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Phase programmed nanofabrication: Effect of organophosphite reactivity on the evolution of nickel phosphide nanocrystals

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A critical aspect of the synthesis and application of nanostructured materials is to precisely control their phase, composition, and consequently, properties. Traditional methods call for fine tuning and optimization of multiple factors to achieve satisfactory levels of phase and composition control, which prove to be significantly time consuming. To overcome this problem, we demonstrated a simple but efficient approach to manipulate the outcome of nanocrystal synthesis by fine-tuning the chemical reactivity of molecular precursors, while keeping all the other conditions constant. Using this chemical reactivity approach that is well established for metal chalcogenides, we have studied how the structure and reactivity of a family of commercially available organophosphite precursors ($P(OR)_3$, R = alkyl or aryl), which are potentially tunable with group (R) substitution, affect the evolution of metal pnictide nanocrystals, explicitly nickel phosphide nanocrystals. Nanostructured nickel phosphides are known to be an excellent catalyst for hydrodesulfurization, hydrodenitrification and hydrogen evolution reactions. The optimized synthetic procedure involves a hot injection of phosphite solution at 275 °C to a reaction mixture of nickel precursor, oleylamine, and 1-octadecene. We optically and structurally characterized aliquots that were taken from the mixture at 1, 10, and 30 min reaction times. Our experimental observations show that different organophosphite precursors selectively yield nickel phosphide ($Ni_{12}P_5$, Ni_2P) or nickel (Ni) nanophases and that these evolve over time through well-defined and separate mechanistic pathways. In agreement with prior literature reports, we find that the formation of a nickel-rich, kinetic tetragonal $Ni_{12}P_5$ phase precedes the formation of the final, thermodynamically preferred hexagonal Ni_2P phase. Some organophosphites such as $P(OiPr)_3$ and $P(OMe)_3$ yield fcc-Ni transiently, while at least one organophosphite, $P(O\text{-}2,4\text{-}tBu_2C_6H_3)_3$, more persistently yields Ni nanocrystals that never evolve into a nickel phosphide phase. With the support of computations, we proposed two separate mechanistic pathways for precursor decomposition and metallic Ni formation. For precursor decomposition, prior phosphite coordination to the nickel precursor, followed by intramolecular arrangement with bonds breaking in a concerted manner is consistent with our observations. Metallic Ni formation involves a direct, outer sphere reduction of nickel(II) to Ni(0) by uncoordinated organophosphite. As a direct result of our study, we have built a chemical reactivity scale for organophosphite precursors. In conclusion, organophosphites are a nifty addition to the synthetic pnictide toolbox and our findings will enable a faster and more systematic approach to control the phase, morphology, and size of similar pnictide nanomaterials for industrial applications.

Keywords: Nickel phosphide, Organophosphite precursors, Phase and composition control

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