

Glucose-functionalized polystyrene particles designed for selective deposition of silver on the surface

Citation for published version (APA):

Mann, D., Chattopadhyay, S., Pargen, S., Verheijen, M. A., Keul, H., Buskens, P., & Möller, M. (2014). Glucose-functionalized polystyrene particles designed for selective deposition of silver on the surface. *RSC Advances*, 4(108), 62878-62881. <https://doi.org/10.1039/C4RA10941D>

DOI:

[10.1039/C4RA10941D](https://doi.org/10.1039/C4RA10941D)

Document status and date:

Published: 01/01/2014

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.



CrossMark
click for updates

Cite this: *RSC Adv.*, 2014, 4, 62878

Received 22nd September 2014
Accepted 7th November 2014

DOI: 10.1039/c4ra10941d

www.rsc.org/advances

Glucose-functionalized polystyrene particles designed for selective deposition of silver on the surface†

Daniel Mann,^a Subrata Chattopadhyay,^a Sascha Pargen,^a Marcel Verheijen,^{bc} Helmut Keul,^a Pascal Buskens^{*ad} and Martin Möller^{*a}

We present the synthesis of glucose-functionalized polystyrene particles through emulsion polymerisation using glucose acrylate as reactive surfactant. Additionally, we present the selective deposition of silver on the surface of these particles yielding well-defined polystyrene–silver composites.

Metal nanoparticles are of interest for a broad variety of applications ranging from sensing^{1–4} to sunlight harvesting^{5–7} and catalysis.^{8–11} For a variety of applications, it is of interest to immobilize such particles on dielectric carrier materials such as silica or polymer particles, *e.g.* for use as building blocks for the preparation of conducting films,¹² or for catalytic conversions.^{13,14} Additionally, the localized plasmon resonance, which is the property of interest for many applications, can be influenced by bringing metallic particles together on the surface of a carrier particle at a distance smaller than the extinction diameter.^{15–19} To date, most routes for the preparation of sub-micron sized dielectric particles decorated with small silver particles or islands, however, suffer from one or more of following drawbacks: (1) the formation of small silver nanoparticles, which are not connected to the dielectric carrier particles, as undesired side product,^{19–22} (2) the presence of non-metallised dielectric

particles after the silver deposition step^{21–23} and (3) poor colloidal stability of the resulting composite particles.

Here, we present the design and synthesis of sub-micron sized polystyrene particles tailored for the deposition of silver, and a procedure for the deposition of silver resulting in well-defined polystyrene–Ag composites, avoiding the above mentioned drawbacks. We applied following design principles for the synthesis of these composites: (a) we used a reactive surfactant (surfmmer)^{24–27} to immobilize the surface active species on the latex surface, (b) we immobilized the reducing agent on the latex surface, (c) we used a secondary mild reducing agent in low concentration which is not able to stabilize silver nanoparticles, and (d) we added a stabilizing agent to ensure the colloidal stability of the particles after metallization. Design principles (a), (b) and (c) should ensure selective deposition of Ag on the surface of the polystyrene particles, avoiding the formation of small silver nanoparticles as side product. Furthermore, they should ensure metallisation of all polystyrene particles, avoiding the presence of non-metallized polystyrene particles after the silver deposition step. Design principle (d) should stabilize the core–shell particles in dispersion without interfering with the silver deposition process.

To combine both the functionality of reducing agent and surfmer in one molecule, we selected glucose acrylate as functional monomer. As recently demonstrated by our group, enzymatic transacylation reactions are efficient for the synthesis of functional (meth)acrylate monomers, *e.g.* dodecylmethacrylate.^{28,29} In analogy to this procedure, we reacted methyl acrylate with α -D-glucose in *tert*-butanol using Novozyme 435 as catalyst (Fig. 1). After 24 h reaction time at 55 °C, we obtained glucose acrylate with a yield of 35% (see ESI†).

To prepare glucose-functionalized polystyrene particles, we reacted styrene, divinyl benzene and glucose acrylate in an emulsion polymerization process using potassium peroxydisulfate as initiator. Instantaneous emulsion formation confirmed the expected surface activity of glucose acrylate. After 14 h reaction time at 80 °C, well defined polystyrene particles

^aDWI – Leibniz Institute for Interactive Materials, Forckenbeckstrasse 50, 52056 Aachen, Germany. E-mail: buskens@dwi.rwth-aachen.de; moeller@dwi.rwth-aachen.de

^bPhilips Innovation Services, High Tech Campus 11, 5656 AE, Eindhoven, The Netherlands

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

^dThe Netherlands Organisation for Applied Scientific Research (TNO), De Rondom 1, 5612 AP, Eindhoven, The Netherlands. E-mail: pascal.buskens@tno.nl

† Electronic supplementary information (ESI) available: Materials, measurements, experimental, kinetic study of glucose acrylate using different solvents and glucose/methacrylate ratios, full characterisation of glucose-acrylate with yield calculation through ¹H NMR, zeta potentials of polystyrene particles with zeta potential study of Sn²⁺-sensitized particles, TGA measurements of polystyrene–Ag composites. See DOI: 10.1039/c4ra10941d

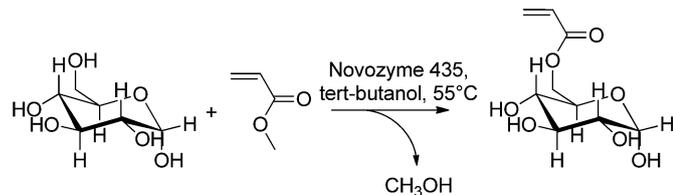


Fig. 1 Reaction of methyl acrylate with α -D-glucose to glucose acrylate.

were formed which were purified through filtration, centrifugation and subsequent dispersion in demineralized water at neutral pH (see ESI†). Based on the high yield (between 89% and 96%, see ESI†), the absence of monomers in the supernatant and the fact that the propagation rate for the polymerization of glucose acrylate in water is very low due to its low concentration (1.07 – $8.54 \mu\text{mol mL}^{-1}$),³⁰ we conclude that glucose acrylate does not form homopolymer under these conditions, but is quantitatively incorporated into the particles as co-polymer with styrene. Using 1, 2, 4 and 8 wt% glucose acrylate based on styrene, we obtained well-defined particles with an average outer diameter D_{av} of 391 nm, 339 nm, 267 nm and 218 nm, respectively (Fig. 2). In all four cases, the size distribution was ≤ 0.05 .³¹

To maximize the amount of reducing agent on the particle surface with the aim of achieving a highly selective Ag deposition, the latex particles prepared with 8 wt% glucose acrylate ($D_{\text{av}} = 218 \text{ nm}$) were treated with a tin(II) chloride solution to obtain Sn^{2+} -modified particles.

Since Sn^{2+} ions serve as nucleation points for the reduction of Ag^+ , it is important that they coordinate to the surface of the latex particles. As starting point, we chose to apply 67 mg SnCl_2 per mg latex. Using this amount of SnCl_2 , we observed an increase in the zeta potential of the particles from -34 mV to 63 mV , which proves that Sn^{2+} ions coordinate to the particle surface. We used this mixture as starting point for the silver deposition and added it to a solution of silver nitrate and aqueous ammonia in water (see ESI†). After 1 h reaction time at $75 \text{ }^\circ\text{C}$, hexamethylene tetramine was added and the resulting reaction mixture was stirred for an additional hour at $75 \text{ }^\circ\text{C}$. Subsequently, the dispersion was cooled to room temperature and poly(vinylpyrrolidone) (PVP, molecular weight 40 000) was added. The resulting particles were purified through centrifugation and subsequent dispersion in demineralized water at neutral pH. After completion of the Ag deposition step, we analysed the resulting particles through SEM analysis and observed that, although Ag was deposited on all latex particles, we formed a large number of small silver particles as undesired side product (Fig. 3a).

We hypothesized that only part of the Sn^{2+} ions coordinated to the latex surface and that the residual ions free in solution caused the formation of small Ag nanoparticles as side product. To validate this hypothesis, we removed excessive Sn^{2+} ions after pre-treatment of the latex with SnCl_2 through centrifugation and demonstrated that three centrifugation cycles led to a starting point (zeta potential = 47 mV , see ESI†), from which all

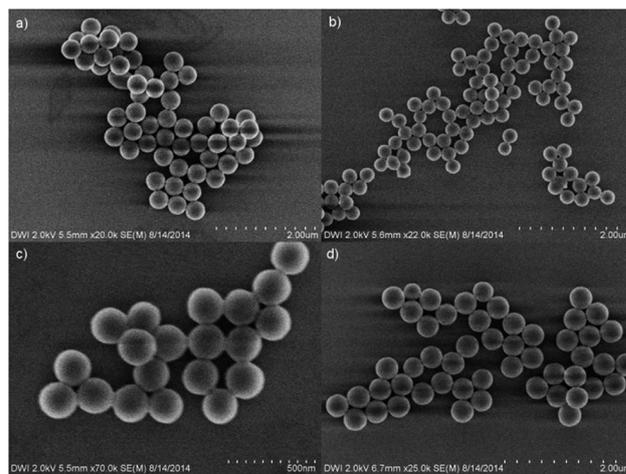


Fig. 2 SEM images of glucose-functionalized polystyrene particles prepared with (a) 1 wt%, (b) 2 wt%, (c) 4 wt% and (d) 8 wt% glucose acrylate based on styrene.

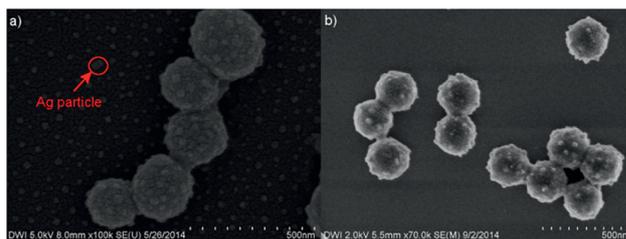


Fig. 3 SEM images of polystyrene–Ag composites (a) with small Ag nanoparticles as side product and (b) without small silver nanoparticles as side product. The latex prepared with 8 wt% glucose acrylate ($D_{\text{av}} = 218 \text{ nm}$) was used.

silver was selectively deposited on the latex particle surface without formation of small silver nanoparticles as side product (Fig. 3b). No non-metallized polystyrene particles were observed after Ag deposition. The resulting particle dispersion was stable for at least two weeks. No agglomeration occurred. Due to gravity, the composite particles sediment. After sedimentation, they can easily be dispersed through shaking of the sample.

To demonstrate that the procedure also works for polystyrene particles of different size and with a different loading of glucose acrylate, we deposited silver on the latex particles prepared with 1 wt% glucose acrylate and a D_{av} of 391 nm. Using the optimized procedure for silver deposition (see ESI†), as described above, we obtained polystyrene–Ag composites similar to those obtained with the particles prepared using 8 wt% glucose acrylate (Fig. 4).

As demonstrated in Fig. 4, silver was selectively deposited on the latex particle surface and no non-metallized polystyrene particles were observed. To obtain more detailed information on the distribution of Ag on the particle surface, we performed HR-TEM and STEM-EDX analyses of the composite particles presented in Fig. 3 and 4 (Fig. 5). These images confirm the selective deposition of Ag on the surface of the particles, and

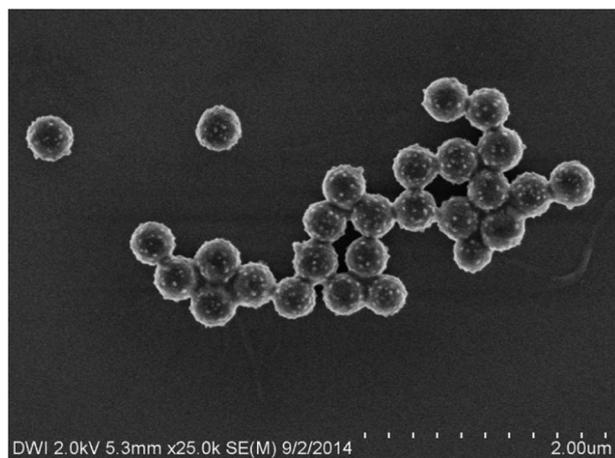


Fig. 4 SEM image of polystyrene–Ag composites. The latex prepared with 1 wt% glucose acrylate ($D_{av} = 391$ nm) was used.

demonstrate the presence of multiple Ag particles of a size between 10 and 20 nm on the surface of the polystyrene particles (Fig. 5a–c). On average, the distance between the silver particles is larger than the extinction diameter. This is confirmed by the absence of a red-shift of the localized plasmon resonance (see ESI†). As expected for polystyrene–Ag composites dispersed in water with a distance between the silver particles larger than their extinction diameter, the plasmon resonance wavelength λ_{max} is in the wavelength regime between 400 and 500 nm.³² In addition, however, these images demonstrate the presence of Sn-containing particles on the composite particles, both in between and on top of the silver islands

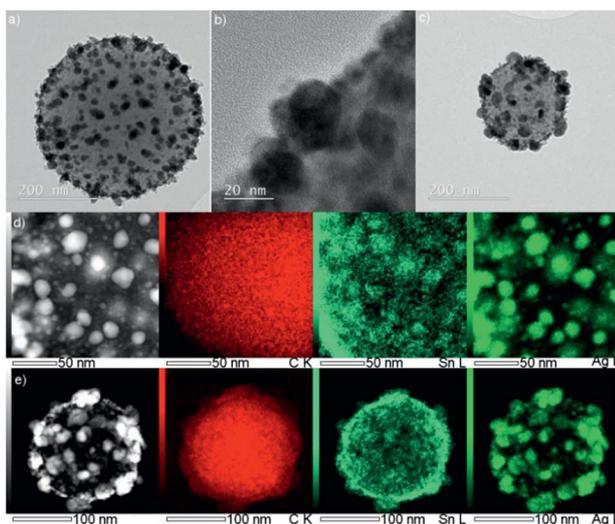


Fig. 5 (a) TEM image of polystyrene–Ag composite particles (1 wt% glucose acrylate), (b) HR-TEM image of polystyrene–Ag composite particles (1 wt% glucose acrylate), (c) TEM image of polystyrene–Ag composite particles (1 wt% glucose acrylate), (d) STEM-EDX image of polystyrene–Ag composite particles (1 wt% glucose acrylate), (e) STEM-EDX image of polystyrene–Ag composite particles (8 wt% glucose acrylate).

(Fig. 5d and e). HR-TEM imaging of the Sn-containing particles displayed that these particles are crystalline. FFT analysis of the HR-TEM images yielded interplanar distances of 3.6 ± 0.1 nm and 2.8 ± 0.1 nm. Accurate compositional determination of the particles was beyond the resolution of the technique. Combining the FFT and EDX data, however, we identified orthorhombic SnCl_2 as most likely candidate based on the matching interplanar distances. The presence of Sn-containing nanocrystals is an important observation, since it may influence the deposition of additional Ag on these particles, or impact the application of these composite particles.

Conclusions

In conclusion, we have successfully developed a synthesis route for the preparation of polystyrene–Ag composite particles. We demonstrated that through use of glucose acrylate, which serves as reactive surfactant during the latex synthesis and as reducing agent for Ag^+ , we obtained polystyrene–Ag composite particles with a polystyrene particle size between 218 and 391 nm and narrow size distribution (≤ 0.05). All polymer particles were covered with Ag islands of a size between 10 and 20 nm, without the formation of small Ag nanoparticles as side product. Through HR-TEM and STEM-EDX analyses, we demonstrated the presence of Sn-containing particles on the composite particles, both in between and on top of the Ag islands. These find their origin in tin(II) chloride, which is used during the silver deposition step, and may influence the deposition of additional Ag on the composite particles, or impact the application of these composite particles. Currently, further studies are ongoing in our laboratory on the deposition of other metals on glucose-functionalized polystyrene particles, and on the development of new latex systems designed for deposition of specific metals or metal oxides.

Acknowledgements

Special thanks to Cornelia Broicher for her assistance in the lab work. Solliance, a solar energy R&D initiative of ECN, TNO, Holst, TU/e, imec and Forschungszentrum Jülich, and the Dutch province of Noord-Brabant are acknowledged for funding the TEM facility at Philips Innovation Services.

Notes and references

- 1 J. N. Anker, W. P. Hall, O. Lyandres, N. C. Shah, J. Zhao and R. P. van Duyne, *Nat. Mater.*, 2008, 7, 442.
- 2 N. Nath and A. Chilkothi, *Anal. Chem.*, 2002, 74, 504.
- 3 K.-S. Lee and M. A. El-Sayed, *J. Phys. Chem. B*, 2006, 110, 19220.
- 4 K. Saha, S. S. Agasti, C. Kim, X. Li and V. M. Rotello, *Chem. Rev.*, 2012, 112, 2739.
- 5 J. R. Cole and N. J. Halas, *Appl. Phys. Lett.*, 2006, 89, 153120.
- 6 P. Wang, B. Huang, Y. Dai and M.-H. Whangbo, *Phys. Chem. Chem. Phys.*, 2012, 14, 9813.
- 7 I. Carmeli, I. Lieberman, L. Kraversky, Z. Fan, A. O. Govorov, G. Markovich and S. Richter, *Nano Lett.*, 2010, 10, 2069.

- 8 P. Herves, M. Perez-Lorenzo, L. M. Liz-Marzan, J. Dzubiella, Y. Lu and M. Ballauff, *Chem. Soc. Rev.*, 2012, **41**, 5577.
- 9 N. Yan, C. Xiao and Y. Kou, *Coord. Chem. Rev.*, 2010, **254**, 1179.
- 10 S. Mukherjee, F. Libisch, N. Large, O. Neumann, L. V. Brown, J. Cheng, J. B. Lassiter, E. A. Carter, P. Nordlander and N. J. Halas, *Nano Lett.*, 2013, **13**, 240.
- 11 P. Christopher, H. Xin and S. Linic, *Nat. Chem.*, 2011, **3**, 467.
- 12 A. Tuerke, W.-J. Fischer, H.-J. Adler and A. Pich, *Polymer*, 2010, **51**, 4706.
- 13 H. Yougen, Z. Tao, Z. Pengli and S. Rong, *Colloid Polym. Sci.*, 2012, **290**, 401.
- 14 Y. Mei, G. Sharma, Y. Lu and M. Ballauff, *Langmuir*, 2005, **21**, 12229.
- 15 J. H. Lee, M. A. Mahmoud, V. Sitterle, J. Sitterle and J. C. Meredith, *J. Am. Chem. Soc.*, 2009, **131**, 5048.
- 16 P. Barnickel and A. Wokaun, *Mol. Phys.*, 1989, **67**, 1355–1372.
- 17 J. Gong, X. Zu, W. Mu and Y. Deng, *Colloid Polym. Sci.*, 2013, **291**, 239.
- 18 C. Song, D. Wang, Y. Lin, Z. Hu, G. Gu and X. Fu, *Nanotechnology*, 2004, **15**, 962.
- 19 S. J. Oldenburg, R. D. Averitt, S. L. Westcott and N. J. Halas, *Chem. Phys. Lett.*, 1998, **288**, 243.
- 20 V. G. Pol, H. Grisar and A. Gedanken, *Langmuir*, 2005, **21**, 3635.
- 21 T. Tuval and A. Gedanken, *Nanotechnology*, 2007, **18**, 255601.
- 22 M. A. Khan, C. Perruchot, S. P. Armes and D. P. Randall, *J. Mater. Chem.*, 2001, **11**, 2363.
- 23 A. B. R. Mayer, W. Grebner and R. Wannemacher, *J. Phys. Chem. B*, 2000, **104**, 7278.
- 24 K. L. Thompson, S. P. Armes, D. W. York and J. A. Burdis, *Macromolecules*, 2010, **43**, 2169.
- 25 K. L. Thompson and S. P. Armes, *Chem. Commun.*, 2010, **46**, 5274.
- 26 K. L. Thompson, S. P. Armes, J. R. Howse, S. Ebbens, I. Ahmad, J. H. Zaidi, D. W. Yoek and J. A. Burdis, *Macromolecules*, 2010, **43**, 10466.
- 27 S. Pargen, C. Willems, H. Keul, A. Pich and M. Möller, *Macromolecules*, 2012, **45**, 1230.
- 28 D. Popescu, H. Keul and M. Moeller, *Macromol. Chem. Phys.*, 2009, **210**, 123.
- 29 D. Popescu, H. Keul and M. Moeller, *Macromol. Rapid Commun.*, 2011, **32**, 559.
- 30 I. Capek, *Chem. Pap.*, 1991, **45**, 481.
- 31 From the images obtained through SEM analysis, the average diameter was calculated from 50 measured particles. The size distribution is defined as standard deviation divided by average diameter.
- 32 K.-T. Yong, Y. Sahoo, M. T. Swihart and P. N. Prasad, *Colloids Surf., A*, 2006, **290**, 89.