Assembling anisotropic colloidal building blocks

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CHAPTER 5

PATCHY PARTICLES OF VARIOUS SHAPES WITH DISTINCT PATCHES

Abstract

We fabricated complex patchy particles with distinct patches by applying the "colloidal recycling" method to binary mixtures of colloidal spheres. Aggregates constructed from the binary mixtures were reconfigured into patchy shapes by the addition of organic solvent. We combined spheres of different size and rigidity which yielded patchy particles of all permutations and therefore various shapes. The rigidity of the seeds influenced the final shape of the binary patchy particle, since soft spheres strongly deformed during reconfiguration whereas rigid spheres remained spherical. At low size ratio, 1.5, the geometry of the patchy particle was determined by the total number of spheres. At size ratio 4.6, the large spheres arranged in a compact geometry and the small particles positioned at the contact areas between these spheres. Large numbers of small spheres formed a 'jacket' around the cluster, where the patches of the small spheres introduced surface roughness at the center of the patchy particle. This yielded particles with both chemical and physical patchiness, which may be used for depletion induced self-assembly in the future.

5.1 Introduction

Functional materials can be realized by the bottom-up assembly of complex building blocks. Since patchy particles can be anisotropic in both shape and surface chemistry, these particles are in particular promising building blocks. Complex colloids with multiple patches are often formed by assembling a number of identical seed particles, such as colloidal spheres[25,153], Janus particles[137] or colloids with liquid protrusions[16], into larger structures. With our recently developed 'colloidal recycling' method we can fabricate patchy particles by recycling aggregates of uniform spheres.[138] The recycling involves the reconfiguration of aggregates induced by the addition of organic solvent. With this method a wide variety of patchy particles can be obtained by tuning experimental parameters such as colloid material, swelling agent and particle rigidity.[138,154]

By assembling non-identical seed particles into larger structures, colloids with different patch types and shapes can be realized. Although this is a promising approach to create complex particles, only a few examples are known where non-identical seeds are combined to form clusters with higher complexity. Ni *et al*. formed colloidal clusters consisting of two to four different spheres using a capillary-assisted assembly technique.[155] Using a template-based substrate the composition and the shape of these clusters could be controlled. However, since this template-based technique cannot be performed in bulk, low quantities were obtained. Cho *et al*. showed that colloidal clusters could be constructed from binary mixtures of spheres by evaporation of emulsion droplets containing a number of spheres. The spherical confinement and strong capillary forces acting on the spheres during evaporation bind the spheres into colloidal clusters of compact shapes.[134,156] Since all possible permutations could be formed, a wide variety of shapes was yielded. The geometry of these clusters was determined by the size ratio between the two seed types. At size ratio's ≥ 3, the geometry of the cluster was determined by the larger spheres whereas at size ratios ≤ 2 it was determined by both components. In all cases the geometries the same as those obtained for clusters of identical spheres. At a fixed number of spheres N, the dumbbell was formed for N=2, the triangle for N=3, the tetrahedron for N=4 and the triangular dipyramid for N=5. In particular particles with distinct and separated patches are highly promising for the bottom-up construction of materials, since the interaction between the patches can be localized and tuned by the size and location of the patches.[157]

We fabricated particles with distinct patches by employing the 'colloidal recycling' method to binary mixtures of colloidal spheres. The spheres differed in size and rigidity, which led to various shapes and patch compositions. Since soft spheres deformed during the reconfiguration process, but the rigid spheres

remained spherical, asymmetric shapes were obtained when the two were combined. We found at size ratio 1.5 that the geometry of the cluster was determined by the total number of spheres, whereas at size ratio 4.6 solely the larger spheres were involved. Interestingly, at size ratio 4.6, we formed particles that were both chemically and physically patchy.

5.2 Experimental Methods

Materials

Styrene ($\geq$99%, contains 4-tert-butylcatechol as inhibitor), divinylbenzene (DVB, technical grade 55%), azobisisobutyronitril (AIBN, $\geq$98%), hydroquinone (HQ, $\geq$99.5%), sodium dodecyl sulfate (SDS, $\geq$98.5%), vinyl acetate (contains 3-20 ppm hydroquinone as inhibitor), potassium peroxodisulfate (KPS, puriss. p.a. ACS reagent, $\geq$99.0%) and perylene (sublimed grade, $\geq$99.5%) were purchased from Sigma-Aldrich. Styrene was passed through an inhibitor remover column (Sigma-Aldrich) before use. Potassium chloride (>99% p.a.) was obtained from Fluka, Germany. The water used was deionized using a Millipore Filtration System (MilliQ Gradient A10), resulting in a resistivity of 18.2 MΩ·cm.
RITC dyed polystyrene spheres of 1.06 ± 0.06 µm with a crosslink density of 10% v/v were purchased from Magsphere Inc.

Methods

Synthesis of 1.6 μm sized polystyrene spheres Linear carboxylic acid functionalized polystyrene spheres of 1.05 ± 0.02 µm in diameter were synthesized by a surfactant free emulsion polymerization procedure[104]. The colloids were stored in water after filtration through glass wool and washing. To 13.5 mL of a 2.29% wt dispersion of these linear seeds, 0.05 g SDS, 0.034 g HQ and 1.7 mL crosslink solution was added to swell and crosslink the particles. The crosslink solution consisted of styrene with 2% wt AIBN, 2% v/v DVB and 15.78 mg perylene. Perylene was added during swelling to allow imaging by confocal microscopy. The mixtures were rotated for 24h on a tumbler at 20 rpm in the dark. Finally, the swollen colloids were polymerized in a 72°C preheated oil bath for 24h while being rotated at 100 rpm at a 45° angle. The polymerized colloids were washed and stored in water. The spheres had a smooth surface morphology and were 1.59 ± 0.07 μm in diameter with a crosslink density of 1.6% v/v (see Figure 5.1).

Synthesis of 0.2 μm sized polystyrene spheres Smaller polystyrene particles were synthesized according to an emulsion polymerization method developed by Mock *et al.*[110] Here, a solution containing 225 mL water, 0.25 g SDS and 21.15

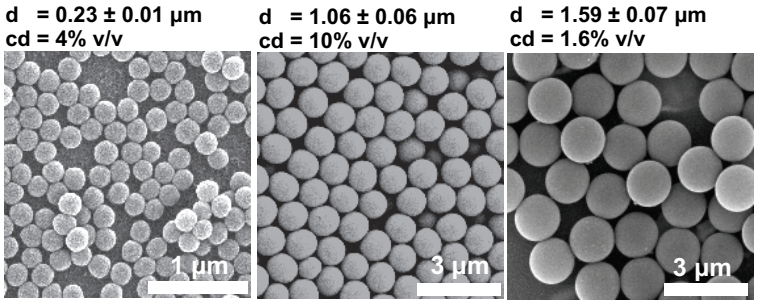

FIGURE 5.1: SEM micrographs of the polystyrene seed particles used in this study. The diameter and crosslink density are listed above the images.

g styrene with 0.97 mL DVB was heated for 1h in a 80°C oil bath under magnetic stirring, before polymerization was initiated by the addition of 0.78 g KPS in 38 mL water. The reaction was continued for 24h yielding 229 ± 8 nm particles with a crosslink density of 4% v/v. To increase the hydrophobicity of the particle surface and therefore the wetting angle of the particles with styrene, the polystyrene particles were coated with vinyl acetate. Here, 100 mL of this dispersion (7.66% wt) was heated in a 80°C oil bath under magnetic stirring for 45 min before a solution of 0.17 g KPS in 25 mL water was added. This was followed by the addition of 183 μL vinyl acetate every 15 min until a total volume of 732 μL (0.68 g) was added, leading to a surface coverage of 3.56 x 10^{-21} g/nm^2.[110] The reaction was stopped after 24h. A SEM micrograph of the colloids is shown in Figure 5.1

Formation of patchy particles Patchy particles were prepared using the 'colloidal-recycling' method.[138] We first formed random aggregates by diffusion limited aggregation of charge-stabilized colloidal spheres. Aggregates of spheres with size ratio 1.5 were formed by adding 100 μL of a 2M potassium chloride solution to a mixture of 60 μL of 1.59 μm (2.9% wt) and 40 μL 1.06 μm polystyrene particles. After an aggregation time, t_a = 6 min, the aggregates were quenched with 20 mL water. For size ratio 4.6, 60 μL of a 2M potassium chloride solution was added to 40 μL of the 1.06 μm sized colloids (1.8% wt) for t_a = 5 min followed by the addition of 40 μL of 229 nm particles (0.3% wt). The total t_a before quenching was 9 min. The aggregates were reconfigured into compact patchy particles by the addition of organic solvent: To 5 mL of the quenched dispersion, 10 μL of aqueous SDS solution (10% wt) and 10 μL of reconfiguration solution, consisting of styrene with 1.5% v/v DVB and 2% wt AIBN, was added. The dispersion was magnetically stirred for 24h to complete reconfiguration of the aggregates. The obtained patchy particles were polymerized for 24h in a preheated oil bath at 80°C. The particles were washed and stored in water.

Imaging and analysis The synthesized polystyrene seed particles and polymerized patchy particles were imaged using a FEI nanoSEM scanning electron microscope (SEM) at 80 kV. The size of the polystyrene seed particles was determined by measuring the circumference of >100 particles in SEM micrographs with ImageJ. The aggregates of the binary mixtures were studied with a Nikon Eclipse Ti microscope with an AIR confocal scan head with a 100x oil immersion objective (NA = 1.4). The 1.06 μm Magsphere particles and the 1.59 μm polystyrene spheres with a crosslink density of 1.59% v/v, were excited with a laser wavelength of 405 or 561 nm, resulting in blue and red fluorescence, respectively.

5.3 Results and Discussion

With the 'colloidal recycling' method randomly shaped aggregates of colloidal spheres are reconfigured into compact shapes by the addition of organic solvent. We have thoroughly investigated the reconfiguration mechanism and the shapes obtained after reconfiguration for aggregates of identical seed particles.[138,154] Well-defined structures were formed for a fixed number of spheres in the cluster, N, for N<6. The geometries obtained include the dumbbell for N=2, triangle for N=3, tetrahedron for N=4 and the triangular dipyramid for N=5. For aggregates of six or more identical spheres the geometry obtained after reconfiguration was determined by the deformability of the seeds.[154] While six soft spheres reconfigured to the polytetrahedron, six rigid spheres assembled into an octahedron. We found that the reconfiguration pathway was largely influenced by confinement of the cluster and geometric contraints.
Our understanding of the reconfiguration mechanism and of the shapes formed by clusters of identical colloids motivated us to explore the colloidal recycling method further using binary mixtures of seeds. The binary mixtures contained spherical colloids of different sizes and with different particle rigidity yielding patchy particles with distinct patches.

5.3.1 Patchy particles of soft and rigid spheres, size ratio 1.5

We applied the colloidal recycling method to mixtures of soft and rigid spheres to obtain particles with distinct patches and shapes. The rigidity of the seed particles was controlled by the crosslink density (cd) of the polystyrene colloids. We previously showed that the final shape of reconfigured clusters depends on the crosslink density of the seed particles.[154] Spheres with low crosslink density (cd$\leq$0.5% v/v) were strongly deformed during reconfiguration by capillary forces, resulting in complete or partial merging of the seeds in the covering droplet. More densely crosslinked seeds reconfigured into patchy particles and the deformation of the spheres decreased with increasing crosslink density.

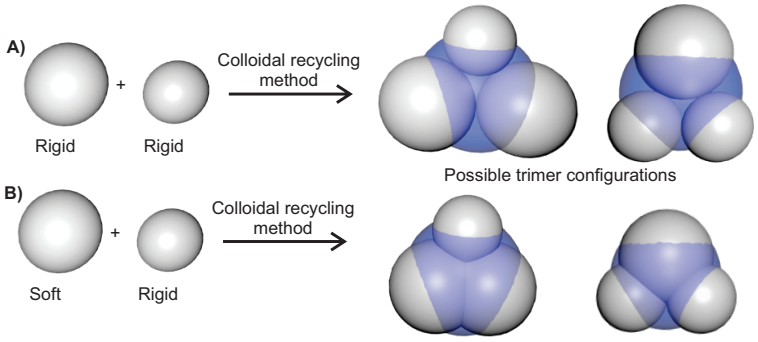

FIGURE 5.2: Illustration of patchy trimers that can be constructed from two seed types with size ratio 1.5. A) Rigid seed particles are not deformed by the capillary forces during reconfiguration, resulting in patchy particle shapes solely determined by the size ratio between the particles. B) By combining soft and rigid seeds the final shape of the patchy particle will be more compact compared to clusters of rigid spheres, since the soft spheres can be deformed by the capillary forces during reconfiguration.

We here employed a binary mixture of polystyrene spheres of 1.06 μm and 1.59 μm in diameter with cd = 10 and 1.6% v/v, respectively. This resulted in a size ratio of 1.5 and a crosslink density ratio of 6.3. If both sphere types would not deform during deformation, the shape of the reconfigured cluster would solely be determined by the size ratio between the particles, see Figure 5.2A. However, if the crosslink density of the larger spheres (cd=1.6% v/v) is insufficient to resist shape deformation induced by the capillary forces, the reconfigured shapes will be more compact (see Figure 5.2B).

Aggregates constructed from both colloid types were formed by exposing the binary mixture of charge-stabilized spheres to a 1M potassium chloride solution for several minutes. The aggregates obtained were of random shape and both components could be distinguished by size with bright field microscopy (see Figure 5.3A). The two seed particle types could also be recognized with confocal microscopy, which was possible since the 1.59 μm and 1.06 μm particles were provided with perylene and rhodamine dye, resulting in blue and red emitting particles, respectively. The confocal microscopy image in Figure 5.3B shows that the two seed types are uniformaly distributed over the aggregates.
After addition of organic solvent, the aggregates reconfigured into compact shapes of different sizes (Figure 5.3C). The reconfigured shapes were examined using high resolution SEM micrographs, where the two seed types could be distinguished by size. For patchy particles constructed from both seed particles different compositions and shapes were observed. The geometries of the

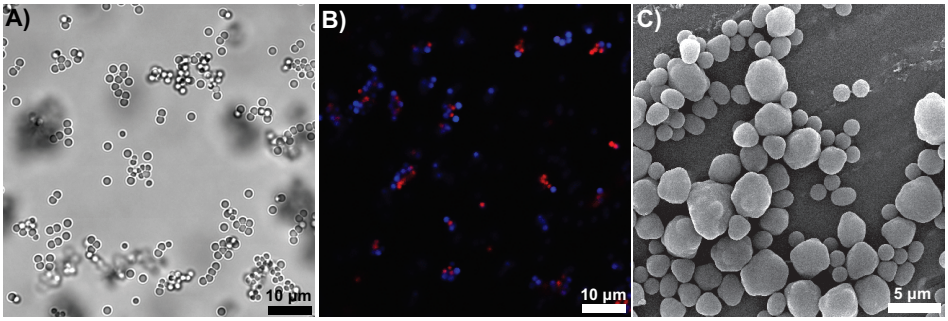

FIGURE 5.3: Applying the colloidal recycling method to a mixture of 1.06 μm polystyrene particles with cd = 10% v/v and 1.59 μm particles with cd = 1.6% v/v (size ratio of 1.5 and a crosslink density ratio of 6.3). A) Bright field microscopy image of randomly shaped aggregates after destabilization of the spheres. B) Confocal microscopy image of the aggregates with the 1.06 μm particles in red and the 1.6 μm seeds in blue. C) SEM micrograph of the reconfigured clusters obtained after reconfiguration and polymerization. Compact patchy shapes are formed of different sizes.

reconfigured clusters were set by both the 1.06 μm and the 1.59 μm spheres and depended on the total number of seeds in the cluster, N. For small patchy particles of N=2 this resulted in assymmetric dumbbells (Figure 5.4A) and aggregates of N=3 reconfigured into triangular shapes formed by two soft and one rigid seed or one soft and two rigid seeds (Figure 5.4B). Aggregates of N=4 yielded the tetrahedron shape (see Figure 5.4C for one permutation). Clusters of five spheres of any permutation reconfigured to triagular dipyramid structures (see Figure 5.4D for one permutation). For clusters of N>5 several three-dimensional shapes where observed where not all original seed particles could be unambiqiously identified from SEM micrographs (Figure 5.4E).

Reconstruction of the spherical seed particles (shown as overlayed on the bottom SEM micrographs in Figure 5.4) shows that the large spheres were partly deformed during reconfiguration while the smaller rigid particles remained spherical (see Figure 5.2). This is in agreement with our previous experiments where we found that the deformability of the seeds by capillary forces decreased with increasing crosslink density. Here, polystyrene spheres with cd = 10% v/v barely deformed.[154]
The geometries for clusters of N=2-5 are similar to those observed for identical spheres. Due to the difference in size and particle rigidity in the binary mixture a larger variety of shapes is observed compared to one-component systems. For colloidal clusters of binary mixtures with size ratio 1.5, formed using an emulsion based droplet evaporation technique, also geometries similar to one-component systems were observed.[156] Since Cho *et al*. used non-deformable spheres less

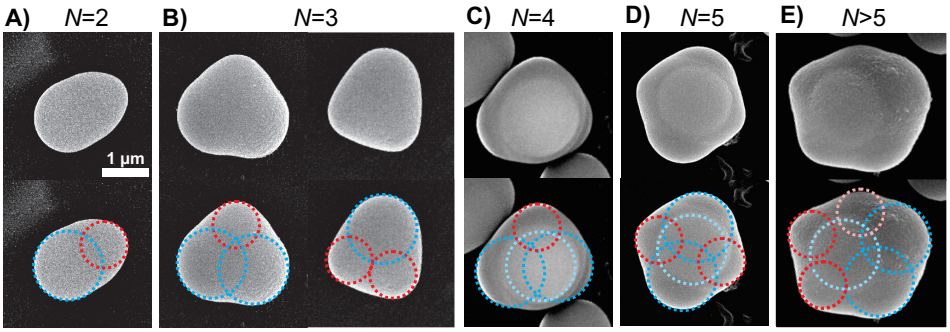

FIGURE 5.4: SEM micrographs of patchy particles constructed by 1.59 μm (cd=1.6% v/v) and 1.06 μm (cd=10% v/v) seed particles. Below the images a reconstruction of the spherical seed particles is shown. A) Asymmetric dumbbell constructed from one large and one small particle. B) The clusters of N=3 reconfigured to triangular shapes and consist of either two large and one small particle or one small and two large particles. C) Tetrahedron particle constructed by three large and one small sphere. D) Pentagonal dipyramid formed by three large and two small particles. E) Example of a cluster consisting of N>5 spheres. Reconstruction of the spherical seed particles indicates that the large spheres strongly deformed, whereas the smaller rigid particles maintaned their spherical sphape.

compact shapes were obtained. Besides the rigidity of the spheres another important difference with our results is the absence of the cluster-spanning droplet. With droplet evaporation techniques the cluster-spanning droplet is completely evaporated, while with the colloidal recycling method the organic droplet remains and is polymerized. The polystyrene spheres also have a preferred wetting angle with the droplet. These factors together with geometric constraints due to an increased contact area between deformed spheres influence the reconfiguration pathway. The patchy particles obtained at size ratio 1.5 have distinct and separated patches. Self-assembly of these complex particles could lead to novel structures.

5.3.2 Patchy particles with chemical and physical patchiness, size ratio 4.6

We examined the shapes obtained after reconfiguration of aggregates of binary mixtures with size ratio 4.6. This was achieved by applying the colloidal recycling method to a binary mixture of 0.23 μm (cd = 4% v/v) and 1.06 μm (cd=10% v/v) polystyrene particles. Since the crosslink density of both seed types was larger than 4% v/v we expect little deformation of the spheres during reconfiguration.[154]

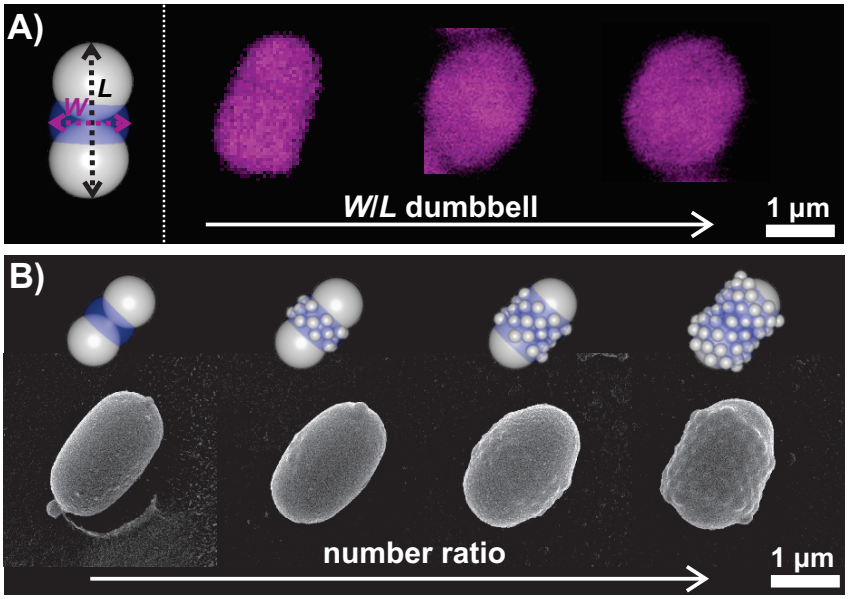

FIGURE 5.5: Dumbbell patchy particles consisting of two 1.06 μm spheres and various 0.23 μm spheres. A) Confocal microscopy images of dumbbell particles shaped from two 1.06 μm spheres with similar dumbbell lengths, but different dumbbell widths. B) SEM micrographs of dumbbells, where 0.23 μm spheres are positioned at the contact area between the large spheres. The width of the dumbbell increases with increasing number of 0.23 μm particles. At large number ratios the 0.23 μm particles arrange on an ordered lattice forming a 'jacket' around the dumbbell.

Aggregates of the 0.23 μm and 1.06 μm spheres were formed by exposing the binary mixture to a 1M potassium chloride solution for a total aggregation time of nine minutes. The composition of the aggregates could not be imaged with optical microscopy, since the 0.23 μm particles are at the diffraction limit of optical microscopy. The larger 1.06 μm spheres could be imaged in both bright field as well as confocal mode due to the rhodamine molecules incorporated in the colloids. Since the rhodamine was non-covalently bound to the 1.06 μm polystyrene particles, the dye-molecules could easily migrate to the organic solvent and smaller particles during reconfiguration. These migrated dye-molecules provided us with additional information on the shape of the reconfigured clusters.

Clusters of two 1.06 μm spheres formed dumbbells with similar dumbbell lengths but divergent widths, see Figure 5.5A. These results differ from one-component systems where uniform shapes were formed with a maximum polydispersity of

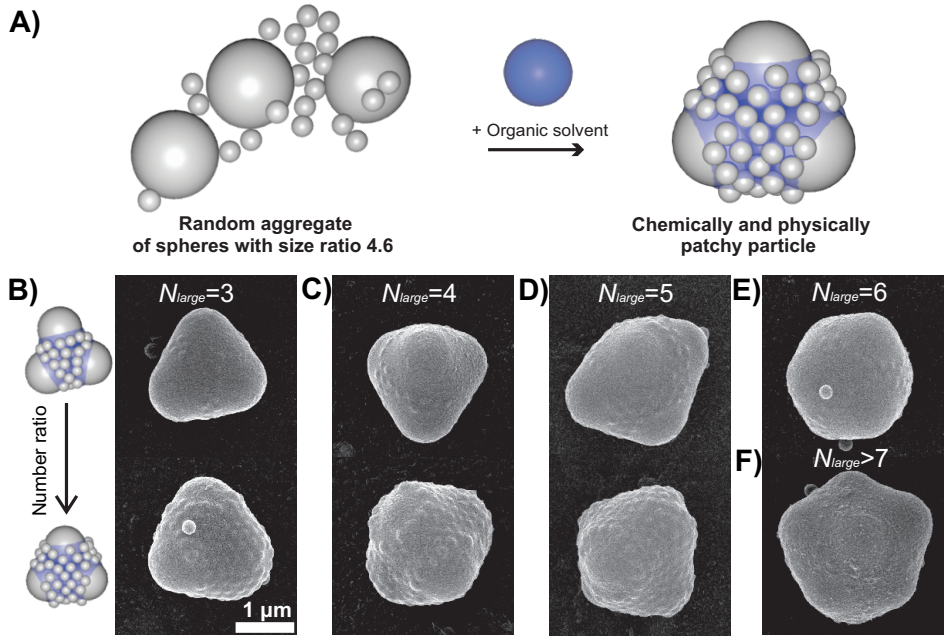

FIGURE 5.6: Chemically and physically patchy particles. A) Illustration of the reconfiguration of an aggregate consisting of spheres with size ratio 4.6. Reconfiguration is induced by the addition of organic solvent. The number of larger spheres, N_{large}, determines the geometry of the patchy particle resulting in the triangle at N_{large}=3, the tetrahedron at N_{large}=4, the triangular dipyramid at N_{large}=5 and the octahedron at N_{large}=6. The small particles position at the contact areas of the larger spheres and determine the final shape of the patchy particle. At large number ratios, the small particles arrange in an hexagonal pattern forming a 'jacket' around the cluster of 1.06 μm spheres. Since the protruding particles introduce surface roughness, the patchy particles own both chemical and physical patchiness.

6% in the length over width ratio (L/W) of dumbbells.[154] Analysis of high resolution SEM micrographs of dumbbell particles revealed that the small spheres all positioned close to the contact area between the larger spheres (see Figure 5.5B). At a given swelling ratio, the width of the dumbbells is therefore influenced by the number ratio between the small and large spheres, where the width increases with increasing number ratio. Large numbers of small particles arranged in a regular pattern forming a 'jacket' around the dumbbell. The patches originating from the small and the large spheres differ in both size and surface chemistry.
At size ratio 4.6, we found that the overall geometry of patchy particles of N>2 was determined solely by the number of 1.06 μm spheres, N_{large}. Similar to one-

component systems of rigid spheres, triangles were formed for N_{large}=3, tetrahedrons for N_{large}=4, the pentagonal dipyramid for N_{large}=5 and the octahedron for N_{large}=6 (Figure 5.6). The geometry of the larger spheres was not influenced by the smaller particles which accumulated at the contact areas between the larger spheres. Similar findings were obtained by Cho *et al*. for colloidal clusters of binary mixtures with size ratio's ≤ 3.[134,156] In our case, patchy particles are formed with both sphere types partly immersed in the cluster spanning droplet. The small spheres determined the exact shape of the patchy particles. At high number ratios, the small particles form an ordered hexagonal pattern at the center of the cluster of larger spheres. The patches of the large particles are especially well-pronounced on these 'jacketed' patchy particles. Additionally, the protruding part of the small particles introduce roughness on the surface of the polymerized droplet. This results in a difference in surface roughness between the patches and the body of the patchy particle, which can be used for depletion induced self-assembly.[29] These particles are therefore both chemically and physically patchy.

The patchy shapes obtained with the colloidal recycling method are not only determined by the size ratio between the particles, but also by the crosslink density and the wetting properties of the spheres. We were therefore able to form a variety of patchy particle shapes with distint patches.

5.4 Conclusions

The colloidal recycling method was used to form particles with distinct patches. This was achieved by employing binary mixtures of colloidal spheres of different size and particle rigidity. Various patchy shapes were formed, since all permutations were possible. At size ratio 1.5, the geometry of the reconfigured clusters was set by both the larger and the smaller particles. Since the larger spheres had a low crosslink density, these particles strongly deformed during reconfiguration. The resulting shapes were therefore more compact compared to clusters of rigid spheres. The geometries obtained were similar to one-component systems and to binary colloidal clusters formed via droplet evaporation methods.
Patchy particles with increased complexity were formed by mixing two types of rigid seed particles with size ratio 4.6. The shapes obtained have patches of different sizes and with different surface chemistry. The larger seeds determined the overall geometry and the small particles positioned at the contact areas between the larger spheres. At high number ratios, the small particles formed a 'jacket' around the clusters. The 'jacket' consisted of the polymerized droplet with the protruding part of the small spheres, which introduced a difference in surface roughness between the body and the patches. These advanced patchy particles are therefore both chemically and physically patchy and may act as complex building blocks for functional materials.