Comment on 'Unconventional gap state of trapped exciton in lead sulphide quantum dots'

R J Curry

Advanced Technology Institute, University of Surrey, Guildford, Surrey, GU2 7XH, UK

E-mail: r.j.curry@surrey.ac.uk

Abstract

In a recent paper Lewis *et al* (2010 *Nanotechnology* **21** 45502) proposed a previously unidentified gap state within lead sulphide nanocrystals (PbS-NCs) based on analysis of their temperature dependent optical properties. In the following we argue that due to oversights in the analysis of the data presented, inconsistencies arise which question their exclusion of 'dark' excitonic states as the origin of the observed effects.

Recently, temperature dependent absorption and photoluminescence (PL) of lead sulphide nanocrystals (PbS-NCs) were presented by Lewis *et al* [1] showing the well known redshift as temperature is reduced. This behaviour is in contrast to most semiconductors which instead display a blueshift with reducing temperature.

Analysis of the temperature dependent PL can provide insight into its origin and which parameters play an important role in determining its behaviour. Plotting the temperature dependence of the relative PL energy shift, ∂E (equation (1)), can be used to infer or exclude the presence of emission from ‘dark’ excitonic states.

$$\frac{\partial E}{\partial T} = \frac{E_2 - E_1}{T} \quad (1)$$

(1)

Figure 3(a) in [1] provides the required data for such analysis which the authors present in figure 4(a). However, as can be clearly seen from figure 3(a) (E should be negative leading to $\partial E/\partial T$ being positive as opposed to that presented in Figure 4(a). Whilst figure 4(a) does show the magnitude of the temperature dependent shift, $|\partial E|$, it is critically important that the direction is also considered along with its gradient. To illustrate this point we can consider a simple 3-level system (figure 1) in which level 1 represents a ‘bright’ excitonic state and level 2 a ‘dark’ excitonic state with populations N_1 and N_2 respectively, separated by an energy ϵ . When $k_B T > \epsilon$ then with an intersystem crossing rate, A_{isc} , being typically orders of magnitude faster than the ‘dark’ radiative recombination rate, $1/\tau_2$, emission is dominated by recombination of the ‘bright’ state as $N_1 > N_2$. We note that A_{isc} must compete with the radiative emission rate from the ‘bright’ excitonic state, $1/\tau_1$, and in these systems is enhanced via the ‘heavy atom effect’. In contrast, when $k_B T < \epsilon$ transfer from the ‘dark’ to ‘bright’ excitonic state is reduced and radiative recombination of the ‘dark’ state can dominate the emission as $N_1 < N_2$.

For systems that display an overall blueshift in emission with reducing temperature such as CdSe-NCs [2] this effect can be seen by analysis of data using (1). The result is that $\partial E/\partial T$ can switch from being negative to positive at very low temperatures when emission from the ‘dark’ excitonic state starts to dominate giving what has been referred to as a ‘hook’ [1,2]. However, for systems in which a redshift of the PL is observed with reducing temperature this effect does not present itself in the same way and no ‘hook’ can be expected. Instead for systems with an appreciable value of ϵ all that might be expected is that $\partial E/\partial T$ remains positive or in extreme cases further increases (i.e. becomes more positive) at very low temperatures. For systems in which the temperature dependent redshift saturates above $T = \epsilon/k_B$ then $\partial E/\partial T$ will start to tend to zero at this temperature though may remain slightly positive until the emission becomes totally dominated by the ‘dark’ state. This leads to a ‘flattening off’ in $\partial E/\partial T$ very similar to that observed when the data in figure 4(a) in [1] is plotted as $-\partial E$ rather than as $|\partial E|$. As such the lack of ‘hook’ in the data presented in Figure 4(a) of [1] is expected and cannot be used as evidence that the PL does not originate from a ‘dark’ excitonic state. Therefore the proposal of a new unconventional gap state in these systems in order to explain the observed behaviour requires further evidence if ‘dark’ excitonic states are to be excluded.

Figure 1. Three-level rate model used to evaluate the temperature dependent behaviour of $\eta E(T)$ defines in (1). N_x is the population of level x with $x = 1$ being a 'bright' excitonic state and $x = 2$ a 'dark' excitonic state. A_{isc} is the intersystem crossing rate, $1/\tau_1$ and $1/\tau_2$ are the radiative recombination rates of the 'bright' and 'dark' states respectively.

References

- [1] Lewis J E and Jiang X J 2010 *Nanotechnol.* **21** 455402.
- [2] Liptay T J *et al.* 2007 *Phys. Rev. B* **76** 155314.