Introduction

The ability to synthesize shape- and size-controlled metallic nanostructures offers tremendous opportunity in a number of areas including catalysis, optics, sensing, and medicine.\(^1\) Gold and silver nanoparticles exhibit remarkable optical properties due to their surface plasmon resonance (SPR) absorption with peak positions that are highly dependent on the size, shape, and composition of nanoparticles and the dielectric constant of the medium.\(^2\) Furthermore, the strong electromagnetic field generated by surface plasmon (SP) excitation can drastically enhance the fluorescence and Raman signal of nearby molecules.\(^3\)–\(^5\)

A range of differently shaped metal nanoparticles have been synthesized including spheres, rods, stars, and hollow particles.\(^6\)–\(^11\)

In particular, metal nanoshells developed by Halas and co-workers have attracted much attention due to their tunable wavelengths in the near-IR range.\(^12\),\(^13\) Metal nanorods synthesized by Murphy and co-workers are another class of metal nanostructures that have been widely studied for their tunable SP wavelengths in the near-IR region and the strong electromagnetic field generated at the tip of the nanorods.\(^14\) Metal nanoshells and nanorods have been shown to be promising materials for various applications including surface enhanced Raman spectroscopy (SERS), in vivo contrast agents, and photothermal therapy.\(^15\)–\(^20\) The syntheses of both metal nanostructures are based on the seeded-growth approach. Metal nanoshells are usually synthesized by the catalytic reduction of metal ions on seed-decorated silica particles.\(^21\)

Metal nanoshells and nanorods have been shown to be promising materials for various applications including surface enhanced Raman spectroscopy (SERS), in vivo contrast agents, and photothermal therapy.\(^15\)–\(^20\) The syntheses of both metal nanostructures are based on the seeded-growth approach. Metal nanoshells are usually synthesized by the catalytic reduction of metal ions on seed-decorated silica particles.\(^21\)

In particular, metal nanoshells developed by Halas and co-workers have attracted much attention due to their tunable wavelengths in the near-IR range.\(^12\)–\(^13\) Metal nanorods synthesized by Murphy and co-workers are another class of metal nanostructures that have been widely studied for their tunable SP wavelengths in the near-IR region and the strong electromagnetic field generated at the tip of the nanorods.\(^14\) Metal nanoshells and nanorods have been shown to be promising materials for various applications including surface enhanced Raman spectroscopy (SERS), in vivo contrast agents, and photothermal therapy.\(^15\)–\(^20\) The syntheses of both metal nanostructures are based on the seeded-growth approach. Metal nanoshells are usually synthesized by the catalytic reduction of metal ions on seed-decorated silica particles.\(^21\)

Nanorods are typically synthesized by the autocatalytic reduction of metal ions on small seed gold particles (diameter: \(\sim 1–4\) nm) in...
the presence of cetyltrimethylammonium bromide (CTAB). Several research groups (see work by the groups of Hafner, Liz-Marzan, and Wei) have used similar approaches to synthesize star-shaped nanoparticles.

Here, we report a novel metal nanostructure of spikey gold shells, which combines the morphological features of nanorods and hollow metal nanoshells (Figure 1). Our synthetic approach is based on the seed-mediated growth method of gold on self-assembled nanostructures of block copolymers or commercially available polymer beads. Note that spikey nanoshells of various shapes can be readily synthesized using diverse polymeric nanostructures obtained through the self-assembly of block copolymers as templates. We also demonstrate that the spikey gold nanoshells can be combined with other types of functional nanoparticles and molecules to generate multicomponent nanostructures utilizing the capability of block copolymers to encapsulate various types of nanoparticles and molecules. The combination of spikey features and the hollow structure opens up many exciting possibilities for multifunctional applications such as simultaneous imaging and drug delivery and potentially plasmon-controlled drug delivery.

**Experimental Section**

**Materials and Instrumentation.** Cetyltrimethylammonium bromide (CTAB), HAuCl₄, AgNO₃, and NaBH₄ were purchased from Sigma. Dimethylformamide (DMF), tetrahydrofuran (THF), dioxane, NH₄OH, and ascorbic acid were purchased from Fisher. Carboxylate-modified Fluospheres (100 nm) were purchased from Invitrogen. Amphiliphic block copolymers composed of poly styrene and poly(acrylic acid) (PAA-b-PS) were synthesized via sequential reversible addition–fragmentation chain transfer (RAFT) polymerization. ZnS-coated CdSe nanoparticles (4.6 nm in diameter) and Fe₃O₄ nanoparticles (5.6 nm in diameter) were synthesized by literature methods. Transmission electron microscope (TEM) images were taken with a Tecnai G² 12 TWIN operating at 80 kV accelerating voltage or a JEOL TEM-2010F operating at 200 kV accelerating voltage. Extinction spectra were measured with an Agilent 8453 UV–visible spectrophotometer.

**Preparation of Block Copolymer Templates.** Block copolymer assemblies of different shapes were prepared with PAA₃₁-b-PS₃₀ or PAA₅₀-b-PS₁₀₂ following the procedure reported by Eisenberg and co-workers. Bilayers were prepared with PAA₅₀-b-PS₁₀₂. All other assemblies were formed with PAA₃₁-b-PS₃₀. Briefly, the self-assembly of block copolymers was induced by the slow addition of water to the solution of block copolymers. The size and shape of the assemblies were controlled by changing the initial solvent for block copolymers. Small spherical micelles (44 ± 6 nm) were prepared by using DMF as the initial solvent. Typically, 150 μL of water was slowly added to the DMF solution of PAA₃₁-b-PS₃₀ (0.5 wt %, 500 μL) at a rate of 5 μL/30 s. After 12 h, the solution of block copolymer assemblies was dialyzed against water for 24 h. Larger spherical assemblies (117 ± 18 nm) were prepared by using DMF containing a small amount of chloroform (1%) as the initial solvent for PAA₃₁-b-PS₃₀ (0.022 wt %, 1.5 mL). Bilayers were prepared by following the same procedure as the large spheres but using PAA₅₀-b-PS₁₀₂. Vesicles and rod-like micelles were formed by following the same procedure used to prepare small spherical assemblies but with different solvent systems. For vesicles, dioxane was used as the initial solvent to dissolve polymers. After dialysis, vesicles were concentrated by centrifugation (1000 rpm, 15 min). Rod-like micelles were formed by using THF/DMF mixtures as the initial solvent. The initial solvent containing 5 wt % THF produced short rod-like micelles. Increasing the THF content to 10 wt % produced worm-like micelles with a higher aspect ratio. The rod-like or worm-like micelles were separated from small spherical micelles by centrifugation (12,000 rpm, 15 min). Block copolymer assemblies encapsulating iron oxide and ZnS-coated CdSe nanoparticles were prepared following previously reported procedures.

**Preparation of Seed-Decorated Polystyrene Beads.** Fluorospheres purchased from Invitrogen (2% solids, 100 μL) was placed in a microcentrifuge tube. An aqueous solution of Ag(NH₃)₂ ÷ (0.01 M, 100 μL), which was prepared by mixing AgNO₃ (0.01 M, 1 mL) and NH₄OH (1 M, 20 μL), was added to the polymer beads.

---

After 30 min, 1 mL of purified water (18.0 MΩ⁻¹) was added to the solution, which was then centrifuged at 18,000 rpm for 30 min to remove unadsorbed silver ions. Supernatant was discarded and the same washing procedure was repeated one more time. 500 μL of water was added to the final precipitate. Finally, an aqueous solution of NaBH₄ (0.01 M, 100 μL) was added to the solution with vigorous mixing to reduce silver ions. The solution was aged for seven hours before use for the shell growth. The resulting seed-decorated PS beads were purified by centrifuging the solution at 18,000 rpm for 30 min and replacing the supernatant with water.

Preparation of Seed-Decorated Block Copolymer Assemblies. Typically, 200 μL of 0.5 wt % solution of block copolymer assemblies was placed in a microcentrifuge tube. Ten microliters of 2% NH₄OH and 200 μL of 0.01 M AgNO₃ were consecutively added to the block copolymer solution. After 30 min, 1 mL of purified water (18.0 MΩ⁻¹) was added to the solution, which was then centrifuged at 18,000 rpm for 30 min. Supernatant was discarded, and the same washing procedure was repeated one more time. 500 μL of water was added to the final precipitate. Finally, an aqueous solution of NaBH₄ (0.01 M, 100 μL) was added to the block copolymer solution with vigorous mixing to reduce silver ions. The resulting seed-decorated block copolymer assemblies were purified by centrifuging the solution at 18,000 rpm for 30 min and replacing the supernatant with water. The solution was aged for seven hours before use for the shell growth.

Preparation of Spiky Gold Nanoshells. For PS beads, the growth solution was prepared by mixing aqueous solutions of CTAB (0.1 M, 10 mL), HAuCl₄ (0.01 M, 421 μL), AgNO₃ (0.01 M, 64 μL), and ascorbic acid (0.1 M, 67 μL). For complete shell formation on PS beads, 10 μL of seed-decorated bead solution described above was added to the growth solution (10 mL) while gently mixing for a few seconds. Color started developing after the described above was added to the growth solution (10 mL) while gently mixing for a few seconds. Color started developing after 30 min. 1 mL of purified water (18.0 MΩ⁻¹) was added to the solution, which was then centrifuged at 18,000 rpm for 30 min. Supernatant was discarded, and the same washing procedure was repeated one more time. 500 μL of water was added to the final precipitate. Finally, an aqueous solution of NaBH₄ (0.01 M, 100 μL) was added to the block copolymer solution with vigorous mixing to reduce silver ions. The resulting seed-decorated block copolymer assemblies were purified by centrifuging the solution at 18,000 rpm for 30 min and replacing the supernatant with water. The solution was aged for seven hours before use for the shell growth.

Results and Discussion

Spiky nanoshells were synthesized using commercial polymer beads as well as block copolymer assemblies as templates. The general synthetic method is outlined in Figure 1A. Virtually, any negatively charged template can be used for the synthesis. In this study, we used two different types of polymeric nanostructures, carboxylate-modified polystyrene (PS) beads (100 nm, FluoSpheres, Invitrogen) and self-assembled nanostructures of anionic amphiphilic block copolymers. In typical experiments, small seed particles of silver (∼2–3 nm) were first synthesized on PS beads by reducing [Ag(NH₃)₂]⁺ adsorbed on PS beads with NaBH₄. To grow spiky nanoshells, the seed-decorated PS beads were placed in a growth solution containing partially reduced gold (i.e., Au⁺) and CTAB. The growth solution was prepared by mixing HAuCl₄, silver nitrate, ascorbic acid, and CTAB. After the solution color was fully developed (∼2 h), the spiky shells were precipitated by centrifugation and redispersed in water.

Transmission electron microscope (TEM) images (Figure 1B–C) revealed that synthesized gold shells were covered with sharp spikes. The yield of spiky nanoshell formation was very high (∼100%), and the final product was free of small particles and other nanostructures (Supporting Information). The synthesis of spiky nanoshells can be carried out in one step if the appropriate amount of gold is used or in consecutive steps where partially covered polymer beads are used to grow complete shells (Figure 1A). Figure 2A presents TEM images of seed-decorated PS beads (left) and metal nanoshells with different gold coverage (i–iii) obtained by varying the amount of seed-decorated PS beads relative to the amount of growth solution. At a high concentration of seed-decorated polymer beads, metal nanospheres were formed on the surface of PS beads (Figure 2A(ii)), which possessed an SP band at 535 nm (Figure 2C(ii)). With an increase of gold precursors, the surface gold coverage was increased with a significant red shift of the SP band to 650 nm (Figure 2A–C(ii)). With a further addition of growth solution, complete shells of gold spikes were formed around PS templates (Figure 2A(iii)). The spiky shells exhibited an extinction coefficient of 2 orders of magnitude higher than that of low coverage beads. Figure 2D showed a gradual red-shift of the SP band into the near-IR region and increases in extinction (Figure 2D,E) with reaction time. The extinction coefficient was calculated using the concentration of FluoSpheres given in the product specification and assuming that there is no loss of polymer spheres during the synthesis. Thus, this estimation provides a minimum possible number, and the actual extinction coefficient can be potentially higher than this estimated value.
spiky nanoshells is substantially higher than that of smooth shells for the same amount of gold.\(^{37}\)

The synthetic method has been extended to make spiky gold nanoshells of various morphologies by using self-assembled nanostructures of amphiphilic block copolymers composed of PS and poly(acrylic acid) (PS-b-PAA) (Figure 3). Amphiphilic block copolymers can be self-assembled into various nanostructures in water including spheres, rods, vesicles, and bilayers by controlling the length of polymers or other self-assembly conditions such as concentration, ionic strength, pH, and solvent.\(^{28}\) In this study, PS-b-PAA was self-assembled by the slow addition of water to the solution of block copolymers following a well-established literature procedure.\(^{28}\) Various morphologies were obtained including spherical micelles, rod-like micelles, and vesicles by controlling the initial solvent that the polymers were dissolved in. The prepared block copolymer assemblies were transferred into water by dialysis and used for the synthesis of spiky nanoshells. Different-sized spherical spiky gold shells were prepared by using spherical assemblies of two different sizes (44 and 110 nm) (Figure 3A,B). The morphology obtained with 110 nm assemblies was similar to that of spiky nanoshells prepared with commercial PS beads (Figure 3B). The nanoshells prepared with 44 nm particles possessed a rough surface, although the rods grown on the surface were not as sharp as the ones made with bigger assemblies (Figure 3A). Block copolymer templates with a higher radius of curvature (diameters smaller than 44 nm) did not form a complete nanoshell due to interparticle aggregation. Micrometer-sized shells were also prepared by using large vesicles as templates (Figure 3C).

The ability to control the shape of nanoshells has been shown to be important for many in vivo applications of nanoparticles.\(^{38}\) For example, it has been shown that the shape of nanoparticles significantly affects the cellular uptake of nanoparticles.\(^{39}\)

Figure 3D–F presents TEM images of anisotropic nanoshells obtained by using rod- and worm-like micelles and bilayers as templates. Currently, silica nanoparticles are the most commonly used template for the nanoshell synthesis,\(^{40}\) partly because silica particles can be easily synthesized in uniform sizes by the well-established Stöber method.\(^{40}\) However, the synthetic method produces only spherical nanoparticles, and the synthesis of anisotropic silica particles is more complex.\(^{41}\) Researchers have also used polymer beads\(^{42,43}\) and copolymers\(^{44,45}\) as the dielectric core for the metal shell formation. However, only spherical polymeric structures have been used in those syntheses. With the block copolymer approach described here, various shapes of nanoshells can be readily prepared as shown in Figure 3. While amphiphilic block copolymers have been widely used as templates to form well-defined metal nanostructures in the core\(^{46–48}\) or on the corona\(^{44}\) of spherical micelles, we believe that our work is the first to synthesize gold shells of various shapes using a range of different polymer templates made through the self-assembly of block copolymers.

More complex nanostructures can be prepared by the self-assembly of nanoparticles and block copolymers. Amphiphilic block copolymers have long been used to encapsulate hydrophobic molecules and nanoparticles in the core of the assemblies.

\(^{37}\) For example, spiky nanoshells composed of 60 cones (radius, 18 nm; height, 35 nm) covering a 20 nm thick gold shell (100 nm core) possess 66% larger surface area compared to the smooth shells with the same amount of gold.


We used this capability to prepare spiky gold nanoshells incorporating Fe₃O₄ (Figure 4B) and ZnS-coated CdSe nanoparticles (Figure 4E). Nanoparticle-encapsulating block copolymer assemblies were first prepared by the simultaneous self-assembly of block copolymers and nanoparticles, following a previously reported procedure. The assemblies were then used as templates for the growth of gold shells, forming magnetically active spiky gold nanoshells (Figure 4C). The photoluminescence of ZnS-coated CdSe nanoparticles in spiky gold shells (Figure 4E) was completely quenched at the current geometry due to the energy transfer to gold. However, with a careful control of the nanoparticle geometry, it might be possible to prepare photoluminescent gold nanoshells. This work demonstrates that the block copolymer templated synthesis described here can be used to generate multifunctional metal nanoshells containing various types of nanoparticles. In addition, unique morphologies such as hammer-like gold shells can be prepared by using the self-assembly of block copolymers and nanoparticles (Figure 4E), which is difficult to achieve by other types of templating materials.

Conclusions

We developed a high-yield synthetic method that generates a new type of metal nanoshells with protruding sharp spikes. The spiky nanoshells possess very high surface roughness, which makes them a promising material for various applications of metal nanoparticles including spectroscopy, imaging, and medicine. We have used block copolymer assemblies as templates to create gold nanoshells of various shapes such as tube-like structures and hammer-shaped shells, which are not easily obtained through typical silica templates. We have also shown that nanoparticle-encapsulating block copolymer assemblies can be used to generate multifunctional nanoshells, demonstrating the versatility of the synthetic approach.

Acknowledgment. This work was supported by NSF career award and ARO new investigator award.

Supporting Information Available: Additional figure as described in the text. This material is available free of charge via the Internet at http://pubs.acs.org.