

Controlled Manipulation of Giant Hybrid Inorganic Nanowire Assemblies

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Received February 11, 2008; Revised Manuscript Received April 28, 2008

ABSTRACT

The ultimate goal of nanotechnology is the design and fabrication of nanosize building blocks with multiple functionalities and their assembly into large-scale functional structures that can be controllably manipulated. Here we show that hybrid inorganic multisegmented nanowires, with hydrophobic carbon nanotube tails and hydrophilic metal nanowire heads, allow the assembly and manipulation of massive ordered structures in solution, reminiscent of the organic molecular micellar assembly. Further, properly designed assemblies can be manipulated using external stimuli such as magnetic field and light. The hybrid nanowires can have multiple segments including magnetic components, allowing the assembly to be manipulated by external magnetic field. The assembled structures can also be manipulated by modifying the hydrophobicity of the respective components via chemical functionalization and optical irradiation. This approach brings the concept of environment sensitive self-assembling nanomaterials closer to reality.

The design and building of mesoscale constructs of multifunctional attributes^{1–3} could have a big impact on technologies such as drug delivery and microfluidics.^{4–6} Recently, Link et al.^{2,7} has demonstrated the use of porous silicon as the building block for making smart materials. However, limited by the simple one-component system, it is difficult to incorporate additional functions into such designs. In order to provide broader capabilities, it is clear that materials of wider functionalities should be considered. One-dimensional nanoscale building blocks⁸ such as nanotubes,^{9–14} nanowires,^{15–19} and their hybrids^{20–23} could prove to be valuable materials in this endeavor. A previous report by Park et al.²² showed that the amphiphilic properties of certain nanowires could be used to assemble structures based on the self-interaction between nanowires. Yet, the true strength of such system lies in the ability to build complex structures that are responsive in real time to their environment. Such ability can be afforded by the interaction between the nanostructure and the environments (akin to surfactants). Here, we show for the first time that appropriately designed hybrid nanowires can be used to generate structures that can respond to their environment and can be manipulated using various external stimuli.

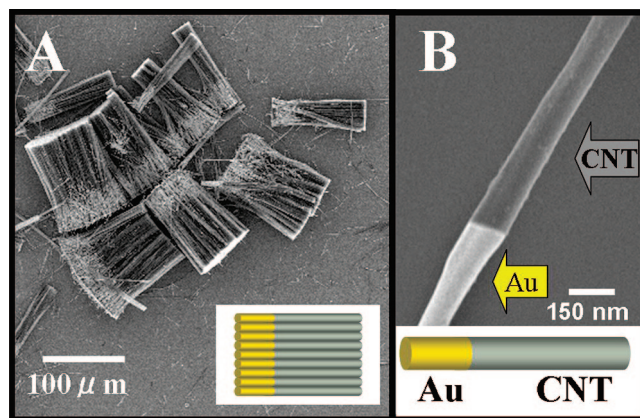


Figure 1. (A) SEM images of carbon nanotube (CNT)–Au hybrid nanowire arrays. The bright and dark segments show the gold and carbon nanotube sections, respectively, as illustrated by the schematic in the inset. The hybrid structures are grown using AAO templates by a combination of electrodeposition and chemical vapor deposition methods. (B) SEM image of a single hybrid nanowire, with (inset) a schematic of a single hybrid CNT–Au nanowire. (See Supporting Information for energy dispersive X-ray analysis and transmission electron microscopy image for the CNT–Au sample.)

Our approach is based on the use of one-dimensional hybrid nanowires consisting of multiple segments with hydrophobic carbon nanotubes on one end and hydrophilic metal nanowires on the other.²³ Through the hard template approach, the hybrid nanowire is fabricated by combination of electrodeposition and chemical vapor deposition for the

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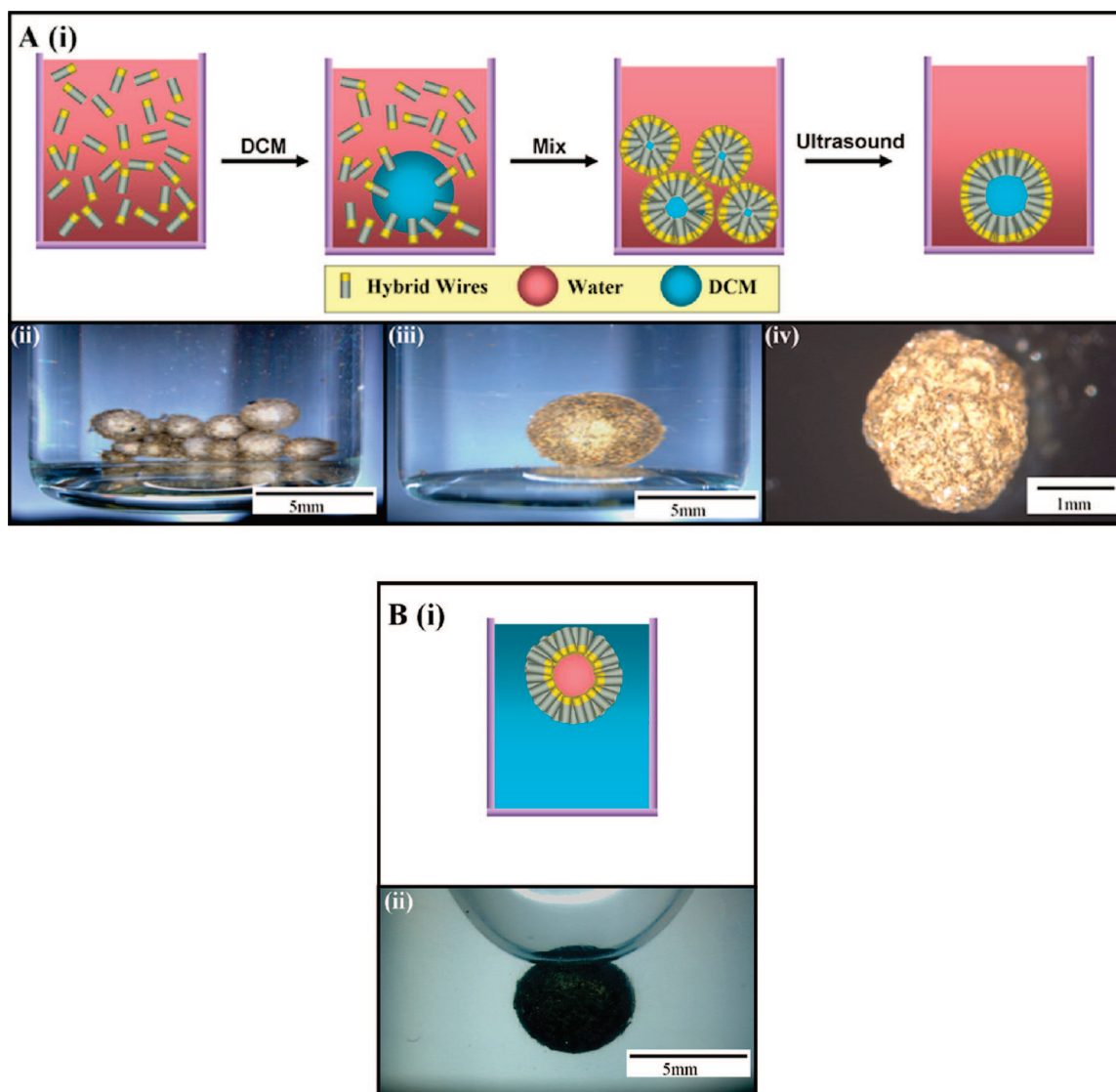


Figure 2. (A) (i) Schematic showing the synthesis of bifunctional assemblies from hybrid CNT–Au nanowire building blocks. The hybrid nanowires are first dispersed in water. With the addition of dichloromethane (DCM), a hydrophobic/hydrophilic interface forms between the two liquids and the hybrid nanowires orient themselves at the interface and form smaller spheres showing a golden surface, upon shaking. Gold segments point outward, while CNT segments face inward. The smaller spheres merge when subjected to ultrasound. (ii) An optical image showing the smaller spheres with a golden surface, resulting from the self-assembly of bifunctional hybrid nanowires. (iii) An optical photograph of the larger golden droplet, formed by merging the smaller spheres using ultrasound. (iv) Optical image of the wrinkled golden sphere which was removed from the solution and dried (also see Supporting Information, S2, for details). Note that the gold sphere appears ellipsoid in the figures due to the fact that the microscope image was taken across the water in the vial. (B) (i) Schematic showing the formation of large black spheres by the reverse assembly of hybrid nanowires when water is added to dichloromethane. The CNT segments face outward, and the gold segments point inward. (ii) An optical image of the black sphere formed by the reverse assembly of the hybrid nanowires. The concave meniscus evidencing the hydrophobic attraction between the DCM and the polypropylene tube can also be clearly seen in this figure.

growth of metal nanowires and carbon nanotubes, respectively (see Supporting Information for method and synthesis schematics). Panels A and B of Figure 1 show the scanning electron microscopy (SEM) images of arrays of these hybrid nanowires and single hybrid nanowires, respectively. The rationale for choosing such hybrid structure as the building block for the assembly was that the hybrid nanowires possess hydrophobic and hydrophilic domains at their terminations. Owing to this bifunctional nature, the assembly of the hybrid nanowires are sensitive to their environment and they can convey the environment change to an outside observer

through the color change induced by the alternation in their assembly.

The ability for the nanowires to sense their environment is demonstrated in a biphasic solution mixture (immiscible) of water and a hydrophobic liquid.²⁴ First, the hybrid nanowires are suspended in water (see Figure 2A(i), schematic). See Supporting Information for the detailed experimental conditions. With the uniform dispersion of the nanowires, the water dispersion appears murky. A droplet of dichloromethane (DCM) was then added to water containing the dispersed nanowires. Upon addition of dichlo-

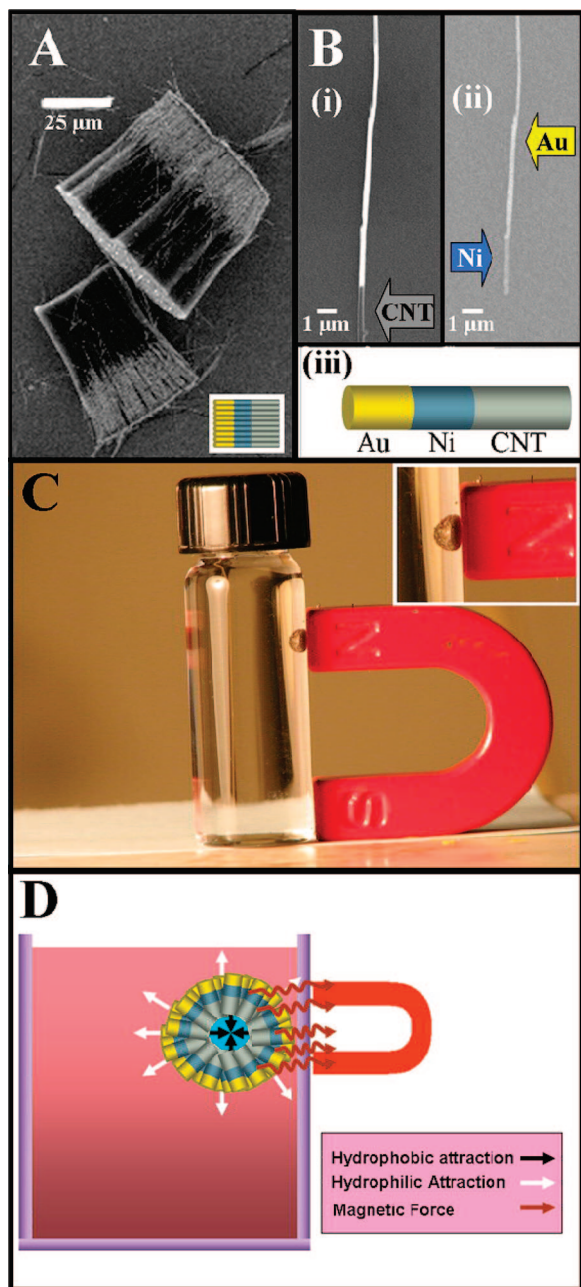


Figure 3. (A) (i) SEM images of multisegmented arrays of CNT-Ni-Au hybrid nanowires. The inset shows the schematic of the multisegmented hybrid nanowire arrays. Insertion of the Ni segment between Au nanowire and CNT makes the hybrid nanowire magnetic, which allows them to be manipulated by an external magnetic field (see Supporting Information for the backscattered SEM image for an array of magnetic hybrid nanowires). (B) (i) Secondary (SE) and (ii) backscattered SEM image of a single hybrid nanowire, showing the multisegments of gold nanowire, nickel nanowire, and CNT, corresponding to the schematic shown in the inset. The distinction between the metal nanowire and carbon nanotube can be noted in the secondary image while the distinction between the Au and Ni nanowires can be noted in the backscattered image. (See Supporting Information for energy dispersive X-ray analysis of the Au-Ni-CNT sample). (C) Photograph showing the manipulation of the self-assembled nanowire sphere using a magnet. The gold sphere could be attracted to the sidewall of the vial using the magnet. Upon removal of the magnet, the sphere drops to the bottom (see Supporting Information for the video). (D) Schematic representation of the gold sphere being attracted to the magnet. The various forces acting on the droplet are illustrated.

romethane, a hydrophilic/hydrophobic interface forms between the two liquids. This interface spontaneously attracts the nanowires to orient and stay at the interface. However, due to the small interfacial area presented by the single large drop and the inability of the nanowires far away from the interface in seeking the interface, only few of the nanowires are able to fall rapidly at the interfaces, while the rest of them remain suspended in water. The water still looks murky at this stage from the dispersion of the nanowires. In order to increase the collision frequency of the nanowires to the solution interface, the solution is shaken to form smaller droplets of dichloromethane. With the formation of smaller dichloromethane droplets, the total water-DCM interfacial area increases significantly and, as a result, rapid orienting and falling of the nanowires at the water-DCM interfaces takes place. This results in the formation of small spheres with golden surface appearance (see Figure 2A(ii)). The surfaces of these spheres appear golden because during assembly at the hydrophobic-hydrophilic interfaces, the gold segments of the nanowires face outside and the nanotube tails face inward; the nanotubes (hydrophobic) are attracted inward by the attraction induced by (hydrophobic) dichloromethane, whereas the gold parts (hydrophilic) pointed outward due to the attraction of water.

Stable CNT-Au nanowire assemblies are obtained when dichloromethane drops are added to water in which the nanowires are suspended, due to the hydrophobic shells (CNT) surrounding the dichloromethane drops and the formation of hydrophilic shells (Au) near water. The micelle size therefore depends on the amount of the dichloromethane added to the water. The selective merging of droplets can be carried out using ultrasound (see Supporting Information for experimental details). When the small golden spheres are subjected to an ultrasound bath for a few seconds, merging of the smaller spheres occurs but, once again, reflecting the same directed assembly, with CNT inside and Au on the outside (figure 2A(iii)). Hence, by using ultrasound, we can control the size of the micelle. The smaller spheres are not deassembled during sonication but coalesce while retaining the preferential orientation of the CNT and Au found in the smaller spheres. This shows that the nanowires at the interfaces are held together by strong forces, and deassembly of the assembled structures into the fully dispersed state is not easily achieved by ultrasound.

The spheres once assembled can also be dried. Figure 2A(iii) shows the optical image of the large sphere that was removed from the solution and dried (see Supporting Information for a zoom in view of the golden surface in Figure S7). It can be determined from the SEM image of the dried micelle that the micelle surface is almost completely covered by the hybrid nanowires. Although the shape of the large sphere has deformed and wrinkled during evaporation of the DCM bubble, the golden surface is retained and primarily constitutes of hybrid nanowires with the Au segments pointing outward. From the scanning electron microscopy (SEM) image (Figure S7), we can also see that not all the gold nanowires are pointing along the same directions, as shown in the schematic in Figure 1. Such

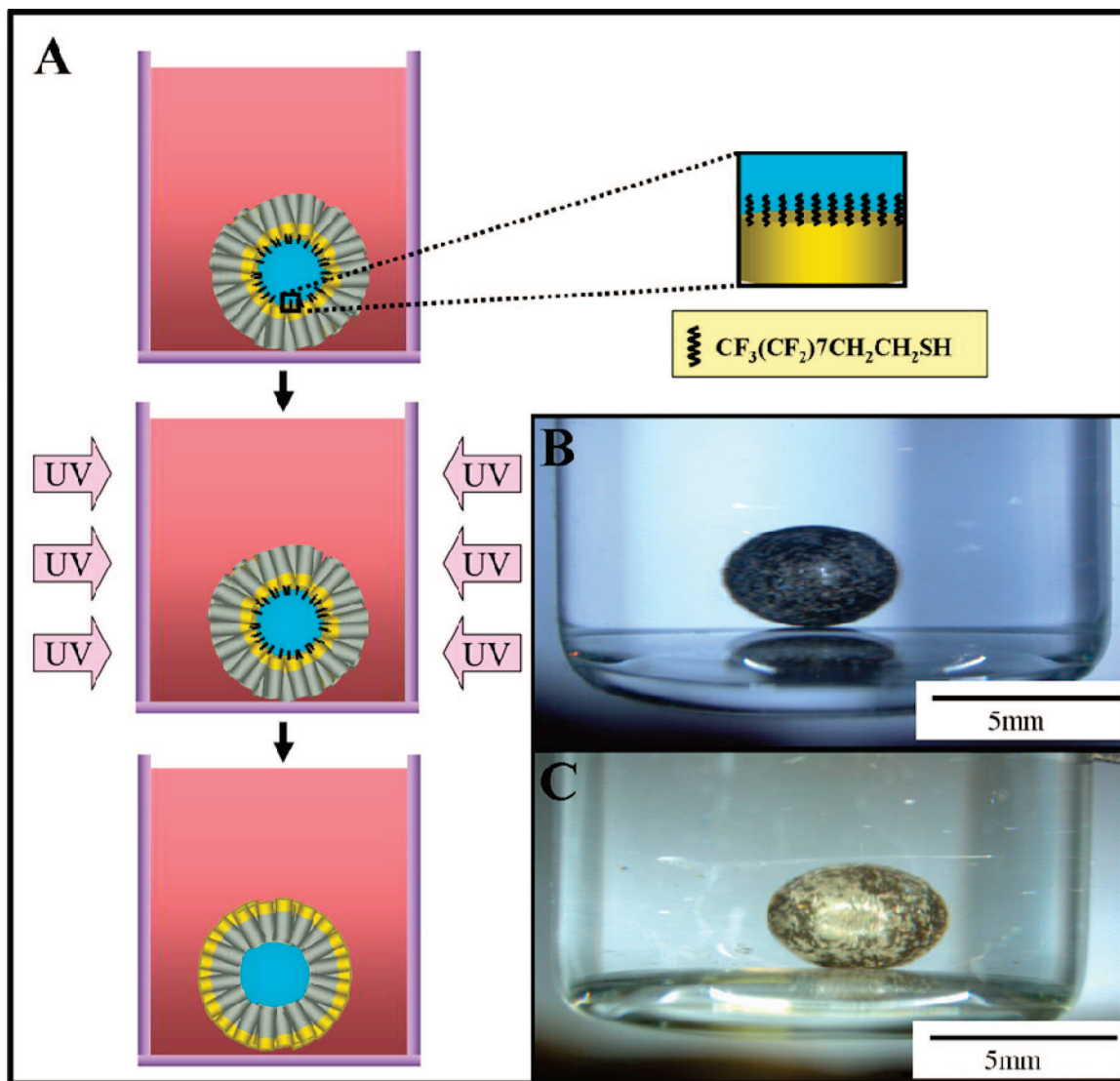


Figure 4. (A) Schematic showing the photoinduced surface modification of hybrid nanowire assembly using UV irradiation. The nanowire assembly from a black sphere (CNT pointing outward) could be reversed to a golden sphere (Au nanowire facing outward) by selective thiol functionalization of the gold segments, followed by UV irradiation. UV light photo-oxidizes the Au nanowire and removes the thiol group, thereby reversing to the original assembly (gold spheres). (See Supporting Information for the chemical structure of 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol that is attached to the gold surface of the hybrid nanowire assembly.) (B) Optical image of the black sphere formed from the assembly of thiol-functionalized Au–CNT hybrid nanowires dispersed in water, when a drop of dichloromethane is added. (C) Optical image showing the gold sphere formed after a drop of dichloromethane is added after the UV irradiation.

misalignment might have very likely arisen during the process of drying and solvent evaporation. By taking advantage of the ability for the micelle to stay in shape even after drying, the approach can provide a new strategy to self-assemble three-dimensional networks of hybrid nanowires on various substrates. The stable organizations shown here are impossible for organic molecular micellar structures to be retained outside the solution phase.

The assembly of the system is reversed when a drop of water is introduced into dichloromethane. In this case the nanowires self-assemble into black spheres (Figure 2B(i, ii)) with CNT segments facing outward (surface) and the Au segments pointing inward. This demonstrates that the bi-functional nanowires are sensitive to the surrounding hydrophobic–hydrophilic environments present in the liquid. The nanowire building blocks act similar to surfactants,

capable of detecting the local environment by directed assembly based on the interaction of its hydrophobic head and hydrophilic tail with the hydrophobic–hydrophilic interfaces that develop in the solution mixtures.

Taking advantage of the ease in introducing different materials into the hybrid nanowire structures, we can also create assembled architectures that allow controlled manipulation. For example, embedded magnetic structures can be used as a practical way to manipulate materials at the nanoscale.^{25–28} In our current system, magnetic segments are easily incorporated into the hybrid framework (see Supporting Information for synthesis details). Here the nanowires were made magnetic by the insertion of nickel segments between the gold and the nanotube parts. Figure 3A shows a SEM image of arrays of three-segmented multifunctional nanowire system with magnetic segments inserted in the

middle; the inset shows the SEM image for such a single magnetic hybrid nanowire. This incorporation of the Ni segment in the hybrid nanowire allows the hybrid nanowires to be manipulated using a magnetic field. By use of an external magnetic field to move the assembled particles (e.g., black, golden spheres as discussed before), our system provides a practical way to remotely deliver species (or even the liquid droplets encapsulated in the assembly, as was shown in Figure 2) that can be either attached to the nanowires or encapsulated within the assemblies. For example, by using a magnet, we can freely attract the golden sphere (and hence the encapsulated DCM drop) to the sidewall of a vial as shown in Figure 3B,C. It is apparent that the collective attraction of the hybrid nanowires on the dichloromethane is strong enough to allow the magnetic field to pick up not only the nanowire assembled sphere along but also the dichloromethane drop surrounded by the nanowires. We can perform various actions on the assembled spheres and the encapsulated liquid droplet including dragging and spinning the droplet at controlled speed without breaking up the sphere or the droplet inside (see videos provided in the Supporting Information).

In addition to the magnetic field, we have also used optical irradiation as another means to manipulate our system of nanowire assemblies. We demonstrate that the optical irradiation can induce the flipping of the nanowire orientations in the assemblies by changing the surface characteristics of the individual segments in the nanowires. For example, we could reverse-assemble the nanowires to change from a black sphere (nanotube-terminated surface) to a gold sphere (gold-terminated surface) in the two-segmented nanowires that we discussed in Figure 1. Here, a hydrophobic thiol such as 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol (PFDT) was first functionalized selectively onto the gold surface (see Supporting Information for details). Since the PFDT functionalization makes the surface hydrophobic,²⁹ the functionalized gold surface becomes relatively more hydrophobic in comparison to the untreated CNT surface. Hence, instead of assembling into a golden sphere as described previously (Figure 1), a black sphere (Figure 4A) is formed when a drop of dichloromethane is introduced into water dispersed with the Au–CNT nanowires. In a subsequent step, the functionalized (thiol) nanowires were irradiated by UV light for 3.5 h so that the UV light photo-oxidizes the gold helping to remove the thiol groups from the gold surfaces,³⁰ and hence allowing the gold to return to a hydrophilic state²⁹ (see Supporting Information for details), once again changing the hydrophobic–hydrophilic balance between the Au and CNT segments and the sphere flipping back to the one with golden surface (Figure 4B) in the presence of the dichloromethane drop. Such turnover and complete reconstruction of the assembled structure, via photoinduced surface modification, could be used effectively in applications such as smart delivery systems, which could be remotely reconfigured (inside out) to release or expose species that could be attached to specific terminal segments of the nanowires.

In conclusion, we have demonstrated the design, assembly, and manipulation of multisegmented inorganic hybrid nano-

wires. We have shown that such constructs are responsive to their surrounding and these changes can be easily visually observed. They can also be manipulated using a magnetic field and optical irradiation. It is shown that by taking advantage of having various components inserted on single nanowires, as well as utilizing their amphiphilic nature to assemble, a true multifunctional material can be realized. This controlled engineering feat at the nanoscale that allows well-controlled assembly and manipulation could lead to the creation of smart materials that are a cornerstone for the development of nanotechnology-based applications.

Acknowledgment. F. Ou thanks Applied Materials, Inc., for a graduate fellowship. We thank the interconnect focus center New York and New York State Foundation for Science, Technology and Innovation (NYSTAR) for supporting this research, L. Ci for TEM assistance, and James Tour for helpful discussions.

Supporting Information Available: Description of experimental methods and figures of TEM and SEM images for the hybrid nanowires. This material is available free of charge via Internet at <http://pubs.acs.org>.

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NL080407I