Electronic Supplementary Information

Synthetic details for the preparation of the ZnTe core

General procedure: The zinc precursor (ZnO or ZnCl₂•2H₂O), fatty acid and ODE were loaded in a 100 mL three-neck flask. The mixture was maintained under vacuum atmosphere for 1 h at 70°C and heated to 120 °C for another 1 h. Meanwhile, the Te solution was prepared in a dry box by mixing the adequate quantity of Te with the phosphine (TBP or TOP) in ODE. The suspension was subjected to 10 min of stirring and sonication and was heated gradually to 170°C to afford a maximum dissolution of the chalcogen. The Zn-containing mixture was heated up to the temperature of nucleation (T

nu

) at which the Te solution was rapidly injected with a syringe from a rubber sealed vial to the reaction vessel. After the Te injection the nanocrystals were allowed to grow at the chosen temperature of growth (T

gr

); the reaction was monitored by taking aliquots at different time intervals, and recording UV/Vis absorption spectra for each aliquot. The reaction was eventually quenched by cooling down to room temperature; chloroform was added at ca. 60 °C to prevent solidification of the mixture. The QDs were isolated by precipitation with methanol or acetone; after centrifugation the supernatant was discarded and the solid nanocrystals were redissolved in chloroform. This procedure was repeated five times by adding chloroform to dissolve the nanocrystals, and methanol or acetone to trigger their precipitation. Finally, the resulting quantum dots were collected as a deep yellow waxy solid.

Protocol 1: This route follows the general procedure described above, with ZnCl₂•2H₂O activated with OA as zinc precursor. A ratio Zn/Te/OA/TOP of 1:1:30:30 was utilised with the following experimental details. Zn Solution: ZnCl₂•2H₂O 13.6 mg (0.1 mmol), OA 0.85 mg (3 mmol), ODE 7.9 g (10 mL); Te Solution: Te 12.8 mg (0.1 mmol), TOP 1 mL (3 mmol), ODE 0.79 g (1 mL); T

nu

 = 285°C; T

gr

 = 250°C. After the injection a slight yellow coloration of the reactive mixture was observed and aliquots were taken over a period of 90 minutes. However, the formation of the nanocrystals was not observed in any of the aliquots.

Protocol 2: This route follows the general procedure described above, with ZnO activated with SA as zinc precursor. A ratio Zn/Te/SA/TBP of 1:2:4:80 was utilised with the following experimental
details. Zn Solution: ZnO 8.2 mg (0.1 mmol), SA 20.2 mg (0.4 mmol), ODE 9.5 g (12.5 mL); Te Solution: Te 25.6 mg (0.2 mmol), TBP 2 mL (8 mmol), ODE 1.6 g (2 mL); $T_{nu} = 300^\circ C$; $T_{gr} = 270^\circ C$; time for size saturation = 90 min. After the injection a yellow coloration was observed and aliquots were taken over a period of 90 minutes. After the purification the quantum dots were isolated as a yellow thin powder.

![Absorption spectrum](image1)

**Figure S1.** Absorption spectrum (CHCl$_3$, room temperature) and TEM image of the QDs obtained with protocol 2.

**Protocol 3:** This route follows the general procedure described above, with ZnO activated with SA as zinc precursor. A ratio Zn/Te/SA/TBP of 1:2:5:80 was utilised with the following experimental details. Zn Solution: ZnO 8.2 mg (0.1 mmol), SA 129 mg (0.5 mmol), ODE 9.5 g (12 mL); Te Solution: Te 27.7 mg (0.1 mmol), TBP 2 mL (8 mmol), ODE 1.58 g (2 mL); $T_{nu} = 300^\circ C$; $T_{gr} = 270^\circ C$; time for size saturation = 10 min. After the injection the solution turned yellow immediately. After 10 minutes, the red shift of the exciton position was over and consequently the reaction was quenched. After purification (explained in the general procedure), the QD were isolated as a deep yellow solid.
**Protocol 4:** This route corresponds to protocol 3 described above, except for the fact that 15 equivalents of ODA were also added to the Te solution. The same results were observed by adding ODA to the Zn solution. Experimental details: Zn Solution: ZnO 8.2 mg (0.1 mmol), SA 129 mg (0.5 mmol), ODE 7.9 g (10 mL); Te Solution: Te 25.7 mg (0.2 mmol), TBP 2 mL (8 mmol), ODA 0.404 g (1.5 mmol), ODE 1.58 g (2 mL); \( T_{nu} = 300^\circ C; \ T_{gr} = 270^\circ C; \) time for size saturation = 20 min. After the injection the solution turned yellow immediately. After 20 minutes, the red shift of the exciton position was over and consequently the reaction was quenched. After purification (explained in the general procedure), the QD were isolated as a deep yellow solid.

**Protocol 5:** This route corresponds to protocol 4 described above, except for the fact that the growth temperature was raised to 285°C. Experimental details: Zn Solution: ZnO 8.6 mg (0.1 mmol), SA 133 mg (0.5 mmol), ODE 10 g (12.6 mL); Te Solution: Te 25.9 mg (0.2 mmol), TBP 2 mL (8 mmol), ODA 0.408 g (1.5 mmol), ODE 1.60 g (2 mL); \( T_{nu} = 300^\circ C; \ T_{gr} = 285^\circ C; \) time for size
saturation = 10 min. After the injection the solution turned yellow immediately. After 20 minutes of growth, the reaction was quenched. Half of the batch was collected and submitted to purification. After, purification (explained in the general procedure 1), the QD were isolated as a deep yellow solid, which exhibited an exciton centred at 508 nm.

![Figure S4. Absorption spectrum (CHCl₃, room temperature) and TEM image of the QDs obtained with protocol 5.](image)

**Protocol 6:** This route corresponds to protocol 5 described above, except for the fact that the nucleation temperature was raised to 320°C. Experimental details: Zn Solution: ZnO 17.4 mg (0.2 mmol), SA 271 mg (0.95 mmol), ODE 7.9 g (10 mL); Te Solution: Te 55.8 mg (0.4 mmol), TBP 4 mL (16 mmol), ODA 0.816 g (3 mmol), ODE 3.2 g (4 mL); Tₙₚ = 320°C; Tₙₙ = 285°C; time for size saturation = 10 min. After the injection the solution turned yellow immediately and the nanocrystals were allowed to grow. After 15 minutes of growth, the reaction was quenched. After purification, the QDs were isolated as a deep yellow solid. See also Figures SX-SX for TEM images and size distribution analysis of samples obtained with this protocol.

![Figure S5. Absorption spectrum (CHCl₃, room temperature) and TEM image of the QDs obtained with protocol 6.](image)
**Protocol 7:** This route follows the general procedure described above, with ZnO activated with SA as zinc precursor. A ratio Zn/Te/SA/TBP of 1:5:4:150 was utilised with the following experimental details. Zn Solution: ZnO 8.7 mg (0.1 mmol), SA 133 mg (0.4 mmol), ODE 5 g (6.3 mL), TOPO 400 mg (1.5 mmol); Te Solution: Te 55.8 mg (0.4 mmol), TBP 3.7 mL (15 mmol), ODA 0.408 g (1.5 mmol), ODE 3.5 g (4.1 mL); $T_{\text{nu}} = 320^\circ\text{C}$; $T_{\text{gr}} = 290^\circ\text{C}$. After the injection no change was observed, and after 60 minutes of stirring at 290°C no sign of QD formation was detected.

**HRTEM characterization of the ZnTe core**

**General procedure:** High Resolution Transmission Electron Microscopy (HRTEM) observations were performed with a FEI Tecnai F20 TEM equipped with a Schottky emitter and operating at 200 kV. ZnTe nanocrystals, obtained with protocol 6, have been deposited on conventional TEM Cu grids covered with holey carbon film, by drop-casting the solution, gentle heated at about 50 °C, and then left at ambient temperature for the evaporation of the solvent residuals.

**ZnTe nanocrystals characterization:** A low magnification panoramic view of a group of particles aggregates is reported in Fig. S6. The nanoparticles aggregate in small agglomerates, but, as reported in the main text, it is still possible to distinguish the shape of the single spherical particles. The Selected Area Diffraction (SAD) pattern reported on the inset, confirms the crystalline nature of the nanoparticles. The diffraction rings indicate d-spacings of 0.35 nm, 0.21 nm, 0.18 nm and 0.12 nm, corresponding, respectively, to (1,1,1), (2,2,0), (3,1,1) and (4,2,2) reflections of a ZnTe crystal in the cubic (sphalerite) structure.

To confirm the shape and crystalline structure of the single nanoparticles, as well as their monodispersion, HREM observations have been carried out. In Fig. S7 is reported one HRTEM image, showing three ZnTe nanocrystals, having comparable spherical shape. Moreover, the measure of the interplanar distances (0.35 nm, 0.30 nm and 0.21 nm) confirm also that the cubic structure of the ZnTe nanocrystals.

Several HREM images have been analysed for the determination of the particle diameter distribution. The results, reported in Fig. S8, show an average diameter of $(7.5\pm1.7 \text{ nm})$ calculated over a sample of about 120 nanoparticles. It is worth noticing that this value is in very good agreement with both the expected average particle size for Protocol 6, and the measurement performed by means of the conventional TEM images (see Figure S9).
**Figure S6.** Low magnification TEM image of a group of nanoparticles aggregates. In the inset is reported the corresponding SAD, showing the typical reflections of ZnTe crystal in the cubic structure.

**Figure S7.** HREM image of a group of spherical and nanocrystals. Three single nanocrystals, marked by the numbers, are clearly visible, confirming the spherical shape, the monodispersion, and the ZnTe cubic crystalline structure.
Synthetic details for the deposition of the ZnS shell

**General procedure:** For the preparation of ZnTe/ZnS core/shell QDs, a SILAR procedure was employed. The solution of the Zn precursor was obtained by mixing ZnO (32.6 mg, 0.4 mmol) and OA (0.9 g, 3.2 mmol) with 7.09 g (9 mL) of ODE; the resulting suspension was stirred and heated at 230°C until everything is dissolved, and then maintained at 80°C. The S solution was prepared dissolving elemental sulphur (12.8 mg, 0.4 mmol) in 7.9 g (10 mL) of ODE at 80°C. The ZnTe nanocrystals were prepared according to protocols 4 and 6 for ZnTe/ZnS (5sh) and ZnTe/ZnS (2sh), respectively, and were allowed to grow for 20 min. The temperature of the reaction mixture was then decreased to 230°C. A solution containing 1 g of ODA and 4 mL of ODE was added, and the SILAR procedure was started. A predetermined amount of Zn precursor solution was added dropwise and the mixture was stirred at 230°C for 20 min. The sulphur solution was then slowly injected and the mixture was kept at 230°C for 20 min. The procedure was repeated for the deposition of more ZnS layers. The purification of the core/shell nanocrystals was performed in a similar manner to that used for the core QDs, i.e., they were precipitated from CHCl₃ upon addition of MeOH or acetone.
Synthesis and characterization of ZnTe/ZnS (5sh): The coating of the core obtained from either protocols 4 or 6 was performed following the general procedure described above. The amount of precursors added is show in Table S1. After the purification by successive precipitations, the QDs were isolated as a yellow solid and stored in the dry box.

Table S1: Volumes of Zn and S precursor solutions used for the SILAR synthesis of the ZnTe/ZnS (5sh) nanocrystals.

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Figure S9. Size distribution histograms of (a) ZnTe nanocrystal cores obtained with protocol 6 \((d = 7.7 \pm 1.2 \text{ nm})\) and (b) ZnTe/ZnS (5sh) core-shell nanocrystals obtained upon coating the particles shown in (a) with 5 ZnS layers \((d = 10.3 \pm 2.4 \text{ nm}; \text{expected diameter, 10.65 nm})\). Notice that the distribution in (a) refers to the same ZnTe nanocrystals analyzed by HREM (Figure S8). In each case, the size analysis was performed by measuring the diameter of more than 100 nanoparticles in several TEM images. Panels (c) and (d) show representative images corresponding to the samples in (a) and (b), respectively.
Figure S10. Size distribution histograms of (a) ZnTe nanocrystal cores obtained with protocol 4 \( (d = 6.1 \pm 0.9 \text{ nm}) \) and (b) ZnTe/ZnS (5sh) core-shell nanocrystals obtained upon coating the particles shown in (a) with 5 ZnS layers \( (d = 9.3 \pm 1.3 \text{ nm}; \text{expected diameter, } 9.25 \text{ nm}) \). In each case, the size analysis was performed by measuring the diameter of more than 100 nanoparticles in several TEM images. Panels (c) and (d) show representative images corresponding to the samples in (a) and (b), respectively.

Synthesis and characterization of ZnTe/ZnS (2sh): The coating of the core obtained from protocol 4 was performed following the general procedure described above. The amount of precursors added is shown in Table S2. After the purification by successive precipitations, the QDs were isolated as a yellow solid and stored in the dry box, except for the sample labelled ‘aero’, which was left in contact with the air.
Table S2: Volumes of Zn and S precursor solutions used for the SILAR synthesis of the ZnTe/ZnS (2sh) nanocrystals.

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<th>$V$ addition (mL)</th>
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Figure S11. Size distribution histograms of (a) ZnTe nanocrystal cores obtained with protocol 4 ($d = 6.0 \pm 0.6$ nm) and (b) ZnTe/ZnS (2sh) core-shell nanocrystals obtained upon coating the particles shown in (a) with 2 ZnS layers ($d = 7.0 \pm 1.2$ nm; expected diameter, 7.12 nm). In each case, the size analysis was performed by measuring the diameter of more than 100 nanoparticles in several TEM images. Panels (c) and (d) show representative images corresponding to the samples in (a) and (b), respectively.

TEM investigations showed that the obtained nanocrystals exhibit a larger dispersion in shape in comparison with the ZnTe and the ZnTe/ZnS (5sh) QDs. In particular, non-spherical objects can be
found in the TEM images, suggesting that in some cases the ZnS shell did not grow uniformly. The size analysis shown in Figure S11 was performed by selecting only roughly spherical, non-aggregated particles.

Figure S12. EDX Spectrum (15 kV) recorded for the ZnTe/ZnS (2sh) sample deposited on a Cu/formvar grid upon solvent evaporation in air. The Si and Cu peaks arise from the grid substrate, whereas the Cl signal may be due to some chloroform solvent that remains entrapped in the nanocrystal solid. Adventitious K is also observed.
Figure S13. EDX Spectrum (15 kV) recorded for the ZnTe/ZnS (2sh) sample deposited on HOPG upon solvent evaporation in air. The Cl signal may be due to some chloroform solvent that remains entrapped in the nanocrystal solid. Adventitious Si is also observed.
**Figure S14.** EDX Spectrum (15 kV) recorded for the ZnTe/ZnS (5sh) sample deposited on Cu/formvar grid upon solvent evaporation in air. The Si and Cu peaks arise from the grid substrate, whereas the Cl signal may be due to some chloroform solvent that remains entrapped in the nanocrystal solid.
Figure S15. TEM Image of the CdSe nanocrystals employed for the photocurrent measurements.
Figure S16. Photocurrent spectrum (left scale) of a bare ITO electrode (green triangles) and the same ITO electrode functionalized with ZnTe/ZnS (2 sh) nanocrystals (black squares). The absorption spectrum of the QDs in CHCl$_3$ solution (black line, right scale) is also shown.

Figure S17. Photocurrent spectrum (left scale) of an ITO electrode functionalized with CdSe nanocrystals (4.7 nm diameter, black squares). The absorption spectrum of the QDs in CHCl$_3$ solution (black line, right scale) is also shown.