Answers to comments of reviewer 3

The paper discusses the deposition by coagulation of small particles generated by spark discharge onto a TiO2 nanopowder to make an unspecified catalyst. Spark ablation is known to generate small particles, but a reliable method to synthesize useful catalysts with them is still lacking. The paper goes in more technical detail than a recent publication with a similar approach (Debecker 2024), and provides several useful insights, and novel approaches compared to the state of the art. The paper does not mention catalytic performance, but focuses on the aerosol synthesis route, and as such is a suitable topic for this journal.

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

1) The introduction seems written as an afterthought: It contains a lot of puzzle pieces, but the reader is left to guess what the motivations are for including these pieces. A clearer focus here helps highlight which parts of the work are novel, and which ones are not.
   The introduction was expanded and the main motivation of our study and open questions addressed are now clearly described (line 73-92). Furthermore, the abstract was also expanded to state these research questions clearly.

Technical issues:

2) Residence time for the different experimental parts aren't completely clear. E.g. Fig 1; L100: The residence time of volume C is specified. But what is the residence time before and after volume C? Figure 2 shows particle size 1.3s "after generation": depending on where you define generation, this can be somewhere before, in, or after volume C…
   We define the three residence times as defined by all the tubing and mixing volumes, through which the particles pass starting from the exit the spark generator to particle sampling point.
   The corresponding text in the manuscript was adapted as suggested by the reviewer (line 120-125).

3) The description of Fig 1. implies coated particles are not analysed (either/or?). Is the deposition tree for coating experiments the same as direct particle deposition without volume C? Were flows/volume adjusted to maintain correct residence time?
   The flow was adjusted in the case of the bi-modal coating. The caption to Figure 1 and the text in section 2.1 (line 120-125) were changed to be more concise.

4) Is the SDG flow on during nebulizer characterization, and is the nebulizer flow on during SDG only characterization? L88: Is the flow rate specified otherwise somewhere? It seems redundant.
   The nebulizer is off during SDG characterization. A sentence stating this was added (line 122-123).

5) Section 3.1.1: It's mentioned later, but already here mention that collection by diffusion will overrepresent small particles. Validity of max. primary particle size and Df of small agglomerates is probably unaffected, but the consideration should be part of the authors

analysis. Differences between the metals are consistent with prior literature on spark discharge, not necessarily new.

A sentence stating the overrepresentation was added in the section (line 179-180). Furthermore another sentence was added to clarify that the presented results are also observed by others (Feng et al., 2016; Grammatikopoulos et al., 2014; José-Yacamán et al., 2005; Debecker et al., 2024; Tabrizi et al., 2010), line 222-224 and line 230-231 respectively).

6) L151 “Fully coalesced particles are defined here as primary particles.” Is this the same as singlet particles (e.g. Feng 2016) ? The circularity criterion for singlet particle identification is a nice addition to previous analyses, and could be more explicit.

Yes, the definition of the spherical particle size is the same as ‘spherical singlet particles’ defined by Feng and coworkers. The ‘primary particle size’ as defined here was also used in (Tabrizi et al., 2009) – we now included this reference in the manuscript (line 187-188). 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.

7. The comparison of electrode mass loss and NP mass on filter is very qualitative. It shouldn't be too difficult to get a first order approximation of expected relative mass rates based on the Llewellyn Jones formula (see Tabrizi 2009, Feng 2016), and confirm whether or not the suggested explanations fit.

We thanks the reviewer for this comment and implemented the energy balance equation by Llewellyn Jones (Jones, 1950) for our system and electrodes and added the results in the corresponding section (line 256-261) as well as Table 2.

8. L193: Charge related losses are significant, but not necessarily majority of losses. Losses due to turbulence / poor flow conditions typically are also significant. Collection efficiency on membrane filters is loading dependent, which causes an underestimation of mass arriving at the filter. This effect is most important for low loadings.

We included in the revised manuscript the additional loss processes mentioned in the comment above in line 237-242.

9. L228-235, Fig 4. Are the concentrations for the TEM samples calculated by the diffusion correction, or only the relative abundance?

Yes, we determine particle concentrations for Fig. 4 from the TEM samples taking into account diffusional processes. We now describe the conversion of size distributions derived from TEM analysis to aerosol concentrations in more detail in the manuscript (line 287-290).

10. L281: please provide clear TEM images in SI for the contact angle measurements.

The angle was added in the main figure (Fig. 5) and shown in a more detailed way also in the appendix in Figure A2.

11. Fig 6: Shouldn’t this be compared to the observed TEM size distribution in figure 3? The reason why the TEM grids collect more of the smaller particles is the same reason why the TiO2 collect more of the smaller particles.

We now include a comparison of Fig. 6 and Figs. 2 and 3 in the manuscript (line 354-357).

12. Fig 8. EDX is difficult to read, in particular the Au sputtering layer mentioned in L333-335. This type of information must be clearly visible in the graph, e.g. using labels in the graph.
    Arrows were added to Fig. 8 (Ni) to make the distinction between Ni particles and Au sputtering layer clearer.

Minor details:

13. L84: The set voltage for the spark generator used is the mean voltage, not the breakdown voltage.
    The term 'breakdown voltage' was changed to 'discharge voltage' in line 105.

14. There is no forward reference to appendix C. If it's not relevant to the work itself, best to include this in the work referred to in L380.
    A forward reference to appendix C was added in line 272.

Literature:

Debecker, D. P., Hongmanorom, P., Pfeiffer, T. V., Zijlstra, B., Zhao, Y., Casale, S., and Sassoye, C.: Spark ablation: a dry, physical, and continuous method to prepare powdery metal nanoparticle-based catalysts, Chem. Commun., 60, 11076–11079, https://doi.org/10.1039/D4CC03469D, 2024.

Feng, J., Huang, L., Ludvigsson, L., Messing, M. E., Maisser, A., Biskos, G., and Schmidt-Ott, A.: General Approach to the Evolution of Singlet Nanoparticles from a Rapidly Quenched Point Source, J. Phys. Chem. C, 120, 621–630, https://doi.org/10.1021/acs.jpcc.5b06503, 2016.

Grammatikopoulos, P., Cassidy, C., Singh, V., and Sowwan, M.: Coalescence-induced crystallisation wave in Pd nanoparticles, Sci Rep, 4, 5779, https://doi.org/10.1038/srep05779, 2014.

Jones, F. L.: Electrode Erosion by Spark Discharges, Br. J. Appl. Phys., 1, 60, https://doi.org/10.1088/0508-3443/1/3/302, 1950.

José-Yacamán, M., Gutierrez-Wing, C., Miki, M., Yang, D.-Q., Piyakis, K. N., and Sacher, E.: Surface Diffusion and Coalescence of Mobile Metal Nanoparticles, J. Phys. Chem. B, 109, 9703–9711, https://doi.org/10.1021/jp0509459, 2005.

Tabrizi, N. S., Ullmann, M., Vons, V. A., Lafont, U., and Schmidt-Ott, A.: Generation of nanoparticles by spark discharge, J Nanopart Res, 11, 315–332, https://doi.org/10.1007/s11051-008-9407-y, 2009.

Tabrizi, N. S., Xu, Q., Van Der Pers, N. M., and Schmidt-Ott, A.: Generation of mixed metallic nanoparticles from immiscible metals by spark discharge, J Nanopart Res, 12, 247–259, https://doi.org/10.1007/s11051-009-9603-4, 2010.