Electronic Supplementary Information

Direct observation of valence band splitting with room temperature photoluminescence of CdS hollow submicrospheres

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Experimental section

Materials: Tetraethyl orthosilicate(l, >98%, TEOS) and ammonia(aq, 25%) were purchased from MERCK-Schuchardt; (3-aminopropyl)triethoxysilane(l, >98%, APTES), $CdCl_2$(s, tech grade) and $Na_2S \cdot 9H_2O$ (s, >99.99%) were purchased from Sigma-Aldrich; 50% HF(aq) was purchased from J.T.Baker and diluted with water to make 1% HF(aq); and glycerol(l, >99.0%) and ethanol(l, >99.0%) were purchased from Daejung Chemicals. Ultrapure deionized water (>17 MΩ cm) from a Millipore Milli-Q system was used throughout the experiments. Hard template silica submicrospheres were initially prepared by mixing 0.520 mL (2.35 mmol) TEOS and 0.313 mL (4.19 mmol, for H1) or 1.253 mL (16.7 mmol, for H2) ammonia(aq) in 8.33 mL ethanol and 3.00 mL water and stirring for 1.5 h; the relative sizes for the silica templates for H1 and H2 were controlled by adjusting the added amount of 25% ammonia(aq). To functionalize the surface of the silica submicrospheres, an excess amount of 1.94 mL (8.33 mmol) APTES was added to the sample and the mixture was further stirred for another 2 h. 159 mg (0.867 mmol) $CdCl_2$ was added as the cadmium source and stirred for 15 h at 60 °C. After centrifugation, half of the cadmium-attached silica spheres were redispersed in a mixture of 10.0 mL H_2O and 10.0 mL glycerol, and 104 g (0.433 mmol) Na_2S was added as the sulfur source. After stirring for 1 h, the mixture was put under microwave irradiation for 10 min with stirring every 20 s. After centrifugation, the resulting SiO_2@CdS core@shell structures were redispersed in 8.0 mL ethanol, submerged in 72 mL of 1% HF(aq) for 2 min, quickly diluted with water, and then centrifuged.

Characterization: EFTEM images were obtained with a Carl Zeiss LIBRA 120 microscope and HRTEM images with a Tecnai F20 one. HRXRD patterns were recorded using a Bruker D8 DISCOVER diffractometer with Cu K_α radiation (λ = 0.154178 nm). Extinction spectra were measured by using a Scinco S-3100 UV/vis spectrometer, and PL spectra were obtained with a Princeton Instruments ICCD579G CCD detector attached to an Acton Research Spectrapro-500 spectrometer having a path length of 50 cm with excitation of 355 nm pulses having a duration time of 6 ns from a Quantel Brilliant Q-switched Nd:YAG laser.
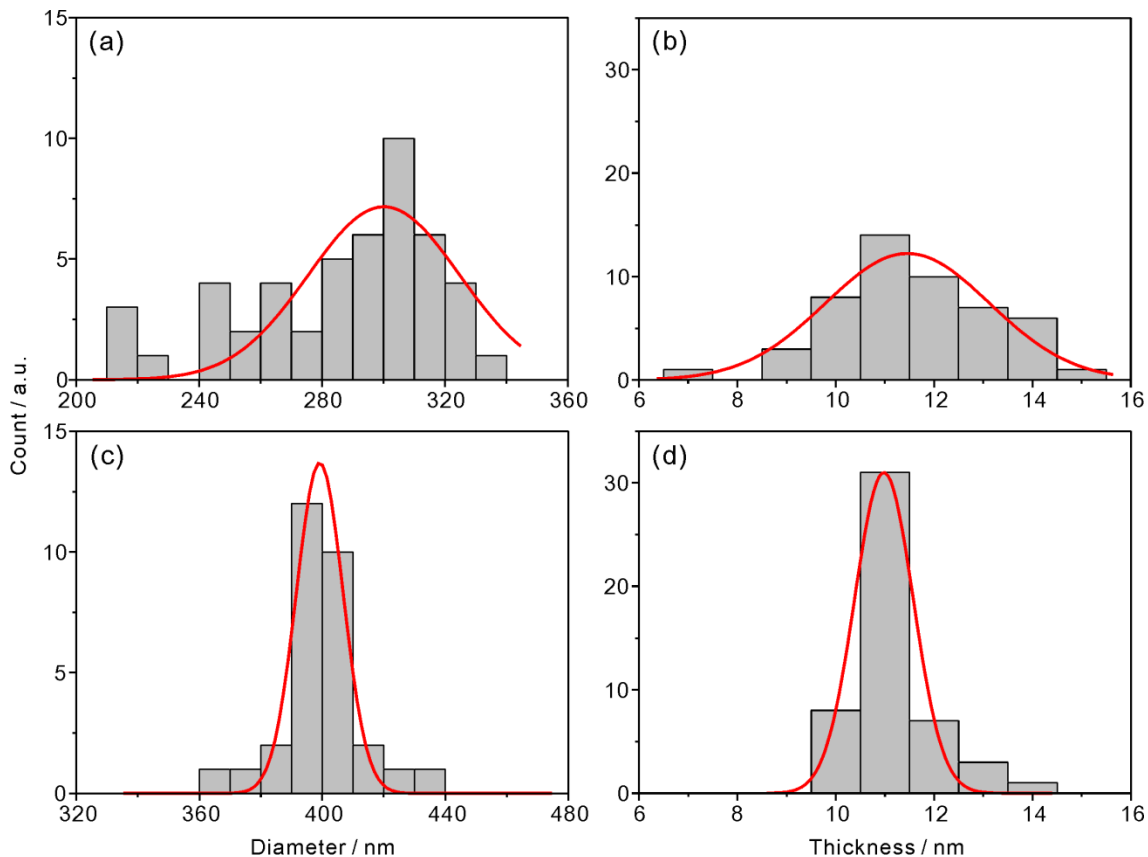

Fig. S1 Histograms showing to the outer diameters (left) and the shell thicknesses (right) of CdS hollow submicrospheres H1 (top) and H2 (bottom). H1 showed an average diameter of 300±25 nm (a) and an average shell thickness of 11±2 nm (b) while H2 showed an average diameter of 399±8 nm (c) and an average shell thickness of 11±1 nm (d).
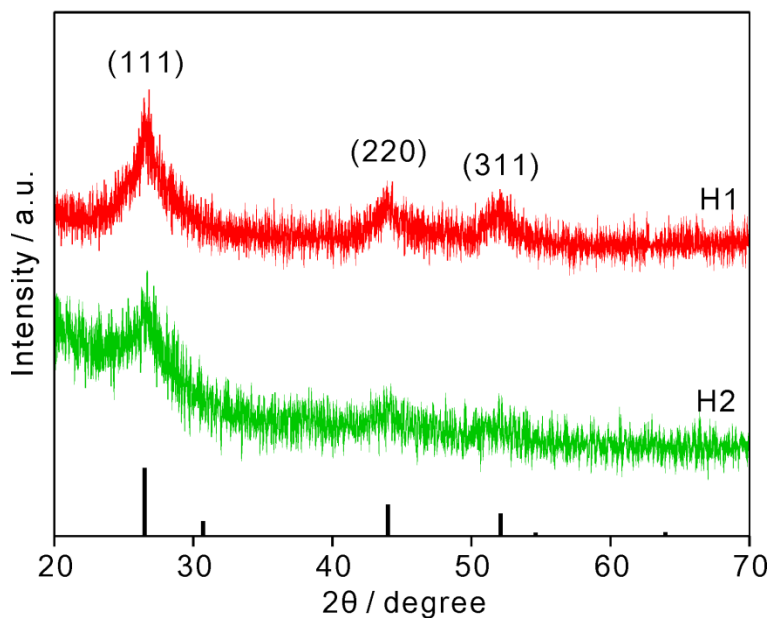
Fig. S2 HRXRD spectra of H1 (red) and H2 (green) revealing the cubic zinc blende crystal lattice (reference shown at the bottom, JPCDS Card No. 04-008-8227).

Table S1 Peak positions and integrated intensity values of the fitted Gaussian curves in Fig. 3

	H1		H2	
Transitions	Position (eV)	Intensity (a.u.)	Position (eV)	Intensity (a.u.)
$1s_e \rightarrow 1S_{3/2}$	2.505 ± 0.151^a	1.00	2.546 ± 0.143^a	1.00
$1s_e \rightarrow 1S_{1/2}$	2.698 ± 0.064	0.22	2.700 ± 0.062	0.26
$1p_e \rightarrow 1P_{3/2}$	2.860 ± 0.073	0.50	2.861 ± 0.073	0.62
$1p_e \rightarrow 1P_{1/2}$	3.034 ± 0.056	0.22	3.034 ± 0.054	0.24

[a] The Stokes shift of H1 is 115 meV while that of H2 is 34 meV. The large difference in magnitudes of the Stokes shift between two samples arises from differences in nanocrystallite sizes and nanocrystallite size distributions.

Table S2 Relative electron population of $1p_e$ to $1s_e$ $(N_{p_e}/N_{s_e})^a$ and relative hole population of $1L_{1/2}$ to $1L_{3/2}$ $(N_{1/2}/N_{3/2})^b$

	N_{p_e}/N_{s_e}		$N_{1/2}/N_{3/2}$	
Sample	$1L_{3/2}{}^c$	$1L_{1/2}{}^c$	$1s_e{}^d$	$1p_e{}^d$
H1	0.48	0.49	0.69	0.71
H2	0.60	0.48	0.81	0.65

[a] Calculated by normalizing the relative transition strength of $1p_e$ and $1s_e$ to a common lower state with the theoretical[15] relative absorption strength of the common lower state to the corresponding upper states.
[b] Calculated by normalizing the relative transition strength of $1L_{1/2}$ and $1L_{3/2}$ from a common upper state with the theoretical[15] relative absorption strength of the corresponding lower states to the common upper state, where L is S or P. [c] Common lower state. [d] Common upper state.