an arrangement reminiscent of 2D thin sheet-like structures, while in the *nf*-Nb₂O₅-550 sample, the particles appear to be fibre-like, which can be attributed to the fibrous nature inherent in CNFs. Upon adjusting the calcination temperature to 700 °C, a different crystal-line phase emerged, as evidenced in Fig. 3b, which shows phase-pure orthorhombic Nb₂O₅ (T-Nb₂O₅) structures. The



Fig. 2 SEM and TEM micrographs of *nc*-Nb₂O₅ and *nf*-Nb₂O₅ synthesised at (a and b) 550 °C, (c and d) 700 °C, (e and f) 800 °C and (g and h) 1100 °C.



Fig. 3 PXRD data (Cu K_{α} , $\lambda = 1.5406$ Å) for (a) nc-Nb₂O₅-550 and nf-Nb₂O₅-550, (b) nc-Nb₂O₅-700 and nf-Nb₂O₅-700, (c) nc-Nb₂O₅-800 and nf-Nb₂O₅-800 and (d) nc-Nb₂O₅-1100 and nf-Nb₂O₅-1100. The reference Bragg diffraction peaks of the corresponding Nb₂O₅ crystalline phases are shown at the bottom of each plot.

particles of orthorhombic nc-Nb₂O₅-700 and nf-Nb₂O₅-700 appear rod-like in shape (Fig. 2c and d). Despite their comparable morphologies, nf-Nb2O5-700 exhibits a larger average crystallite size of 56 nm compared to nc-Nb₂O₅-700 which has an average crystallite size of 34 nm. Increasing the calcination temperature to 800 °C did not lead to a transition in the crystalline phase of the Nb_2O_5 structure (Fig. 3c). However, the PXRD peaks of nc-Nb₂O₅-800 and nf-Nb₂O₅-800 narrowed due to increased growth in their crystallite sizes, which are calculated to be 68 nm and 94 nm. This was verified by SEM and TEM images (Fig. 2e and f), in which the longitudinally arranged particles of nc-Nb2O5-800 and nf-Nb2O5-800 have average diameters of 80 nm and 131 nm, respectively. It is well known that monoclinic Nb₂O₅ typically forms above 1000 °C. However, for our samples, further raising the temperature to 1100 °C only induced particle sintering, resulting in larger particles, while the crystalline phase remained in the orthorhombic structure (ESI, Fig. S6[†]). Therefore, the heating time was subsequently increased from 2 hours to 10 hours, which successfully yielded highly crystalline monoclinic Nb₂O₅

(Fig. 3d). In stark contrast to the previously discussed nc-Nb₂O₅ and nf-Nb₂O₅, prismatic crystals were obtained for nc-Nb₂O₅-1100 and nf-Nb₂O₅-1100 (Fig. 2g and h). nc-Nb₂O₅-1100 exhibits rod-like prismatic crystals that have not been reported in the literature for monoclinic Nb₂O₅. However, the prismatic crystals of monoclinic nf-Nb2O5-1100 are comparatively more compact, no longer inheriting the fibre-like morphology characteristic of CNFs. At high temperature, Nb₂O₅ often undergoes partial melting followed by recrystallisation and the molten Nb₂O₅ solidifies to form the prismatic crystals that we observed in the monoclinic Nb₂O₅ samples. Thus, the more intertwining fibrous network of nf-NbOxA likely facilitated the solidification of more molten Nb₂O₅ in the vicinity to form larger prismatic crystals. Despite reaching the micron range, both monoclinic nc-Nb₂O₅-1100 and nf-Nb₂O₅-1100 particles are more structured with a larger intergranular space compared to the monoclinic Nb₂O₅ synthesised without the nanocellulose templates (ESI, Fig. S7[†]).

The photocatalytic efficiencies of the various Nb_2O_5 samples were assessed by their ability to degrade rhodamine B

when exposed to UV irradiation. The concentrations of rhodamine B were determined using Beer's law, with absorbance readings at 554 nm recorded at 30-minute intervals over a span of 120 minutes (Fig. 4). The results in Fig. 4 show that solutions containing either nc-Nb₂O₅ or nf-Nb₂O₅ exhibit accelerated degradation rates compared to the control solution without a Nb₂O₅ catalyst and the solution containing bulk pseudohexagonal Nb₂O₅ synthesised at 550 °C (bulk Nb₂O₅-550)



Fig. 4 Absorbance spectral changes of rhodamine B solutions under UV light irradiation in the presence of *nc*-Nb₂O₅ or *nf*-Nb₂O₅ prepared at (a and b) 550 °C, (c and d) 700 °C, (e and f) 800 °C and (g and h) 1100 °C.

(ESI, Fig. S8[†]). In particular, among the different Nb₂O₅ samples studied, *nc*-Nb₂O₅ presents the highest photocatalytic activity, followed by nf-Nb₂O₅, achieving nearly complete rhodamine B degradation within 120 minutes, with degradation percentages of 98% and 96%, respectively. However, degradation percentages declined as the calcination temperatures rose to 700 °C and 800 °C and then to 1100 °C. For nc-Nb₂O₅, the degradation percentages decreased from 63% to 37% and further to 13%. Similarly, for nf-Nb₂O₅, the degradation percentages decreased from 51% to 21% and then to 16%. The representative decolouration of rhodamine B solutions is shown in Fig. S9,† comparing the colour change of the solutions with and without the nc-Nb₂O₅-550 and nf-Nb₂O₅-550 photocatalysts. The difference in the photocatalytic efficiencies among the nc-Nb₂O₅ and nf-Nb₂O₅ samples can be related to the crystal structure of the photocatalyst. Different Nb₂O₅ crystal structures can result in distinctive physicochemical properties.^{22,25,39} From Fig. 4 and Fig. S10,† we see that pseudohexagonal Nb₂O₅ (nc-Nb₂O₅-550 and nf-Nb₂O₅-550) shows the highest rhodamine B degradation, followed by orthorhombic Nb₂O₅ (*nc*-Nb₂O₅-700, *nf*-Nb₂O₅-700, *nc*-Nb₂O₅-800 and nf-Nb₂O₅-800) and monoclinic Nb₂O₅ (nc-Nb₂O₅-1100 and nf-Nb₂O₅-1100). Taken together, these results suggested that as the temperature rises, the crystal structure of Nb₂O₅ becomes more crystalline and organised. We believe that this change distorts the polyhedral structure of Nb₂O₅, decreasing their photocatalytic activity.25

Conclusions

We have demonstrated the use of nanocelluloses as sustainable biomaterials to structure Nb₂O₅ polymorphs using polymer-grafted cellulose nanocrystals and cellulose nanofibers. The fabrication of Nb₂O₅ polymorphs was achieved by simple electrostatic complexation between the NbOxA precursor and the PDMAEMA shell of the nanocellulose polymer templates. Upon heat treatment, one-dimensional Nb₂O₅ was synthesized, inheriting the interconnected structure of the nanocelluloses. Specifically, by controlling the calcination temperature, we produced phase-pure TT-Nb₂O₅, T-Nb₂O₅ and H-Nb₂O₅, with particle sizes ranging from the nanoscale to the microscale. In addition, we tested the photocatalytic ability of the as-synthesized nc-Nb₂O₅ and nf-Nb₂O₅ to break down rhodamine B under UV light. Specifically, pseudohexagonal nc-Nb₂O₅ and *nf*-Nb₂O₅ show the highest photocatalytic activity among the nc-Nb₂O₅ and nf-Nb₂O₅ samples tested which we attribute to having more active sites associated with lower crystallinity.

Author contributions

M. M. conceived the idea and supervised the research with C. D. L. Y. T. C and M. M. planned and developed the experimental setup. Y. T. C. performed all the experiments and ana-

lysed the data. S. S. A. and N. A. provided the pristine CNC and CNF materials. All the authors discussed the results. Y. T. C. and M. M. co-wrote the manuscript with inputs from all the authors. The authors declare no conflict of interest.

Data availability

The authors declare that the data supporting the findings of this study are available within the paper and its ESI.† Raw data files can be found on the OSF server using this read-only link: https://osf.io/wstby/?view_only=1ffef41b4daa4ee2b00d218629c8f938. Should any raw data files be needed in another format, they are available from the corresponding author upon reasonable request.

Conflicts of interest

There are no conflicts to declare.

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