Polymer/Nanoparticle Hybrid Materials of Precise Dimensions by Size-Exclusive Fishing of Metal Nanoparticles

Ziyin Fan, Melissa Köhn Serrano, Andreas Schaper, Seema Agarwal, and Andreas Greiner*

The size and shape of metal nanoparticles are crucial for material properties in various applications, e.g., in optics and catalysis.

The direct synthesis of nanoparticles with precisely defined size and size distribution is still a challenge. Many efforts have been carried out to provide versatile separation techniques for size sorting of nanoparticles, such as membrane filtration, size exclusion chromatography, gel electrophoresis, asymmetric-flow field flow fractionation, and ultracentrifugation using viscosity or density gradient. The use of novel polymer materials for size-selective separation of metal nanoparticles is highlighted in the present work. In contrast to already known separation techniques for nanoparticles, our method separates directly the nanoparticles of desired size and thereby creates novel hybrid materials. A straight-forward “fishing” process is demonstrated for the separation of gold nanoparticles (AuNPs) as a model with high size selectivity using polymer cages of predetermined size quasi as “mesh bag.” Previously, we have developed a novel concept for the preparation of core (AuNP)/shell (polymer) nanoparticles with predetermined functional groups by radical polymerization of thiol-functionalized vinyl monomers on the surface of AuNPs. This method is defined as “grafting around” of polymer on nanoparticle surfaces. As ligand, 4-vinylbenzenethiol was immobilized onto the AuNP surface using the Brust–Schiffen method using dodecyl trimethylammonium bromide (DTMABr) as phase transfer catalyst. Subsequent free radical polymerization using carboxylic acid-functionalized azo-initiator enabled monofunctionalization of AuNP with carboxylic acid group within single step. The surface polymerization should be much faster than the decomposition of the initiator. Therefore, the overall concentration of the radical was low, which enabled the stoichiometric functionalization of AuNPs. The monofunctionality of AuNP was demonstrated by Krüger et al. using coupling reactions.

The “grafting around” method generates nanoparticles coated with single polymer chain with precisely controlled functionality. This provides in an easy way a new type of polymerizable vinyl monomers with AuNPs as substituents at the vinyl bond and their copolymers with other conventional vinyl monomers like methyl methacrylate (MMA) (Figure 1). The utility of such interesting copolymers with AuNPs as substituents along the polymer chain for the size-selective separation of metal particles is discussed in the present work. The AuNPs from the core of the substituents were etched for getting an empty polymer cage with coordinating thiol groups hanging on MMA backbone (cage-co-PDMA). The size-selective fishing of metal nanoparticles was carried out using these specially designed polymer cages for the separation of nanoparticles from a mixture of particles of different sizes. It should be mentioned as well that refilling of previously etched polymer hollow capsules, prepared differently, were used for the encapsulation of uranyl acetate without any report on encapsulation efficiency.

In the present work as a concrete example, the monovinyl-substituted AuNPs (AuNP 3) were made by reaction of carboxylic acid group on single-polymer-chain-stabilized AuNP (AuNP 2) surface with 4-vinylaniline using N,N′-disopropylcarbodiimide (DIC) as coupling catalyst (Figure 1). The AuNP core had a diameter of 4.5 ± 2.3 nm, as measured by transmission electron microscopy (TEM) (Supporting Information). Further, the copolymers (AuNP-co-PDMA) of MMA with small amounts (2 wt%) of AuNP 3 were made by radical polymerization using azobisisobutyronitrile (AIBN) as initiator, according to our previously published procedure. The reason for copolymerization with MMA will be explained below. The details for preparation and characterization of the copolymer are presented in the Supporting Information.

The selective etching of the AuNPs from the core of the core-shell substituent of the copolymer by NaCN at room temperature led to the formation of empty polymer cages of poly(4-vinylbenzenethiol) covalently attached as side chains to the PMMA backbone (Figure 1, cage-co-PDMA). The quantitative removal of AuNP for the formation of empty polymer cages was proven by UV–vis spectroscopy and elemental analysis (Supporting Information).

To deduce the morphology of the polymer cage, the AuNP template was etched after the “grafting around” process (AuNP 2) leaving the pure polymer cage without attached PMMA chain. The TEM image in Figure 2a presents a globular shape of the empty polymer cage stained with osmium tetraoxide (OsO4) at its dry state. Moreover, the polymer cage exhibited high content of disulfide instead of thiolate, as measured by Raman spectroscopy. The disulfide bond was responsible for the crosslinking of the polymer cage (Figure 2b). The average diameter of the empty polymer cage was 40 nm, which was larger than the size of the AuNP core. It is speculated that the disulfide crosslinking...
not only occurred within a single polymer cage but also with each other. Thus, the polymer cage in Figure 2a was revealed as a large crosslinked polymer network.

To evaluate the shell crosslinking of the “grafting around” process, we investigated the stability of AuNPs before (AuNP \(_1\)) and after (AuNP \(_2\)) surface polymerization upon adding excess of dodecanethiol (DDT), according to the study of Schacher and co-workers.\(^\text{[20]}\) The thiolate ligand can be replaced by the competing ligand DDT in excess. DDT-coated AuNPs are not stable in \(N,N'\)-dimethylacetamide (DMAc), which leads to the precipitation of AuNPs. Based on this principle, the UV–vis measurements were carried out for AuNP dispersions (AuNP \(_1\) and \(_2\)) in DMAc charged with excess of DDT and recorded every hour. The corresponding UV–vis spectra of AuNP \(_1\) and \(_2\) are shown in Figure 2c,d. The absorption maxima of AuNP \(_1\) decreased continuously to 22% of the initial value after 48 h when a black brown precipitate was already observed at the bottom of the cuvette (for pictures see the Supporting Information). On the contrary, AuNP \(_2\) after surface polymerization showed much higher stability in the presence of DDT than AuNP \(_1\). The absorption maxima of AuNP \(_2\) decreased only to 80% of the initial value in the first hour and kept almost constant accompanying slightly decline after 48 h. Comparable results were obtained by Schacher and co-workers to study the shell crosslinking efficiency of the thiolate-terminated block copolymer on AuNP surface. In our case, the difference of the stability between AuNP \(_1\) and \(_2\) provided convincing arguments not only for the successful polymerization of vinyl-ligand around AuNP but also for the shell crosslinking of the polymer chain during the “grafting around” process. The crosslinking of the macromolecule could be attributed to the chain transfer reaction or entanglement. As for AuNP \(_2\), DDT could attach to the vacant space in between the single crosslinked macromolecule around AuNP surface. This led to the change of the electronic structure and consequently the decline of the absorption maxima. In combination with the results from TEM and Raman analysis, we consider that the polymer cages consists of crosslinked macromolecules, which results from disulfide bonds and backbone crosslinking. The polymer cage is similar to a “mesh bag” without a rigid structure.

Citrate-stabilized gold nanoparticles (Ct@AuNP) of different sizes ranging from 57 to 3 nm prepared by using the Turkevich method\(^\text{[21]}\) were used as representative examples for the size-selective separation of metal nanoparticles. The size-selective nanoparticle separation process was carried out using ligand exchange reactions in a biphasic chloroform/water system (polymer cages in chloroform and Ct@AuNP in water) using the phase transfer catalyst (tetraoctyl ammonium bromide (TOAB)) at room temperature. As the polymer cage contained numerous thiolate and disulfide groups that have high affinity to AuNP surface, the citrate ligand was replaced by thiol groups. The ligand exchange occurred at the interface, where AuNPs were partially covered by citrates and the polymer cages. Due to the lowered surface electrostatic repulsion, AuNPs tended to agglomerate in this stage at the interface.\(^\text{[22]}\) To prevent the agglomeration and increase the interface, TOAB was used as the phase transfer catalyst as is well-documented for the interfacial ligand exchange reactions involving silver nanoparticles.\(^\text{[23]}\) The ligand exchange reaction was followed by the transfer of the characteristic red-violet color of AuNPs from the aqueous phase to the organic phase. The organic phase was separated followed by precipitation in methanol and vacuum drying. The covalently bound PMMA chains served quasi as an “auxiliary grip for polymer cages” that increased the hydrophobicity and enabled...
the completion of the ligand exchange within one minute. As a side remark: PMMA chains were used here as a model polymer matrix and could be replaced by any other radical polymerizable hydrophobic monomer, which opens a wide field for fabrication of novel hybrid materials with nanoparticles of definite size.

The efficiency of the separation process was analyzed qualitatively by UV–vis spectroscopy and TEM and quantitatively by inductive coupled plasma–optical emission spectroscopy (ICP-OES). Experiments were carried out both with AuNPs of discrete size range with relatively narrow size distribution and also using a mixture of particles with different size and size distribution. The characterization of Ct@AuNP and AuNP after size separation (cage-co-PMA@AuNP) using discrete sized Ct@AuNP is presented in Table 1.

Table 1. Analysis data of AuNP before and after size separation using discrete sized nanoparticles with narrow distribution.

| Entry | Ct@AuNP | AuNP in polymer cages |
|-------|---------|-----------------------|
|       | Diameter$^a$ [nm] | Absorption$^b$ [nm] | Abs. $^b$ | Diameter$^a$ [nm] | Absorption$^b$ [nm] | Abs. $^b$ |
| 1     | 56.5 ± 10.2 | 532 | 0.463 | 3.1 ± 0.7 | 545 | 0.005 |
| 2     | 41.0 ± 7.3  | 536 | 0.988 | 4.1 ± 2.1 | 568 | 0.011 |
| 3     | 34.2 ± 5.6  | 532 | 0.943 | 3.9 ± 1.1 | 567 | 0.005 |
| 4     | 30.9 ± 5.6  | 530 | 0.952 | …$^c$ | 577 | 0.007 |
| 5     | 20.5 ± 3.2  | 522 | 0.774 | 22.1 ± 3.4 | 526 | 0.024 |
| 6     | 15.3 ± 1.8  | 519 | 0.780 | 14.5 ± 2.4 | 525 | 0.075 |
| 7     | 12.4 ± 1.9  | 517 | 0.813 | 13.6 ± 2.1 | 524 | 0.078 |
| 8     | 3.4 ± 0.6   | 506 | 0.666 | 5.0 ± 2.1 | 526 | 0.127 |

$^a$The diameter of AuNPs was determined from TEM images. For each sample, more than 200 particles were measured; $^b$Absorption peak and absorbance (Abs.) were determined from UV–vis spectra; $^c$In this sample, only three particles were found in TEM images.
Using Ct@AuNP with a diameter over 30 nm (entries 1–4, Table 1), neither absorption of the organic phase typical for AuNPs nor AuNPs with corresponding size were observed in UV–vis spectra and in TEM images (Figure 3b), separately. ICP-OES measurements also showed negligible transfer, i.e., only 3.4% of gold in polymer cages in the organic phase (Figure 3c). This indicated that the majority of AuNPs from the water phase could not undergo ligand exchange reaction since they did not fit into the polymer cages. As shown in Figure 3a, conspicuous increase of the absorption maxima of AuNP in polymer cages occurred by samples of Ct@AuNP smaller than 20 nm (entries 5–8, Table 1). Here, quantitative analysis of the AuNP in polymer cages by ICP-OES showed that 14.4% of gold was transferred from the aqueous phase to the chloroform phase. The polymer cages were most suitable for the ligand exchange reactions with AuNPs (Ct@AuNP) with diameter under 15 nm, since they fitted well into the polymer cages in the chloroform phase. This was verified by TEM analysis as AuNPs of the aqueous phase were identified after ligand exchange reaction in the chloroform phase. Correspondingly, ICP-OES analysis showed a large uptake of gold by the chloroform phase as high as 57.6%.

So far, only the separation of AuNPs by polymer cages was applied to AuNP dispersions with a discrete size range of AuNP and a relatively narrow size distribution. Further, the concept was verified for the size-selective separation by taking a mixture of nanoparticles with different sizes: 31, 15, and 3 nm in equal volume ratio. Comparing the TEM images before and after ligand exchange reaction, preferentially small AuNPs were found in the organic phase whereas the oversized gold nanoparticles (31 nm) were not found (Figure 4c). The polymer cages clearly filtered off the bigger nanoparticles and thereby providing decreased size and size distribution of AuNPs after the separation process.

To verify the size selectivity of the polymer cage, we chose a linear polymer of thiol-terminated PMMA (PMMA-SH) and a block copolymer of polystyrene-block-poly(4-vinylpyridine) (PS-b-PVP) as comparison groups. PMMA-SH extracted AuNPs up to 30 nm quantitatively from aqueous phase to chloroform phase. Even larger AuNPs of about 40 nm were found in the organic phase when using Ct@AuNP with corresponding sizes in the aqueous phase. However, only a small portion of AuNPs was transferred to the organic phase, as a significant amount of AuNPs were aggregated at the interface (for TEM images and UV–vis spectra see the Supporting Information). Taking the mixture of Ct@AuNP of different sizes (30, 14, and 4 nm) as precursors, all sizes of AuNP were found in the organic phase after ligand exchange (Figure 3a). Hence, there was no change in size distribution after ligand exchange reaction using PMMA-SH.

In the case of PS-b-PVP, the pyridine moiety of the PVP block served as ligand for AuNPs. In contrast with the polymer cage, the PVP block is a non-crosslinked linear polymer that can wrap the AuNPs. The PS block increased the hydrophobicity of the PS-b-PVP-stabilized AuNP (PS-b-PVP@AuNP), which enabled the ligand exchange reaction in a biphasic system. The PS block consists of 77 units, while the repeat unit of PVP block is calculated with 34 units. The full characterization of PS-b-PVP is shown in the Supporting Information. The ligand exchange reactions using Ct@AuNP with discrete sizes were carried out under similar conditions. Quantitative phase transfer of AuNP
up to 30 nm was also observed as in the case of PMMA-SH. Meanwhile, PS-b-PVP showed no size selectivity when using a mixture of Ct@AuNP in size as precursor (Figure 4b). As a side mark, the polymer cage is not restricted to the thiolate ligand. Other ligands containing nitrogen like 4-vinylpyridine or sulfur can be fabricated into polymer cage for separation of AuNPs. The “fishing” concept is therefore universal for applications in different nanoparticle systems with suitable ligands.

Neither PMMA-SH nor PS-b-PVP had the ability to narrow the size distribution of AuNP by means of a biphasic ligand exchange. We attribute the difference of the size selectivity between these three types of polymers to how the polymer chain behaves at the interface during ligand exchange. PMMA-SH owns one thiol endgroup that can replace the citrate ligands. The rest of the PMMA chain has no direct interaction with AuNP. We define this behavior as a “plug in” process. As for PS-b-PVP, each 4-vinylpyridine unit in a single chain can be attached to the AuNP surface by ligand exchange. As a consequence, the whole PVP chain is relatively fixed on the AuNP surface in an equilibrium, which is called a “wrapping” process. The polymer cage is less flexible than PMMA-SH or PS-b-PVP due to disulfide and backbone crosslinking. Considering the polymer cage as a “mesh bag,” then the cage should be open and nonrigid in order to encapsulate AuNP. As shown in the TEM image (Figure 2a), the polymer cage forms a spherical pad at its dry state with a mean radius of about 20 nm, the theoretical coating area is calculated of 800 $\pi \times 10^4$ nm$^2$ under the assumption that the pad consists of a double layer. This corresponds to the surface area of AuNP with a diameter of 20 nm. In other words, the polymer cage is only able to encapsulate AuNPs under 20 nm, which was proven by ligand exchange reaction using Ct@AuNPs with discrete sizes. If the polymer cage encounters an AuNP of 30 nm at interface, it could not expand or immobilize around the AuNP beyond its limit of coating area. This long-time insufficient coating hindered the transfer reaction of AuNP to the organic phase due to the lack of hydrophobicity. The large AuNPs were thus agglomerated because of the decrease of the electrostatic repulsion before they could be immobilized into the organic phase. As a result we denote the ligand exchange using the polymer cage as a “folding” process.

Copolymers of core (AuNP)/shell (polymer) monovinyl-functionalized nanoparticles and MMA as templates for polymer cages were synthesized using the “grafting around” method, where thiol-functionalized vinyl monomers were radically polymerized around the AuNP surface. Polymer cages with a distinct size were prepared by etching of AuNPs from the copolymer. The polymer cages were crosslinked as derived from TEM, Raman spectroscopy, and study of the long-time stability of the AuNP after “grafting around” process using UV–vis spectroscopy. The empty polymer cages were used for the ligand exchange reaction using the polymer cage as a “folding” process. The ligand exchange process using the polymer cage was proven by TEM images (Figure 2a) and size distribution (Figure 4b).
size-selective separation of AuNPs with an excellent size resolution by comparison with PMMA-SH and PS-b-PVP. The separation efficiency was verified qualitatively by UV–vis spectroscopy and TEM and quantitatively by ICP-OES. Despite numerous nice reports regarding nanoparticle syntheses with narrow size distribution,\textsuperscript{224} the size selective separation of nanoparticles is of great importance, which offers a broad choice for polymer/nanoparticle hybrid material synthesis with precisely designed dimensions. Although the polymer cage showed better size selectivity than linear (PMMA-SH) and block copolymer (PS-b-PVP), AuNPs under 15 nm cannot be separated efficiently. Future work is focused on altering of the size and exploring the 3D structure of the polymer cage to achieve higher selectivity and efficiency. Surely, the concept of size-selective separation of nanoparticles with polymer cages, in analogy to fishing, is not restricted to metal nanoparticles when other ligands in the polymer cages are provided. So far, the polymer cage has been successfully applied to the silver nanoparticle system (data not shown). The next is now to expand selective separation of nanoparticles with respect to shape and chemistry for making hybrid materials in a single step. Based on the separation concept, novel materials could be created, e.g., by arrangement of different metal nanoparticles in the same polymer cages, which offers interesting perspective for new property profiles.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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