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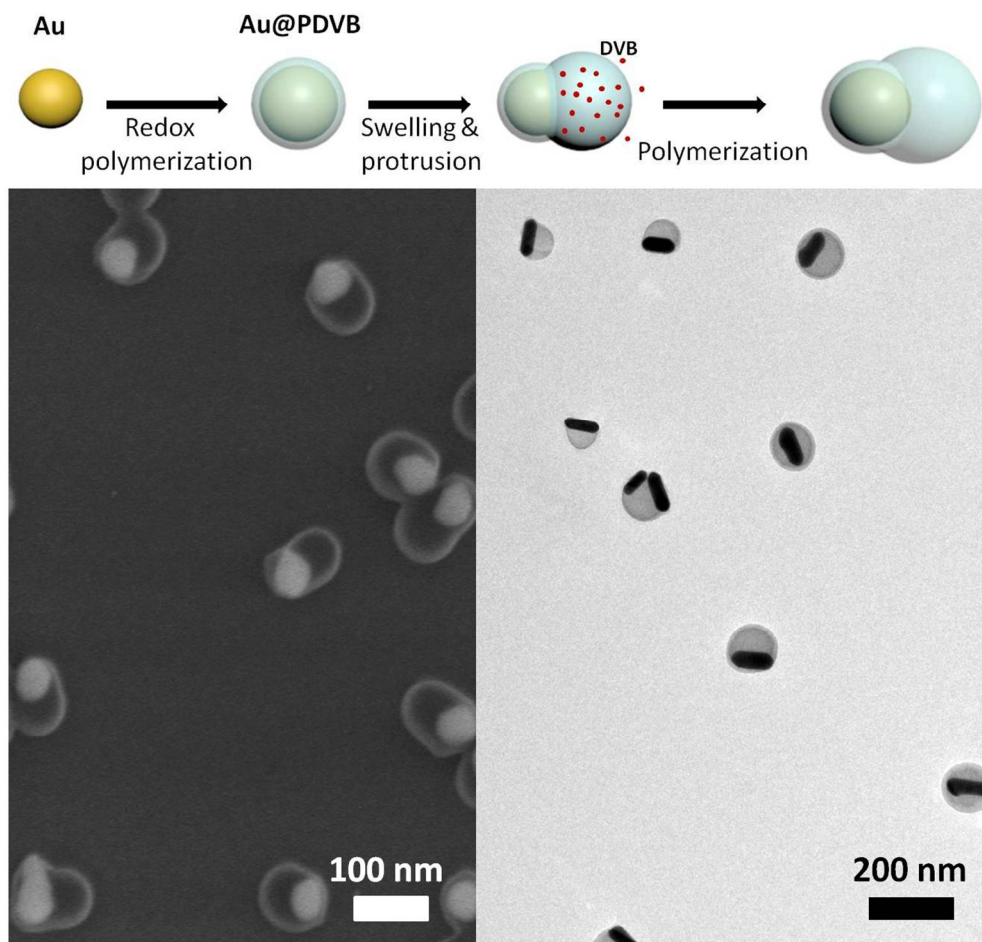


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Harnessing Nonlinear Rubber Swelling for Bulk Synthesis of Anisotropic Hybrid Nanoparticles

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Asymmetric hybrid nanoparticles are at the forefront of colloidal chemistry as building blocks for novel structures and applications, as well as for exploring fundamental ways of breaking symmetry in physical systems. Current methods of synthesis have significant limitations in terms of control over synthesis, particle size ranges and polydispersity. We report a facile and scalable synthesis based on the anisotropic swelling of rubber to obtain metal-(polymer rubber) hybrid nanoparticles. Initial Au nanoparticle (NP) seeds are grown larger by reducing HAuCl₄ with divinyl benzene (DVB), while simultaneous radical polymerization of DVB forms a cross-linked rubber layer of PDVB on the Au NP surface. The propensity of the rubber to swell nonlinearly in the presence of DVB monomers amplifies initial asymmetries to break the symmetry of the PDVB shell, causing growth of asymmetric protrusions on one side of the core-shell particles, which are fixed by further polymerization. Plasmonic absorption of the Au allows us to follow the Au reduction reaction, and also suggests potential applications of some of the asymmetric particles in plasmon-enhanced sensing. The polydispersity, determined statistically from TEM and SEM images, of the resulting particles is low (<10%) and their sizes, shapes and metal/polymer ratio are easily tunable.

Introduction

Anisotropic hybrid colloidal particles have aroused interest in the last few years for uses in multi-functional diagnostics and therapeutics,¹ catalysis,^{2,3} with potential as solid stabilizers in foams and emulsions,⁴ and suitability for novel self-assemblies of multi-configurations and multi-functionality that cannot be easily achieved from spherical building blocks.⁵⁻⁹ In the last decade methods for formation of anisotropic hybrid particles have been greatly developed and can generally be classified into physical fabrication and chemical synthesis approaches. Physical fabrication techniques involve lithography,¹⁰ sputter deposition,¹¹ electric field co-jetting,¹² and microfluidics.¹³ They produce relatively large nanoparticles, but at the same time lack volume scalability. Chemical approaches overcome the volume scaling limitation, but often produce mostly spherical shapes since interfacial energies favor the lowest surface-to-volume ratio shapes. Additional potentials need to be applied to favor (thermodynamically or kinetically) nonspherical shapes. Facet control¹⁴ and ligand control¹⁵ have been successfully applied to inorganic composite nanoparticles, however, for organic / inorganic hybrid nanoparticles, the main challenge still remains.

One way to affect the shape of hybrid colloids is hydrophilic-hydrophobic ligand segregation on the surface of metal particles so that the diblock polymers can be self-assembled on the hydrophobic domains.¹⁶ Controllability of the sizes of the polymer component is poor however, and

limited to a small range of thicknesses from 10 to 20 nm. A more robust and scalable way to create hybrid asymmetric nanoparticles is to initiate polymerization on inorganic nanoparticles or their precursors. The group of Xia introduced a scalable method by initiating precipitation polymerization of PS in the presence of Au NPs.¹⁷ However subtle effects from the addition time (~2s after initiating the polymerization) and sensitivity to reactant ratios, makes this method difficult in terms of reproducibility. Hybrid nanoparticles have also been made by interfacial polymerization,¹⁸ but reactions at interfaces also require delicate control, and occasionally sophisticated manipulation of one of the suspending phases.

Seeded polymerization is a versatile method for generating nonspherical polymer-polymer hybrid particles. The shapes and ratios of the particles are tunable, driven by the phase separation of polymers.¹⁹⁻²¹ This technique has also been used to create hybrid metal-polymer particles via partial wetting of the metal particles before polymerization, though the surface wetting properties are not easy to control.²² Polydispersity is also significant, controlled by an Ostwald ripening mechanism.

New methods that are easier to control, and which would expand the range of polymers and metals used are highly desired in this field. Here we initiate polymerization of divinyl benzene (DVB) on AuNP seeds to generate a cross-linked rubber coating, but a similar procedure could be used with most rubber coating materials. We use the non-uniform swelling of the rubber by its liquid monomer to break the symmetry, and

form hybrid particles of AuNPs anisotropically encapsulated in poly(divinylbenzene) (PDVB).

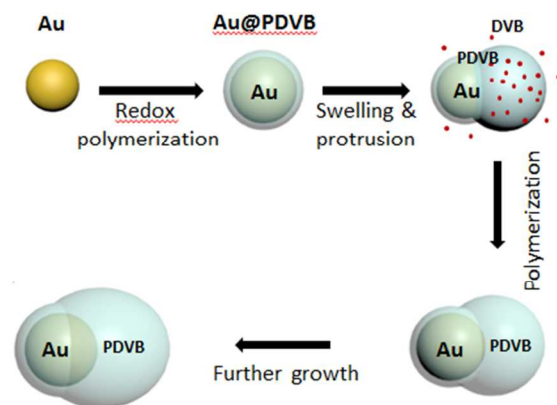
Results and discussion

The synthesis of asymmetric hybrid nanoparticles is based on a combination of seeded polymerization and dispersion polymerization. The detailed growth mechanism is shown in Scheme 1. We used citrate stabilized Au NPs as the seeds. The redox reaction between HAuCl_4 and DVB will preferentially deposit the reduced Au(0) onto the Au NP seeds along with a uniform coating of PDVB on the surface. The solubility parameter of PDVB is 9.1, which matches quite well with DVB ($\delta=8.5$)²³ and makes DVB a good solvent/swelling agent for it, as well as its second function as a cross-linker. The DVB would swell/uncoil any regions between cross-links until the swelling pressure is balanced by the elastic stress from the network, but the reaction process is proceeding in parallel. The elasticity of a network (and its resistance to swelling) is directly proportional to its crosslink density. So any initial asymmetries in swelling are later amplified, since the DVB would swell new lightly cross-linked regions more than heavily cross-linked regions. In this paper we have aimed to produce a simple synthetic procedure, but if one is willing to separate the swelling and reaction processes, one could conceivably control these effects using Flory and Rehner's theory to measure formalized these interactions.^{24, 25} Such control on a larger scale was recently used to produce asymmetric particles from two polymers (PS And PDVB)²⁰ and could be an inspiration for the development of more complex nanoparticles as well.

In our case, the swelling of low crosslink density regions results in breaking of the spherical PDVB shell symmetry to form a DVB-swollen lobe.¹⁹ The swollen rubber lobes of particles continue to swell in a self-catalytic process, as they keep growing and crosslinking, while preserving the particle asymmetry. At the same time, the reaction rates allow us, by the amount of DVB and Au salt added, to tune the ratio between metal and polymer components. Figure 1a shows SEM and TEM images of the colloids. For a typical reaction, 0.5 ml aqueous solution of Au seeds is sequentially mixed with 40 μl PVP (20 mg/ml), 1 μl DVB and 30 μl HAuCl_4 (10 mM) and sonicated for 2 hrs. After this 50 particle images in SEM were measured to quantitate their anisotropy and polydispersity, summarized in Figure 1b. The diameter of the Au component increases from 32 nm (for the initial seeds) to 45 nm. The long and short axes of the PDVB ellipsoids are 68 and 96 nm with relative standard deviation of 10%. The reaction kinetics was monitored by UV-Vis spectroscopy as shown in Figure 1c and d. The TEM image at the initial stage of growth (5 mins reaction) shows that ~ 3 nm of PDVB is wrapped on the surface of Au nanoparticles to form concentric core-shell structure (see left inset in Fig. 1d). As the polymerization proceeds, the sizes of both the Au NP and the PDVB components increase, but the encapsulation evolves quite eccentrically due to the nonlinear swelling of PDVB as shown in the middle and right insets in Figure 1d. The reaction usually finishes in just over an hour, when the plasmonic absorption peak has red-shifted from 524 to 543 nm, which is mainly due to the increase of the size of Au NPs.

We use water as the dispersant medium and PVP as the stabilization agent. Assuming full coverage of the resulting particles, it is estimated from the amount of PVP added, that around 10^5 PVP molecules were absorbed on the surface of the Au-PDVB nanoparticles. Without PVP, the hybrid

nanoparticles of Au-PDVB aggregate (see SI-Fig. S1). The cross-linking is critical for the generation of anisotropic nanoparticles since if styrene (with only one vinyl bond) is used as the monomer, only a very thin layer of PS shells are coated on the surface of the Au NPs and no protrusion is observed (see SI- Fig. S2). It is possible that the mismatch of interfacial energy between the PDVB and Au NP may also cause anisotropic growth, but this would be more likely to produce hetero-dimers rather than ellipsoids.²²



Scheme 1. Formation of anisotropic hybrid nanoparticles made of Au-PDVB. The yellow sphere is the AuNP, the red dots represent DVB monomers, which swell, crosslink and enlarge the light blue region representing the PDVB coating.

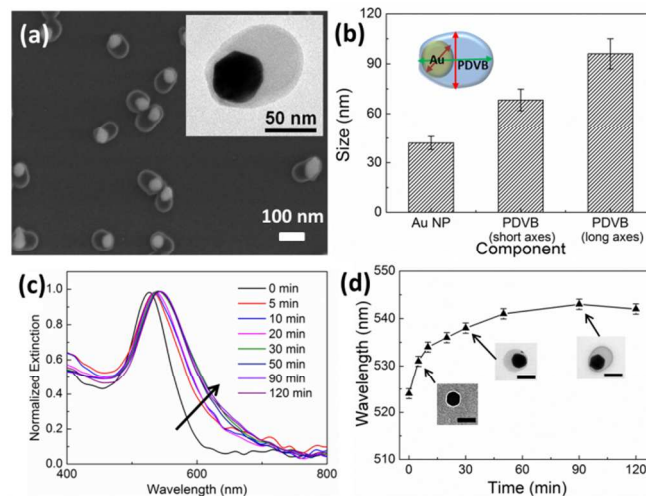


Figure 1. Seeded growth of asymmetric hybrid Au-PDVB colloids. (a) SEM image of the hybrid hetero-dimers with inset of the corresponding TEM image, (b) histogram of the sizes of different components of the hybrid Au-PDVB nanoparticles. (50 particles) The inset shows the way sizes were measured, Au NP: dark red arrow; Short axes: red arrow; Long axes: green arrow. (c) UV-vis extinction spectra of the hybrid Au-PDVB particles measured at different reaction times, and (d) wavelength shift of the peaks in (c) with time, with insets showing TEM images of Au-PDVB hybrid nanoparticles evolving from spherical core-shell to anisotropic encapsulation. Scale bars are 50 nm.

By adjusting the amount of HAuCl_4 the absolute size of the Au NP cores can be controlled independently (Figure 2). We start with 32 nm diameter Au NP seeds and vary the amount of

H₂AuCl₄ added while keeping the same amount of DVB. With increasing amounts of H₂AuCl₄, the size of the Au NP increases gradually, as does also the size of the PDVB shell, since H₂AuCl₄ also initiates conversion of DVB in solution to PDVB. The PDVB shell size gradually reaches a plateau beyond 100 μ l H₂AuCl₄, implying that full conversion from the DVB monomers to PDVB has occurred. The hybrid nanoparticles maintain the same asymmetric shape throughout the growth process as shown in Figures 2b-d. The statistical range of sizes of the Au and PDVB components in the hybrid nanoparticles is shown in Figure 2e, with polydispersity remaining small. The plasmonic properties of the hybrid nanoparticles are characterized with UV-Vis spectroscopy (Figure 2f), showing the absorption peak red-shifts from 524 nm to 567 nm with increasing amounts of H₂AuCl₄. At the same time the spectral half width of the plasmonic peak increases considerably from 60 to 100 nm. These measurements can be explained by both the increase in the size of the Au NPs, as well as the increase in the effective refractive index surrounding them. We note that such solution measurements average over the anisotropy of the hybrid NPs, combining plasmons across the short axis with those along the long axis (which see more PDVB), thus broadening the measured linewidth.

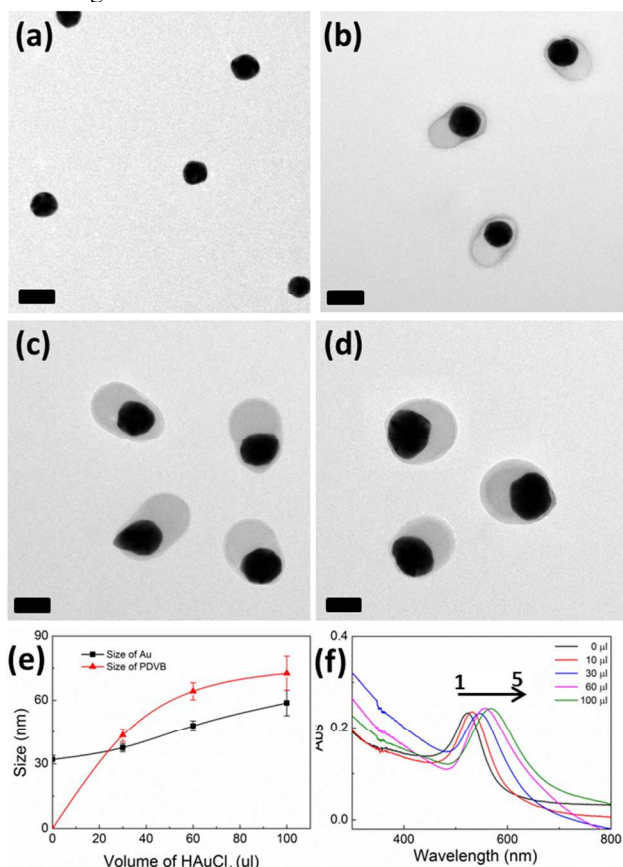


Figure 2. Increasing size of hybrid Au-PDVB hetero-dimers with increasing amounts of H₂AuCl₄. (a-d) TEM images with increasing 10 mM H₂AuCl₄ from (a) 0 μ l, (b) 30 μ l, (c) 60 μ l, to (d) 100 μ l, with fixed 1 μ l DVB. Scale bars are 100 nm. (e) Measured size of Au and PDVB particles (short axis) with increasing H₂AuCl₄. (f) Corresponding UV-Vis absorption spectra of the Au-PDVB hetero-dimer nanoparticles. Spectra 1 to 5 correspond to particles with increasing H₂AuCl₄ added, 1: 0 μ l, 2: 10 μ l, 3: 30 μ l, 4: 60 μ l, 5: 100 μ l.

We also examined the size change with increasing volumes of DVB from 1 μ l to 5 μ l, while keeping the amount of H₂AuCl₄ fixed (Figure 3). The PDVB particle size increases gradually from 40 to 50 nm, while the size of Au NP increases only slightly from 32 to 37 nm (Figure 3a-d), perhaps due to a higher conversion ratio of Au(I) to Au(0) with excess reductant (DVB). In all cases, the amount of DVB is in excess and the amount of the H₂AuCl₄ is the limiting factor for the growth of both PDVB and Au NP components. The absorption spectra of the plasmonic nanoparticles (Figure 3e) show little peak shift, confirming our previous hypothesis that the peaks red-shift mainly due to increasing Au NP size, with less dependence on PDVB shell size.

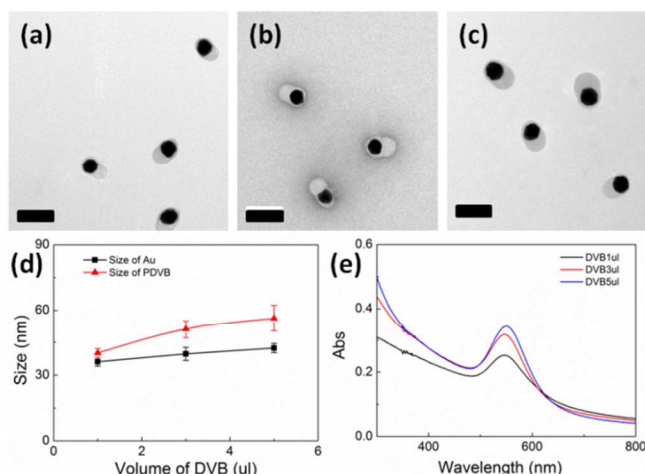


Figure 3. Size of hybrid Au-PDVB hetero-dimers with increasing DVB of (a) 1 μ l, (b) 3 μ l, (c) 5 μ l, while keeping fixed 0.6 mM concentration of H₂AuCl₄. Scale bars are 100 nm. (d) Size dependence of Au and DVB components of hybrid nanoparticles vs DVB volume, with (e) corresponding absorption spectra.

We normally carried out the experiment near 45 $^{\circ}$ C. The process is one of seeded-growth, so small temperature variations should not change the final particle size, which is determined by the exhaustion of the reactants (H₂AuCl₄) and DVB monomer used. The kinetics of the process may change but the number of Au and Au-PDVB hybrid nanoparticles stays constant.

In order to increase the asymmetry of the hybrid particles, we attempted to use Au NRs as the seeds (Figure 4a) on which to grow the PDVB shell. Two options are then possible: a) that one side would start swelling more and thus dominate with growth on just one side of the rods, or b) that if the two sides are sufficiently separate, both may grow independently. In fact (Figure 4b), the Au NRs grew PDVB lobes exclusively on just one side. Partly this may be because the high curvature of the Au NRs prevents complete wetting of the rods with DVB, and only the side initially wetted grows, since in the presence of swellable PDVB no further nucleation or wetting of DVB on Au takes place. Statistical measurements of the Au NRs (50 particles) sizes (Figure 4c) shows that their length increases (from 80 to 87 nm) and width increases (from 23 to 30 nm), implying deposition of Au(0) on the NRs is uniform all over the surface. The NR aspect ratio thus reduces from 3.5 to 3.0, which in the extinction spectra of the hybrid AuNR-PDVB nanoparticles (Figure 4d) produces a blue-shift of the longitudinal mode (from 769 to 731 nm) and a red-shift of the transverse mode (from 513 to 526 nm) compared to the original Au NR seeds.^{26, 27} The basic mechanism appears to be the same

as with Au NP seeds. The reduced Au(0) heterogeneously grows on the Au NRs along with a thin layer of PDVB oligomers formed at the surface. The DVB monomer droplets partially wet the Au NR surface and grow anisotropically on one side. The contact angle between PDVB and Au NR becomes consistently $\sim 80^\circ$ (Figure 4e). Although the number of Au NRs on the PDVB lobe can vary up to three (Figure 4f insets), the majority of products are AuNR-PDVB particles with a single rod (90%). Particles with two (8%) or three rods (2%) may possibly be generated at the initial stage of the dispersion polymerization when the DVB lobe is not totally solidified and occasional collisions can occur between the particles. The high stabilization from PVP molecules prevents much aggregation, resulting in the near-uniform monodisperse distribution of rods in particles.

The near hemispherical shape of these hybrid nanoparticles containing a single rod is interesting from both assembly and sensing perspectives. The almost complete absence of polymer on one side of the particles implies large differences in polarization, which has been used before in the assembly of similar Janus particles in electric²⁸ and magnetic fields.²⁹ Furthermore, when the lobes are grown to larger diameters, due to their size and symmetry, the particles would only be able to assemble in pairs (when aggregated by electric or optical fields), since the sideways hemispherical protrusion would prevent a third particle from coming in contact with the rods. Knowing only two particle cores could interact, this polarization enhancement could be used for quantitative and sensitive detection. This is a unique advantage in suspensions, as traditionally such enhancement has been possible only through the laborious fabrication of nanolithography patterns,³⁰ and has long been sought after in self-assembly of plasmonic structures.³¹

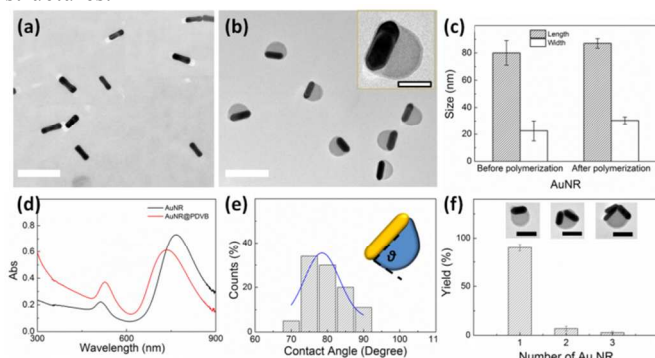


Figure 4. Growth of asymmetric hybrid nanoparticles using Au NR seeds. (a) Seed Au NRs, and (b) as-grown asymmetric AuNR-PDVB hybrid nanoparticles. Scale bars are 200 nm and 50 nm in inset. (c) Statistical distribution of Au NRs dimensions before and after growth of asymmetric AuNR-PDVB hybrid nanoparticles. (d) Absorption spectra of Au NRs and AuNR-PDVB hybrid nanoparticles. (e) Statistical distribution of the observed angle between PDVB and AuNRs, with Gaussian fit (blue line). (f) Yields of anisotropic hybrid nanoparticles with different number of AuNRs encapsulated.

Experimental

The Au seeds (AuNPs and Au NRs) were obtained from Sigma-Aldrich, and used as received. Typically, 40 μ l of PVP (20 mg/ml) was mixed with 0.5 ml of the Au aqueous solution in a 1.5 ml Eppendorf tube. The aqueous solution of HAuCl₄ (10 mM) was introduced into the mixture under vortex mixing

followed by the addition of the monomer of DVB. The amount of HAuCl₄ and DVB are adjusted to tune the relative sizes of Au and PDVB in the hybrid nanoparticles. The entire Eppendorf tube was kept in an ultrasonic bath (600 W, 45 $^\circ$ C) for 2 hrs. The final products of Au/PDVB asymmetric hybrid nanoparticles were harvested after 3 cycles of centrifugation and redispersion.

The morphology of asymmetric hybrid nanoparticles were characterized in a Scanning Electron Microscope (Zeiss) and Transmission Electron Microscope (FEI Tecnai 20). For clear observation of the polymers, some of the samples were stained with (NH₄)₆Mo₇O₂₄. The plasmonic property of the hybrid nanoparticles was characterized using a UV-Vis spectrometer (Ocean optics QE65000).

Conclusions

The conclusions section should come at the end of article, before the acknowledgements. In this paper, we report a facile approach for asymmetric hybrid plasmonic nanoparticles made of Au and PDVB. This synthetic approach is easy to control, and superior to physical approaches both in terms of scalability, control of small size, and uniformity. Specifically, we synthesized hybrid nanoparticles of Au and PDVB rubber. After initial formation of the thin rubber shell, nonlinear swelling by the monomer in suspension causes a self-amplifying bulge on one side of the Au particle, which continues to grow as long as there is monomer in the suspension. By adjusting the size of initial seeds, the amount of Au precursor added, and amount of DVB monomer, we can tune the size of Au core and the polymer shell and achieve good monodispersity. The hybrid particles are stable and do not easily aggregate, due to the lower van der Waals interactions of their polymer shells, which makes them good for plasmonic probes. We can fine-tune the plasmon resonance wavelength of the cores to match specific requirements.

The strategy we have used here is not only applicable to Au and DVB, but also relies on the non-linear swelling of the rubber shell. It should thus be possible to use it with any cross-linked rubber shell material which is swollen by its liquid monomer. Similarly, the Au core could be replaced by another metal, which if Ag or Cu, could also exhibit plasmonic properties, but for other metals may at least be protected from the environment by the polymer shell.

Potential applications for the hybrid plasmonic particles include sensing, which may be especially true for the hybrid particles starting from Au NR, which we demonstrated. Including magnetic cores could allow various particle assemblies in the presence of electric or magnetic fields. We hope the fundamental insight of breaking symmetry for hybrid particles through rubber swelling, the scalability of this dispersion method, its ease of use, and low polydispersity will enable the synthesis of a whole class of such particles.

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Notes and references

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