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Mechanical Nanosprings: Induced Coiling and Uncoiling of Ultrathin Au Nanowires

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Abstract: We report the controllable coiling of colloidal gold nanowires induced by the contraction of their polymer shells. The mechanical energy stored in this process can be released upon removal or swelling of the polymer shells.

A common strategy in nanoscience is to mimic the structure and concept of macroscopic devices to achieve novel functions. Coiled springs are elastic metal objects with structural memory. Their ability to store and release mechanical energy has led to their widespread applications. Likewise, controlling mechanical energy at nanoscale would be an important step toward nanoengineering. A tremendous amount of research effort has been devoted to mimicking coiled springs in nanoscale, but the methodologies are still quite limited. Most of the coiled nanofilaments in the literature were directly synthesized by gas-phase deposition of a material on a substrate at a high temperature. The structural twisting was proposed to be caused (a) by a dislocation-driven growth mode;[1a−c] (b) by the surface charge imbalance on oxide nanowires (NWs) or nanobelts;[1d−f] or (c) by the anisotropy in the extrusion of carbon nanotubes (CNTs) from catalytic particles.[1g,h] Single-wire studies have demonstrated the mechanical flexibility of several helical nanosprings.[1e,h] In addition, CNTs were known to spontaneously coil under various treatments,[2a−c] likely to maximize packing among the overlapping loops. However, these methods are generally not applicable for coiling metallic filaments, which has been rarely reported.[2d] Just as in macroscopic springs, metal would be a favored material owing to its flexibility and resilience.

Here, we report a new approach to induce the coiling of prefabricated AuNWs in high yield (Figure 1), giving a structure resembling that of torsion springs. The mass transformation of straight wires to circular rings is achieved in a colloidal solution by modulating the contraction of encapsulating shells made of polystyrene-*block*-poly(acrylic acid) (PSPAA). Unlike most of the existing nanosprings, the *induced* coiling stored elastic energy in the stressed AuNWs. As a proof-of-concept demonstration, this energy was released when the nanosprings spontaneously uncoiled upon removal or swelling of the polymer shells.

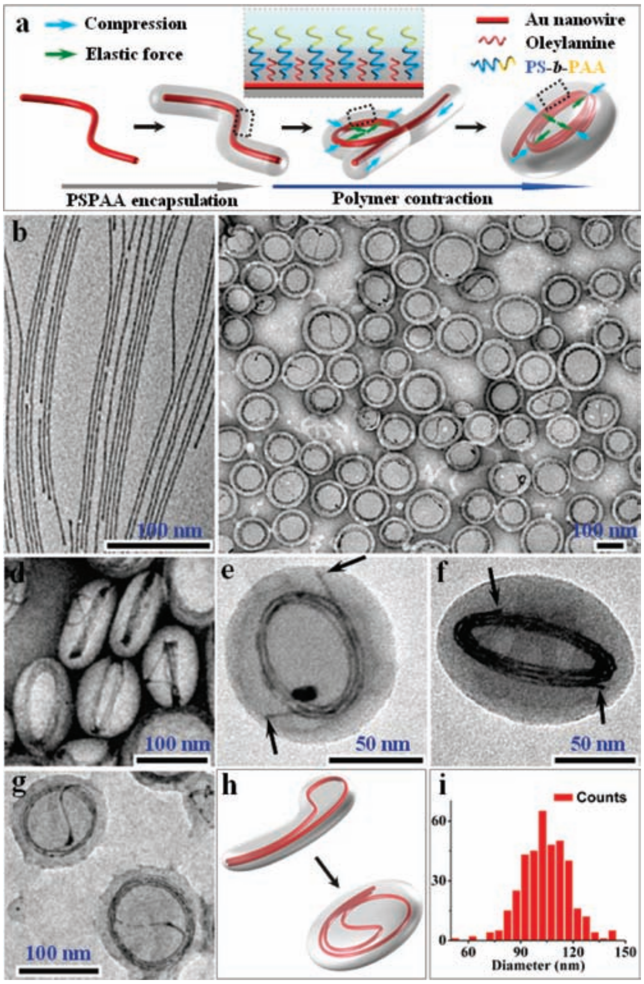

Figure 1. (a) Schematics showing the polymer-induced coiling of AuNWs. TEM images of (b) as-synthesized oleylamine-stabilized AuNWs; (c, d) coiled nanosprings embedded in PS$_{154}$-*b*-PAA$_{49}$ micelles; (e, f) two typical Au nanosprings from different perspectives, with arrows indicating their ends. (g, h) TEM image and schematic illustration of a typical Au nanospring that did not coil along its first loop but via a new loop formed by the folded double-wire. (i) Diameter distribution of the Au nanosprings.

Surface-templated self-assembly of PSPAA provides a facile route to fabricate uniform shells on various types of nanoparticles, where PS blocks attach to the hydrophobically functionalized particle surface and PAA blocks dissolve in water facing outward.[3a−d] The minimization of the PS−solvent interface typically makes free PSPAA micelles spherical in shape. On Au nanorods, the encapsulating PSPAA micelles were often thinner on the ends and thicker on the sides; this deformation of the shell structure manifested sizable surface tension.[3e,f,4] We were intrigued by the notion that, conversely, the cores might be made to deform with the force exerted by polymer shells. Thus, we tested this idea on ultrathin AuNWs[5a] that were expected to have low flexural strength.

The oleylamine-stabilized AuNWs were synthesized[5a] and purified[5b] as previously reported (Figure 1b). However, our standard encapsulation methods[3b−f] did not work as the ultrathin AuNWs

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were prone to aggregation in DMF solutions and they easily fused or dissolved away upon heating.[4] A room temperature method was thus developed: the as-synthesized AuNWs were mixed with PS_{154}-*b*-PAA_{49} dissolved in a ternary solvent mixture, DMF/THF/H_2O (4:4:1, v/v/v), and then incubated for 24 h. THF was used to improve the solubility of the oleylamine-stabilized AuNWs, and the large percentage of organic solvents was intended to swell the polymer and facilitate its assembly at room temperature. The sample was then diluted by water to deswell the polymer shells and centrifuged to remove the excess solvent and free PSPAA micelles.

Instead of random coils, however, the originally straight AuNWs were unexpectedly transformed into orderly structures (Figure 1c), with each polymer micelle containing one coil of 5−10 loops (AuNW@PSPAA). The Au nanosprings appeared highly circular (94% yield) for the well-separated ones on a TEM (transmission electron microscopy) grid. At crowded regions (e.g., Figure 1d), some nanosprings offered side views showing that the overall PSPAA shells had shapes of circular discs and that the metal coils consisted of closely packed coplanar rings. Considering the radii of the nanosprings (52.1 ± 6.7 nm) (Figure 1i), the overall circumferences of the loops were in general agreement with the original length of the AuNWs (ca. 1−2 μm;[4] the AuNWs often break during TEM characterization, e.g., Figure 2b). Close inspection showed that the nanosprings often revealed two ends (Figure 1e, f) with arguably chiral structures, suggesting that they each originated from a single wire. A slightly different polymer, PS_{144}-*b*-PAA_{22}, could also be used to fabricate similar nanosprings.[4]

Since the AuNWs cannot spontaneously coil up, the PSPAA must have played a critical role. To trap the coiling intermediates, amine-functionalized TEM grids (positively charged) were used to fix the negatively charged PSPAA micelles.[4] Most of the AuNW@PSPAA directly trapped from the encapsulation solution (4:4:1 DMF/THF/H_2O, 11% water) were single wires with cylindrical shells of 20 nm (72% yield, Figure 2a),[4] supporting our assertion that the nanosprings were single-wire coils. The shells were thicker than those on nanoparticles in our previous reports,[3b−d] presumably because they were trapped and fixed to the substrate before the deswelling with the addition of water. The free spherical micelles in this sample showed that the PSPAA cannot form cylindrical micelles[6a] by itself under the same conditions. Importantly, this result indicated that the coiling of the AuNWs must have occurred *after* the PSPAA attachment, and probably during the addition of water. In general, addition of water deswells the PSPAA micelles, increasing the PS−solvent interfacial tension[6] and decreasing the mobility of polymer.

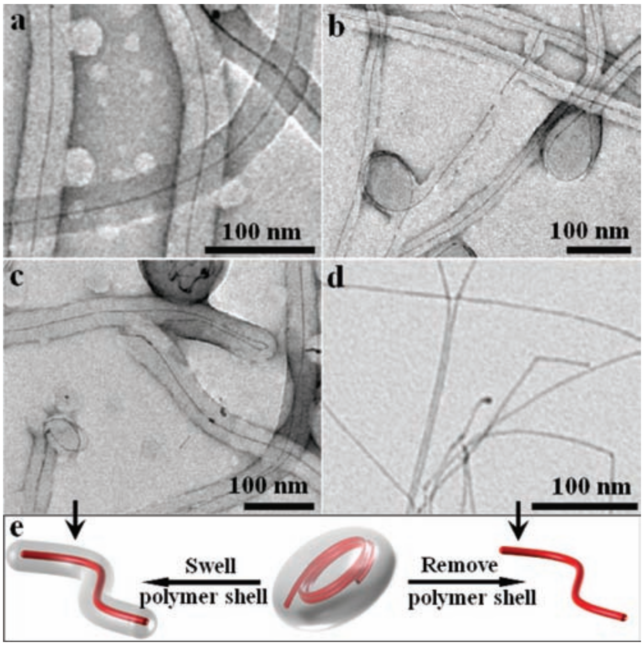

Figure 2. TEM images of AuNW@PSPAA trapped under the conditions of (a) 11% water, giving coaxial core/shell structures; (b) 23% water, giving racket-shape intermediates; (c) after swelling the nanosprings using 4:4:1 DMF/THF/H_2O; and (d) after dissolving the nanosprings in THF. (e) Schematic showing the spontaneous uncoiling of AuNWs.

After addition of water (23% v/v) and incubation for 20 min, racket-shaped structures[7] were found with 50% yield among the trapped AuNW@PSPAA (Figure 2b). At 41% water, most of the AuNW@PSPAA turned into nanosprings, which are stable with further addition of water. The incubation in the low-water solvents allowed the AuNWs to equilibrate in the viscous polymer and improved the yield of nanosprings. After this step, the nanosprings can be redispersed in pure water, where they remained stable for weeks. Quick addition of a large amount of water (>99%) to the AuNW@PSPAA in 4:4:1 DMF/THF/H_2O gave mostly random coils,[4] but we were not able to trap intermediates from the redistribution of PSPAA.

Thus, the increase of PS−solvent interfacial tension likely led to the contraction of the polymer micelles, which initiated the coiling of AuNWs. We postulate that the PSPAA shell exerted a compressive force on the AuNW, causing it to bend and then twist to form the first loop (Figure 1a). The PSPAA shell on the metal coil maintained inward compression, counteracting the induced elastic tension. Some of the first loops after incubation at 23% water can be trapped as rackets[7] or folded single wires (Figure 2b). Once formed, the first loop could template the formation of the subsequent loops, possibly assisted by weak van der Waals attraction among the loops. At the final state, the AuNW formed a circular ring to evenly distribute its internal stress. Apparently, some of the AuNWs did not coil along their first loops and the racket-shaped intermediates were further coiled via new loops of the folded double wires (Figure 1g−h). About 8% of the nanosprings were coiled through this pathway, as judged from the remaining racket heads (Figure 1c).

In the literature, the coiled nanofilaments from direct synthesis[1] were probably at thermodynamic minima (not global minima), and the spontaneous coiling of CNTs[2a−c] was likely driven by the attraction among the loops. As such, it remains challenging to exploit the uncoiling of these nanostructures.[1e] In contrast, the coiling of AuNWs here was driven by the energy minimization of the combined AuNW−polymer system. As a PSPAA micelle lowered its surface energy by contraction, the strain energy in the AuNW increased as its outer surface stretched in tension while the inner surface compressed. Thus, the AuNW stabilized as a circular coil when its outward elastic tension reached a balance with the isotropic inward compression from the ellipsoidal PSPAA shell (Figure 1a).

To probe the tension in the AuNWs, the polymer shell on the nanosprings were swelled in DMF/THF/H_2O (4:4:1) in the presence of excess PSPAA (Figure 2c) or dissolved away by pure THF (Figure 2d). As a result, the coiled AuNWs spontaneously sprang back to give nearly straight wires, releasing the internal stress. Apparently, the elastic potential energy stored in the nanosprings was larger than the attractive interactions among the loops. However, a significant number of kinks were observed in the uncoiled AuNWs. Since the addition of organic solvent affected both the surface tension and the liquidity/mobility of the polymer shells, it is conceivable that the swelling may not have occurred uniformly within the shells as the AuNWs uncoiled. This would focus the released mechanical energy onto a few spots and cause inelastic deformations of the AuNWs.

In summary, we report the first example of storing and releasing mechanical energy at nanoscale by a simple solution-phase process. The self-assembled polymer shells served as a unique tool to manipulate the entire population of colloidal gold nanowires. This simple methodology could be potentially applied to other systems involving different nanofilaments, such as nanowires or nanotubes,[8] and different polymer shells such as polystyrene or conductive polymers.[9] We believe the environment-responsive transformation of AuNWs and the control of their mechanical energy could be applied to fields such as biology, nanofabrication, and nanoengineering.

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Supporting Information Available: Details for experimental procedures, large-area views of TEM images. This material is available free of charge via the Internet at http://pubs.acs.org.

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