J|A|C|S
COMMUNICATIONS

Published on Web 07/19/2006

Directed Self-Assembly of Gold-Tipped CdSe Nanorods

Asaf Salant, Ella Amitay-Sadovsky, and Uri Banin*

Institute of Chemistry and the Center for Nanoscience and Nanotechnology, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

Received May 7, 2006; E-mail: uri.banin@huji.ac.il

A primary challenge of the bottom-up approach to nanomaterials is the construction of complex architectures from the nanoscale building blocks. Self-assembly is the main paradigm to achieve this goal, where previous work focused primarily on spherical-shaped nanocrystals[1a−h] forming ordered monolayers, superlattices, and molecular-like dimers, trimers, and additional structures. Due to the spherical symmetry of the building blocks, there are no preferred orientations in such assemblies. Recent advances led to the development of shape-controlled nanocrystals, where a particularly important family includes that of rod-shaped particles.[2a−d] For such nanorod structures, orientation of self-assembly of the building blocks is important and can lead to diverse structures. Only a few results have been reported for self-assembly of nanorods, with particular focus on large metal rods.[3a−f] Simple conjugation can be done using dithiol molecules as linkers,[3f,4a] but the control is limited as the assembly cannot be easily stopped, resulting in the distribution of chain lengths. Using more sophisticated biomolecular linkers allows improved control over the self-assembly because of their specificity and the ability to suppress their reactions. For metal nanorods, assemblies were previously prepared using DNA[3a] linking, and for long rods, chains were prepared using streptavidin−biotin hybridization,[3b,c,e] while under different conditions, side-to-side assembly was preferred.[3d]

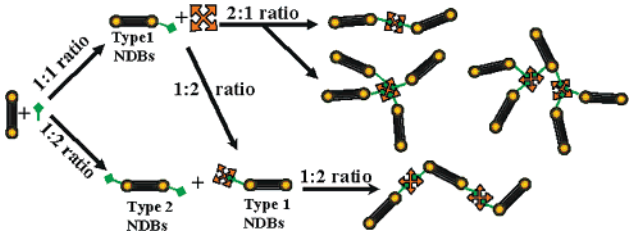
We have recently developed hybrid metal-tipped semiconductor nanorods termed nanodumbbells (NDBs),[4a−b] and demonstrated the use of the gold tips as anchor points for self-assembly using simple dithiol molecules, resulting in chain formation.[4a] Here we report applying a biochemical linking strategy for creating dimer and trimer chains of NDBs. This establishes the concept of using Au tips as anchor points for directed self-assembly, employing linker molecules that have a high affinity to gold.

We use the strong and specific avidin−biotin interaction[5] to construct head-to-tail assemblies of NDBs. Disulfide modified biotin was used to conjugate the disulfide end to the gold tip of the NDBs. The biotin end remained available to conjugate to the avidin, which can conjugate up to four biotin molecules. This can be used to form flowerlike shapes of the NDBs as well. A separation method using a concentration gradient was applied to the conjugated NDBs, providing further control of the obtained structures.

NDBs (40 × 4 nm) were synthesized according to the method reported earlier[4] and were solubilized in aqueous phase using a ligand exchange method (see Supporting Information). EZ-Link biotin HPDP (Pierce, Scheme S1) was added to the aqueous NDBs and mixed overnight in the refrigerator, resulting in biotinylated NDBs. The addition of biotin was done in two mole ratios, mole ratios of 1:1 (type1 NDBs) and 1:2 (type2 NDBs), as seen in Scheme 1, to control the assembly of NDBs.

First we show the preferential formation of dimers by using type1 NDBs in which we expect on average one biotin molecule per particle. To this solution, avidin (Sigma), at a 1:2 ratio to the NDBs, was introduced and mixed. Excess D-biotin was then added to stop the reaction by blocking unbound sites on the avidin. Figure 1a shows TEM images of this sample. Dimer formation is identified with clear preference for head-to-tail binding through the Au tips. This is in contrast with unconjugated NDBs and nonbiotinylated NDBs with avidin, which show strongly preferential side-to-side arrangement due to strong van der Waals interactions (Figures S1−S3). Carrying out the same experiment in similar conditions for CdSe rods without gold tips did not lead to preferential head-to-tail dimer or chain formation (Figures S4 and S5). This clearly shows the selective conjugation of NDBs through the gold tips using a disulfide modified biotin molecule and linking with avidin. The spacer between the disulfide and the biotin molecule is not rigid, hence, different angles and distances of conjugated NDBs can be seen.

Scheme 1. Reacting Biotin Disulfide (Green) with NDBs and Avidin (Orange) Using Different Mole Ratios, Resulting in Dimers, Flowers, and Trimers



A different distribution of chain lengths favoring trimers was targeted by changing the concentration ratios and reacting type 1 NDBs with 1:2 excess of avidin. The avidin in this case will mostly link to biotin on NDBs and will not lead to dimer formation because excess avidin is present and it diffuses more rapidly then the larger NDBs. Next, these avidin-terminated type 1 NDBs were combined with type 2 NDBs, which on average have biotin on each Au tip in a mole ratio of 2:1, and mixed again, followed by adding excess D-biotin. Figure 1b shows the TEM image of this preparation revealing trimers along with dimers and individual NDBs. Once again, the selective conjugation through the gold tips is clearly observed.

To further emphasize the differences in self-assembly in the two approaches and to purify the distributions of chain lengths, we performed separations using a concentration gradient recently applied to separate conjugates of gold nanoparticles.[6] Dimer and trimer solutions of conjugated NDBs were centrifuged in a sucrose gradient. After the centrifugation, bands were seen, extracted, and examined by TEM (Figures S6 and S7). The distributions for the dimer and trimer cases before and after separations are shown in Figure 2a and b, respectively, and compared with biotinylated NDBs. In the dimer experiment, before adding avidin (Figure 2a), most of the population consists of monomers, and some NDBs are assembled in a dimer head-to-tail configuration due to nonselective aggregation. After the protein was added, an increase in the dimer conjugated NDBs population is seen of more than 35%. The

10.1021/ja063192s CCC: $33.50

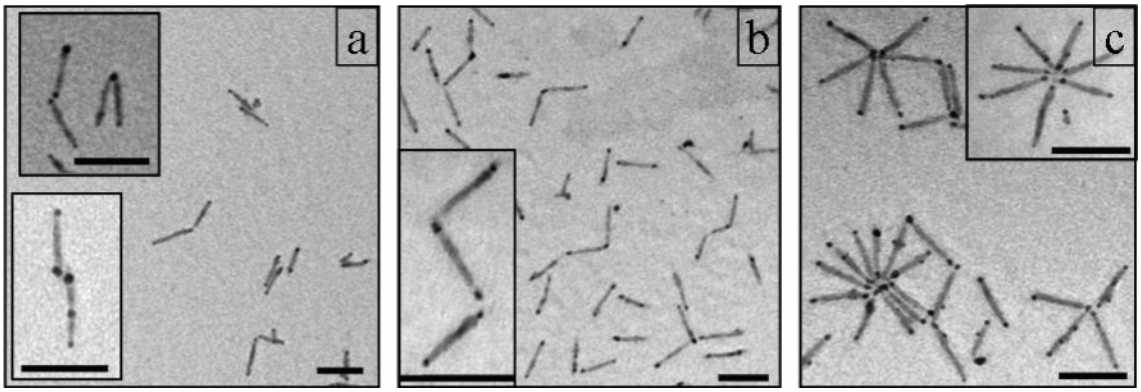


Figure 1. TEM images (taken prior to separation) of (a) dimers of NDBs in different conjugation angles, (b) trimers, and (c) flowers (50 nm scale bars).

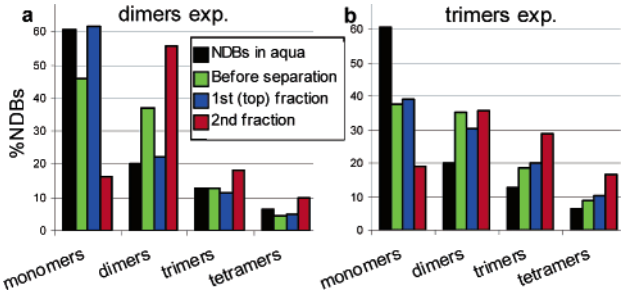


Figure 2. Statistics of (a) dimer-induced experiment and (b) trimer-induced experiment. Black column, in aqua before avidin addition; green column, after addition of avidin and before gradient separation; blue column, top fraction taken from the gradient after centrifugation; red column, second fraction taken from the gradient after separation. In each experiment, more than 700 NDBs were counted.

relatively large fraction of monomers results from the low ratio of NDB to biotin used in the first step and required for better control of the assemblies. After separation, the top band extracted contains mostly monomers, as expected, while the lower fraction has more than 55% dimers, achieving a reasonably pure distribution of the desired dimer species.

The statistics of the trimer experiment (Figure 2b) show that, after avidin addition, before the separation (green), ~20% of the population are trimers and ~35% are dimers. After separation, the top fraction (blue) contains only 20% of trimers. The trimer population increases in the lower fraction to almost 30%. In this trimer case we observe, therefore, a broader distribution, which is to be expected from the added possibilities for conjugation combinations. This shows also the limitations of the avidin−biotin conjugations to control specific chain lengths of NDBs.

Finally, a unique structure we observed along with dimer formation is shown in Figure 1c. These are flowerlike arrangements of NDBs which conjugate to a central point. This can be explained through the tetramer binding sites of the avidin yielding an "X"-like arrangement. Moreover, more elaborate flower shapes are seen and are explained by having more than one disulfide biotin molecule reacting with the NDB gold tip. Such structures were not reported for the larger metal rods, likely because of steric hindrance in that case. Because of the small diameter of the gold tips and rods used here, such structures are indeed feasible (Scheme S2). We note that the flowerlike structure is not favorable in the dimer case conditions and is seen in small quantities relative to dimers.

In summary, we use avidin−biotin conjugation to create rod dimers, trimers, and flowers based on linking through the gold tips of the NDBs. This establishes the use of such tips as anchor points for self-assembly. More controlled assemblies can be envisioned using also one-sided gold-tipped rods[4b] and more sophisticated linking schemes such as DNA hybridization.

Acknowledgment. Taleb Mokari is thanked for helpful discussions, Avi Vilentz is thanked for assistance in TEM studies, and Joseph and Ruth Sperling are thanked for assistance in the separations. This work was supported by the European Union under project SA-NANO.

Supporting Information Available: Solubilization method of NDBs in aqua, description of control experiments, and TEM images. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Alivisatos, A. P.; Johnson, K. P.; Peng, X.; Wilson, T. E.; Loweth, C. J.; Bruchez, M. P., Jr.; Schultz, P. G. *Nature* **1996**, *382*, 609−611. (b) Mirkin, C. A.; Lestinger, R. L.; Mucic, R. C.; Storhoff, J. J. *Nature*, **1996**, *382*, 607−609. (c) Bethel, D.; Brust, M.; Schiffiin, D. J.; Kiely, C. *J. Electroanal. Chem.* **1996**, *409*, 137−143. (d) Loweth, C. J.; Caldwell, W. B.; Peng, X.; Alivisatos, A. P.; Schultz, P. G. *Angew. Chem., Int. Ed.* **1999**, *38*, 1808−1812. (e) Connolly, S.; Nagaraja, R.; Fitzmaurice, D. *J. Phys. Chem. B* **2000**, *104*, 4765−4776. (f) Kanaras, A. G.; Wang, Z.; Bates, A. D.; Cosstick, R.; Brust, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 191−194. (g) Fu, A.; Micheel, C. M.; Cha, J.; Chang, H.; Yang, H.; Alivisatos, A. P. *J. Am. Chem. Soc.* **2004**, 126, 10832−10833. (h) Shevchenko, E. V.; Talapin, D. V.; Murray, C. B.; O'Brien, S. *J. Am. Chem. Soc*. **2006**, *128*, 3620−3637.

(2) (a) Peng, X.; Manna, L.; Yang, W.; Wickham, J.; Scher, E.; Kadavanich, A.; Alivisatos, A. P. *Nature* **2000**, *404*, 59−61. (b) Jun, Y. W.; Lee, S. M.; Kang, N. J.; Cheon, J. *J. Am. Chem. Soc*. **2001**, *123*, 5150−5151. (c) Kan, S.; Mokari, T.; Rothenberg, E.; Banin, U. *Nat. Mater.* **2003**, *2*, 155−158. (d) Sau, T. K.; Murphy, C. J. *Langmuir* **2004**, *20*, 6414−6420.

(3) (a) Dujardin, E.; Hsin, L.; Wang, C. R. C.; Mann, S. *Chem. Commun.* **2001**, *14*, 1264−1265. (b) Caswell, K. K.; Wilson, J. N.; Bunz, U. H. F.; Murphy, C. J. *J. Am. Chem. Soc.* **2003**, *125*, 13914−13915. (c) Salem, A. K.; Chen, M.; Hayden, J.; Leong, K. W.; Searson, P. C. *Nano Lett.* **2004**, *4*, 1163−1165. (d) Gole, A.; Murphy, C. J. *Langmuir* **2005**, *21*, 10756−10762. (e) Chen, M.; Guo, L.; Ravi, R.; Searson, P. C. *J. Phys. Chem. B* **2006**, *110*, 211−217. (f) Shibu Joseph, S. T.; Ipe, B. I.; Pramod, P.; Thomas, K. G. *J. Phys. Chem. B* **2006**, *110*, 150−157.

(4) (a) Mokari, T.; Rothenberg, E.; Popov, I.; Costi, R.; Banin, U. *Science* **2004**, *304*, 1787−1790. (b) Mokari, T.; Sztrum, C. G.; Salant, A.; Rabani, E.; Banin, U. *Nat. Mater*. **2005**, *4*, 855−863.

(5) Green, N. M. *Adv. Protein Chem.* **1975**, *29*, 85−133.

(6) Dadosh, T.; Gordin, Y.; Krahne, R.; Khivrich, I.; Mahalu, D.; Frydman, V.; Sperling, J.; Yacoby, A.; Bar-Joseph, I. *Nature* **2005**, *436*, 677−680.

JA063192S