Supplementary information for:

Tunable synthesis of poly(ethylene imine)-gold-nanoparticle clusters

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Materials and Instrumentation:

DMF (anhydrous, amine free, 99.9%) and hydrogen tetrachloroaurate(III) trihydrate (99.99%) were purchased from Alfa Aesar. Silver nitrate (>99.8%), ethanol, branched PEI (bPEI; 25 kDa), PAAm (17 kDa, 20 wt% aqueous solution) and sodium citrate dihydrate (>99%) were purchased from Sigma-Aldrich. Linear PEI (lPEI; 25 kDa), bPEI (0.6, 1.8 and 10 kDa) was purchased from Polysciences Inc.. Potassium cyanide (techn.) was obtained from Riedel De Haen. Ammonium chloride (>99%) was purchased from Roth. Water (< 0.1µS/cm) was purchased from an ELGA Purelab Prima. All chemicals were used as received.

UV-vis absorption spectra were recorded on a Perkin Elmer Lambda 750 spectrometer in 1 cm quartz cuvettes at room temperature. TEM measurements were performed on a Philips CM-120. 15 µL of the sample solution were blotted onto clean carbon coated TEM grids (Mesh 400, Quantifoil, Jena) and excess material was removed by a filter paper (Whatman No. 1); the samples were allowed to dry prior to the transfer to the microscope. Grid cleaning was performed by UV-ozone treatment for 40 s. Particle sizes were determined from the TEM

images utilizing ImageJ. Centrifugation was performed with a Heraeus Biofuge Primo with a fixed angle rotor in 1.5 mL Eppendorf tubes.

Synthesis of the clusters with different PEI/$HAuCl_4$ ratios and different PEIs:

A solution of bPEI (25 kDa 2.5; 3.3; 5; and 10 mg/mL DMF) and a solution of $HAuCl_4 \times 3 H_2O$ (10 mg/mL DMF) were prepared. To 1 mL DMF in a small glass vial 40 µL of each solution were added and the mixture was immersed in an oil bath at 150 °C (corresponding to an internal temperature of ~130 °C after 20 min) and stirred for 20 min at 700 rpm and afterwards cooled to room temperature. In the same way particles with bPEI 0.6; 1.8; 10 kDa and lPEI 25 kDa were prepared (10 mg/mL of the reactants, 1:1 ratio).

Synthesis of PEI clusters with NH_4Cl:

To 1 mL of a solution of bPEI (25 kDa, 4 mg/mL DMF) 100 µL NH_4Cl (10 mg/mL H_2O) was added and the solution immersed in an oil bath at 150 °C and stirred for 20 min at 700 rpm and then cooled to room temperature.

Synthesis of gold nanoparticle–PAAm clusters:

A solution of PAAm (66.5 mg/mL water) and a solution of $HAuCl_4 \times 3H_2O$ (10 mg/mL DMF) were prepared. To 1 mL DMF in a small glass vial 40 µL of each solution were added. The mixture was immersed in an oil bath at 150 °C and stirred for 20 min at 700 rpm and then cooled to room temperature.

Synthesis of single gold particles and differently sized gold nanoparticle–PEI clusters:

Solutions of 1 mg/mL, 10 mg/mL, 20 mg/mL, 50 mg/mL, 100 mg/mL of bPEI (25 kDa) and $HAuCl_4 \times 3 H_2O$ were prepared. To 1 mL DMF 40 µL of each solution were added under

stirring and the mixtures were immersed in an oil bath at 150 °C. After stirring for 20 min at 700 rpm the mixtures were cooled to room temperature.

Transfer into water, etching of the particles and synthesis in water/ethanol:

All experiments were conducted with the solutions synthesized with bPEI 25 kDa at a 1:1 ratio. 40 µL of each solution were added to 1 mL DMF (concentration of 10 mg/mL for each reactant).

To transfer the clusters into water 1 mL of the solution was centrifuged at 5.000 rpm for 90 min, afterwards 950 µL of the supernatant solution was taken off, 950 µL of water were added and the procedure was repeated two more times. Etching of the gold cores was accomplished by addition of 100 µL of a KCN solution (10 mg/mL H_2O) to 1 mL of the cluster solution.

In case of water and ethanol as the solvents the reaction was conducted at 95 °C and 70 °C oil bath temperature, respectively, for 20 min. The synthesis of the clusters at room temperature was conducted by stirring the reaction for one week.

Synthesis of silver nanoparticles:

The synthesis was performed with a fresh solution of $AgNO_3$ (4.3 mg/mL DMF) and bPEI (25 kDa, 10 mg/mL). 40 µL of each solution were added to 1 mL DMF and the mixture was immersed in an oil bath (temperature 150 °C) and stirred for 20 min at 700 rpm. Subsequently, the mixture was cooled to room temperature.

Synthesis of citrate stabilized gold nanoparticles:

In a 250 mL round bottom flask 200 mL of a $HAuCl_4 \times 3H_2O$ (1 mM) solution was heated to 100 °C while stirring at 700 rpm. To the refluxing solution 1 mL of a sodium citrate solution (0.78 mM) was added at once. The color of the solution turned red after ~ 30 seconds.

Heating was continued for 30 minutes, afterwards the solution was cooled down and stored in the dark at 4 °C.

Synthesis of clusters with increased gold particle size and filling fraction:

For clusters with a low concentration of initial nanoparticles, 1 mL of the citrate nanoparticles were centrifuged in a plastic vial at 5000 rpm for 90 min and 950 µL of the supernatant solution was taken off. Afterwards 100 µL of a PVP solution (10 mg/mL DMF) and 850 µL DMF were added and the particles were redispersed by simple shaking. The solution was centrifuged two times at 5000 rpm for 2.5 h and each time 950 µL supernatant was taken off and the particles were redispersed in 950 µL DMF. For solutions with a high concentration of initial gold particles ten 1 mL solutions were processed in the same way. As an additional step the solutions were centrifuged again, 900 µL of the supernatant was taken off, and all the solutions were combined.

For the synthesis of small clusters, to 1 mL of the low or high concentrated particle solution 40 µL PEI (10 mg/mL DMF) and 40 µL $HAuCl_4 \times 3H_2O$ (10 mg/mL DMF) were added under stirring at 1200 rpm. The solution was then immersed in an oil bath at 150 °C and stirred for 5 minutes at 700 rpm; afterwards it was cooled to room temperature.

For the synthesis of large clusters, to 1 mL of the low or high concentrated particle solution 40 µL PEI (50 mg/mL DMF) and 40 µL $HAuCl_4 \times 3H_2O$ (50 mg/mL DMF) were added under stirring at 1200 rpm. The solution was then immersed in an oil bath at 150 °C and stirred for 5 minutes at 700 rpm; afterwards it was cooled to room temperature.

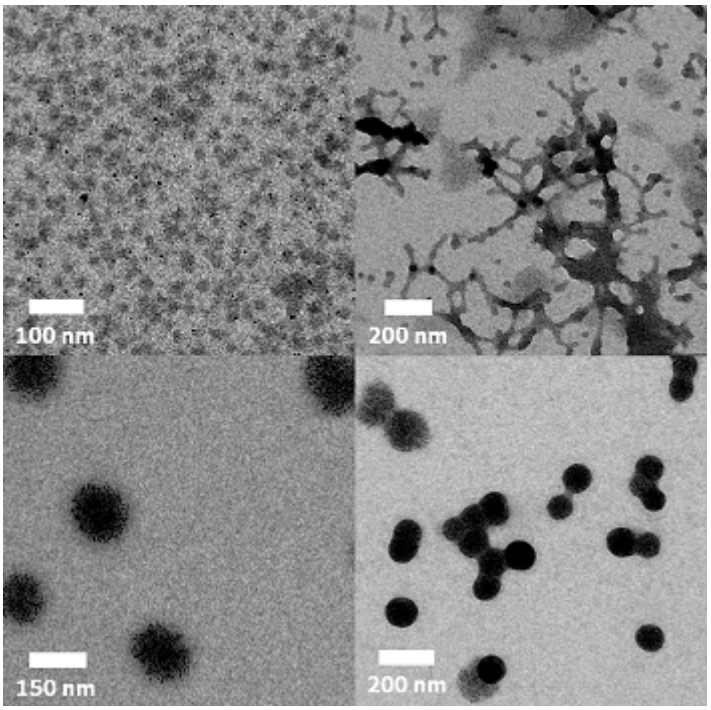

Figure S1. TEM images at different stages of the nanoparticle synthesis. After 30 sec (top left), 45 sec (top right), 1 min (bottom left) and 2 min (bottom right).

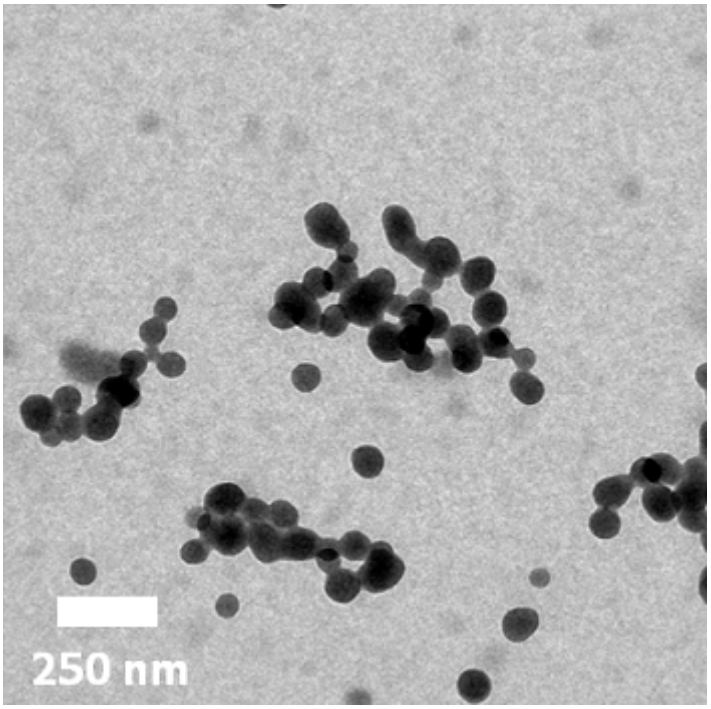

Figure S2. TEM image of the control solution with NH_4Cl instead of $HAuCl_4$.

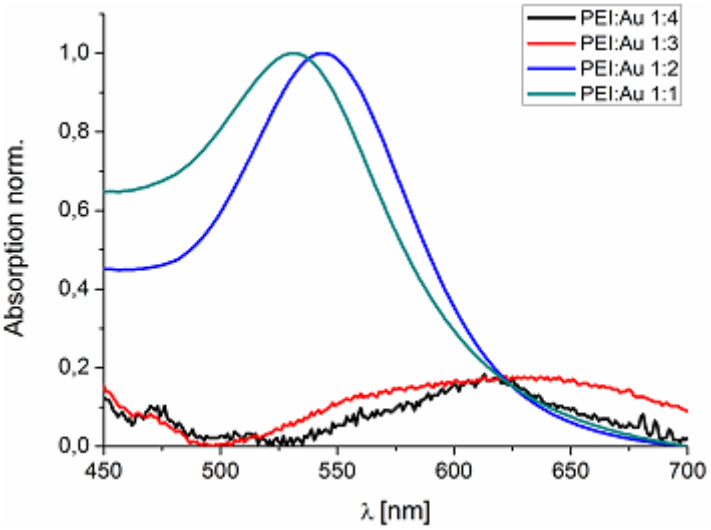

Figure S3. UV-vis spectra of particles synthesized with different PEI/$HAuCl_4$ ratios (in DMF).

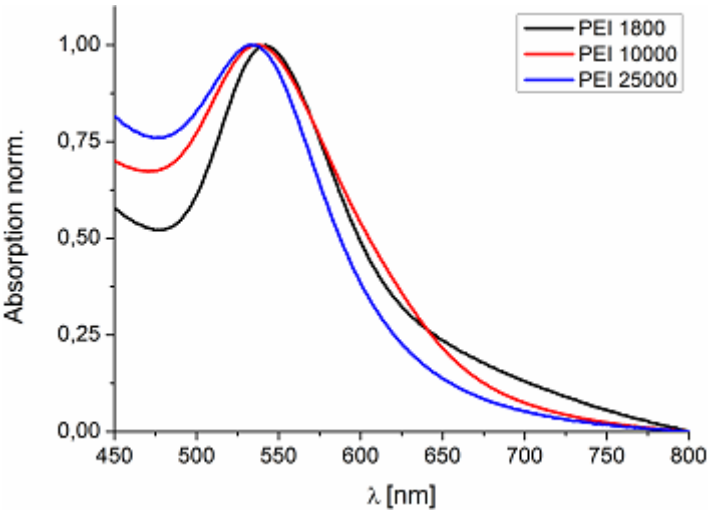

Figure S4. UV-vis spectra of clusters synthesized with PEIs of different molar masses (in DMF).

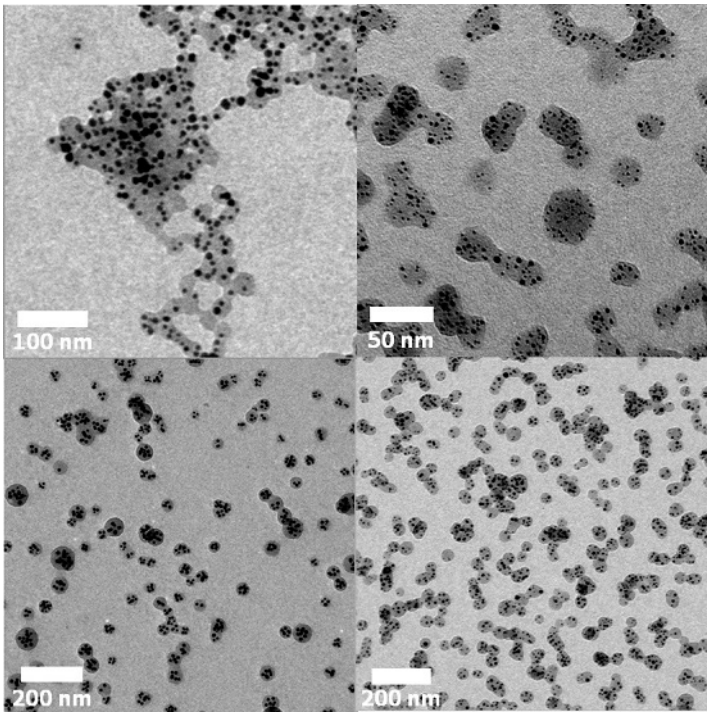

Figure S5. TEM images of particles synthesized with a 1:2 ratio (top left), with PAAm (top right), bPEI 1.8 kDa (bottom left) and bPEI 10 kDa (bottom right).

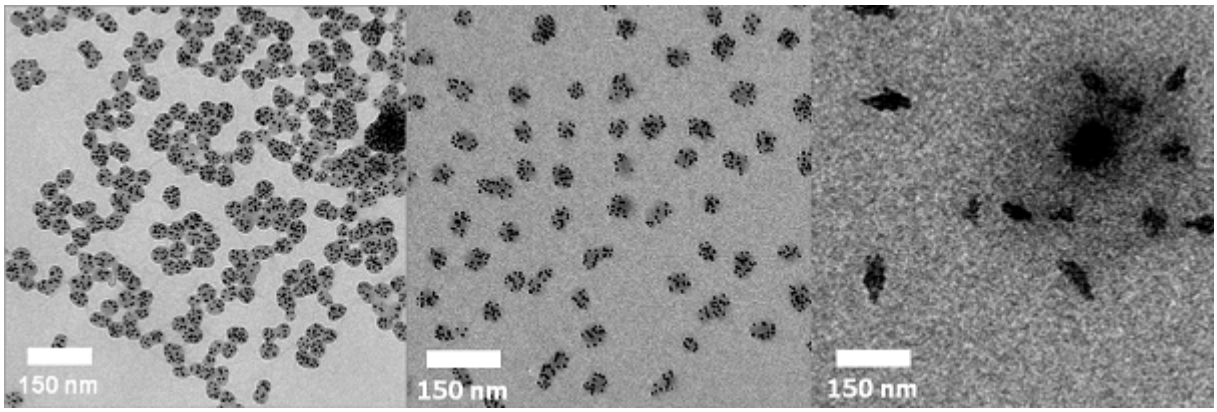

Figure S6. TEM images of as synthesized particles with bPEI 25 kDA and a 1:1 ratio, after three times centrifugation and redispersion in water and after etching with KCN (left to right).

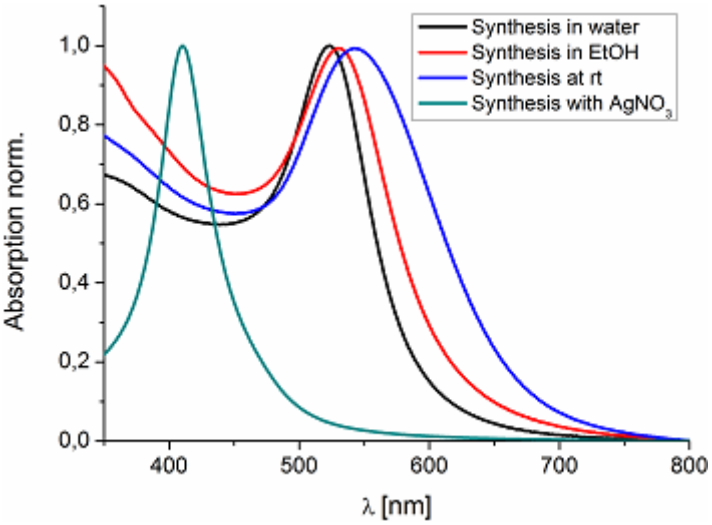

Figure S7. UV-vis spectra of particles synthesized in water, ethanol, at room temperature (in DMF) and with silver nitrate (in DMF).

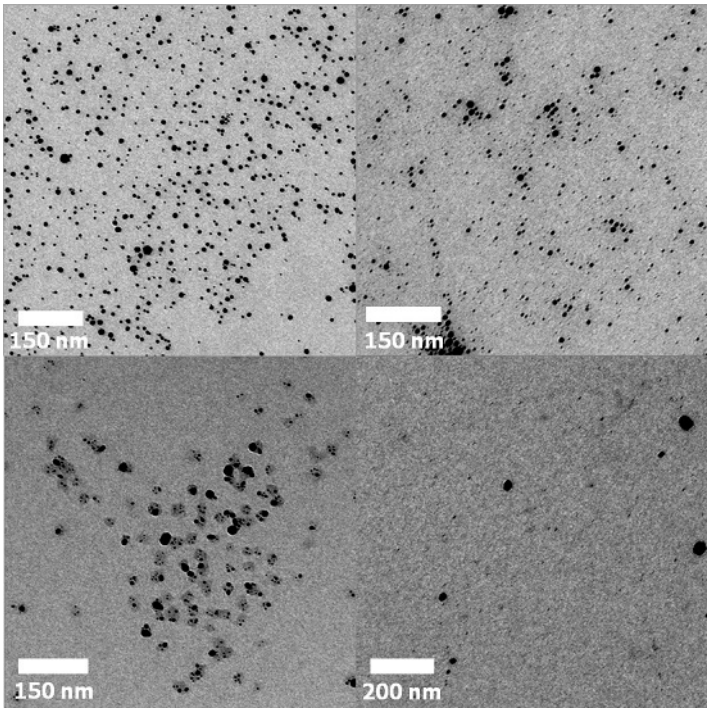

Figure S8. TEM images of particles synthesized in water (top left), ethanol (top right), at room temperature (bottom left) and with silver nitrate (bottom right).

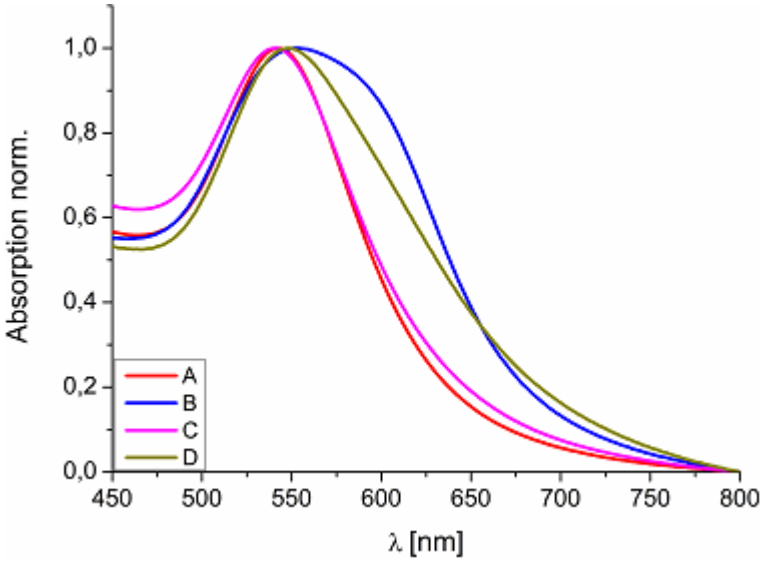

Figure S9. UV-vis spectra of clusters of different size and filling fractions: A - small clusters, low filling fraction; B - small clusters, high filling fraction; C - large clusters, low filling fraction; D - large clusters, high filling fraction (in DMF).

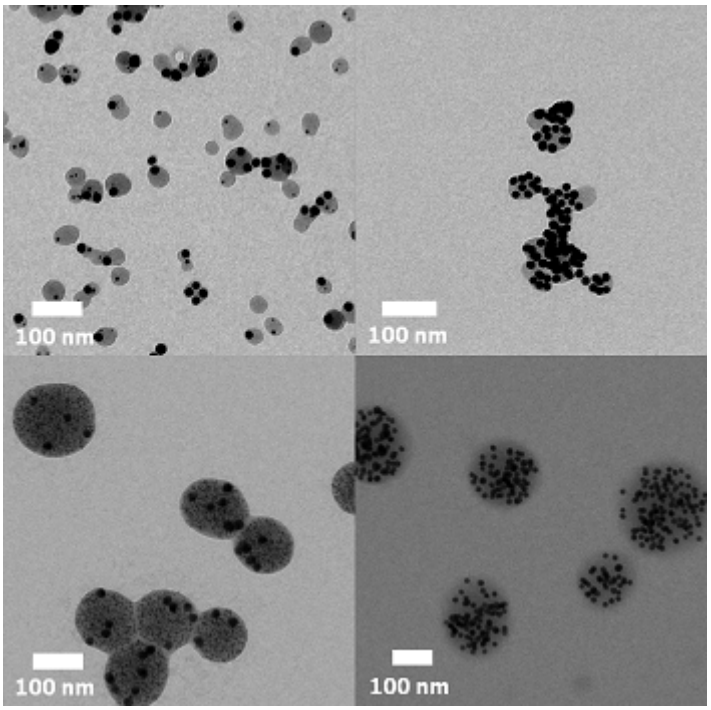

Figure S10. TEM images of clusters of different size and filling fractions: top left - small clusters, low filling fraction; top right - small clusters, high filling fraction; bottom left - large clusters, low filling fraction; bottom right - large clusters, high filling fraction.