Dynamic Processes in Metal-Semiconductor Nanoparticle Heterostructures

Michael S. Seifner[1, 2], Markus Snellman[2, 3], Daniel Jacobsson[1, 2, 4], Knut Deppert[2, 3], Maria E. Messing[2, 3], and Kimberly A. Dick[1, 2, 3]

[1]*Centre for Analysis and Synthesis, Lund University, 22100 Lund, Sweden*
[2]*NanoLund, Lund University, 22100 Lund, Sweden*
[3]*Solid State Physics, Lund University, 22100 Lund, Sweden*
[4]*National Center for High Resolution Electron Microscopy, Lund University, 22100 Lund, Sweden*
Corresponding author: Michael.Seifner@chem.lu.se, Kimberly.Dick_Thelander@chem.lu.se

Over the last years, there have been huge research efforts in the synthesis of advanced nanoparticle heterostructures to promote their performance in photocatalysis.[1] Especially, the combination of metals with semiconductors has been identified as a potential approach to enhance the photocatalytic activity via efficient charge carrier separation enabled by plasmon-exciton coupling.[2] The physical properties of such heterostructures highly depend on the present crystal facets and heterointerfaces.[3] Consequently, a detailed characterisation of nanoparticle heterostructures to determine the impact of morphological/structural properties on the photocatalytic activity is of high importance in this research field and paves the way towards facet-engineered surface and heterointerface design via advanced synthesis procedures. In this study, we combine $Cu_{3-x}P$ – a p-type semiconductor with a band gap of ~1.5 eV[4] – and Ag to form a metal-semiconductor nanoparticle heterostructure with potential in water splitting and investigate dynamic processes occurring around the synthesis of such structures.

For that purpose, Ag-Cu nanoparticle heterostructures synthesised in a spark ablation system[5] were deposited on a heating chip for *in situ* transmission electron microscopy (TEM) investigations. Subsequently, the heating chip was transferred to an environmental TEM with integrated metalorganic chemical vapour deposition (MOCVD) system. The controlled supply of phosphine (PH_3) at moderate temperatures initiated the Cu-$Cu_{3-x}P$ phase transformation in a Ag-Cu nanoparticle heterostructure with a Ag($\bar{1}$11)/Cu($\bar{1}$11) interface oriented parallel to the electron beam and both phases tilted in their [110] zone axes. We characterized the present phases via high-resolution TEM imaging and energy dispersive X-ray spectroscopy (EDS). The analysis of selected averaged frames of a high-resolution TEM movie capturing the phase transformation reveals the dynamic processes occurring in the nanoparticle heterostructure.

The nucleation of the $Cu_{3-x}P$ phase occurred at the triple phase boundary of the Ag-Cu nanoparticle heterostructure and the chemical reaction proceeded perpendicular to the formed growth front. We identified epitaxial relations dominating the arrangement of the phases and observed faceting of the $Cu_{3-x}P$ phase. After the complete transformation of the Cu phase, an additional heterointerface formed and grew at the cost of the heterointerface being initially present in the nanoparticle heterostructure. Several factors promoted the rearrangement of the phases including a well-matched interplanar spacing of planes perpendicular to the new heterointerface. Moreover, we observed an inhomogeneous strain distribution in the Ag phase caused by the presence of two heterointerfaces. As part of the post-synthesis annealing, corner truncation of the faceted $Cu_{3-x}P$ phase to reduce the total surface free energy was observed. The rearrangement process could be accelerated by increasing the temperature resulting in a Ag-$Cu_{3-x}P$ nanoparticle heterostructure with a single interface. The involved planes forming the interface in the observed nanoparticle heterostructure were different to the ones observed in the most common product of the here presented synthesis procedure.

Our results show different scenarios occurring during the phase transformation and highlight potential ways to control the synthesis of Ag-$Cu_{3-x}P$ nanoparticle heterostructures with well-defined facets and heterointerfaces via a gas phase approach using Ag-Cu nanoparticle heterostructures as templates. Future experiments will focus on the impact of morphological and structural properties of those nanoparticle heterostructures on their photocatalytic activities.

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