Supporting Information

Shell thickness-induced thermal dependence: highly sensitive core-shell CdSe/ZnS/POSS-based temperature probe

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Method:

Transmission electron microscopy (TEM) and high resolution TEM (HR-TEM) were recorded using a FEI G2F30 electron microscope with a Gatan SC 200 CCD camera. To characterize the crystal structure of the material, X-ray diffraction (XRD) patterns were recorded at a wavelength of Cu K (1.79) using a Bruker AXS D8 Discover X-ray diffractometer. An AXIS ULTRA (Kratos Analytical Ltd.) was used to evaluate the elemental composition of the samples via an Al mono K X-ray source (1486.6 eV). A Steady State & Lifetime Fluorescence Spectrometer was used to obtain the excitation spectra. An Edinburgh Instruments FLS920 spectrophotometer with an integrated nanowire was used to record the fluorescence spectra. Temperature dependence and temperature-dependent reversibility data of the material were obtained from the temperature-dependent experimental platform,[13] consisting of a laser, a spectrometer, a fiber optic, a digital thermostat, an MX 100 data collector, and a platinum resistance temperature sensor. The Agilent Cary 7000 Universal Spectrophotometer (UMS) was used to measure the absorbance of a quantum dot solution.

Calculations of the precursors for the shell growth:

(1) NC Correlation ε of CdSe NCs:

$$\varepsilon = 5857(D)^{2.65}$$

where D is the the diameter of the NCs.

(2) The concentration of a dispersion containing NCs of quantum dots can be determined by UV/Vis spectroscopy using the Beer–Lambert law:

$$A = \varepsilon * c * l$$

where A, ε, c, and l are absorbance, molar absorbtivity (L mol cm^{-1}), NC concentration (mol L^{-1}), and path length of the cuvette in which the sample is contained (cm), respectively.

(3) Lattice constant of Zinc blende ZnS: a=0.5406 nm.
The volume of ZnS molecular: $V_{ZnS}=a^3/4$.
The average thickness of one monolayer of ZnS (d): $d=\sqrt{3}/3*a^3$

(3) The amount of precursor required to grow a shell material with x monolayer thicknesses on the surface of NCs can be calculated knowing the size and molar quantity of NCs and the lattice constant of one monolayer of ZnS shell:

(3.1)The amount of Zn and S precursor for the 1 monolayer ZnS (1 ML):

$$V_{ZnS}(1ML)=\frac{3}{4}*\pi*((R_{core}+d)^3-R_{core}^3)$$

The amount of ZnS moleculars (1ML) in one quantum dot: $n_{1ML}= V_{ZnS}(1ML)/V_{ZnS}$

The amount of Zn/S precursor (1ML):

$B_{ZnS}(1ML)= (n_{core}\times N)\times n_{1ML}/N=n_0\times n_1$; n_{core} is the number of CdSe core particles calculated from the quantum dot solution volume and NC concentration c. N is Avogadro's constant.

(3.2) The amount of Zn and S precursor for the x monolayer ZnS (x ML):

Repeating the above calculation process, the amount of Zn/S precursor required for each layer of ZnS shell can be obtained.

Figure S1 shows the particle size distribution of CdSe/ZnS quantum dots with different shell layers.

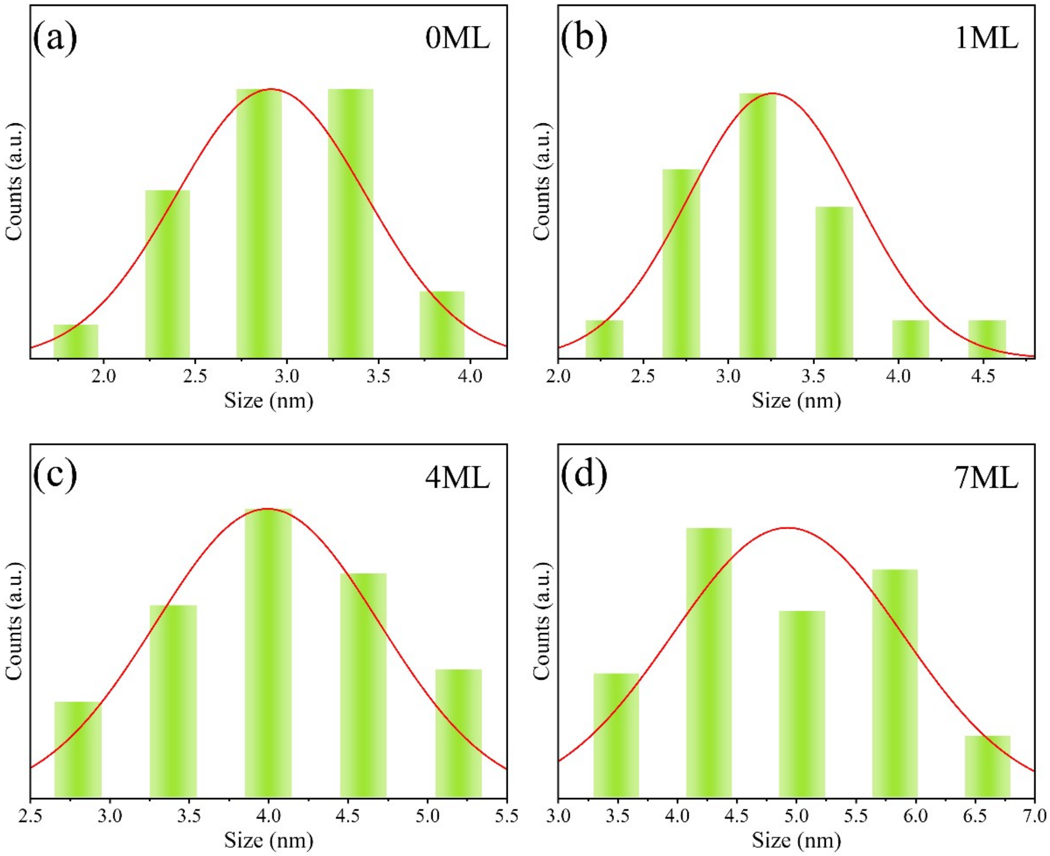

Figure S1. The particle size distribution of CdSe/ZnS quantum dots with different shell layers. (a) 0ML. (b) 1ML. (c) 4ML. (d) 7ML.

Figure S2 shows the fine XPS spectra of the CdSe/ZnS quantum dots.

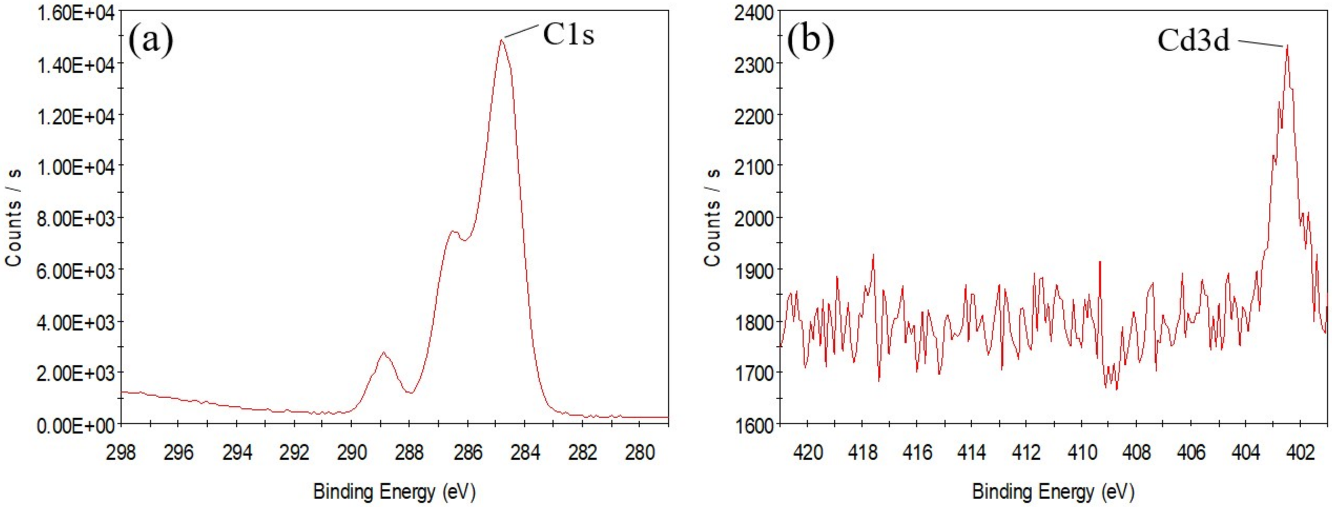

Figure S2. The fine XPS spectra of the CdSe/ZnS quantum dots.

Figure S3 demonstrates the temperature-dependent characterization of the peak intensity versus temperature for CdSe/ZnS quantum dot film probes with various shell thicknesses.

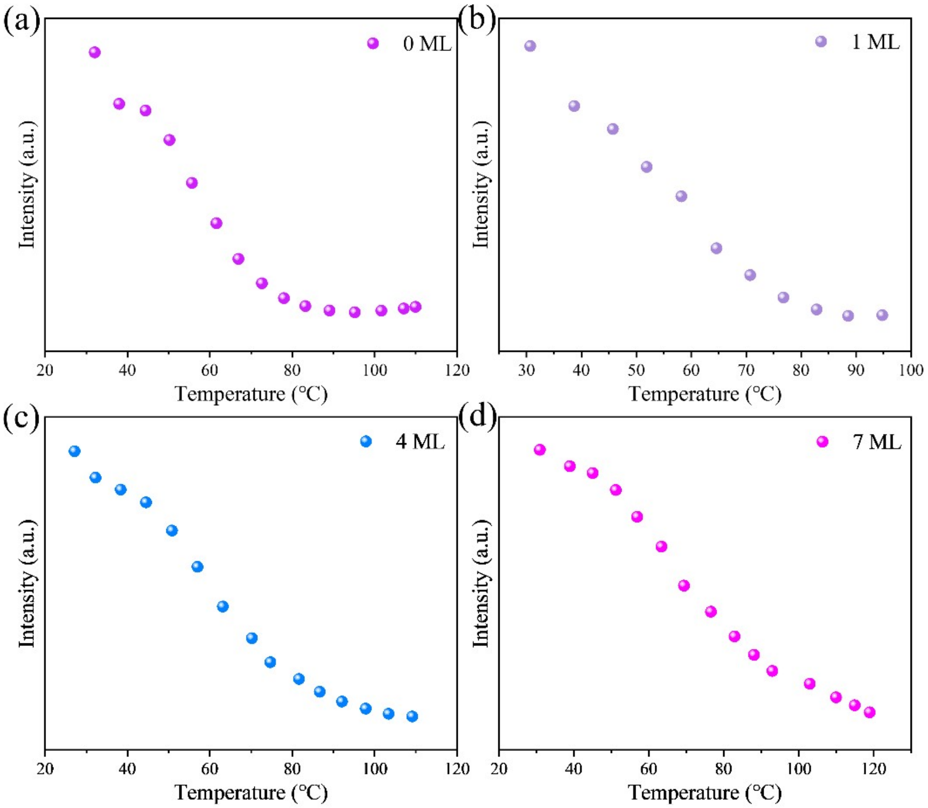

Figure S3. Temperature response characteristics of CdSe/ZnS films. (a) PL peak intensity variation during heating of the core CdSe film temperature probe. (b) PL peak intensity variation during heating of the CdSe/ZnS (1ML) film temperature probe. (c) PL peak intensity variation during heating of the CdSe/ZnS (4ML) film temperature probe. (d) PL peak intensity variation during heating of the CdSe/ZnS (7ML) film temperature probe.

Figure S4 illustrates the temperature-dependent characterization of the full width at half maxima (FWHM) of CdS/ZnS quantum dot thin-film probes with different shell thicknesses.

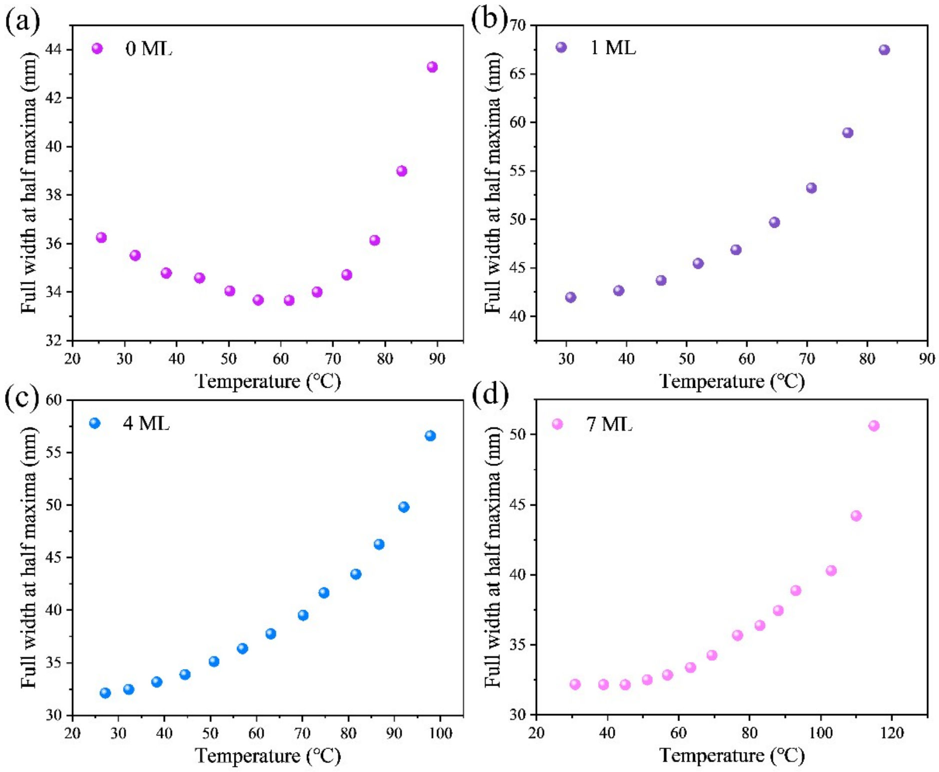

Figure S4. (a) Full width at half maxima variation during heating of the core CdSe film temperature probe. (b) Full width at half maxima variation during heating of the CdSe/ZnS (1ML) film temperature probe. (c) Full width at half maxima variation during heating of the CdSe/ZnS (4ML) film temperature probe. (d) Full width at half maxima variation during heating of the CdSe/ZnS (7ML) film temperature probe.

Table S1 shows the fitted expressions for the temperature-dependent curves of CdSe/ZnS films possessing different shell thickness as well as the degree of linearity of the fit (R^2).

Film Probes	Temperature Range	Fitting expressions	Pearson's R^2 (COD)
CdSe	20-70℃	$y = 545.90152 - 0.21649x$	0.99062
CdSe/ZnS (1ML)	20-75℃	$y = 570.72034 + 0.23381x$	0.99529
CdSe/ZnS (4ML)	20-80℃	$y = 564.73052 + 0.11633x$	0.99465
CdSe/ZnS (7ML)	20-100℃	$y = 561.38497 + 0.08513x$	0.94612

Table S2. Comparison of the temperature sensing characteristics of the CdSe/ZnS based temperature probe with other similar nanothermometers.

Material	Temperature Range	Reversibility	R^2	Ref.

Mn4+/Er3+ co-activated double perovskite	303-523 K	1	0.981	[1]
PbS@CdS@CdS GQD	10-40 °C	/	0.97	[2]
CdSe/ZnS@PCF	-10-120 °C	3	0.99	[3]
CdTe/ZnS	20-60 °C	/	0.955	[4]
CdSe	225−375 K	/	0.995	[5]
Graphene QDs	10-80°C	3	0.99	[6]
$NaYF_4$: Yb^{3+}/Er^{3+}	20-60 °C	5	0.997	[7]
CdSe/ZnS film (4ML)	20-80 °C	5	0.995	this work*

Figure S5 illustrates the changes in peak fluorescence wavelengths of four different CdSe/ZnS quantum dot membranes during heating and cooling cycles (the photoluminescence curves have been normalized during heating and cooling).

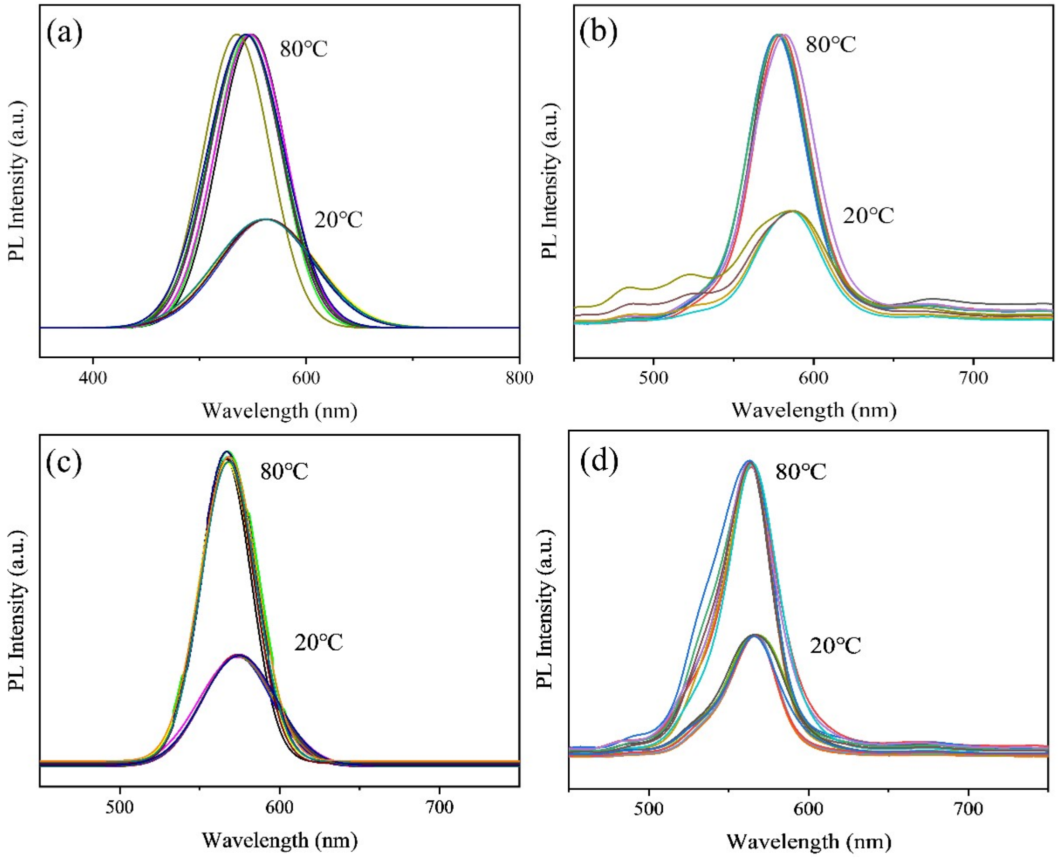

Figure S5. Four different CdSe/ZnS quantum dot membranes during heating and cooling cycles (a) 0 ML. (b) 1 ML, (c) 4 ML, (d) 7 ML.

Figure S6 demonstrates the X-ray photoelectron spectra of CdSe cores and CdSe/ZnS core-shell QD/POSS-based films with different ZnS monolayers after 10 heating and cooling cycles, which did not change significantly compared to the unheated quantum dot film.

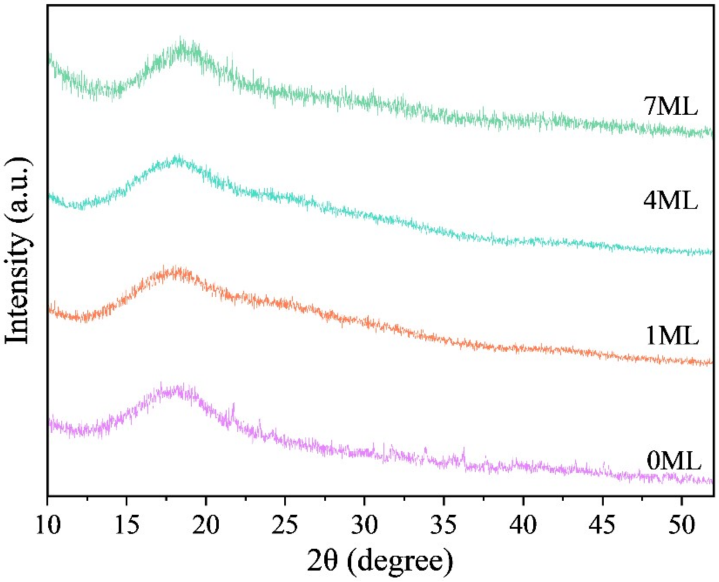

Figure S6. X-ray photoelectron spectra of CdSe cores and CdSe/ZnS core-shell QD/POSS-based films with varying ZnS monolayers.

Reference:

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