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Near-Infrared Ag₂Se Quantum Dots with Distinct Absorption Features and High Fluorescence Quantum Yields

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EXPERIMENTAL SECTION

Chemical Materials.

Selenium powder ($\geq 99.5\%$), indocyanine green (ICG), 1-Octadecene (ODE, 90%), 1-octanethiol ($\geq 98.5\%$), octylamine ($\geq 99\%$), were purchased from Sigma Aldrich. Trioctylphosphine (TOP, 90%, Alfa), Tetrachloroethylene (C_2Cl_4 , 99%, Alfa), polyacrylic acid (Aladdin, PAA, MW 2,000,). Silver acetate (AgAc), sodium borate, boracic acid, NaOH, concentrate nitric acid, n-hexane, methanol, dimethyl sulfoxide (DMSO), ethanol and acetone were purchased from China national medicines corporation, Ltd. Ultrapure water was purified using a Milli-Q water purification system.

Preparation of Se Stock Solution.

ODE-Se stock solution: First, 10 mL of ODE in a three-neck flask was heated to 110 °C for 30 min under Ar flow to remove moisture and oxygen. Then 1 mmol selenium powder was swiftly added into the flask under positive Ar pressure, the mixture were heated to the critical temperature of 210 °C for 30 min, after which elemental selenium was completely dissolved to form an optically clear yellow solution.

TOPSe stock solution: 0.1 M of TOPSe was prepared by dissolving 0.1 mmol of selenium powder in 1 mL of TOP under inert atmosphere in the glovebox.¹

Synthesis of Ag₂Se QDs

In a typical reaction, 0.2 mmol of AgAc, 1.61 mmol of 1-octanethiol were added into 5 mL of ODE in a three-neck flask under Ar flow, and then the mixture was heated to 165 °C. At this temperature, 1 mL of ODE-Se stock solution was swiftly injected into the heated mixture under vigorous stirring. The reaction solution began turning dark brown immediately after injection. Subsequently, the reaction temperature was reduced to 110 °C for the growth of the nanocrystals. Different sized Ag₂Se QDs were synthesized by tuning the initial ratios of Ag/Se. The products were precipitated with ethanol, washed with methanol, and redispersed in nonpolar solvents for further characterization.

Synthesis of Water-Soluble Ag₂Se QDs²

The surfaces of Ag₂Se QDs were modified by hydrophobic encapsulation with amphiphilic polymers octylamine-modified polyacrylic acid (OPA).² Both the hydrophobic QDs and OPA were dissolved in chloroform ($CHCl_3$), the mass ratio of the QDs and OPA was 1:8, and mixed in a vial. The $CHCl_3$ was evaporated under reduced pressure, leaving an OPA/QDs film. Borate saline buffer (pH 12.0) was added and the solution was vortexed and sonicated to dissolve the coated QDs, leaving a highly fluorescent, transparent solution. All the hydrophobic Ag₂Se QDs were transferred into the water with a yield of $\sim 100\%$ after capping the OPA.

Extinction Coefficient Measurements^{3,4}

The concentrations of the Ag₂Se QDs dispersed in n-hexane were adjusted by the intensities of the exciton absorption peaks in the UV-vis-NIR absorption spectra. The samples were digested with concentrate nitric acid and diluted to certain volume with ultrapure water. The Ag ion concentrations were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (IRIS Intrepid II XSP).

Characterizations

The UV-vis-NIR absorption spectra were obtained on a UV-3600 ultraviolet-visible-near-infrared (UV-vis-NIR) spectrophotometer (SHIMADZU). The size and morphology of the samples and the HRTEM images were examined on a JEM-2010FEF (UHR) electron microscope operated at 200 kV equipped with an Energy dispersive X-ray spectrometer (EDAX Inc.). EDX measurements were performed on it. X-ray photoelectron spectroscopy (XPS) spectra were obtained on an ESCALAB 250Xi X-ray Photoelectron Spectrometer (Thermo Scientific, US). Powder X-ray diffraction (XRD) patterns of the dried samples were performed on a Bruka D8 Advanced X-Ray diffractometer (Bruker axs) at a scanning rate of $0.5^\circ \text{ min}^{-1}$ using Cu K α radiation (wavelength 1.5406 Å). The NIR fluorescence spectra were recorded on a Fluorolog-3 fluorescence spectrophotometer (HORIBA JOVIN YVON INC.) equipped with a liquid nitrogen cooled InGaAs detector (between 800 and 1600 nm). ICG ($\Phi \approx 0.13$ in DMSO) was used as the reference to determine the fluorescence QY. Fourier transform infrared spectroscopy (FT-IR) tests were conducted on a Thermo Scientific Nicolet iS10 spectrometer.

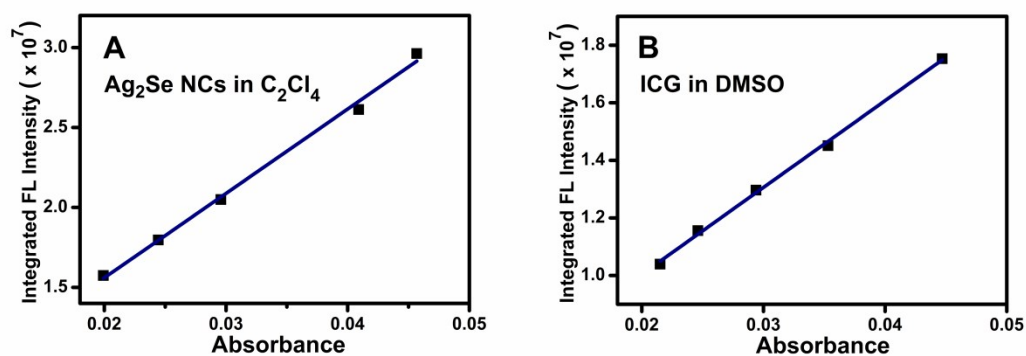


Fig S1. Integrated fluorescence intensity versus absorbance^{3,4} of the as-prepared Ag₂Se nanocrystals in C₂Cl₄ (A) and ICG in DMSO (B).

Table S1. Comparison of different characteristics of synthesized Ag₂Se QDs with different Se precursors.

Ref	Se precursor	Absorption (nm)	Emission (nm)	FWHM (nm)	Size (nm)	FL QY _{max} (%)
Our manuscript	ODE-Se	830~954	958~1020	142~164	1.9~3.1	23.4%
10	TOPSe	770, 1000	1030, 1250	250~300	2.0, 3.4	1.76%
3	TOPSe	770~1070 (Tauc plot)	1080~1330	200~300	3.1~3.9	9.58%
17	TOPSe	810~1085 (Gaussian fit)	—	—	1.9~9.4	—
8	NaHSe	—	1300	125~140	3.4	29.4%
2	GSSeH	—	700~820	90~120	1.5~2.4	3.09%
11	Hydrazine hydrate-Se complex	—	966~1228	49~61	3.3~6.1	12.2%

Note: The FWHM of the reported Ag₂Se QDs of the references (ref. 10, 3, 17, 8, 2) are approximate.

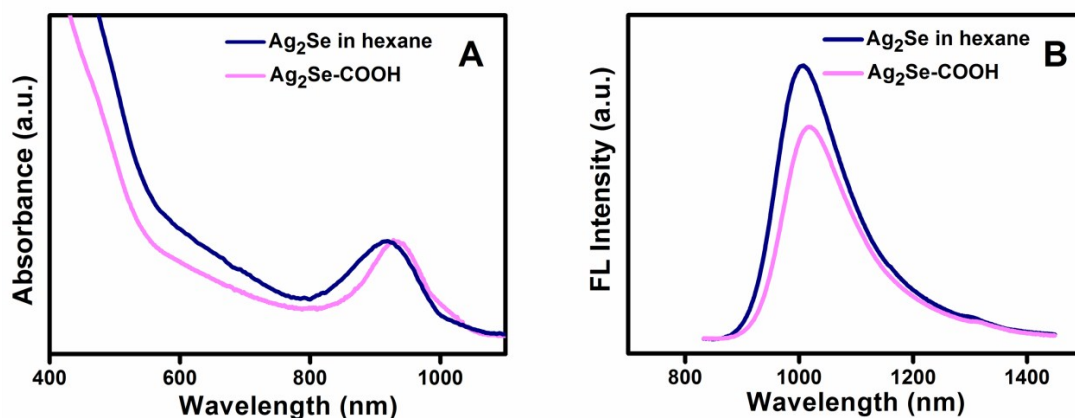


Fig S2 UV-vis-NIR absorption (A) and fluorescence emission (B) spectra of hydrophobic Ag₂Se QDs and hydrophilic Ag₂Se -COOH QDs.

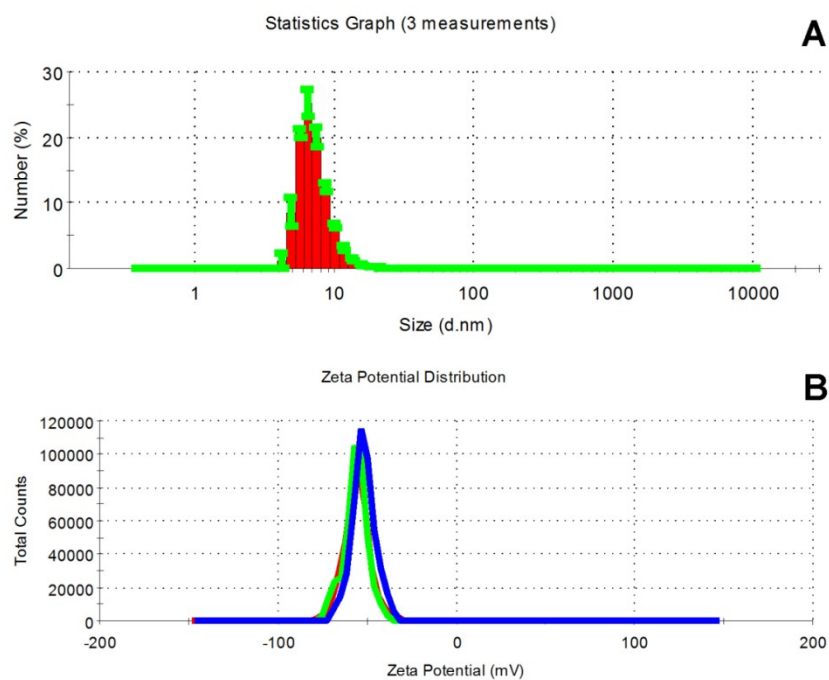


Fig S3. (A) Dynamic hydrogen diameter (8.13 ± 0.60 nm) and (B) zeta potential distributions (-52.1 ± 2.41 mV) of the $\text{Ag}_2\text{Se-COOH}$ QDs with emission at 1010 nm.

Table S2. ICP-AES results of the Ag_2Se nanocrystals with different sizes

sample	d (nm)	c (Ag) (ppm)	c (Se) (ppm)	atomic ratio of Ag/Se
a	1.9	21.64	5.651	2.80:1
b	2.6	30.82	8.141	2.77:1
c	2.8	22.38	6.06	2.70:1
d	3.1	19.58	6.159	2.33:1
e	3.3	20.84	8.091	1.89:1

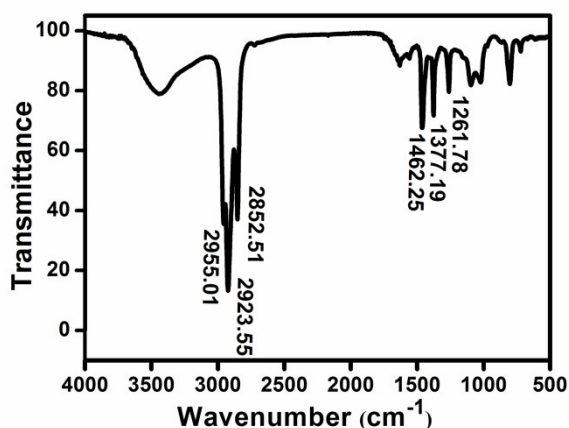


Fig S4. FT-IR spectrum of the as-prepared Ag_2Se nanocrystals. The peaks at 2955 cm^{-1} , 2924 cm^{-1} , and 2853 cm^{-1} were ascribed to the stretching vibrations of CH_2 and CH_3 in the alkane chain. The bending vibrations of C-CH_3 and CH_2 were located at 1377 cm^{-1} and 1464 cm^{-1} respectively. The peak of 1262 cm^{-1} was ascribed to $\text{CH}_2\text{-S}$. The above vibration absorption peaks of alkane and $\text{CH}_2\text{-S}$ matched well with the IR peaks of the pure 1-octanethiol.

Table S3. The evolution of the absorption peaks with different injection temperature and growth time.

Injection temperature ($^{\circ}\text{C}$)	125	145	165
1 min (nm)	910	920	940
5 min (nm)	930	934	945
15 min (nm)	938	944	950
30 min (nm)	944	948	952

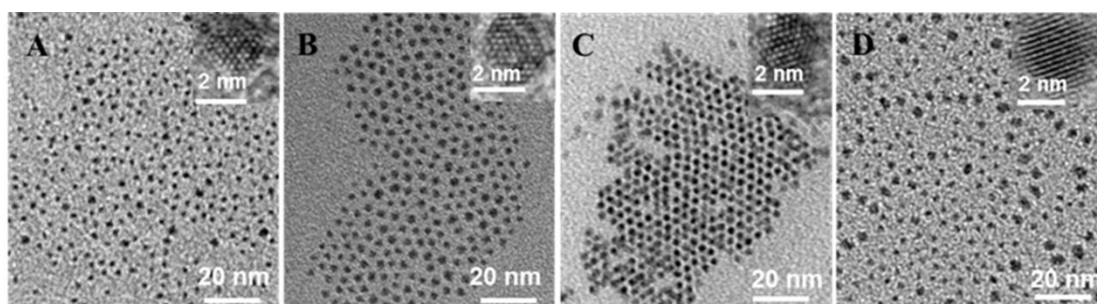


Fig S5. TEM images (A, B, C, D), HRTEM images (A, B, C, D, inset) of Ag_2Se nanocrystals with different initial ratios of Ag to Se: (A) 6:1, $1.9 \pm 0.26\text{ nm}$; (B) 4:1, $2.6 \pm 0.39\text{ nm}$; (C) 2:1, $2.8 \pm 0.35\text{ nm}$; (D) 1:1, $3.1 \pm 0.63\text{ nm}$.

Table S4. The different ϵ for the lowest transitions of different sized Ag_2Se QDs.

sample	absorption peak (nm)	size measured by TEM (nm)	extinction coefficient $\epsilon (10^5\text{ cm}^{-1}\text{ M}^{-1})$
a	830	1.9	0.17

b	895	2.6	0.32
c	944	2.8	0.55
d	954	3.1	1.15

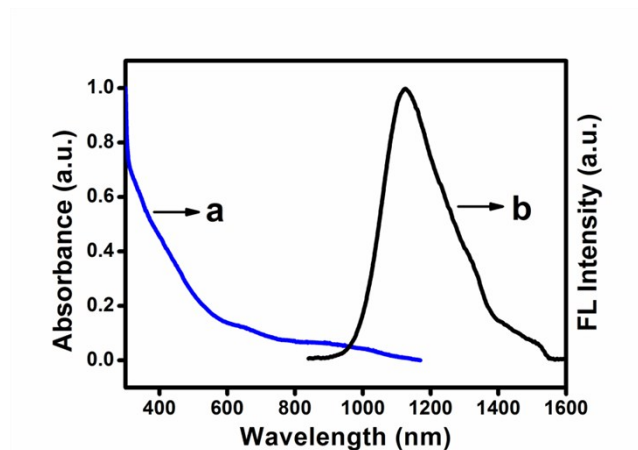


Fig S6. UV-vis-NIR absorption (a) and fluorescence emission spectra (b) of the 3.3 nm Ag₂Se nanocrystals.

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