Pushing PbS/Metal-Halide-Perovskite Core/Epitaxial-Ligand-Shell Nanocrystal Photodetectors beyond 3 μm Wavelength

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PbS nanocrystals have been proven to be highly suitable for photodetector fabrication by facile solution processing, and have been successfully tested as photosensitive material in imaging devices. So far, their spectral response has been blue-shifted with respect to that of commercial bulk PbS detectors, due to quantum confinement in nanostructures smaller than the exciton Bohr radius. Here, a PbS nanocrystal synthesis approach is introduced, allowing to surpass this limit, and thus to push the cut-off wavelength to the value of the bulk material. To avoid self-absorbance from ligands within the spectral range of the photoconducting signal, an all inorganic metal-halide-perovskite is applied to form a semiconducting ligand shell. The photoconductors, which are provided from a single drop, do not only show a record in long wavelength operation for PbS nanocrystal detectors but also a room temperature detectivity $> 10^{10}$ Jones, which is on par with that of commercial bulk PbS detectors. Combining these properties might find application in future low-cost infrared imagers, which are currently still elusive due to their high prices.

1. Introduction

Photoconducting materials are widely used in daily life for instance as major components in cameras integrated into smartphones and webcams. While such imaging devices in the visible region experiences radical economic growth,^[1] cameras operating at longer wavelengths that are of considerable significance for medical applications,^[2] night-time surveillance,^[3] defense,^[4] and environmental monitoring^[5] are in limited use

due to their high cost. The predominance of visible imaging technologies has been provided by undisputed small feature sizes and thus high integration densities possible with silicon electronics, in addition to low costs as result of mass production. Cameras operating in the infrared spectral region require alternative semiconductors, integrated onto silicon based CMOS chips for read out and processing of signals.^[6,7] Traditionally, epitaxially grown III–V photodiodes or Hg containing II–VI single crystals are in use for that purpose, which require a cumbersome microbump soldering procedure^[8] in the final stage of production. Infrared imagers have additional disadvantages such as the necessity of cooling the photosensitive chips to obtain high sensitivity at long wavelengths.^[9] Colloidal nanocrystals offer an attractive

alternative, despite facile and low temperature processing from solution they provide outstanding optoelectronic properties.^[10] PbS nanocrystals in particular have demonstrated exemplary figures of merit for photodetection in a variety of architectures^[11] and PbS nanocrystal-CMOS hybrid imagers have been demonstrated recently in literature with photosensitivity up to 1840 nm.^[12] A challenge as yet remains to obtain operation at longer wavelengths. While record values with respect to operation wavelengths have been achieved with Hg-chalcogenide nanocrystals,^[13–16] these materials are strongly restricted substances in electronic devices due to safety regulations.^[17] Lead chalcogenides, PbSe and PbS, have thus far demonstrated photoconductors with reliable operation up to wavelengths of 2400^[18] and 2250 nm^[19] respectively (cut off is defined as the wavelength where responsivity drops to 20% of its peak value, $\lambda_{0.2}$), however, with rather modest detectivity at this limit. Here we show significant improvements in these respects, by (i) introducing a synthetic route to obtain PbS nanocrystals with controlled sizes between ≈ 6 and ≈ 170 nm, (ii) introducing an epitaxial metal-halide perovskite ligand shell with no absorption bands arising from organic ligands within the desired photoresponsivity region, and (iii) demonstrating photoconductivity properties from nanocrystal films that are similar to those of a bulk material with detector response at wavelengths over 3000 nm. Critically, these photoconductive

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devices are prepared via a drop and dry procedure with no high temperature steps or aggressive ligand exchange procedures required, making them ideal candidates for integration onto delicate read out electronics, as is used for imaging devices.

2. Results and Discussion

2.1. Nanocrystal Synthesis—Shape and Size Control

The nanocrystals synthesis performed in this work was developed by taking into account two successful approaches reported in literature. (i) The most commonly used synthesis by Hines and Scholes^[20] that makes use of bis(trimethylsilyl) sulfide and lead oleate as precursors, where elegant size tuning is enabled by controlled excess of oleic acid concentration and growth temperature. (ii) The more recently introduced syntheses by Hendricks et al.^[21] who proposed a library of substituted thioureas as sulfur precursors of varying reactivity that can be used for size tuning. With both approaches, highly monodisperse PbS nanocrystals have been demonstrated, however all batches which were obtained based on these syntheses provided nanocrystals with diameters well below the 18 nm excitonic Bohr radius of PbS.^[22–28] To obtain larger sizes, we

combined these two approaches by selecting a disubstituted thiourea compound as sulfur precursor and making use of size control by excess ligand content. According to Hendricks et al.^[21] the reactivity of the thiourea is related to the size and chemical nature of the selected side groups. Here we use oleyl, phenyl *N,N'*-substituted thiourea (**Figure 1a**), for which the large electron donating groups of the substituents reduce access to the reactive center of the thiourea molecule. The oleyl (C₁₈H₃₆) group used here is substantially larger than any substitution groups used by Hendricks et al.^[21] guaranteeing low reactivity. This slows down the monomer generation rate and thus nucleation rates, followed by growth enabled by a steady supply of monomers. The thiourea precursor was prepared by mixing phenyl isothiocyanate and oleylamine in octadecene (ODE) under nitrogen atmosphere. Nanocrystals were synthesized in octadecene by reacting Pb oleate at 135 °C with the disubstituted thiourea for 20 min. As oleate was used as ligand, its presence and concentration strongly affects the final nanocrystal size and shape.

A series of monodisperse samples was achieved at constant temperature (135 °C) by varying the concentration of oleic acid, between 1.5 and 3.5 mL (**Figure 1b**). The monodispersity of all these samples, for which values down to ±3% were obtained, is underlined by their tendency to form ordered superstructures.

Figure 1. a) Synthetic route to large PbS nanocrystals. b) FE-SEM images of typical series of syntheses carried out using disubstituted thiourea as sulfur precursor with corresponding c) statistical size dispersion and d) photoconductivity curves after ligand exchange. No size selective precipitation was carried out prior to SEM or photoconductivity spectra.

The oleic acid concentration behave here as the tuning knob for size control, with which the mean size of the nanocrystals characteristic dimensions (diameters in case of spheres, side lengths in case of truncated cubes, distances between the tips of legs in case of hexapods) could be effectively varied from 6 to 38 nm (size distributions are given in Figure 1c) and the meaning of the provided characteristic dimension is sketched in Figure 1d. Nanocrystal sizes were reproducibly obtained for a rather wide variety of temperatures as well as precursor concentrations (Figures S1 and S2, Supporting Information). While the monodisperse nanocrystals with 38 nm characteristic dimensions are already significantly larger than previously nanocrystals obtained by hot injection methods, even larger sizes resulted from an increased oleic acid concentration of 10 mL. In this case the average characteristic dimension was 170 nm, and the size dispersion broadened to $\pm 34\%$. Besides size control, oleic acid concentration also strongly affected the nanocrystal shapes. The smallest nanocrystals exhibit a spherical shape, caused by minimization of the surface to volume ratio. By increasing the oleic acid concentration first truncated cubes with smooth edges were observed (Figure S3, Supporting Information), followed by nanocrystals exhibiting stubs of legs, growing from the center of the cubes (for 3.5 mL of oleic acid). The resulting hexapods exhibit legs growing in {100} directions (Figure S4, Supporting Information). Finally, for 10 mL oleic acid polydispersity in sizes and shapes was obtained, with large nanocrystals dominantly observed with octahedral shapes and {111} facets. It should be mentioned that all these shapes have been observed previously, albeit under completely different synthetic conditions.^[29,30] Hexapods and octahedrons, for instance, have been reported to be synthesized in aqueous solvents.^[31] In all cases the ligand concentration played a decisive role in the shape control. While for small sizes minimization of surface to volume ratio provides the spherical shape, in thermodynamic equilibrium the facet energies provide crystallite shapes. Thus, the octahedral shapes observed for the largest sizes result from minimal surface energies of the {111} facets, exhibiting eventually also surface reconstructions and only partial ligand coverages.^[32]

With increasing size, the optical properties of the PbS nanocrystals are tuned. The most important property here is the shift of the fundamental absorption edge.^[27] Probed in solution, the absorbance of the 6.2 nm nanocrystals exhibits a clearly resolved 1S excitonic peak at 1740 nm and further features at smaller wavelengths (Figure S5, Supporting Information). The onset of the absorption spectrum is found at longer wavelengths. It is measured here at 20% of the peak absorbance providing $\lambda_{0.2} = 1850$ nm. When a solid film is formed from these nanocrystals (after appropriate ligand transfer described below) a photoconductivity spectrum can be measured providing a $\lambda_{0.2} = 2080$ nm which is very close to that observed in the absorption spectrum (Figure 1d). By increasing the nanocrystal size, the photoconductivity onsets are clearly red shifted. The largest monodisperse sample (hexapods with 38 nm length (leg to leg) and ≈ 10 nm leg diameter) reaches a $\lambda_{0.2} = 2870$ nm (0.430 eV), which is exceeded by that of the polydisperse nanocrystals (octahedrons with average 170 nm side lengths) only slightly (by 23 meV) because both these nanocrystal batches exhibit already some characteristic

dimensions larger than the exciton Bohr radius (18 nm),^[33] thus providing close to bulk like bandgap energies.

The nanocrystals produced by the procedure described above are surface capped with oleate moieties. A film of such nanocrystals is insulating as a result of the relatively long alkyl chains of the oleate. Thus, it is necessary to replace the ligands by other species. While a large variety of possible small organic^[19,34] and inorganic^[35,36] ligands been introduced, metal halide perovskite type ligands,^[37,38] have been shown to be especially beneficial for PbS nanocrystals. First, they allow to prepare functional inks,^[39,40] providing high performance field effect transistors and solar cells in a single step deposition, and secondly they provide a crystalline shell around the PbS nanocrystals, exhibiting a close lattice matching to the core.^[41] The perovskite quasi-epitaxial shell exhibited advantageous photoconducting properties in films together with reasonable mobility and carrier lifetimes. From a selection of studied perovskite ligands, methyl-ammonium-iodobismuthate exhibited the best performance in photoconducting devices. Thus, here we have chosen the same ligand exchange procedure as described in ref. [41]; however, instead of methyl ammonium we used potassium as counter ions to the iodobismuthates, forming the quasi-epitaxial ligand shell. This choice was made to avoid infrared absorption within the range of the PbS nanocrystal photoconductivity spectra, due to the organic methyl ammonium cations, causing N–H bond stretching vibrations between 3100 and 3225 nm.^[42]

2.2. Ligand Exchange and Transmission Electron Microscopy (TEM) Analysis of Epitaxial Interface

In our previous work, we demonstrated the ligand exchange and the formation of an epitaxial shell rather indirectly, by a combination of nuclear magnetic resonance, small and wide angle X-ray diffraction, and optical experiments.^[41] Here we attempt to confirm the epitaxial ligand shell directly by dedicated TEM analysis including aberration-corrected high resolution TEM (AC-HRTEM). A selected area electron diffraction (SAED) pattern of the nanocrystals was taken (Figure S6a, Supporting Information) and compared with that of an ideal PbS powder, demonstrating a perfect match, confirming a pristine rock-salt PbS structure. Ring widths are broadened owing to the small size of the nanocrystals. The scanning transmission electron microscopy-high angle annular dark field (STEM-HAAD; Z-contrast) image in Figure S6b (Supporting Information) evidences a cubic shape of the nanocrystals chosen for the TEM analysis, together with a mono-disperse size distribution. At higher magnified Z-contrast image (Figure 2a), one nanocrystal is observed very close to a <110> projection. From this cubic nanocrystal two intensity profiles are displayed as insets, taken along the marked positions/directions. Profile 1, measured along a thickness gradient in between the edges, exhibits the expected linear intensity increase towards the center of the cube, plus small signal enhancements close to the cube edges (arrows in inset 1). Profile 2 was measured perpendicular to the first one. Beginning from the nanocrystal center it shows a plateau, however, close to the surface again a signal maximum is observed. These signal enhancements have a measured width

Figure 2. (S)TEM analysis of core/shell PbS/BiI nano-particles. a) STEM-HAADF image, with insets showing intensity profiles extracted along marked directions, below is a sketch of the analyzed nanoparticle, aligned closely to the $[110]$ zone axis. b) Magnified AC-HRTEM image of a single nanocrystal shows the almost perfect alignment along $[110]$ projection. Lower inset image is a simulation of a rigid PbS/BiI crystal model with interface location indicated, calculated for thickness $t = 13$ nm and defocus $\Delta f = -14$ nm (see Experimental Section for more information).

of 1.5–2 nm, suggesting a core/shell structure, where the shell is composed of elements heavier than that of the interior of the cube. Such a core–shell structure is confirmed by energy dispersive X-ray spectral imaging (EDX-SI, Figure S6c–g, Supporting Information), provided by evaluated atomic percentages normalized to the local thickness of the sample. Supporting Information Figure S6 (Supporting Information) exhibits clearly higher portion of the Bi and I signals as a shell surrounding the PbS nanocrystals core. Clearer information was obtained by AC-HRTEM imaging of a single nanocrystal oriented along the $\langle 110 \rangle$ projection (Figure 2b). As the optical parameters of the TEM were carefully controlled during these experiments, the image contrast could be compared to simulations (Figure S7, Supporting Information), predicting the different phases at core and shell, as well as the interfacing at atomic scale. In Figure 2b, bright spots can be assigned to heavy atom columns, i.e., Pb, Bi, and I, due to the negative spherical-aberration imaging condition being fulfilled and the fact that the dynamic extinction distance of these atom columns coincide with the range of sample thickness. In contrast, S columns shows very little contrast because only half its dynamic extinction distance is fulfilled at this thickness range. Based on these contrast features one can distinguish the shell from the PbS core, judging from the lattice motif features of the nanocrystals, as is marked by the diamonds in the simulated inset image and on the experimental image. The shell can be seen to be 4–5 of the $\{002\}$ lattice planes (or monolayers), and is coherently connected to the PbS core. The two outer most layer of the shell show a slightly irregular arrangement of bright spots, indicating the presence of strain resulting in a distortion of the lattice. While the simulation of the lattice assumed simply a replacement of Pb atoms by Bi and of S by I in a 1:1 manner, charge neutrality requires an excess of I in the lattice. In this

respect it should be noticed that the potassium iodo-bismuthate used for ligand exchange provides a surface charge, stabilizing the nanocrystals in the dimethylformamide (DMF) solution (Ref. [41]), and that the small potassium ions can be intercalated in the shell lattice structure to provide partial charge compensation.

2.3. Bulk-Like Photoconductivity

The PbS nanocrystals with potassium iodo-bismuthate epitaxial ligand shells allow the preparation of photoconducting devices by simple drop casting of the nanocrystal ink on various substrates. In particular, 20 μL of a concentrated lead sulfide nanocrystal ink (75 mg mL^{-1} in DMF) were drop casted onto a pair of interdigitated electrodes with a distance of 10 μm . The solvent was dried at 100 $^{\circ}\text{C}$ for 30 min. The devices fabricated from the largest nanocrystals, forming a film with a

thickness of 5 μm , exhibited a resistivity of 24 500 $\Omega\text{ cm}$ in darkness. Under illumination the current increased and the photocurrent showed a linear response on bias (Figure S8, Supporting Information) and the photoresponsivity spectrum was measured under a bias of 11 V, under which a stable operation of the photoconductor was observed. While such detectors operate over the whole visible spectral region, here we especially focus on the wavelengths range for which so far no photoconductivity was achieved from colloidal PbS nanocrystals.^[19] Thus, the photoresponsivity spectrum in Figure 3a starts at 2400 nm and is shown to up to ≈ 3350 nm. There the responsivity, however, is rather low. Thus, as a wavelength limit of usable operation we provide the value, at which the photoresponsivity drops to 20% of its peak value. $\lambda_{0.2} = 3050$ nm for the present device, which is at least 700 nm further in the infrared than what was reported previously for PbS based nanocrystal detectors.^[19] In particular it is similar to the cut off wavelength of commercial bulk-like PbS photodetectors (20% point at 2900 nm^[43]). Furthermore, the peak responsivity of $\approx 0.12\text{ A W}^{-1}$, measured after the light passed through a 2300 nm long pass filter, is found at 2600 nm. To provide detectivity as a figure of merit to compare the current device with others, a noise analysis was performed. The noise current, which was found to be in the order of 100 pA $\text{Hz}^{-0.5}$ exhibited a $1/f$ like dependence (Figure 3b) which can be attributed to thermally induced generation and recombination, as can be expected due to the small bandgap of the PbS nanocrystals. The responsivity shows a less dramatic decrease with increasing frequency up to a cut off value (taken at 3 dB) of 5030 Hz (Figure 3c). A detectivity is obtained at 2000 Hz and amounts to 1.3×10^{10} Jones. Overall, these figures of merit are comparable to those achieved by bulk-like lead sulfide photodetectors available on the market today,^[43] with the advantage that nanocrystal devices are fabricated via simple drop casting.

Figure 3. Photoconductor figure of merits for bulk-like lead sulfide, with detectivity of 1.1×10^{10} Jones at 2 kHz, 3 dB at 5030 Hz and $1/f$ dependency of noise on measurement frequency.

For applications it is important that it demonstrates a linear detector response with respect to incident power, i.e., responsivity is independent of light intensity. This was tested and found to be the case, over almost three orders of magnitude (Figure S9, Supporting Information). Thus, the overall performance of the PbS nanocrystal photodetector is comparable to that of commercial PbS bulk detectors, however, with the advantage that they are processed from solutions and at low temperatures. We made also an attempt to obtain a photovoltaic device with these large PbS nanocrystals. Although a device, based on a nanocrystal film deposited on an indium tin oxide covered glass and a conjugated polymer as top layer showed fairly low responsivity at long wavelengths, it nicely revealed the onset of the absorption of the low dimensional iodo-bismuthate perovskite material used as ligand shell. As shown in the supplementary Information Figure S10 (Supporting Information) the photovoltaic device showed a clear onset of photoconductivity at the bandgap energy of the ligand, close to 1.9 eV, which is close to the bandgap energies of related iodo-bismuthates with intercalated potassium ions as reported in ref. [44]. It should be also mentioned that there is a stability issue. While we have chosen Bi based perovskites as ligands due to its good lattice match to the PbS core and its reported superior stability in comparison

to Pb based perovskites,^[45–47] the devices show a transient behavior after switching on the bias voltage. This transient behavior is caused by ion currents, which last for ≈ 15 min until a stable response could be measured. To improve stability, strategies currently investigated for perovskite solar cells^[48,49] could be implemented to the long wavelength nanocrystal photodetectors, including addition of long chain alkyl ligands and proper device encapsulation. Irrespective of that, detector production could be scaled up easily by making use of printing techniques, which also enables fabrication of highly integrated devices and image arrays.

3. Conclusion

In conclusion, a synthetic route has been introduced for PbS nanocrystals, which is especially capable in producing large sizes, tunable by ligand concentration. The large sizes are enabled by a slow nucleation rate, provided by the selected disubstituted thiourea sulfur precursor. For sizes well above the exciton Bohr radius in PbS, monodisperse nanocrystals are achieved, with well controlled shapes, including spheres, cubes, and hexapods. Most importantly, the optical response, measured here in photoconductivity, could be tuned to approach the bulk bandgap of PbS, which is in the mid infrared spectral region. To provide a nanocrystal ink, from which photoconductive devices can be prepared simply by drop casting, a ligand exchange was performed in solution. High resolution transmission electron microscopy proved the inorganic ligand shell to be crystalline, with an epitaxial relation to the PbS core. It shows a cubic crystal structure and is related to a metal-halide perovskite, built up from $[\text{BiI}_6]^{3-}$ octahedrons, for which K was used as additional cation to enable charge neutrality. In contrast to more common organic counterions, K results in a perovskite shell with minimal near infrared vibrational absorption, critical for the operation of an infrared detector operating in this spectral region. Thus, photoconductivity could be obtained up to a record cut-off wavelength of 3030 nm, with figures of merit which are comparable to commercially available PbS photodetectors. The advantage is the simple processing of the detector by drop casting and drying at low temperature, which makes CMOS based read out electronics possible, enabling future cost reliable and sensitive near to mid-infrared imager devices.

4. Experimental Section

Sulfur Precursor Preparation: The slow reacting thiourea for use in synthesis of lead sulfide was prepared by mixing equimolar amounts of phenylisothiocyanate (2.28 g) with oleylamine (4.51 g) in octadecene (3.21 g). The oleylamine was slowly added dropwise to the octadecene/phenylisothiocyanate mixture under nitrogen environment

while being stirred and left overnight. The result was a white amorphous solid with a low melting point.

Lead Sulfide Preparation: A 50 mL three neck round bottom flask was charged with octadecene (15 mL), lead oxide (0.45 g), and oleic acid (between 1.5 and 10 mL). The mixture was placed under vacuum and degassed for 1 h at 120 °C. The temperature was raised to 135 °C and thiourea/ODE mixture (0.8 g) prepared as above was injected into the rapidly stirring mixture which steadily turned black over the course of a few minutes. The temperature was maintained at 135 °C for 20 min to facilitate the reaction before being removed and resultant lead sulfide allowed to cool to room temperature before being loaded into a centrifuge and spun at 6000 rpm to recover the nanocrystals from the mother solution. Small nanocrystals required the addition of a small amount of ethanol to facilitate flocculation. The nanocrystals were redispersed in hexane and centrifugation repeated three times.

Ligand Exchange: The ligand exchange procedure analog to that reported previously^[41]; performed there for methyl ammonium BiI₆. In particular 6% by weight K₃BiI₆ in DMF solution was prepared by dissolving KI (52 mg) with BiI₃ (62 mg) in DMF (2 mL) at 80 °C for 1 h. 1 mL of the resultant ligand solution was mixed with PbS nanocrystals (75 mg) dispersed in n-hexane (1 mL). Over the course of approximately one minute the PbS was completely transfer to the polar DMF phase leaving the hexane phase clear. The PbS nanocrystals were washed five times with hexane, followed by centrifugation at 14 500 rpm for three min to collect the product. The black sediment was dispersed in DMF (0.5 mL) and again centrifuged at 14 500 rpm for 3 min, before disposing of the supernatant. For device fabrication, the sediment was dispersed into DMF (0.1 mL).

(Scanning) Transmission Electron Microscopy: The studies were performed on a Titan3 Themis microscope operating at 300 kV, equipped with Cs-correctors both at the illumination/probe and imaging side, and a Super-X EDX detector. The Super-X detector comprises four silicon drift detectors (SDD) symmetrically placed around the optical axis, close to the sample area, with a detection solid angle of about 0.9 sr. All four signals are combined into one spectrum to improve the collection efficiency in spectrum imaging (SI) acquisition. Probe corrector was set to guarantee an aberration-free opening angle better than 20 mrad, but the probe-forming semiangle was set to a smaller value of about 16 mrad in order to reduce channeling effect in EDX analysis. The inner collection angle of the high-angle annual dark-field (HAADF) detector was set to about 60 mrad, with which the STEM-HAADF signal should be dominated by Z-contrast. The probe current of 200–500 pA, dwell time 20–50 μs was applied in STEM imaging and EDX-SI, which was found to be a compromise to balance drift, beam damage, contamination, and detectable signal. For HRTEM imaging, the image corrector was set to negative Cs imaging (NCISI) condition,^[50] with the first pass band of the phase contrast transfer function (PCTF) corresponding to a resolution of 1 Å. Under this condition, with a small over-focus (≈10 nm, set by the defocus knob during experiment), bright spots in HRTEM images can be in correspond to atomic column location. HRTEM Contrast Simulation was performed as described with example result in the Supporting Information.

Preparation of Photoconducting Devices: Gold contacts (Au/Ti with 40/10 nm thickness) were prepared on glass substrates by optical lithography and thermal evaporation followed by a lift-off process. The size of the gap between electrodes was 10 μm and the total active area was $4.12 \times 10^{-7} \text{ m}^2$. The photoconducting nanocrystal layers were deposited and dried as described in the main text.

Photoconductivity Characterization: Illumination was provided via a tungsten lamp monochromatized through an Acton SP2150i monochromator. Spectra were recorded for light modulated through a mechanical chopper with a frequency of 10 Hz, where the signal was recorded by a Signal Recovery 7265 DSP lock-in amplifier. Bias was provided by a Keithley 2612B SMU at 11 V. The setup was controlled by a home-written software in LabView IV. Frequency dependency was measured using a LED1550E (Thorlabs) controlled by square shape pulses. Light intensity dependencies were measured using a series of linear attenuator. Noise characterization was measured at the same voltage but instead using a Stanford Research Systems Model SR830.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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