Doping nanocrystals by *in situ* layer-by-layer overcoating

Hsueh-Shih Chen,[1,a] Ramachandran Vasant Kumar,[1] and Hsin-Yen Hong[2]
[1]*Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ, United Kingdom*
[2]*Material and Chemical Laboratories, Industrial Technology Research Institute, Kuan-Fu Road Sec. 2, Hsinchu 300, Taiwan*

We demonstrate that internally doped nanocrystals can be obtained by an *in situ* overcoating process. In the case of ZnSe doped with iodine, ZnSe cores are overcoated by interlaced iodine layers and ZnSe layers to incorporate the iodine atoms into the ZnSe matrix. Photoluminescence from the ZnSe band edge is gradually depressed, while emission from the deep-level recombination caused by iodine is dramatically improved up to fourfolds with increasing number of iodine/ZnSe overcoats. This result suggests that the impurity atoms are incorporated into the host matrix. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3115035]

Intrinsic semiconductors are usually intentionally doped with impurities to alter their electric, optical, magnetic, and superconducting properties.[1–4] It is found that doping colloidal nanocrystals (NCs) is particularly difficult due to certain reasons that remain unclear.[5] A general approach to dope colloidal NCs is to directly mix dopant monomers with host monomers as a precursor. However, a doping level achievable in this method, based on probabilistic collisions between impurities and host monomers, is either zero or is very limited.[6] Despite some studies that have announced the doping by using specific monomers, there is no general approach to synthesize internally doped NCs.[7] Most of the cases show that dopants are predominantly bounded on the NCs surface.[8] For this phenomenon, it has been suggested that impurities are expelled from a host matrix due to a thermodynamic surface-purification process as the formation energies of defects increase with decreasing size,[9] or a kinetic limit as the doping of impurities mainly occurs on the specific facets having higher surface energy.[10]

Unfortunately, surface doped NCs may not show desired properties completely, e.g., entirely switch an emission from a host to an impurities-related recombination.[10] Moreover, surface-adsorbed impurity atoms may not sustain a post treatment, e.g., surface functionalizations.[11] In this letter, we present an approach to incorporate impurities into NCs matrix by alternately *in situ* overcoating of impurity layers and host layers.

In situ overcoating of NCs has been reported.[12,13] In the present study, several sets of alternating impurity monomer injection and host monomer injection were conducted to overcoat ZnSe cores. ZnSe cores were first produced before the *in situ* overcoating process was carried out. A Zn precursor was prepared by mixing 2.5 mmol ZnO, 8 mmol lauric acid, and 8 mmol hexadecylamine at 280 °C under an argon flow. TOP-Se and TOP-Se-I precursors were prepared separately for the alternating injection process. The TOP-Se precursor was prepared by dissolving 1.5 mmol Se into 1 ml trioctylphosphine (TOP) and diluted by toluene to 5 ml. The TOP-Se-I precursor was prepared by 0.1 mmol iodine de-

gassed in vacuum for 1 h, 1.5 mmol Se, 1 ml TOP, and diluted by toluene to 5 ml in an ultrasonic bath at 50 °C. ZnSe cores were produced by introducing 1 ml of the TOP-Se into the hot Zn precursor at 280 °C and reacted at 260 °C for 2–3 min depending on the desired size. Then, alternating TOP-Se-I (0.5 ml) and TOP-Se (0.5 ml) injections were carried out every 30 s. Samples prepared by the *in situ* layer-by-layer overcoating method are named as ZnSe:[I/ZnSe]$_n$ NCs, where n is the number of the I/ZnSe pair overcoat. ZnSe:I NCs prepared by a monomers mixing method with a mixture of TOP-Se (Se/TOP=1.5 mmol/ 1 ml) and TOP-I (iodine/TOP/toluene=0.1 mmol/1 ml/ 1 ml) are named mix-ZnSe:I NCs (injection/growth= 280/260 °C). In a purification process, 50 ml methanol was poured into the reaction vessel under argon flow at 150 °C. Then the mixture was moved to an ultrasonic bath for 60 min. Samples were separated by a centrifugation. The precipitated solids were further washed by hot methanol (~50 °C) for several times. In etching experiments, dried ZnSe:I NCs were dispersed into 50 ml pyridine in an ultrasonic bath at 50 °C for 3 h. The samples were collected by adding 1 ml of hexane before centrifugation and dried by vacuum. Photoluminescence (PL) measurement was performed at 325 nm excitation wavelength.

X-ray diffraction patterns (XRD) show that ZnSe and mix-ZnSe:I samples have wurtzite characteristics (Fig. 1). (002) peak appears to have higher intensity due to the addition of intensity from the adjacent peaks. PL and absorption spectra from ZnSe and mix-ZnSe:I NCs are shown in Fig. 2. For the ZnSe NCs, the first excitonic absorption and PL exhibit sharp peaks at 410 and 416 nm, respectively, corresponding to about 4.5 nm in diameter.[12] For the mix-ZnSe:I NCs, the excitonic absorption becomes slightly broader and the PL spectrum display a sharp peak at 418 nm together with a broadband at 512 nm, indicating iodine doping causes a change in the optical property of the ZnSe NCs. The sharp PL peak at 418 nm is the band edge emission from the recombination of the quantum confined excitons. The broadband is due to the recombination of carriers at the deep levels caused by the iodine doping. This duality of PL is thought to be an incomplete incorporation of impurities in a host, for example, by surface doping of impurities on NCs.[10] A slight

a)Electronic mail: hsc28@cam.ac.uk. Tel.: +44 1223 334315. FAX: +44 1223 334567. Also at MCL, Industrial Technology Research Institute, Kuanfu Road Sec. 2, Hsinchu 300, Taiwan.
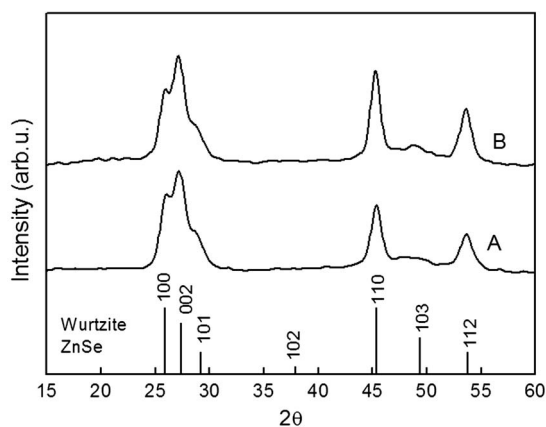
FIG. 1. XRD of ZnSe (curve A) and mix-ZnSe:I NCs prepared by mixing monomers and impurities (curve B).

FIG. 3. (Color online) Doping NCs by mixing monomers/impurities (a) and *in situ* layer-by-layer overcoating approach (b).

peak at around 380 nm is from monomers as confirmed by a blank test.

Internal doping of semiconductor NCs was thought to be difficult as the self-purification or the binding energy between a dopant and a facet limits the incorporation of impurities into NCs matrix.[9] Despite the fact that the impurities were difficult to be completely incorporated into NCs matrix in the previous studies, it did show that surface-adsorbed impurities could be covered by an additional passivation layer.[10] Moreover, it has been shown that a passivation layer could be epitaxially grown on a NC core by *in situ* overcoating in the atomic scale by an additional injection of monomers.[12] Taken together, if an impurity overcoat followed by a host overcoat could be produced layer by layer, it would be able to completely encapsulate dopants into NCs matrix. This can be done by a series of alternating dopant-host monomers injections, as schematically shown in Fig. 3. In a conventional process, dopant monomers are mixed with host monomers. Dopant atoms may finally locate at the NCs surface [Fig. 3(a)]. For the *in situ* layer-by-layer overcoating process, dopant layers and host layers are grown alternately. Despite that dopants may locate at the surface region of NCs cores after an injection of impurity monomers, the NCs surface could be subsequently covered by a ZnSe overcoat, covering and fixing the surface impurity atoms, as shown in Fig. 3(b).
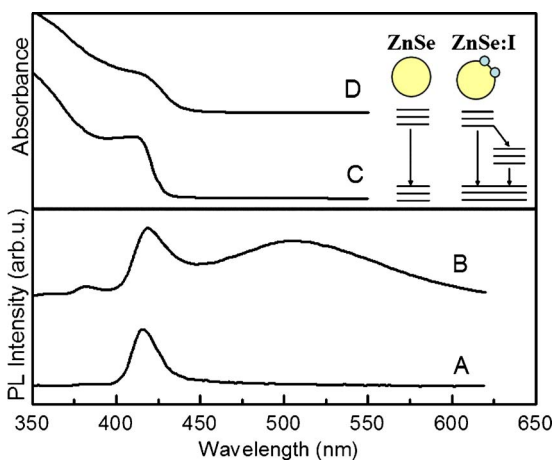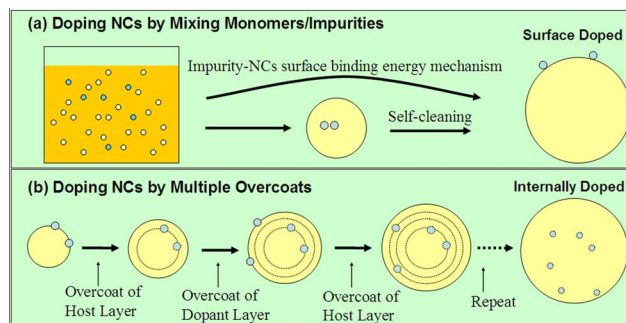
According to PL spectra (Fig. 4), PL of ZnSe NCs gradually transits from the band edge emission to the deep-level emission with increasing number of impurity/host layers. Bare ZnSe cores have a band edge emission at 416 nm before doping is conducted (curve A). When the bare ZnSe NCs are overcoated by a pair of an I layer and a ZnSe layer, forming $ZnSe:[I/ZnSe]_1$ NCs, an impurity-related emission band at about 512 nm appears, as shown in curve B. This PL spectrum is quite similar to that of the mix-ZnSe:I NCs, showing that iodine doping does not completely switch the band edge emission to the deep-level emission. The data also demonstrate that the duality of PL spectra of mix-ZnSe:I NCs are caused by the surface-adsorbed iodine atoms. As the $ZnSe:[I/ZnSe]_1$ NCs are overcoated by more I/ZnSe layers, the band edge emission intensity steadily decreases, while the iodine-related emission intensity dramatically improves, as shown from curves B to D in Fig. 4. The disappearance of the PL duality elucidates that the deep-level emission from iodine doping finally dominates the PL of $ZnSe:[I/ZnSe]_n$ NCs. Relative concentrations of dopants in NCs can be associated with the PL intensity ratio of NCs cores to dopants.[10] Estimated PL intensity ratios of the band edge emission to the deep-level emission are 0.75, 1.28, and 4.57 for $n=1$, 3, and 5, indicating the relative concentration of iodine atoms in $ZnSe:[I/ZnSe]_n$ NCs increases with increasing number of the overcoats. This proves that overcoating of I/ZnSe effectively incorporate iodine atoms into the ZnSe matrix. Curve E shows as ZnS layer is further grown as a passivation layer on the $ZnSe:[I/ZnSe]_5$ NCs, further increasing the PL intensity about 34% has taken place.
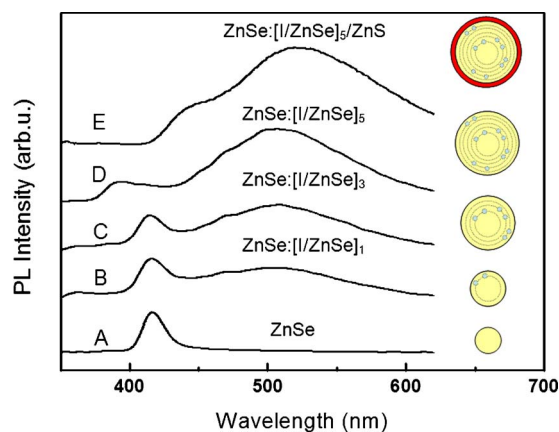

FIG. 2. (Color online) PL and optical absorption spectra from ZnSe (curve A and C) and mix-ZnSe:I NCs (curve B and D).

FIG. 4. (Color online) PL spectra from bare ZnSe NCs and I-doped ZnSe NCs by *in situ* overcoating.

FIG. 5. TEM image of ZnSe:$[I/ZnSe]_5$/ZnS NCs.

FIG. 6. (Color online) Effects of pyridine treatment on PL spectra for ZnSe:$[I/ZnSe]_1$ NCs. Inset shows changes in integration intensity of the band edge and the deep-level emissions for ZnSe:$[I/ZnSe]_n$ NCs.
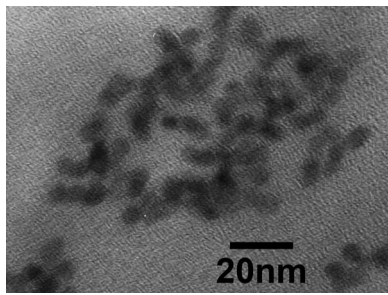
Transmission electron microscopy (TEM) images of ZnSe:$[I/ZnSe]_5$ NCs are shown in Fig. 5. The mean size of the ZnSe:$[I/ZnSe]_5$ NCs slightly increases from 4.5 to 5.1 nm after the overcoating process. The *in situ* layer-by-layer overcoating does not lead to an obvious redshift of 416 nm PL peak, implying that the interlaced impurity-host overcoating result shows no increase in the pure ZnSe cores. In addition, some shoulders are observed for the doped ZnSe NCs, e.g., ~450/470 nm in the curve D, and ~450 nm in the curve E, which are possibly due to the specific placement of dopant in the NCs that might change the local environment and the luminescence.[5] Further work is needed to research the PL mechanism of doped NCs by the *in situ* layer-by-layer overcoating.

To examine the degree of doping, an etching experiment is conducted for the iodine-doped ZnSe NCs. Because pyridine could remove surface species by the ligand exchange, it provides a convenient way to observe the surface doping.[6] Fig. 6 plots the PL integration intensities of 416 nm peak (400–440 nm) and 512 nm PL peak (450–650 nm) measured before and after the etching experiment is carried out. The pyridine treatment leads to intensity decreases of both 416 and 512 nm PL peaks of all ZnSe:$[I-ZnSe]_n$ samples. For ZnSe:$[I-ZnSe]_1$ NCs, intensity decays of 512 and 416 nm peaks are about 57% and 61%, respectively after an etching treatment (Fig. 6). The shape of the PL shows no significant difference. This implies that the etching removes both impurity and host atoms, and induces some nonirradiative defects. Considering the decay of the 416 nm peak for ZnSe:$[I/ZnSe]_n$ NCs with regard to different overcoats, it shows that $n=1$, 3, 5, 7, and 10 have about 61%, 51%, 49%, 43%, and 24% reductions in intensity, respectively, as shown in Fig. 6 (inset). The amount of intensity reduction decreases with increasing overcoats after the treatment of pyridine. This is reasonable as more overcoats are capable of preventing ZnSe cores from etching. Interestingly, intensity decays of the 512 nm peak reduces about 57%, 38%, 53%, 44%, and 49% for $n=1$, 3, 5, 7, and 10, respectively, which are roughly half their original intensities. This may indicate that all samples have about the same amount of impurity atoms on the near surface region so that the etching causes a similar degree of intensity decay. Theoretically, if the impurity atoms are immobile in the matrix, the impurity content inside ZnSe:$[I/ZnSe]_n$ NCs should increase with increasing number n. Therefore, the amount of the intensity decay of 512 nm PL should decrease with increasing n as the etching only removes surface species. Presumably, this event is resulted by the migration of the impurity atoms to the near surface
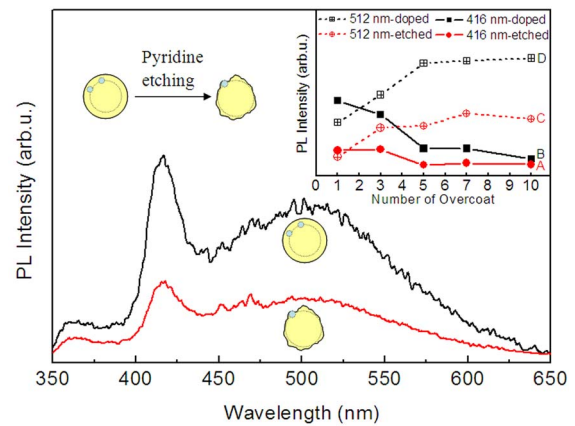
region in the NCs in the overcoating process. The migration may be driven by the thermal energy. Unfortunately, it is difficult to identify the migration of the impurity atoms arising after the growth of the next host layer (via bulk diffusion) or during the host layer growth (via surface diffusion) or both. It appears that the arrangement of impurity atoms on the surface is more possible as the activation energy of diffusion on a surface is lower than that in a bulk. This viewpoint may bring an alternate explanation of doping of colloidal NCs; if the growth of NCs is a layer-by-layer atomic accumulation process, which is likely for the growth of colloidal NCs, bound impurity atoms may be mobile via the surface diffusion and finally locate themselves at the surface region after the NCs growth.

In summary, internal iodine doping of ZnSe NCs has been established by an *in situ* layer-by-layer overcoating process via alternating iodine precursor and ZnSe precursor injections. The ratio of the band edge emission intensity from the ZnSe cores to the deep-level emission caused by the iodine doping increases with increasing number of I/ZnSe overcoats. With five I/ZnSe overcoats, the band edge emission is nearly depressed, while the deep-level emission dramatically increase about four times.

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