Colloidal Antimony Sulfide Nanoparticles as a High-Performance Anode Material for Li-ion and Na-ion Batteries

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To maximize the anodic charge storage capacity of Li-ion and Na-ion batteries (LIBs and SIBs, respectively), the conversion–alloying-type Sb2S3 anode has attracted considerable interest because of its merits of a high theoretical capacity of 946 mAh g⁻¹ and a suitable anodic lithiation/delithiation voltage window of 0.1–2 V vs. Li⁺/Li. Recent advances in nanostructuring of the Sb2S3 anode provide an effective way of mitigating the challenges of structure conversion and volume expansion upon lithiation/sodiation that severely hinder the Sb2S3 cycling stability. In this context, we report uniformly sized colloidal Sb2S3 nanoparticles (NPs) as a model Sb2S3 anode material for LIBs and SIBs to investigate the effect of the primary particle size on the electrochemical performance of the Sb2S3 anode. We found that compared with microcrystalline Sb2S3, smaller ca. 20–25 nm and ca. 180–200 nm Sb2S3 NPs exhibit enhanced cycling stability as anode materials in both rechargeable LIBs and SIBs. Importantly, for the ca. 20–25 nm Sb2S3 NPs, a high initial Li-ion storage capacity of 742 mAh g⁻¹ was achieved at a current density of 2.4 A g⁻¹. At least 55% of this capacity was retained after 1200 cycles, which is among the most stable performance Sb2S3 anodes for LIBs.

Lithium-ion batteries (LIBs) are the most well-known rechargeable electrochemical energy storage devices, and they are a key component of electric mobility and portable electronics1–4. Sodium-ion batteries (SIBs) are conceptually similar, and they have attracted enormous attention in recent years because of the higher natural abundance of sodium and more favorable distribution of sodium reserves compared with lithium5–13. Although graphite is currently the main commercialized anode material for LIBs, its low theoretical charge storage capacity (372 mAh g⁻¹) limits its application in new generation batteries, requiring exploration of new electrode materials with higher capacity and stable cycling performance14. With respect to SIBs, the search for efficient Na-storing anodes is a high priority, because graphite shows low Na-ion capacities of 30–35 mAh g⁻¹15, while other carbonaceous materials have low tap densities and exhibit capacities of less than 300 mAh g⁻¹16. Additionally, the relatively low potential of carbon sodiation (~0 V vs. Na⁺/Na) leads to deposition of sodium metal on the carbon electrode surfaces, which may eventually result in compromised safety17.

Over the past decade, much attention has been focused on development of alternative anode materials for both LIBs and SIBs12. In particular, low-cost and environmentally benign Sb2S3 anodes have attracted great interest because of their high capacities and relatively low redox lithiation/sodiation potentials18–45. Theoretically, Sb2S3 can generate a specific capacity as high as 946 mAh g⁻¹ through conversion and alloying reactions (corresponding to 12 mol of lithium/sodium and electrons per formula unit). However, harnessing this storage potential of Sb2S3 is hindered by its poor capacity retention owing to the structural (conversion) and volume (alloying) changes during discharging/charging, which lead to mechanical disintegration of the electrodes and thus loss of electrical connectivity. These difficulties can be mitigated by nanostructuring, particularly when the active material is embedded in an elastic and conductive network that helps to enhance electronic transport and reduce the cycling instability caused by volumetric changes in the conversion–alloying-type anode material36,46,47. Specifically, in the last few years, extensive effort has focused on various forms of nanostructured Sb2S3, such as

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Sb$_2$S$_3$ nanowires$^{24,48–51}$, nanorods$^{45,52,53}$, nanoparticles (NPs)$^{37,54–57}$, nanocables$^{58}$, and Sb$_2$S$_3$/C nanocomposites$^{23}$, to maximize the anodic charge-storage capacity and improve the cycling performance. Notably, the electrochemical performance of highly uniform colloidal Sb$_2$S$_3$ NPs has not been reported. Such NPs are an ideal platform for studying the effects of the size and electrode morphology on the charge storage capacity and cycling stability of Sb$_2$S$_3$ anodes.

In this study, we synthesized uniformly sized colloidal Sb$_2$S$_3$ NPs whose size is tunable in 10–200 nm size range, which allowed us to comprehensively investigate the effect of the primary particle size on the electrochemical behaviour of Sb$_2$S$_3$ as the anode material for LIBs and SIBs. We assessed the pros and cons of nano-Sb$_2$S$_3$ anodes in comparison with commercial microcrystalline Sb$_2$S$_3$ (hereafter denoted bulk Sb$_2$S$_3$, Figure S1). We note that although synthesis of Sb$_2$S$_3$ NPs might be prohibitively expensive for practical application in commercial batteries, the insight gained from using such precisely tunable model NPs can guide development of Sb$_2$S$_3$ anodes for both LIBs and SIBs. We found that at current rates of 0.3–12 A g$^{-1}$, the Li-ion storage capacities for anodes composed of ca. 20–25 nm (1055–608 mAh g$^{-1}$) and ca. 180–200 nm Sb$_2$S$_3$ (970–574 mAh g$^{-1}$) were significantly higher than for their bulk counterpart (683–418 mAh g$^{-1}$). For Na-ion storage, the capacities of nano-Sb$_2$S$_3$ and bulk Sb$_2$S$_3$ anodes were similar. Regarding the cycling stability, the major finding was that nano-Sb$_2$S$_3$ exhibited significantly higher capacity retention for both Li-ion and Na-ion storage than bulk Sb$_2$S$_3$. Notably, unprecedented Li-ion capacity retention of 55% was achieved for ca. 20–25 nm Sb$_2$S$_3$ NPs at a current density of 2.4 A g$^{-1}$ after 1200 cycles.

**Results and Discussion**

The general synthetic route for preparation of ca. 20–25 nm amorphous antimony sulfide NPs using octadecene (ODE) as a solvent in the presence of oleylamine (OAm) as a surface capping ligand is shown in Fig. 1a. In a typical synthesis, the Sb$_2$S$_3$ NPs were synthesized by the hot-injection technique using antimony(III) chloride and bis(trimethylsilyl)sulfide ((TMS)$_2$S) as the antimony and sulfur precursors, respectively. After injection of (TMS)$_2$S into the SbCl$_3$/ODE mixture, the color of the reaction solution rapidly changed to red-orange. The reaction temperature was maintained at 120 °C for 15 min. Transmission electron microscopy (TEM) and X-ray diffraction (XRD) analysis confirmed formation of amorphous spherical ca. 20–25 nm Sb$_2$S$_3$ NPs with a narrow size distribution (Figs. 1c and S2a). A longer reaction time of 30 min resulted in formation of ca. 1.5–2.0 μm long crystalline Sb$_2$S$_3$ nanorods with diameters of ca. 150–200 nm (Figure S3). When the (TMS)$_2$S solution was injected at 100 °C and maintained at this temperature for 15 min, ca. 8–10 nm amorphous Sb$_2$S$_3$ NPs were obtained (Figure S4). Scanning transmission electron microscopy with energy-dispersive X-ray spectroscopy (STEM-EDXS) measurements of the as-synthesized ca. 20–25 nm Sb$_2$S$_3$ NPs revealed that Sb and S were homogeneously distributed throughout each NP (Fig. 1e,f,g,h). From scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDXS) analysis, the atomic ratio of Sb, S and O was about 1:1.4:0.1 (Figure S5). The presence of detectable oxygen in the EDS spectrum could be because of oxidation of the NPs during synthesis, cleaning, or preparation of the specimen. Notably, similar synthesis of Sb$_2$S$_3$ NPs was reported...
by Bakr et al.\textsuperscript{59} using SbCl\textsubscript{3} and (TMS)\textsubscript{2}S in ODE with oleic acid (OAc) as a ligand. The synthesis yielded relatively polydisperse ca. 30–50 nm Sb\textsubscript{2}S\textsubscript{3} NPs with a chain-like structure. In our synthesis, the use of the OAm ligand resulted in slower reaction kinetics, causing more homogeneous nucleation and growth of Sb\textsubscript{2}S\textsubscript{3} NPs in comparison with the OAc ligand.

Larger Sb\textsubscript{2}S\textsubscript{3} NPs of approximately ca. 180–200 nm were synthesized in a similar way to the ca. 20–25 nm Sb\textsubscript{2}S\textsubscript{3} NPs by replacing the antimony(III) chloride precursor and OAm ligand with antimony acetate and OAc, respectively (Figs. 1b,d and S2b, S6; for details see the experimental section). By changing of the (TMS)\textsubscript{2}S sulfur source to S/OAm (elemental sulfur dissolved in OAm), crystalline Sb\textsubscript{2}S\textsubscript{3} nanoplates were obtained (Figure S7).

The galvanostatic cycling measurements of the Sb\textsubscript{2}S\textsubscript{3} NPs are summarized in Figs. 2 and 3. For electrochemical testing, the Sb\textsubscript{2}S\textsubscript{3} NPs were treated with a 1 M solution of hydrazine in acetonitrile for 2 h\textsuperscript{60,61}. The untreated NPs gave no operational electrodes because of the isolating long-chain capping molecules surrounding the as-synthesized Sb\textsubscript{2}S\textsubscript{3} NPs. In addition to the effect of the active material, the charge storage capacity of the electrode strongly depends on the electrode formulation (the origin and amounts of the binder and conductive additive), electrode thickness, porosity, temperature, electrolyte, and so forth. Therefore, with the aim of distinguishing the size effect from the other factors, the following experimental parameters were fixed for all of the electrodes: (i) the choice and mass fractions of the binder and carbon black and (ii) the electrolyte composition. All of the electrodes contained 64 wt\% of the active material, 15 wt\% carboxymethylcellulose as a binder, and 21 wt\% carbon black as a conductive additive. The electrochemical tests were performed in Li-ion or Na-ion half-cells with elemental lithium or sodium acting as both the counter and reference electrodes, respectively. Further details of electrode preparation and assembly of the batteries are given in the Supporting Information.

The cyclic voltammetry (CV) curves of electrodes composed of ca. 20–25 nm and ca. 180–200 nm Sb\textsubscript{2}S\textsubscript{3} NPs (hereafter denoted small and large Sb\textsubscript{2}S\textsubscript{3} NPs, respectively) measured in Li-ion electrolyte at a scan rate of 1 mV s\textsuperscript{−1} are shown in Fig. 2a. In the first cathodic cycle, the broad peak at about 1.2–1.4 V vs. Li\textsuperscript{+}/Li can be attributed to formation of a solid electrolyte interphase (SEI) layer and the conversion reaction of Sb\textsubscript{2}S\textsubscript{3} NPs (Sb\textsubscript{2}S\textsubscript{3} + 6Li\textsuperscript{+} + 6e\textsuperscript{−} → 2Sb + 3Li\textsubscript{2}S). Upon further lithiation, two reduction peaks at 0.7 and 0.5 V vs. Li\textsuperscript{+}/Li appeared, which are ascribed to formation of Li\textsubscript{2}Sb and Li\textsubscript{3}Sb alloys, respectively. In the reverse scan, the Sb\textsubscript{2}S\textsubscript{3} electrode
showed two peaks at 1 and 1.9 V, which are associated with delithiation of the Li₃Sb alloy phase following formation of Sb₂S₃. The discharge voltage profiles of the Sb₂S₃ NPs are shown in Fig. 2b. The profiles of the Sb₂S₃ NPs are similar to the CV curves, showing two-step reduction of Sb₂S₃ eventually resulting in formation of metallic Sb (conversion reaction, voltage range 1.7–1.2 V \text{vs} \ Li^+/Li) and the Li₃Sb alloy (alloying reaction, voltage range 0.4–1.0 V \text{vs} \ Li^+/Li). As follows from CV measurements, alloying of Sb in bulk Sb₂S₃, large and small Sb₂S₃ NPs takes place differently. In the bulk system, it appears that the lithiation proceeds through the direct formation of Li₃Sb alloy. On the contrary, in the case of Sb₂S₃ NPs, the lithiation takes place through sequential formation of Li₂Sb and Li₃Sb alloys, respectively.

The Li-ion discharge capacities of Sb₂S₃ anodes composed of small Sb₂S₃ NPs, large Sb₂S₃ NPs, and microcrystalline Sb₂S₃ at charge/discharge current densities of 0.3–12 A g⁻¹ are shown in Fig. 2c. At a low current density of 0.3 A g⁻¹, the anodes composed of small and large Sb₂S₃ NPs exhibited theoretical capacities of about 1000 mAh g⁻¹ with Coulombic efficiency of 97%–98% (Figure S10). The capacity retention values of the Sb₂S₃ anodes composed of small and large Sb₂S₃ NPs were 60% and 61% at 12 A g⁻¹, respectively. The slightly higher discharge capacity of the anode composed of small Sb₂S₃ NPs during the first few cycles at a low current density of 0.3 A g⁻¹ can be attributed to formation and stabilization of a SEI layer. For the bulk Sb₂S₃ system, the anode composed of microparticles of Sb₂S₃ exhibited only 60% of the theoretical capacity at 0.3 A g⁻¹, but it retained 57% of its initial charge-storage capacity at high current density, similar to the Sb₂S₃ NP anodes. Regarding the cycling performance, the Sb₂S₃ NP and bulk Sb₂S₃ anodes showed stable capacities for the first 200 cycles (Fig. 2d). However, upon prolonged cycling, the capacity of the bulk Sb₂S₃ anode gradually decreased.

The capacities of the anodes composed of small and large Sb₂S₃ NPs were stable for 1200 cycles. The anode composed of small Sb₂S₃ NPs systematically showed at least 5% higher capacity than the anode composed of large NPs. In all cases, the Coulombic efficiency was relatively low for the initial 10–20 cycles (95%–97%), but it then increased to more than 99% upon cycling. As mentioned above, the higher cycling stability of the anode composed of Sb₂S₃ NPs compared with that composed of bulk Sb₂S₃ probably originates from the lower kinetic constraints of nanomaterials for conversion and alloying reactions. For instance, for alloying anode materials.
(e.g., Sn, Si, and Ge), several studies have demonstrated the existence of a critical size of the particles below which they do not fracture.\(^\text{22,23}\) Furthermore, we speculate that the amorphicity of the Sb\(_2\)S\(_3\) NPs aids in isotropic expansion/contraction upon their lithiation/delithiation, eventually resulting in reduction of the amount of anisotropic mechanical stress within the electrode.

In Na-ion cells with Sb\(_2\)S\(_3\) NP electrodes, CV measurements showed three peaks at ca. 1, 0.7, and 0.27 V associated with formation of a SEI layer/intercalation of sodium ions into Sb\(_2\)S\(_3\), conversion, and alloying reactions, respectively (Fig. 3a, see Figure S12 for details). Upon desodiation (reverse scan), the Sb\(_2\)S\(_3\) electrode showed two peaks at 0.8 and 1.3 V vs. Na\(^+\)/Na, which are associated with dealloying of Sb and recombination of the Sb\(_2\)S\(_3\) phase. The third peak at a higher potential of 1.6 V can be assigned to desinsertion of Na\(^+\) ions from Sb\(_2\)S\(_3\). In general, the CV curves (Fig. 3a) and shape of the voltage profiles (Fig. 3b) suggest conversion and the alloying mechanism of sodiation of the Sb\(_2\)S\(_3\) NPs in the voltage ranges 0.6–1 V and 0.1–0.5 V vs. Na\(^+\)/Na, respectively.

In Na-ion cells, the nano-Sb\(_2\)S\(_3\) and bulk Sb\(_2\)S\(_3\) electrodes showed similar charge storage capacities of ~580–620 mAh g\(^{-1}\) at current densities of 0.3–1.2 A g\(^{-1}\) (Fig. 3c). The similar capacities of the nano-Sb\(_2\)S\(_3\) and bulk Sb\(_2\)S\(_3\) anodes in Na-ion cells can be explained by the presence of an amorphous surface oxide shell on the Sb\(_2\)S\(_3\) NPs (see Figures S5 and S6 for EDS spectra). This leads to formation of Na\(_2\)O, eventually resulting in irreversible capacity loss in the first discharge cycle. The much smaller differences among the capacities of the electrodes composed of small Sb\(_2\)S\(_3\) NPs, large Sb\(_2\)S\(_3\) NPs, and bulk Sb\(_2\)S\(_3\) for Na-ion cells than Li-ion cells can be explained by the different properties of Li\(_2\)O and Na\(_2\)O. We suspect that Li\(_2\)O acts as a relatively benign impurity covering the Sb\(_2\)S\(_3\) NPs because of its high Li-ion conductivity. In contrast, Na\(_2\)O is a much poorer Na\(^+\) conductor, leading to exclusion of some Sb\(_2\)S\(_3\) NPs from the reversible charge/discharge storage capacity. The results of stability tests for 500 cycles at a high current density of 2.4 A g\(^{-1}\) are shown in Fig. 3d. In general, the charge storage capacities were consistently higher for nano-Sb\(_2\)S\(_3\) than bulk Sb\(_2\)S\(_3\), although the capacities remained stable for only about 50 and 100 cycles for bulk Sb\(_2\)S\(_3\) and nano-Sb\(_2\)S\(_3\), respectively.

Conclusions

In summary, we have reported facile colloidal synthesis of highly uniform colloidal Sb\(_2\)S\(_3\) NPs with mean particle sizes in the ranges ca. 20–25 nm and ca. 180–200 nm. The underlying chemistry is based on the reaction of antimony(III) chloride/acetate and (TMS)\(_2\)S in ODE using OAm/OAc as a coordinating ligand at high temperature of 120/130 °C for small/large Sb\(_2\)S\(_3\) NPs. Both the small and large Sb\(_2\)S\(_3\) NPs showed electrochemical cyclic stability superior to that of bulk Sb\(_2\)S\(_3\) in both LIBs and NIBs. In particular, the small NPs exhibited high retention of the capacity upon extended cycling, losing only 55% of their initial capacity over 1200 cycles at a high density of 2.4 A g\(^{-1}\).

Methods

Chemicals. Oleic acid (OAc, Sigma-Aldrich), oleylamine (OAm, Acros, 80–90%), octadecene (Sigma-Aldrich), octadecene (ODE, Sigma-Aldrich), antimony (III) chloride (ABCR), antimony (III) acetate (Sigma-Aldrich), bis[trimethylsilyl]sulfide (Sigma-Aldrich), chloroform and acetone were used as received.

Synthesis of ~20–25 nm spherical amorphous NPs. In a typical synthesis 0.5 mL oleylamine, OAm, (Acros, 80–90%) and 4 mL octadecene (ODE) were loaded into 25-mL flask and dried at 100 °C for 30 min. Then, 114 mg (0.5 mmol) SbCl\(_3\) were added to the flask under argon. The reaction mixture was heated up to 120 °C and 0.5 mmol bis[trimethylsilyl]sulfide (100 μL, (TMS)\(_2\)S) in 2 mL dried ODE was then injected into the reaction flask. The color of the solution has changed to orange-red. In 15 min reaction mixture was cooled down to room temperature and washed 2 times by chloroform/acetone and separated by centrifugation. After washing step, Sb\(_2\)S\(_3\) NPs were re-dispersed in oleic acid (OAc)/chloroform mixture (50 μL OAc in 2–3 mL chloroform) and stored under ambient condition. Injection of (TMS)\(_2\)S solution at 100 °C and maintaining this temperature through the reaction for 15 min leads to formation of 8–10 nm amorphous Sb\(_2\)S\(_3\) NPs. Injection of (TMS)\(_2\)S solution at 170–180 °C and maintaining this temperature through the reaction for 3–5 min leads to formation of micrometer-sized crystalline rods (Figure S3a). Powder XRD of as-prepared NRs shows that they are highly crystalline and their XRD pattern corresponds to stibnite phase of antimony sulfide (Figure S3b). Crystalline rods could be also obtained at 120 °C in case of longer growth time. In 30 min after injection of (TMS)\(_2\)S the orange color of the reaction mixture started to change into a gray-black.

Synthesis of ~180–200 nm spherical amorphous NPs. In a typical synthesis, 2.5 mL OAc, 2.5 mL ODE and 0.5 mmol antimony (III) acetate were loaded into 25-mL flask and dried at 100 °C for 30 min. The reaction mixture was heated up to 130 °C under argon. At 130 °C, 0.375 mmol (TMS)\(_2\)S (78 μL) in 2.5 mL dried ODE was then injected into the reaction flask. The color of the solution has changed to orange-red. In 3–5 min, reaction mixture was cooled down to room temperature and final product was washed 2 times by chloroform/acetone and separated by centrifugation. After washing Sb\(_2\)S\(_3\) NPs were re-dispersed in OAc/chloroform mixture (50 μL OAc in 2–3 mL chloroform) and stored under ambient condition.

Synthesis of thin crystalline Sb\(_2\)S\(_3\) nanoplatelets. We have found that another sulfur source such as elemental sulfur in OAm effects on the morphology of Sb\(_2\)S\(_3\) NPs yielding the formation of thin crystalline Sb\(_2\)S\(_3\) nanoplatelets (Figure S7a). Their average size is approximately several hundred nanometers and their XRD pattern suggest that they are highly crystalline (Figure S7b). In a typical synthesis, 5 mL OAm (Acros) and 0.25 mmol (57 mg) antimony (III) chloride were loaded into 25-mL flask and dried at 80 °C for 30 min. The reaction mixture was heated up to 110 °C under argon. At 110 °C, 1 mmol (32 mg) sulfur dissolved in 2 mL OAm (Acros) was then injected into the reaction flask. Then temperature of reaction mixture was increased to 180 °C and kept for 15 min. The final product was washed 2 times by chloroform/acetone and separated by centrifugation. Sb\(_2\)S\(_3\) nanoplatelets were also synthesized for 30 min at 210 °C, yielding yellow crystalline rods (Figure S8a).
were re-dispersed in OA/3-chlorofor mixture (50 μL OAc in 2–3 mL chloroform) and stored under ambient condition.

**Battery components.** Carbon black (Super C65, TIMCAL), carboxymethyl cellulose (CMC, Grade: 2200, Lot No. B1118282, Daicel Fine Chem Ltd.), NaClO4 (98%, Alfa Aesar, additionally dried), propylene carbonate (BASF, battery grade), 4-fluoro-1,3-dioxolan-2-one (FEC, Hisunny Chemical, battery grade), 1 M solution of LiPF6 in ethylene carbonate/dimethyl carbonate (EC/DMC, Novolyte, Celgard separator (Celgard 2400, 25 μm microporous monolayer polypropylene membrane, Celgard Inc. USA), glass microfiber separator (GF/D, Cat No. 1823–257, Whatman, Al foil (MTI Corporation), Na foil (Sigma-Aldrich), Li foil (MTI Corp.), Sb2S3 (99.995%, Sigma Aldrich), Coin-type cells (Hohnsen Corp., Japan).

**Electrochemical characterization of antimony sulfide.** Coin-type cells were assembled in an argon-filled glove box (O2 < 1 ppm, H2O < 1 ppm) using one layer separator (glass fiber) for NIBs and two layers of separators (Celgard and glass fiber) for LIBs. Elemental sodium or lithium served as both reference and counter electrodes. As electrolyte 1 M NaClO4 in PC was used for Na-ion batteries and 1 M LiPF6 in EC:DMC (1:1 by wt.) for Li-ion batteries. To improve cycling stability 3% of FEC were added to both electrolytes. Electrochemical measurements were performed using constant current mode for both, charge and discharge steps between 0.01–2.5 V for both Na and Li-ion batteries on a MPG2 multi-channel workstation (Bio-Logic).

**Materials characterization.** TEM samples were prepared by dropping a solution of Sb2S3 NPs onto standard amorphous carbon-coated TEM grids. TEM images were recorded using JEOL JEM-2200FS microscope operated at 200 kV. STEM images and EDXS spectrum were collected on FEI Talos F200X operated at 200 kV and equipped with Super-X EDS system (4 detector configuration). Scanning electron microscopy (SEM) measurements were done on a Quanta 200 F microscope (Thermo Fisher Scientific) operated at an acceleration voltage 20 kV. 45 kV. Energy-dispersive X-ray spectroscopy (EDXS) was performed with an Octane SDD detector (EDAX (Ametec)) attached to the microscope column. Powder X-ray diffraction pattern was collected with STOE STADIP powder diffractometer.

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Author contributions
The manuscript was written through contributions of all authors. K.V.K., M.I.B. and M.V.K. designed the experimental work. M.I.B. synthesized Sb$_2$S$_3$ NPs and performed XRD, TEM, and STEM-EDXS measurements. K.V.K. conducted all electrochemical measurements reported in the paper. K.V.K. and M.V.K. wrote the paper. All authors have given approval to the final version of the manuscript.

Competing interests
The authors declare no competing interests.

Additional information
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