

# Directed Assembly of Multisegment Au/Pt/Au Nanowires

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## ABSTRACT

We demonstrate directed end-to-end assembly of Au/Pt/Au multisegment nanowires using the biotin/avidin linkage. The formation of a self-assembled monolayer on the central platinum segments is essential to avoid nonspecific binding of the linker group and hence to minimize lateral assembly.

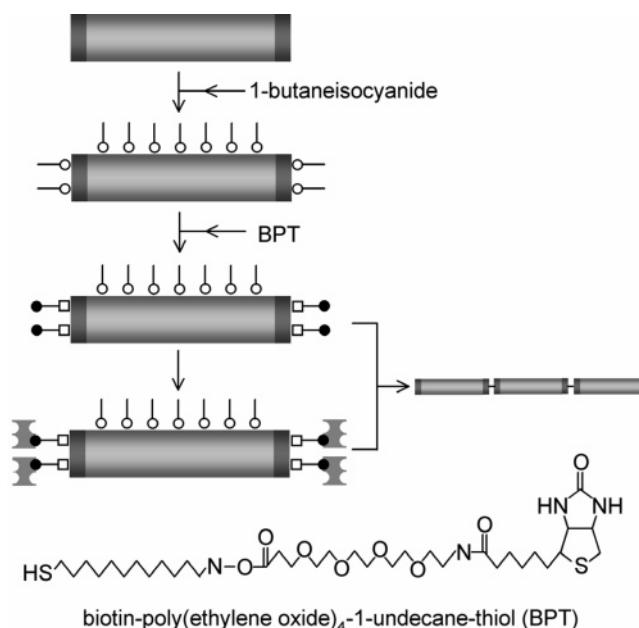
The bottom up approach to device fabrication involves the synthesis and assembly of nanoscale building blocks. With advances in synthesis of nanoscale particles, there is increasing interest in assembly of higher order structures through particle–particle or particle–substrate interactions.

In comparison to spherical particles, asymmetric particles such as nanowires offer additional degrees of freedom in self-assembly due to their inherent shape anisotropy.<sup>1,2</sup> Furthermore, the ability to synthesize particles with different segments along the length of a nanowire provides the opportunity to introduce multiple chemical functionalities by exploiting the selective binding of different ligands to the different segments.<sup>3–6</sup>

Here we report on the directed end-to-end assembly of Au/Pt/Au multisegment nanowires using the biotin/avidin linkage. The biotin/avidin linkage is one of the strongest known biological interactions<sup>7,8</sup> and has been used for the assembly of single-component gold nanoparticles<sup>9–11</sup> and nanorods.<sup>12</sup> We show that bifunctionalization is essential to avoid nonspecific binding of the linker group and hence to minimize lateral assembly. Further we show that the length of the gold end segment can be used to control the number of nanowires connected at each node.

The overall strategy for directed end-to-end assembly is shown in Figure 1. Au/Pt/Au nanowires 300 nm in diameter and 4.5  $\mu\text{m}$  in length were synthesized by electrochemical template synthesis. Selective functionalization was achieved through a thiol linkage on the gold segments and an isocyanide linkage on the central platinum segment.<sup>3,13</sup>

Nanowires were fabricated by electrodeposition into an  $\text{Al}_2\text{O}_3$  template (Anodisc, Whatman) with a nominal pore



**Figure 1.** Schematic illustration of a general approach for directed end-to-end assembly of Au/Pt/Au nanowires. Biotin-terminated thiol (BPT) is bound to the gold segments and butane isocyanide is bound to the platinum segments. Avidin is bound to the biotin groups on the gold end segments in aliquots of bifunctionalized nanowires. Coupling between nanowires with avidin-terminated and biotin-terminated gold end segments results in directed end-to-end assembly.

diameter of 300 nm. An evaporated silver film on one side of the template served as the working electrode in a three-electrode configuration. A thin layer of silver was first electrodeposited from 50 mM  $\text{KAg}(\text{CN})_2$  and 0.25 M  $\text{Na}_2\text{CO}_3$  buffered to pH 13 at  $-1.0$  V (Ag/AgCl) in order to ensure easy release of the nanowires from the template. The

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Au segments of the nanowires were deposited from a commercial gold plating solution (Technic) at  $-1.0$  V (Ag/AgCl), and the Pt segments are deposited from a solution of  $0.015$  M of  $(\text{NH}_4)_2\text{PtCl}_6$  and  $0.2$  M  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$  at  $-0.4$  V (Ag/AgCl). The silver layers were dissolved in 70 vol. % nitric acid, and the alumina template was then dissolved in  $2$  M KOH. The nanowires were washed repeatedly using  $2$  M KOH, deionized water, and ethanol.

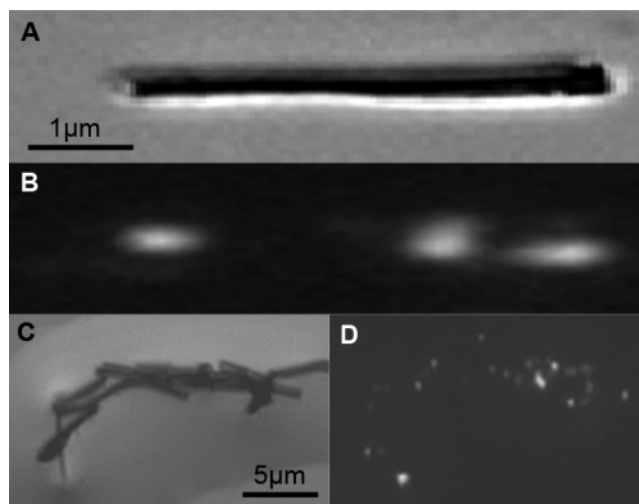
Biotin-poly(ethylene oxide)<sub>4</sub>-1-undecane-thiol was synthesized by reacting  $2.4$  mg 11-amino-1-undecanethiol (Dojindo) with  $5.89$  mg *N*-hydroxy-succinimide-poly(ethylene oxide)<sub>4</sub>-biotin (Pierce) in  $5$  mL of a 50:50 mixture of dimethyl formamide and dimethyl sulfoxide overnight under an argon blanket at room temperature. A tetra(ethylene oxide) spacer group was placed between the biotin and the alkane chain to provide greater hydrophilicity and flexibility for ligand-receptor interaction. The increased hydrophilicity can reduce undesirable nonspecific protein interactions while the long flexible chain increases the efficiency of avidin binding.<sup>7</sup>

In the first series of experiments, Au/Pt/Au nanowires with a  $3.5$   $\mu\text{m}$  platinum segment and  $500$  nm gold end segments were functionalized only with the biotin-terminated thiol.  $2$  mL of the biotin-terminated thiol in DMF/DMSO was added to a  $2$  mL suspension of Au/Pt/Au nanowires ( $\approx 10^9$  mL<sup>-1</sup>) in ethanol at a concentration of  $2$  mM. The suspension was agitated using rotation for  $24$  h. The nanowires were then washed with ethanol and finally with deionized water using centrifugation. The aqueous suspension was then divided into two portions. Neutraavidin tetramethyl rhodamine (NATR, Molecular Probes) was added in excess to one volume of the nanowire suspension for  $5$  min, followed by further washing with deionized water. Saturation of the biotin binding sites with free avidin reduces aggregation by decreasing the probability of nanowire-nanowire binding.<sup>10,11</sup>

Figures 2A and 2B show light microscope and fluorescence microscope images of the functionalized nanowires. Figure 2B shows that the NATR is bound to the gold segments as well as to parts of the platinum segment. This suggests that the biotin-terminated thiol forms an incomplete monolayer on the platinum segment<sup>3</sup> and implies that the binding of thiol to platinum is weaker than on gold.

When a suspension of nanowires functionalized with biotin-terminated thiol is mixed with an equal volume of nanowires where the biotin groups have been saturated with avidin, lateral assembly is significant, as illustrated in Figures 2C and 2D. The formation of aligned bundles of nanowires indicates strong end-to-end assembly as well as lateral assembly. The lateral component is similar to cross-linking in polymers and may be useful in increasing the stiffness in self-assembled nanowire fibers.

In the second series of experiments, nonspecific binding of the biotin-terminated thiol was eliminated by functionalizing the platinum segments with butaneisocyanide (BIC). A suspension of Au/Pt/Au nanowires in  $2$  mL hexane was added to  $2$  mL of  $2$  mM BIC and mixed using rotation for  $24$  h. The nanowires were then washed repeatedly with



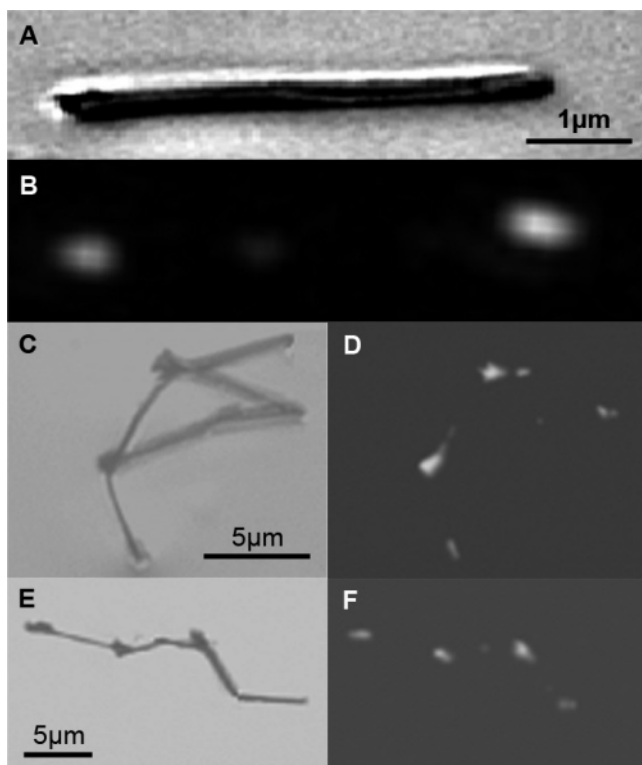
**Figure 2.** (A) Light and (B) fluorescence microscope images of Au/Pt/Au nanowires functionalized with biotin-terminated thiol and exposed to NATR (emission  $580$  nm). (C) Light and (D) fluorescence microscope images of a self-assembled cluster of nanowires.

deionized water using centrifugation and transferred to ethanol. The nanowires were then treated with the biotin-terminated thiol as described above. After washing, the nanowire suspension was divided into two portions and NATR added to one volume.

Figures 3A and 3B show light and fluorescence microscope images of a Au/Pt/Au nanowire with a  $3.5$   $\mu\text{m}$  platinum segment and  $500$  nm gold end segments selectively functionalized with BIC and biotin-terminated thiol. The fluorescence image shows that the NATR is bound to the gold end segments with minimal nonspecific binding to the platinum segment. This shows that the BIC is displaced from gold segments by the biotin-terminated thiol, but not from the central platinum segment. Similar results have been reported by Mallouk and co-workers.<sup>3</sup>

In control experiments, Au/Pt/Au nanowires were functionalized with BIC and then exposed to 1-decanethiol. Subsequent addition of excess NATR and washing did not result in selective functionalization of the gold end segments, indicating that the binding of NATR is a specific receptor-mediated interaction with biotin. Similarly, selective functionalization of the gold end segments was not observed when excess NATR was added to unfunctionalized nanowires.

When nanowires with biotin-terminated gold segments and isocyanide-functionalized platinum segments are mixed with an equal volume of similarly functionalized nanowires that have been treated with avidin, end-to-end binding is observed. With  $500$  nm long gold segments, a significant fraction of the nodes connect three nanowires, as shown in Figure 3C. The corresponding fluorescence image (Figure 3D) clearly shows emission from the NATR at the nodes. The number of nanowires at each node can be limited to two by decreasing the length of the gold segments. Figures 3E and 3F show light and fluorescence microscope images of Au/Pt/Au nanowires with  $10$  nm gold segments and  $4.5$   $\mu\text{m}$  platinum segments using the same procedure as described above.



**Figure 3.** (A) Light and (B) fluorescence microscope images of Au/Pt/Au nanowires functionalized with BIC, biotin-terminated thiol, and exposed to NATR. (C) Light and (D) fluorescence microscope images of a self-assembled cluster of Au/Pt/Au nanowires with 500 nm gold segments. (E) Light and (F) fluorescence microscope images of Au/Pt/Au nanowires with 10 nm gold segments.

The 10 nm long gold end segments minimize binding of three or more nanowires at one node and maximize end-to-end assembly.

In summary, we have demonstrated directed end-to-end assembly of Au/Pt/Au multisegment nanowires using the biotin/avidin linkage. The formation of a self-assembled monolayer on the central platinum segments is essential to

avoid nonspecific binding of the linker group and hence to minimize lateral assembly. We also show that the number of nanowires connected at each node is dependent on the length of the gold end segments.

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**Note Added After ASAP Posting.** This article was posted on the web on 5/11/2004. The spelling of the first author's name has been corrected to "Aliasger K. Salem". The correct version was posted on 5/18/2004.

## References

- (1) Sun, L.; Searson, P. C.; Chien, C. L. *Appl. Phys. Lett.* **2001**, *79*, 4429.
- (2) Chen, M.; Sun, L.; Bonevich, J. E.; Reich, D. H.; Chien, C. L.; Searson P. C. *Appl. Phys. Lett.* **2003**, *82*, 3310–3312.
- (3) Martin, B. R.; Dermody, D. J.; Reiss, B. D.; Fang, M. M.; Lyon, L. A.; Natan, M. J.; Mallouk, T. E. *Adv. Mater.* **1999**, *11*, 1021–1025.
- (4) Nicewarner-Pena, S. R.; Freeman, R. G.; Reiss, B. D.; He, L.; Pena, D. J.; Walton, I. D.; Cromer, R.; Keating, C. D.; Natan, M. J. *Science* **2001**, *294*, 137–141.
- (5) Salem, A. K.; Searson, P. C.; Leong, K. W. *Nature Mater.* **2003**, *2*, 668–671.
- (6) Salem, A. K.; Chao, J.; Leong, K. W.; Searson, P. C. *Adv. Mater.*, in press.
- (7) Salem, A. K.; Cannizzaro, S. M.; Davies, M. C.; Tandler, S. J. B.; Roberts, C. J.; Williams, P. M.; Shakesheff, K. M. *Biomacromolecules* **2001**, *2*, 575–580.
- (8) Diamandis E. P.; Christopoulos, T. K. *Clin. Chem.* **1991**, *37*, 625–636.
- (9) Mann, S.; Shenton, W.; Li, M.; Connolly, S.; Fitzmaurice, D. *Adv. Mater.* **2000**, *12*, 147–150.
- (10) Salem, A. K.; Rose, F.; Oreffo, R. O. C.; Yang, X. B.; Davies, M. C.; Mitchell, J. R.; Roberts, C. J.; Stolnik-Trenkic, S.; Tandler, S. J. B.; Williams, P. M.; Shakesheff, K. M. *Adv. Mater.* **2003**, *15*, 210–213.
- (11) Connolly, S.; Cobbe, S.; Fitzmaurice, D. *J. Phys. Chem. B* **2001**, *105*, 2222–2226.
- (12) Caswell, K. K.; Wilson, J. N.; Bunz, U. H. F.; Murphy, C. J. *J. Am. Chem. Soc.* **2003**, *125*, 13914–13915.
- (13) Hickman, J. J.; Laibinis, P. E.; Auerbach, D. I.; Zou, C. F.; Gardner, T. J.; Whitesides, G. M.; Wrighton, M. S. *Langmuir* **1992**, *8*, 357–359.

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