A simple template-based synthesis of three-component nanorods with flexible central sections is discussed. These nanorods become flexible by dissolving their central silver sections in dilute hydrogen peroxide, to leave behind a flexible yet robust residue. It is also shown that the flexible region can be reinforced by adding a polymer additive to the plating mixture.

Nanowires have seen a host of new applications in recent years from self-propulsion and transportation of colloidal cargo to energy generation, biosensing, and the fabrication of advanced optical and acoustic devices. One factor that has undoubtedly contributed to the rise of nanowire technology has been the ability to grow these nanowires and modify their surfaces via a variety of methods. Recently, Ozin and coworkers reported the first synthesis of nanorod structures with well-defined flexible regions. Wang and coworkers followed by publishing a second, simpler synthetic procedure for making flexible nanorods in a communication that focused on the applications of the rods rather than a detailed characterization. This paper explores the makeup of these as-yet ill-defined flexible nanorods and describes a related method to prepare a new type of more robust, reinforced flexible nanorods.

Flexible nanorods were prepared by a method similar to that reported by Wang and coworkers (see Methods). Briefly, when three-segmented gold-silver-gold, \{Au-Ag-Au\}, nanorods that had been synthesized via the template method were placed in solutions of dilute H\(_2\)O\(_2\) (~1% v/v) and imaged under a microscope, their central sections became transparent over the course of a few minutes. This length increase came at a cost however, as very long tethers had a tendency fold back on themselves, collide and entangle with other nanorods, or break apart.

When these three-segment \{Au-Ag-Au\} nanorods were initially exposed to H\(_2\)O\(_2\), during the brief time interval before the central section became completely transparent, the nanorods were observed to slowly translate and flex their central regions in a non-Brownian fashion. As the peroxide concentration was increased, this non-Brownian motion became more vigorous, often leading to mechanical breaking of the nanorods at higher peroxide concentrations (25% v/v). This non-Brownian motion was most likely due to self-electrophoresis of the nanorods, a propulsion mechanism which has been well-studied for other bimetallic nanorods in H\(_2\)O\(_2\) solutions. In these previously reported systems, the nanorods studied were intentionally made asymmetric in order to induce motion in one direction. Since the rods in this communication are relatively (but not completely) symmetric, the translation that was observed was much slower than that reported in previous systems. In the rare event that a rod with a partially intact, semi-transparent, central silver section cleaved in half during etching, two very asymmetric \{Au-Ag-Au\} nanorods were prepared by a method similar to that reported by Wang and coworkers (see Methods). Briefly, when three-segmented gold-silver-gold, \{Au-Ag-Au\}, nanorods that had been synthesized via the template method were placed in solutions of dilute H\(_2\)O\(_2\) (~1% v/v) and imaged under a microscope, their central sections became transparent over the course of a few minutes. (Fig. 1, Supporting Video 1). Although the central sections of these partially cleaved \{Au-Ag-Au\} nanorods could not be observed directly via optical microscopy, the central region was obviously still present in some form, since the two gold ends of the rods remained translationally paired in dilute peroxide even after enduring the randomization associated with Brownian motion in dilute hydrogen peroxide for 24 h (Supporting Video 2). In addition, these nanorods with their flexible, transparent centres remained intact even when subjected to the chaotic fluid motions associated with gentle pipette transfers.

If more concentrated solutions of H\(_2\)O\(_2\) were used to etch the silver regions, the onset of transparency and flexibility was much more rapid (< 5 s for 25% v/v H\(_2\)O\(_2\)). However, for these more concentrated solutions of H\(_2\)O\(_2\), this period of was not as long lived, and the nanorods quickly cleaved in half (Supporting Video 3).

In addition to varying the H\(_2\)O\(_2\) concentration, the length of the central silver section was also varied. As the length of the central section was increased (from 2.5 \(\mu\)m to 17 \(\mu\)m), the freedom of motion of the two ends also increased, and the central section began to behave less like a rusty hinge and more like a flexible tether (Supporting Video 4). This length increase came at a cost however, as very long tethers had a tendency fold back on themselves, collide and entangle with other nanorods, or break apart.
nanorods resulted, and as expected, the speed of these end fragments approached that of other known asymmetric self-electrophoretic nanorod systems (Supporting video 5). An alternative mechanism which may explain the observed non-Brownian motion of these rods during etching is one which involves self-diffusiophoresis. In this mechanism, the silver ions produced by the gentle etching of the silver segment create an electric field in solution which acts back on the rod resulting in motion.\(^\text{22,23}\) Likely both of these mechanisms are at play to some degree in this current system.

This chemically induced method of preparing flexible nanorods presents an interesting question: Once the silver central sections of these nanorods were dissolved away by the excess H\(_2\)O\(_2\), what was it that held the two gold tips of each nanorod together? FE-SEM images reveal that the transparent central sections of these peroxide-etched \{Au\textendash\textendashAu\} nanorods consists of spherical nanoparticles encased in a substance which has a net-like morphology (Fig. 2). TEM images confirm this structure, and also highlight that the trapped spherical nanoparticles are sensitive to the microscope’s high energy electron beam (Fig. 3). This sensitivity suggests that the nanoparticles trapped within the net are relatively electrically non-conductive.

Elemental analyses (ESI, Fig. S1, S2) indicate that the trapped nanoparticles are comprised primarily of silver. A significantly attenuated silver signal was recorded from the net-like structure. Additional signals from carbon and oxygen were present in the spectra, but did not map significantly above the naturally high background noise to any particular region of the rods. A degree of polycrystallinity was noted in the selective area electron diffraction pattern from the entrapped spherical nanoparticles (although this may be associated with an annealing of the particles by the TEM’s high energy electron beam), whereas the diffraction pattern of the net-like moiety revealed an amorphous structure (ESI, Fig. 3).

From this data, our working hypothesis became that the spherical nanoparticles trapped within the flexible region were comprised of undissolved silver oxide. These nanoparticles were protected from further dissolution by a mechanically robust net, whose exact composition and origin required further investigation. It was initially hypothesized that this net-like region was comprised of proprietary additives from the commercial plating solutions used to synthesize the nanorods; however, the net-like structure remained present even when home-made plating solutions containing only AgCN, AuCN, KCN, and deionized water were used to synthesize the nanorods.

Also helping to rule out the influence of proprietary additives from the metal plating solutions was the fact that when pure silver foil (Sigma Aldrich, 99.99\%) was exposed to 10\% v/v H\(_2\)O\(_2\) a similar amorphous network formed on the surface of the metal. During the formation the network, the colour of the H\(_2\)O\(_2\) supernatant solution gained a yellow tint. Decanting and evaporation of this yellowish

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**Fig. 2** FE-SEM images of a \{Au\textendash\textendashAu\} nanorod with a long central silver section that has been exposed to 2\% v/v H\(_2\)O\(_2\) for 5 min, creating a flexible \{Au\textendash\textendashAu\} nanorod. Large boxed inset is a higher resolution image of the smaller green-boxed region of the main image. Scale bar for larger image is 200 nm.

**Fig. 3** TEM images of a silver nanowire after being etched by 2\% v/v VWR-H\(_2\)O\(_2\) for 5 min. (a) Overview of the resulting network; (b) magnified view of the fiber-like morphology; (c) magnified view of the nanoparticle; (d) magnified view of the nanoparticle after 2 min electron beam irradiation.

**Fig. 4** SEM images of a) Silver nanowire reacted with 2\% v/v H\(_2\)O\(_2\)-Sigma. b) Silver foil after reacted with 10\% v/v H\(_2\)O\(_2\)-Sigma. c) Dried residues from the solution obtained by reacting silver foil with 30\% v/v H\(_2\)O\(_2\)-EMD. d) Residue from dried 30\% v/v H\(_2\)O\(_2\)-EMD.
H$_2$O$_2$ supernatant also yielded an amorphous residue (Fig. 4c). Subsequent experiments showed that the amorphous residue could be obtained even in the absence of silver metal, just by the simple evaporation of the H$_2$O$_2$ solution (Fig. 4d).

Since H$_2$O$_2$ can be catalytically decomposed by a variety of trace impurities, often commercial sources of H$_2$O$_2$ contain a stabilizer chemical. Although the manufacturer of the H$_2$O$_2$ used for all the above experiments, EMD Chemical (distributed by VWR, cat. WV3690, hereafter referred to as “H$_2$O$_2$-EMD”), claimed that no stabilizer was added to their product, for completeness, the above experiments were repeated with H$_2$O$_2$ from a second supplier with a similar claim, Sigma Aldrich (cat. 95313, “H$_2$O$_2$-Sigma”). In these experiments with H$_2$O$_2$-Sigma, no amorphous network was observed either on the etched pure Ag nanorods (Fig. 4a), or the etched segmented Au-Ag-Au nanowires (see ESI, Fig. S4), or the silver foil surfaces. Instead, the reaction of H$_2$O$_2$-Sigma with the silver foil left behind a collection of nanoparticles (Fig. 4b). Notably, in their original report describing the synthesis of these flexible rods, Wang and coworkers employed stabilized H$_2$O$_2$ (Sigma Aldrich cat. 216–763 and Fischer cat. H325). 24

XPS on the silver foil both before and after the reaction with H$_2$O$_2$-Sigma shows that the binding energies of the surface were shifted by −0.4 eV during the formation of the nanoparticle coating, indicating the formation of Ag$_2$O (ESI, Fig. S5). 25 The fact an electrical insulator, Ag$_2$O is formed on Ag surfaces exposed to H$_2$O$_2$ is consistent with the TEM observation of non-conductive nanoparticles trapped within the flexible rod’s amorphous matrix.

While it is reasonable to surmise that the amorphous network that comprises the flexible regions of the rods in this paper is derived from a stabilizer/impurity in the H$_2$O$_2$-EMD etchant, the net’s exact composition remains unknown at this time. XPS analysis of the residue from the evaporation of a H$_2$O$_2$-EMD aliquot, however, does indicate the presence of a tin(II) compound (Fig. 5), along with ubiquitous signals from oxygen and carbon, which suggests that the stabilizer may be an organic tin(II) compound. Indeed, a search of the literature reveals that tin(II) polycarboxylic acids are common stabilizers for H$_2$O$_2$. 26

Since the above experiments show that a trace organic compound may be inadvertently incorporated into a nanorod’s structure and can impart a surprising amount of mechanical stability once the metal nanorod matrix is dissolved, we have explored the possibility of creating flexible nanorods which incorporate intentionally added organic components. To do this, a polymer additive, poly(allylamine hydrochloride) (PAA) was simply added in excess to the aqueous silver plating solution used to synthesize the central section of these three-component {Au-Ag/PAA-Au} nanorods. Poly(allylamine hydrochloride) was chosen as it is a simple, readily available, water-soluble polymer with pendant amine groups. These amine groups are deprotonated in the cyanide-based silver plating solution (pH 13) and can coordinate to the silver ions in solution.

As can be seen in the FE-SEM images in Fig. 6, once the metal components of the nanorods were electrodeposited and the sacrificial silver component of the central region was dissolved away in dilute peroxide, the polymer additive remained in place, readily incorporated into the flexible region of the nanorods. As observed by SEM, these flexible Au-Ag/PAA-Au nanorods tend to bent as much as 60 degrees (see ESI, Fig. S6). The resulting morphology of these polymer-reinforced flexible rods thereby became that of a rope-like structure, as opposed to the ragged net-like morphology associated with the un-reinforced flexible regions of the earlier-described nanorods. While it is not entirely clear, the shape retention by the PAA segment is probably due to a combination of chain entanglement and H$_2$O$_2$-induced oxidative cross-linking of the polymer.

Conclusions

In conclusion, we have shown that the flexible regions of the three-component nanorods first described by Wang are likely the result of an organic tin(n) stabilizer contained within the H$_2$O$_2$ etchant solution, and the silver nanoparticles trapped within the resulting amorphous matrix are Ag$_2$O in composition. We have also demonstrated a simple process for the incorporation of an organic, flexible, nonconductive polymer region into a metallic nanorod structure. This method of synthesizing polymer/metal-composite nanorod nunchucks can potentially be extended to other functional polymers and co-polymers. The in situ nature of this synthesis method also represents a significant simplification to the existing process of

![Fig. 6 FE-SEM images of a {Au-Ag/PAA-Au} nanorods with a long central silver sections containing poly(allylamine hydrochloride). These rods have been exposed to 3.3% v/v H$_2$O$_2$ for 5 min, creating flexible {Au-PAA-Au} nanorods. Inset at top right is a higher resolution image of the polymer-metal junction, with the polymer region on top. Scale bar for larger image is 2 µm. Scale bar for inset image is 200 nm.](image-url)
creating such composite materials, which are generally fabricated one component at a time, either by surface modification of metal nanoparticles\textsuperscript{27,28} or by encapsulation of polymer particles in a metal shell.\textsuperscript{29,30} These flexible multicomponent nanostructures can be viewed as multifunctional building blocks for the assembly of nanoscale analogs of macroscopic objects, a part of the growing field of nanomechanics.

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**Notes and references**


24. J. Wang, personal communication.