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Protecting patches in colloidal synthesis of Au semishells†

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Protecting groups are commonly applied in multi-step molecular syntheses to protect one or multiple functional groups from reacting. After the reaction, they are removed from the molecule. In full analogy to this concept, we report the practical and scalable colloidal synthesis of Au semishells using polyphenylsiloxane protecting patches to prevent part of the surface of polystyrene nanoparticles from being covered with Au. After Au deposition, the patches are removed yielding Au semishells. We anticipate that this strategy can be extended to the synthesis of other types of non-centrosymmetric nanoparticles.

For a long time, protecting groups have been used in multistep organic syntheses of complex molecules.^{1–8} They are applied to protect one or multiple functional groups present in one molecule from reacting in a specific step, and are removed from the molecule afterwards. Many different functional groups can be protected in such a way, e.g. amino-,^{1,2,4–7} carbonyl-,^{1,7} carboxyl-,^{1,7} hydroxyl-^{1,3,7,8} and thiol-groups.^{1,7} The enormous potential of using molecular protecting groups is depicted by the wide range of different fields of organic chemistry in which they are applied, such as synthesis of polysaccharides,³ peptides and proteins^{4–6} and in the synthesis of complex polymers.^{7,8}

For the synthesis of non-centrosymmetric nanoparticles starting from perfectly symmetric nanospheres, the concept of using some kind of protection to selectively functionalize only part of the surface of the nanosphere has been reported.^{9,10} Prototypical examples of such syntheses are the preparation of Janus particles *via* plasma treatment of polymer-entrapped silica particles by Ling *et al.*,¹¹ the synthesis of colloidal particles with chemically distinct surface patches to create colloids with valence and specific directional bonding by Wang *et al.*,¹² the utilization of a molten wax in water emulsion with subsequent partial embedding of silica particles in the solidified wax to synthesize different kinds of Janus particles by Hong *et al.*,¹³ and various strategies to synthesize metal semishells *via* entrapment of silica particles in macroscopic polymer films^{14,15} or micron sized particles.¹⁶ These examples all demonstrate that the concept of “protecting groups” is highly promising for colloidal synthesis. However, these examples lack full analogy to the concept of protecting groups in molecular syntheses because of (a) the inability to remove the protecting material after synthesis,¹² (b) the immobilization of particles on macroscopic surfaces or embedding in macroscopic films^{11,14,15} for protection, or (c) the protection of multiple particles through partial embedding in the same micron sized protecting particle.^{13,16} This also limits the practical, large scale application of these routes. To genuinely transfer the concept of protecting groups, with all its benefits, from molecular to colloidal synthesis, a protecting patch has to be developed that can be applied to individual particles in dispersion, prevents part of the particle surface from reacting and is easily removable after synthesis. Here, we demonstrate the potential of protecting patches – in full analogy to protecting groups in molecular synthesis – in the 3-step colloidal synthesis of Au semishells.

Reduced-symmetry 3D metal nanostructures such as Au semishells are of interest because of their localized plasmon resonance. They consist of a spherical dielectric core particle decorated with a hemispherical shell of Au. Based on their reduced symmetry when compared to Au nanoshells,¹⁷ such semishells display an electric axial and magnetic transverse plasmon mode at two distinct resonance frequencies. Both modes display distinct and

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very different light scattering characteristics, which can be used to direct light in complex optical structures and photonic devices.^{18–24}

To date, such Au semishells are prepared in processes which are not practical for large scale synthesis. In most cases, Au semishells are prepared through anisotropic etching of Au nanoshells immobilized on a planar substrate. The Au nanoshells are produced through chemical plating of dielectric nanospheres.^{23,25} Alternatively, dielectric core particles are deposited on a macroscopic flat substrate, coated with Au through thermal evaporation, sputtering or plating, and subsequently removed from the substrate surface in a complicated lift-off process.^{25,26} Only few approaches have been reported for full colloidal synthesis of metal semishells in dispersion. These methods, however, all lack control over the degree of metal coverage and typically result in poorly defined metallic partial shells.^{27–29} The most promising approach reported to date involves embedding of nanoparticles in polymer films, and therefore protecting one side of the particles. Here the particles can be chemically¹⁴ or physically^{15,16} entrapped into a polymer film^{14,15} or micron sized particles¹⁶ after a “sinking-in” immobilization. For this synthetic strategy, the release of the semishells is optimized but the reaction scale is still a limiting factor for practical application.

For a practical, large scale synthesis a low cost synthetic strategy to realize metallic semishells in aqueous dispersion is needed. The introduction of a colloidal protecting patch, that protects part of the surface of the dielectric particle during metallization and can easily be removed afterwards, would enable this. To function as a protecting patch, a material is needed that is able to cover a nanoparticle only partly, therefore forming a patch that protects part of the nanoparticle surface. For polystyrene spheres, this is accomplished by Mo *et al.*³⁰ who used tetraethoxy silane in a Stöber synthesis to form silica nanobowls on polystyrene particles. Another important requirement for the protecting patch is that it can be removed under mild conditions. Unfortunately, this is not the case for silica, which is typically removed using hydrofluoric acid. But changing the silica precursor to phenyltrimethoxy silane (Ph-TMS), we anticipate that polyphenylsiloxane patches can be synthesized, that can be dissolved in toluene.^{31–33} Furthermore, for the synthesis of metallic semishells, substrate particles are needed that can be covered with a homogeneous and well defined metal shell. As recently demonstrated by our group, this can be accomplished by using glucose functionalized polystyrene particles, which we were able to cover with Au and Ag shells in a two-step seed-growth reaction.^{17,34}

Combining all the above mentioned systems, we developed a synthesis strategy, in which we use Ph-TMS in a sol-gel reaction to form polyphenylsiloxane patches on glucose functionalized polystyrene particles. We assume that the uncapped part of the polystyrene particles is subsequently coated with a thin Au shell in a seeding-plating sequence. In the last step, the polyphenylsiloxane patches should be removed through addition of toluene yielding Au semishells (Fig. 1a).

For the synthesis of polyphenylsiloxane patches, a dispersion of glucose functionalized polystyrene particles with a radius of 141 nm, which are cross-linked with 5 wt% divinylbenzene,³⁴ was stirred with Ph-TMS in an ice bath for one hour.

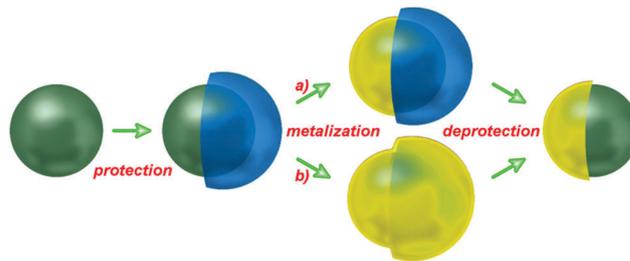


Fig. 1 (a) Synthesis strategy and (b) actual reaction pathway to realize Au semishells using a polyphenylsiloxane protecting patch (green = cross-linked polystyrene, blue = polyphenylsiloxane, yellow = gold).

Subsequently, the reaction mixture was placed in an oil bath at 80 °C and an ethanolic ammonia solution was added to facilitate the hydrolysis and polycondensation of Ph-TMS. After a reaction time of two hours and a subsequent work up by centrifugation, polystyrene particles decorated with a polyphenylsiloxane patch with a radius of 185 nm were isolated, as demonstrated by scanning electron microscopy (SEM, Fig. 2a and b) and scanning transmission electron microscopy (STEM, Fig. 2c). STEM-energy-dispersive X-ray spectroscopy (EDS) analysis shows that the patch comprises Si, and that the polyphenylsiloxane patch is attached to the surface of the polystyrene particle (Fig. 2d). In the SEM analysis, we observed that small spherical polyphenylsiloxane particles were formed as side product (Fig. 2b). The side product was removed by centrifugation.

For the synthesis of Au semishells, the polystyrene particles protected with polyphenylsiloxane patches were covered with a Au shell in a two-step seeding-plating sequence according to the procedure recently published by our group.¹⁷ SEM analyses show that the entire composite particle is covered with small Au particles after seeding, and with a thin Au shell after plating

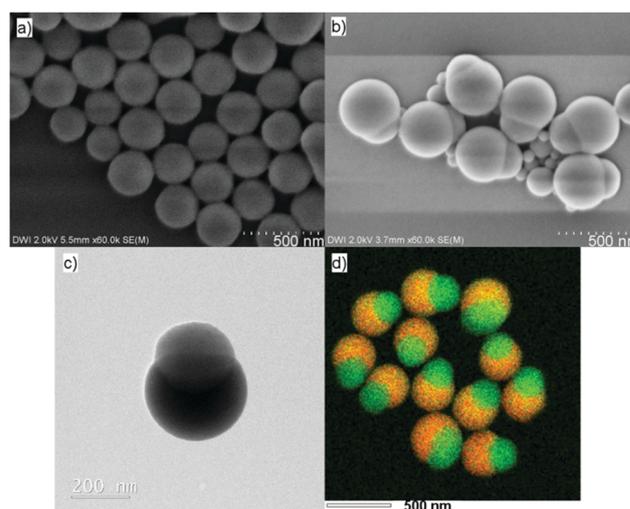


Fig. 2 (a) SEM image of cross-linked polystyrene particles (radius = 141 nm); (b) SEM image, (c) STEM image and (d) EDS mapping of polystyrene particles protected with a polyphenylsiloxane patch (radius = 185 nm; green = carbon, red = silicon).

(Fig. 3a and b), which is confirmed by STEM-EDS measurements (Fig. S1, ESI[†]). This observation, schematically represented in Fig. 1b, deviates from our synthesis strategy, in which we aimed at selectively covering only the polystyrene part of the composite particle with Au (Fig. 1a). However, by synthesizing a porous Au shell that allows toluene to penetrate into the polyphenylsiloxane patch, the patch and the corresponding part of the Au shell were removed through washing with toluene (Fig. 3c and d). Ergo, after washing the dispersion of Au plated composite particles with toluene, the polyphenylsiloxane patch is dissolved and the Au shell is removed from this side of the particle creating Au semishells (Fig. 3c and d). We observed that by removing the Au shell from the polyphenylsiloxane part, small Au particles were formed as side product (Fig. 3c). These side products were removed by centrifugation. The removal of the protecting group was confirmed by SEM-EDS analysis (Fig. 3d).

The optical properties of the Au plated polystyrene-polyphenylsiloxane composite particles (nanoshells), and the Au semishells formed after deprotection, were analysed using UV-Vis extinction spectrophotometry. Comparing both spectra, we observed a change from one distinct extinction maximum at 1072 nm for the nanoshells to two extinction maxima at 906 nm and 1008 nm for the semishells (Fig. 4). To explain these experimental results, we performed optical simulations using finite element method for the composition and dimensions of the Au nanoshells and semishells depicted in Fig. 3b and c, respectively. We neglected the imperfections (roughness/porosity) of the Au (semi-)shell because of its minor impact on the plasmon resonance, and simulated smooth (semi-)shells.¹⁷ Our simulations demonstrate that the asymmetric nature of the semishells leads to an angle-dependent plasmon resonance, which is in agreement with previously reported systems.^{18,19} Consequently, the optical response depends on the polarization of light and its propagation direction (Fig. S2 and S3, ESI[†]). For the nanoshells and semishells, we calculated extinction spectra averaged over

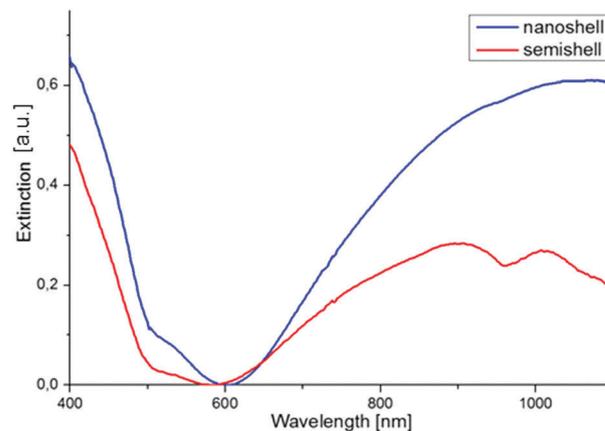


Fig. 4 UV-Vis extinction spectra of polystyrene-polyphenylsiloxane composite particles plated with a thin Au shell (nanoshell, blue), and Au semishells after deprotection (red).

all polarizations and angles. The simulated spectra are in good agreement with our experimental data (Fig. S2 and S3, ESI[†]). Furthermore, our results are in good agreement with data on the optical properties of previously reported similar particles.^{18,19}

After proving the concept that Au semishells can be prepared in dispersion using polyphenylsiloxane patches as protecting groups, a short study concerning the scope of this newly developed synthetic procedure was performed. Firstly, we changed the amount of Ph-TMS used for forming the polyphenylsiloxane protective patch, whilst keeping the amount of polystyrene particles in the dispersion constant. This led to polystyrene particles (diameter = 282 nm) with a patch of 121 nm radius for the lowest amount Ph-TMS (16% of the amount used to prepare patches with 185 nm radius), up to particles with patches of 221 nm radius for the highest amount (150%). With increasing patch size, an increased part of the polystyrene particle surface was covered with polyphenylsiloxane, and therefore protected (Fig. 5 and Fig. S4, ESI[†]). By performing thermogravimetric

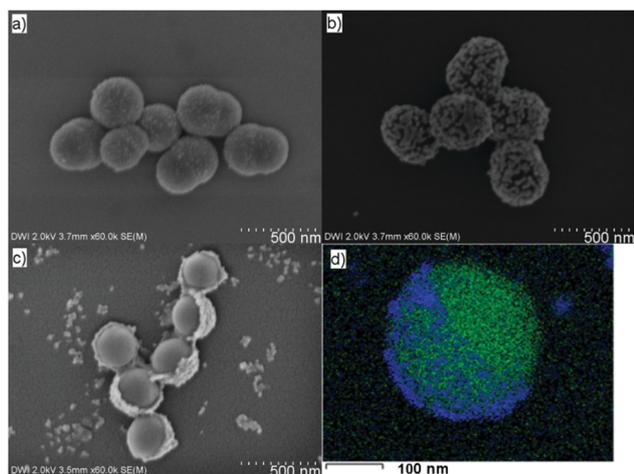


Fig. 3 SEM images of polystyrene-polyphenylsiloxane composite particles covered with (a) small Au particles and (b) a thin Au shell; (c) SEM image and (d) EDS mapping of Au semishells after deprotection (green = carbon, blue = gold).

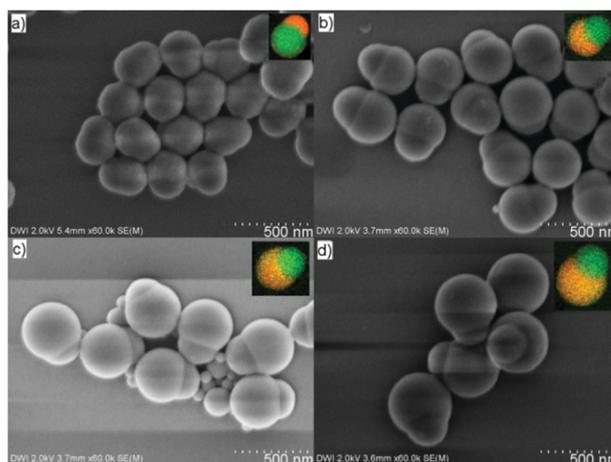


Fig. 5 SEM images of polystyrene-polyphenylsiloxane composite particles with increasing patch size synthesized with (a) 13 μ L, (b) 50 μ L, (c) 80 μ L and (d) 120 μ L Ph-TMS (Inlays show STEM-EDS mappings; green = carbon, red = silicon).

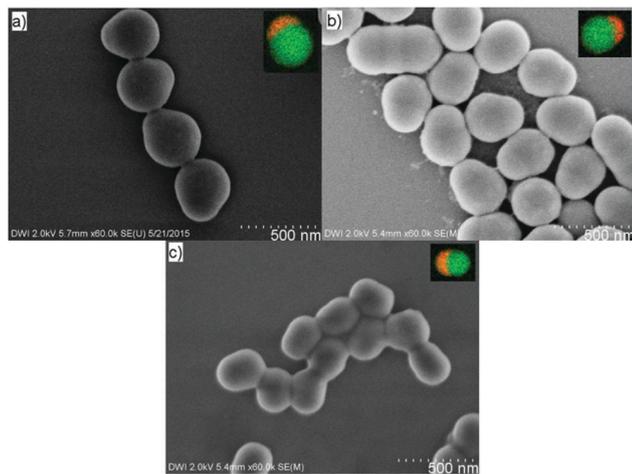


Fig. 6 SEM images of polystyrene-polyphenylsiloxane composite particles with template particles of (a) 386 nm, (b) 338 nm and (c) 218 nm diameter (Inlays show STEM-EDS mappings green = carbon, red = silicon).

analysis (TGA) on these particles, a composition resembling the ratio of starting materials used in the synthesis was found for all four composite particles (Table S2 and Fig. S5, ESI[†]). Ergo, the surface area that will be protected can simply be varied through variation of the ratio of Ph-TMS to polystyrene.

Secondly, polystyrene particles with different particle diameters were used. By using particles with diameter of 386, 338 and 218 nm we demonstrated that the reaction forming a protecting group can be accomplished for a range of differently sized polystyrene particles (Fig. 6 and Fig. S6, ESI[†]). The TGA study showed a composition resembling the ratio of starting materials for all three composite particles (Table S2 and Fig. S7, ESI[†]). Combined with the fact that we are able to coat polystyrene particles of different diameters with well-defined Au shells,¹⁷ it is reasonable to assume that our newly developed procedure can yield Au semishells with varying core diameter and degree of Au coverage.

In conclusion, we developed a practical and scalable 3-step synthesis of Au semishells using polyphenylsiloxane protecting patches to prevent part of the surface of glucose-functionalized polystyrene nanoparticles from being covered with Au. After Au deposition, the patches were easily removed through dissolution in toluene yielding Au semishells. The synthesis strategy is in full analogy to the concept of protecting groups in molecular synthesis, and eliminates the drawbacks of previously reported methods for the synthesis of Au semishells. We optically characterized the resulting Au semishells through UV-Vis extinction spectrophotometry combined with optical simulations using finite element method. Furthermore, we demonstrated that the synthesis strategy is applicable for Au semishells with varying polystyrene core diameters and degree of surface coverage. We anticipate

that this synthesis procedure can be extended for other types of polymer particles and shell materials. A complete analysis of the reaction mechanism that underlies the formation of polyphenylsiloxane patches on polystyrene particles will be presented in a follow up paper.

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