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Protecting "Groups" in Colloidal Synthesis of Au Semishells

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Supporting Information

Materials

Chloroauric acid (≥99.9 %), sodium borohydride (99 %), poly(ethylene glycol) methyl ether thiol (average Mn 6000), Trimethoxyphenylsilane (Ph-TMS) and ammonia solution (2.0 M in ethanol) were purchased from Sigma Aldrich. Toluene was purchased from Acros Organics. Tin(II) chloride (anhydrous) was purchased from Merck. Hydrochloric acid was purchased from TH Geyer. Formaldehyde was purchased from KFM optiChem. Potassium carbonate was purchased from Fluka. Glucose-functionalized polystyrene particles were synthesized according to a previously published procedure.[34]

Measurements

UV/VIS measurements were conducted at 25 °C using a Jasco V-6300 UV/Vis spectrometer with a range from 190 to 1100 nm. Therefore, disposable polystyrene cuvettes from Brand GMBH & CO KG were used.

FESEM images were acquired using a Hitachi S4800 FESEM. For sample preparation, one droplet of the particle dispersion was placed on a silicon wafer and dried at room temperature. The samples were sputtered with gold. Particle diameters from FESEM images were determined using MATLAB. For average diameter and size distribution, at least 200 particles per sample were measured.

TEM studies were performed using a JEOL ARM 200 probe-corrected TEM, operated at 200 kV. Imaging of the particles was performed in high-angle annular dark field (HAADF)-scanning TEM (STEM) mode. EDS spectra were recorded using a 100-mm2 Centurio SDD detector.

EDS mappings were obtained in STEM mode by acquiring full spectra in grids of either 256 × 256 or 512 × 512 pixels. All mappings were obtained by summation of 50–100 frames, each having 0.1 ms acquisition time per pixel per frame. In this way, the particles remained unaffected by the impact of the incident electron beam.

Thermogravimetric analysis (TGA) was performed using a Discovery TGA (TA Instruments). Samples were loaded in platinum pans and ramped at 10°C/min to 900°C under dry air with a flow rate of 20 mL/min.

Protection

Glucose functionalized polystyrene particle dispersion (5.0 mL, 0.74 wt. %) was cooled to 0°C in an ice bath and was subsequently dosed with Ph-TMS (80 µL). The reaction mixture was stirred for 1 h at 0°C and afterward transferred to a preheated oil bath at 80°C. Ethanoic ammonia solution (2M; 0.5 mL) was added and the mixture was stirred for 2 h at 80°C. The mixture was centrifuged at 5000 rpm for 20 min and after redispersion in water again for 15 min with subsequent redispersion in water.

All other particle protections were performed according to this procedure (Table S1). Weight percentage was calculated to accomplish a constant amount of polystyrene particle overall.

Table S1. Reaction parameters for polystyrene particle protection with polyphenylsiloxane caps.

particle diameter [nm]	particle concentration [wt.%]	amount Ph-TMS [µL]	radius polyphenylsiloxane cap [nm]
282	0.74	13	121
282	0.74	50	174
282	0.74	80	185
282	0.74	120	221
386	1.90	13	152
338	1.27	13	136
218	0.42	13	109

Polystyrene-Si-Au composites

Au seeding and plating of polystyrene-polyphenylsiloxane composite particles was performed according to previously published procedure.[17]

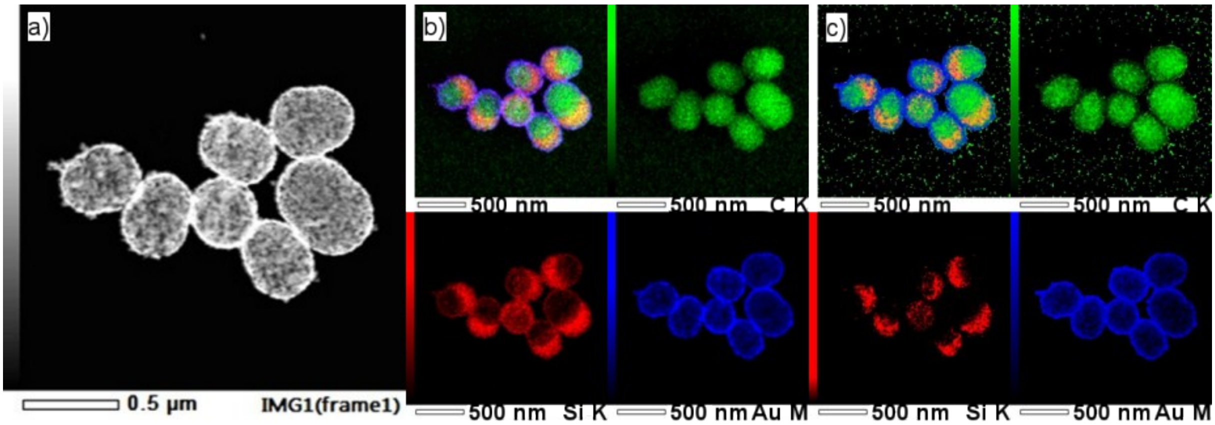

Figure S1. a) TEM image, b) raw count and c) quantified EDS mappings of polystyrene-polyphenylsiloxane composite particles plated with a thin Au shell (nanoshells). The thin Si shell that seems to be present around the entire polystyrene part in the raw count EDS mapping is an artefact due to partial peak overlap between the Si-Kα line and the Au-Mz line.

Deprotection

Aqueous dispersion of Au plated polystyrene-polyphenylsiloxane composite particles was treated with toluene for 10 min. The Mixture was centrifuged at 5000 rpm for 20 min and redispersed in water.

Optical Analysis

Since the semishells and the polystyrene-polyphenylsiloxane composite particles plated with a thin Au shell (nanoshells) are not symmetric, it is important to consider different optical responses that depend on the polarization of light and its propagation direction. Essentially, one may consider three different situations: *z*-polarized light propagating in *x* direction (k:[1,0,0]; Pol:[0,0,1]), *x*-polarized light propagating in *z*-direction (k:[0,0,1]; Pol:[1,0,0]), and *y*-polarized light propagating in *z* direction (k:[0,0,1]; Pol:[0,1,0]). All other possibilities are either equivalent to or a linear combination of the three cases.

To measure the optical response of the particles, they are dispersed in DI-water and illuminated with unpolarized broadband light. Due to the randomness of the process, the measured absorbance is a weighted combination of all possible cases discussed above, in which the weight is the probability of each situation to occur. Assuming there is not a preferential one, the absorbance is a simple average of these three cases. The same approach is used for the numerical calculation of the total extinction efficiency.

The extinction efficiency is defined as the ratio between the extinction cross-section and the cross-sectional area of the particle. The extinction cross-section is calculated using the finite element method (frequency domain solver) of the 3D electromagnetic simulation software CST STUDIO SUITE 2016 (Service Pack 6) [CST STUDIO SUITE 2016 (SP6). https://www.cst.com].

The geometry describing the Au semishell consists of a polystyrene sphere (core), with 293 nm of diameter, surrounded by a Au half-sphere (shell), 8 nm thicker than the inner sphere. For the nanoshells, one considers two overlapping spheres, 60 nm apart from each other, with different diameters: 293 nm (polystyrene) and 320 nm (polyphenylsiloxane). They are surrounded by a 8-nm-thick Au shell. The models are designed with open boundary conditions (add space), and excited by linear polarized plane waves. The refractive index of polystyrene and silica is, respectively, 1.590 and 1.458, and the background material is water (1.330). For Au, the wavelength-dependent refractive index is based on Johnson & Christy's handbook [Johnson PB, Christry RW (1972) Optical Constants of the Noble Metals. Phys Rev B 6:4370–4379. doi: 10.1103/PhysRevB.6.4370]. All simulations are performed using 10 meshing points per wavelength.

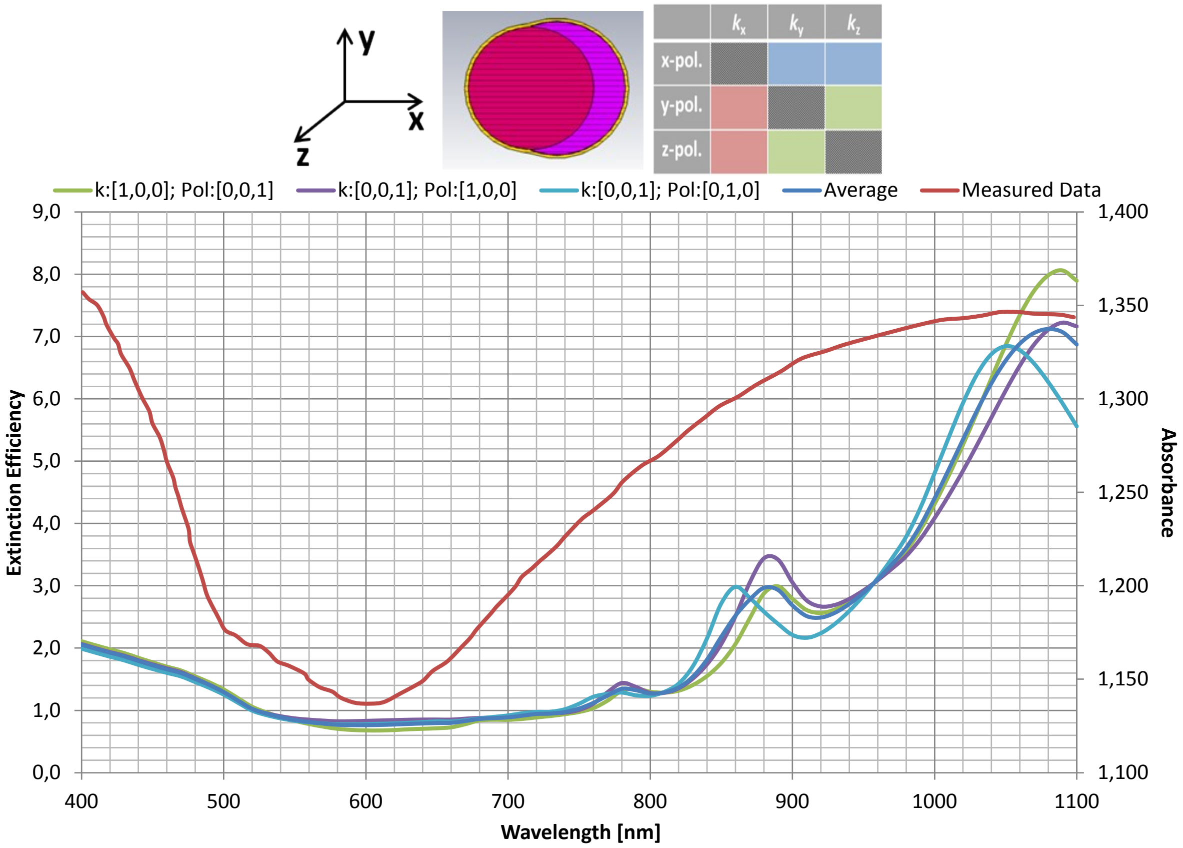

Figure S2. UV/VIS measurements and theoretical calculations using finite element method of polystyrene-polyphenylsiloxane composite particles plated with a thin Au shell (nanoshells).

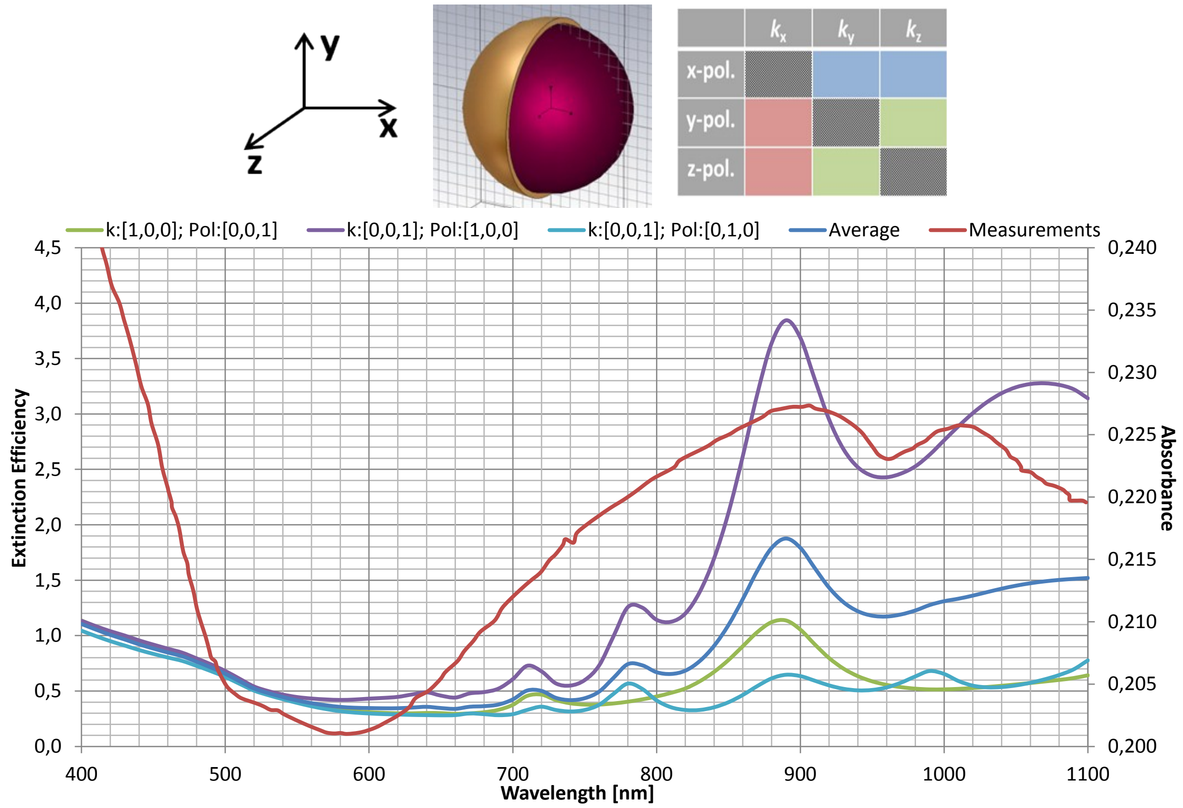

Figure S3. UV/VIS measurements and theoretical calculations using finite element method of Au semishells after deprotection.

Additional TEM/EDS data

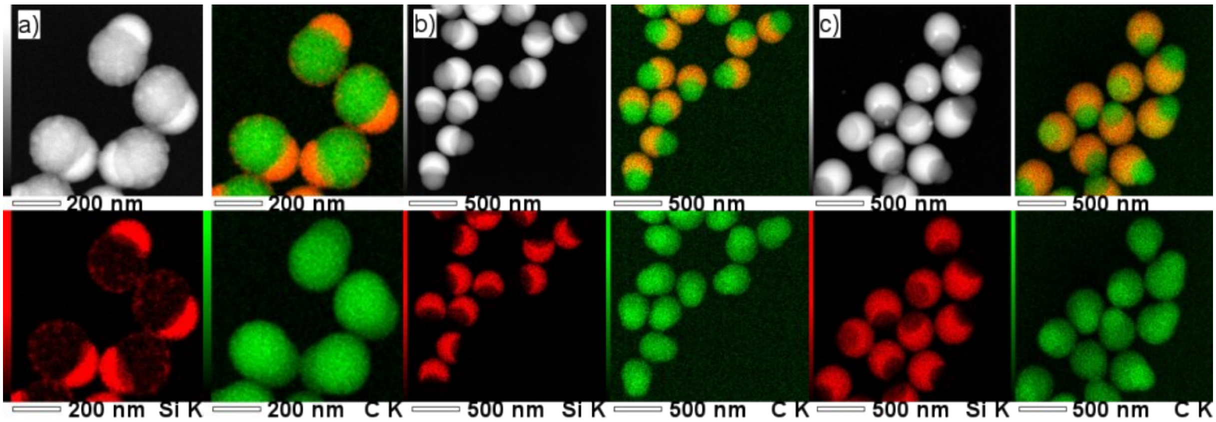

Figure S4. TEM-EDS images of polystyrene particels (d=281 nm) with polyphenylsiloxane caps of various sizes synthesized with a) 13 µL, b) 50 µL and c) 120 µL Ph-TMS.

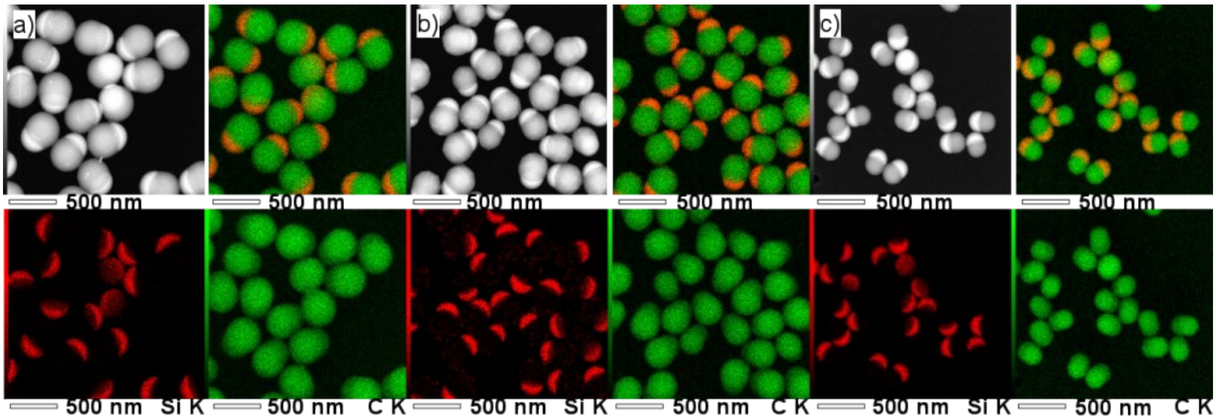

Figure S6. TEM-EDS images of polystyrene particels (d=386 nm (a), 338 nm (b), 218 nm (c)) with polyphenylsiloxane caps synthesized with 13 µL Ph-TMS.

TGA measurements

Table S2. Composition of polystyrene-polyphenylsiloxane composite particles analyzed by TGA

particle diameter [nm]	radius polyphenylsiloxane cap [nm]	polystyrene [wt. %]	polyphenylsiloxane [wt. %]	ratio starting material (PS:Ph-TMS)
282	121	64	36	73:27
282	174	42	58	41:59
282	185	30	70	30:70
282	221	22	78	22:78
386	152	84	16	80:20
338	136	76	24	72:28
218	109	53	47	40:60

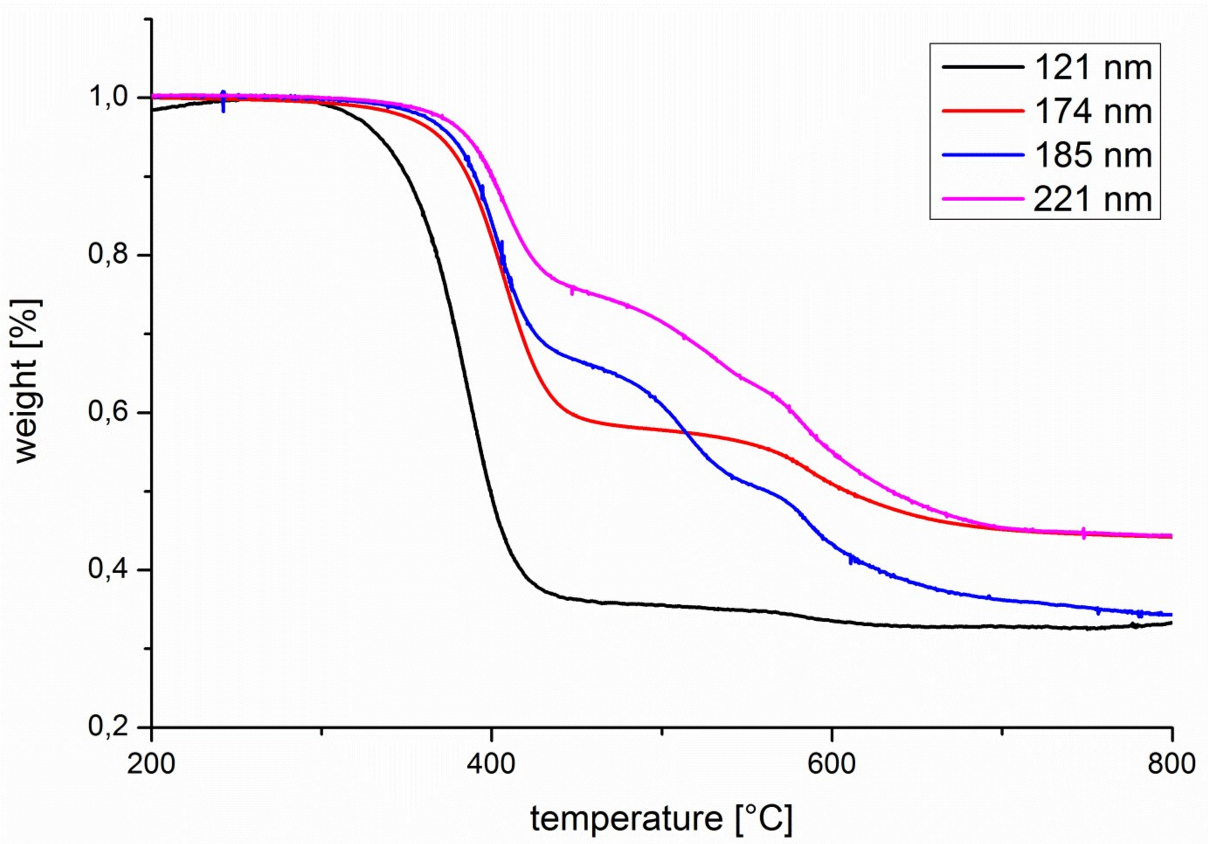

Figure S5. TGA measurements of polystyrene-polyphenylsiloxane composite particles with core diameter of 281 nm and different cap sizes.

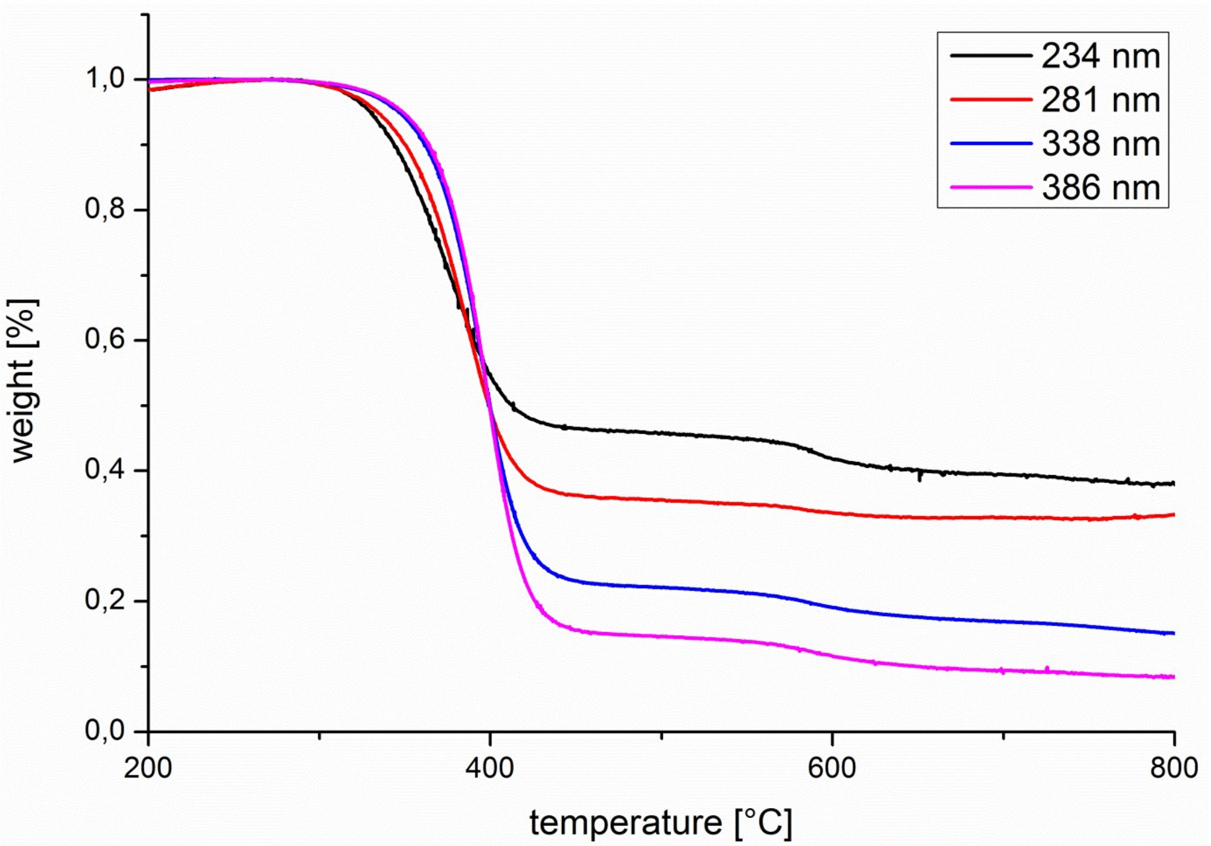

Figure S7. TGA measurements of polystyrene-polyphenylsiloxane composite particles with different core diameters nm and cap sizes around 130 nm (radius).