

### Three-dimensional metamaterials made from engineered oligonucleotides and nanoparticles

Angela F. De Fazio<sup>a</sup>, Afaf H. El-Sagheer<sup>b,c</sup>, Tom Brown<sup>b</sup>, Otto L. Muskens<sup>a</sup>, Antonios G. Kanaras<sup>\*a</sup>

<sup>a</sup> *Physics and Astronomy, Faculty of Physical Sciences and Engineering, University of Southampton, Southampton, SO17 1BJ, UK.*

<sup>b</sup> *Department of Chemistry, Chemistry Research Laboratory, University of Oxford, Oxford, OX1 3TA, UK.*

<sup>c</sup> *Chemistry Branch, Department of Science and Mathematics, Faculty of Petroleum and Mining Engineering, Suez University, Suez 43721, Egypt.*

\*Corresponding Author e-mail: [A.Kanaras@soton.ac.uk](mailto:A.Kanaras@soton.ac.uk)

The ability to assemble nanoparticles into programmed 2D or 3D structures by means of synthetic oligonucleotides<sup>1–3</sup> has resulted into the fabrication of novel nanomaterials with unique physical and chemical properties. In particular this bottom-up approach allows routes to flexible and precise design of featured materials which can be tuned by varying the constituent building blocks. These combine the advanced programming of the assembly processes to the use of innovative ligation techniques.

Despite the promising results achieved towards the engineering of different shaped materials<sup>4</sup>, by using different size, shape<sup>5,6</sup> and composition<sup>7</sup> particles, DNA-nanoparticles materials lack in stability, which limits their application.

Herein we present a method to fabricate self-assembled materials based on synthetic oligonucleotides and metallic nanoparticles endowed with enhanced stability thanks to the introduction of a tunable covalent bond within the sequences. This opens the way to a broad series of possible applications, including their use on surfaces coating and incorporation in hybrid systems.

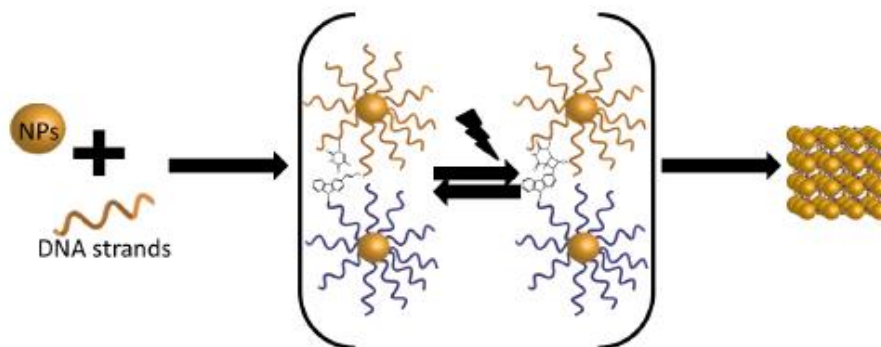


Fig. 1 Synthetic scheme of the synthesis on DNA-NP assemblies, using a covalent bond approach between previously hybridised oligonucleotides.

- (1) Alivisatos, a. P.; Johnsson, K. P.; Peng, X.; Wilson, T. E.; Loweth, C. J.; Bruchez, M. P.; Schultz, P. G. Organization of “Nanocrystal Molecules” Using DNA. *Nature*, 1996, 382, 609–611.
- (2) Park, S. Y.; Lytton-Jean, A. K. R.; Lee, B.; Weigand, S.; Schatz, G. C.; Mirkin, C. a. DNA-Programmable Nanoparticle Crystallization. *Nature* 2008, 451, 553–556.
- (3) Mirkin, C. a; Letsinger, R. L.; Mucic, R. C.; Storhoff, J. J. A DNA-Based Method for Rationally Assembling Nanoparticles into Macroscopic Materials. *Nature*, 1996, 382, 607–609.
- (4) Liu, W.; Tagawa, M.; Xin, H. L.; Wang, T.; Emamy, H.; Li, H.; Yager, K. G.; Starr, F. W.; Tkachenko, A. V; Gang, O. Diamond Family of Nanoparticle Superlattices. 2015, 3–8.
- (5) O’Brien, M. N.; Jones, M. R.; Lee, B.; Mirkin, C. a. Anisotropic Nanoparticle Complementarity in DNA-Mediated Co-Crystallization. *Nat. Mater.* 2015, 14, 833–839.
- (6) Jones, M. R.; Macfarlane, R. J.; Lee, B.; Zhang, J.; Young, K. L.; Senesi, A. J.; Mirkin, C. a. DNA-Nanoparticle Superlattices Formed from Anisotropic Building Blocks. *Nat. Mater.* 2010, 9, 913–917.
- (7) Sun, D.; Gang, O. Binary Heterogeneous Superlattices Assembled from Quantum Dots and Gold Nanoparticles with DNA. *J. Am. Chem. Soc.* 2011, 133, 5252–5254.