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Polarized luminescence of MoS_2 nanodots

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The effect of temperature on the polarization of the luminescence of the colloidal system of MoS_2 nanodots in n-methylpyrrolidone is studied under the condition of linearly polarized excitation. Nanodots are obtained by chemical exfoliation and dispersion of MoS_2 microcrystals in a liquid medium under the action of ultrasound. The photoluminescence spectrum of the ensemble of MoS_2 nanodots is significantly shifted towards shorter wavelengths with respect to the luminescence spectrum of bulk crystals, which is explained by the quantum-size effect in the electronic spectrum of MoS_2 nanocrystals. It is shown that the temperature dependence of the anisotropy of the radiation of nanodots is described by the Levshin−Perrin equation, which takes into account the rotational diffusion of luminescent particles in the liquid matrix. The size of photoexcited nanodots in the framework of the Levshin−Perrin model turns out to be ≥ 1.5 nm and increases with increasing the emission wavelength. It is shown that the sizes of MoS_2 nanodots obtained by analyzing the temperature dependence of the emission anisotropy are in satisfactory agreement with the data obtained by analyzing the quantum-size effect in the electronic spectrum of nanodots.

Keywords: polarized luminescence, molybdenum disulfide, nanodots, colloidal systems.

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1. Introduction

Molybdenum disulfide belongs to a group of layered crystals, characterizing with explicit anisotropy of mechanical and crystallographic properties. Layered crystals are easily split in planes, parallel to crystal layers. Such features of crystals demonstrates, that chemical bonds of atoms inside the layer are much stronger, than between layers, and, thus, some physical properties of layered crystals (not necessarily all) have two-dimensional nature [1]. Layered structure of molybdenum disulfide causes, particularly, excellent antifriction properties of this compound, widely used in technics [2].

Discovering of unique properties of monolayer graphite — graphene [3] gave impetus to study the properties of thin films and monolayers of other layered crystals, including molybdenum disulfide [4–9]. Transition from a bulk crystal of MoS_2 to monolayer is accompanied with changes in the crystal band structure, particularly, unlike a bulk crystal the monolayer of MoS_2 is a direct band semiconductor, that is significant for its application in photonics and optoelectronics [10].

Optical properties of nanodots of MoS_2 [11–13] and their electron structure features are studied much less. For the first time the quantum size effect in absorption spectra of MoS_2 nanoparticles was probably observed in sols, formed as a result of MoS_2 crystal powders dissolution in acetonitrile [14,15]. Later on the other methods of MoS_2 nanoparticles producing [16–18] were developed, the possibilities of MoS_2 nanodots application for catalysis in energy storage devices, and optoelectronics were studied (see review [19]). Considering the low toxicity of molybdenum disulfide, nanodots based on it are considered as the prospective materials for application in biomedicine [20].

The fundamental task of MoS_2 nanodots photophysical properties studying is determination of the properties of emissive states in these objects. Spectra of optical absorption and luminescence of MoS_2 nanodots are represented by broad bands. Effective method of studying the properties of emissive states, forming the broadband spectra, is studying the influence of external factors (temperature, polarization and intensity of optical excitation) on their luminescence properties. Particularly, the polarized luminescence method [21,22] allows to obtain information on elementary radiators properties, their interaction between each other and with environment even in case of broadband spectra. The purpose of this work was to study an influence of temperature on polarization of luminescence of MoS_2 nanodots, obtained using a method of chemical exfoliation of massive MoS_2. It was established, that temperature increase results in luminescence depolarization (under conditions of linearly polarized excitation). It is shown, that emission depolarization is described with Levshin−Perrin equation, connecting luminophore emission depolarization with its rotation. Within the Levshin–Perrin model, the size of emitting nanoparticles was estimated, which is in satisfactory agreement with the results of the analysis of the emission spectrum of MoS_2 nanodots, taking into account the quantum size effect.

2. Experimental procedure

MoS_2 nanoparticles were produced by chemical exfoliation and dispersion of massive MoS_2 („top-down" method) in alkali solutions under ultrasound exposure [23]. Molybdenum disulfide powder (MoS_2, particles size $< 2\,\mu$m, 98%, Aldrich) with a mass of 1.5 g was put into 10M water solution of LiOH and NaOH (mole ratio is 1 : 2). The obtained suspension were processed with ultrasound (22 kHz, 250 W) at 30°C for 80 hours with constant stirring. MoS_2 nanoparticles were separated from coarse fraction by means of centrifugation at 8000 g at Sigma 6−16 centrifuge for 30 min, the target fraction was deposited at 12000 g for 1 hour. For cleaning from Na^+ and Li^+ ions the nanoparticles were re-dispersed three times in deionized water with the following centrifugation. After that the obtained MoS_2 nanoparticles were dried at 70°C and re-dispersed in n-methylpyrrolidone (NMP, Aldrich, spectrophotometric grade, $\geq 99\%$), containing 0.2M of NaOH. MoS_2 nanoparticles concentration in NMP was 1 mg/ml.

For luminescence study the synthesized samples were put into thin-walled quartz cuvettes. Studies of polarized luminescence of colloidal solutions of MoS_2 in NMP are performed at excitation of nanodots with continuous radiation of semiconductor laser with a wavelength of $\lambda_{\text{exc}} = 405$ nm ($h\nu_{\text{exc}} = 3.061$ eV). Radiation power was ~ 0.1 W. Luminescence polarization degree was measured using a quartz modulator [24] and a linear polarizer combined with two-channel photons counting system. The exciting light, polarized with $\mathbf{E} \parallel z$, was propagated along y axis, sample radiation was registered at a right angle, in x axis direction. Spectra registration was performed using diffraction spectrometer.

3. Results and discussion

Luminescence spectrum of colloidal solution of MoS_2 nanodots in NMP at excitation with a light with $h\nu_{\text{exc}} = 3.061$ eV is presented in Fig. 1. It consists of a broad weakly-structured band with the main maximum at ~ 2.8 eV, located in a region of fundamental absorption of molybdenum disulfide bulk crystal. The spectrum significantly differs from photoluminescence spectrum of a bulk molybdenum disulfide, in which a broad emission band dominates with maximum at $h\nu = 1.3$ eV [25], located in a region of an edge of indirect interband transitions of bulk MoS_2 ($E_{\text{gi}} \approx 1.3$ eV [26]). Two weak short-wave radiation bands at 1.8 and 2.0 eV are associated with direct exciton transitions in K point of Brillouin zone of MoS_2 hexagonal crystal [25]. Significant shift of emission spectrum of MoS_2 nanodots towards short-wave side relative to bulk crystals spectrum is naturally to associate with quantum size effect in electron spectra of nanodots. Reduction of sizes of semiconductor nanocrystal is accompanied with increase of its forbidden band width [27], resulting in a crystal edge emission spectrum shift towards short-wave side. The effect is the most noticeable, when the nanocrystal reaches sizes, comparable or less than Bohr radius of exciton in the bulk crystal.

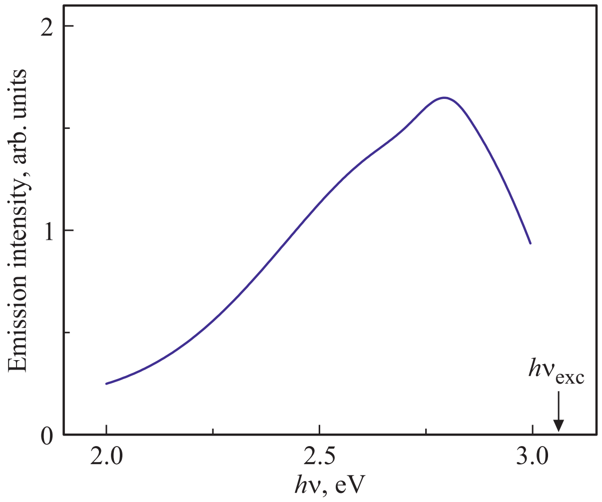

Figure 1. Emission spectrum of colloidal solution of MoS_2 nanodots in NMP. $h\nu_{\text{exc}} = 3.061$ eV. $T = 303$ K.

At excitation with linearly polarized light the emission of nanodots in solution becomes primarily linearly polarized in the same plane as the exciting light. State of linear polarization of emission is easy to characterize with the emission anisotropy r, related to a degree of linear polarization P with a relation:

$$r = \frac{I_z - I_y}{I_z + 2I_y} = \frac{2P}{3 - P}, \tag{1}$$

where I_z and I_y — intensities of emission components, polarized with $\mathbf{E} \parallel z$ and $\mathbf{E} \parallel y$ respectively. At constant temperature the nanodots emission anisotropy in NMP is maximum at a short-wave edge of radiation band and decreases with wavelength increase. Increase of colloidal solution temperature results in radiation depolarization, while dependence $r(h\nu_{\text{emis}})$ becomes less explicit (Fig. 2). It should be noted, that at nanodots excitation with circularly polarized light the circular emission polarization was missing (at measurement of circular polarization of luminescence the radiation detection was performed at small angle to the exciting light propagation direction).

It is known, that in the absence of external fields the colloidal system with liquid medium is optically isotropic [28]. The observed photoinduced linear emission polarization indicates the hidden optical anisotropy of the system. Features of the polarized luminescence of nanodots can be explained within oscillatory model [21]. Within this model the ensemble of photoexcited nanodots should be considered as a system of linear fully-anisotropic dipole oscillators, which orientations in space has a random nature. Linearly polarized light excites primarily oscillators, dipole moments of which are oriented parallel to light vector $\mathbf{E}$. If during a lifetime of radiative state (oscillator decay time)

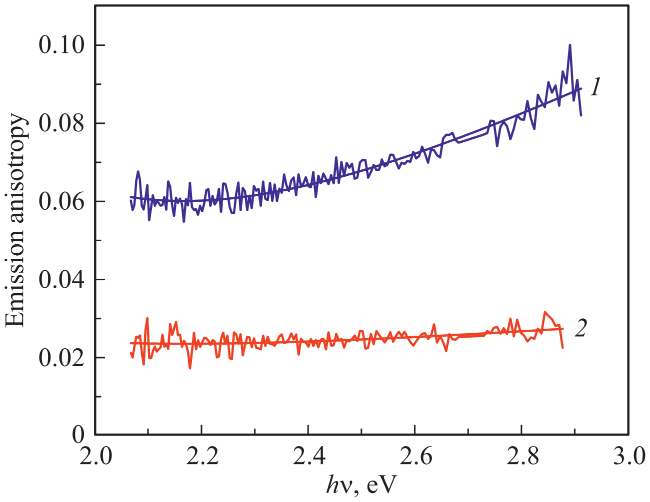

Figure 2. Dependence of emission anisotropy of MoS_2 nanodots in NMP on the emitted photons energy at $T = 254$ K (*1*) and $T = 303$ K (*2*). $h\nu_{\mathrm{exc}} = 3.061$ eV.

the orientation of the dipole moments does not change significantly, the radiation of oscillators system will be primarily polarized in the same plane as the exciting light.

In diluted solutions the energy migration between various nanodots can be neglected. In this case, as molecular spectroscopy experience shows, the determining mechanism of depolarization of colloidal solutions radiation is the Brownian rotation of particles (and, consequently, the related dipole oscillators). Thermal motion of the solution molecules disrupts the initial (created by light) anisotropic oscillators distribution by directions of their dipole moments, reaching to isotropization of distribution function. Emission depolarization is a result of this isotropization. Depolarization degree is determined by the rotation angle of a luminous particle, which depends on its size, lifetime of radiative state, medium temperature and viscosity. Dependence of emission anisotropy of nanoparticles in a shape of a hard sphere (or oblate ellipsoid [29]) on solution temperature is described with Levshin–Perrin equation [22]:

$$\frac{1}{r(T)} = \frac{1}{r_0} + \frac{kT\tau(T)}{r_0\eta(T)V} = \frac{1}{r_0} + \frac{x}{r_0V}. \qquad (2)$$

where k — Boltzmann constant, T — solution temperature, $\tau(T)$ — radiative state lifetime, $\eta(T)$ — solvent dynamic viscosity, V — nanoparticle volume, $x \equiv kT\tau/\eta$, r_0 — anisotropy limit value (at $\eta \to \infty$). At random orientation of molecules in solution the maximum value of $r_0 = 0.4$ is reached at the same orientation of photoexcited and light-radiative dipoles. Temperature increase results in Brownian motion intensification and the viscosity reduction, which as per equation (2), contributes to reduction of emission anisotropy.

Experimental dependencies $r^{-1}(x)$ for various spectral regions of emission bands of MoS_2 nanodots in NMP (in maximum and at a long-wave edge of the band) are presented in Fig. 3. Values of x were calculated considering temperature dependence $\eta(T)$ [30]. Value of τ within examined temperature interval of 254 K–323 K was taken as temperature-independent $\tau \approx 5.5$ ns [31]. As seen from Fig. 3, experimental dependencies $r^{-1}(x)$ are well described with equation (2), that confirms the „rotational mechanism" of emission depolarization of nanodots. Theoretical dependencies in Fig. 3 were obtained at the following parameter values: $V = 1.8\,\mathrm{nm}^3$ ($h\nu_{\mathrm{emis}} = 2.82$ eV) and $V = 2.7\,\mathrm{nm}^3$ ($h\nu_{\mathrm{emis}} = 2.14$ eV). Parameter V depends on emission wavelength: the longer the wavelength, the greater V. Considering, that volume of crystal lattice cell of hexagonal molybdenum disulfide $\nu_0 = 0.106\,\mathrm{nm}^3$ [32], for nanodot with $V = 2.7\,\mathrm{nm}^3$ we have $V \approx 25\nu_0$ (or 50 molecules of MoS_2). For spherical nanoparticles $V = 4\pi R^3/3$, from where the size (diameter) of nanoparticles, emitting in the region $h\nu_{\mathrm{emis}} = 2.82$ eV and $h\nu_{\mathrm{emis}} = 2.14$ eV is $d = 2R = 1.5 \pm 0.3$ nm and $d = 2R \approx 1.7 \pm 0.2$ nm respectively. From the other side, if we assume, that MoS_2 nanodots have a shape of oblate spheroid („disc") with a small axis („thickness") equal to thickness of MoS_2 monolayer (~ 0.6 nm [32]), their larger axes (diameters of „discs") are ~ 2.4 nm at $V = 1.8\,\mathrm{nm}^3$ and ~ 2.9 nm at $V = 2.7\,\mathrm{nm}^3$.

Limit values of anisotropy r_0, corresponding to emission anisotropy of immobile nanodots, also differ for various spectral regions of emission band: $r_0 \cong 0.26$ for $h\nu_{\mathrm{emis}} = 2.82$ eV, $r_0 \cong 0.25$ for $h\nu_{\mathrm{emis}} = 2.61$ eV and $r_0 \cong 0.16$ for $h\nu_{\mathrm{emis}} = 2.14$ eV. Within oscillatory model the drop of r_0 in this series can be explained with increase of an angle between absorbing and emitting dipoles with increase of energy difference of the corresponding optical transitions. Values of $r_0 > 0.1$ allow to consider, that polarization properties of the corresponding optical transitions truly have properties of linear oscillator. Ra-

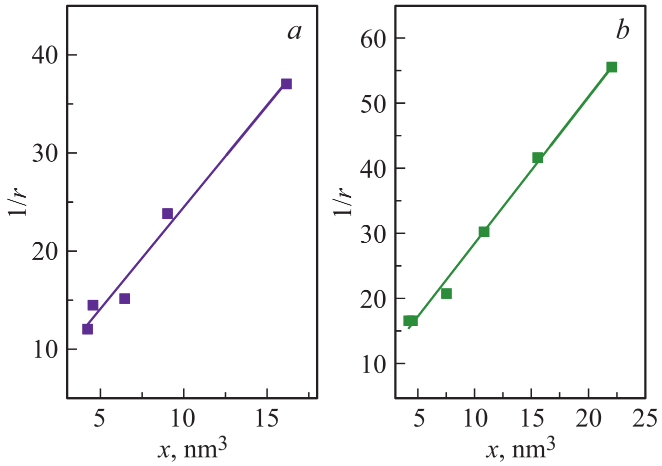

Figure 3. Dependencies $r^{-1}(x)$ for various spectral regions of emission band of MoS_2 nanodots in NMP: $h\nu_{\mathrm{emis}} = 2.82$ eV (*a*) and $h\nu_{\mathrm{emis}} = 2.14$ eV (*b*). $x \equiv kT\tau/\eta$. $h\nu_{\mathrm{exc}} = 3.061$ eV. Points are experimental values, solid lines are approximations of experimental dependencies with equation (2).

diative transitions in low-dimensional structures based on MoS_2 are usually associated [19,31,33] with direct electron transitions between the states, in bulk crystals corresponding to conductivity band (K_5) and valence band (K_4, K_1 [34]) in K point of Brillouin zone. Radiative transitions $K_5 \rightarrow K_{1,4}$ are allowed in light polarization $\mathbf{E} \perp c$ (c — crystal optical axis) [35] and equally probable for any vector $\mathbf{E}$ orientation in layer plane („plane oscillator"). In this case, if polarization characteristics of nanodots radiation are similar to characteristics of a bulk crystal radiation at K point, the maximum anisotropy of radiation of nanodots ensemble under conditions of linearly polarized excitation can not exceed 0.1 [36]. It is obvious, that values of $r_0 \leq 0.1$ do not correspond to the abovementioned values of r_0. On the other hand, it is known, that in bulk MoS_2 the forbidden band width in K point ($E_{g\mathrm{K}0}$) is very close to the forbidden band width in H point of Brillouin zone ($E_{g\mathrm{H}0}$): $E_{g\mathrm{H}0} - E_{g\mathrm{K}0} \approx 50\,\mathrm{meV}$ [37]. Radiative transitions at H point of bulk crystal $H_3 \rightarrow H_3$ [34] are polarized with $\mathbf{E} \parallel c$ and polarization properties of the corresponding radiation can be described in terms of linear oscillators, which ensemble is characterized with $r_0 \leq 0.4$. Therefore, it can be assumed, that transition from bulk molybdenum disulfide to nanocrystal is accompanied with modification of its electron spectrum, resulting in dominant contribution to the radiative transitions of the states at H point (transitions of $H_3 \rightarrow H_3$ type).

Analysis of polarized luminescence of molybdenum disulfide nanodots shows, that there is a correlation between the emitted photons energy and volume of dots: the higher photon energy, the lower dot volume. It is natural to associate this correlation with quantum size effect in electron spectrum of nanodots, resulting in dependence of the forbidden band width of a nanodot on its size. Under conditions of strong quantum confinement the forbidden band width (ground state energy of electron-hole pair) of spherical semiconductor nanodot is defined with relation [38]:

$$E_{g\mathrm{ND}}(R) = E_{g0} + \frac{\hbar^2\pi^2}{2\mu R^2} - 1.786\,\frac{e^2}{4\pi\varepsilon_0\varepsilon R} - 0.248E_{\mathrm{Ry}}, \tag{3}$$

where μ — exciton reduced mass, $\hbar$ — Plank constant, e — electron charge, ε_0 — electric constant, ε — dielectric constant of nanodot material, E_{Ry} — excitonic rydberg. At room temperature the radiative transitions energies, responsible for luminescence bands in bulk crystals of MoS_2 [25], are close to E_{g0}: $h\nu_{\mathrm{emis}} \approx E_{g0}$. Assuming for the sake of simplicity, that for nanodots $h\nu_{\mathrm{emis}}(R) \approx E_{g\mathrm{ND}}(R)$, let's assess based on (3) the sizes (diameters) of nanodots d, forming various regions of emission spectrum in Fig. 1. The estimate gives $d = 2R = 1.6\,\mathrm{nm}$ ($h\nu_{\mathrm{emis}} = 2.82\,\mathrm{eV}$), $d = 1.9\,\mathrm{nm}$ ($h\nu_{\mathrm{emis}} = 2.41\,\mathrm{eV}$) and $d = 2.3\,\mathrm{nm}$ ($h\nu_{\mathrm{emis}} = 2.14\,\mathrm{eV}$), which are close to the values, obtained from polarization measurements. The following parameters of MoS_2 were used during the assessment: $E_{g0} = E_{g\mathrm{H}0} = 2.0\,\mathrm{eV}$ [39,40], $\mu = 0.33m_0$ [41,42] (m_0 — free electron mass), $\varepsilon = 3.3$ [43], $E_{\mathrm{Ry}} = 0.05$ [44]. It should be noted, that equation (3) overstates the value of $E_{g\mathrm{ND}}$ [45], not considering, particularly, dependencies of an effective mass μ [46,47] and ε [48] on nanoparticle size.

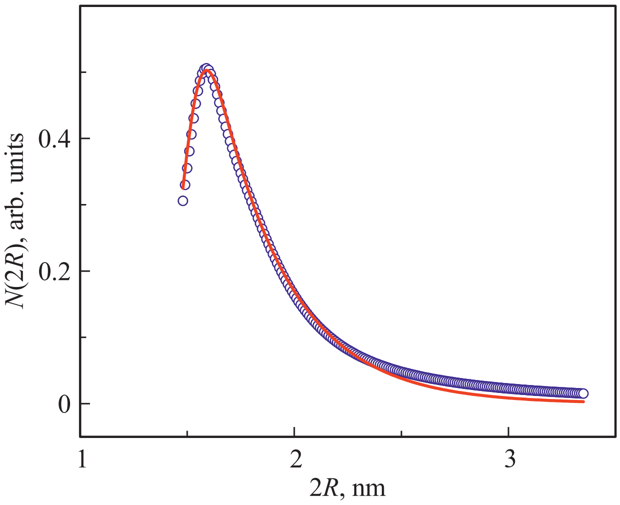

Figure 4. Size distribution of photoexcited nanodots of MoS_2 in NMP at light excitation with $h\nu_{\mathrm{exc}} = 3.061\,\mathrm{eV}$. Points represent distribution density of $N(2R)$, calculated based on (5), solid line — approximation of $N(2R)$ with a density function of probability of exponentially modified normal distribution.

In approximation of $h\nu_{\mathrm{emis}}(R) \approx E_{g\mathrm{ND}}(R)$ the relation (3) allows to obtain the function of the size distribution density of photoexcited nanodots in solution. Emission intensity of an ensemble of nanodots

$$I(E) \propto N(E)W_{\mathrm{r}}(E), \tag{4}$$

where $N(E)$ — energy distribution density of photoexcited nanodots $E \equiv h\nu_{\mathrm{emis}}(R) \approx E_{g\mathrm{ND}}(R)$, $W_{\mathrm{r}}(E)$ — probability of radiative electron-hole recombination in a nanodot. In its turn, the size distribution density of photoexcited nanodots $N(R)$ is associated to $N(E)$ with relation $N(E)|dE| = N(R)|dR|$, from where

$$N(R) = N\big(E(R)\big)\left|\frac{dE(R)}{dR}\right| \propto I\big(E(R)\big)W_{\mathrm{r}}^{-1}(R)\left|\frac{dE(R)}{dR}\right|, \tag{5}$$

where $E(R)$ is described with relation (3). At known dependence $W_{\mathrm{r}}(R)$ [49] the relation (5) allows to define the main features of $N(R)$ function.

Functional dependence $N(2R)$ calculated on the basis of (5) characterizing size distribution of photoexcited nanodots of MoS_2, is presented in Fig. 4. Shape of distribution $N(2R)$ is well approximated with exponentially modified normal distribution with maximum at $d_{\mathrm{M}} = 1.6\,\mathrm{nm}$, shown in Fig. 4 with a solid line.

4. Conclusion

Chemical exfoliation and dispersion of MoS_2 micropowder in solutions under ultrasound exposure allow to obtain the nanodots of molybdenum disulfide, which luminescence covers a wide spectral range, located in a region of fundamental absorption of bulk crystals. Studies of polarized luminescence of colloidal system of nanodots under conditions of linearly polarized excitation show, that different spectral regions of radiation band are formed with nanodots of different volume. This indicated the significantly inhomogeneous broadening of the spectrum, related to the size dispersion of the luminous nanodots. Analysis of spectra of polarized luminescence of MoS_2 nanodots shows, that in assumption of their sphericity the diameter of photoexcited dots is within a range of $1.5-1.7$ nm. Dependence of nanodots emission wavelength on their size can be explained with quantum size effect. Considering the connection between luminescence spectrum shape and size distribution density of photoexcited nanodots of MoS_2, the shape of distribution density function is assessed and it is shown, that it is characterized with a maximum at $d_M = 1.6$ nm. It is shown, that the results of MoS_2 nanodots sizes assessment using polarized luminescence method and based on relation (3) are in satisfactory agreement with each other.

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Conflict of interest

The authors declare that they have no conflict of interest.

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