Directed Assembly of Nanodumbbells via Nano-Lithographic Docking

A. Marcovici[1,3], G. Le Saux[1,3], P. Rukenstein[2,3], T. Mokari[2,3], M. Schvartzman[1,3]
[1]Department of Materials Engineering, Faculty of Engineering, [2] Department of Chemistry, Faculty of Science, [3]Ilse Katz Institute for Nanoscale Science and Technology Ben Gurion University of the Negev, Be'er Sheva, Israel, 8410501

avichaim@post.bgu.ac.il

Realization of the bottom-up nanofabrication approach requires the placement of synthesized building nano-blocks. In particular, 1D nano-blocks have great potential for the future bottom-up functional nano-devices and circuits. Several approaches for the placement of different types of 1D nanostructures have been evolved and studied, including microfluidic channels[1], dielectrophoresis[2] , and surface patterning[3] . However, these and other approaches have been limited so far to nanowires whose width is usually scaled by few tens of nm and length is scaled by microns. Controlled placement of inorganic 1D nanostructures with sub-100 nm length has not been explored, to the best of our knowledge.

Inorganic nanodumbbells were first synthesized more than a decade ago by attachment of Au nanotips to CdS nanorods [4, 5]. The main motivation for the Au nanotips was the formation of natural anchoring points for directed self-assembly, yet this assembly concept has not been implemented up today. Here, we introduce, for the first time, the programmed assembly of nanodumbbells onto arrays of functionalized nanodots that serve as docking points. Notably, similar approaches have been applied for organic molecules with functionalities that bind to nanodots[6, 7, 8], but not yet on inorganic nanostructures.

The docking arrays of 5-10 nm AuPd nanodots were produced by nanoimprint lithography, followed by angle-evaporation pattern transfer[9] (*Fig. 1a*), and functionalized by thiol molecules terminated to bind Au tips of nanodumbbells. To dock the nanodumbbells, we used thiols with various terminal functionalities including thiol, biotin, and cyste-amine hydrochloride. Nanodumbbells (*Fig. 1b*) functionalized to bind the docking nanodots were introduced to the arrays, forming higher 2D architectures, whose geometry is encoded by the nanodots pattern (*Fig. 1c*). Theoretical models aimed at the prediction of the docking behavior of the nanodumbbells to the nanodots array were based on probabilistic & kinetic approaches, showing a good agreement with the experimental data (*Fig 2)*. We believe that our approach opens a pathway to the future nanostructured materials and functional systems with the nano-dimensions and functionalities unachievable by current technologies.

1. L. J. Guo, Nano Lett. **4**, 69 (2004).
2. E. Freer et al, Nat. Nanotechnol. **5**, 525 (2010).
3. Y. Huang et al, Science . **291**, 630 (2001).
4. T. Mokari et al, Science. **304**, 1787 (2004).
5. T. Mokari et al, Nat. Mater. **4**, 855 (2005).
6. P. Morales et al, Small **12**, 169 (2016).
7. H. Cai et al, J. Vac. Sci. Technol. B **31**, 06F902 (2013).
8. M. Palma et al, J. Am. Chem. Soc. **133**, 7656 (2011).
9. M. Schvartzman et al, Nano Lett. **9**, 3629 (2009).

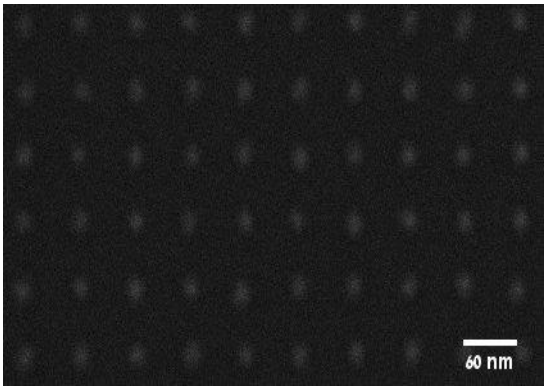

Figure 1a - SEM Micrograph of AuPd docking array, dots are 60nm apart

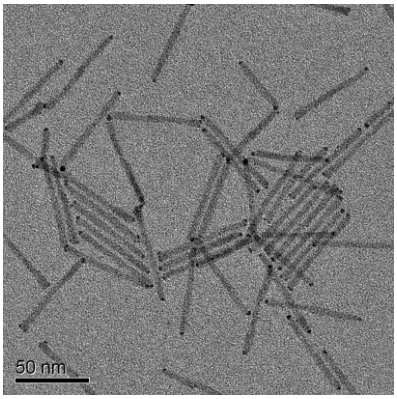

Figure 1b – TEM micrograph of 60nm long CdS nanodumbbells with Au tips

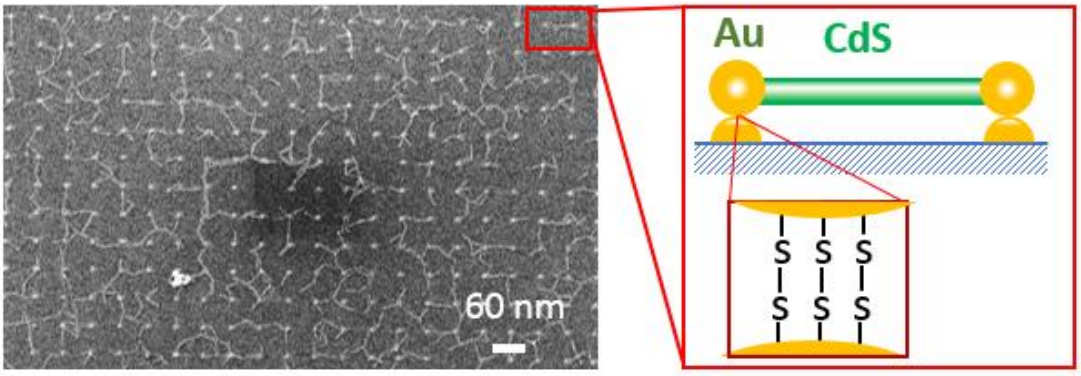

Figure 1c – SEM micrograph showing docking of nanodumbbells onto array of dithiol functionalized AuPd nanodots, scheme on the right showing docking of a single nanodumbbell to a neighboring pair of nanodots

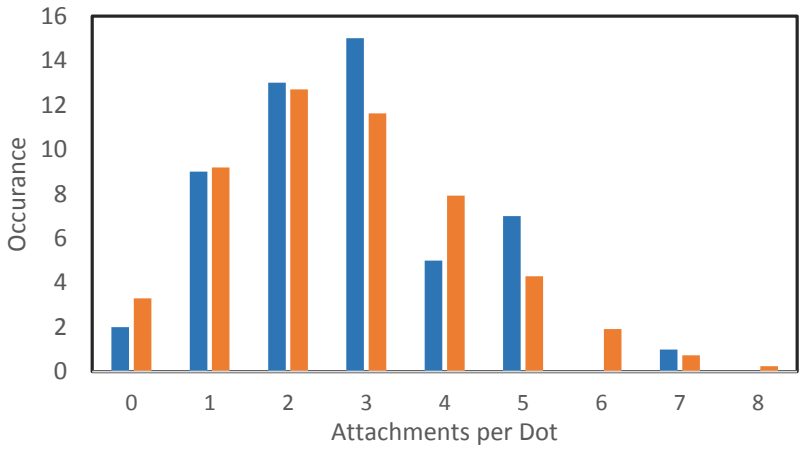

Figure 2 – Comparison between random attachment model & experimental results for attachment of nanodumbbells to a single dot