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Preparation of Asymmetric Nanostructures through Site Selective Modification of Tetrapods

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ABSTRACT. CdTe tetrapods have been deposited on a substrate, and partially coated with a protective polymer layer, exposing just one arm. The exposed arm was then decorated with Au nanoparticles in a site selective fashion. The modified arms were readily broken off from the remainder of the tetrapods, and released from the substrate, yielding CdTe nanorods asymmetrically modified with Au nanoparticles. These nanostructures with reduced symmetry may show interesting optoelectronic properties.

Asymmetry is a common feature of the building blocks in many self-assembled structures. For example, phospholipids, molecules that have polar groups on one end and non-polar ones on the other, are basic building blocks for cell membranes. The asymmetry in hydrophilicity enables them to self-assemble into bilayer structures in water. Another very good example is diblock copolymers, which can self-assemble into different morphologies such as spheres, cylinders, and lamellae. In this case, the self-assembly depends not only on the existence of asymmetry, i.e. the two different blocks, but also on the degree of asymmetry, which is the volume ratio between them.

In the field of nanoscience, to build self-assembled structures from nanocrystals has been a long term goal. The ability to build controlled nanocrystal assemblies, or “artificial molecules”, from nanocrystal “artificial atoms”¹⁻³ allows us to mimic the molecular world in a much larger dimension. State of the art nanomaterial syntheses can now produce colloidal nanoparticles (NPs) with controlled sizes, shapes, and compositions^{4,5}. However, only highly symmetric NPs, such as spheres⁶, rods^{7,8}, and more recently tetrapods⁹ have been well studied. Nanometer sized materials of greater complexity can be built with components of lower symmetry, offering the possibility of creating materials with a higher level of integrated functionality.

Asymmetric nanostructures are more versatile building blocks compared to their symmetric counterparts. For example, when a gold NP is asymmetrically modified with only one single strand DNA (ssDNA), it can be used as the building block to prepare more complex structures such as dimers and trimers^{1,3}. Recently, it has been shown that asymmetric diblock Au-polymer nanorods can self-assemble into bundles, tubes, and sheets¹⁰. The degree of asymmetry of the nanorods, which is the length ratio of the two blocks, determines the final assembled structure, similar to the case of the diblock copolymer.

Some asymmetric structures have been prepared using post synthesis modifications. For example, gold half-shell structures were produced by evaporating gold onto an array of silica colloidal particles¹¹. Heat treatment of these structures gave gold–metal oxide asymmetric dimers¹². In a similar approach, gold shell structures have been grown from Au NP seeds on a silica surface to produce gold cups or caps¹³. Direct synthesis of asymmetric structures has also been realized in nanowire systems using chemical vapor deposition¹⁴⁻¹⁶. Similarly, asymmetric rods can be prepared using template directed growth^{10,17}.

In many of the above examples, relatively large particles were prepared. For example, the gold–metal oxide asymmetric dimers can only be prepared from metal oxide particles larger than 200 nm. The gold-polymer asymmetric nanorods have diameters around 200 nm and lengths over one micrometer. As a result, they can only be used to prepare assemblies in micrometer or even larger dimensions. To prepare

sub-micrometer sized assemblies, smaller asymmetric building blocks are needed. Furthermore, it is desirable to develop a range of methods that can yield such structures.

CdTe tetrapods were recently prepared in high yield in our group⁹. The structure of the tetrapod is topologically similar to that of a sp^3 hybridized carbon atom. With the possibility to mimic the bonding between carbon atoms in organic molecules, this type of structure can serve as a very interesting building block to prepare superstructures, especially three dimensional ones. For example, it would be very interesting to modify each of the four arms differently, to produce a chiral “nanocrystal molecule”. Another advantage of using tetrapods as building blocks lies in the fact that the dimension of tetrapods can be tuned over a wide range. For example, the arm length can be made from less than 20 nm to over 200 nm, while keeping the arm diameter unchanged. This feature makes it possible to use tetrapods to prepare structures over a wide range of sizes and complexities.

In this communication, we show the first step toward this direction: the preparation of asymmetric tetrapods. We show it is possible to modify only one of the four arms of the tetrapod with Au NPs. It is further shown that asymmetrically modified CdTe nanorods can be produced by breaking this structure. The structures prepared here are potential building blocks to more complex assemblies. The tetrapod arms were modified with Gold NPs instead of small molecules, mainly for ease of visualization. It is difficult to characterize organic species on the semiconductor NP surface with nanometer spatial resolution using current instrumentation. However, use of NPs as tags allows us to use transmission electron microscopy (TEM) or scanning electron microscopy (SEM) to directly image the modified structures. In addition, the surface chemistry of gold is well developed. Attaching gold particles to tetrapods provides a surface with unique chemical properties which can be used for further functionalization or preparation of nanostructure assemblies. Finally, Banin and coworkers have recently prepared CdSe nanorods and tetrapods with single Au nanoparticles directly attached to the ends¹⁸. It should be of interest to compare the properties of those systems with the asymmetric ones produced here.

Results and Discussions.

In order to selectively modify only one of the four arms, the approximate T_d symmetry of the tetrapods must be broken first. This was realized by putting tetrapods onto a flat silicon surface. Because of the unique geometry of the tetrapods, three arms contacted with the surface and the last one pointed away from the surface. To produce high density tetrapod films with minimum aggregation, spin-coating and Langmuir-Blodgett techniques were first tested but both produced a high degree of aggregation. To our surprise, slow evaporation of tetrapod solutions in pyridine produced uniform tetrapod coverage with almost no aggregation over the range of 100 μm (Figure 1).

To achieve modification of only one arm of the tetrapods, a polymer film was then spin-coated to cover the bottom three arms, exposing only part of the top arm (Scheme 1, step A). So far, two polymers have been tested: poly (3-hexyl-thiophene) (P3HT) and poly (methyl methacrylate) (PMMA). Because P3HT is a semiconductor polymer, SEM can be used to characterize the surface before and after spin-coating. After a ~ 40 nm thick P3HT layer was spin-coated, the bottom three arms showed reduced contrast in SEM images, which suggested that they were covered by the polymer film (data not shown). Atomic force microscopy (AFM) was used to further characterize the composite. Figure 2 shows the height image of the polymer-tetrapod surface. Separated dots can be found, which correspond to the exposed top arms. The heights of the dots roughly match the estimated exposed arm lengths.

The composite film was then treated with an isopropanol solution of hexanedithiol overnight to modify the exposed top arms (Scheme 1, step B). P3HT and PMMA are not soluble in isopropanol so the bottom three arms remained covered throughout this process. Thiol groups readily bind to the CdTe surface. In the case of hexanedithiol, one thiol group binds to the CdTe surface while the other one remains free. Gold NPs coated with trioctylphosphine (TOP) were then used to modify the top arms via the dithiol linkers (Scheme 1, step C)¹⁹. TOP coated NPs instead of thiol coated ones were used because TOP can be easily replaced by the thiol groups. The diameters of the gold NPs and arms of the tetrapod we used here were around 5 nm and 10 nm, respectively. As a result, multiple gold NPs bound to the top arms in this step. After the modification, the polymer film was removed by dissolving it in organic

solvent such as chloroform (for P3HT) or pyridine (for PMMA) to expose the whole structure (Scheme 1, step D).

SEM and TEM were used to characterize the prepared asymmetric tetrapods. Figure 3 shows the SEM images of the resulting asymmetric tetrapods using PMMA as the protecting layer. It can be clearly seen that the tips of the top arms have larger diameters compared with the bottom parts, as a result of the attachment of large numbers of Au NPs. The fine structure is revealed in the selected higher resolution images, shown at the bottom of figure 3. Individual gold NPs can be seen on the top arm while the other three arms are clean. Similar results were obtained using P3HT as the protecting polymer.

Control experiments demonstrate that the modification is indeed mediated by the dithiol linker instead of nonspecific adsorption. A silicon chip was spilt into two halves after deposition of tetrapods and spin-coating of the P3HT film. One of the pieces was treated with hexanedithiol solution and the other was not. Both of them were then treated with Au NPs and the polymer layers were removed afterwards. Shown in figure 4, the sample without hexanedithiol treatment shows no binding of gold NPs while the other one shows successful asymmetric modification.

In one experiment, two cycles of hexanedithiol and gold NP modifications were performed before the polymer protecting layer was removed. This procedure produced two layers of gold NP shells on the exposed top arms. A much larger cluster of gold NPs can be seen on the top arms (Figure 5). In a different approach, the thickness of the polymer layers was varied to control the exposed arm length in order to control the degree of modification (data not shown).

It is desirable to release the modified tetrapods intact from the substrate. So far this has not proven possible, because of the very strong interaction with the substrate. When the tetrapods are first deposited, the capillary force from solvent evaporation slams the tetrapods onto the surface, flattening the three arms that are pointing down towards the substrate. This effect has been visualized previously in experiments where the tetrapods were deposited to the side walls of trenches and could be viewed from the side²⁰. It also has been seen by C. Kieselowski for tetrapods deposited on flat surfaces using tomographic reconstruction in the TEM²¹. In the future, it may be possible to gently deposit the

tetrapods using supercritical fluid, to avoid strong capillary forces. In the meantime, we have learned how to break off the uppermost arm of the tetrapod, which is asymmetrically modified with Au NPs.

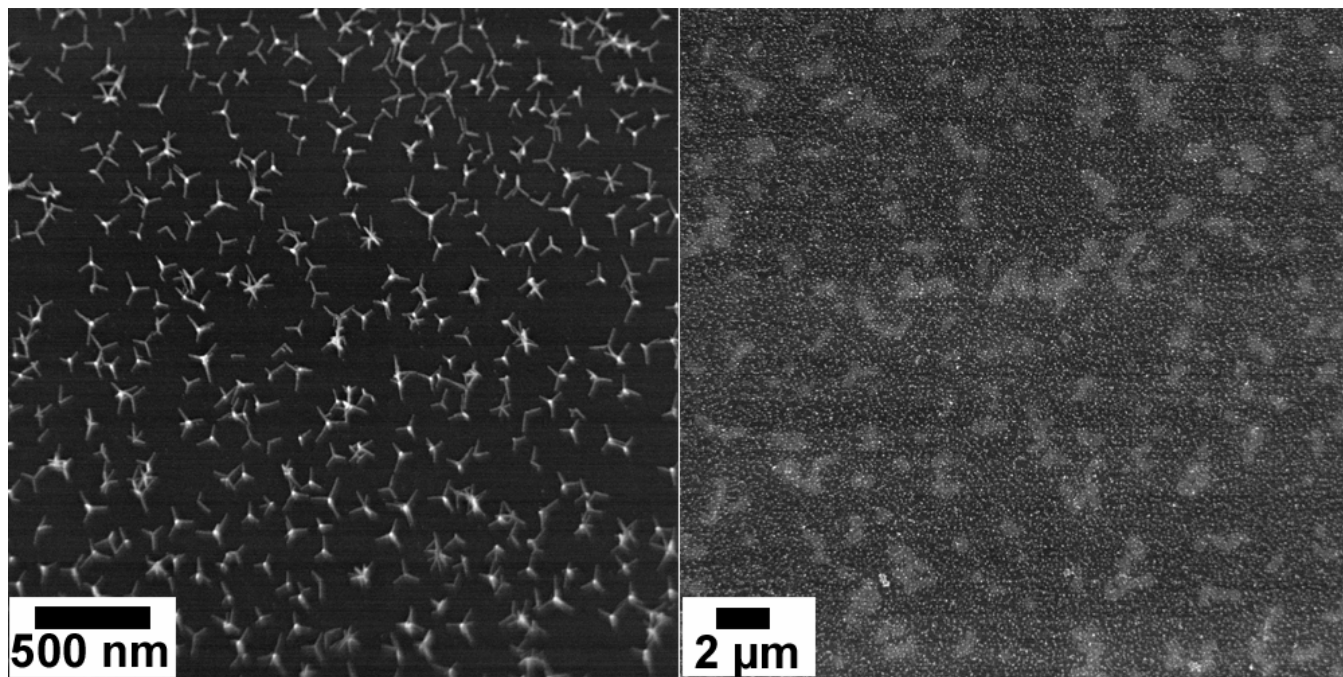
This was accomplished by pressing a TEM grid onto the silicon surface. During this process, particles were transferred to the TEM grid. Indeed, we were able to find a few asymmetrically modified tetrapods on some rare occasions (Figure 6). However, to our surprise, the majority of the materials on the TEM grid were nanorods (Figure 7, top left). Under higher magnification, it can be seen that the nanorods were asymmetrically modified with gold NPs (Figure 7, top right) formed by breaking the modified top arms (Scheme 2) by the TEM grid. We found that this break-and-transfer process could be applied to other substrates as well. The bottom of Figure 7 shows SEM images of the broken asymmetric CdTe nanorods transferred to a Si substrate. We want to emphasize here that this simple method produces asymmetric nanorods which are very hard to prepare in other ways. Besides the interesting semiconductor-metal heterostructure itself, these asymmetric nanorods can also be used as useful basic building blocks. For example, if functionalized by appropriate organic molecules on the gold NPs; they can be potentially made into nanocrystal amphiphiles. Furthermore, they should exhibit anomalously large transient electric birefringence²², and may have interesting non-linear optical properties.

In conclusion, we successfully prepared asymmetrically modified CdTe tetrapods and nanorods via a site selective modification method. These novel structures can be potentially used as basic building blocks to prepare more complex nanostructures. The mild preparation process makes it possible to modify other tetrapod shaped substrates, for example, CdSe⁸ and ZnO tetrapods²³ in the future. By using different material specific linker molecules, other NPs can also be used in the modification.

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Figure 1. SEM images (top down view) of the prepared tetrapod film on Si wafer. Left: High resolution image showing individual tetrapods. The top arms appear as bright spots. Right: Low resolution image showing the large area homogenous film. Each tiny white spot corresponds to one tetrapod top arm. The large white islands result from organic contamination.



Scheme 1. Preparation of asymmetric tetrapods. A: Spin-coat polymer to partially cover tetrapods. B: Treat with hexanedithiol solution. Hexanedithiol modified surface is shown in blue color. C: Attach gold NP (shown as red dots) onto modified tetrapod surface. D: Dissolve the polymer layer.

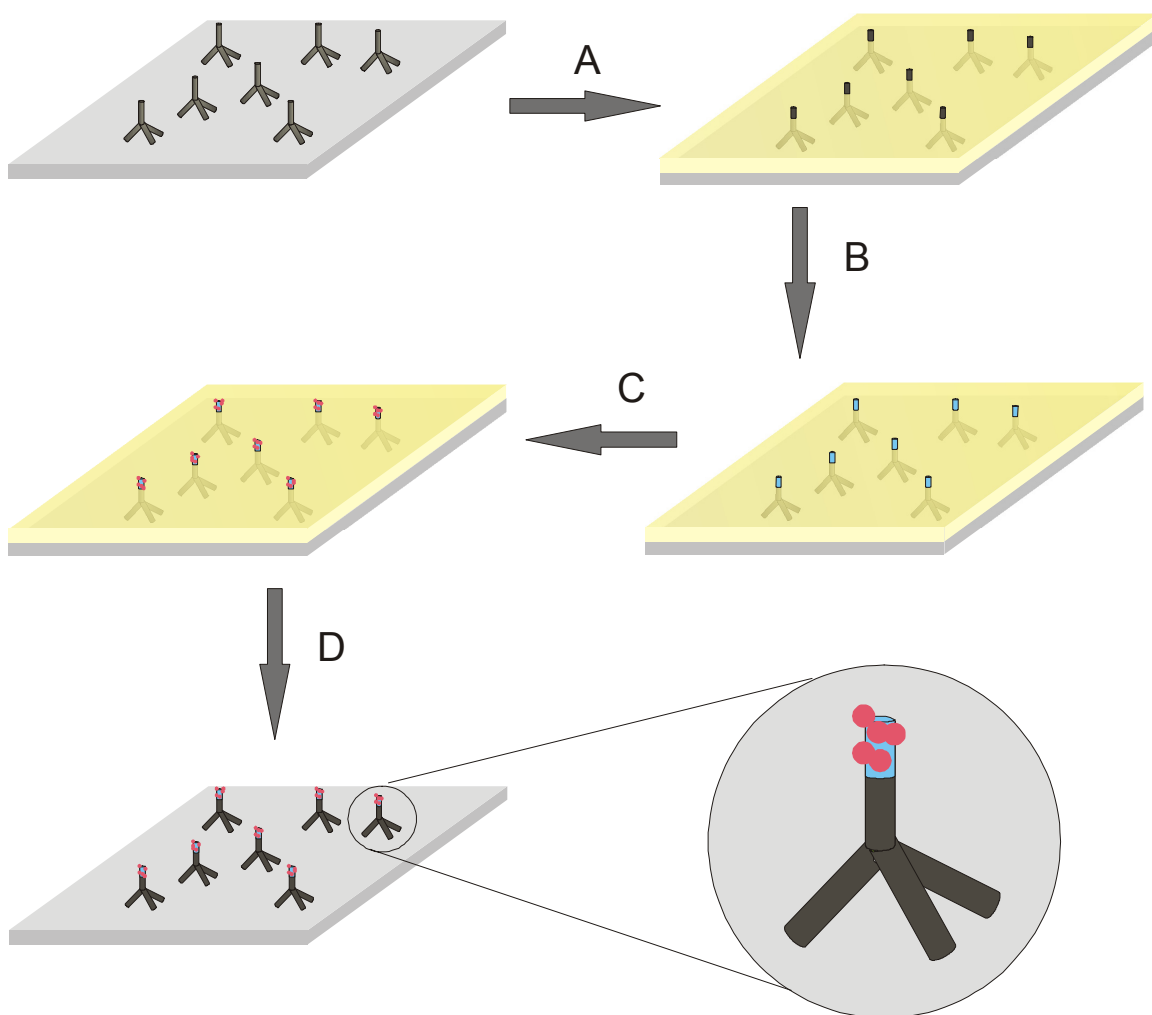


Figure 2. Tapping mode AFM height image of the tetrapods partially covered with polymer. The image size is 1 μm x 1 μm . The high spots correspond to exposed top arms.

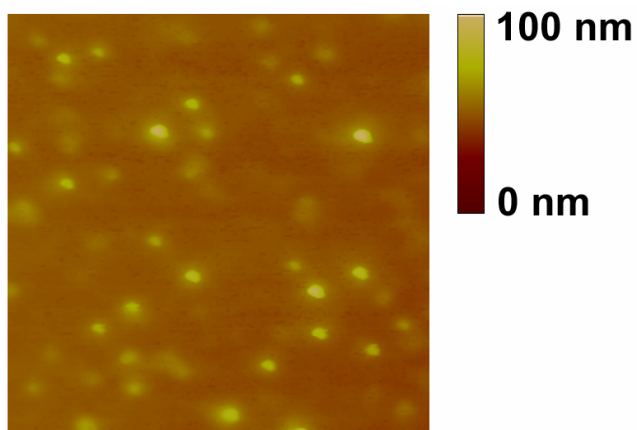


Figure 3. SEM images (tilted 30 degrees) of as prepared asymmetric tetrapods on Si surface. The top arms were modified with many gold NPs. Top: large area view. Bottom: selected high resolution images.

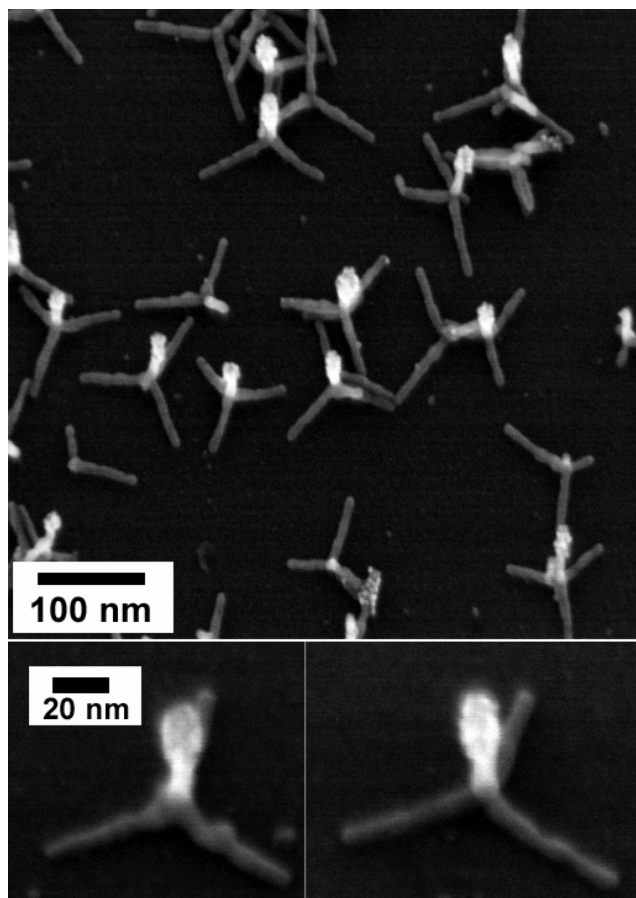


Figure 4. Control experiment result supports that the modification is a chemical one. Left: SEM image of CdTe tetrapods obtained after treating with hexanedithiol and Au NPs. Right: SEM image of CdTe tetrapod obtained after treating with Au NPs only. The tetrapods were not modified with Au NPs in this case.

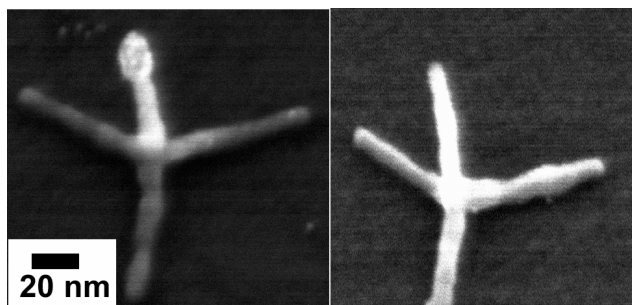


Figure 5. SEM images of asymmetric tetrapods prepared using two cycles of hexanedithiol, Au NP modifications. There are much more Au NPs on the top arm compared to those in the figure 3.

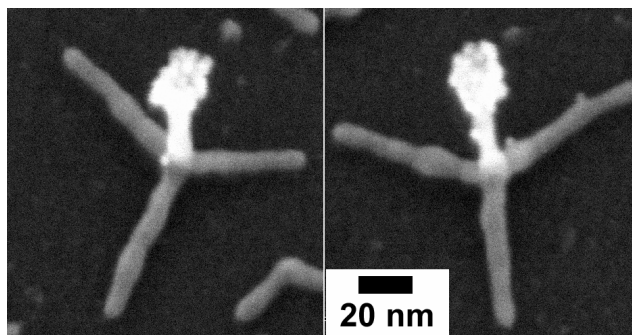
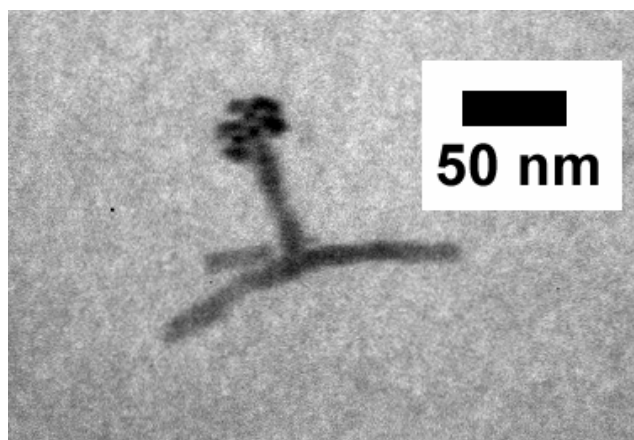


Figure 6. TEM image of asymmetric tetrapod.



Scheme 2. Asymmetric tetrapods are broken to produce asymmetric rods.

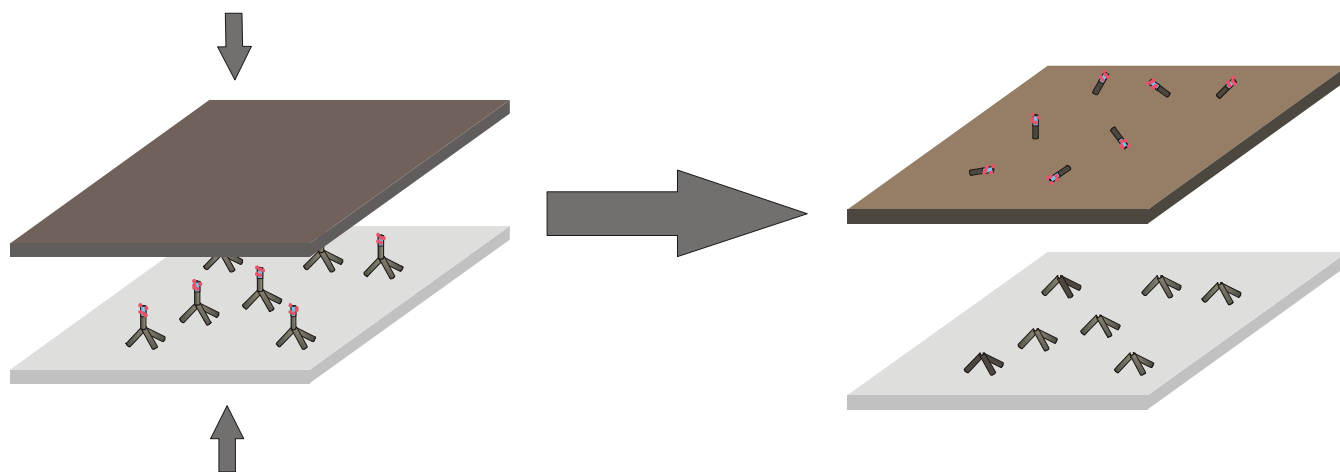
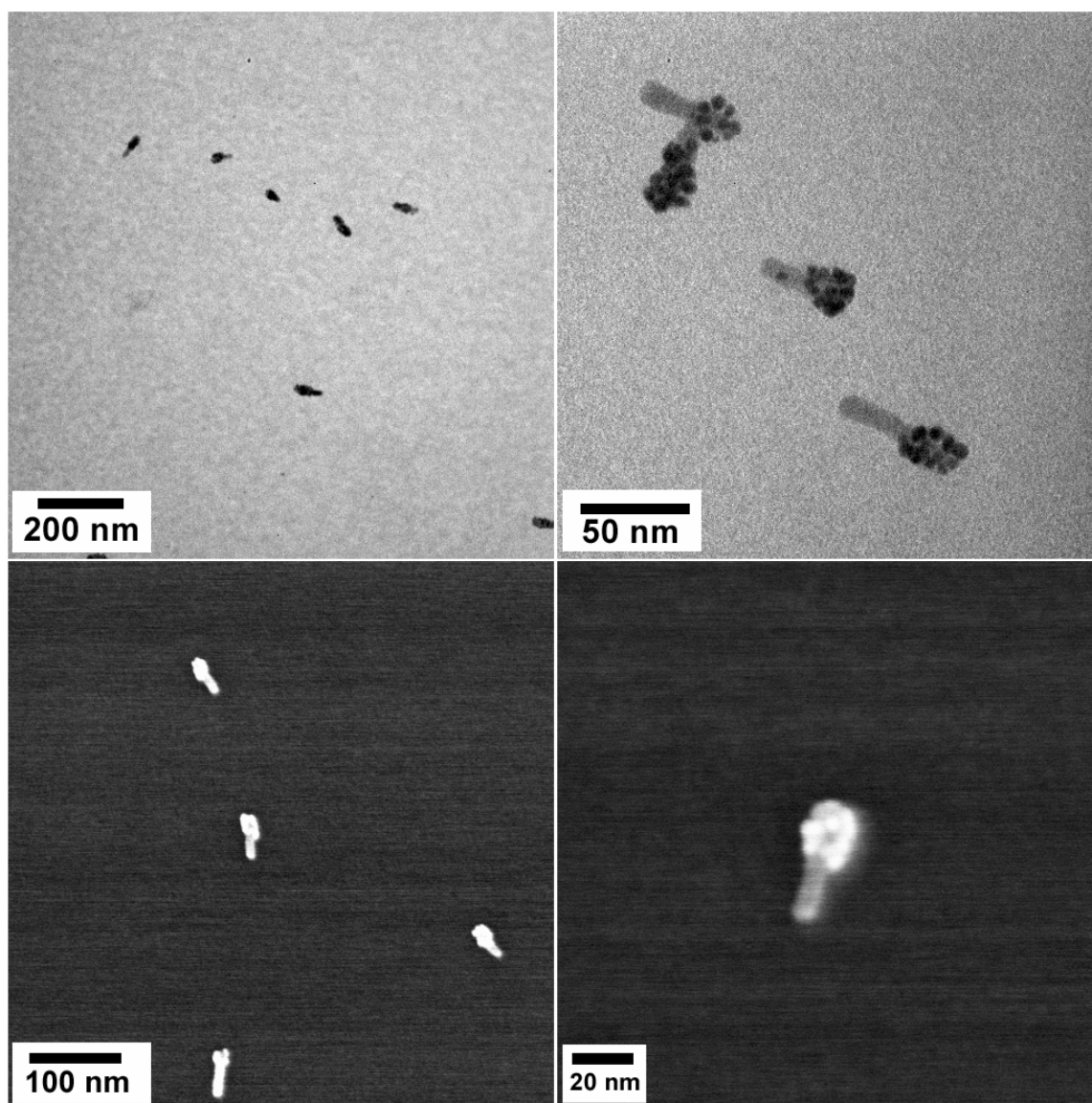


Figure 7. TEM (top) and SEM (bottom) images of asymmetrically modified CdTe rods.



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