

A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

Accepted Article

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To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201805264 Angew. Chem. 10.1002/ange.201805264

Link to VoR: http://dx.doi.org/10.1002/anie.201805264 http://dx.doi.org/10.1002/ange.201805264

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Supporting Information for

Multistage Microfluidic Platform for the Continuous Synthesis of III-V Core/Shell Quantum Dots

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Experimental Section

Materials. Octane (anhydrous) and dodecane (anhydrous) were purchased from Sigma-Aldrich. The solvents were degassed by freeze-pump-thaw method and further dried with 4 Å molecular sieves. Trino-octylphosphine (TOP, Strem) was dried with 4 Å molecular. Tri-no-octylphosphine oxide (TOPO, Sigma-Aldrich) and 1-dodecanethiol (Sigma-Aldrich) were dried under vacuum (< 70 mTorr) at 100 °C for 2 hours before use. The following chemicals were used as received. Bis(trimethylsilyl) sulfide ((TMS)₂S), myristic acid (MA), oleic acid (OA), and 1-hexanethiol were purchased from Sigma-Aldrich. Tris(trimethylsilyl)phosphine ((TMS)₃P) and cadmium acetate (Cd(Ac)₂, anhydrous) were purchased from Strem. Zinc acetate (Zn(Ac)₂, anhydrous) was obtained from Alfa Aesar, and Tris(trimethylsilyl)arsine ((TMS)₃As was obtained from Nanomeps.

Precursor preparation. All the precursor preparation and transfer were performed under nitrogen or vacuum in a Schlenk line or glove box. $In(MA)_3$ was synthesized as previously reported^[1]. The indium precursor solution was prepared by dissolving $In(MA)_3$ in octane with 10% TOP. $Zn(OA)_2$ or $Cd(OA)_2$ was prepared by reacting $Zn(Ac)_2$ or $Cd(Ac)_2$, with oleic acid under vacuum (<70 mTorr) at 140 °C for 2 hours. TOP-S were prepared by dissolving elemental sulfur in TOP (concentration 1.5 M). TOP-S was used for CdS shell synthesis, while (TMS)₂S was used for ZnS shell overcoating. (TMS)₃P and (TMS)₃As were diluted to pure octane. All the shell precursors were diluted to octane containing 20% TOP. The concentration of the core precursors was 30mM, and that of shell precursors was 20 mM if it was not specified in the later discussion.

Ligand exchange reaction. The synthesized InP/ZnS QDs were purified by precipitation using ethanol and acetone as the anti-solvents, and then redisperesed in chloroform. The purified QD samples were mixed with a solution of excess 3-mercaptopropionic acid in water. The biphasic mixture was stirred vigorously until the non-polar phase became colorless.

Microreactor fabrication and system operation. Preparation of the silicon-based microreactors was conducted based on a previously reported precedure^[2]. We first assembled 4.5 µm silicon oxide as a hard mask onto the 6 inch silicon wafer (the thickness was 800 µm); then 0.5 µm silicon oxide layer was grown on the silicon wafer by wet-oxidation process (MRL industries, Model 718), and 4 um silicon oxide layer was further grown by dielectric Plasma-enhanced chemical vapor deposition (PECVD) process (Applied Materials, Centura 5300). Thin positive photoresist with a thickness of 1 µm was spin-coated on the top of the silicon oxide layer. Model MA6 (Karl Suss) was used as a mask-aligner. This process allowed for precise channel development. For the shell growth chip reactors, the width and depth of the main channel were 400 μ m and 420 μ m and corresponding dimensions of the side channels were 80 μ m and 100 μ m respectively. Each side channel had 40 - 60 times higher flow resistance than the main channel to prevent any backflows. This high flow resistance also helped to maintain uniform flow distribution when the flowrates of each injection (main, and two side injections) changes. After patterning the wafer, the channels were sealed by the covalent bonding of a Pyrex wafer through the anodic bonding process. The reaction platform is illustrated in Figure S1, and the picture of differently designed reactors are shown in Figure S2 and S3. The growth of nanocrystals was monitored by a custom designed in-line UV-vis measurement device, which was connected with Ocean Optics DH-2000 light source and SD2000 fiber-optics spectrometer. Stainless steel tubes with an inner diameter of 0.02 inch were used for connections between reactors.

Characterization. All the solutions were diluted in hexane for the bench-top optical measurements. Absorbances were measured by Hewlett Packard 8452 diode-array spectrometer. Emissions spectra were recorded by an SD2000 fiber-optics spectrometer. TEM images were acquired by JEOL 200CX transmission electron microscope. XRD data were measured using PANalytical X'pert Pro Multipurpose Diffractometer and Rigaku H3R. Quantum yields were measured by comparing the integrated emission of the QDs in hexane to that of the dyes (rhodamine or indotrycarbocyanine) in methanol and ethanol. The QY was calculated based on the integrated intensities of the emission spectra, the absorption at the excitation wavelength and the refraction index of the solvent using the equation:

 $QY_{QDs} = QY_{dye} * \frac{Absorbance_{dye}}{Absorbance_{QDs}} * \frac{Emission\ integral_{QDs}}{Emission\ integral_{dye}} * \frac{Refraction\ index_{toluene}^{2}}{Refraction\ index_{ethanol}^{2}}$



Figure S1. A picture of the multistage set-up under ambient light (top) and UV light (bottom). The pictures were taken after cooling down the system to room temperature.



Figure S2. Differently designed chip reactors used for the multistep synthesis of core/shell nanocrystals. These reactors were used for mixing, aging and sequential growth steps (from left to right).



Figure S3. Shell-formation microreactor with ten sub-channels

605

630

Photoluminescence	In	Р	Zn	S
Emission Peak (nm)	(atomic %)	(atomic %)	(atomic %)	(atomic %)
554	20.4	16.5	26.5	36.6
599	21.4	18.1	25.6	34.9

18.9

17.6

27.5

28.0

32.6

36.1

21.0

18.2

Table S1. Compositions of InP / ZnS core-shell QDs measured with wavelength dispersive spectroscopy (WDS).

Table S2. Lattice constants of the bulk materials in zinc blende structure at 300K

Material	InP	ZnS	ZnSe	CdS
Lattice Constant (Å)	5.87	5.82	5.41	5.67



Figure S4-1 Emission spectra of InP/ZnSe QDs



Figure S4-2 TEM images of InP / ZnSe core-shell QDs emitting at 582 nm. The scale bar corresponds to 20 nm.

Photoluminescence Emission Peak (nm)	Total CdS precursor Flow (µl / min)	Temperature at the sequential injection stage (°C)	Temperature at the annealing stage (°C)	FWHM (nm)
608	10	280	280	75
648	20	280	300	74
683	20	290	320	74
702	50	290	320	81
721	70	290	330	84
768	90	290	330	102

Table S3. Experimental conditions for the synthesis of InP/CdS QDs and the corresponding emission properties



Figure S5. TEM images of InP / CdS core-shell QDs emitting at 721 nm (left) and 768 nm (right) respectively. The scale bar corresponds to 20 nm.



Figure S6–1 The absorption (left) and emission (right) spectra of InAs/InP QDs. The arrow indicates an increasing thickness of the InP shell on the InAs core.



Figure S6–2 TEM images of InAs/InP core-shell QDs emitting at 744 nm (A) and 783 nm (B) respectively. The scale bar corresponds to 20 nm.

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