Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

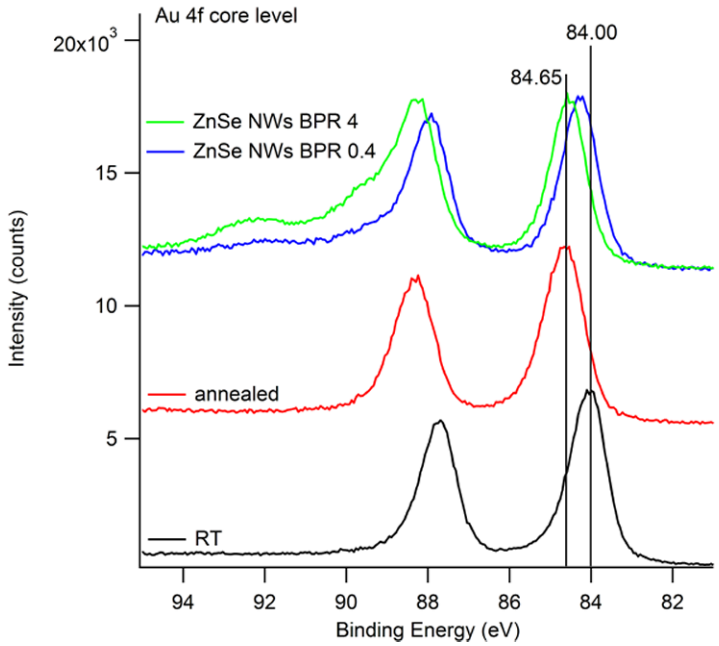

Figure S1. XPS spectra in the 80-95 eV range of binding energy measured after 1 minute ZnSe NWs growth using the two opposite beam pressure ratios. The Au 4f core level (spin-orbit split pair) in the 82-90 eV range is the most intense signal, but the Zn 3p core level (85-95 eV) is also detected. The spectra of the Au layer after the room temperature deposition and after the annealing at 450°C are also reported for sake of comparison.

As explained in the main text, the Au $4f_{7/2}$ core level measured after the annealing at 450°C is centered at 84.65 eV, due to the formation of a Au-Ga surface alloy. The ZnSe deposition for 1 minute at BPR 4 (Zn-rich) does not change the Au 4f binding energy, indicating that the nanoparticles assisting the growth of ZnSe NWs are still made of Au-Ga alloy. On the other hand, ZnSe deposition with an excess of Se (BPR 0.4) causes a shift of the Au 4f core level toward the metallic gold position (84.00 eV). This suggests a decrease of the amount of Ga into the nanoparticles, due to the reaction of the Ga atoms with the incoming Se ones. Therefore, the removal of Ga from the Au-Ga alloy nanoparticles occurs at the very beginning of the NWs growth under Se-rich conditions.

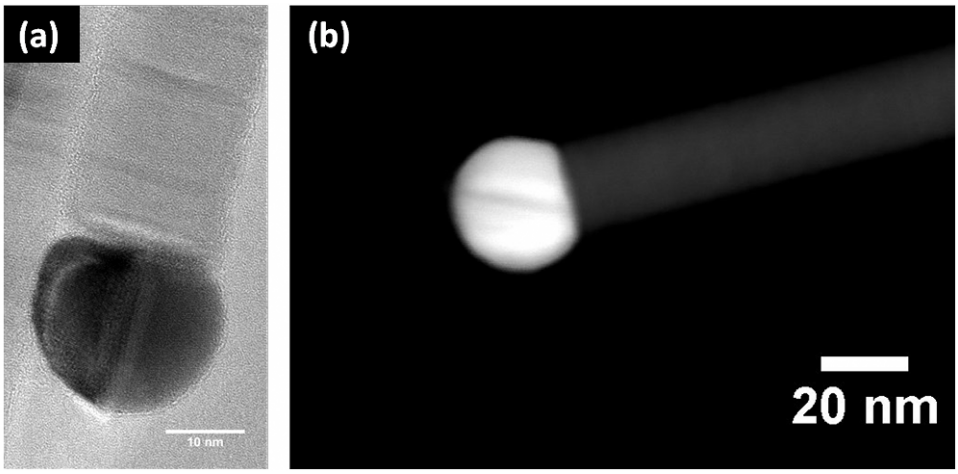

Figure S2. TEM and STEM images of the tips of ZnSe NWs grown with Se-rich conditions (BPR 0.4).

Both the images indicate the presence in the nanoparticle of two grains (in some cases even more grains have been observed). The analysis of fringes in TEM and the contrast in STEM indicate that the composition is not significantly different in the two grains, and the lattice parameter of both is consistent with that of fcc Au. The presence of two grains is possibly due to the initial coexistence of two phases (a gold solid core and a Au-Ga liquid alloy shell), followed by the fast solidification of the liquid phase due to the Ga removal by the Se-rich fluxes. Indeed the rapid cooling changes abruptly the volume inside the particle, causing grain formation.