

Electronic Supplementary Material

Helium droplet assisted synthesis of plasmonic Ag@ZnO core@shell nanoparticles

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Additional STEM images of Ag@ZnO nanoparticles

Additional sets of high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) images in different magnifications are provided to complement the information about sizes, shapes, and distribution of the synthesized nanoparticles on the amorphous carbon support. The four images in Fig. S1 give an overview at lower magnification. Note that in panel (b) the scale differs from the other images. It can be observed, that elongated and kinked wire-like nanoparticles exhibit a broad distribution of sizes and lengths. Some of these larger particles are folded and form broad and massive structures upon deposition. The smaller spherical nanoparticles, on the other hand, appear very regularly distributed, as discussed in the main manuscript.

In Fig. S2 the nanoparticles are shown in more detail at higher magnifications. Panels (a)-(c) focus on spherically shaped particles, while in panel (d) examples for wire-like structures can be seen. As noted also in the main manuscript, a ZnO shell with uniform thickness is formed around the Ag cores for both particle types.

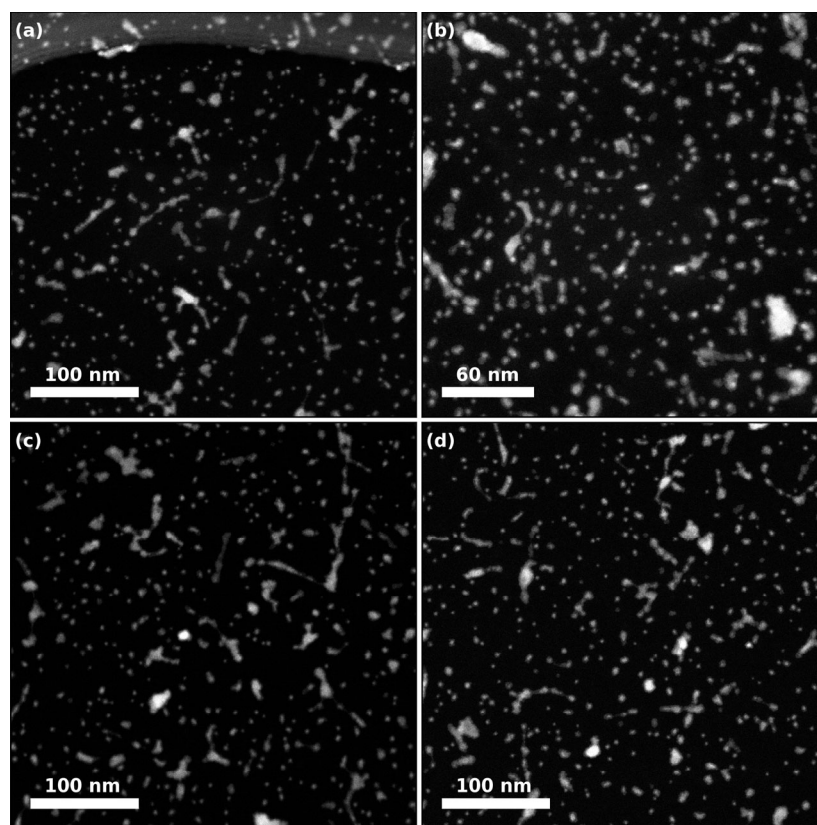


Figure S1 (a)-(d) HAADF STEM overview images of the Ag@ZnO nanoparticles deposited on an amorphous carbon support. Both synthesized particle types are present: smaller spherically shaped and elongated, kinked wire-like nanoparticles. An example for the analysis of the surface coverage using these STEM images is presented in Fig. S4. Contrast and brightness of the images were adjusted for better visibility.

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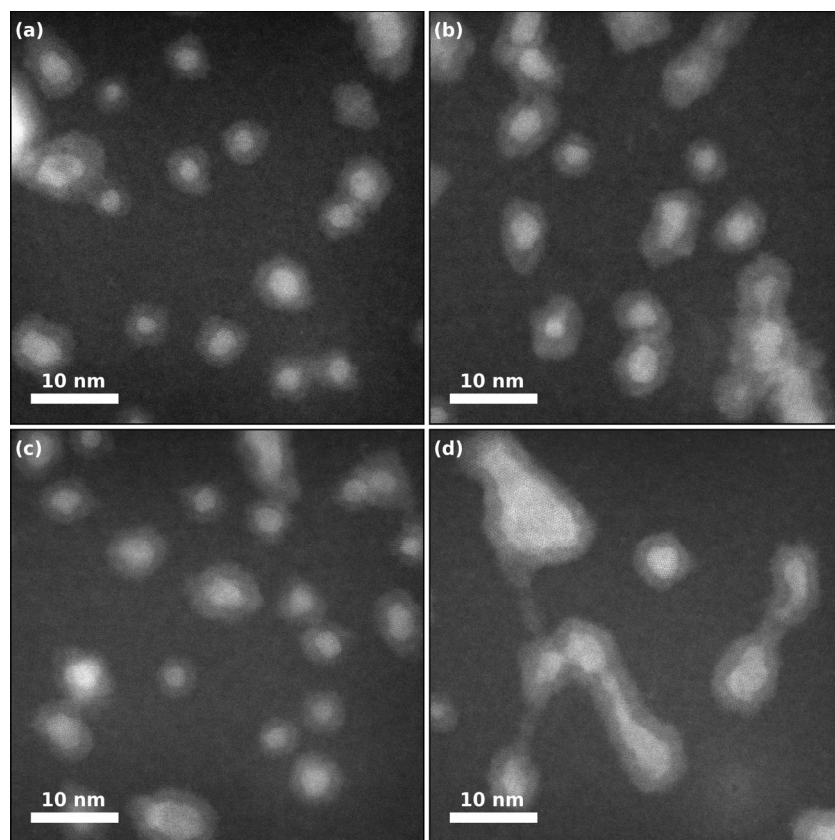


Figure S2 High magnification HAADF STEM images of Ag@ZnO nanoparticles deposited on an amorphous carbon support. (a)-(c) Areas on the sample where mostly spherical nanoparticles are present, which were synthesized at 20 bar and 8 K with a deposition time of 40 min. The particle shape and size are uniformly distributed. As the deposition process is random, some particles are deposited on top of each other or in such proximity that they are connected. (d) Wire-like particles, synthesized at 20 bar and 5 K with a deposition time of 3 min, showing an example of possible sizes and shapes. Note that for both types of nanoparticles the ZnO shell layer is very uniform and completely covers the Ag core. Contrast and brightness of the images were adjusted for better visibility.

ZnO structure determination

To support the conclusion that in the synthesized particles the ZnO shell preferably forms in a wurtzite structure, another set of HAADF STEM images, in which lattice plans are visible, is presented in Fig. S3 in the top panels (a)-(d). The region of interest (ROI) in every image, where the ZnO lattice is clearly visible, is marked by a colored frame. The respective fast Fourier transform (FFT) images obtained from the ROIs are shown in Fig. S3 in the bottom panels (e)-(h). Only selected areas of the ZnO shells in the STEM images are used for the generation of FFT data to avoid any influence of the Ag cores, which would impact the obtained data and obscure the lattice spacing of ZnO. Note that the FFT images are not at the same scale due to the varying sizes of the ROIs.

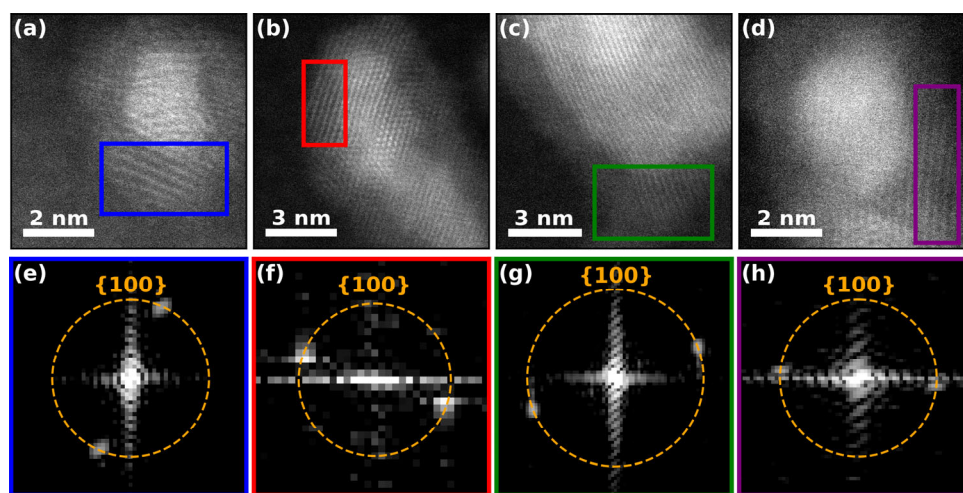


Figure S3 (a)-(d) HAADF STEM images at high magnification showing parts of spherically shaped and wire-like Ag@ZnO nanoparticles. Areas of the ZnO shell, where a lattice structure is clearly visible, are marked as ROIs with colored frames. Contrast and brightness of the images were adjusted for better visibility. (e)-(h) FFT images obtained from the ROIs showing the diffraction patterns. The found lattice distances from left to right are (0.30 ± 0.03) nm, (0.28 ± 0.03) nm, (0.28 ± 0.02) nm, and (0.28 ± 0.03) nm, respectively. They can all be assigned to the {100} planes of wurtzite ZnO as indicated by the annotation of the orange circles.

The diffraction spots visible in the FFT images correspond to the crystal planes in the ROIs. The obtained lattice spacing is (0.30 ± 0.03) nm for panel (a), (0.28 ± 0.03) nm for panel (b), (0.28 ± 0.02) nm for panel (c), and (0.28 ± 0.03) nm for panel (d). All measured lattice distances can be assigned to the {100} planes of wurtzite ZnO with a reported lattice spacing of 0.2814 nm, obtained from the Crystallography Open Database (COD) [S1].

Surface coverage evaluation

The employed procedure for the evaluation of the surface coverage with nanoparticles obtained by synthesis with the helium nanodroplet approach is exemplarily shown in Fig. S4. The HAADF STEM image shown in panel (a), serving as starting point, is modified with help of the ImageJ 1.52p software package [S2]. From this image a mask plot, as displayed in panel (b), is generated. Discriminating by particle sizes allows for the creation of mask plots containing only smaller spherically shaped nanoparticles, shown in panel (c), or wire-like structures, as presented in panel (d). This procedure was applied to all four overview images shown in Fig. S1 and yielded an estimated average rate for the surface coverage of $(9.3 \pm 0.5)\%$ per hour for the spherically shaped particles and about $(110 \pm 30)\%$ per hour for the wire-like structures, as stated in the main manuscript. For lower source temperatures and larger helium droplets the deposition rate, which can be achieved by the approach, is strongly enhanced.

SEM imaging of nanoparticle sample

Scanning electron microscopy (SEM) provides an additional imaging method with a resolution in the nm regime. It can be used for substrates that cannot be investigated by STEM because of constraints concerning the sample thickness or size, as, for example, the glass coverslips coated with indium tin oxide (ITO) in this work. Consequently, in order to obtain information on the substrates decorated with spherically shaped nanoparticles (source conditions: 20 bar and 5 K, deposition time: 5 h) for analysis in the NanoESCA system, SEM was used as additional analysis method. Figure S5 shows an overview image of the spherical Ag@ZnO nanoparticles on the ITO surface. The SEM image was taken with a Zeiss Sigma 300 VP scanning electron microscope. The inlens detector for secondary electrons (Inlens SE) and an acceleration voltage of 15 kV at a working distance of 2.3 mm were used for the measurement. It can be seen in Fig. S5, that the nanoparticles are uniformly distributed on the ITO surface. Note that at the given magnification the bright spots associated with the particles appear enlarged.

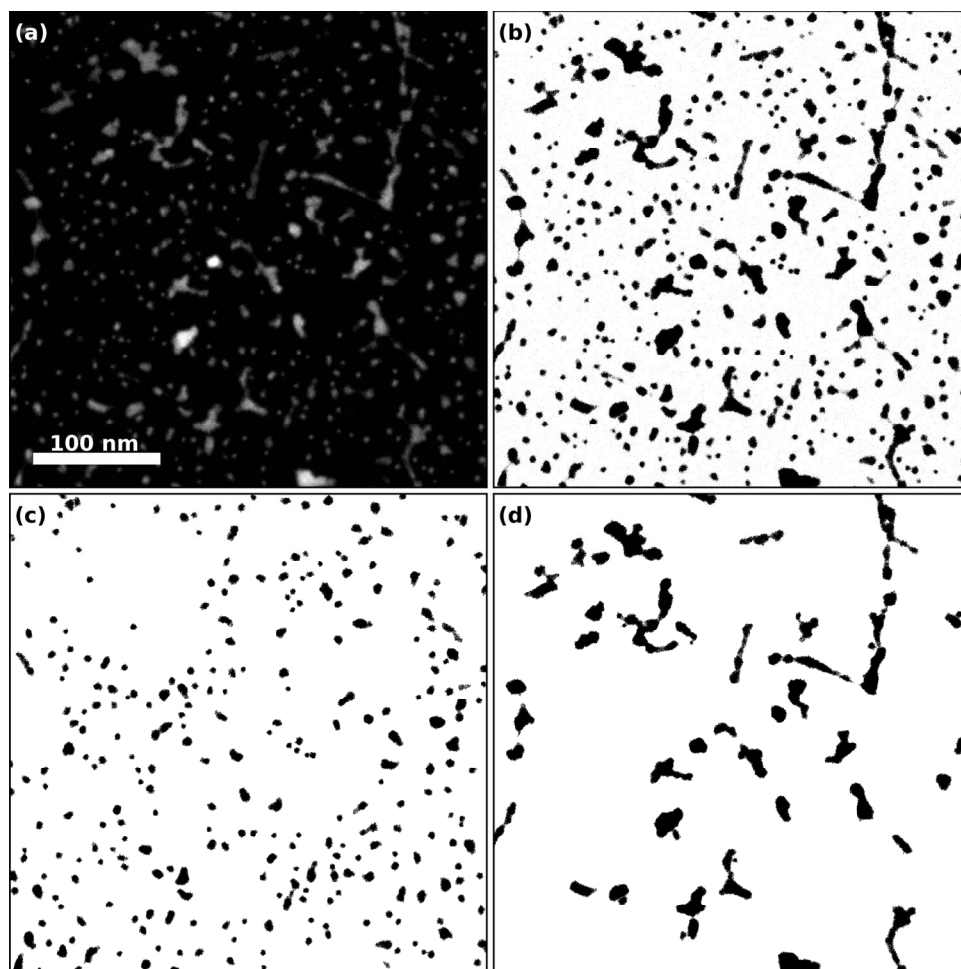


Figure S4 (a) HAADF STEM overview image with both nanoparticle types deposited on amorphous carbon. (b) A mask plot, marking all of the deposited particles, was obtained by introducing a brightness threshold to the STEM image and is further discriminated by particle size. This leads to a mask plot in panel (c), containing only smaller spherically shaped nanoparticles, and yields an estimated rate for the surface coverage of 9% per hour. (d) A mask plot for the longer wire-like structures yields an estimate for the surface coverage rate of 136% per hour.

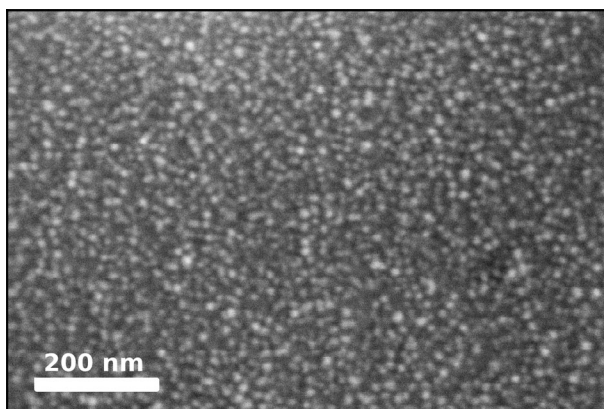


Figure S5 Overview SEM image of Ag@ZnO nanoparticles deposited on an ITO substrate for analysis in the NanoESCA system with a deposition time of 5 h. The sub-monolayer of nanoparticles is uniformly distributed on the surface.

References

- [S1] Schreyer, M.; Guo, L.; Thirunahari, S.; Gao, F.; Garland, M. Simultaneous determination of several crystal structures from powder mixtures: The combination of powder X-ray diffraction, band-target entropy minimization and Rietveld methods. *J. Appl. Cryst.* **2014**, *47*, 659-667.
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