

Synthesis and characterization of hybrid particles obtained in a one-pot process through simultaneous sol-gel reaction of (3-mercaptopropyl)trimethoxysilane and emulsion polymerization of styrene

Citation for published version (APA):

Segers, M., Vermeer, I., Moeller, M., Verheijen, M., & Buskens, P. (2017). Synthesis and characterization of hybrid particles obtained in a one-pot process through simultaneous sol-gel reaction of (3-mercaptopropyl)trimethoxysilane and emulsion polymerization of styrene. *Colloids and Interfaces*, 1(1), [7]. <https://doi.org/10.3390/colloids1010007>

Document license:
CC BY

DOI:
[10.3390/colloids1010007](https://doi.org/10.3390/colloids1010007)

Document status and date:
Published: 01/12/2017

Document Version:
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Article

Synthesis and Characterization of Hybrid Particles Obtained in a One-Pot Process through Simultaneous Sol-Gel Reaction of (3-Mercaptopropyl)trimethoxysilane and Emulsion Polymerization of Styrene

Margot Segers^{1,2,3}, Isabel Vermeer⁴, Martin Möller^{1,2}, Marcel Verheijen^{5,6}
and Pascal Buskens^{1,2,3,4,*}

¹ DWI—Leibniz Institute for Interactive Materials e.V., Forckenbeckstrasse 50, 52056 Aachen, Germany; margot.segers@tno.nl (M.S.); moeller@dwi.rwth-aachen.de (M.M.)

² Institute for Technical and Macromolecular Chemistry, RWTH Aachen University, Worringerweg 2, 52074 Aachen, Germany

³ TNO/Brightlands Materials Center, Urmonderbaan 22, Postbus 18, 6167 RD Geleen, The Netherlands

⁴ Faculty Beta Sciences and Technology, Research Group Nanostructured Materials, Zuyd University of Applied Sciences, Nieuw Eyckholt 300, Postbus 550, 6400 AN Heerlen, The Netherlands; isabelvermeer@hotmail.com

⁵ Philips Innovation Labs, High Tech Campus 11, 5656 AE Eindhoven, The Netherlands; m.a.verheijen@philips.com

⁶ Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

* Correspondence: pascal.buskens@tno.nl; Tel.: +31-88-866-2990

Received: 27 October 2017; Accepted: 14 November 2017; Published: 16 November 2017

Abstract: Hybrid particles consisting of an organic polymer and silica or polyorganosiloxanes are interesting building blocks for nanocomposites. The synthesis of such particles typically requires multiple reaction steps involving the formation of polymer colloids and the subsequent deposition of silicon-containing material either inside or on the surface of these colloids, or vice versa. In 2014, we reported a facile method for the one-pot synthesis of sub-micron sized hybrid particles based on simultaneous sol-gel conversion of organotrimethoxysilanes and emulsion polymerization of a vinylic monomer, illustrated by the synthesis of polystyrene-polyphenylsiloxane particles from the monomers styrene and phenyltrimethoxysilane (Segers et al (2014)). In this process, the required surface active species was formed in situ through hydrolytic conversion of phenyltrimethoxysilane to phenylsilanol oligomers. Introduction of thiol groups in such hybrid particles should yield particles suited for functionalization with small metal nanoparticles, e.g., Au. Here, we present the synthesis of thiol-containing hybrid particles consisting of poly(3-mercaptopropyl)siloxane and polystyrene using the one-pot synthesis method based on simultaneous conversion of (3-mercaptopropyl)trimethoxysilane and styrene. We prepared particles from different volume ratios of (3-mercaptopropyl)trimethoxysilane and styrene, ranging from 1:99 to 80:20. The resulting spherical hybrid particles displayed different sizes, compositions, and architectures (including core-shell), which were studied in detail using scanning electron microscopy, thermogravimetric analysis, and scanning transmission electron microscopy combined with energy dispersive x-ray spectroscopy. The composition of these particles, and consequently the number of thiol groups available for further functionalization such as metal anchoring, was tunable.

Keywords: polystyrene; silica; surfmer; multidomain; core-shell; phase separation; thiol

1. Introduction

Hybrid nanoparticles, or particles derived thereof, are interesting materials for use in a broad range of applications [1–3] including coatings [4–6]. In particular, hybrid particles of which the properties can be tailored for a specific application through precise control over size, composition, and architecture are highly desired [7,8]. Such particles, however, are typically prepared in a multi-step synthesis involving the formation of polymer colloids followed by the deposition of inorganic material inside or on the surface of these colloids [1,9,10], or vice versa [11–14]. Therefore, such particles are costly and/or challenging to prepare at the pilot or industrial scale, which limits their application. In 2014, our group reported a method for the one-pot synthesis of sub-micron sized hybrid particles in aqueous ammonia, based on simultaneous sol-gel conversion of organotrimethoxysilanes and emulsion polymerization of vinylic monomers (styrene or methyl methacrylate) [15]. Using the combination of phenyltrimethoxysilane (Ph-TMS) and styrene as prototypical example, we demonstrated that well-defined spherical hybrid particles consisting of polyphenylsiloxane and polystyrene could be produced [15]. The mechanism of formation of these particles involved the formation of an oil-in-water (o/w) emulsion comprising a mixture of Ph-TMS and styrene as the oil phase, which was stabilized by surface active phenylsilanol oligomers formed in situ through the hydrolytic conversion of Ph-TMS. Ergo, Ph-TMS serves as monomer and precursor for the surface active species in this synthesis route (surfmmer) [15]. The formation of these surface active species has been confirmed in multiple studies, as well as exploited for the synthesis of hollow and porous polyphenylsiloxane spheres [16,17], and polystyrene-polyphenylsiloxane Janus particles [18,19].

In addition to use in composites and coatings, hybrid spheres may also be particles suited for further functionalization, e.g., surface decoration with small metal nanoparticles, or even nanoshells [20,21], e.g., of Au. Based on their localized surface plasmon resonance, such composite particles are of interest for a wide range of applications in which plasmonic absorption and/or scattering play a key role. Examples of such applications are plasmon-mediated chemical conversions [22,23], surface enhanced Raman scattering [24,25], and photothermal tumor treatment [26,27].

Since thiol moieties are attractive groups for further functionalization, e.g., for anchoring of noble metal nanoparticles, the aim of this study was to prepare hybrid particles comprising a tunable number of thiol groups using the previously developed one-pot conversion method. For this purpose, we selected the combination of styrene and the thiol-containing sol-gel reagent (3-mercaptopropyl)trimethoxysilane (MPTMS, Figure 1).

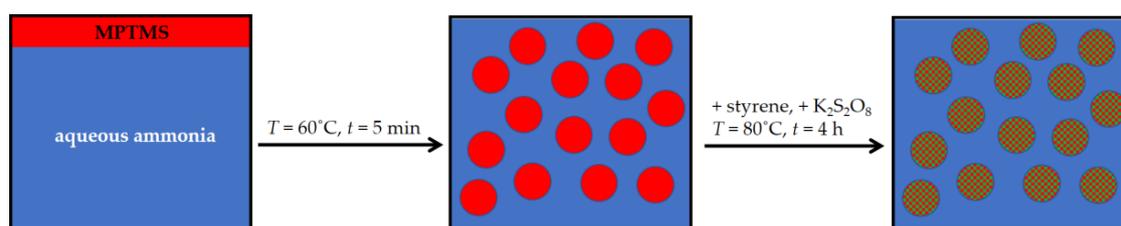


Figure 1. Schematic representation of the synthesis of hybrid particles consisting of poly(3-mercaptopropyl)siloxane and polystyrene.

We present the synthesis of spherical hybrid particles consisting of poly(3-mercaptopropyl)siloxane and polystyrene, and demonstrate the effect of varying the ratio of styrene to MPTMS on the size, composition, and architecture of the resulting hybrid spheres.

2. Materials and Methods

2.1. Materials

MPTMS (95%), styrene ($\geq 99\%$), potassium peroxodisulfate (99%), and aqueous ammonia (30–33%) were purchased from Sigma-Aldrich (Zwijndrecht, The Netherlands). Prior to use, styrene was purified through removal of the inhibitor via filtration over a short aluminum oxide column. Styrene and potassium peroxodisulfate were degassed and stored under nitrogen at 4 °C. MPTMS and aqueous ammonia were used without purification.

2.2. Synthesis of Hybrid Particles

The synthesis was performed under a nitrogen atmosphere. Degassed Milli-Q water (340 mL) was heated to 60 °C in a glass reactor equipped with an overhead stirrer. Subsequently, aqueous ammonia (30 mL, 30–33%) and MPTMS (3–x mL) were added. After 5 min stirring at 350 rpm, the reaction mixture became turbid white, indicating that an emulsion was formed. Then, styrene (x mL) and a solution of potassium peroxodisulfate (0.150 g) in water (3.0 mL) were added. The resulting mixture was heated to 80 °C for 4 h. Subsequently, the mixture was cooled to 0 in an ice bath, and the particles were purified through centrifugation and washing with Milli-Q water. The purified particles were dispersed in Milli-Q water.

2.3. Characterization and Measurement Methods

2.3.1. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was performed using a Discovery TGA (TA Instruments, New Castle, PA, USA). Samples were loaded in platinum pans and ramped at 10 °C·min⁻¹ to 700 °C or 900 °C under dry air with a flow rate of 20 mL·min⁻¹.

2.3.2. Scanning Electron Microscopy

Scanning electron microscopy (SEM) measurements were carried out using a FEI quanta 600 microscope. Samples were prepared by drying a dispersion droplet on a cleaned microscope slide and were subsequently sputtered with a gold coating. The accelerating voltage used was 15 kV.

2.3.3. Transmission Electron Microscopy

Transmission electron microscopy (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. Energy dispersive X-ray spectroscopy (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 the 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.

3. Results and Discussion

To successfully perform the emulsion polymerization of styrene in the presence of MPTMS and obtain corresponding hybrid particles consisting of poly(3-mercaptopropyl)siloxane and polystyrene, it is of vital importance that styrene and MPTMS are miscible in all mixing ratios, and that MPTMS forms a surface active species through hydrolytic conversion. Through macroscopic mixing experiments, we confirmed that styrene and MPTMS are miscible in all mixing ratios. To validate the formation of the surface active species from MPTMS, we added MPTMS to aqueous ammonia at pH 11 (volume ratio 1:100) at a temperature of 60 °C. After 5 min, we observed the formation of a turbid white emulsion of MPTMS in aqueous ammonia, which confirmed the formation of the surface active species through hydrolytic conversion of a small amount of MPTMS. This is in agreement with

previous results obtained for Ph-TMS and other organotrimethoxysilanes [15–19]. After confirming that both reagents were fully miscible and MPTMS formed a surface active species through hydrolytic conversion, we performed the particle synthesis at a volume fraction of 8.04×10^{-3} (=0.084 vol %) monomers (sum of MPTMS and styrene) in aqueous ammonia. After the formation of the emulsion of MPTMS in aqueous ammonia at 60 °C, we added styrene and potassium peroxydisulfate to the reaction mixture. After 4 h reaction time at 80 °C, the particles were purified through centrifugation and washing with water, and redispersed in water. We performed experiments at four different volume ratios of MPTMS:styrene, viz. 1:99, 20:80, 50:50, and 80:20, and analyzed the resulting particles using SEM (Figure 2).

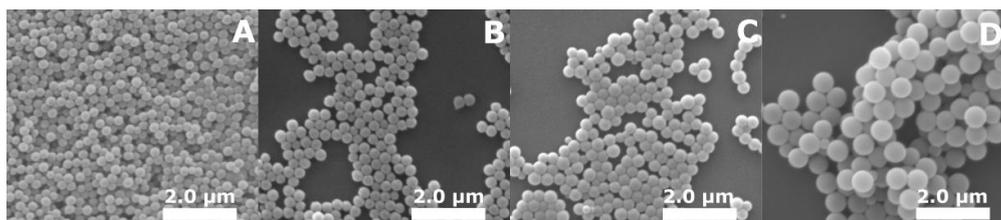


Figure 2. SEM images of hybrid particles obtained at a volume ratio of MPTMS:styrene of (A) 1:99, (B) 20:80, (C) 50:50, and (D) 80:20.

The SEM images clearly display that the size of the particles produced from MPTMS:styrene mixtures at volume ratios of 1:99 (Figure 2A), 20:80 (Figure 2B), and 50:50 (Figure 2C) are similar. All reactions were carried out in triplicate, and the average particle size was determined from the SEM images through analysis of at least 100 particles (Supplementary Materials Figures S1–S4). The average particle diameters were determined as 288 nm (1:99), 312 nm (20:80), and 305 nm (50:50). The particles produced from the 80:20 mixture were substantially larger with a diameter of 556 nm (Figure 2D). All batches displayed a reasonably narrow size distribution with a ratio of standard deviation to particle diameter between 0.052 and 0.14. As a reference material, we synthesized particles without styrene using only MPTMS as a monomer. The resulting poly(3-mercaptopropyl)siloxane spheres display an average diameter of 557 nm (Supplementary Materials S5). Although the hybrid spheres formed in this study are slightly smaller, a similar trend in particle size was observed for hybrid particles derived from the previously reported Ph-TMS:styrene system [15]. Similar to miniemulsion polymerization, we expect that the particle size could be reduced using e.g., sonication, and smaller hybrid spheres should be achievable. Up to a ratio of Ph-TMS:styrene of 40:60, the particle size was approximately 350 nm. At a ratio of 50:50 and upwards, a particle size of approximately 600 nm was reported.

The composition of the particles was analyzed using TGA. As displayed, the particles decompose in two steps (Figure 3): polystyrene decomposes at about 300 °C, and poly(3-mercaptopropyl)siloxane at 400 °C.

From the TGA analysis, we obtained the following weight percentages of silica: 19.7% (20:80), 32.7% (50:50), and 39.0% (80:20) (Table 1). The particles obtained at a ratio of 1:99 could not be analyzed using TGA due to the limited accuracy of the technique. In previous work, we demonstrated through Raman spectroscopic analyses that the thiol group of MPTMS does not react under the reaction conditions applied for the synthesis of the hybrid spheres [15]. Based on that, we conclude that they are available for further chemical reactions applied for the functionalization of the hybrid spheres.

Table 1. Experimentally obtained and theoretical silica content at different mixing ratios.

Ratio MPTMS:Styrene	Theoretical wt % Silica	Experimental wt % Silica
20:80	7.49	19.7
50:50	20.3	32.7
80:20	35.5	39.0

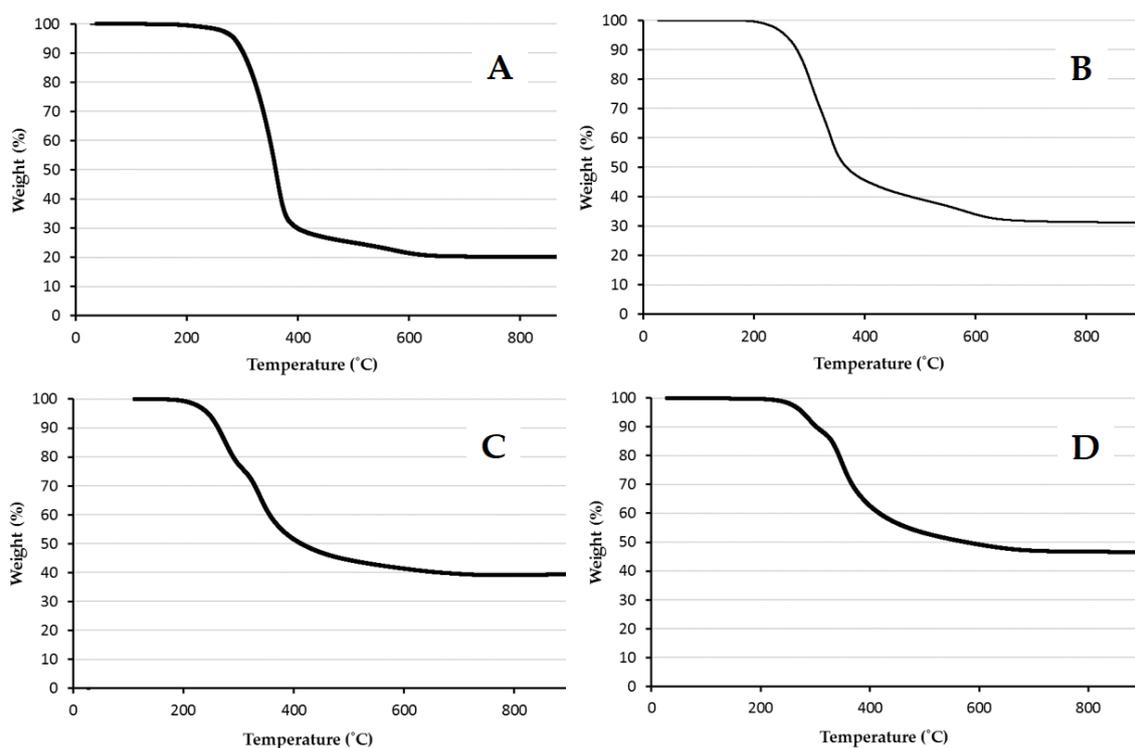


Figure 3. Thermogravimetric analysis (TGA) of particles obtained from a mixture MPTMS:styrene of (A) 20:80, (B) 50:50, (C) 80:20, and (D) 100:0.

At low to medium ratios of MPTMS: styrene (20:80 and 50:50, Figure 3A,B), the amount of silica present in the sample is higher than the theoretical value. The reason for this could be that the polymerization of styrene is hampered, and unreacted styrene monomer is lost in the purification process. At a ratio of 80:20 (Figure 3C), the amount of silica in the sample is close to the theoretical value. Particles obtained from MPTMS only have a theoretical and experimental silica content of 47.2% and 46.3%, respectively (Figure 3D). This behavior deviates from the previously reported Ph-TMS:styrene mixtures, in which for all investigated monomer ratios the experimentally obtained silica percentage was very similar to its theoretical value [15].

To demonstrate that the particles are really hybrid, and to study the architecture of the particles, we performed STEM-EDS analyses (Figure 4 and Supplementary Materials Figures S6 and S7).

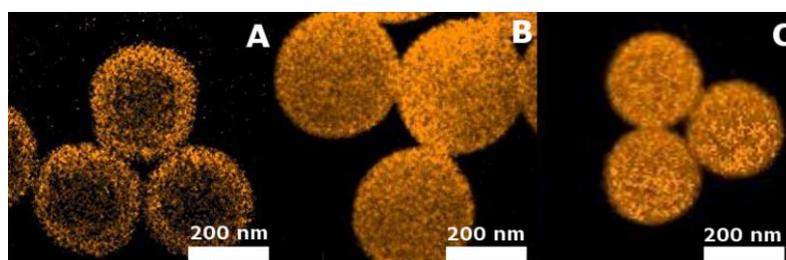


Figure 4. Scanning transmission electron microscopy–energy dispersive X-ray spectroscopy (STEM-EDS) mappings displaying the distribution of silicon in hybrid particles obtained at a ratio of MPTMS:styrene of (A) 20:80, (B) 50:50, and (C) 80:20.

These STEM-EDS analyses clearly confirm that the particles obtained from the 20:80, 50:50, and 80:20 mixtures consist of polystyrene and poly(3-mercaptopropyl)siloxane. There are neither pure polystyrene nor pure poly(3-mercaptopropyl)siloxane particles present in the samples. Although the

monomers are miscible, the particle architectures seem to be the result of the phase separation of the polymers during the polymerization processes. At a ratio of 20:80, the resulting particles display a core-shell architecture with a core of polystyrene and a shell of poly(3-mercaptopropyl)siloxane. Although both polymers seem rather homogeneously distributed for the MPTMS:styrene ratios 50:50 and 80:20, the images show signs of the formation of small domains which seem more or less randomly distributed throughout the spherical particle. When compared to the previously reported polystyrene-polyphenylsiloxane spheres, we observe that in both cases particles with a polystyrene core and polyorganosiloxane shell are formed at low volume ratios. Large differences occur at a 50:50 ratio. In the case of MPTMS:styrene, both polymers seem rather homogeneously distributed. For Ph-TMS:styrene, phase separation results in inhomogeneous polymer particles with rather large domain structures. At high ratios (80:20 or higher), the resulting spheres show rather homogeneous distributions of both polymers for the MPTMS and Ph-TMS cases.

4. Conclusions

In conclusion, we successfully prepared hybrid particles consisting of polystyrene and poly(3-mercaptopropyl)siloxane in a one-pot process. The process involves the formation of an o/w emulsion of polystyrene and MPTMS in aqueous ammonia, which is stabilized by in situ formed surface active (3-mercaptopropyl)silanolate oligomers. After the formation of the emulsion, styrene is converted to polystyrene through radical polymerization, and at the same time MPTMS reacts to poly(3-mercaptopropyl)siloxane through hydrolysis and polycondensation in a sol-gel reaction. The resulting hybrid spheres have a diameter between 288 nm and 556 nm, with a reasonably narrow particle size distribution. The composition of the spheres is tunable through the variation of the monomer ratio of MPTMS:styrene, albeit that at low and medium ratios (20:80 and 50:50) the silica content of the hybrid particles is higher than expected. This indicates a loss of styrene. At high ratios (80:20), the silica content is very similar to its theoretical value. The hybrid nature of the particles is confirmed through STEM-EDS analyses. At a MPTMS:styrene ratio of 20:80, the resulting particles have a core-shell architecture with a polystyrene core and a poly(3-mercaptopropyl)siloxane shell. At medium and high ratios, the distribution of both polymers seems rather random. Ergo, we managed to prepare hybrid spheres with a tunable amount of thiol groups, as well as tunable size and architecture. Therefore, these spheres should be of interest for further functionalization via their reactive thiol groups, e.g., for decoration with noble metal nanoparticles. This will be the subject of future investigations.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2504-5377/1/1/7/s1>, Figures S1–S5: SEM images of hybrid particles obtained at a volume ratio of MPTMS:styrene of 1:99, 20:80, 50:50, 80:20, and 100:0, each in three independent synthesis experiments; Figures S6 and S7: STEM-EDS mappings displaying the distribution of carbon and oxygen in hybrid particles obtained at a ratio of MPTMS:styrene of (A) 20:80, (B) 50:50 and (C) 80:20.

Acknowledgments: P.B. and M.S. acknowledge TNO for funding. Solliance and the Dutch province of Noord-Brabant are acknowledged for funding the TEM facility.

Author Contributions: M.S., P.B. and M.M. conceived and designed the experiments; M.S. and I.V. performed the experiments; I.V. and M.S. analyzed the data; M.V. performed and assisted in the interpretation of the electron microscopy analyses; P.B. and M.S. wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Van Bommel, K.J.C.; Friggeri, A.; Shinkai, S. Organic templates for the generation of inorganic materials. *Angew. Chem. Int. Ed.* **2003**, *42*, 980–999. [[CrossRef](#)] [[PubMed](#)]
2. Klapper, M.; Clark, C.J., Jr.; Müllen, K. Application-directed syntheses of surface-functionalized organic and inorganic nanoparticles. *Polym. Int.* **2008**, *57*, 181–202. [[CrossRef](#)]
3. Kidsaneepoiboon, P.; Wanichwecharungruang, S.P.; Chooppawa, T.; Deephum, R.; Panyathanmaporn, T. Organic-inorganic hybrid polysilsesquioxane nanospheres as UVA/UVB absorber and fragrance carrier. *J. Mater. Chem.* **2011**, *21*, 7922–7930. [[CrossRef](#)]

4. Schottner, G. Hybrid sol-gel-derived polymers: Applications of multifunctional materials. *Chem. Mater.* **2001**, *13*, 3422–3435. [[CrossRef](#)]
5. Fielding, L.A.; Mykhaylyk, O.O.; Schmid, A.; Pontoni, D.; Armes, S.P.; Fowler, P.W. Visible Mie scattering from hollow silica particles with particulate shells. *Chem. Mater.* **2014**, *26*, 1270–1277. [[CrossRef](#)]
6. Buskens, P.; Burghoorn, M.; Mourad, M.C.D.; Vroon, Z. Antireflective coatings for glass and transparent polymers. *Langmuir* **2016**, *32*, 6781–6793. [[CrossRef](#)] [[PubMed](#)]
7. Truong, N.P.; Quinn, J.F.; Anastasaki, A.; Rolland, M.; Vu, M.N.; Haddleton, D.M.; Whittaker, M.R.; Davis, T.P. Surfactant-free RAFT emulsion polymerization using a novel biocompatible thermoresponsive polymer. *Polym. Chem.* **2017**, *8*, 1353–1363. [[CrossRef](#)]
8. Truong, N.P.; Quinn, J.F.; Anastasaki, A.; Haddleton, D.M.; Whittaker, M.R.; Davis, T.P. Facile access to thermoresponsive filomicelles with tuneable cores. *Chem. Commun.* **2016**, *52*, 4497–4500. [[CrossRef](#)] [[PubMed](#)]
9. Caruso, F.; Caruso, R.A.; Möhwald, H. Nanoengineering of inorganic and hybrid hollow spheres by colloidal templating. *Science* **1998**, *282*, 1111–1114. [[CrossRef](#)] [[PubMed](#)]
10. Tissot, I.; Reymond, I.P.; Lefebvre, F.; Bourgeat-Lami, E. SiOH-functionalized polystyrene latexes. A step toward the synthesis of hollow silica nanoparticles. *Chem. Mater.* **2002**, *14*, 1325–1331. [[CrossRef](#)]
11. Pyun, J.; Matyjaszewski, K. Synthesis of nanocomposite organic/inorganic hybrid materials using controlled/“living” radical polymerization. *Chem. Mater.* **2001**, *13*, 3436–3448. [[CrossRef](#)]
12. Pietrasik, J.; Hui, C.M.; Chaladaj, W.; Dong, H.; Choi, J.; Jurczak, J.; Bockstaller, M.R.; Matyjaszewski, K. Silica-polymethacrylate hybrid particles synthesized using high-pressure atom transfer radical polymerization. *Macromol. Rapid Commun.* **2011**, *32*, 295–301. [[CrossRef](#)] [[PubMed](#)]
13. Moraes, J.; Ohno, K.; Maschmeyer, T.; Perrier, S. Synthesis of silica–polymer core–shell nanoparticles by reversible addition–fragmentation chain transfer polymerization. *Chem. Commun.* **2013**, *49*, 9077–9088. [[CrossRef](#)] [[PubMed](#)]
14. Hartono, S.B.; Phuoc, N.T.; Yu, M.; Jia, Z.; Monteiro, M.J.; Qiao, S.; Yu, C. Functionalized large pore mesoporous silica nanoparticles for gene delivery featuring controlled release and co-delivery. *J. Mater. Chem. B* **2014**, *2*, 718–726. [[CrossRef](#)]
15. Segers, M.; van Zandvoort, R.; Sliepen, M.; Arfsten, N.; Verheijen, M.; Keul, H.; Buskens, P.; Möller, M. Facile and versatile platform approach for the synthesis of submicrometer-sized hybrid particles with programmable size, composition, and architecture comprising organosiloxanes and/or organosilsequioxanes. *Chem. Mater.* **2014**, *26*, 5718–5724. [[CrossRef](#)]
16. Segers, M.; Arfsten, N.; Buskens, P.; Möller, M. A facile route for the synthesis of sub-micron sized hollow and multiporous organosilica spheres. *RSC Adv.* **2014**, *4*, 20673–20676. [[CrossRef](#)]
17. Segers, M.; Sliepen, M.; Kraft, D.J.; Möller, M.; Buskens, P. Synthesis of sub-micron sized hollow, and nanoporous phenylsiloxane spheres through use of phenyltrimethoxysilane as surfmer: Insights into the surfactant and factors influencing the particle architecture. *Colloids Surf. Physicochem. Eng. Asp.* **2016**, *497*, 378–384. [[CrossRef](#)]
18. Mann, D.; Voogt, S.; van Zandvoort, R.; Keul, H.; Möller, M.; Verheijen, M.; Nascimento-Duplat, D.; Xu, M.; Urbach, H.P.; Adam, A.J.L.; et al. Protecting patches in colloidal synthesis of Au semishells. *Chem. Commun.* **2017**, *53*, 3898–3901. [[CrossRef](#)] [[PubMed](#)]
19. Mann, D.; Voogt, S.; Keul, H.; Möller, M.; Verheijen, M.; Buskens, P. Synthesis of polystyrene-polyphenylsiloxane Janus particles through colloidal assembly with unexpected high selectivity: Mechanistic insights and their application in the design of polystyrene particles with multiple polyphenylsiloxane patches. *Polymers* **2017**, *9*, 475. [[CrossRef](#)]
20. Mann, D.; Chattopadhyay, S.; Pargen, S.; Verheijen, M.; Keul, H.; Buskens, P.; Möller, M. Glucose-functionalized polystyrene particles designed for selective deposition of silver on the surface. *RSC Adv.* **2014**, *4*, 62878–62881. [[CrossRef](#)]
21. Mann, D.; Nascimento-Duplat, D.; Keul, H.; Möller, M.; Verheijen, M.; Xu, M.; Urbach, H.P.; Adam, A.J.L.; Buskens, P. The influence of particle size distribution and shell imperfections on the plasmon resonance of Au and Ag nanoshells. *Plasmonics* **2017**, *12*, 929–945. [[CrossRef](#)] [[PubMed](#)]
22. Meng, X.; Liu, L.; Ouyang, S.; Xu, H.; Wang, D.; Zhao, N.; Ye, J. Nanometals for solar-to-chemical energy conversion: From semiconductor-based photocatalysis to plasmon-mediated photocatalysis and photo-thermocatalysis. *Adv. Mater.* **2016**, *28*, 6781–6803. [[CrossRef](#)] [[PubMed](#)]

23. Baffou, G.; Quidant, R. Nanoplasmonics for chemistry. *Chem. Soc. Rev.* **2014**, *43*, 3898–3907. [[CrossRef](#)] [[PubMed](#)]
24. Chen, X.-J.; Cabello, G.; Wu, D.-Y.; Tian, Z.-Q. Surface-enhanced Raman spectroscopy toward application in plasmonic photocatalysis on metal nanostructures. *J. Photochem. Photobiol. C Photochem. Rev.* **2014**, *21*, 54–80. [[CrossRef](#)]
25. Cialla, D.; März, A.; Böhme, R.; Theil, F.; Weber, K.; Schmitt, M.; Popp, J. Surface-enhanced Raman spectroscopy (SERS): Progress and trends. *Anal. Bioanal. Chem.* **2012**, *403*, 27–54. [[CrossRef](#)] [[PubMed](#)]
26. Boisselier, E.; Astruc, D. Gold nanoparticles in nanomedicine: Preparations, imaging, diagnostics, therapies and toxicity. *Chem. Soc. Rev.* **2009**, *38*, 1759–1782. [[CrossRef](#)] [[PubMed](#)]
27. Hirsch, L.R.; Stafford, R.J.; Bankson, J.A.; Sershen, S.R.; Rivera, B.; Price, R.E.; Hazle, J.D.; Halas, N.J.; West, J.L. Nanoshell-mediated near-infrared thermal therapy of tumors under magnetic resonance guidance. *Proc. Natl. Acad. Sci. USA* **2003**, *100*, 13549–13554. [[CrossRef](#)] [[PubMed](#)]



© 2017 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).