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基于 DNA 自组装的手性等离子体纳米结构研究进展

王猛, 董今一, 王强斌*

中国科学院苏州纳米技术与纳米仿生研究所, 苏州 215123
* 联系人, E-mail: qbwang2008@sinano.ac.cn

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摘要 自然界中的手性现象广泛存在. 近年来, 具有在可见光波段手性光学响应特性的等离子体金属纳米结构吸引了越来越多的关注. DNA自组装技术以DNA分子为基元构筑纳米材料, 具有根据实际需求精准调控并组装得到复杂纳米结构的优点, 可以用来构建从静态到动态的各种手性等离子纳米结构. 本文综述了基于DNA自组装的手性等离子体纳米结构的研究历程和最新进展, 并对相关研究做进一步展望.

关键词 DNA 纳米技术, DNA 自组装, 手性等离子体, 金属纳米粒子

手性作为物体与其镜像不对称的结构特性, 是科学界一个非常重要且广泛的研究领域[1], 如各种蛋白质大分子药物的手性对映体具有不同的毒性和药理特征, 化学不对称合成、手性催化等在研究和生产中都有重要意义[2]. 贵金属纳米颗粒可以在三维空间以手性方式排列, 并通过其表面等离子基元的耦合产生特殊的光学手性信号[3~5]. 表面等离子体激元是当光波(电磁波)入射到金属与介质分界面时, 金属表面的自由电子发生集体振荡的行为[6]. 当表面等离子体激元被局域在粒径远小于入射光波长的金属纳米颗粒表面上时, 即可形成局域表面等离子体共振效应[7], 赋予了贵金属纳米材料(金、银、铜)优异的物理、化学性质. 相比生物大分子在紫外光波段的光学手性响应, 手性等离子体纳米结构可以在可见光波段使手性信号得到极大增强, 并由此带来很多新的光学现象, 如手性传递、负折射等, 一直受到科学家的关注[8~10].

DNA自组装技术提供了在溶液中构建手性等离子纳米颗粒的有效手段. DNA是脱氧核糖核酸的简称, 是大自然中普遍存在的遗传物质, 两条互补的单链DNA严格遵循Watson-Crick碱基互补配对原则形成稳定的DNA双螺旋结构, 因而DNA自组装可靠性高而又易于重复. 1982年, Seeman研究组[11]从Holliday模型得到灵感, 在体外首次构建了稳定的Holliday结构, 奠定了DNA结构组装的基础. 在此之后, Yan研究组[12,13]和Mao研究组[14,15]等对模块化组装策略拓展, 利用结构可控、稳定的多臂单元自组装得到二维阵列和立体结构. Yin研究组[16]在2008年以两对互补序列构成一个具有4片不同的结合域的模块进行组装, 即单链结构模块(single-stranded tile, SST)方法, 可以组装为纳米带、纳米管、三维结构和复杂精细结构[17~19]. 2006年, Rothemund[20]提出了一种全新的自组装的方法——DNA折纸术(DNA origami), 可以由一条固定的DNA长链和预设计的短链自组装形成所设计的构型, 研究人员利用DNA折纸术又发展了一系列的设计精确、结构复杂的DNA纳米结构[21~29], 进一步推动了纳米结构组装和器件的发展. 等离子纳米颗粒可以通过DNA互补精准地固定在DNA折纸

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结构的表面构成特定的手性等离子纳米结构.

1 以球形金属纳米材料组装手性等离子体纳米结构

基于DNA纳米技术组装手性等离子体超结构初期研究主要采用球形金属纳米材料作为构筑基元, 这是由于球形金属纳米材料自身的各项同性, 在调节手性超结构的构型时主要考虑整体空间构型的几何手性, 调控比较方便, 利用这种优势可以将球形金属纳米粒子组装拓展到数量更多、造型复杂的手性超结构. Zhao等人[30]构建了椭球形的金属纳米颗粒异二聚体(图1(a)); Mastroianni等人[35]利用DNA连接金纳米颗粒得到了手性金字塔结构, 在此基础上, Yan等人[31]利用双链DNA连接不同尺寸的金纳米颗粒、银纳米颗粒和量子点, 形成具有光学手性的金字塔结构(图1(b)), 这种结构的产率可以达到80%并且可以在350~550 nm观察到3个CD信号峰.

以DNA折纸结构为模板构筑手性等离子超结构

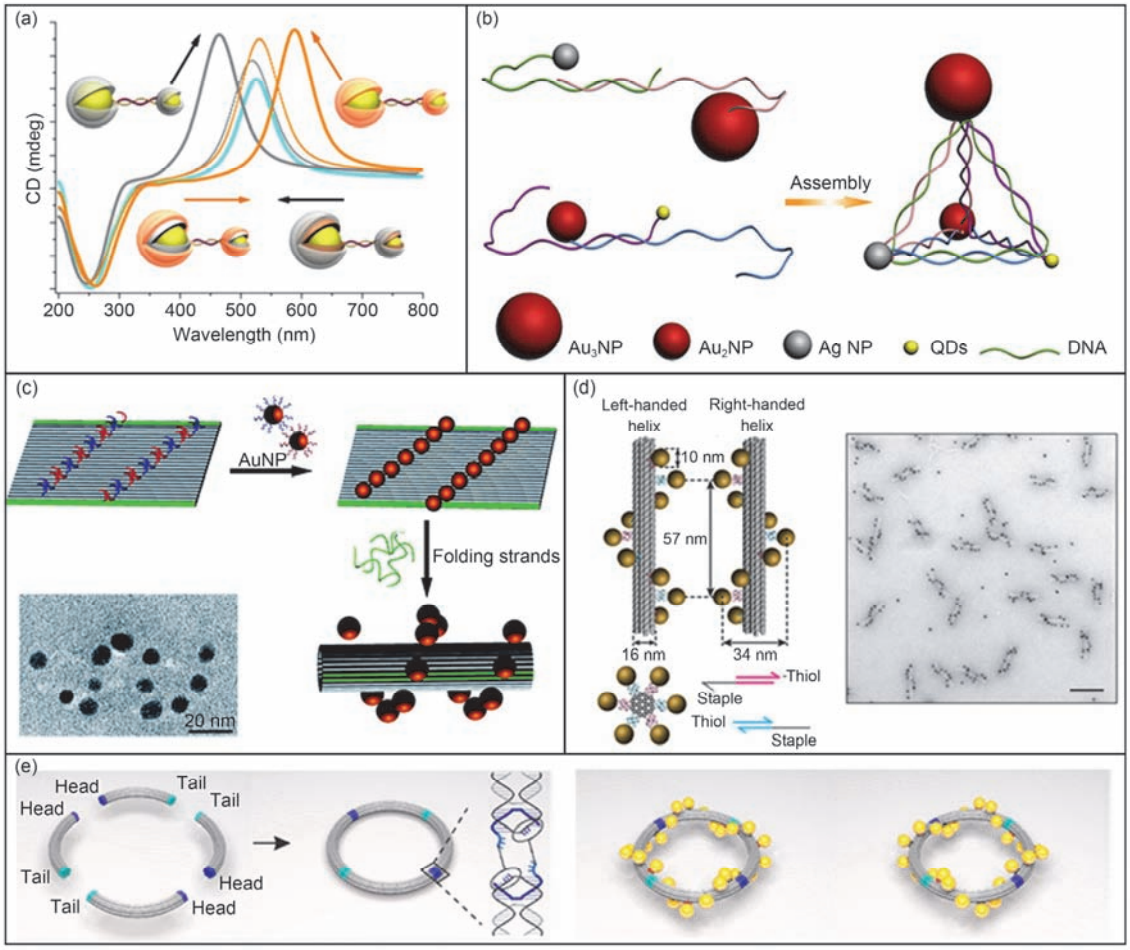

图 1 (网络版彩色)以球形金属纳米材料组装手性等离子体纳米结构. (a) DNA连接的金纳米颗粒-银壳异二聚体, 这种结构可以在 400~600 nm 波段调节手性光谱[30]; (b) 不同尺寸的金纳米颗粒、银纳米颗粒和量子点, 形成具有光学手性的金字塔结构[31]; (c) 以矩形DNA折纸为模板, 通过加入闭合链使得平面矩形片卷曲得到中空的管状结构, 构筑得到了 15 个金纳米粒子的三维螺旋的手性等离子纳米结构[32]; (d) 以柱状DNA折纸结构为模板构筑左手螺旋和右手螺旋的金纳米颗粒单螺旋结构[33]; (e) 以环形的DNA折纸结构为模板组装金纳米颗粒的环状手性螺旋超结构[34]

Figure 1 (Color online) Spherical metal nanomaterials are assembled into chiral plasma nanostructures. (a) DNA-bridged pairs of gold and silver shells around the nanoparticle heterodimers enables spectral modulation of their chiral plasmonic bands in 400–600 nm region[30]. (b) A family of self-assembled chiral pyramids made from multiple metal and/or semiconductor nanoparticles[31]. (c) Fifteen AuNPs are assembled on a rectangular origami sheet. Addition of the folding strands leads to rolling and subsequent stapling of the 2D sheet into a hollow tube. As a consequence, the AuNPs are arranged into a 3D helix[32]. (d) Plasmonic helices created by arranging AuNPs on origami bundles and the measured CD spectra[33]. (e) AuNPs are assembled in a helical fashion along an origami ring to form a chiral plasmonic toroidal structure[34]

在设计上更加简洁明了且具有较高的稳定性，Shen等人[36]在DNA折纸矩形片上下两面设计捕获位点并分别装载了4个20 nm的金纳米颗粒，相比于Mastroianni等人[35]所设计的手性金字塔结构，这种四面体的等离子结构由于尺寸增加具有更强的光学响应，同时DNA折纸作为模板比双链DNA的连接方式更加稳定，因此金纳米颗粒的四面体结构拥有更明显的CD吸收．同时Shen等人[32]以矩形DNA折纸为模板构筑双螺旋的手性等离子纳米结构(图1(c))，纳米粒子之间的空间位置由捕获链的位点决定，加入的闭合链使得矩形片在卷曲的同时降低金纳米粒子间的斥力，最终构成手性的螺旋结构，调节纳米粒子的尺寸可以获得不同强度的光学响应．Kuzyk等人[33]以100 nm长的刚性柱状DNA折纸结构为模板，将10 nm的金纳米颗粒分别排列成左手螺旋和右手螺旋的单螺旋结构(图1(d))，这种精确排列的纳米粒子螺旋在近场耦合作用下产生了手性光学信号，同时作者利用银纳米粒子增强了CD信号，组装得到可调节的等离子手性结构．Urban等人[34]组装了利用环形的DNA折纸结构组装得到了更为复杂的24个金纳米颗粒的环状手性螺旋超结构(图1(e))，DNA折纸模板由4段圆弧首尾相连拼接而成，模板表面的设计位点能够精准地捕获金纳米粒子从而获得DNA纳米粒子环状复合结构，这种手性等离子超结构在可见光区具有明显的光学活性．随着研究的深入，球形金属纳米材料超结构产生光学活性的机制也已经被阐明[37~39]．

2 以金纳米棒为基元组装手性等离子体纳米结构

各项异性材料的部分化学、物理等性质随着方向的改变而有所变化，在不同的方向上呈现出差异的性质，结合手性等离子体纳米结构的概念可以发掘更多新奇的性质和特征，DNA折纸纳米模板可以根据需要调整金属纳米基元的间距以及空间构型，进而实现对手性光谱的调控，目前研究人员以棒状金属纳米材料作为构筑基元组装更有挑战性的等离子体手性结构．Pal等人[40]在金纳米棒表面修饰上单链巯基DNA并将其连接到预先设计好的位点的三角形DNA折纸上，得到了两个金纳米棒分别排列成0°，60°，90°和180°等不同角度的二聚体结构(图2(a))，实现了对金纳米棒的精确排布．Zhan等人[41]利用角度可调的DNA折纸三脚架为模板，成功地对金纳米棒的三维空间构型进行了可逆地动态调节(图2(b))．本课题组[43,44]采用DNA模板开展了一系列精确组装等离子手性纳米结构的研究，以矩形片DNA折纸为模板，将金纳米棒组装成“L”形的金纳米棒二聚体[45]，通过调整表面位点改变两根金纳米棒的位置，获得了不同的手性光学响应；在此基础上进一步优化设计，成功构筑了多根金纳米棒排列而成的手性螺旋超结构[42](图2(c))，以双层、双面正方形 DNA折纸为模板，通过设计中心对称功能区域组装金纳米棒，分别获得了左手型和右手型金纳米棒螺旋超结构，其

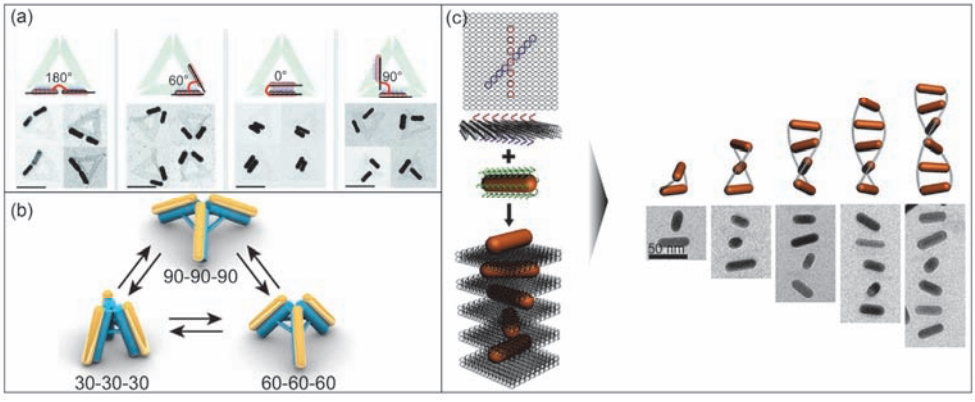

图 2 (网络版彩色)以金纳米棒为基元组装手性等离子体纳米结构．(a) 以三角形DNA折纸为模板构筑特定角度和间距的金纳米棒二聚体结构[40]；(b) 以角度可调的DNA折纸三脚架为模板构筑具有三维空间构型的金纳米棒三聚体[41]；(c) 通过在矩形片折纸上下表面设计“X”形位点，金纳米棒可以连接到矩形片表面并形成手性螺旋超结构[42]

Figure 2 (Color online) Gold nanorods (AuNRs) are assembled into chiral plasmonic nanostructures. (a) AuNR dimer structures with various predetermined inter-rod angles and relative distances via triangular DNA origami[40]. (b) A 3D reconfigurable plasmonic nanostructure with controllable, reversible DNA origami tripod[41]. (c) By designing the “X” pattern of the arrangement of DNA capturing strands on both sides of a two-dimensional DNA origami template, AuNRs were assembled into AuNR superstructures with the origami intercalated between neighboring AuNRs[42]

中金纳米棒的间距和夹角均得到精确控制，分别为14 nm和45°，这种超螺旋结构由于其强耦合效应，其光学活性达到了与宏观金纳米棒-纤维复合材料相接近的水平. Liu等人[46]提出了一种可编程自组装成各种手性超分子结构的策略，以DNA三角框螺旋超支架为模板，通过模板边缘上下键合和表面位点设计，将金纳米棒组装成旋转的阶梯式手性超结构. 这些结构在可见光波段都具有显著且可调制的手性光学信号.

3 手性等离子纳米结构的动态调控

DNA纳米技术得益于DNA分子自组装高水平的结构可编程性，即DNA纳米结构大小、空间指向性以及表面功能化单元(如靶向配体、多肽、寡核苷酸、药物和纳米颗粒等)都可以精确控制[47~51]，在上述静态组装手性等离子超结构的基础上，研究人员开发了一系列可动态调控的手性等离子超结构. Jiang等人[52]将DNA折纸模板扩展到两个三角形片并在单个片上固定金纳米棒，获得了L形的金纳米棒二聚体和固定的手性光学响应，之后他们在三角形片的键合处设计不同的条件来响应外界刺激(图3(a))，从而可以改变金纳米棒二聚体的构型而获得不同的光学响应. Kuzyk等人[53]报道了一种可调节的三维等离子复合结构(图3(b))，通过精巧的设计，两个DNA折纸的纳米带可以装载两根金纳米棒得到金纳米棒复合结构，通过加入DNA“燃料”作为“钥匙”，在Toehold介导的链置换反应下，金纳米棒复合结构的构型会发

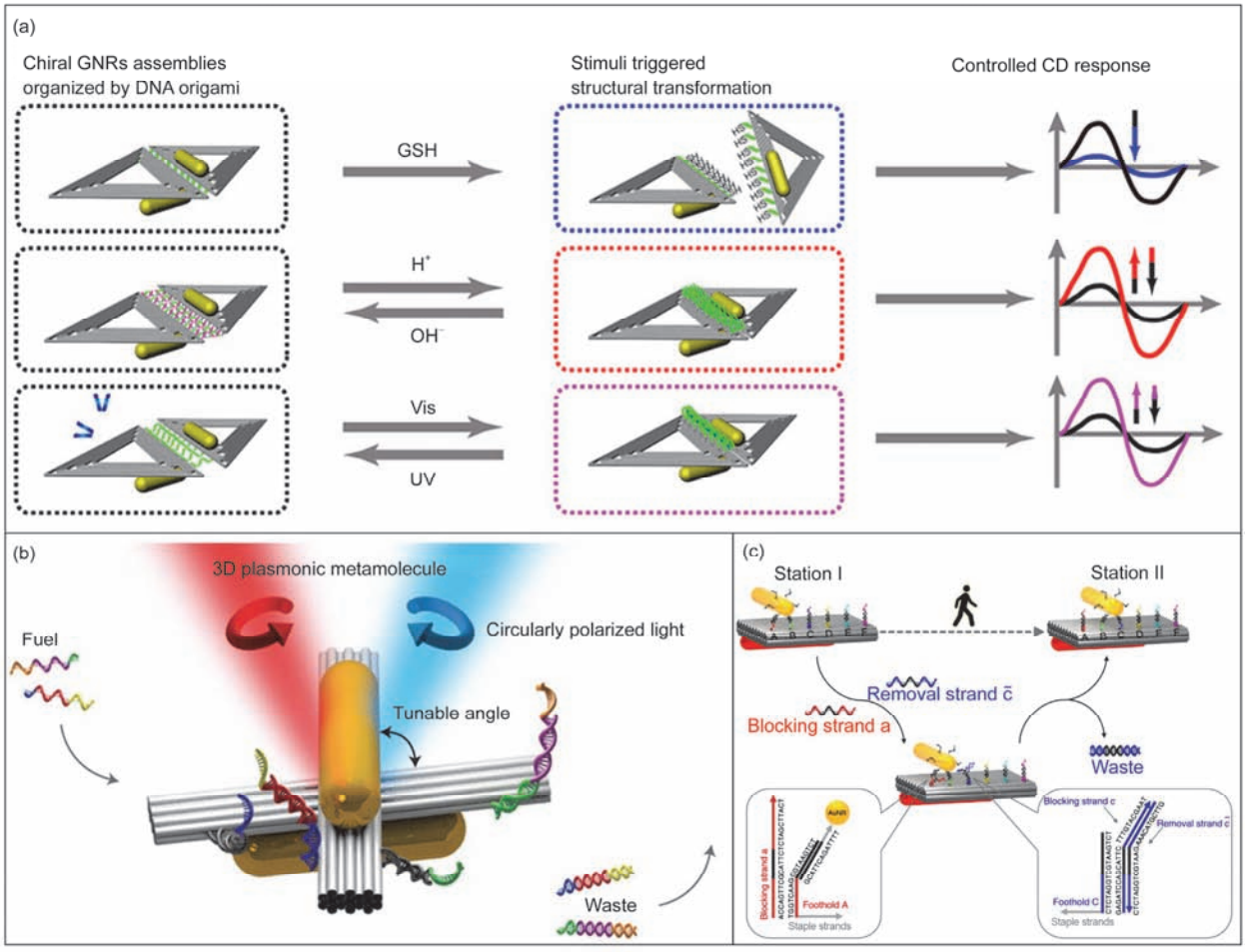

图 3 (网络版彩色)DNA自组装得到可动态调控的等离子体超结构. (a) 响应外界刺激的金纳米棒二聚体[52]; (b) 基于Toehold介导的链置换反应的动态三维等离子体纳米结构[53]; (c) 可以在DNA折纸上进行分步行走的等离子体行者[54]

Figure 3 (Color online) DNA-assembled plasmonic nanostructures for dynamic manipulation. (a) A stimulus-responsive plasmonic nanosystem based on DNA origami-organized gold nanorods[52]. (b) Reconfigurable 3D plasmonic nanostructures consist of AuNRs hosted on switchable DNA origami templates based on toehold mediated chain replacement[53]. (c) Plasmonic walker that can perform stepwise walking on origami[54]

生左旋结构、右旋结构、松弛状态之间的转变，其光学响应强烈且在可见光区．Yan等人[55]利用相似的策略将偶氮苯修饰的DNA插入到“钥匙”之中，通过偶氮苯分子响应不同光照条件后产生的*cis*/*trans*构型变化引导金纳米棒二聚结构的构型变化，从而产生可调节的手性等离子结构．Zhou等人[54]提出了一种动态操控的等离子组装体系(图3(c))，两根不同功能的金纳米棒(一根锚定于模板表面另一根可以在反面行走)排布在矩形片DNA折纸的上下两侧，在一侧的DNA模板表面以不同的位点设计了5个“站台”，通过加入DNA转移链可以让一根金纳米棒在模板表面行走，并可以实时检测到CD信号．当然，在引入不同尺寸和形貌的等离子体纳米基元混合组装之后，更多结构新颖、光学性质独特的手性等离子体纳米结构还亟待探索．

4 总结和展望

手性与自然界息息相关，手性等离子体结构利用其自身等离激元能够增强电磁场从而达到放大和调控光场的性质，为进一步研究手性光效应与其应用开拓了广阔的前景；自Seeman教授第一次应用DNA分子作为自组装材料以来，研究人员已经能够对DNA纳米结构的几何形状、三维结构、尺寸大小和多元功能化进行精确控制．近年来，科学家利用DNA纳米结构作为工具和载体研究手性等离子体组装行为和结构特性，已经从静态组装和动态调控两个方面对不同的金属纳米粒子和半导体量子点等基元组装取得了丰硕的成果．虽然如此，手性等离子体超结构研究领域依然面临许多挑战，如在三维尺度上多组分体系的精确组装与性能的精确调控、复杂环境下分子间弱相互作用及动态组装的开展以及手性等离子体超结构作为智能载体的探索等，这些挑战有希望在研究人员的共同努力下得以突破，将更复杂的手性等离子纳米结构在三维空间、更大尺度进行精确组装从而构建手性超结构，获得新型的纳米材料的有序组装体．

参考文献

1 Zhang S, Park Y S, Li J, et al. Negative refractive index in chiral metamaterials. Phys Rev Lett, 2009, 102: 023901
2 Agranat I, Caner H, Caldwell J. Putting chirality to work: The strategy of chiral switches. Nat Rev Drug Discovery, 2002, 1: 753
3 Ma W, Xu L, de Moura A F, et al. Chiral inorganic nanostructures. Chem Rev, 2017, 117: 8041–8093
4 Ma W, Hao C, Sun M, et al. Tuning of chiral construction, structural diversity, scale transformation and chiroptical applications. Mater Horiz, 2018, 5: 141–161
5 Zhao Y, Sun M, Ma W, et al. Biological molecules-governed plasmonic nanoparticle dimers with tailored optical behaviors. J Phys Chem Lett, 2017, 8: 5633–5642
6 Ozbay E. Plasmonics: Merging photonics and electronics at nanoscale dimensions. Science, 2006, 311: 189–193
7 Schuller J A, Barnard E S, Cai W, et al. Plasmonics for extreme light concentration and manipulation. Nat Mater, 2010, 9: 193
8 Wang Z, Cheng F, Winsor T, et al. Optical chiral metamaterials: A review of the fundamentals, fabrication methods and applications. Nanotechnology, 2016, 27: 412001
9 Valev V K, Baumberg J J, Sibilia C, et al. Chirality and chiroptical effects in plasmonic nanostructures: Fundamentals, recent progress, and outlook. Adv Mater, 2013, 25: 2517–2534
10 Luo Y, Chi C, Jiang M, et al. Plasmonic chiral nanostructures: Chiroptical effects and applications. Adv Opt Mater, 2017, 5: 1700040
11 Seeman N C. Nucleic acid junctions and lattices. J Theor Biol, 1982, 99: 237–247
12 Zhang F, Jiang S, Wu S, et al. Complex wireframe DNA origami nanostructures with multi-arm junction vertices. Nat Nanotechnol, 2015, 10: 779–784
13 Yan H, Park S H, Finkelstein G, et al. DNA-templated self-assembly of protein arrays and highly conductive nanowires. Science, 2003, 301: 1882–1884
14 He Y, Tian Y, Chen Y, et al. Sequence symmetry as a tool for designing DNA nanostructures. Angew Chem Int Ed, 2005, 44: 6694–6696
15 He Y, Chen Y, Liu H, et al. Self-assembly of hexagonal DNA two-dimensional (2D) arrays. J Am Chem Soc, 2005, 127: 12202–12203
16 Yin P, Hariadi R F, Sahu S, et al. Programming DNA tube circumferences. Science, 2008, 321: 824–826
17 Wei B, Dai M, Yin P. Complex shapes self-assembled from single-stranded DNA tiles. Nature, 2012, 485: 623–626
18 Ke Y G, Ong L L, Shih W M, et al. Three-dimensional structures self-assembled from DNA bricks. Science, 2012, 338: 1177–1183
19 Ong L L, Hanikel N, Yaghi O K, et al. Programmable self-assembly of three-dimensional nanostructures from 10000 unique components. Nature, 2017, 552: 72–77

20 Rothemund P W. Folding DNA to create nanoscale shapes and patterns. Nature, 2006, 440: 297–302
21 He Y, Ye T, Su M, et al. Hierarchical self-assembly of DNA into symmetric supramolecular polyhedra. Nature, 2008, 452: 198
22 Douglas S M, Chou J J, Shih W M. DNA-nanotube-induced alignment of membrane proteins for NMR structure determination. Proc Natl Acad Sci USA, 2007, 104: 6644–6648
23 Douglas S M, Dietz H, Liedl T, et al. Self-assembly of DNA into nanoscale three-dimensional shapes. Nature, 2009, 459: 1154
24 Dietz H, Douglas S M, Shih W M. Folding DNA into twisted and curved nanoscale shapes. Science, 2009, 325: 725–730
25 Han D, Pal S, Nangreave J, et al. DNA origami with complex curvatures in three-dimensional space. Science, 2011, 332: 342–346
26 Song J, Li Z, Wang P, et al. Reconfiguration of DNA molecular arrays driven by information relay. Science, 2017, 357: eaan3377
27 Tikhomirov G, Petersen P, Qian L. Programmable disorder in random DNA tilings. Nat Nanotechnol, 2017, 12: 251–259
28 Tikhomirov G, Petersen P, Qian L. Fractal assembly of micrometre-scale DNA origami arrays with arbitrary patterns. Nature, 2017, 552: 67–71
29 Fang W N, Fan C H, Liu H J. Effect of pH on the stability of DNA origami. Acta Polym Sin, 2017, (12): 1993–2000
30 Zhao Y, Xu L, Ma W, et al. Shell-engineered chiroplasmonic assemblies of nanoparticles for zeptomolar DNA detection. Nano Lett, 2014, 14: 3908
31 Yan W, Xu L, Xu C, et al. Self-assembly of chiral nanoparticle pyramids with strong R/S optical activity. J Am Chem Soc, 2012, 134: 15114–15121
32 Shen X, Chen S, Wang J, et al. Rolling up gold nanoparticle-dressed DNA origami into three-dimensional plasmonic chiral nanostructures. J Am Chem Soc, 2012, 134: 146–149
33 Kuzyk A, Schreiber R, Fan Z, et al. DNA-based self-assembly of chiral plasmonic nanostructures with tailored optical response. Nature, 2012, 483: 311–314
34 Urban M J, Dutta P K, Wang P, et al. Plasmonic toroidal metamolecules assembled by DNA origami. J Am Chem Soc, 2018, 138: 5495–5498
35 Mastroianni A J, Claridge S A, Alivisatos A P. Pyramidal and chiral groupings of gold nanocrystals assembled using DNA scaffolds. J Am Chem Soc, 2009, 131: 8455–8459
36 Shen X, Asenjo-Garcia A, Liu Q, et al. Three-dimensional plasmonic chiral tetramers assembled by DNA origami. Nano Lett, 2013, 13: 2128–2133
37 Fan Z, Zhang H, Govorov A. Plasmonic circular dichroism of chiral nanoparticle assemblies. Nano Lett, 2010, 10: 2580–2587
38 Fan Z, Zhang H, Govorov A O. Optical properties of chiral plasmonic tetramers: Circular dichroism and multipole effects. J Phys Chem C, 2013, 117: 14770–14777
39 Ferry V E, Smith J M, Alivisatos A P. Symmetry breaking in tetrahedral chiral plasmonic nanoparticle assemblies. ACS Photonics, 2014, 1: 1189–1196
40 Pal S, Deng Z, Wang H, et al. DNA directed self-assembly of anisotropic plasmonic nanostructures. J Am Chem Soc, 2011, 133: 17606–17609
41 Zhan P, Dutta P K, Wang P, et al. Reconfigurable three-dimensional gold nanorod plasmonic nanostructures organized on DNA origami tripod. ACS Nano, 2017, 11: 1172–1179
42 Lan X, Lu X, Shen C, et al. Au nanorod helical superstructures with designed chirality. J Am Chem Soc, 2014, 137: 457–462
43 Shen C, Lan X, Zhu C, et al. Spiral patterning of Au nanoparticles on Au nanorod surface to form chiral AuNR@AuNP helical superstructures templated by DNA origami. Adv Mater, 2017, 29: 1606533
44 Shen C, Xiang L, Lu X, et al. Site-specific surface functionalization of gold nanorods using DNA origami clamps. J Am Chem Soc, 2016, 138: 1764–1767
45 Lan X, Chen Z, Dai G, et al. Bifacial DNA origami-directed discrete, three-dimensional, anisotropic plasmonic nanoarchitectures with tailored optical chirality. J Am Chem Soc, 2013, 135: 11441–11444
46 Liu Y, Lan X, Su Z, et al. Programmable supra-assembly of DNA surface adapter for tunable chiral directional self-assembly of gold nanorods. Angew Chem Int Ed, 2017, 56: 14824–14828
47 Hong F, Zhang F, Liu Y, et al. DNA origami: Scaffolds for creating higher order structures. Chem Rev, 2017, 117: 12584–12640
48 Hu Q, Li H, Wang L, et al. DNA nanotechnology-enabled drug delivery systems. Chem Rev, 2018, doi: 10.1021/acs.chemrev.7b00663
49 Lan X, Wang Q. Self-assembly of chiral plasmonic nanostructures. Adv Mater, 2016, 28: 10499–10507
50 Liu N, Liedl T. DNA-assembled advanced plasmonic architectures. Chem Rev, 2018, 118: 3032–3053
51 Zhang Y, Chao J, Liu H, et al. Transfer of two-dimensional oligonucleotide patterns onto stereocontrolled plasmonic nanostructures through DNA-origami-based nanoimprinting lithography. Angew Chem Int Ed, 2016, 55: 8036–8040
52 Jiang Q, Liu Q, Shi Y, et al. Stimulus-responsive plasmonic chiral signals of gold nanorods organized on DNA origami. Nano Lett, 2017, 17: 7125–7130
53 Kuzyk A, Schreiber R, Zhang H, et al. Reconfigurable 3D plasmonic metamolecules. Nat Mater, 2014, 13: 862–866
54 Zhou C, Duan X, Liu N. A plasmonic nanorod that walks on DNA origami. Nat Commun, 2015, 6: 8102
55 Yan Y, Chen J I, Ginger D S. Photoswitchable oligonucleotide-modified gold nanoparticles: Controlling hybridization stringency with photon dose. Nano Lett, 2012, 12: 2530–2536

Summary for “基于 DNA 自组装的手性等离子体纳米结构研究进展”

Chiral plasmonic nanostructures via DNA self-assembly

Meng Wang, Jinyi Dong & Qiangbin Wang*

Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou 215123, China
* Corresponding author, E-mail: qbwang2008@sinano.ac.cn

Controlling molecular chirality is of great importance in nanotechnology. Many biologically active molecules are chiral, including the naturally occurring amino acids, nuclear acids and sugars. In biological systems, most of these compounds are of the same chirality and the circular dichroism (CD) response of natural molecules is very weak. On the other hand, when metallic nanostructures, especially noble metal, illuminated by light with proper energy and momentum, surface plasmons can be excited, which have been used to enhance the electric field and excite higher electric and magnetic modes, leading to a series of fantastic optical phenomena and applications. Chirality of natural molecules can be manipulated by reconfiguring molecular structures through light, electric field, and thermal stimuli. While, the fabrication of complex metal structures is limited by the condition of current technology, especially for the precise fabrication and manipulation molecules at the nanoscale. Moreover, how to achieve chiroptical response in the visible range needs more efforts. In recent years, DNA nanotechnology, using DNA as building blocks of self-assembly, could be finely engineered into desired nanoarchitectures with high complexity and precision. It provides an effective way to easily control and tailor the arrangement of nanoparticles, and to form chiral metamolecules with complicated geometry. Among a variety of functionalized particles, metal nanoparticles such as gold nanoparticles feature an important pathway to endow DNA origami assembled nanostructures with tailored optical functionalities. Such DNA nanostructures were used for building versatile chiral plasmonic nanostructures from static to dynamic. Taking advantages of the spherical metal nanomaterials own isotropy and the programable of DNA nanostructures, the chiral configuration of self-assembled plasmonic nanostructures mainly consider the overall geometry of chiral space, which is easy to expand to more chiral and complex structure. Researchers can arrange achiral metal nanoparticles including gold nanoparticles, silver nanoparticles and quantum dots to fabricate chiral plasmonic nanostructures by analyzing and simulating the optically active molecular analogs. In addition, the interest in self-assembly of chiral plasmonic nanostructures, such as gold nanorods, as anisotropic building blocks is growing quickly. Researchers have developed a variety of complex superstructures such as chiral tetrahedral nanoparticles, pyramid nanoparticles, helical structures and three-dimensional plasmonic nanostructures. DNA nanotechnology provides one of the few ways to form designed, complex structures with precise control over nanoscale features. As a result, plasmonic chiral nanostructures assembled by DNA allow for dynamic manipulation of chirality and reversible switching of strong CD responses, hold great promise for applications in adaptable nanophotonic circuitry, artificial nanomachinery, as well as optical sensing of molecular binding and interaction activities. This article briefly reviews the developments and achievements of chiral plasmonic nanostructures enabled by DNA nanotechnology. Firstly, we show chiral plasmonic nanostructures based on spherical AuNPs, including plasmonic helices, tetramers, and chiral geometric conformations. Then, to challenge the complex configurations and enhance the CD responses, anisotropic gold nanorods with larger extinction coefficients are utilized to fabricate chiral plasmonic nanostructures including dimers, tripod and superhelix. Finally, we introduce dynamic manipulation based on DNA nanostructures with the fast development of this interdisciplinary field. We envision that the combination of DNA nanotechnology and plasmonics will open an avenue toward a new generation of functional plasmonic systems with tailored optical properties and useful applications, including polarization conversion devices, biomolecular sensing, surface-enhanced Raman and fluorescence spectroscopy, and diffraction-limited optics.

DNA nanotechnology, DNA self-assembly, chiral plasmonic nanostructures, metal nanoparticles

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