Supporting Information

Solution phase synthesis of homogeneously alloyed ultrathin CdS_xSe_{1-x} nanosheets

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1. Experimental

Materials. Cadmium chloride (CdCl₂, 99.99%), selenium (200 mesh, 99.99%), sulfur, octylamine (OA) (99%), oleylamine (OLA) (70%) and trioctylphosphine (TOP, 90%) were purchased from Sigma-Aldrich and used without further purification.

Synthesis of ultrathin CdS nanosheets. Single-layered CdS nanosheets were synthesized from the reaction of CdCl₂ (OA, OLA)₂ complex and S powder in a mixture of octylamine and oleylamine. A CdCl₂ (OA, OLA)₂ complex solution was prepared by heating 1.5 mmol (275 mg) of CdCl₂ in 5 ml of octylamine and 5 ml of oleylamine at 120 °C for 2 h. After 2 h it was cooled down to room temperature. In a separate vial, 4.5 mmol (144 mg) of sulfur powder was dissolved in a mixture of 2.5 ml of octylamine at 2.5 ml of oleylamine at room temperature. The sulfur solution was injected into the CdCl₂ (OA, OLA)₂ complex solution at room temperature and the resulting mixture was slowly heated to 95 °C and maintained at this temperature for 16 h. The nanosheets were precipitated by adding excess ethanol and centrifuged. For characterization, the

nanosheets were dispersed in toluene containing a small amount of octylamine and oleylamine with mild sonication.

Synthesis of ultrathin CdSe nanosheets: Single-layered CdSe nanosheets were prepared in a similar procedure as for the CdS nanosheets by using a $CdCl_2$ (OA, OLA)₂ complex and a Se powder dispersion instead of sulfur. During the purification process, the resulting turbid yellow solution was washed with ethanol containing TOP to remove unreacted Se.

Synthesis of ultrathin CdS_xSe_{1-x} nanosheet: Single-layered CdS_xSe_{1-x} nanosheets were synthesized using a slight modification of the above procedure. A (S-Se) precursor was prepared with varying amount of S and Se (total amount of S + Se is 4.5 mmol) and an equivalent amount of NaBH₄. This (S-Se) precursor was injected swiftly into the CdCl₂ (OA, OLA)₂ complex at room temperature. After precursor addition, the reaction temperature was slowly increased to 95 °C and kept for 16 h at that temperature. After ~16 h, it was cooled to room temperature and washed with ethanol containing small amount of TOP to remove unreacted precursors.

Preparation of TEM samples: CdS_xSe_{1-x} nanosheets in chloroform were precipitated with ethanol and re-dissolved in chloroform. Then, a drop of the solution was placed on graphene TEM grids (CVD graphene film on Lacy carbon 300 mesh, Graphene Supermarket, NY, USA) and left to evaporate. The dried grids were cleaned with a custom-made apparatus combining gentle heating (50°C) and vacuum (10⁻⁷ mbar) for 5 days under N₂ and kept in an inert atmosphere until mounting on the TEM.

TEM measurements

TEM images were acquired on a CM120 Super Twin TEM (Philips) operating at 120 kV and JEOL JEM-2010 electron microscope operating at 200 kV

Low energy aberration corrected TEM measurements were performed using the spherical and chromatic double aberration-corrected FEI 60-300 Ultimate ³ ('PICO') at the Ernst Ruska-Centre, Germany. TEM images were acquired at 80 kV acceleration voltage with a 3rd order spherical aberration value of -5 μ m, a fifth order spherical aberration value of +2 mm and a chromatic aberration value smaller than 1 μ m. Optimized phase contrast for TEM images was achieved at a slight overfocus of +5 nm with a point resolution better than 1 Å.

Energy-filtered TEM images were taken on the 'PICO' instrument at an acceleration voltage of 80 kV using a Gatan Quantum ERS energy filter. Axial chromatic dispersion, defocus and astigmatism aberrations were corrected resulting in an effective chromatic disc of confusion that is less than 1.4 Angstrom for the largest energy slit width chosen. Optimum amplitude contrast was chosen for the recording of energy-filtered images, which were achieved at a slight overfocus of about +2 nm at a 3rd order spherical aberration value of $-5 \mu m$ and a 5th order spherical aberration value of +2 mm.

High-resolution STEM images were recorded using probe aberration-correction on the 'PICO' instrument at an acceleration voltage of 80 kV. Axial aberrations were corrected over the the probe forming aperture with a diameter of 30 mrad. HAADF images were taken with a Fischione Detector with an inner collection angle of 83 mrad.

Preparation of XRD samples: The CdS_xSe_{1-x} samples in chloroform was dropped onto a small Si wafer, and the solvent was evaporated on a heating mantle under mild heating. Data were collected on Panalytical Empyrean Powder Diffractometer equipped with position sensitive (PSD) X'Celerator detector using Cu K_a radiation (λ =1.5405 Å) and operated at 40 kV and 30 mA. The usual Bragg-Brentano $\theta/2\theta$ and grazing incident beam geometry were employed. The grazing incident scan was performed at a constant incident beam angle of 2° in a 2 θ range of 20°-80° with a step of 0.05° and 2 s per step.

Optical measurements: A small amount (0.1 ml) of sample was taken from each batch and diluted with chloroform to an optical density of 0.1- 0.2. UV absorption spectra were measured with a Shimadzu UV-3600 spectrophotometer. Photoluminescence (PL) emission spectra were measured with a Shimadzu spectrofluorophotometer RF-5301pc.

Atomic Force Microscopy: AFM measurements were performed on drop casted films on a silicon water at ambient conditions using a Thermomicroscopes CP Research Instrument mounted on an active antivibration table. A 100 μ m scanner was used. Microfabricated Si oxide ultralevers (Thermomicro) with integrated pyramidal tips were used. The 512 pixel x 512 pixel images were taken in a noncontact mode with a scan size of up to 60 μ m, at a scan rate of 1 Hz.

2. Preliminary results of reactions without NaBH₄



Figure S1. TEM images of the CdS_xSe_{1-x} with the composition of $CdS_{0.25}S_{0.75}$ prepared without NaBH₄ (Inset showing the high resolution TEM images of the same samples).

3. Additional TEM images of pure and alloyed samples



Figure S2. High-resolution TEM images of pure and alloyed ultrathin nanosheets.

4. Lattice parameters and elemental composition of pure and alloyed samples

Sample	a (Å)	c(Å)	c/a
CdS	4.1019	6.6709	1.626
$CdS_{0.6}Se_{0.4}$	4.2089	6.8009	1.616
$CdS_{0.4}Se_{0.6}$	4.2124	6.8260	1.620
$CdS_{0.3}Se_{0.7}$	4.2595	6.8920	1.618
CdSe	-	-	-

Table S1. Lattice parameters 'a' and 'c' calculated from powder XRD.

Table S2. Elemental composition (atomic %) by EDS analysis.

Sample	CdS _{0.6} Se _{0.4}	CdS _{0.4} Se _{0.6}	CdS _{0.3} Se _{0.7}
Cd	48.7	49.5	23.2
S	18.3	19.3	8.3
Se	32.9	31.2	68.5

5. Element distribution by energy filtered TEM (EFTEM)



Figure S3. EFTEM images of the CdS_xSe_{1-x} nanosheets with the composition $CdS_{0.3}Se_{0.7}$; at zero-loss (A) and at an energy loss of 90eV, showing the signal from Se-M₄₅ core-loss excitation (B)

Se elemental images taken with energy-filtered TEM prove the compositional homogeneity of the CdS_xSe_{1-x} nanosheets. Figure S3 shows two energy-filtered images of $CdS_{0.3}Se_{0.7}$ nanosheets. Figure S3(a) is a zero-loss image taken with elastically scattered electrons and a small energy-selecting slit of 10 eV width. The contrast variations in the zero-loss images are related to thickness variations, the low-frequency fringes observable in smaller regions are Moire contrasts of superimposed nanosheets with crystallographic domains of different orientation. The image in Figure S3(b) was taken with a 30 eV window around an energy loss of 90 eV. Electrons contributing to this image have suffered from one energy loss to a characteristic Se-M₄₅ core-loss excitation with an onset at 45 eV, but not to a characteristic S-K excitation for which the energy onset is at 165 eV. Figure S3(b) therefore qualitatively displays the Se distribution. The Se signal in Figure S3(b) correlates with the thickness and is homogeneous for domains of equal thickness in figure S3(a).

6. Height measurements of $CdS_{0.3}Se_{0.7}$ by AFM



Figure S4. Non-contact-mode AFM image and the height along the corresponding line in the AFM images.

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Sample	Absorption max (nm)	QY (%)	Thickness (nm)
CdS _{0.6} Se _{0.4}	473, 503	1.5	3.77-2.2= 1.57
CdS _{0.4} Se _{0.6}	464, 490	1.2	3.79-2.2=1.59
CdS _{0.3} Se _{0.7}	484, 517	3.1	4.00-2.2=1.80