Up to now only a few synthetic routes for the colloidal synthesis of intermetallic NCs were published [1], despite the recent intensive study on properties of these materials.[2] In this context, we report the synthesis of colloidal heterostructures made of a core of Au2Cd alloy surrounded by a shell of CdSe via a one-pot approach. Gold NCs, acting as seeds, were converted to AuCd alloy NCs as intermediate step. The formation of a CdSe shell was triggered as soon as a Se precursor was injected in the solution containing the AuCd NCs. One peculiarity of our synthesis method is that the Cd atoms employed for the formation of the shell seem to be supplied by the AuCd alloy NCs with minor or no contribution from residual Cd species present in solution. This assumption is supported by the fact that the composition of the core varied from AuCd to Au2Cd upon CdSe shell growth, then the shell growth stopped spontaneously. Therefore, both the initial AuCd core synthesis (from Au NCs to AuCd NCs) and the following shell growth are self-limited by the formation of Au-Cd alloy NCs with two compositions that are particularly stable also in the bulk, namely AuCd and Au2Cd. The AuCd NCs were therefore acting as a reservoir of Cd atoms. This synthesis approach results in a drastic reduction or total absence of byproducts (i.e. CdSe), while yielding more symmetric core/shell structures with variable core size.

Metal-semiconductor NC heterostructures are model systems for understanding the interplay between the localized surface plasmon resonances in the metal domain and the relaxation of the excited carriers in the semiconductor domain. Since the spectral features of the individual Au2Cd and CdSe domains in our core/shell NCs overlap in the visible range, in order to better understand the hot electrons relaxation dynamics of these systems we recorded transient absorption spectra by pumping either below (800 nm) or above the CdSe bandgap (400 nm). We obtained similar spectral shape and lifetime for the plasmon peak in both cases, which indicates that most of the photons were absorbed by the Au2Cd core. By fitting the decay of the transient absorption signal at the plasmon peak position for different pump power levels, we extracted a low-power limit of half a picosecond for the hot electrons relaxation lifetime. Almost the same relaxation time was found for the core/shell NCs and for the AuCd NCs seeds used for their synthesis. This indicates that in the Au2Cd/CdSe core/shell NCs the relaxation of hot charge carriers is determined mainly by their interaction with the bulk phonons, while surface modes seem to play a minor role.

Fig. 1: a,b) TEM images of Au and AuCd alloy NCs. c) HRTEM image of AuCd NCs. d) HAADF STEM image of AuCd NCs and their EDX spectrum with the Cd and Au peaks. Cu peaks come from Cu TEM grid. The chemical composition is consistent with an atom ratio Au:Cd of 1:0.94. e) Static absorption spectra of Au and AuCd alloy NCs. f) XRD pattern of AuCd alloys NCs.

Fig. 2: TEM image of Au2Cd/CdSe core/shell NCs. b) HRTEM image of a single Au2Cd/CdSe core/shell. c) HAADF STEM image of Au2Cd/CdSe core/shell NCs. EDX line profile (red line) exhibits Au, Cd, and Se distribution across the cores and the shells. d) Static absorption spectra of Au, AuCd and Au2Cd/CdSe samples. e) XRD pattern of the Au2Cd/CdSe sample.