Inclusion of supported gold nanoparticles into their semiconductor support

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These supporting information provide additional information on the properties of the materials. It is demonstrated how the particle mass load can be determined and a correlation between the mass and volume load is given. Further all UV-vis extinction spectra and additional size measurements determined by an analytical disc centrifuge are shown. Beside this, additional SEM images are provided, as the manuscript just shows a representative selection.

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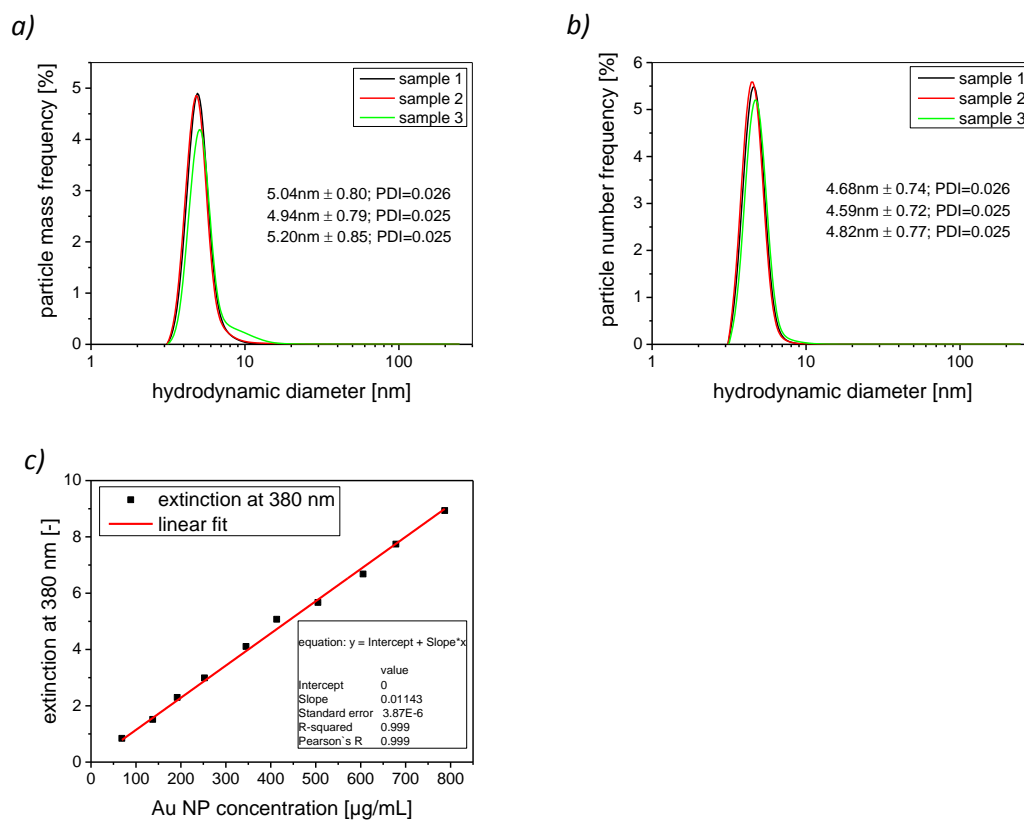
Supporting Information

Fig. S1: particle size distribution detected in an analytical disc centrifuge of monodisperse Au NP colloids before adsorption onto zinc oxide support a) as weight distribution and b) as number distribution of three different samples; c) extinction at 380 nm for different Au NP colloid concentrations and linear fit used to determine Au NP concentration after centrifugation and prior to adsorption on zinc oxide

For calibration at an extinction wavelength of 380 nm laser ablation time was varied from 1 to 10 minutes in 1 minute steps. The concentration of obtained gold colloids was determined by differential weighing of the target before and after laser ablation. The colloids were diluted to receive an extinction value around 1 where the extinction scales linearly with the Au NP concentration. Subsequently the measured extinction value was multiplied by the dilution factor and plotted versus the concentration as shown in Fig. S1 c).

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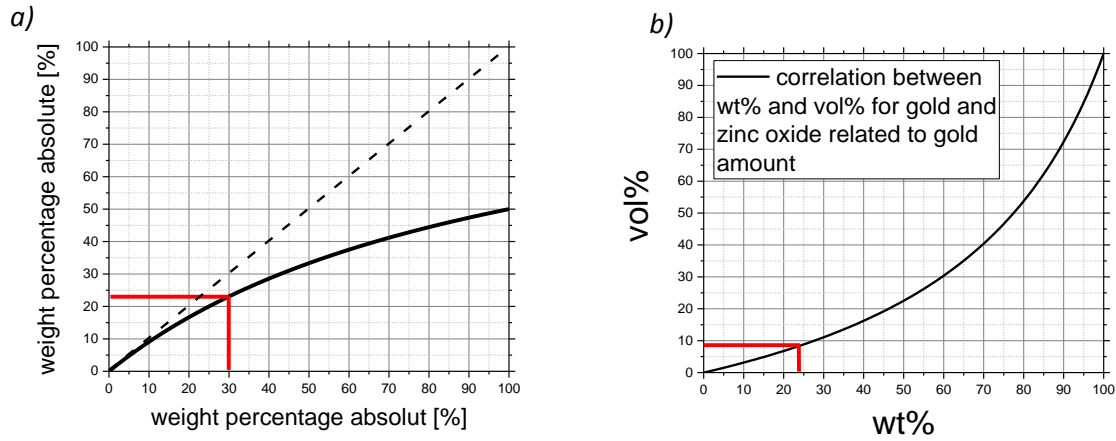

Fig. S2: a) correlation between the absolute weight percentage and the weight percentage referred to supports mass; b) correlation between volume percentage and weight percentage for the material composition of gold and zinc oxide referred to gold amount. Red lines mark the experimental values used for this study

Values for the curves shown in Fig. S1 a) and b) can be calculated by the following equations:

$$\frac{mass\ Au\ [g]}{mass\ ZnO\ [g]} \cdot 100 = weight\ percentage\ referred\ to\ support\ [wt\%]$$

$$\frac{mass\ Au\ [g]}{mass\ ZnO\ [g] + mass\ Au\ [g]} \cdot 100 = weight\ percentage\ absolute\ [wt\%]$$

$$\frac{\dfrac{mass\ Au\ [g]}{\rho_{Au}\ [\frac{g}{cm^3}]}}{\dfrac{mass\ ZnO\ [g]}{\rho_{ZnO}[\frac{g}{cm^3}]} + \dfrac{mass\ Au\ [g]}{\rho_{Au}\ [\frac{g}{cm^3}]}} \cdot 100 = volume\ percentage\ [vol\%]$$
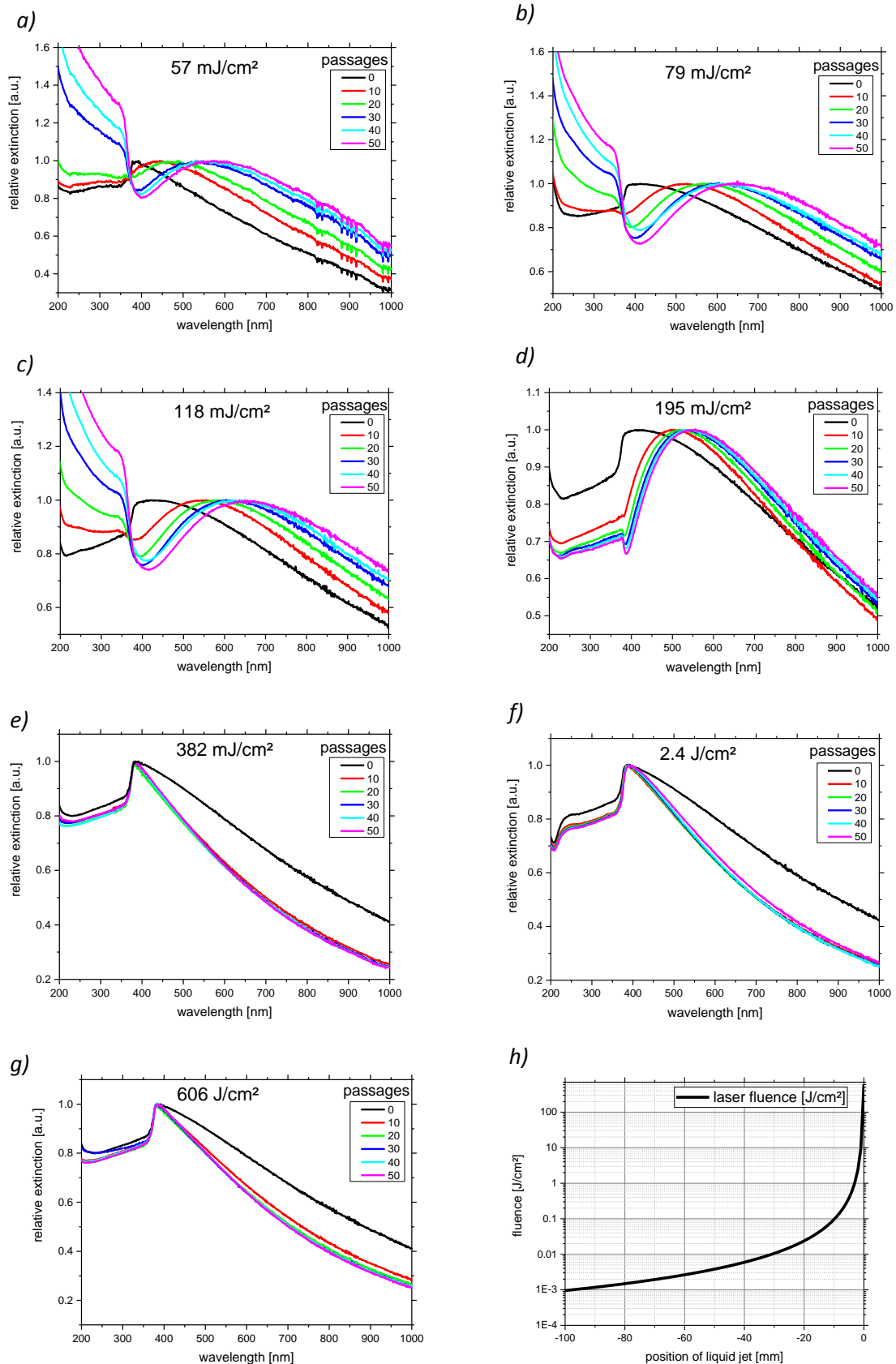
Fig. S3: UV/vis spectra of the pure zinc oxide particle suspensions for laser irradiation with 355 nm for increasing laser fluecnes (a-g) and calculated laser fluences for the different positions of the liquid jet relative to the focal plane of a 100 mm lens (h)

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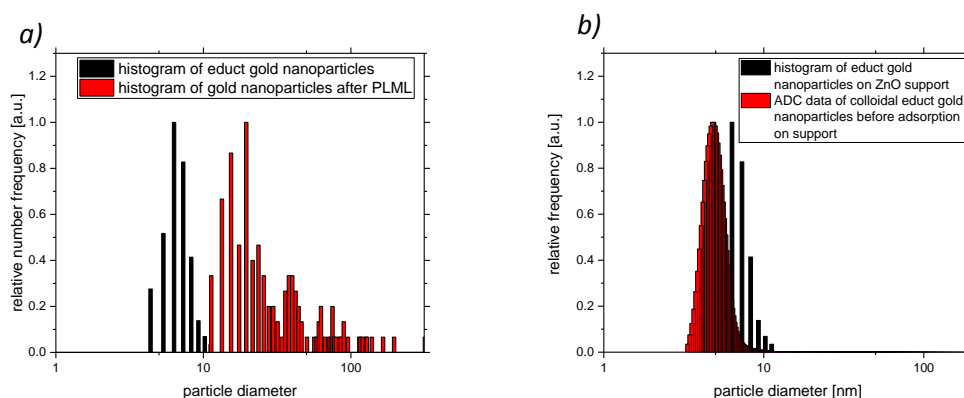

Fig. S4: Histogram of particle size distribution of gold nanoparticles on ZnO support before (black bars) and included in ZnO SMS after PLML derived from SEM images (red bars) (a)) and comparism of the Au NP particle size distributions derived from analytical disc centrifuge (ADC, red bars) before deposition onto ZnO and histogram from SEM images after Au NP deposition (black bars) (b))

Fig. S3 shows that gold nanoparticle size does not change after deposition onto the zinc oxide support but for PLML bigger gold nanoparticles are obtained. This is in agreement with findings of Marzun et al. [Marzun, G.; Nakamura, J.; Zhang, X.; Barcikowski, S.; Wagener, P. Size control and supporting of palladium nanoparticles made by laser ablation in saline solution as a facile route to heterogeneous catalysts. *Appl. Surf. Sci.* **2015**, *348*, 75-84] and Lau et al. [Lau, M., Haxhiaj, I.; Wagener, P.; Intartaglia, R.; Brandi, F.; Nakamura, J.; Barcikowski, S. Ligand-free gold atom clusters adsorbed on graphene nano sheets generated by oxidative laser fragmentation in water. *Chem. Phys. Lett.* **2014**, *610*, 256-260]. Further it demonstrates that high loadings can be achieved without causing significant particle aggregation or agglomeration.
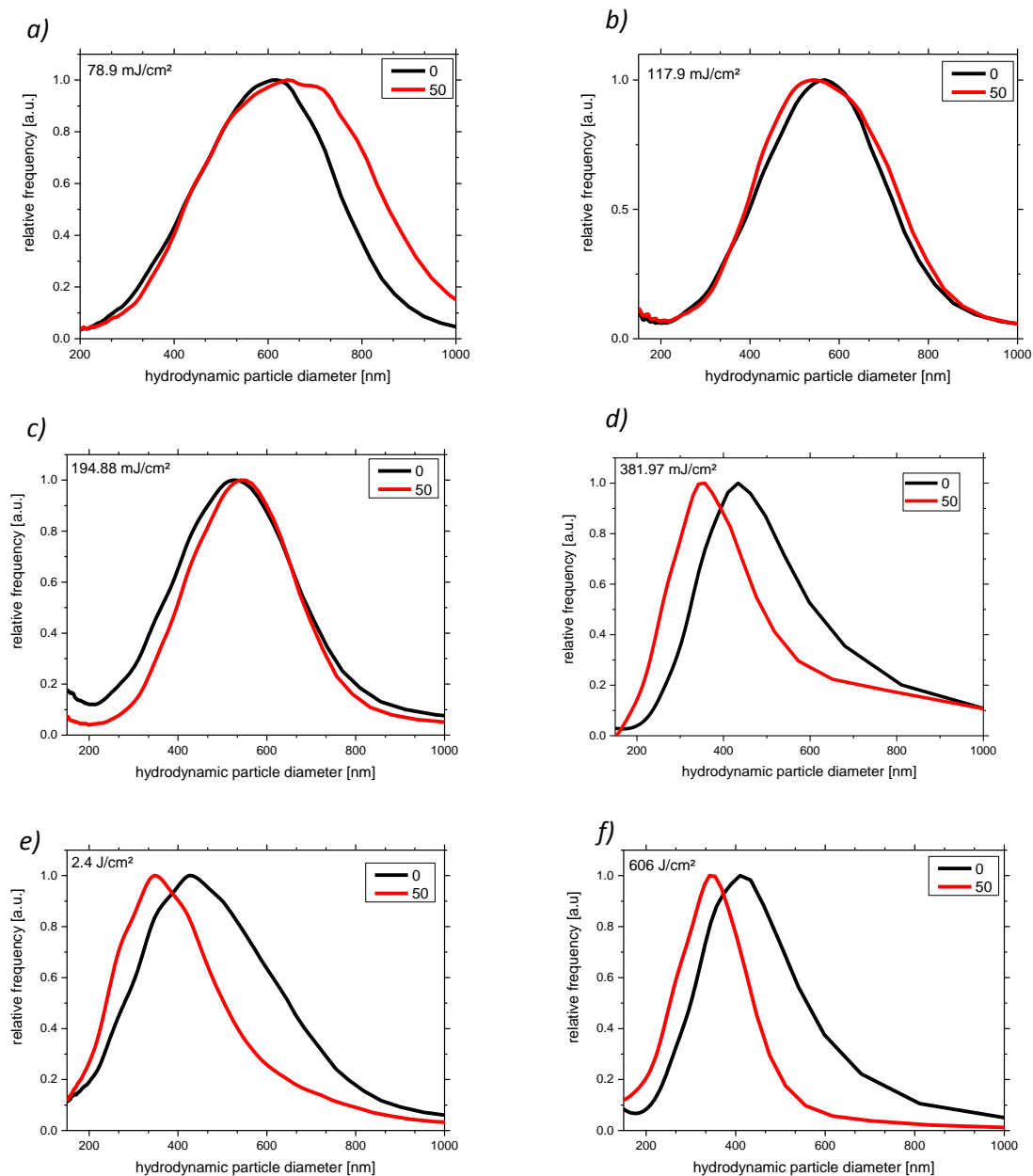
Fig. S5: Particle size distribution determined by analytical disc centrifugation before and after 50 passages of pulsed laser melting of pure zinc oxide in pure water for increasing laser fluences (a-f)
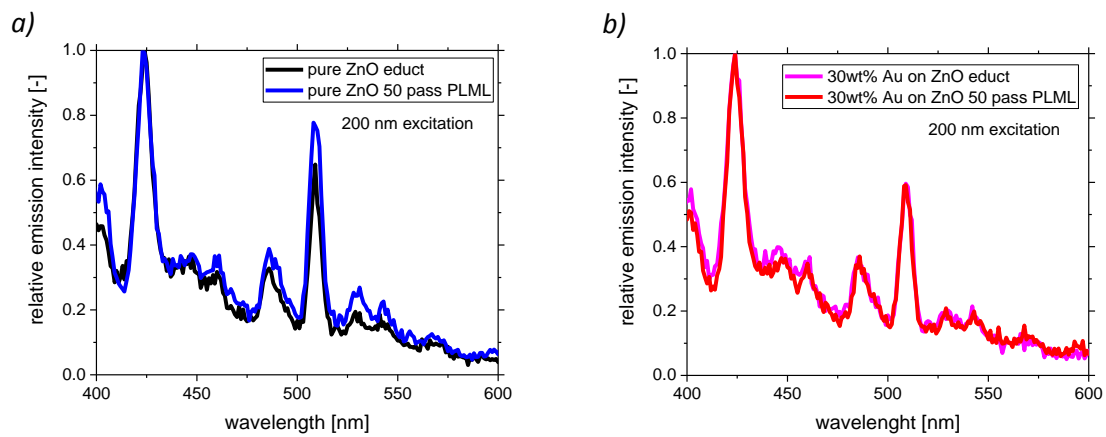
Fig. S6: Fluorescence spectra of the pure ZnO before and after PLML a) and of 30 wt% Au NP ZnO particles before and after PLML b)
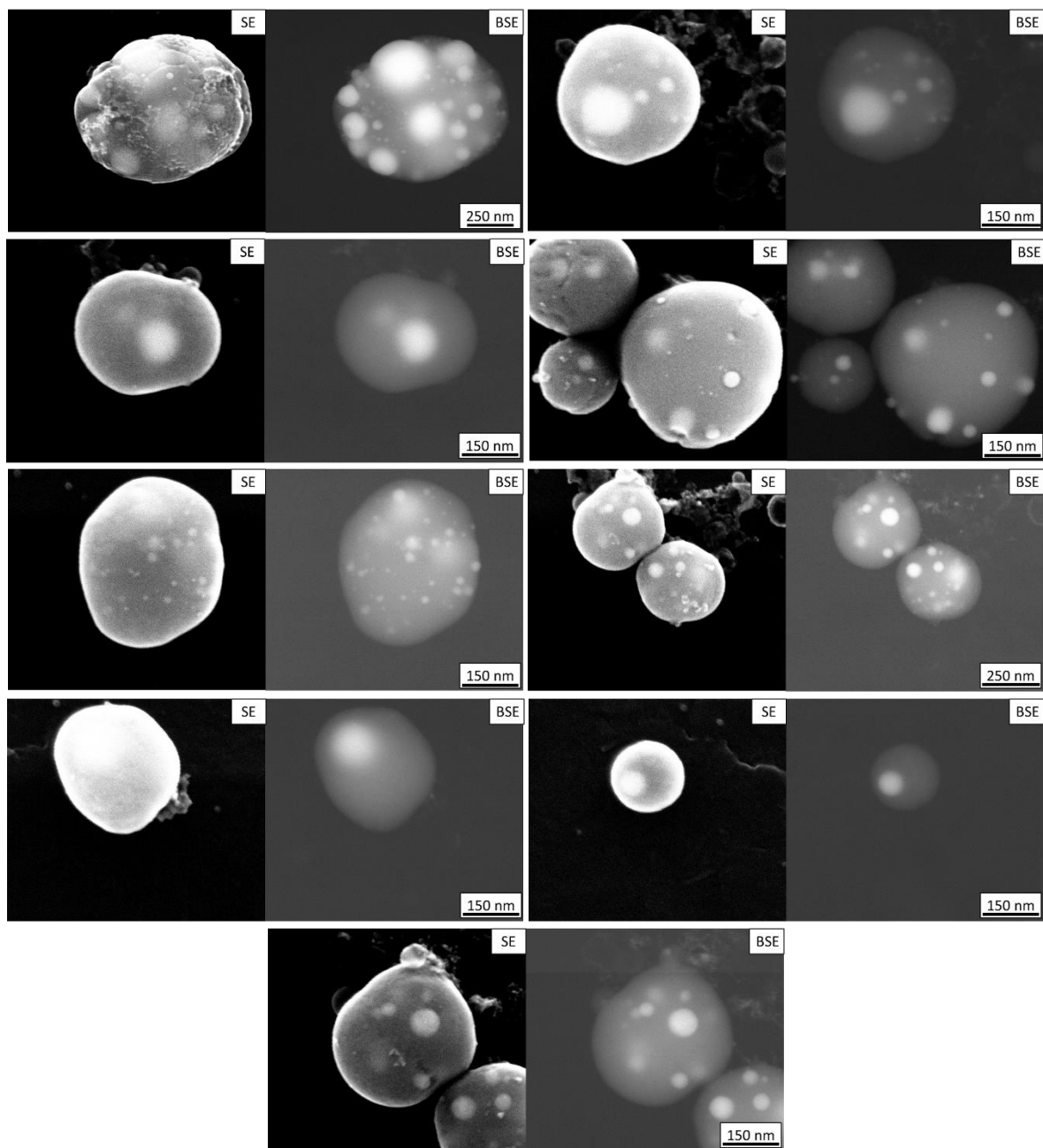
Fig. S7: Correlated SEM images of gold nanoparticle inclusions in zinc oxide matrix forming sub-micrometer spheres after 50 passages PLML with 79 mJ/cm², 355 nm and 40 ns detected with a secondary electron detector (SE) and back scattered electron detector (BSE)
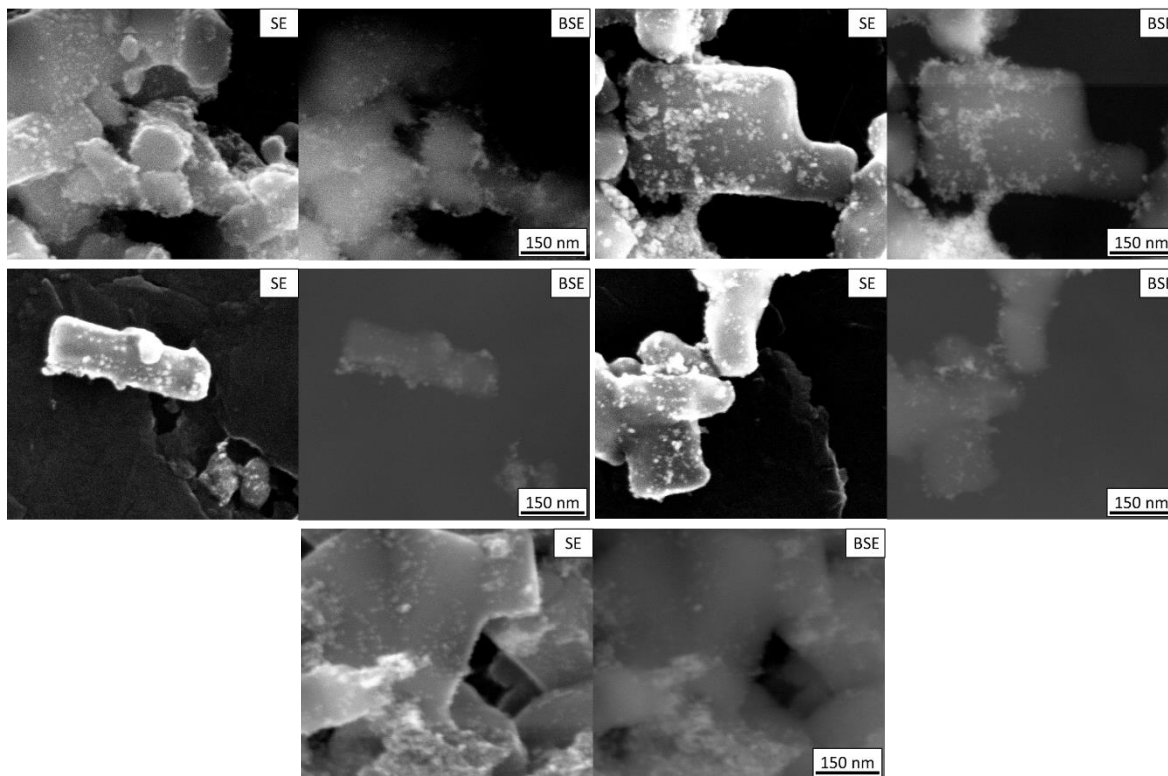
Fig. S8: Correlated SEM images of gold nanoparticles supported on zinc oxide particles before PLML detected with a secondary electron detector (SE) and back scattered electron detector (BSE)

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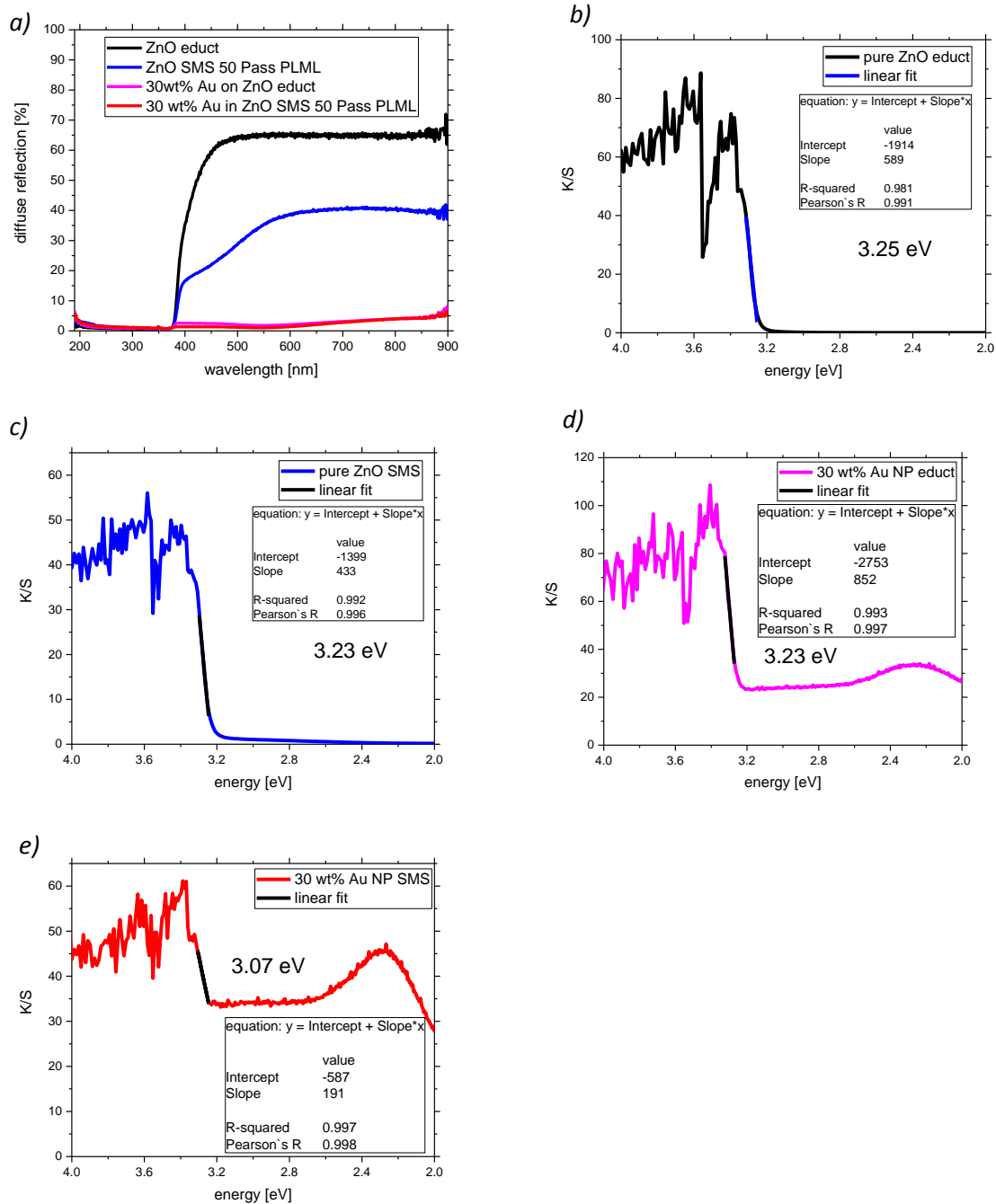

Fig. S9: a) diffuse reflection spectra for the different particle materials before and after 50 passages PLML; b)-e) determination of bandgap energy from linear fit by plotting the Kubelka-Munk function versus the electron energy for b) pure ZnO, c) ZnO SMS after 50 passages PLML, d) 30 wt% Au NP on ZnO and e) 30 wt% Au NP in ZnO SMS after 50 passages PLML

The ratio of absorption to scattering (K/S) can be determined by the following equation (Kubelka-Munk theory), with R_∞ as reflection of the infinite thick sample:

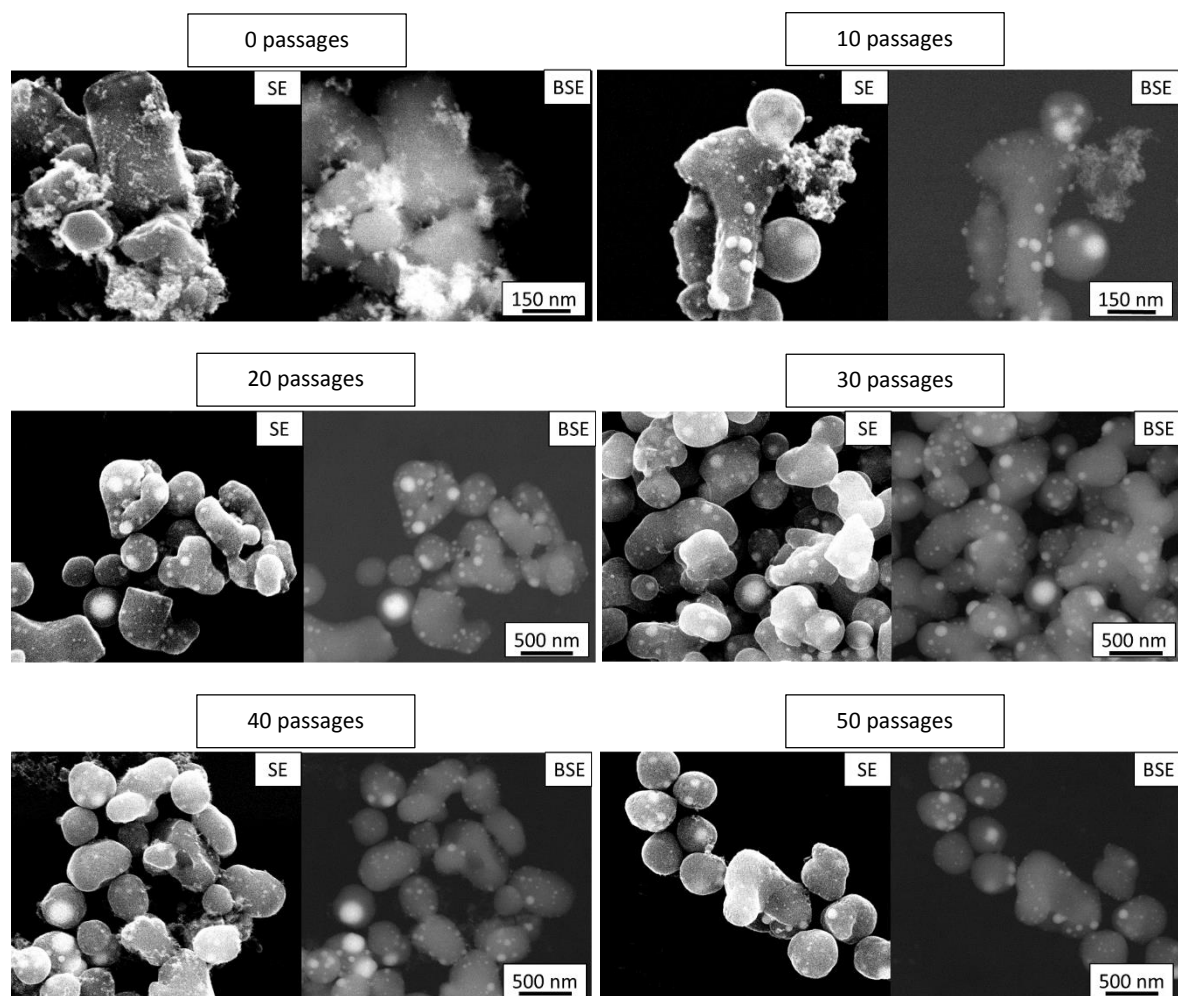$$\frac{K}{S} = \frac{(1-R_\infty)^2}{2R_\infty}$$

Fig. S10: SEM images of particles after 0, 10, 20, 30, 40 and 50 passages of PLML with 30 wt% Au NP on ZnO detected with secondary electrons and back scattered electrons, respectively