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# Nanorice and Nanospears from Polymer Nanospheres\*\*

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Nanometer-sized functional particles are attractive for optical, electrical, magnetic, and biological applications. Recently, in addition to size, the shape of a nanoparticle was reported to be crucial, for example, to how it interacts with light, as presented by Halas and co-workers.<sup>[1]</sup> They found that rice-shaped nanoparticles made of gold and iron oxide are the most sensitive surface plasmon resonance (SPR) nanosensors yet devised. They hope to get a clearer picture of proteins and unmapped features on the surfaces of cells by attaching them to scanning probe microscopes.

Although there are tremendous potential advantages of using anisotropic nanoparticles like nanorice instead of conventional spherical nanoparticles, the development of controlling such shape on the nanoscale is in its early stages. Some controlled growth of the end shape of nanorods with specific equipment at specific conditions has been reported for inorganic or metallic nanoparticles.<sup>[2,3]</sup> Even though polymer nanorods and nanotubes have commonly been produced since the fabrication was introduced by Wehrspohn and co-workers,<sup>[4]</sup> terminal contour control of polymer nanoparticles like nanorice or nanospears has remained a challenging task. If functional polymer nanoparticles can be shaped in the desired forms on the nanoscale, they can easily be functionalized to have much enhanced multifunctional properties using them as templates or substrates. In the fabrication of nanorods and nanotubes, template-assisted fabrication is gaining widespread interest because of its simplicity. Such novel nanostructures are expected to provide new functions in optoelectronic and biological applications that can not be attained with conventional spherical nanoparticles. Researchers have used various kinds of membranes such as polycarbonates and anodized alumina membranes as templates for the fabrication of nanotubes and nanorods.<sup>[5-9]</sup> However, no report of polymer nanorods has shown control of both aspect ratio and terminal contour. Additionally, no polymer nanospheres have been incorporated into the production of nanorods. Mostly, monomers, polymer melts, or solutions are introduced into the

nanopores for the production of nanorods and nanotubes. Other template-assisted techniques use the step-edge method<sup>[10-12]</sup> and other methods involving template molecules in solution.<sup>[13]</sup> Other nanorod-production techniques that do not require templates include the electrospinning of nanofibers<sup>[14,15]</sup> and also the use of biomolecules and self-assembly processes.<sup>[16,17]</sup>

The techniques that use membranes as templates include electrodeposition,<sup>[18]</sup> layer-by-layer deposition,<sup>[19-21]</sup> and methods using commercially available metal-plating solutions.<sup>[22,23]</sup> Zheng et al. have fabricated copolymer nanotubes and nanowires by having polymerizing copolymers inside the pores of alumina membranes.<sup>[24]</sup> Anisotropic metallic nanoparticles like conical nanotubes rather than cylindrical nanotubes and nanorods have also been fabricated. Such anisotropic nanoparticles were fabricated using either a complex chemical vapor deposition setup<sup>[25]</sup> or a tapered pore that was coated with gold.<sup>[26]</sup> However, in this paper we report, for the first time, the fabrication of tapered nanorods of varying aspect ratio and controlled terminal contour (e.g., from nanorice to nanospears) using a simple method. First, our method exploits the injection of a controlled amount and size of nanospheres into the cylindrical nanopores of an alumina substrate. Second, the resulting nanostructures are controlled during the nonuniform heating of the polymer nanospheres by capillary forces, and wetting (or dewetting) onto the cylindrical alumina walls.

To achieve faster production and also obtain subtle variation in the shape, size, and aspect ratio of nanoparticles, we created a fabrication method using polymer nanospheres and anodized alumina membrane templates that controls the structure of the resulting nanoparticles. Our system for fabricating novel nanorice and nanospears is easy to set up and perform on a laboratory bench top. Nanoscale fabrication was made possible without the use of an elaborate setup involving vacuum chambers or expensive equipment that are normally required for lithography-based fabrication. The cost of running the experiment was very low and the fabrication of different types of nanostructures was easily performed by changing key parameters, such as the particle size, template pore size, duration of ultrasonication, and temperature or heating time.

In this work, we used commercially available alumina membranes (Whatman anodized alumina membrane) as templates and polystyrene (PS) nanospheres (neutral, carboxylated, or sulfated PS) for the fabrication of controlled aspect ratio and terminal-contour-controlled nanoparticles (i.e., nanorice and nanospears). The pores of these membranes were filled with

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nanospheres by a solvent-aided injection. Subsequent heat treatments then allowed the nanoparticles to coalesce and wet (or dewet) from the alumina nanopore walls and form nanoparticles with a controlled aspect ratio and an interesting terminal curvature (i.e., round to sharp or pointed). We assembled a small solvent-aided nanoinjection unit for injecting materials into the cylindrical alumina nanopore membranes, as shown in Figure 1.

Figure 2 illustrates the overall process. A specific amount of PS nanosphere suspension was put in the reservoir and then it was pumped through membranes with desired pore sizes in series (first large and then small pores) or a membrane having

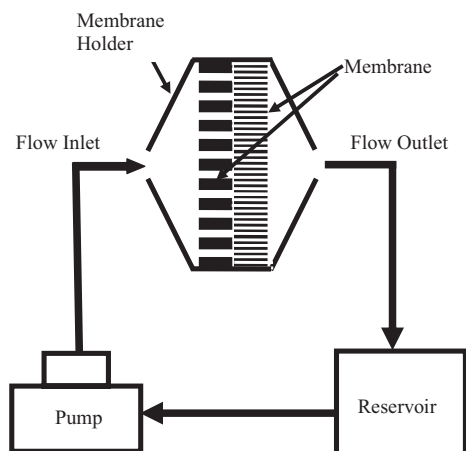


Figure 1. A system for solvent-aided nanoinjection of nanospheres.

both large and small pores on each side. The size of the nanospheres was in between the large and the small pores so that the nanospheres are trapped only in the large pores. Once the large-pore membrane was filled with the desired amount of nanospheres it was carefully taken out, heated at 120 °C (above the glass-transition temperature,  $T_g$ , of the polymer) for various amounts of time, and then placed in a 3 M NaOH aqueous solution where the alumina membranes dissolved. Then, the remaining polymer nanoparticles were filtered using a centrifuge and washed several times in deionized (DI) water to remove any residual NaOH. To image the resulting structure of nanoparticles, a drop of the sample suspension was put on a glass slide and then dried. The dried samples on the glass slide were sputtered with gold (around 5 nm thick) for scanning electron microscopy (SEM) analysis. The scanning electron microscope used for high-resolution imaging was a JEOL 6300F with field emission.

Figure 3A shows that the resulting nanorods tapered at the ends were made of (8.1 mg of 140 nm PS nanoparticles in 200 mL of water) PS nanospheres in a 200 nm pore-sized alumina membrane stacked against a 20 nm pore-sized membrane. A unique and peculiar terminal contour was observed in these polymer nanorods (i.e., nanospears). As far as we know, there has been no report on such sharply pointed polymer nanorods that were fabricated with a uniform size at the nanometer scale. Figure 3B shows tapered nanorods of smaller aspect ratio (i.e., nanorice) that were fabricated by reducing the amount of nanospheres injected through the membrane. Figure 3C shows a higher-magnification image of the nanorice. In addition, we used smaller nanospheres and a

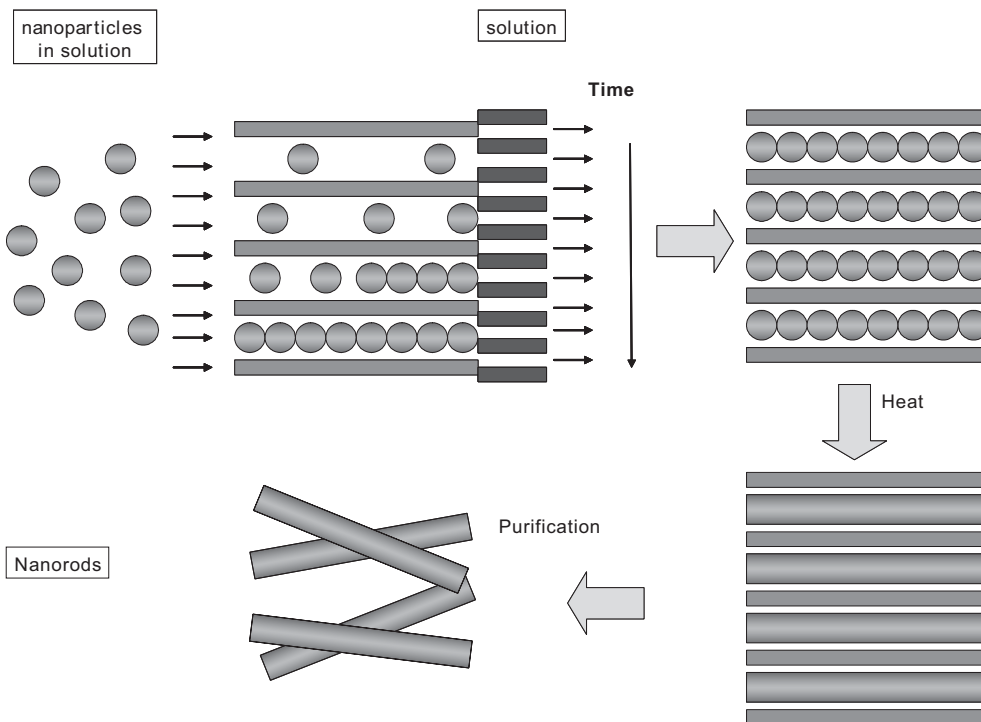
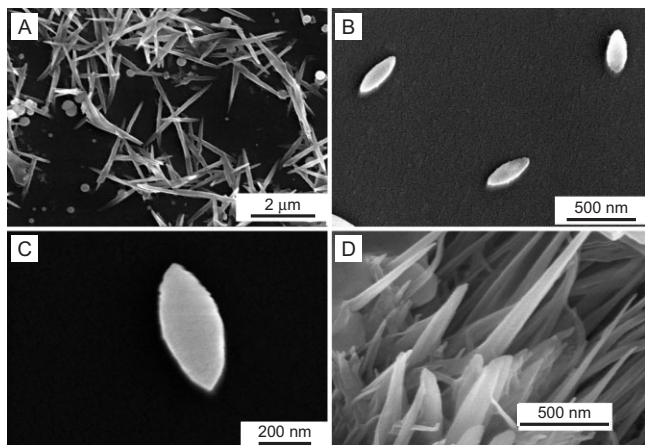


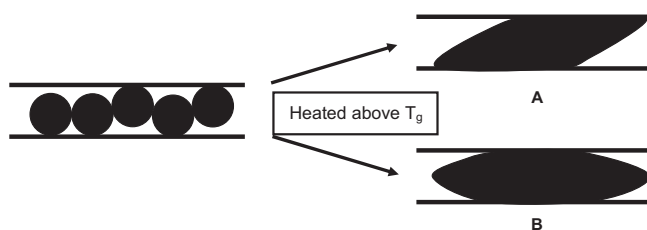
Figure 2. Schematic illustration of the solvent-aided nanoinjection molding process using alumina membranes with cylindrical nanopores.



**Figure 3.** SEM images of novel tapered nanorods. A) Nanospears made of PS nanospheres (aspect ratio  $\sim 10$ ). B) Nanorice (small aspect ratio ( $\sim 2$ ) tapered nanorods). C) Higher-magnification image of nanorice. D) Nanospear bundles formed by pumping 50 nm PS particles into a single membrane that has 20 and 200 nm pore sizes at either ends. The nanospheres were pumped into the 200 nm pore side.

smaller membrane. This membrane had two pore sizes at each end, 20 and 200 nm. Both pores were cylindrical and they met at around 2  $\mu\text{m}$  from the 20 nm end. The concentration for 50 nm PS nanospheres was 2.3 mg in 200 mL of DI water. 100 mL of this suspension was injected from the large-pore side to the small-pore side and then heated at 120  $^{\circ}\text{C}$  for 2 h. Since these nanospheres (50 nm) were much smaller than the large pores (200 nm) they must have been closely packed and in this case we observed much longer and sharper tapered nanowires, as shown in Figure 3D. The composition of the particles was confirmed to be mainly carbon without Al by energy dispersive X-ray (EDX) spectroscopy analysis (data not shown).

A possible explanation for the formation of the tapered tip is illustrated in Figure 4. When the cylindrical pore diameter of the membrane was 200 nm and the PS nanospheres were 140 nm in diameter, nanospheres aligned themselves in the cylindrical pores. The pore diameter was larger than the nanosphere diameter. Hence, all the nanospheres (140 nm) had only a small contact area with the pore wall, as shown in the left side of Figure 4. This figure illustrates an exaggerated ef-



**Figure 4.** A) Schematic representation of forming tapered nanorods and nanospears forming due to wetting. B) Schematic representation of forming tapered nanorods and nanospears due to dewetting.

fect of nonuniform heating resulting in the coalescence of nanospheres, and the shape change caused by wetting (or dewetting) and capillary forces.

As the nanospheres-filled membrane was heated above the glass-transition temperature of the polymer used, there would be two main heating mechanisms: conduction through the alumina wall and convection via air. The radiation would be negligible because of the low temperature. In the first case the pore wall is a better heating source than air. There would be more heat transfer through the small contact area between the wall and nanospheres than through air. Hence, the nanospheres would start to partially deform and wet at the pore wall. As polymers are being softened in the cylindrical nanodomain, capillary forces play an important role in moving and shaping the softened polymer.

Capillary forces can allow these softened polymers to flow slowly onto the nanopore walls; thus,<sup>[4,27]</sup> adjacent nanospheres coalesce to form a continuous shape. The nanosphere at the end just stretches further along the cylindrical nanopores. As the temperature is slightly above the glass-transition temperature of PS, there is only partial wetting of the pores by the softened PS, as discussed by Zhang et al.<sup>[28]</sup> This implies that the softened PS forms a meniscus at the ends, as is observed by Zheng et al. in the formation of PS nanorods. But, in our case, as PS nanoparticles are used, this partial wetting and limited supply of polymer leads to the formation of tapered nanospears and nanorice. Alternatively, as the end nanosphere does not have another nanosphere to coalesce with it forms a tapered end due to partial wetting, as illustrated in Figure 4A. On the other hand, when heat convection is dominant, the softened polymer parts will be on the outside of nanoparticles, rather than the nanosphere-wall contact region. The softened polymers can connect neighboring nanoparticles together to form nanorods. At both ends, the softened polymers from the outsides of nanoparticles which can be further extended to the empty sides by capillary forces, resulting in the formation of nanorounded (nanorice) or nanosharpened edges (nanospears), as illustrated in Figure 4B.

The terminal contour development of nanorice or nanospear is somewhat similar to that of icicles, in which water added to the outside icicles moves toward the narrow tip by the force of gravity. In this system, the external force analogous to the gravitational force will be the capillary forces which lead to the tapering of the ends to form tapered nanorods. Hence, in the formation of nanorods with sharp terminal contours, capillary forces along with wetting (Fig. 4A) or dewetting (Fig. 4B) may play an important role, which can be related to the nonuniform heating by either conduction or convection at the nanometer scale. In summary, the softened polymer nanospheres nonuniformly heated to a temperature above the glass-transition temperature tend to stretch slowly to form tapered nanorods.

During the solvent-aided nanoinjection process, the nanospheres tend to stay separated from each other rather than sit adjacently. Intermediate ultrasonication of the membrane is required to tightly pack the nanospheres into the membrane

pores. This intermediate step of ultrasonication after pumping the specified amount of nanosphere suspension also helped to remove excess particles that tend to stay on the membrane surface. These particles could prevent further nanospheres from being delivered to the membrane pores and reduce the aspect ratio of the nanorods.

As shown in Figure 5, we also observed various other nanostructures like incomplete nanotubes (i.e., perforated nanotubes) (A, B, and C), broken nanodoughnuts (D), and nanodiscs (E). These nanostructures show evidence of the thermal wetting of PS onto the cylindrical alumina nanopore walls as heat transfers to PS nanospheres through the wall. It is expected that further variation of the PS nanosphere packing, heating temperature, and time would allow the fabrication of novel nanostructures. Figure 5F illustrates the intermediate step in the coalescence of the particles. Due to a short heating time, the spherical particles have not completely lost their structure. The nanospheres towards the middle can be seen merging together, whereas the nanospheres at the end tend to form a slightly tapered shape.

Currently, we are further modifying our method to achieve better control of the aspect ratio and terminal contour of the elongated nanoparticles. The key parameters governing the final shape of the nanostructures are the nanopore and nanosphere sizes along with heating temperature and time. Experiments are being conducted to observe the effects of these parameters and how the fine tuning of other key parameters can lead to more interesting shapes.

In conclusion, we present a very versatile and effective approach for shaping nanoscale structures using ordered nanopored membranes and a simple solvent-aided nanoinjection

molding process of polymer nanospheres. By exploiting nonuniform heating and resulting wetting or capillary forces of nanospheres filled inside the cylindrical nanopores of membranes we obtained novel nanostructured, anisotropic nanoparticles such as nanorice and nanospears. As far as we know, these nanostructures are unique and have not been prepared using other methods. This method is very easy to implement without any complicated chemistry or expensive equipment. Therefore, after obtaining spherical nanoparticles of any materials, this method can easily change the symmetrical nanoparticle into other geometries with less symmetry.

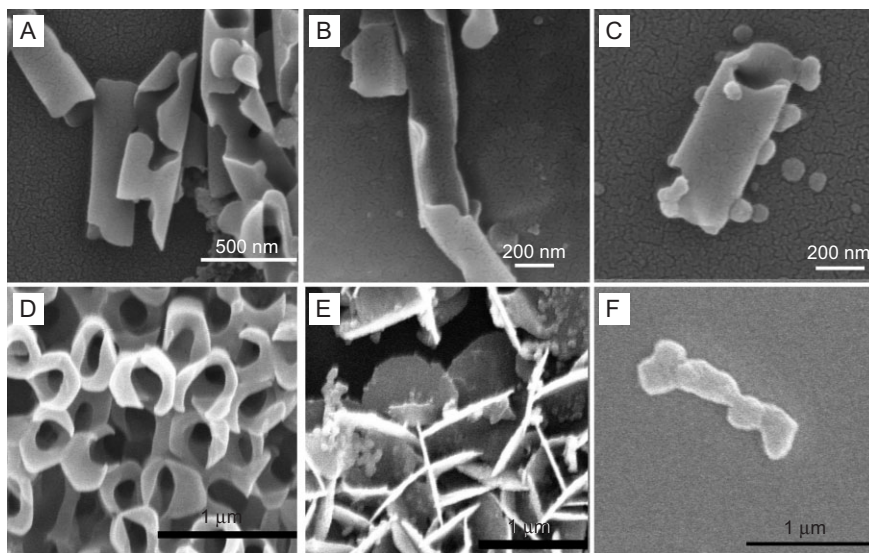
### Experimental

A system was assembled as shown in Figure 1. For nanospears 8.1 mg of 140 nm diameter PS nanoparticles (Polysciences) were suspended in 200 mL of DI water. This solution was pumped through a 200 nm pore-sized alumina membrane (Whatman) stacked against a 20 nm pore-sized membrane. The membranes were removed and the 200 nm pore-sized membrane was heated at 120 °C for 2 h. The membrane was dissolved in 3 M NaOH and subsequently washed in DI water and dried on glass slides for imaging using SEM. For nanorice, only 25 mL of the same solution was pumped and the rest of the procedure was exactly the same. The concentration for 50 nm PS nanospheres was 2.3 mg in 200 mL of DI water. It was pumped through a membrane which has 200 nm pore sizes on one end and 20 nm pore sizes on the other end. 100 mL of this suspension was injected from the large-pore side to the small-pore side and then was heated at 120 °C for 2 h. For 100 nm PS particles the concentration used was 2.63 mg in 200 mL of DI water.

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**Figure 5.** SEM images of incomplete nanorods using nanospheres. A) Incomplete nanotubes were observed after sintering of 140 nm PS nanoparticles inside 200 nm pore-sized membranes. B) A half open nanotube formed inside a 200 nm pore-sized membrane. C) A small-aspect-ratio nanotube. D) Broken nanodoughnuts using 140 nm particles in a single 200–20 nm pore-sized membrane. E) Nanodiscs formed using 100 nm PS spheres in a single 200–20 nm membrane without ultrasonication. F) An intermediate structure with incomplete melting of the polymer nanospheres.

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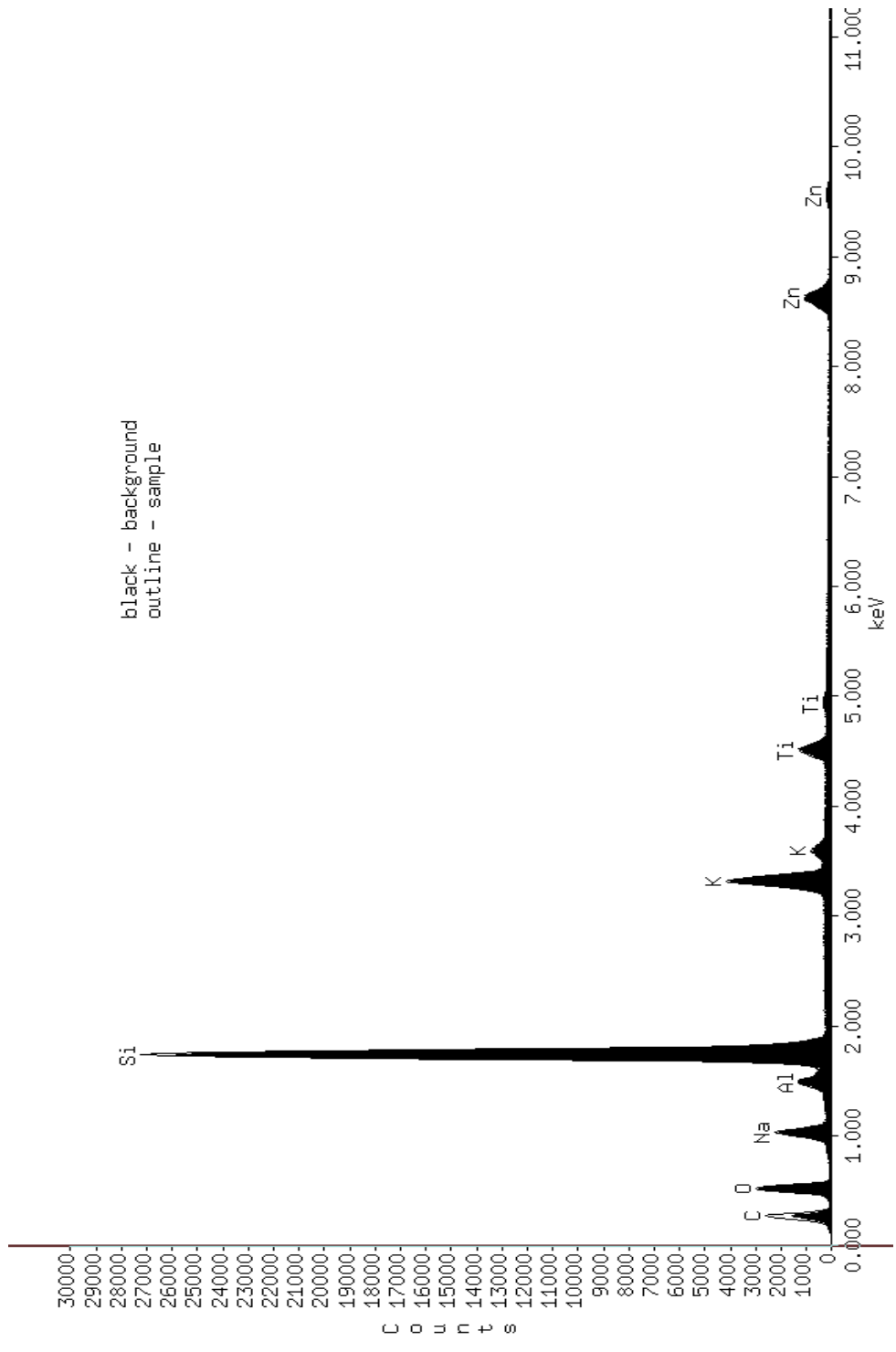
# ADVANCED MATERIALS

**Supporting Information**

for

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Energy dispersive spectrum (EDS) of fabricated nanoparticles is shown above. The black spectrum is the background and the line is the spectrum of the fabricated nanoparticles. The difference in the count of carbon content shows the presence polystyrene which is composed of carbon and rest of the elements do not show any increase.