

TEM study of bimetallic nanoparticles for optical and catalytic applications: comparison of different synthesis routes

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The tunability of optical and electronic properties of bimetallic nanoparticles (NPs) by shape, size, and composition makes them potentially versatile active elements of a wide range of supported catalysts as well as optical and electronic devices.[1] For example, their tunable plasmon resonance renders bimetallic Au-Ag NPs particularly interesting for application in SERS, and recent studies show that Au-Ag alloy NPs have a higher catalytic activity than pure Au and Ag NPs for CO oxidation. As another example, bimetallic CoPd systems are of high interest for several reactions such as, e.g., the Fischer-Tropsch synthesis of high-value hydrocarbons (synthetic fuel).

In particular for catalysts, one of the standard methods employed to produce bimetallic NPs is the incipient wetness impregnation, where the NPs are directly formed on an oxide support. However, problems associated with this synthesis route emerge when the reducibilities of the two metals are different or when the metals interact differently with the support material, bearing the danger of monometallic particles formation. More control over composition is obtained when the NPs are synthesized in a colloidal solution and then deposited on the support. As one of these methods with independent control over size and composition, the NP synthesis in block copolymer (BCP) micelle nanoreactors has attracted much attention. [2] Selectively the micelle cores are loaded with metal salts. There, NPs form in a subsequent reduction step that is induced chemically. Self-assembly of BCP micelles on a support provides a simple way of creating regular arrays of uniform NPs. [3]

We will show a TEM study of bimetallic Au/Ag and Co/Pd NPs that we achieved to prepare inside polystyrene-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP) micelles by loading the P4VP cores with two metal salts (Fig. 1) and subsequently reducing them using $N_2H_4 \cdot H_2O$. [4] TEM revealed stable and spherical NPs with a narrow size distribution around a diameter of 3 nm. The atomic ratio of the metals was determined by EDX at single particles and is in good agreement with nominal amounts of precursor metal salts used. For Au/Ag we varied the atomic Au:Ag ratio between 3:1 and 1:3. UV-Vis spectroscopy revealed one well-defined plasmon band, the wavelength of which could finely tuned by the Au:Ag ratio from 415 to 538 nm (Fig. 1). These results corroborate the formation of bimetallic alloy NPs with controllable composition.

In comparison to the BCP route, CoPd NPs were also prepared using a modified polyol method in two different ways: (i) NPs were formed directly on a support, (ii) NPs were first prepared using Poly(*N*-vinyl-2-pyrrolidone) (PVP) as stabilizing agent and then deposited on a support. TEM revealed rather wide size distributions for NPs prepared in the presence of the support. Furthermore, EDX showed high Pd content in the particles and Co distributed over the entire support, suggesting the formation of monometallic Pd NPs and a Co film on the support. In contrast, NP preparation with PVP stabilization in solution, i.e., before deposition on a support, resulted in very monodisperse NPs. Signals for both metals were observed in EDX at single NPs confirming the formation of bimetallic particles.

AgAu and CoPd NPs prepared by the aid of BCPs were deposited on different oxide supports, as required for the production of catalysts. TEM and EDX showed that the polymer shell could be completely removed by heating at 400 °C in H_2 atmosphere for 30 minutes. The polymer shell was fully removed revealing a smooth “sinking” of the NPs onto the support surface while, in the case of CoPd, the particle size remained unaltered (Fig. 2). Furthermore, EDX revealed that the problem of Co film formation on the support could be avoided, i.e., no Co was detected apart from the NPs.

Thus the BCP-based NP preparation methods presented permit an excellent control over structure and composition, turning the bimetallic NPs obtained in this work into promising building blocks for materials with potential applications in catalysis or optics. [5] [6]

References

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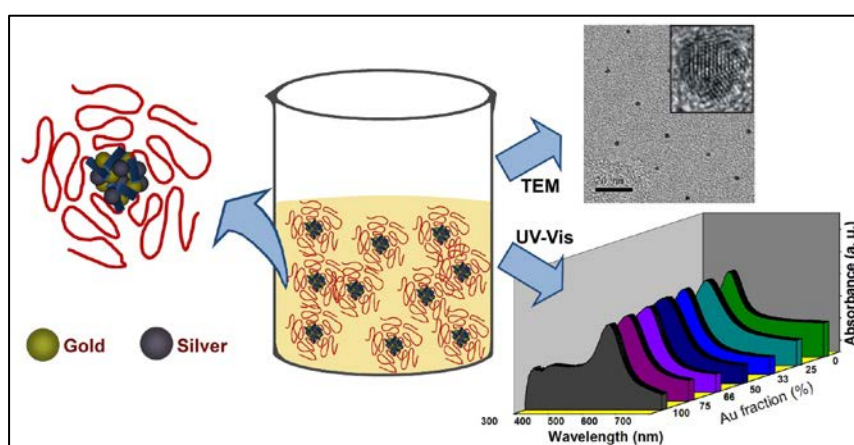


Figure 1. Scheme of AuAg NPs encapsulated in PS-P4VP micelles, and the UV-vis spectra showing the tuned Plasmon band from AuAg NPs.

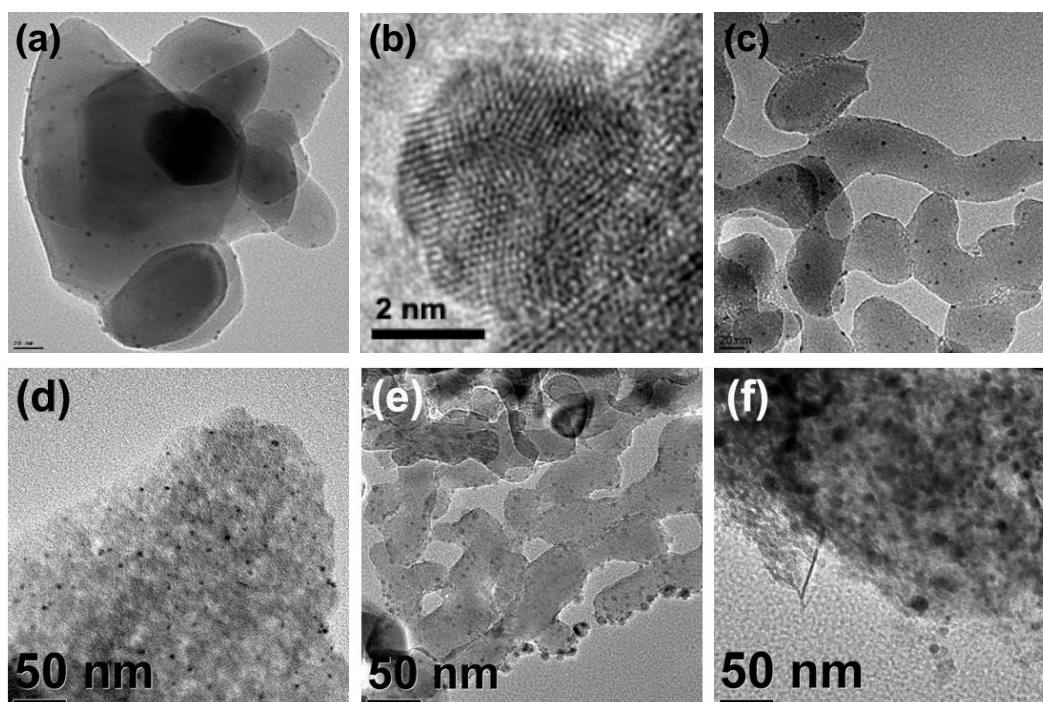


Figure 2. TEM images of different catalysts: (a) AuAg/n-TiO₂, (b) HRTEM from image (a), (c) CoPd/MgO, (d) CoPd/active carbon, (e) CoPd/MgO and (f) CoPd/Al₂O₃.