Answers to comments of reviewer 1

The manuscript (MS) describes the production and characterization of aerosol nanoparticles (NP) as single material form and as hetero-aggregates (HA) using a spark discharge generator (SDG) combined with a nebulizer. The HA consist of TiO2-NP, on which four different metal NPs are deposited. The pure metallic particles and the HA are characterized online and offline using a variety of methods such as SMPS and TEM-EDX.

The authors like to thank the reviewer for their constructive comments. Our answers to their questions and comments are given below in blue font.

General comments

The MS contains many valuable and original results, which, however, still need to be bundled and formulated much better. In particular, there is no common thread linking the research question addressed, its answer and further consequences of the results. What are, up to the conclusion, new findings the authors want to report about the coating of larger NPs with metal NPs from spark ablation? The authors are encouraged to thoroughly rewrite the manuscript with a clear story line and targeted motivation. One interesting part to focus on could be the metal-depending layer quality (layer porosity, thickness, contact angles etc.) of spark generated NPs on TiO2 surfaces. In this context, the oxide affinity of certain metals, e.g. Au vs. Cu or Ni, could be systematically investigated, including many of the already presented data in a condensed way. The individual points are explained in more detail below, with the page (P) and line (L) indicated.

In the revised manuscript we describe in more detail the motivation of our study and the open questions our results address (line 73-92), see also comment below, point 1.
We like to point out that we present here a study with a strong focus on the methodology of metal nanoparticle production and the characterization of their number size distributions. Therefore, the related research aims are also largely method related.

1) Introduction
   The spark ablation section is well described; however, a detailed motivation for coating TiO2 NPs with spark generated particles is missing. Topical literature regarding this aspect is missing, too. While the introduction covers many interesting topics a clear focus of the presented work at the end of the introduction is missing. i.e. which open research questions should be addressed here. This goes beyond the listing of the performed investigations and covers rather the coherence of the results presented here.
   We now added a more detailed paragraph at the end of the introduction detailing the motivation of the presented study and the open research questions they address. (line 73-92)

2) P 4, L 104-108: Collecting small particles by diffusional deposition leads to a size-biased representation of the particle, which is specially agravated for small nanoparticles as outlined in the MS. However, also the amount of deposited particles differs substantially from the number of particles in the aerosol. Therefore, the question needs to be discussed how the fraction of nanoparticles sampled on the TEM grid (and on the Teflon filters) in relation to the total aerosol particles is determined. It is surprising that the number of deposited particles and aerosol particles are so close to each other (e.g. Fig. 4). Which

approach was taken to quantify the fraction of deposited particles? Please explain this point in more detail.

We calculate the number size distribution of the particles in the aerosol phase by combining the measured number size distribution derived via counting of the TEM pictures and the calculated diffusion of particles from the aerosol flow onto the TEM collection grid. To calculate this particle size distribution in the aerosol phase the following parameters were required: The dimension of the collection chamber, the diffusion coefficient of the particles and the flowrate of the aerosol stream. The detailed analysis can be found in the available excel files on the data repository. First, the 'diffusional losses' onto the TEM grid are calculated following the method described by von der Weiden et al. (2009), i.e. calculation of losses in a tube with the flowrate and the length of the TEM grid. After calculating the fraction of particles deposited from the aerosol phase onto the grid, the total amount of particles passing over the grid can be calculated. This is now stated in revised version in more detail in line 287-290.

3) How does a quantitative NP sampling work on Teflon filters with 2 µm pore size and NPs being smaller than approx. 50 nm?

   The primary collection process is diffusion, thus, sampling efficiencies of nearly 100% are reached for particles below 100 nm. (see e.g., W.C. Hinds, Aerosol Technology, Wiley, Second Edition, p. 202 – 203, Figure 9.12; second edition). This reference is now explicitly mentioned in line 241-242.

4) P 5, L 126: What is the motivation for depositing agglomerate NPs on a solid TiO2 film and the subsequent sputter coating with a 100 nm Au layer? It is not clear why such a thick platinum layer needs to be applied. Does this not lead to a significant loss on resolution?

   We changed the description of the lamella experiments (line 148-157).

5) P 6, L 151ff: The idea of employing the circularity to define the spherical particles is very good. This approach could make an important contribution to the issue about the first nucleating clusters and their further fate. This approach is certainly a highlight of the MS and would deserve some more evaluation. Why was the limit of 90% also applied for sphericities staring well below 1.0 (cf. Fig. A1, e.g. Pt for 1.3 s residence time)? Is the fact that some particles start already with sphericities well below 1.0 an indication that in fact they consist of much smaller units, i.e. atomic clusters? In Fig. 3 for Pt 3 residence times were analyzed with respect to size distribution. Why was the results for 26 s not also included in Fig. A1 in the Pt column?

   Why was the limit of 90% also applied for sphericities staring well below 1.0?

   Primary particle (PP) size differs greatly for the different metals (see Fig. 2). The smaller the maximal PP size is, the more pixelated the analyzed PPs are in image processing. This effect, which is most pronounced for Cu and Ni but was also observed for Pt can lead to an underestimation of the circularities (i.e. a pixelated, elongated shape rather than a smooth spherical structure; for the present analyses 2.8 pixels per nm resolution were determined). Thus, the sphericity of the detected PPs can be lower than one. As the pixilation is size dependent (i.e. more pronounced for smaller particles) and thus also metal specific, no absolute circularity value can be defined for which on average full sphericity occurs. In the case of Pt 1.3 s this is clearly visible by the broad circularity distribution below 2 nm.

   Due to these uncertainties, we introduced an estimated 10% limit of the drop of the fitted line as limit value for particle sphericity.

Why does for Cu and Ni sphericity start below 1.0, i.e. due to atomic clusters?
The observation that the sphericity for Ni and Cu starts below 1.0 is mostly due to analysis limitations discussed above, i.e. pixel size.

Why were the results for 26 s not also included in Fig. A1 in the Pt column?
No spherical primary particles were found anymore on the grids for a 26 s coagulation time, but only large agglomerates. Therefore, no curve could be fitted and no PP size could be determined. For this reason, the plot is not shown in Fig. A1.
This is mentioned in the caption to figure A1.

Additionally, one sentence is added in line 192-193 highlighting the suitability of using the sphericity as a parameter to quantify primary particle size limits.

6) The authors state that the coagulation time influenced the primary particle size of the respective materials. How is that possible when primary particle formation is completed approx. 100 µs after the spark discharge? And how can the sphericity of the Pt increase with longer residence time (from 1.3 s to 2.2 s) in Fig. A1?
Given the discussion in 5) above, the data does not definitively indicate that particle sphericity increases with increasing coagulation time, which is due to the pixilation and resulting uncertainties as mentioned in 5).

7) P 7, L 155 and Table I: The authors refer to “primary particle size” and “agglomerate particle size”. Please include a detailed description which size (primary vs. agglomerate) is shown in the size distributions. What equivalent diameter is presented here?
All diameters presented are projected area equivalent diameters. They are defined in line 144 of the manuscript. This definition is now also added in Fig. 1, Table 1 and also further below in subsection 3.1.3 (Line 268)

8) P 7, L 169-171: The authors state that Au NPs might form oxides as a consequence of using N2 5.0 with oxygen impurities. This argument holds certainly for Cu and Ni. Pt NPs from spark ablation can exhibit thin oxide layers on the particle surface; however, for Au, an oxidation is impossible under the mentioned experimental circumstances. This fact supports, in turn, the relatively large primary particle size of <6 nm for Au NPs with a circularity of C=1 that is mentioned by the authors.
We agree with this statement. We deleted our comment that of Au particles could form oxides. (L 264)

9) Besides the low melting point, especially the absence of oxidation of the surface of Au NP contributes to the strong necking and coalescence growth of Au primary particles/clusters. On the other hand, oxygen-sensitive materials such as Ni and Cu experience a so called "pinning effect" by adsorption/reaction of the surface with oxygen (e.g. Seipenbusch et al. J. Aerosol Sci. 34, 2003). Such a pinning effect can increase the activation energy for coalescence from typically 50 kJ/mol (clean metal surface) to about 80 kJ/mol (partly oxidized metal surface, e.g. Ni). This point should be more elaborated here.
Thank you for the explanation, we were not aware that this effect. We added a sentence

explaining this effect (line 217-219) in the revised manuscript and added the reference mentioned above.

10) P 8, L 193-195: Regarding the generally poor charging of very small NP it is surprising that losses due to electric fields should accumulate to such an important amount. Are the substantial losses in the SDG chamber not rather related to the high particle diffusivity?
    We added this in the MS in line 237-242.

11) P 8, L 206-208: The authors mention the ejection of micron sized particles during spark erosion and a subsequent deposition of those within the housing of the spark discharge generator. The observation of Tabrizi et al. is very interesting and is also found for other processes where metal surfaces are locally heated up by sparks or pulsed lasers. It is also reasonable to attribute a high mass loss to the deposition of large micron sized particles. However, since the significance of this mass loss channel is expected to depend very much on the material properties, a more direct confirmation of these droplet-based particles would improve the convincing power of the argument. For instance, samples from the SDG chamber could be taking a wipe sample and analyzing it with electron microscopy (SEM/EDX or TEM/EDX) for micronic spherical particles.
    This would indeed be an interesting way to check if micron size particles are present in the spark chamber. However, as this is not the main focus of the manuscript, such measurements were not performed.

12) P 12, L 281: The authors derived contact angles for Au and Pt on TiO2. Please show a TEM image with a magnification where the contact angle is outlined. Please increase also the size of the TEM micrographs shown in Fig. 5. The inserts are very hard to see.
    The size of Fig. 5 was increased such that the contact angles are now clearly visibly. Furthermore, contact angles are drawn in the same figure and the corresponding angles are inserted. The micrographs with the drawn angels were also enlarged and included in the appendix (Fig. A2).

13) P 13/14/18, Fig.6, 8, B1: The coloring of the EDX maps is confusing. Please use a defined color for each element to distinguish, e.g., background from sputter layers from NPs from TiO2 support. Fig.6: The authors present dark field (DF) and bright field (BF) TEM(STEM) images. Please refrain from using BF images for Pt@TiO2 since Pt has a high contrast in HAADF, such as Au in Fig.6 top left.
    In all EDX recordings, the metal is colored green and the Ti(O_2) is colored blue consistently. Sputter layers are not visualized; the green color in the Figures B1 solely refers to Cu. The large features which are also colored green are also originating (falsely) from the Cu signal. This is, as discussed in the manuscript (e.g. in the caption to Fig. B1), due to a strong Cu signal caused by Cu parts within the instrument. We are not showing the sputtering layers as they are not of relevance.

    We are aware that HAADF usually gives better contrast than BF for high Z elements. However, the analyses we obtained for Pt on TiO_2 using BF detection resulted in a better resolved STEM image than the respective HAADF image. Due to the thickness of the TiO_2 particles and the difference in density of Ti and Pt, it was difficult to correctly set the intensities for the recordings and thus, as the Pt particles are visible better with the BF, the BF image was chosen to be shown in the manuscript.

14) P 15, L 328: The authors mention a continuous layer of Au on the TiO2 substrate after deposition. This observation can be related to the oxygen affinity of the metals used. Due to the absence of oxygen in Au NPs, partial sintering and necking can be observed even at room temperature.
We thank the author for this comment and added a sentence describing the reason why a continuous layer of Au forms on the TiO_2 substrate (due to the absence of oxygen in Au NPs, partial sintering and necking at RT) (line 387-389).

15) P 19, L 370-371: The calculation of the corresponding aerosol concentration based on the TEM micrograph is still not clear (cf. comment above). How was this done?
See 2). Details were added in the main text as described in 2).

16) P 19, Caption of Fig. C1: The diffusion losses in laminar flow in tubes does not depend on the tube diameter! Therefore, this argument about the influence of the larger tube does not apply. There must be another reason for the similar losses at different residence times since the amount of loss depends critically on the duration.
Thank you for pointing this out. It is correct, there is no dependence of the diffusion losses on the tube diameters. The reason why particle losses of the 2.2 s and 26.0 s are similar is due to how the losses accumulate non-linearly (in fact, exponentially):
In the beginning, when the concentration is high, way more diffusional losses occur compared to when the particles passed already a certain length through the tubing. So, the higher total length of the 2.2 s configuration does not result in much more losses than in the shorter 26.0 s configuration.
The caption to Fig. C1 was changed to highlight the above described.

Literature

von der Weiden, S.-L., Drewnick, F., and Borrmann, S.: Particle Loss Calculator – a new software tool for the assessment of the performance of aerosol inlet systems, Atmospheric Measurement Techniques, 2, 479–494, https://doi.org/10.5194/amt-2-479-2009, 2009.