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Comments on the published article “The synthesis and optical properties of GaSe/InSe core/shell nanoparticles”☆

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The above titled paper [1] was published without my knowledge, with Shuming Yang as the corresponding author. The results presented in this paper were largely obtained in my laboratory at U C Merced by S. Yang, who was then a postdoctoral researcher in my group. We had pursued the project of attempting to synthesize GaSe/InSe core/shell particles, thinking that they were likely to have interesting spectroscopic and dynamical properties. However, following a few attempts to synthesize these particles, the spectroscopic results made it clear that such particles were not being formed. These exact same data are presented in reference [1], with the opposite conclusion. I disagree with the conclusions in reference [1], for reasons discussed below.

GaSe and InSe are both layered semiconductors consisting of Se–M–M–Se sheets, where M = Ga or In. Nanoparticles of these materials consist of single tetralayer sheets. One would expect a “core/shell” particle to also be a single tetralayer, and thus, such a structure might better be described as a disk/annulus particle. The valence and conduction band offsets of GaSe and InSe are such that they form a “type II” heterojunction. Specifically, the valence and conduction bands of InSe are 0.1 and 0.9 V, respectively, below those of GaSe [2]. A photogenerated exciton will therefore undergo at least partial charge separation, with the hole on the GaSe portion of the particle, and the electron on the InSe portion. An electron initially in the GaSe portion of the particle loses on the order of 0.9 eV of energy upon relaxation to the InSe potion of the particle. This sort of charge-separated excited state has distinct, characteristic spectroscopic properties. Radiative recombination of the electron in the lower energy InSe conduction band with the hole in the lower energy GaSe valence band results in far red-shifted luminescence. In the present case, one would expect the luminescence to be red shifted by close to 0.9 eV, compared to luminescence from the parent GaSe nanoparticles. GaSe nanoparticles typically luminesce with a maximum at about 475 nm. In the case of complete charge separation, a GaSe/InSe core/shell particle would be expected to have a luminescence maximum at 725 nm. Partial charge separation would result in less, but still significantly red-shifted luminescence. Alternatively, in the case of a very thin InSe shell, charge separation may be described in terms of the less electronegative indium atoms at the particle edges having larger positive charges than the gallium atoms and therefore acting as electron traps. Radiative recombination of an indium “trapped” electron with a hole would lead to red-shifted luminescence. In either case the conclusion is the same: the characteristic spectroscopic signature of any hybrid semiconductor nanoparticle having offset valence and conduction bands is luminescence that is red shifted from that of the parent semiconductor nanoparticles. This is consistently observed in other type II nanostructures, specifically CdSe/CdTe, CdSe/ZnTe heterostructures [3]. Inspection of Figure 4 in reference [1] reveals that red-shifted luminescence is totally absent. The luminescence anisotropy results are also inconsistent with the formation of core/shell particles. The charge transfer transition in a planar core/shell particle is in the plane of the nanoparticle. The lowest transition of the GaSe portion of the nanoparticle is polarized normal to this plane [4,5]. Thus, luminescence from core/shell particles is expected to have a polarization that is orthogonal to that of the excitation. This would result in a negative luminescence anisotropy, in contradiction to the results shown in Figure 5 of reference [1]. Both of these simple, unambiguous considerations lead to the same conclusion: core/shell nanoparticles are not formed.

In retrospect, this conclusion is easy to understand. The ability to form such a core/shell (or disk/annulus) nanoparticles depends on several factors, including the lattice mismatch and the reactivity of the shell precursors. In the case of GaSe and InSe the lattice mismatch is about 6.5%. This is quite significant, but not sufficient to preclude the formation of epitaxial structures. However, the deposition of InSe on an existing GaSe nanoparticle will be energetically quite unfavorable and may proceed rather slowly. Epitaxial growth must compete with nucleation of new InSe nanoparticles, and the rate of nucleation depends, in part, on the precursor reactivity. In this synthesis, the indium source is the highly reactive organometallic, $In(CH_3)_3$ and reaction with trioctylphosphine selenium results in very rapid nucleation. These results make clear that the strained-lattice deposition to form core/shell particles does not compete with nucleation.

The analytical results in reference [1] show that both gallium and indium are present in the sample. Consistent with the presence

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☆ The following represents a comment on the recently published paper entitled “The synthesis and optical properties of GaSe/InSe core/shell nanoparticles” by Shuming Yang, Hongjun Wang, Wenhong Fu, and David F. Kelley (*Journal of Photochemistry and Photobiology A: Chemistry* **2007,** 192, 159). The first author, Dr. S. Yang, was provided with a copy of the comment and given the opportunity to write a rebuttal. Dr. Yang wishes to provide no written rebuttal to Dr. Kelley’s statement.

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of both metals, all of the spectroscopic and dynamical results are strongly reminiscent of those seen from GaSe and InSe nanoparticles. Thus, the results presented in reference [1] can be easily understood in terms of a mixture of GaSe and InSe nanoparticles.

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