Electronic Supplementary Material (ESI) for Nanoscale.

Electronic supplementary information

Coherent InP/ZnS Core@Shell Quantum Dots with Narrow-Band Green Emission

Kazuhiro Nemoto,[a,b] , Junpei Watanabe,[a,c] Hong-Tao Sun,[a] and Naoto Shirahata*[a,b,c]

[a]International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, 305-0044, Japan.

[b]Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo 060-0814, Japan.

[c]Department of Physics, Chuo University, 1-13-27 Kasuga, Bunkyo, Tokyo 112-8551, Japan.

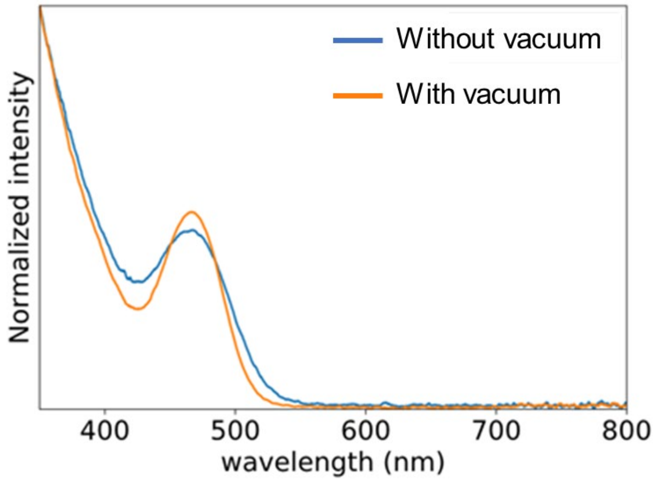

Figure S1. Optical absorption spectra of the InP core QD samples.

NOTE:

The spectrum color-coded in orange has a sharp first-exciton absorption peak while the other spectrum color-coded in blue has a relatively broad peak. The sharp peak was obtained from the sample which was prepared by injection of [P(TMS)$_3$] solution, followed by degassing at 30 Pa of vacuum condition. The other sample exhibiting a broad peak was prepared without the degassing of [P(TMS)$_3$] solution.

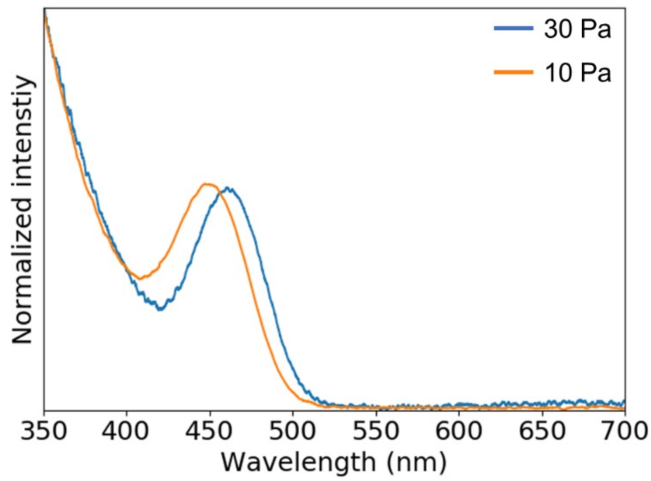

Figure S2. Normalized UV-vis spectra of InP core QD samples prepared using the precursor solutions degassed under 10 Pa (color-coded with orange) and 30 Pa (color-coded with blue). The first exciton peak of the sample (blue) is narrower and sharper than that of the sample (orange).

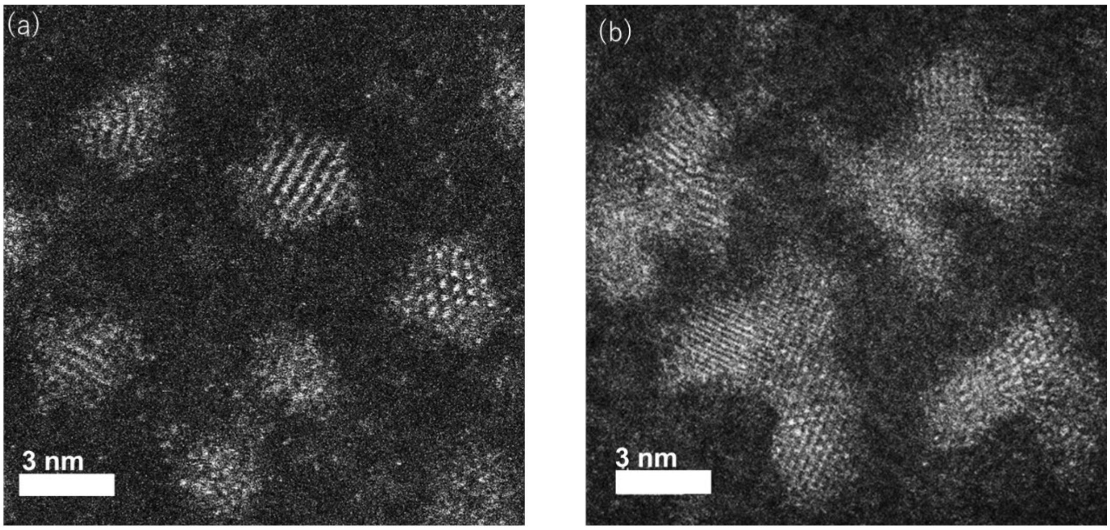

Figure S3. The typical HAADF-STEM images of (a) InP/ZnS (3ML) and (b) InP/ZnS (6ML) core/shell QD samples.

NOTE: The photographs (b) indicate that the roughened shape is based on the S-K growth mode.

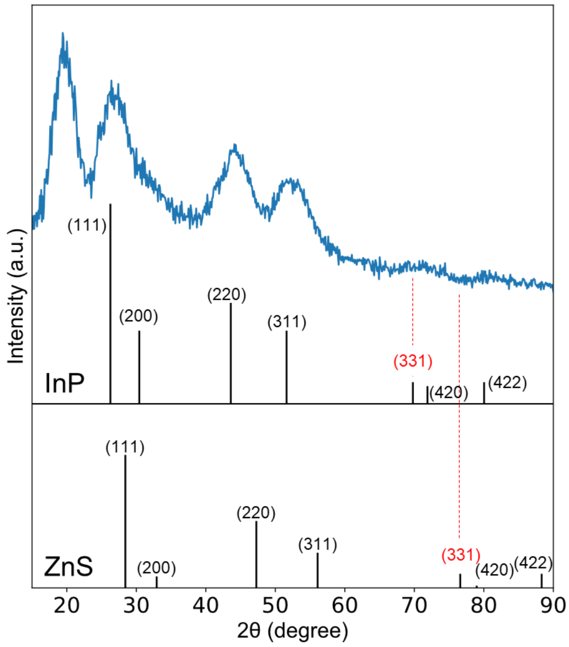

Figure S4. XRD pattern of InP/ZnS (2ML)

NOTE: The XRD peaks are very broad due to reduction in diameter of the QDs. There are tiny peaks at around 71.9° and 80.0°, corresponding to the (420) and (422) planes of InP. However, there is no peak corresponding to the (331) plane of ZnS, suggesting the disappearance of any Bragg diffractions of ZnS crystal planes in the XRD pattern. As a result, the shift of the diffraction angles observed in the XRD pattern appears due to the compressed crystalline lattice of InP.

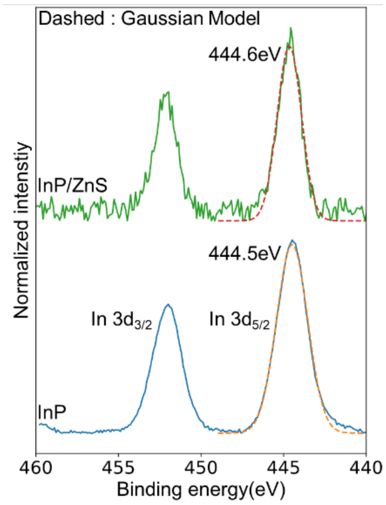

Figure S5. In3$d_{5/2}$ XPS signal of the the InP and InP/ZnS (3ML) core/shell QDs with Gaussian fitting.

NOTE

It has been reported that the crystalline In_2S_3 gives a peak at 445.3±0.1 eV (J. Appl. Phys. 1989, 65, 4051; J. Appl. Phys. 1997, 81, 6986). In our XPS spectrum after 3ML ZnS formation, the 3$d_{5/2}$ peak is centered at 444.6 eV and does not have a shoulder at a higher binding energy side. Thus, we concluded the absence of In_2S_3. The result of curve fitting with a single Gaussian function reveals the formation of not-alloyed core QDs. If Zn ions diffuse into InP core to form an alloy structure, In3$d_{5/2}$ XPS peak shifts from 444.4 eV to 445.0 eV (ACS Appl. Mater. Interfaces 2014, 6, 18233). But such a shift was not observed after 3ML-shell formation.

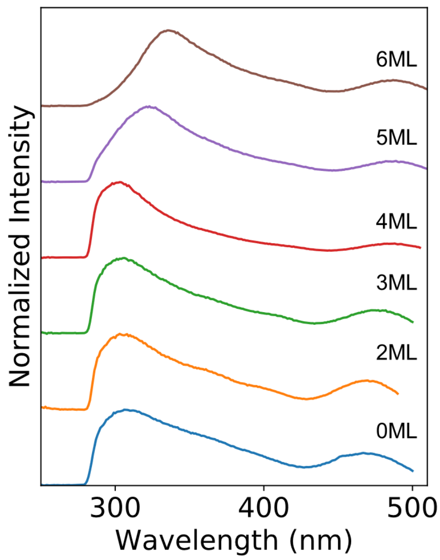

Figure S6. PLE spectra of the InP QDs covered with ZnS shells of different thicknesses.

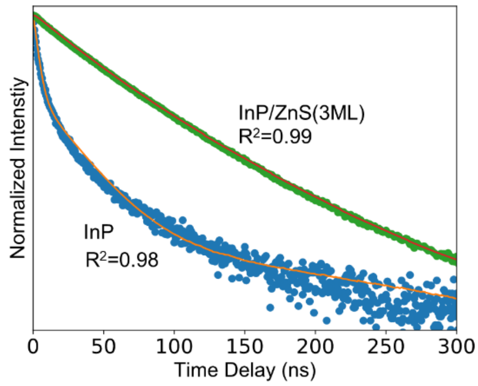

Figure S7. PL decay profiles of the InP core QD (blue dots) and the InP/ZnS (3ML) core/shell QD (green dots), respectively. Both PL decay curves were measured for each PL maximum estimated in Figure 3b. The measured decay curves were fitted with the di-exponential functions (as shown by solid lines color-coded with orange), which are as expressed by the equation (S1):

$$I(t) \approx B_1 exp\left[-\frac{t}{\tau_1}\right] + B_2 exp\left[-\frac{t}{\tau_2}\right] \qquad (S1)$$

where τ_1, and τ_2 are the first, second, and third components of the PL lifetime, and B1 and B2 are the amplitudes of each component, respectively.

Table S1. Parameters obtained by fitting with the equations (S1) and (S2).

sample	$A_1(10^{-2})$	τ_1(ns)	$A_2(10^{-2})$	τ_2(ns)	τ_{avg}(ns)	PLQY	kr(ns^{-1})	knr(ns^{-1})
InP	6.17	26.4	39.1	3.00	6.19	0.03	0.005	0.157
InP/ZnS(3ML)	31.4	32.2	30.2	63.8	47.7	0.70	0.015	0.006

Note: The amplitudes and the average values of PL lifetime were calculated by the equation (S2) which is expressed:[1,2]

$$\tau_{avg} = \sum_{i=1}^{n} A_i\,\tau_i \qquad (S2)$$

References

1. Y. Altıntas, M. Y. Talpur, M. Ünlü and E. Mutlugün, *J. Phys. Chem. C*, 2016, **120**, 7885–7892.

2. J. R. Lakowicz, *Principles of fluorescence spectroscopy*, Springer, New York, 3rd ed., 2006.

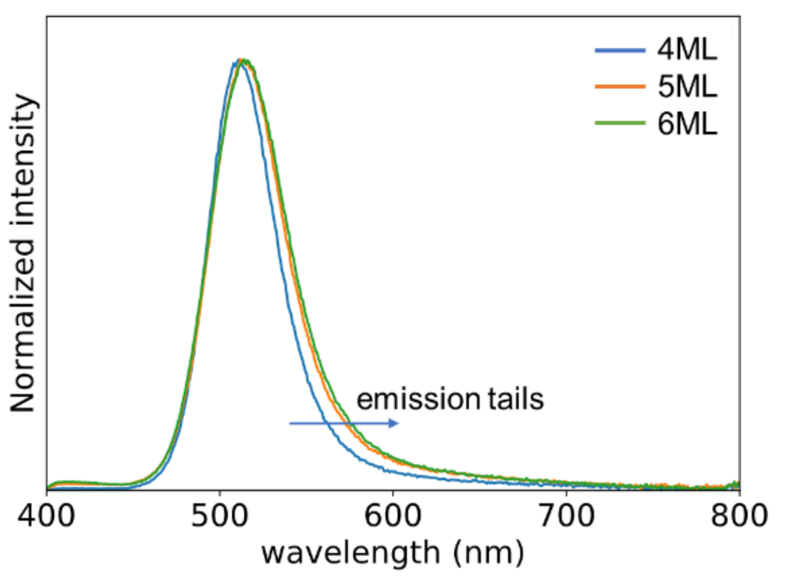

Figure S8. PL spectra of InP QDs coated with ZnS shells of 4ML, 5ML and 6ML.

NOTE: The spectrum of the 4ML-coated QD has a tiny emission tail at a longer wavelength. As is predicted, we see the growing emission tails after coating with 5ML- and 6ML shells. The PL spectral peaks of the 5ML- and 6ML-coated QDs are pulled to long wavelengths due to contribution of the emission tails, resulting in a PL peak shift to longer wavelengths as shown in Figure 2b.

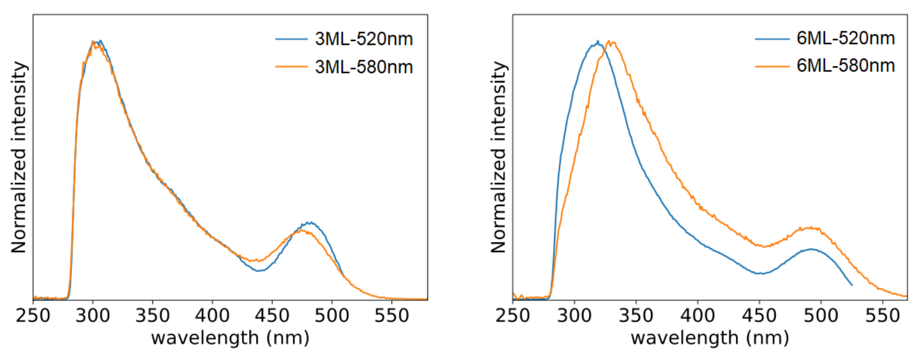

Figure S9. PLE spectra recorded for the PL peaks at 520 nm and the tail-emission peaks at 580 nm for the InP QDs with ZnS shells (3ML) and (6ML), respectively.