Supporting Information for

Core-shell microgels as thermoresponsive carriers for catalytic palladium nanoparticles

Viktor Sabadasch, Lars Wiehemeier, Tilman Kottke and Thomas Hellweg

Physical and Biophysical Chemistry, Department of Chemistry, Bielefeld University, Universitätsstr. 25, 33615 Bielefeld, Germany, E-mail: thomas.hellweg@uni-bielefeld.de

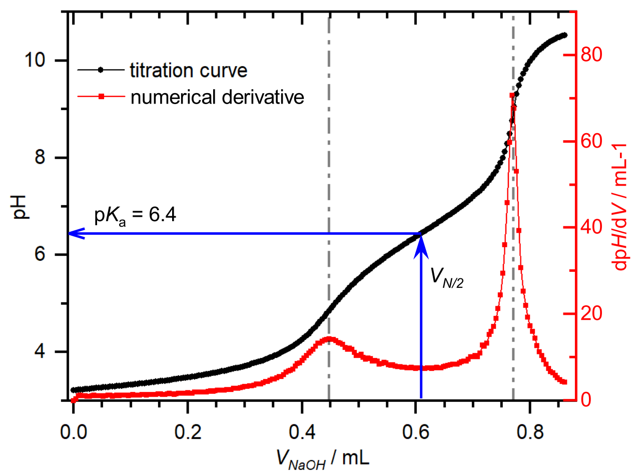

Figure S1 Exemplary titration curve and numerical derivative of the core system plotted against the titrated volume of NaOH. The measurements were performed three times and the calculated data shown in Figure S1 correspond to the averaged values. The grey dashed lines indicate the respective neutralisation points of the hydrochloric acid and copolymerized methacrylate.

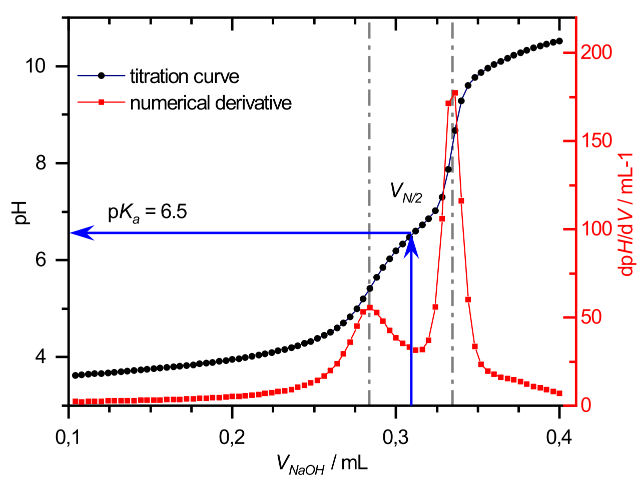

Figure S2 Exemplary titration curve with numerical derivative of the core-shell system. Three measurements were performed and the averaged data can be found in Figure S1.The grey dashed lines indicate the respective neutralisation points.

The acid content derived from the potentiometric titration data can be normalized with respect to the used dry mass of polymer material within the titration experiment to obtain the determined acid content. This determined acid content per dry mass of microgel can be related to the applied acid content per mass of applied educts used for synthesis. The ratio of determined acid content to applied acid content in the core system was obtained with 113 %, resulting in a microgel core system containing 13 % more methacrylic acid than one would have expected from the applied acid content during synthesis. This value is comparable to PNIPAM-co-methacrylic acid systems from Hoare et al., for which an incorporation feed of 110 % was obtained, as derived from their data.[1] The incorporation rate is most likely above 100% because some of the other compounds (NIPAM, BIS and APS) were not copolymerized and were separated from the microgel system in the purification process.

Table S1 Applied and determined methacrylic acid content per dry mass of respective microgel system, incorporation feed as relative ratio of determined to applied acid content per dry mass of microgel, the apparent acid constant pK_a and mass of incorporated palladium per microgel suspension m for the PNNPAM-co-MAc core and PNNPAM-co-MAc@PNIPMAM core-shell microgel systems. An incorporation feed and applied acid content for the core-shell system is not applicable since no additional methacrylic acid was added during the synthesis of the shell. The pK_a was determined by the half equivalence point of the respective titration.

Microgel-system	Core	Core-Shell
applied acid content / mol g^{-1}	$3.68 \cdot 10^{-4}$	-
determined acid content / mol g^{-1}	$4.15 \cdot 10^{-4}$	$1.88 \cdot 10^{-4}$
incorporation feed / %	113	-
pK_a	6.4 ± 0.1	6.5 ± 0.1
m / ppm	16	17

In order to determine the size of the nanoparticle, we performed a size evaluation via the image processing software *ImageJ*.[2] The program converts the transmission electron microscopy image into a binary picture, where solely the nanoparticles are shown in white (Fig. S3). Subsequently the program determines the area a single nanoparticle occupies. The gathered data can then be plotted in a histogram (Figure S4 and S5).

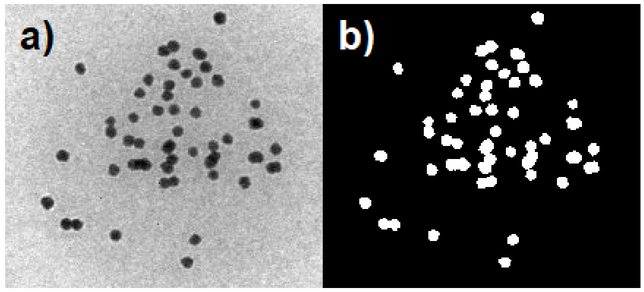

Figure S3 Conversion of a partial section of a TEM image (a) into a binary picture (b) via the image processing software *ImageJ*. As can be seen from the binary, some of the nanoparticles are merged together and will be evaluated as a single area. However, since the nanoparticles are only merged slightly, we can approximate that the accessible surface area of the nanoparticles can be determined by the first mode of the multi-modal size distribution. (see Fig. S4 and S5)

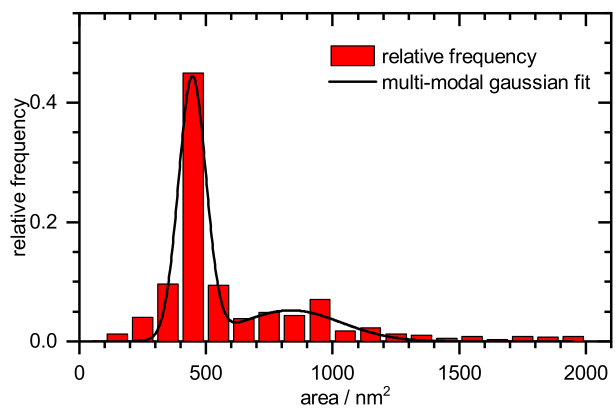

Figure S4 Histogram of the particle size distribution of the core system loaded with palladium nanoparticles.The relative frequency was plotted against the 2D area of a nanoparticles with a bin size of $100\,\mathrm{nm}$. A total of 584 particles were analyzed.

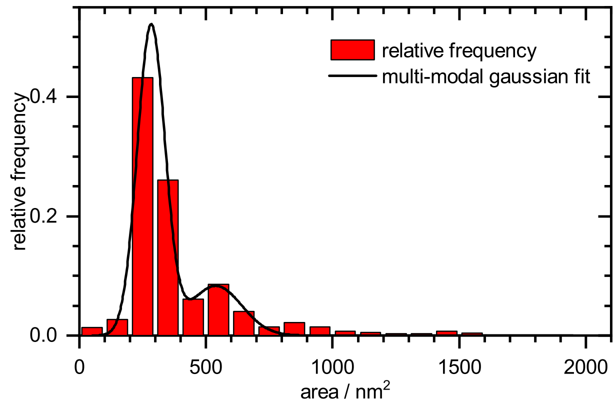

Figure S5 Histogram of the particle size distribution for the core-shell system loaded with palladium nanoparticles. Based on a total of 746 analyzed particles distributed onto bins with a size of $100\,\mathrm{nm}$.

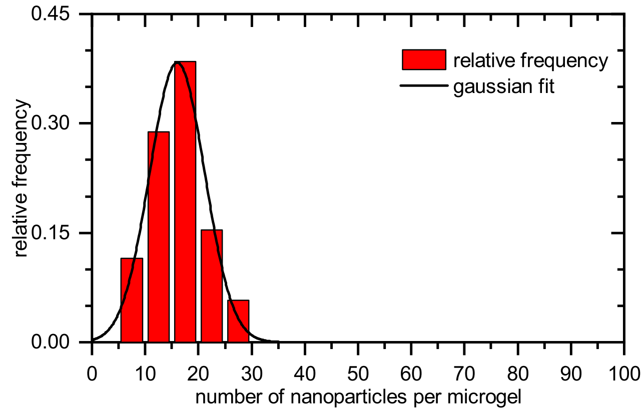

Figure S6 Distribution of the number of palladium nanoparticles embedded in the core system. A total of 52 microgel particles were analyzed.

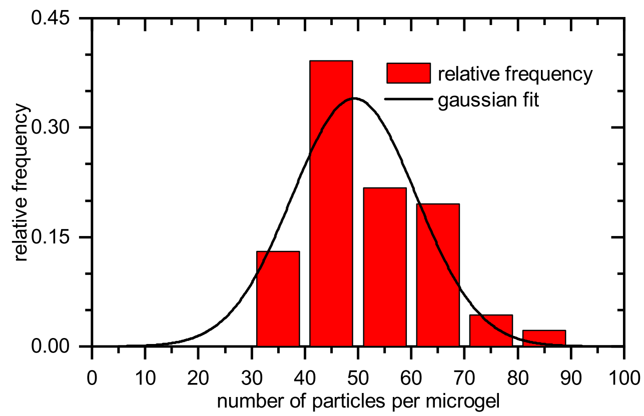

Figure S7 Histogram of the number of palladium nanoparticles embedded in the core-shell system. A total of 46 microgel particles were analyzed.

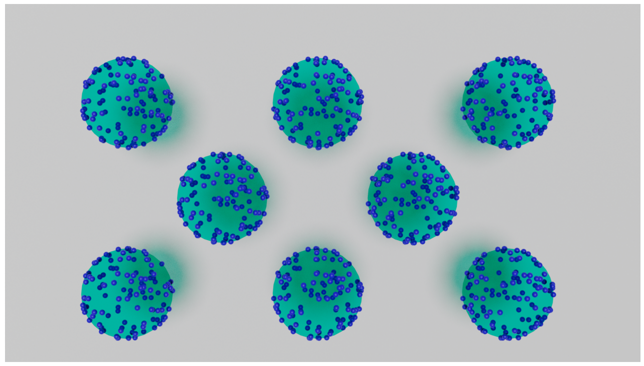

Figure S8 Image of a 3D animation, in which spherical carrier particles (turquoise coloured) were decorated with several randomly distributed small blue particles. The image was taken in a top-down view with a transparent volume for the carrier system. The blue particles create a halo-like distribution density. The simulation was performed via the 3D computer graphics toolset *Blender*.[3]

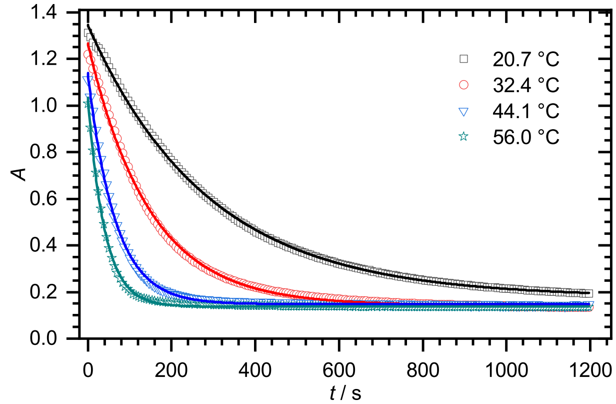

Figure S9 Absorption at a wavelength of 400 nm during a catalysis of *p*-nitrophenol to *p*-aminophenole plotted against the time. A mono-exponential decay is shown as solid line. The baseline absorption at $t \rightarrow \infty$ corresponds to a decreased transmittance mainly contributed by the scattering of the microgel.[4,5]

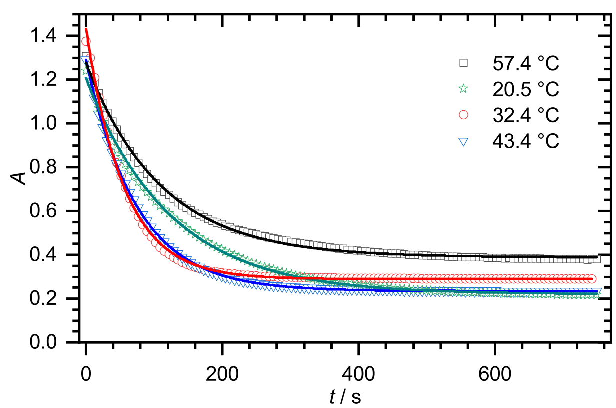

Figure S10 Absorption at a wavelength of 400 nm plotted against the time. Additionally a mono-exponential decay is shown as solid line. The increased baseline absorption with increasing temperature is caused by the microgel-shell collapse.

Notes and references

1 T. Hoare and R. Pelton, *Macromolecules*, 2004, **37**, 2544–2550.

2 W.S. Rasband, ImageJ, U. S. National Institutes of Health, Bethesda, Maryland, USA, https://imagej.nih.gov/ij/, *ImageJ, version 1.52a*, 1997-2018.

3 B. O. Community, *Blender - a 3D modelling and rendering package*, Blender Foundation, Stichting Blender Foundation, Amsterdam, 2018.

4 B. Wedel, M. Zeiser and T. Hellweg, *Z. Phys. Chem.*, 2012, **226**, 737–748.

5 E. Kano, Mamoru; Kokufuta, *Langmuir*, 2009, **15**, 8649–8655.