Turkevich synthesis of plasmonic gold-silver bimetallic nanoparticles revisited

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The synthesis and characterization of metal nanoparticles has gained a lot of attention during the last decade due to their unique electronic, thermal, optical, and catalytic properties leading to important technological applications such as plasmonic photocatalysis, surface-enhanced Raman-spectroscopy, sensors, biosensors, and nano-electronic devices. Bimetallic nanoparticles are of specific interest because of their versatility and tunability mainly for (photo)catalytic applications. Especially the gold-silver combination is of interest due to the optical surface plasmon resonance (SPR) effect that can be tuned over the entire visible range of the electromagnetic spectrum depending on the composition of both metals. Various methods have been applied to synthesize Au-Ag bimetallic nanoparticles, of which the most widely used is the Turkevich method\[1,2\]. This method is based on the co-reduction of metal salt precursors in the presence of a stabilizing agent, usually sodium citrate, in water at elevated temperature. Until now it has always been presumed that, based on this method, perfect alloys are obtained\[3\]. This assumption is mainly based on UV-Vis absorption data that provide information on the optical properties of the bimetallic nanoparticles. Since only one plasmon band appears in the spectra, this leads to the assumption that an alloy is created, since conversely two separate plasmon bands are observed in the case of a core-shell structure.

In this work, we show that actually a core-shell type of particle is formed, in which the metal composition changes in the radial direction. To achieve these results, an in-depth experimental study, an advanced electron microscopy analysis including 3D EDX tomography, and extensive modelling to support the experimental results were performed. In figure (left), the results are shown from the EDX mapping, that clearly shows the formation of a gold enriched core (80% gold, 20% silver) and a silver enriched shell (80% silver, 20% gold). However, in the UV-VIS spectrum (figure, right), only one plasmon band is visible. Therefore, simulations were performed that indicate this is in fact possible because the shell is thick enough (ca. 5 nm).

Figure. Left. EDX map of AuAg nanoparticles. Right. Comparison between experimental and simulated UVVis spectra of a AuAg nanoparticle.


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