

gallium acetylacetonate, silver iodide, and elemental sulphur/dodecanethiol as the metal and sulphur sources, respectively, and oleylamine as the solvent (*cf.* Fig. 1(a)). Fig. 1(b) shows the UV-VIS absorption and photoluminescence (PL) spectra of the AGS QDs. While the absorption spectrum is featureless as in the overwhelming majority of ternary chalcogenide QDs, the PL spectrum shows a small, narrow peak at 442 nm and a broad peak centred at around 520 nm, tentatively attributed to band-edge and trap state-assisted emission.¹⁷ It should be specified that only when using good vacuum conditions during the

degassing step (around 5×10^{-2} mbar), the small peak at 442 nm is visible in the final sample. The inset of Fig. 1(b) illustrates the Tauc plot obtained from the absorption spectrum used to determine the optical band gap of the AGS QDs of 2.89 eV. For the growth of the gallium sulphide (GS) shell, the same gallium precursor was applied whereas diphenylthiourea was selected as the sulphur precursor (*cf.* Fig. 1(a)). Substituted thioureas have been proven to be very versatile precursors in the synthesis of PbS QDs, as they can be easily synthesised and their reactivity readily tuned by changing the substituents.³⁰

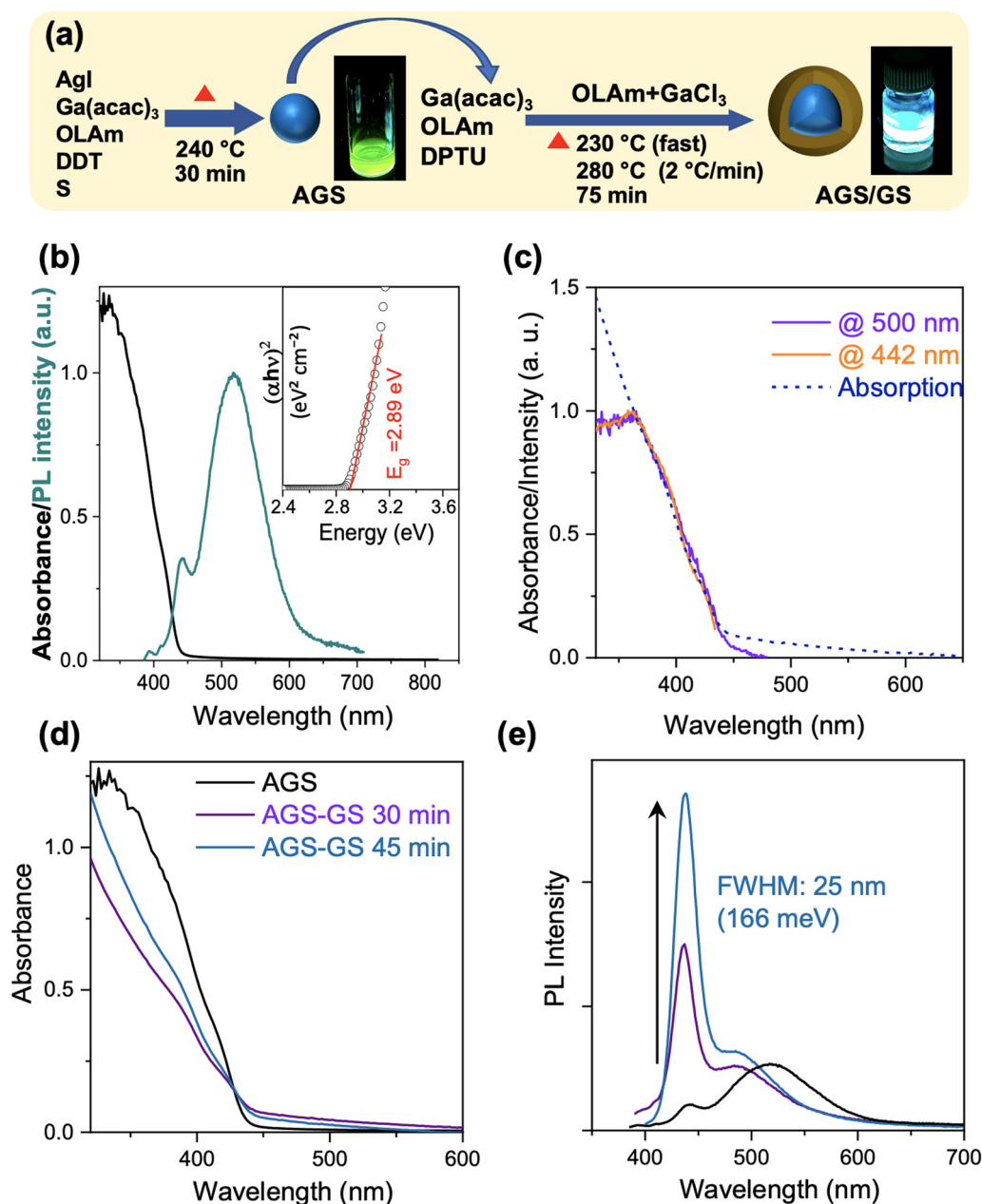


Fig. 1 (a) Schematic representation of the synthesis method for AGS core and AGS-GS core-shell QDs. (b) UV-VIS absorption (black) and PL spectra (dark cyan) of AGS core QDs. The inset shows the Tauc plot used to determine the optical band gap. (c) PLE scan of AGS-GS core-shell QDs (30 min reaction time) measured at the 442 and 500 nm emission peaks in comparison with the absorption spectrum (dashed line). (d) Absorption spectra of AGS core and AGS-GS core-shell QDs obtained with reaction times of 30 min and 45 min. (e) PL spectra of the same samples, normalised for absorbance at the excitation wavelength of 350 nm.



While the core AGS QDs show green emission, AGS-GS core-shell QDs exhibit blue emission under UV light exposure. Fig. 1(d) and (e) show the comparison of the UV-VIS absorption and PL spectra of AGS core and AGS-GS core-shell QDs obtained with different times of shell growth. With the growth of the Ga_2S_3 shell, the broadband trap-state emission of the AGS core QDs is successively suppressed, while the shorter wavelength band-edge peak was enhanced resulting in an intense and sharp blue emission at 442 nm (full width at half maximum, FWHM = 25 nm). This behaviour is attributed to the efficient surface passivation of the AGS core with the larger band gap Ga_2S_3 shell. To further study the origin of the sub-band-gap and band-gap transitions, we recorded the PL excitation (PLE) spectra. Fig. 1(c) shows the PLE scans of the AGS-GS sample obtained after 30 min, collected for the PL emissions at 442 and 500 nm, respectively. Both PL excitation spectra are very similar to the absorption spectrum suggesting that, while the emission occurs through both defect states and band edges, light absorption is dominated by the host semiconductor's bandgap.

To get more insight into the nature of the PL emission, we recorded time-resolved photoluminescence (TRPL) spectra at 442 and 520 nm (Fig. 2(a) and (b)). The TRPL data are summarised in Table 1. The decay curves were fitted using tri-exponential functions resulting for the AGS core QDs in an average lifetime of 45 ns at 442 nm and 118 ns at 520 nm. The significantly longer lifetime of the broad peak suggests trap-assisted emission involving mid-gap states. On the other hand, the relatively short lifetime with the peak position 2.82 eV, similar to the bandgap determined from the absorption spectrum, support the assumption that the 442 nm peak is related to band-edge emission.¹⁸

Noteworthy, the average lifetimes of both the band-edge and mid-gap-related emissions decreased from AGS to AGS-GS QDs due to the suppression of surface defect states. The lifetime value of the mid-gap peak of the gallium sulphide capped AGS-GS QDs is much smaller than that reported by Guo and coworkers for zinc sulphide capped AGS-ZnS QDs²⁶ where a value of 1723 ns was obtained, demonstrating the passivation mechanism is completely different.

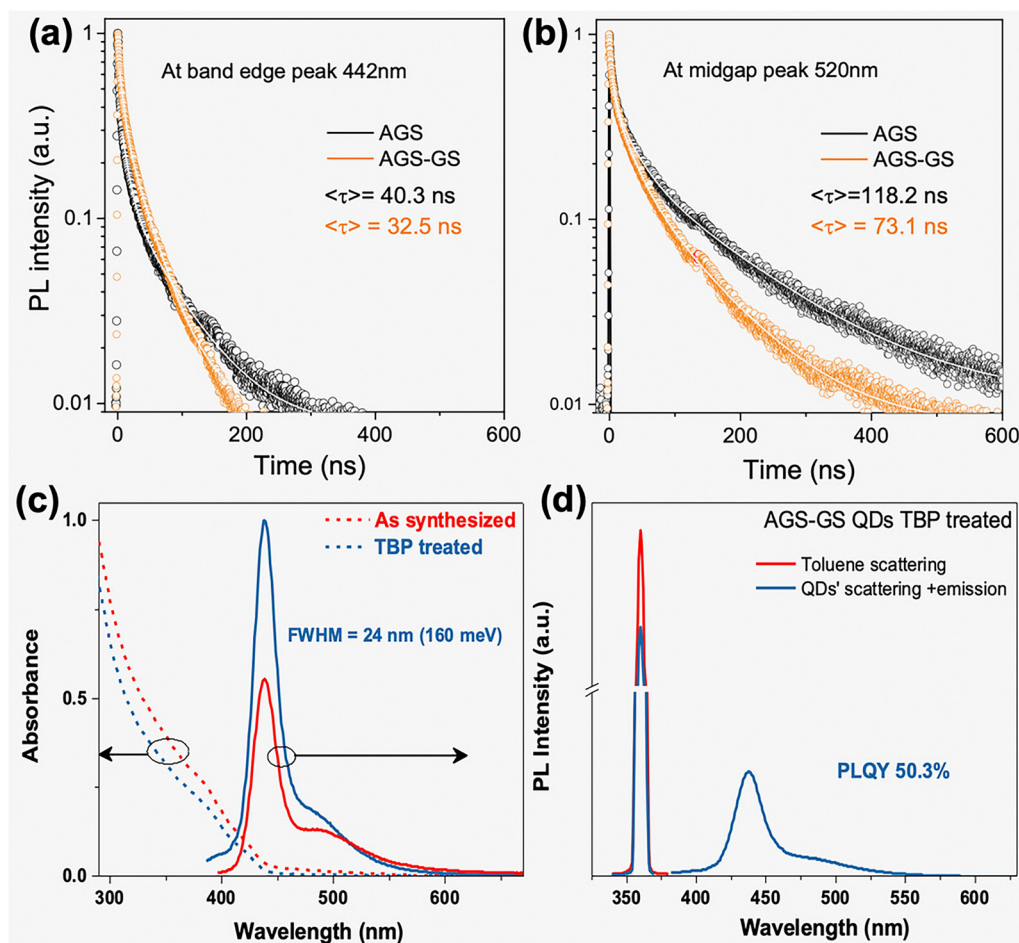
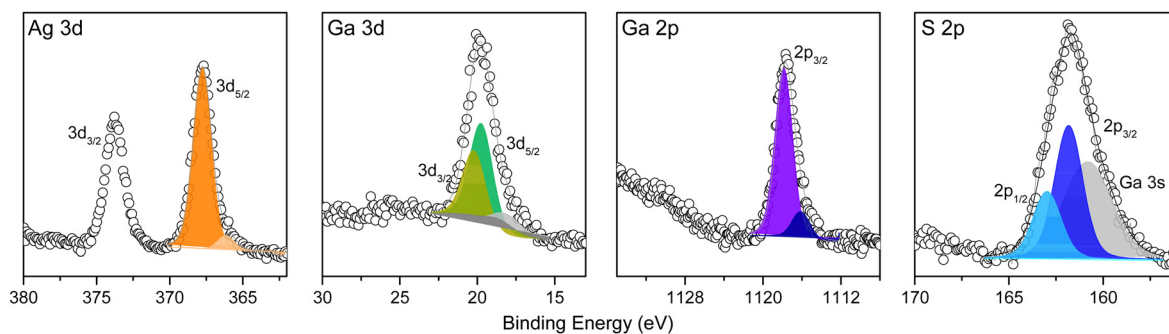


Fig. 2 PL decay curves measured at (a) 442 nm and (b) 500 nm for the AGS core and AGS-GS core-shell QDs fitted with tri-exponential functions (solid lines). (c) UV-vis and PL spectra of the AGS-GS core-shell QDs before and after TBP treatment. (d) Absolute PLQY measurement of the TBP-treated AGS-GS QDs using an integrating sphere.



a) AGS core



b) AGS-GS

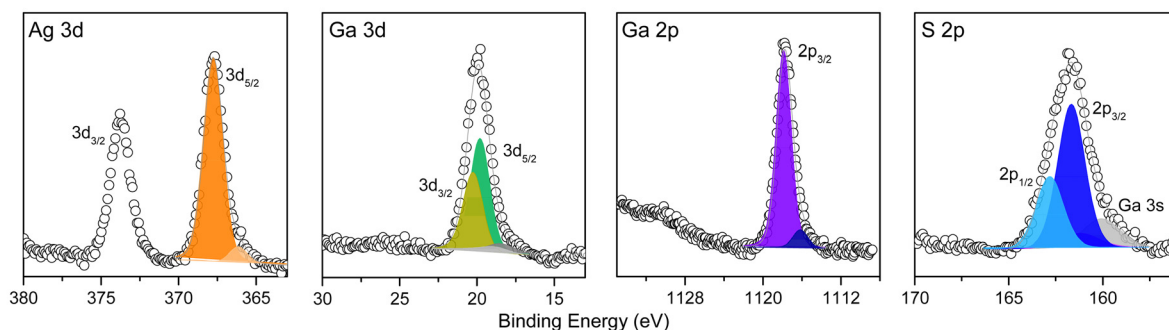


Fig. 5 High-resolution XPS spectra of Ag 3d, Ga 3d, Ga 2p_{3/2}, and S 2p regions for (a) AGS core and (b) AGS-GS core-shell QDs. N.B.: the small peak visible at lower energies is related to the sample charging due to the presence of insulating organic ligands.

oxidation, as well as S²⁻ (Fig. 5(b)). These results, along with the XRD, TEM and optical properties, unambiguously confirm the formation of AGS core and AGS-GS core-shell quantum dots.

To further elucidate the mechanism behind the trap-state passivation upon shell formation, we performed temperature-dependent PL studies in a range of 78–298 K using a liquid nitrogen-cooled cryostat. The qualitative behaviour of the three samples studied – AGS core, AGS-GS core-shell, and TBP-treated AGS-GS QDs – is visible in Fig. 6.

The most striking difference between the core and core-shell samples is the fact that at temperatures below 200 K, the core QDs do not show two distinct emission peaks but only one broad feature, which exhibits high intensity for the lowest temperatures studied (78–108 K). On the contrary, the core-

shell samples show the band-edge and trap-related peaks throughout the whole temperature range studied. For the TBP treated sample, the intensity of the 442 nm band edge peak is always higher than that of the trap-related one, while for the pristine AGS-GS QDs a crossover takes place at around 150 K. A more detailed analysis is provided in Fig. S4, which compares the 2D PL spectra, peak intensity, energy, and line width as a function of the temperature for the three samples. Considering the PL intensity (Fig. S4b, f and j), the two core-shell samples exhibit a sharp increase in the band edge emission at 200–230 K, which is almost 6-fold for AGS-GS and 3-fold for AGS-GS-TBP. This increase is much lower for the trap-state emission due to its different origin. While the intensity decrease on the longer wavelength side likely originates from the thermal activation of non-radiative recombination pathways,^{42,43} the drop in intensity at temperatures below 200 K

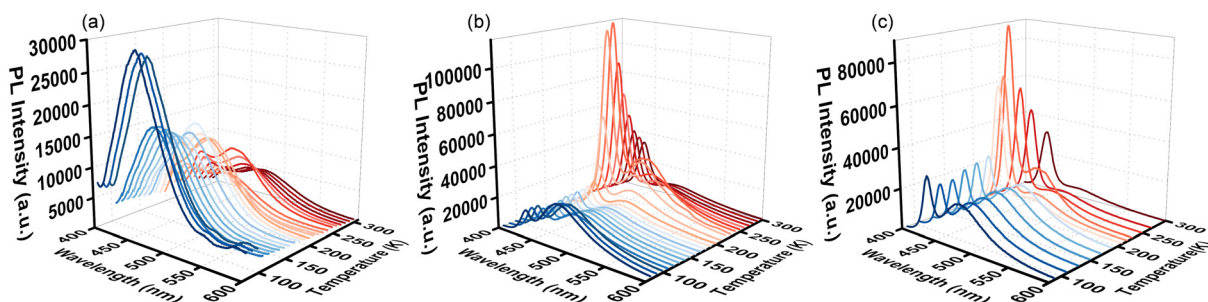


Fig. 6 Temperature-dependent PL spectra of AGS core (a), AGS-GS core-shell (b) and AGS-GS-TBP (c) QDs, using an excitation wavelength of 360 nm and hexane as the solvent (N.B.: the slit widths had to be reduced for the AGS-GS-TBP sample due to the higher intensity leading to saturation).



