Selective agglomeration as a powerful method for scalable, multidimensional classification of colloidal NPs

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Abstract

Nanoparticles like quantum confined semiconductors (quantum dots, QDs) and noble metal nanoparticles represent unique structure-dependent properties. This leads to their broad applications in dye sensitized solar cells, light emitting diodes, or in the area of energy conversion and storage (photocatalysis or fuel cells), as active materials [1, 2, 3]. To improve the product performance, a narrow particle size distribution is usually one important factor [4]. While nanoparticle synthesis is developing into scalable and continuous processes, post-synthetic separation of such small nanoparticles is lacking even in this "simplest" dimension. In this regard, size selective agglomeration (based on the titration of a poor liquid into a stable dispersion of nanoparticles) has already been proven as an effective post processing strategy for size classification of ZnS QDs (<10 nm) [5, 6, 7]. However, apart from size, colloids are also found as mixtures of nanoparticles with different composition and different surface properties (surface ligands), e.g. during recycling. Thus, a minimized dispersity beyond size, i.e. including composition and surface chemistry is essential to achieve well-defined nanoparticulate products [4].

In this study, we realize a multidimensional separation (size and surface property; size and composition) of colloidal NPs below 20 nm using selective agglomeration as the main method. This is done based on the flocculation of less stable nanoparticles (e.g. larger nanoparticles in case of classification by size) induced by the addition of a proper poor liquid into a stable dispersion. Afterwards, the flocks are separated, while the more stable nanoparticles stay as well-dispersed primary particles in solution (see Figure 1). To prepare the model systems in this work, different ZnS QDs (<10 nm) including thioglycerol capped ZnS 1-octadecylamine capped ZnS and 3-mercaptopropionic acid capped ZnS QDs (achieved by ligand exchange), as well as

citrate-stabilized Au nanoparticles (< 20 nm) were synthesized based on previously developed methods [8, 9]. Then, their colloidal mixtures in different combinations were considered as model systems for 2-dimensional classification (size and composition or size and surface properties). In order to classify nanoparticles based on their size and surface properties/composition, first a suitable separation window was identified with regard to the mixtures' chemistry and concentration. Then we realized an appropriate sequence of individual agglomeration steps combined with separation processes (centrifugation or filtration to separate the flocks) to reach the final 2-dimensional fractionation of our system.

In conclusion, here we demonstrated selective agglomeration as a powerful method for the 2-dimensional classification of model systems including QDs and noble metal NPs. These fundamental studies show the high potential of this method and are thus laying the foundation for applying selective agglomeration to more complex systems.

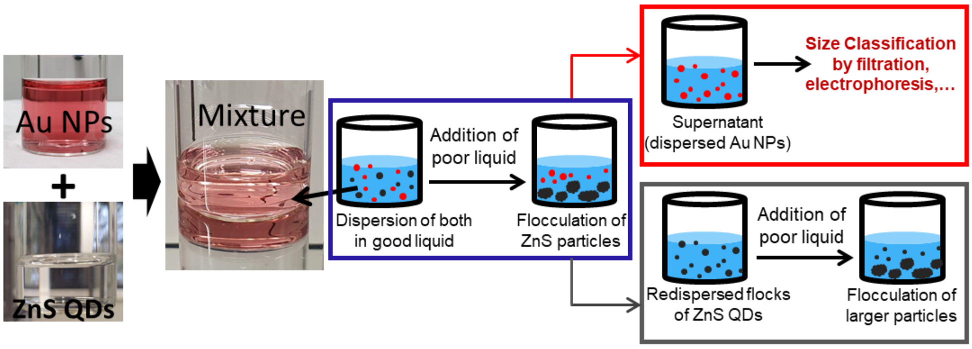

Figure 1: Nanoparticle classification by selective agglomeration

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