Temperature dependent optical properties of PbS/CdS core/shell quantum dot thin films: probing the wave function delocalization

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ABSTRACT

Colloidal semiconductor quantum dots (QDs) are extraordinarily appealing for the development of cheap and large area solar cells, due to high absorption efficiency, tunable bandgap energies and solution processability. Understanding and controlling electronic wavefunction delocalization in QD thin films is therefore pivotal for realizing efficient optoelectronic devices. Here, a detailed study of the exciton recombination dynamics in PbS/CdS core/shell films as a function of temperature and surface chemistry is reported. By decreasing the temperature from 295 K to 5.4 K, electronic wave-function delocalization from the PbS core to the monolayer CdS shell is observed, demonstrating a reduction of the conduction band offset at low temperature and the formation of a quasi-type-II band alignment. Interestingly, films made with core-shell particles, where the shell is thicker than a monolayer, display type-I alignment also at low temperature.

TOC GRAPHICS

KEYWORDS

Colloidal quantum dots, core-shell quantum dots, lead sulfide, low-temperature, nanocrystals

Colloidal QDs form an emerging class of functional materials for novel photovoltaic technologies and light emitting devices.^{1,2} They allow low-cost solution-based deposition of thin films for large area device fabrication, which are compatible with lightweight and flexible substrates. In addition, they have high absorption efficiency and their bandgap energy can be tuned continuously to match the solar spectrum or the desired specific emission wavelength.³ Moreover, enhanced multiple exciton generation in QDs, if harnessed, could lead to a break in the Shockley-Queisser limit of the power conversion efficiency of solar cells.⁴

Lead sulfide (PbS) colloidal QDs currently top the photovoltaic efficiency tables in this class, with rapid advances in photovoltaic performance by improving device architectures,^{5,6} transport properties,⁷⁻⁸ and surface chemistry.^{9,10} Overcoating a core-only QD with an inorganic shell allows to perform band-gap engineering and to passivate trap states at the nanocrystal surface.¹¹ Recently, CdS has been used coating material on PbS QDs to improve the device performance and stability.¹²⁻¹⁴ Others and we demonstrated a substantial increase of the open circuit voltage of QD-based solar cells, through the use of PbS/CdS instead of PbS QDs.¹⁵⁻¹⁸ Apart from the surface defect passivation, the bandgap (mis)alignment of the core and shell materials can be used to control the optical properties and the electron-hole delocalization upon photo-excitation.¹⁹⁻²¹

When the band gap of the shell encloses the band gap of the core, the so-called type-I band alignment occurs. Electrons and holes are confined primarily in the core after photo-excitation, decoupling them from possible trap states at the shell surface, thus slowing down non-radiative recombination pathways. When the core and the shell are in type-II configuration, the staggered energy level alignment results in the spatial separation of electron and hole, facilitating exciton dissociation and charge extraction. Therefore, to harness the unique optoelectronic properties of core/shell QDs for device applications, understanding the band alignment and wave function distribution in these heterostructures is essential.^{19, 22-25}

The optoelectronic properties of such QD solids can be also tailored by choosing their surface-ligands, which control the inter-QD separation-dependent degree of electronic coupling.

The degree of electronic coupling between QDs not only affects charge transport properties as demonstrated by several authors,^{26,27} but also determines the fate of the photogenerated excitons, which is of outmost importance in QD-based optoelectronic devices. At this point, very little is known about the photophysics of core-shell QD solids, especially when they are assembled in thin films with different degrees of interaction.¹³⁻¹⁶

Here, the optical properties of samples prepared with monodisperse PbS/CdS QDs in a transparent polymer matrix, close-packed films of QDs with oleic acid (OA) and shorter ligands (3-mercaptopropionic acid, MPA) are investigated as a function of temperature. At room temperature a quasi type-II band alignment is observed for PbS/CdS QDs with monolayer shell thickness, while the band alignment of thick shell QDs is determined to be of type-I. By means of time-resolved photoluminescence measurements, a temperature-dependent band offset with a different degree of localization for the electron wave function in thin shell PbS/CdS QDs is observed. Electronic wavefunction delocalization in short ligand treated films of PbS/CdS QDs with monolayer shell thickness, is found to lead to a shortening of 3 orders of magnitude of the exciton lifetime respect to the isolated QDs. Conversely, in films of thicker shell QDs, the photoluminescence spectra at every temperature confirm the formation of a type I heterojunction between core and shell, less than a factor two of lifetime variation between the long and the short ligands is observed.

The absorption and photoluminescence spectra of thin shell PbS/CdS QD (monolayer CdS shells) samples capped with oleic acid (OA) in solution are shown in Figure 1a. The sample exhibits the excitonic peak at about 1049 nm. Following the empirical formula relating the bandgap to the diameter of PbS QDs,²⁸ the average size d of the QDs is determined to be ~ 3.5 nm. The temperature dependent photoluminescence (PL) spectra of the QD films in PMMA-matrix

(PbS/CdS@PMMA), of close-packed films made with oleic acid coated QDs (PbS/CdS-OA) and 3-mercaptopropionic acid treated films (PbS/CdS-MPA) are shown in Figure 1b, c and d.

Figure 1. (a) Absorption and photoluminescence spectra of PbS/CdS QDs (monolayer shell) capped with oleic acid (OA) in chloroform solution. Inset: Scanning transmission electron microscopy (STEM) image of a PbS/CdS QD. (b)-(d). Photoluminescence (PL) spectra of core-shell dots from 295 K to 5.4 K for the (b) film of QDs in PMMA matrix (PbS/CdS @ PMMA), (c) closed-packed film (PbS/CdS-OA) and (d) film of PbS/CdS treated with 3-mercaptopropionic acid (PbS/CdS-MPA).

The QDs in the PMMA matrix allow studying the temperature dependence of the optical properties of an assembly of non-interacting QDs. The emission of close-packed (PbS/CdS-OA) (Fig. 1c) films shows a redshift of ~50 nm (from 1125 nm to 1175 nm) compared with the one of

the QDs in the PMMA matrix (Fig. 1b), suggesting that energy transfer (ET) between the close-packed QDs takes place. Any ensemble of QDs has a distribution of sizes, and energy transfer can occur from the population of smaller diameter to the population of bigger diameter QDs. An even larger red shift (to 1213 nm) is observed in 3-mercaptopropionic acid (MPA) (Fig. 1d) treated samples, which can be attributed to the increase of electronic wave function overlap between the QDs, as the inter-QD spacing is reduced after ligand exchange, as has been amply documented by many authors.^{27, 29}

Since temperature-dependent PL measurements can help to unravel the relaxation pathway of the photogenerated excitons, with this purpose we have investigated the variation of the PL spectra of QDs with different packing and interactions as a function of temperature. The temperature dependent measurements are reported in Fig 1b, c and d, while Figure 2 summarizes the key parameters obtained from these measurements: integrated PL intensity (Fig. 2a), peak position (Fig. 2b) and full-width at half maximum (FWHM) (Fig. 2c). The photoluminescence experiences an increase of the overall intensity at lower temperatures. For instance, the PL of PbS/CdS @PMMA QDs at 295 K shows a maximum at 1125 nm and a red-shift to 1240 nm at 5.4 K. This red-shift is possibly related to the temperature dependence of the energy bandgap (E_g) of PbS, namely that E_g decreases with decreasing temperature.²⁹ The PL intensity at 5.4 K is about 2 times increased respect to the emission at room temperature. In addition to the red-shift of the peak wavelength and increase of PL intensity, the FWHM of the PL decreases from 164 nm (295 K) to 120 nm (5.4 K). This could be partially attributed to the suppression of the phonon-carrier interactions at low temperature.

Figure 2. Temperature dependence of (a) the integrated intensity, (b) the peak position and (c) the peak width of the PL emission for the PbS/CdS-MPA, PbS/CdS-OA and PbS/CdS@PMMA samples.

A much stronger temperature dependent intensity variation is measured in the case of MPA treated thin film in comparison to both PbS/CdS @ PMMA and PbS/CdS-OA, as shown in Figure 2a. The comparison of the PL intensity vs. temperature for these three samples suggests that the increased degree of electronic coupling introduced by the shorter ligands contribute significantly to the PL quenching by opening new non-radiative channels. Interestingly, PbS/CdS-MPA films also display an anomalous PL shift towards the blue region of the PL spectrum at low temperature, from 1366 nm (150 K) to 1317 nm (5.4 K), which is similar to what has been recently reported for shell-free PbS QDs.³⁰ There are several contributions to temperature coefficients dE/dT in lead-salt QDs: lattice thermal expansion, electron–phonon coupling, thermal expansion of the wave function envelope, and mechanical strain. The first two

contributions are positive, while the last two are negative. In PbS/CDS-MPA films, QDs are surrounded by short MPA ligands, which could contribute more negatively to dE/dT . On the other hand, in PbS/CDS-MPA films, QDs are strongly coupled. Exponential band tails may form in the PbS/CDS-MPA films. As temperature decrease, the occupation of the shallow states, which give rise to the high-energy part of the PL spectrum, increases, and the overall spectrum shifts to high energy.

All samples show a decrease in FWHM as temperature approaches 5.4 K (see Fig. 2c), but at room temperature the FWHM is much broader for PbS/CdS-MPA compared to PbS/CdS@PMMA and PbS/CdS-OA. At about 50 K, it reaches a similar FWHM of PbS/CdS @ PMMA. We interpret the broader emission at room temperature of the PbS/CdS-MPA sample as a result of the distribution of different degree of coupling among the QDs. Considering the similarity in magnitude of the coupling energy and of the exciton binding energy in PbS QDs,^{27,31-32} we anticipate that the coupling significantly influences the fate of photogenerated excitons, which we shall discuss below.

To gain more insight into the underlying decay process of photogenerated excitons, we carried out time-resolved PL measurements from room temperature to 5.4 K. Figure 3 reports streak camera data of the three samples at selected temperatures (295 K, 100 K, and 5.4 K), along with the PL spectra extracted at different time delays at 5.4 K. At room temperature (Fig. 3a₁-c₁), we observe a time dependent red-shift for each sample. As the temperature is decreased, a much more pronounced spectral shift over the same time scale is observed (Fig. 3a₂-c₂). This effect becomes extreme at 5.4 K, as shown in Fig. 3a₃-c₃. All the samples exhibit a very fast decaying

blue emission band (region I) and a slow decaying red emission band (region II). Figure 3(a)-

Figure 3. Spectrogram of time-revolved photoluminescence from (a) PbS/CdS @ PMMA matrix film, (b) close-packed film (PbS/CdS-OA) and (c) 3-mercaptopropionic acid capped thin films (PbS/CdS-MPA). Bottom panel: Spectra A and B for each sample were obtained by integrating the streak camera images in the time windows labelled accordingly.

(c_i) show the spectra (A and B) by integrating the streak data in the time windows labelled accordingly in Figure 3(a_i)-(c_i). Immediately after excitation ($<0.2 \mu\text{s}$), the corresponding PL spectrum (spectrum A) reveal emission in both spectral regions (I and II), while emission from region I is not detected at longer delays after photoexcitation, as shown in the spectrum B of Figure 3a_i-c_i. The PL decays of the three samples at 5.4 K along with room temperature measurements for region I and II, are shown in Figure 4. The PL decays are fitted by mono- or bi-exponential functions depending on the chi-squared test. The average lifetime at room temperature for PbS/CdS@PMMA is 761 ns and decreases for the samples with interacting particles to become 389 ns for PbS/CdS-OA and 346 ps for PbS/CdS-MPA. When the temperature is lowered till 5.4 K, the decay of the emission in region I shows a much faster decay for all of the three samples, and in the case of the PbS/CdS-MPA (Fig. 4c) sample the shorter decay is limited by the instrumental resolution. One can assume that the short lifetime emission is due to recombination of carriers within the core, whereas the long lifetime emission is a result of recombination between holes from the core and the electrons from the shell. At 5.4 K, the decay dynamics at region II can be fitted with bi-exponential function with a fast component τ_1 and a slower component τ_2 . The fitted lifetime τ_1 is 0.09 μs and τ_2 is 0.77 μs for PbS/CdS-OA. τ_1 is 0.1 μs and τ_2 is 1.8 μs for PbS/CdS@PMMA, and τ_1 is 7.8 ps and τ_2 is 2051 ps for PbS/CdS-MPA. Thus the average lifetime calculated at low temperature (for PbS/CdS@PMMA is 1.7 μs , for PbS/CdS-OA is 0.7 μs and for PbS/CdS-MPA is 2 ns) is much longer in comparison to room temperature emission.

The low temperature behaviour of the PL could be interpreted as a further indication that energy or charge transfer occurs in these films.³³⁻³⁶ As already mentioned, since size polydispersity is inevitable for QD ensembles, exciton migration can be observed in closed-packed QDs films. However, such behaviour should be suppressed in the PMMA matrix sample, where the spacing between QDs is too large for the energy transfer to occur.³³ For far apart dipoles in Förster resonant energy transfer processes, a substantial rise time of the acceptor emission should be

observed.³⁷⁻³⁸ When probed in the lower energy range of the emission spectrum, the rise time of the emission of the PbS/CdS@PMMA is instrumental-response-limited, suggesting that the contribution of energy transfer in PbS/CdS@PMMA for the observed phenomena is from small to negligible.³⁹ Therefore, the supposed energy transfer mechanism cannot explain the low temperature behaviour of the PbS/CdS@PMMA sample and the appearance of a fast (region I) and a slower decaying (region II) feature.

Figure 4. Photoluminescence decay curves from (a) PbS/CdS @ PMMA matrix film, (b) close-packed film (PbS/CdS-OA) and (c) 3-mercaptopropionic acid capped thin films (PbS/CdS-MPA) extracted from figure 3.

As for core-shell QDs, the relative energy alignment of the core and shell is one of the important factors that may affect the exciton recombination pathway. In PbS/CdS heterostructures, it is reported that the LUMO levels are very close to each other so that electron wavefunctions in the core's LUMO may leak into the shell volume.⁴⁰ In view of this fact, we attribute the temperature dependent appearance of the fast component at high energy in these samples, to a temperature dependent variation of the band alignment.

To verify this hypothesis, the optical properties of thick-shell PbS/CdS-OA QDs (see Figure S1 in Supporting Information) were investigated. Compared to PbS/CdS-OA QDs with monolayer shell samples, the PL spectra of the thick shell sample does not display spectral shift going from room temperature to 5.4 K. This may be the consequence of limited lattice dilation of the PbS cores and interface strain due to the thermal lattice mismatch at the core-shell interface, which contributes opposing effect on dE/dT .¹⁴ The decay of the PL at room temperature is characterized by a lifetime of 0.46 μ s, which increases to 0.8 μ s at 5.4 K. Importantly, for the thick shell samples, the fast component observed in the samples fabricated with the monolayer shell QDs (Fig. 3), was not detected at any temperature.

Since the two types of core-shell QDs have the same surface ligands, only differences in the electronic structure and in the confinement of the electron and hole wavefunctions can justify these optical features. Importantly, in our previous work,¹⁷ we have demonstrated that in comparison with core only PbS QDs, solar cell devices fabricated with monolayer-shell (CdS) QDs give rise to an increase in the V_{oc} , and longer photoluminescence lifetime, demonstrating the suppression of non-radiative charge recombination in core-shell QDs. This means that trap concentration is lower in the thin-shell materials, and no traps are generated during the shell growth. Moreover, core only QDs synthesized in the same way do not display the fast blue-shifted emission displayed by the thin shell QDs (Figure S3, Supplementary Information), ruling out a possible interpretation of the slow emission features as originating from trap states.

Figure 5. (a) Sketch illustrating the proposed energy level configuration for a single thin shell PbS/CdS QD, conduction band offset (ΔE) between core and shell decrease as the temperature T is lowered. (b) Schematic of exciton dissociation via charge tunnelling in the PbS/CdS-MPA and resonant energy transfer in the PbS/CdS-OA films at room temperature and in thick shell samples.

Recently, it is reported that monolayer core-shell QDs of InP/CdS exhibit type-II electronic structure.⁴¹ Since the conduction level of PbS is close to CdS,¹³ it is reasonable to form quasi type-II energy alignment in monolayer-shell PbS/CdS QDs. Figure 5a displays a schematic of the electronic level configuration as can be deduced from our measurements; in the thin shell PbS/CdS QD, the conduction band offset (ΔE) between core and shell is very small, therefore the electron wavefunctions can spill out and extend into the CdS shell, leading to a partial spatial separation between the electron and hole wavefunctions (quasi-type II heterojunction). As the temperature T is lowered, the energy level of conduction band in CdS shell is lowered in comparison to PbS core, resulting in greater delocalization of the electron wavefunctions, which derive in a red-shifted emission and a longer radiative lifetime in region II at low temperature because of the lower electron-hole wavefunction overlap (see Figure 5a).⁴² In the thick shell sample, band gap alignment is of type-I with high band offset; both electrons and holes are

confined in the core region strongly, thus PL decay has similar behaviour for every emission wavelength and is insensitive to the temperature in comparison to thin shell samples (Fig. S1).

As already mentioned, not only the heterostructure composing the QDs but also the ligands are fundamental to determine the fate of the photoexcitation. Compared to the closed packed thin shell PbS/CdS-OA samples, the lifetime of PbS/CdS-MPA is much shorter, as shown in Figure 4. The transient PL data of PbS/CdS-OA thin shell films (Figure 4b) show a long effective average lifetime of ~ 389 ns at room temperature, while PbS/CdS-MPA samples (Figure 4c) show exciton lifetimes on the order of hundreds of picoseconds (346 ps). The pronounced shortening of the overall exciton lifetime in the core shell QDs suggests that the de-excitation pathways for MPA treated films are fundamentally different from that of the PbS/CdS-OA films. MPA ligand used in experiment can effectively replace oleic acid and reduce the inter-particle spacing, leading to increased electronic coupling between QDs.⁴³ When the coupling energy is comparable to the exciton binding energy, excitons can dissociate via tunneling of charges between neighbouring QDs, leading to a shortened exciton lifetimes, as demonstrated recently by Choi *et al.*³² Figure 5b illustrates the two different fates of excitons in QD thin films depending on the barrier between them. When the barrier is thin, as in PbS/CdS-MPA thin films, the excitons dissociate via charge tunnelling with the consequence that the PL lifetime is significantly shorter. In case of a thicker barrier, namely the OA coated samples, resonant energy transfer through dipole-dipole interactions between QDs is the dominant effect. The dissimilar coupling obtained with different ligands is in agreement with the electronic wave functions not being confined in the core for thin shell QDs. In case of thick-shell QD films, the exciton dissociation rate is expected to be less sensitive to the ligand than in the thin-shell films, due to larger core-core distance (2.1 nm for thick-shell PbS/CdS-BDT and 3.6 nm for PbS/CdS-OA) and weaker inter-QD electronic coupling. This is confirmed by the dynamics of the PbS/CdS with thick shell with OA and the short BDT ligands, which show a factor of 2 difference in lifetime (the average lifetime is 0.25 μ s for BDT ligand and 0.46 μ s for OA ligand, Fig. S2). The ligand length dependent energy transfer rate in thick-shell QD films will be further investigated.

In summary, we reported on the steady-state and time-resolved photoluminescence process occurring in PbS/CdS QDs vs. temperature and chemical treatments. In contrast to thick shell PbS/CdS QDs, where the electronic wave functions are fully localized in the QD core, we observed a temperature-dependent energy level alignment in heterostructures with monolayer shell coverage, which results in a fast blue shifted emission decay and a slower red-shifted emission. A clear increase of the radiative lifetime of this second emission with decreasing temperature is observed, owing to the variation of the conduction band offset and different degree of localization of the electronic wave functions. Films fabricated with thin shell QDs displayed also an elevated sensitivity to the ligand size, which allow tuning the degree of wave function delocalization. Finally, by enlightening the detail of the electronic structure of these PbS/CdS core-shell QDs, these results can give important indications for the design of the future quantum dots heterostructures for optoelectronics.

Experimental details

Material synthesis and sample fabrication

PbS/CdS QDs with monolayer CdS shells were synthesized using a previously described procedure.¹³ Briefly, parent PbS particles were synthesized using a hot injection method, then coated with a thin shell of CdS through a monolayer cation exchange. In a typical experiment, 1 g of CdO (Aldrich, 99.99%), 20 mL of octadecene (ODE, Aldrich, 90%) and 6 mL of oleic acid (Aldrich, 90%) were loaded into a 100mL three-neck flask, and were heated up to 240°C until colorless Cd-oleate was formed. The temperature was then decreased to 100°C and the mixture was kept under vacuum for 1 h. In the next step, 120 mg of washed PbS nanoparticles were injected in the flask and kept at 40 °C for 10 min. The crude solution was finally cooled down using water base, and the particles were washed with hexane (Aldrich, 95%) and ethanol (Fluka, 99.98%). PbS/CdS QDs with thick-shell (about 0.8 nm) were synthesized by Successive Ion Layer Adsorption and Reaction (SILAR) deposition method on the thin-shell species (see above).

The precursors were prepared according to literature.⁴⁴ The Cd-oleate precursor was obtained by mixing 0.5439 g CdO, 7.5 mL oleic acid, and 30 mL ODE in a 100 mL three-neck flask. The mixture was exposed to vacuum for 10 min at RT, then heated under N₂ at 240°C until the solution became colourless. The precursor was degassed at 100°C for 1 h and kept at 70°C under N₂. For the S-ODE (0.1M) precursor 0.096g S (Aldrich, 99.998%) and 30 mL degassed ODE were loaded into a 100 mL three-neck flask, heated to 180°C for 30 minutes and finally cooled down. For the SILAR process, 5 mL ODE and 2 mL oleylamine (Aldrich, 70%) were degassed in a 100 mL three-neck flask at 100°C for 1 h. First, 29 mg of the thin shell PbS/CdS QDs dispersed in 1 mL toluene (Aldrich) was injected, and kept in vacuum/N₂ for 5 min. During the SILAR process the temperature was kept at 100°C. Cd-oleate and S-ODE were alternatively injected every 10 min, increasing successively the volume: 0.49 mL, 0.62 mL, 0.77 mL, 0.92 mL, 1.1 mL, 1.28 mL, 1.49 mL, 1.7 mL, 1.9 mL, and 2.18 mL. The final solution was then cooled down using a water base, and the particles were washed with toluene and ethanol.

Sample preparation

After the last washing step, all nanocrystals were dispersed in chloroform (CF). PbS@PMMA and PbS/CdS@PMMA samples were prepared by dissolving PMMA in CF and mixing it with the QD solutions in a PbS:PMMA:CF weight ratio of 1:49:950. The solutions were spin-casted onto quartz substrates at 1000 rpm for 90 s. PbS/CdS-OA films were prepared by drop-casting 2.5 mg/ml solutions onto quartz substrates at 55°C. PbS-MPA and PbS/CdS-MPA films were deposited in a layer-by-layer manner onto quartz substrates; QD films spun from a 5 mg/ml solution at 4000 rpm for 45 s were exposed to 0.1% mercaptopropionic-acid (MPA) solution in

methanol for 30 s and spin-dried at 4000 rpm for 45 s, followed by annealing at 140°C for 20 min.

Spectroscopic measurements

Photoluminescence measurements were performed exciting the samples with the second harmonic (400 nm) of a mode-locked Ti:Sapphire laser (Mira 900, Coherent). The laser power was attenuated to 100 μW using neutral density filters in order to avoid unnecessary irradiation during the measurement. The excitation beam was spatially limited by an iris and focused with a 150 mm focal length lens. For steady-state photoluminescence spectra, the excitation power density is estimated to be 60 nJ/cm^2 . For the time-resolved PL measurement, a pulse-picker was used to divide the Ti:Sapphire oscillator frequency. The laser power density is increased to be 5.6 $\mu\text{J}/\text{cm}^2$. The estimated exciton number per QD is 0.07, which is low enough to avoid Auger and multiexcitonic effect. Fluorescence was collected into a spectrometer with a 30 lines/mm grating and recorded by a cooled array-detector (Andor, iDus 1.7 μm). Time-resolved traces were recorded with a Hamamatsu streak camera with a near infrared sensitive photocathode working in synchroscan mode and single sweep mode, depending on the lifetime range to analyse. The excitation source was the same mode-locked femtosecond laser with a repetition rate of 76 MHz; a pulse picker was inserted in the optical path to decrease the repetition rate of the laser pulses when needed. All samples were installed in a liquid helium continuous flow optical cryostat (Oxford Optistat) inside a Nitrogen-filled glovebox to limit exposure to oxygen and moisture.

ASSOCIATED CONTENT

Supporting Information. Photoluminescence spectra and time-revolved photoluminescence of thick shell PbS/CdS close-packed film, and time-revolved photoluminescence of core-only PbS@PMMA materials. The supporting information is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interests.

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