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## Research Update: Progress in synthesis of nanoparticle dimers by self-assembly

Yuri Diaz Fernandez, Lanlan Sun, Tina Gschneidtner,  
and Kasper Moth-Poulsen<sup>a</sup>

*Department of Chemical and Biological Engineering, Chalmers University of Technology,  
SE-412 96 Göteborg, Sweden*

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This article highlights recent advances in the controlled self-assembly of nanoparticles to produce dimeric nanoparticle structures. The relevance of this emergent field is discussed in terms of recent applications in plasmonics and chemical catalysis. The concept of bond-valence applied to nanoparticles will be discussed, emphasizing some general approaches that have been successfully used to build these structures. Further, the asymmetric functionalization of nanoparticles surfaces as a path to drive selective aggregation, the use of biomolecules to self-assemble nanoparticles into dimers in solution, and the confinement of aggregates in small cavities are discussed. © 2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4858295>]

The synthesis of heterogeneous nanomaterials is a challenging area of research that has found applications in different research fields, such as chemistry, physics, and bio-medical sciences. The ability of metal nanoparticles (NP's) to enhance the Raman signals from molecules adsorbed on the surface (surface enhanced Raman scattering, SERS) has become a useful analytical tool, able to increase the sensitivity of molecular detection to the single-molecule level.<sup>1-5</sup> New developments on molecular electronic devices have highlighted the necessity of robust synthetic routes to control NP aggregation.<sup>6-10</sup>

In chemical catalysis, the combination of two or more materials within the same catalyst has been proven to increase the catalytic activity and selectivity of the catalytic reactions.<sup>11-18</sup> In this regard, special interest has been devoted to the synthesis of hybrid materials combining noble metal and metal-oxide catalytic nanoparticles. These hybrid materials have been successfully obtained by different procedures, including solution based “total-synthesis,”<sup>14,19,20</sup> photodeposition,<sup>11,15,21-23</sup> co-precipitation,<sup>24</sup> and on-wire lithography.<sup>25</sup> Metal nanoparticles on metal-oxides surfaces can behave as electron traps, retarding the recombination of electron-hole pairs, and thereby improving catalyst activity.<sup>13,26,27</sup> The enhancement of photocatalytic activity has also been associated with the localized surface plasmon resonance effect,<sup>28,29</sup> while the plasmonic signal has been used as a probe for catalytic events.<sup>30-33</sup> A comprehensible review on the use of plasmonic nanostructures for light-to-chemical energy conversion has been published recently by Linic *et al.*<sup>34</sup>

The accurate control of morphology and chemical composition of self-assembled materials is a challenge that has attracted the interest of the scientific community for several years. The versatility of self-assembly concepts is broadly claimed; but the experimental methods available in this field are rather specific and there are some relevant limitations, like low yields of tailored structures, poor reproducibility, low stability under “real-life” conditions, and impracticable scaling-up, currently reducing the possible applications of these systems to fundamental studies and proof-of-principle experiments.<sup>1-10</sup> At the same time, the potential use of self-assembly to solve several

<sup>a</sup>Author to whom correspondence should be addressed. Electronic mail: [kasper.moth-poulsen@chalmers.se](mailto:kasper.moth-poulsen@chalmers.se)



technological challenges related to miniaturization of electronic and medical devices has still a privileged place in the collective thoughts among scientists and for the general public.<sup>35-41</sup> In reality, artificial nanodevices based on nanoparticles have still a long way to go in terms of complexity and performance when comparing to the biological machines that constitute the basement of life.<sup>42-46</sup> The major reasons for this huge gap can be found in the delicate balance of interactions involved in self-assembly processes that require the precise design of the interactions among the building-blocks. Colloids are often quasi-stable systems and, under certain conditions, spontaneously undergo bulk aggregation.<sup>47-54</sup> Hence, the challenge of building up small self-assembled clusters of nanoparticles relies on the ability to tune the interactions that keep the nanoparticles far from each other in the colloidal solution, allowing for controlled self-assembly while avoiding bulk aggregates.

Self-assembly has been used for controlling NP aggregation to produce small oligo-aggregates.<sup>55,56</sup> Single-molecule functionalized NPs are often required in order to selectively achieve dimerization,<sup>57,58</sup> but controlled self-assembly can also be achieved by asymmetric functionalization of the NP surface.<sup>59,60</sup> The use of biomolecules to self-assemble NPs into dimeric structures has launched new perspectives for the application of these structures as “molecular rulers,”<sup>61-63</sup> for sensing<sup>64,65</sup> and for probing the dynamics of biochemical processes.<sup>66,67</sup> The considerable effort that has been devoted to the synthesis of dimeric assemblies of nanoparticles is motivated by the possible use of these small-size structures to interface sub-nanometer objects (i.e., single molecules, quantum dots) with macroscopic electrodes, optical instruments, and handling tools.<sup>10,68-70</sup> Nanoparticle dimers are intrinsically anisotropic structures, and their optical and electrical response to external signals can be used to perform controlled movements at the nano-scale and to place molecules with nanometric spatial resolution.<sup>71,72</sup> Furthermore, nanoparticle dimers can be used as building block for complex hierarchical structures, that will definitely play a role in the development of lithography-free assembly of devices in the future.

Previous reviews have exhaustively described the use of nanoparticles as advanced building blocks for nanoscale self-assembled systems.<sup>73-75</sup> The present paper is therefore focused on recent advances on the synthesis of NP dimers by self-assembly, and highlights some relevant results from the last 5 years. The discussion of the recent contributions is preceded by a historical overview of this field, mentioning the general strategies that have been used to build defined NP's aggregates.

Since the pioneering work of Weitz *et al.*,<sup>76</sup> NP aggregation has been studied from both fundamental<sup>48,53,77</sup> and applicative points of view.<sup>55,56,78-80</sup> One major challenge is the controlled self-assembly of small aggregates with a well-defined composition, since NPs tend to coalesce in the absence of protecting capping agents or in high ionic-strength conditions.<sup>47,48</sup> The experimental conditions leading to aggregation of nanoparticles are therefore intrinsically incompatible with the conditions of general stability of the colloids in solution. The challenge of establishing methods for controlled aggregation to form nanoparticles small-aggregates lies on the control of kinetics and thermodynamics processes occurring on the borderline between stable colloids and bulk aggregation processes.

Controlled self-assembly may be achieved only through the delicate balance between repulsive interactions, responsible for colloidal stability, and attraction forces leading to aggregation. Typically, the repulsive forces in colloids arise from long-range electrostatic interactions between the electric double layers of the nanoparticles.<sup>48</sup> These interactions depend on several experimental variables, i.e., surface charge of the colloid, dielectric properties of the solvent, temperature, and ionic strength. Playing with these variables it is possible to finely tune the entity of the repulsion forces, addressing favorable conditions for controlled self-assembly. Conversely, attractive forces involved in controlled self-assembly of colloids are usually strong short-range van der Waals and London-dispersion interactions, that can be exploited to lock the self-assembled structures, considering that the energy involved in these interactions is often higher than the thermal energy of the nanoparticles.<sup>48</sup>

The stochastic aggregation of colloids has been used to self-assemble NP oligomers (i.e., dimers, trimers).<sup>81-83</sup> Depending on the preparation method, the yields of dimers for this approach vary from 19% to 32%, before purification. The NP aggregation process can be quenched by polymer encapsulation or by coating with silica shells. Accurate control of NP aggregation-rates is required, and small variations in experimental conditions can lead to large variations in the results obtained. Furthermore, encapsulation of the aggregates with rigid shells creates diffusion barriers on the

surface of the nanostructures, precluding many applications. The systems obtained by this synthetic path consist of single particles and aggregates with different sizes (dimers, trimers, multimers), and despite the distribution of aggregate populations can be controlled to a certain extent, post-synthesis separation procedures are often required to increase the purity of the desired nanostructures.<sup>81–83</sup>

Tailoring more specific interactions, the control over NP aggregation can be improved, increasing the stochastic probability of forming specific structures.<sup>84,85</sup> The yields can be improved with respect to the purely stochastic self-assembly up to 75% by designing the specific experimental conditions. Alivisatos *et al.* used ligand exchange with bi-functional molecules having specific interactions with the surfaces to form discrete aggregates of semiconductor NPs.<sup>86</sup> The controlled formation of mixed self-assembled molecular monolayers on NP surface has also been exploited to address directionality in NP aggregation<sup>87–89</sup> while protocols for surface-temple asymmetric functionalization of NP's surface have been used to control the stoichiometry and three-dimensional structure of NP aggregates.<sup>58,90</sup>

Bar-Joseph *et al.*<sup>91</sup> developed a procedure to obtain high-purity samples of single-bond gold NP dimers (typical yields of 45%–50%). The self-assembly process was controlled to yield single-molecule linked dimers by using large molar excess of gold NPs with respect to the linker molecule, resulting in statistical distributions mainly formed by non-functionalized single NPs and dimeric structures linked by a single molecule. Following the enrichment of the dimers population by post-synthetic separation methods, the authors have been able to measure electronic transport properties through the NP-molecule-NP junction, pioneering the use of self-assembled devices to build molecular electronic devices<sup>91</sup> and to control optical properties of molecules at the nanoscale.<sup>92</sup>

The methods discussed above often involve many surface-groups interactions and are unable to address discrete NP-NP bond formation. Although the size of the aggregates can be controlled to a certain extent, using the term of NP-valence (in analogy to the concept of atomic valence) is not appropriate for the above mentioned systems. Starting from single nanoparticles in solution, the self-assembly of dimers can be seen as a step-growth reaction, and the ability of increasing the yield of the dimers is directly related to the probability of binding, determined by the specificity of local interactions. While using many-molecules functionalization, the specificity of NP-aggregate stoichiometry can be obtained by delicate tuning of experimental conditions, controlling the balance of repulsive and attractive interactions among the NPs. If attractive forces prevail, the system evolves towards bulk aggregation, conversely if repulsive forces are strong, the NPs will not be able to form any kind of aggregates.<sup>48,54</sup> Therefore, the emergence of discrete numbers on inter-particle bonding (dimers, trimers, etc.) is the result of the dynamic behavior of the whole system.

In order to achieve intrinsically discrete valence of NPs, the use of single-molecule specific interactions and functionality have to be obtained. DNA-NP conjugates have been the best candidates for this approach, since several methods have been developed for the synthesis of nanoparticles functionalized with single DNA molecules, being able to form discrete numbers of molecular bridges between NPs with high selectivity and specificity. By using the recognition of complementary DNA-strands anchored on the surface of NPs, Alivisatos *et al.* introduced in 1996 the concept of nanocrystal molecules, i.e., small aggregates in which the constituent NPs behave as pseudo-atoms, forming discrete bonds with well-defined stoichiometry.<sup>93</sup> Independently, Mirkin *et al.* presented a similar approach to build macroscopic materials formed by self-assembly of DNA modified NPs.<sup>94</sup> These approaches have been further developed, establishing an active research community.<sup>75,95,96</sup> Several experimental techniques and theoretical concepts originally used for studying molecules and materials have been successfully applied to these nanocrystal molecules and self-assembled super-lattices of nanoparticles.<sup>97–100</sup>

The appropriate design of the DNA-NP building blocks allows the self-assembly of these pseudo-atoms into lattices with precise stoichiometry and crystallographic structure that follow a set of constraints somewhat equivalent to Pauling's rules for atomic lattices.<sup>98,101</sup> It is important to note that the atomistic description of the NPs and the application of bond valence phenomenology in the formation of these nanostructures should not be considered as a simple analogy with classical chemistry concepts, but an interpretation of the fundamental properties of this new kind of "molecules." At the same time, the atomic bond valence theory is intrinsically different from this extended valence concept, since the discrete characteristics of bond formation for atoms arise

from the quantum properties of electrons in the electric field of the nucleus,<sup>102</sup> while in nanocrystal molecules, the discrete bonding results from the specific interactions between molecules and the accurate control of NP-surface functionalization. Recently Mirkin *et al.* have presented a discussion of these aspects, suggesting the birth of a new Table of Elements, in which NPs building blocks can be combined like atoms to form new materials.<sup>75</sup>

A different approach to address directionality of nanoparticle self-assembly exploits the formation of patches with specific functional groups on the surface of the nanoparticles. If a perfect surface phase-separation of molecular monolayers on the surface of the nanoparticle can be achieved, the so called Janus particles can be obtained. These structures are named after a double-faced Roman Divinity (Janus, in Latin), and described nanoparticles having phase-separated domains on the surface.<sup>103</sup> The anisotropic Janus particles can self-assemble into well-defined structures, based on selective chemical reactions or collective interactions that involve one of the two different chemical domains on the surface.<sup>104–107</sup> The development of experimental techniques able to characterize the self-organized structures on the surfaces of nanoparticles is a pre-requisite for the application of these systems in more advanced procedures.<sup>104</sup> Theoretical simulations of the dynamics of self-assembly in patched-nanoparticles have considerably contributed to the understanding of the potentials of this approach to control the directionality and stoichiometry of self-assembled nanomaterials based on Janus particles.<sup>108–112</sup> Considerable effort is still needed in order to develop general protocols to predict the behavior of these complex systems.<sup>55</sup>

The patched-nanoparticle approach can address directionality and stoichiometry to nanoparticle self-assembly, although it relies on multi-molecular interactions. The systems obtained by these methods could be potentially more robust than single molecule systems, for this reason the development of more efficient strategies to synthesize Janus nanoparticles, independent from size, shape, and chemical composition, could have a tremendous impact in the future of this field.

Nanoparticle dimers can be obtained by direct self-assembly of single nanoparticles in solution, without the formation of any covalent molecular bridge between the two NPs. Electrostatic self-assembly has been used by Crut *et al.* to produce hybrid nanostructures formed by Au-NP's and core-shell Ag@SiO<sub>2</sub> NP's heterodimers.<sup>113</sup> The binding between the components of the dimer was achieved through surface modification of the Ag@SiO<sub>2</sub> particles with a positively charged polyelectrolyte that interacts with the slightly negatively charged Au NP's.

Chen *et al.*<sup>114</sup> obtained dimers by the direct self-assembly of citrate-capped gold nanoparticles in the presence of NaCl. The extent of the aggregation can be roughly controlled by shielding the electrostatic repulsion between the nanoparticles by increasing the ionic strength. The small aggregates were stabilized by polymer encapsulation, and purified by density-gradient centrifugation protocols. Although the dimers can be obtained with high purity after centrifugation in gradients of CsCl (about 95%), the overall yields of this method are low considering the unspecific mechanisms of formation of the dimeric structures, and the unavoidable coexistence of single NP's and larger aggregates in the population.

Basche *et al.*<sup>115</sup> assembled oligomers of colloidal semiconductor quantum dots (QDs), by repeated precipitation from a good solvent by adding a poor solvent. The amount of dimers and trimers increased after several cycles of precipitation and re-dispersion. The dimeric structures were separated from higher multimers by density-gradient ultracentrifugation. The authors applied a similar procedure for the synthesis of oligomers bridged by a rigid terylene diimide molecule, demonstrating by HR-TEM the presence of the molecular gap between the assembled NP's. Moreover, the energy transfer from QDs to the spacer-molecule was observed.

Using pH-induced aggregation of cysteine-capped Au NP's, Wang *et al.* have produced self-assembled aggregates of small sizes.<sup>116</sup> By quenching the aggregation process after the addition of silver ions, the yield of dimers could be considerably increased, avoiding bulk aggregation. The obtained aggregates showed interesting optical properties in the near-infrared region.

Wolf *et al.*<sup>117</sup> presented a method to assemble well-defined arrays of oriented nanorod dimers in a co-aligned configuration onto a nanostructured surface. The capillary assembly process was performed in topographical trapping sites that measure approximately 50 nm × 200 nm in size. Upon drying, capillary immersion forces push apart the two assembling nanorods, and the gap width in the assembled dimers was defined by the thickness of the cetyl trimethyl ammonium bromide

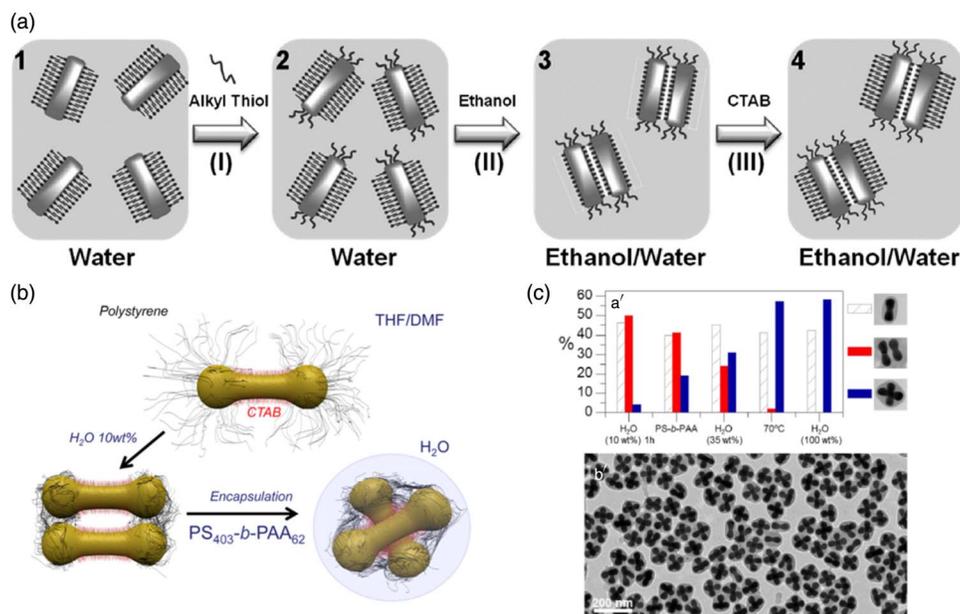


FIG. 1. Strategy for the self-assembly of anisotropic nanostructures by using surface patches. (a) Aggregation induced by weakening of surfactant bilayers. Reprinted with permission from D. Nepal, K. Park, and R. A. Vaia, *Small* **8**, 1013–1020 (2012). Copyright 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) Self-assembly induced by hydrophobic interactions and polymer encapsulation.<sup>125</sup> (c) Experimental yields (a') and representative TEM image of dimers (b') by the method depicted in (b). Reprinted with permission from M. Grzelczak, A. Sánchez-Iglesias, H. H. Mezerji, S. Bals, J. Pérez-Juste, and L. M. Liz-Marzán, *Nano Lett.* **12**, 4380–4384 (2012). Copyright 2012 American Chemical Society.

(CTAB) shell. In this approach non-specific interactions set the limit of the functionality of the obtained dimers, but the possibility of building up ordered meso-structures on surfaces represents a fundamental breakthrough towards applications of self-assembled NP dimers.

Vaia *et al.* developed a solution method for producing large quantities of side-by-side self-assembled Au-nanorods dimers.<sup>118</sup> Combining selective functionalization of the nanorod-ends and ethanol-mediated destabilization of the surfactant bilayer, the self-assembly of the nanorods was induced and subsequently quenched at initial aggregation-stages by increasing the concentration of surfactant (Figure 1(a)). The stability of the dimers allowed further processing, including purification and encapsulation by silica, leading to solutions with 99% of dimeric structures. The silica encapsulated dimers exhibit thermal stability up to 700 °C, suggesting the relevance of this kind of structures for high-temperature plasmonic applications.<sup>119–124</sup>

Following a similar approach, Liz-Marzán *et al.* have recently self-assembled gold nanodumbbell building blocks into crosslike dimers with well-controlled interparticle distance and relative orientation. The method exploited hydrophobic patchiness and shape induced steric-hindrance to induce self-assembly, followed by polymer encapsulation (Figure 1(b)).<sup>125</sup> Through the control of experimental variables, the authors demonstrated the capability of this method to tailor different nano-structures, being able to reach more than 50% of dimers, over single particles and larger aggregates (Figure 1(c)). The yields of the tailored structures are impressively high, considering the non-specific interactions involved in the self-assembly process. This interesting approach opens new possibilities for the study of plasmonic properties in low-symmetry structures.

The versatility of non-covalent self-assembly approaches to build nanoparticle dimers can be illustrated by comparing the two strategies proposed by Liz-Marzán *et al.*<sup>125</sup> and Vaia *et al.*<sup>118</sup> Both methods rely on hydrophobic interactions, confined in surface patches, to drive the self-assembly of the structures and both used post-encapsulation procedures to stabilize the formed oligo-aggregates. Despite these similarities, the two methods are essentially different, if one considers the way in which hydrophobic interactions are used. In the case of Vaia *et al.*<sup>118</sup> the self-assembly is induced after the weakening

water/alcohol mixtures). Conversely, for Liz-Marzán *et al.*<sup>125</sup> the hydrophobic interactions are the direct driving force for the self-assembly process. These representative examples demonstrate how the clever design of experimental strategies can exploit the same kind of interactions in similar systems, but in completely opposite ways, to address similar results.

Bifunctional molecules, such as dithiol or diamine, have been used as linkers to prepare NP's dimers.<sup>126,127</sup> Bjørnholm *et al.*<sup>128</sup> have obtained dimers of gold NP's linked by dithiol-functionalized polyethylene glycol. These dimeric structures can be used as seeds to grow rod dimers in the presence of stabilizing surfactants. The seed-growth approach is a promising strategy able to address single-molecule linking between nanostructures that can be integrated in more complex devices.<sup>129</sup>

Using magnetic colloidal substrates, Sun *et al.*<sup>130</sup> have investigated a generic approach for the synthesis of dimer nanoclusters with a yield of about 54%. Tailored surface modification and controlled physical confinement were applied, to prevent the formation of large aggregates, promoting the formation of dimers.

Li *et al.* have used asymmetric nanoparticles to assemble dimers, using a surface template to induce the asymmetric functionalization of the nanoparticles.<sup>131</sup> The pre-synthesized Janus nanoparticles of two different kinds were assembled in a second step by click-peptide reaction. This general approach can in principle be used to fabricate nanoparticle homo- and hetero-dimers, having control of the interparticle gap size by varying the structure of the linker molecule.

Mixed monolayers of 4,4'-biphenyldithiol and  $\omega$ -mercapto-alkanoic acids have been used by Guttman *et al.*<sup>132</sup> to obtain dimers of Au NP's. The process of dimerization required the NP's to overcome their electrostatic repulsion and to reach a distance of 1 nm from each other. This condition was achieved by screening the repulsive electrostatic forces, after varying the ionic strength of the solution. The dimerization process yielded a solution containing mainly single NP's and dimers, which could be separated by gel electrophoresis.

Reich *et al.*<sup>133</sup> have built SERS-capsules formed by silver NP dimers. The nanostructures were linked through alkane- $\alpha,\omega$ -diamines and different polymers were used to stabilize the obtained nanostructures and quench the aggregation process. The yield of dimers was 25%. Stabilization by protein-encapsulation was also investigated, allowing the use of the assembled NP dimers as *in vitro* SERS imaging-probes.

The ability of acetylene-monofunctionalized multidentate thioether dendrimers to form Au-NP dimers or trimers has been investigated by Mayor *et al.*<sup>134,135</sup> The linker molecule used presented the acetylene moiety at the end of a rigid ethynylene phenylene spacer or at the root of dendrimeric architectures. Acetylene undergoes oxidative coupling leading to NP-NP bridging with yields of 47%.

The synthesis of Au-TiO<sub>2</sub> nanoparticle heterodimers has been presented by Chen *et al.*<sup>26</sup> exploiting the affinity of different chemical moieties for metal and metal oxide surfaces. Au NP's were asymmetrically functionalized at the water-glass interface after building a Langmuir-Blodgett film. The pseudo-Janus Au NP's were then self-assembled with TiO<sub>2</sub> NP's to form dimeric structures. Graf *et al.*<sup>136</sup> also reported a method for controlled formation of gold nanoparticle dimers with yields of 24%, using multivalent thiol ligands and surface-templated asymmetric functionalization of NP surface (Figure 2). This method is based on a locally confined surface modification of gold nanoparticles followed by bridging two nanoparticles with an organic linker. The surface-template strategy for asymmetric modification of NP surface presented in these reports results a very attractive route for the selective formation of NP aggregates with controlled composition and complex architectures,<sup>90</sup> and deserves particular attention.

The selective affinity of thiols for noble metal surfaces, combined with steric hindrance concepts, has been exploited by Grzybowski *et al.* to self-assemble nanoparticles dimers.<sup>137</sup> In this method, composite Fe<sub>3</sub>O<sub>4</sub>/Au nanoparticles were linked by a di-thiol molecule through the gold spots. The combination of pre-synthesized heterogeneous nanoparticles with the self-assembly approach produced high yields of dimeric structures (~75%).

The toolbox of metallo-organic supramolecular chemistry has been used by Waterland *et al.*<sup>138</sup> to develop an interesting approach for the synthesis of self-assembled gold and silver NP aggregates. The authors have designed a polyoxyethylene glycol (PEG) thiol-functionalized bis(phenanthroline) copper(I) complex that was able to mechanically interlock nanoparticles. This method, like many

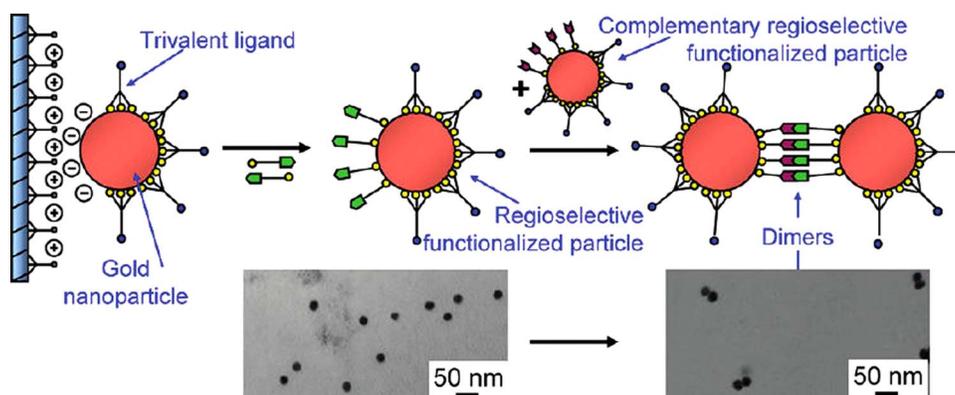


FIG. 2. Addressing the selective formation of dimers by asymmetric functionalization of NP's surface. Reprinted with permission from A. Hofmann, P. Schmiel, B. Stein, and C. Graf, *Langmuir* **27**, 15165–15175 (2011). Copyright 2011 American Chemical Society.

other procedures in catenane chemistry,<sup>139</sup> presents several experimental challenges, but demonstrates the necessity of multidisciplinary research to afford the complex tasks of NP self-assembly and highlights the elegance of the fundamental concepts in supramolecular chemistry.

Biomolecules have the natural ability to self-assemble into well-defined structures via specific “lock and key” interactions. The structural plasticity and the reversibility of the interactions in these complex systems can result in the controlled self-assembly of NP dimers in high yields. DNA has been used as a model system to demonstrate the formation of stoichiometric bonds between NP's.<sup>75</sup> The high programmability of complementary DNA strands allows the selective formation of single molecule-bridges between NP's.<sup>61,140</sup> The yields of the dimeric structures can vary from 48% to 73%, depending on the preparation method, and on the length of the DNA molecule.

Wang *et al.*<sup>141</sup> reported DNA-based assembly of symmetric and asymmetric gold nanoparticles dimers with exceptional purity. The interparticle distance could be tuned by using DNA-molecules with different number of nucleotide bases. For the synthesis of symmetric gold nanodimers, a dithiolated-dsDNA was directly added to the gold colloidal solution and self-assembly occurred. Conversely, to obtain asymmetric gold nanodimers, a two-steps synthesis procedure was required, starting from the monofunctionalization of larger gold nanoparticles and subsequent polyvalent modification of smaller counterparts. These assembled structures can be purified using gel electrophoresis methods to obtain a purity of 80%–90%.

Gang *et al.*<sup>142</sup> reported the switching of binary states of nanoparticle superlattices and dimers by DNA strands. They succeeded in the assembly of nanoparticles into three-dimensional superlattices and dimer clusters with 79% of purity, using a reconfigurable DNA-based device that acts as an inter-particle linker. Similarly, Sturla *et al.*<sup>143</sup> recently succeeded in the sequence-controlled disaggregation of DNA-gold NP hybrids by employing two complementary oligonucleotides. Gang *et al.*<sup>144</sup> also investigated the structure of Au nanoparticle dimers obtained by DNA hybridization with yields of 70%, and concluded that the interparticle distance within the dimer is controlled primarily by the number of linking DNA molecules. Their findings may play an important role in designing novel materials based on nanoparticles and polymers.

The optical and topological properties of gold nanoparticle dimers linked by a single DNA double strands have been investigated by Bidault *et al.*<sup>140</sup> In this work, the gold nanoparticles with a single DNA strand were separated using gel electrophoresis. The surface-to-surface distance within these NP dimers can be reversibly varied by a factor of 3 when hybridizing or removing a single target DNA strand.<sup>145</sup> The yields of the close-dimers was 92%, while the yield of the open-dimers was 88%. The ability to trigger NP-NP distance by molecular signals has a significant relevance in sensing and diagnosis, opening new perspective for the application of self-assembled NP dimers in biomedical and analytical sciences.

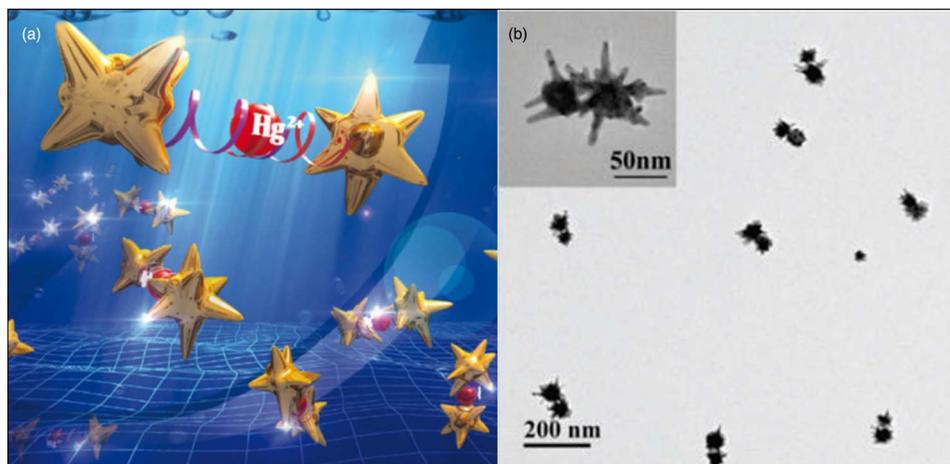


FIG. 3. (a) Artistic representation of the mercury-induced self-assembly of gold nano-stars. Reproduced by permission from W. Ma, M. Sun, L. Xu, L. Wang, H. Kuang, and C. Xu, *Chem. Commun.* **49**, 4989–4991 (2013). Copyright 2013 The Royal Society of Chemistry. (b) TEM image of nano-stars dimers at different magnifications. Reproduced by permission from W. Ma, M. Sun, L. Xu, L. Wang, H. Kuang, and C. Xu, *Chem. Commun.* **49**, 4989–4991 (2013). Copyright 2013 The Royal Society of Chemistry.

Antibody molecules have been used by Huang *et al.*<sup>146</sup> to obtain NP's dimers. Two gold nanoparticles were assembled bearing a receptor unit in the nano gap where the attachment of a CdSe quantum dot was possible. These devices can be assembled in solution or on the surface of electrodes, using different experimental approaches. When the self-assembly process was investigated in solution, the ratio of dimer to monomer formed was found to be temperature-dependent, accounting for the reversibility of antibody-target interactions.

Protein-DNA interactions within self-assembled NP aggregates can be exploited to detect disease-biomarkers. Ginger *et al.*<sup>147</sup> have built gold NP dimers supported on a substrate by using single strand DNA. Gold nanoparticles were functionalized with DNA and linked by a hairpin-loop structure to form dimers on glass slides. These structures behave as actuators triggered by biomolecular interactions, and have a plasmonic read-out. *In vitro* detection of one type of *E. coli* protein was successfully performed using this approach.<sup>148</sup>

Kuang *et al.* have presented an interesting approach to achieve mercury(II) sensing in ultra-trace amounts using the SERS effect from DNA-conjugated gold anisotropic nano-objects (Figure 3).<sup>149</sup> The gold “nano-stars” were functionalized with thiol-modified DNA strands that promote inter-particle dimerization upon the addition of  $\text{Hg}^{2+}$ . A Raman reporter (4-amino-thiophenol) was used to quantify the SERS effect after the formation of plasmonic hot-spots within the dimeric NP's structures. The selectivity of the sensor was tested against different metal ions, and the analytical response was quantitative even below the detection limits for conventional determination methods for mercury(II) in water.<sup>150–153</sup>

Recently Quidant *et al.*<sup>154</sup> have presented a novel strategy exploiting cooperative-effects in the gap of a NP dimer to address the binding of a third nano-object acting as a bridge. The initial dimers were fabricated on glass surfaces by e-beam lithography, while the third NP was assembled into the dimer-gap by protein-recognition interactions. Although the overall method is not strictly based on self-assembly, the relevance of the results for the development of this field justifies its mention in this review. Furthermore, the ability of exploiting the hot-spot over-heating to trigger the binding capacity of molecules, opens new perspectives for the controlled self-assembly of nanomaterials.

Since the pioneering works of Alivisatos *et al.*<sup>93</sup> and Mirkin *et al.*<sup>94</sup> back in 1996, the concept of addressing directionality and discreteness to inter-particle interactions has been considerably developed and spread towards more general applications.<sup>75</sup> Controlled NP aggregation to selectively obtain dimeric structures has been used to obtain active components for single-molecule electronics<sup>91,146</sup> and sensing of chemical and biological species.<sup>147,149</sup> Although the promising perspective of controlled self-assembly in terms of synthesis of new materials<sup>75</sup> and bottom-up building

of functional nano-machines,<sup>155,156</sup> several challenges affecting the yield of the tailored structures still need to be solved. A common feature that becomes evident while reviewing the recent advances in the synthesis of NP dimers is the inability of many of these methods to uniquely address the stoichiometry of inter-particle bonds. The methods typically rely on separation methods to enrich dimer populations or affording dispersity as an intrinsic property of self-assembled systems. In this respect, the development of more efficient size- and shape-sensitive NP separation protocols would contribute to the practical use of self-assembled NP dimers, and should be considered as a priority for the research community.

On the other hand, the biomimetic self-assembly of NP's have provided a selective path for the synthesis of dimers and other oligomers with complex architectures and functions, playing with the delicate energetic balance of biomolecular interactions that are sensible to the experimental conditions. The synthesis of self-assembled NP's dimers based on biomolecules imposes the use of collective interactions of many chemical moieties arranged in topographical motifs within the structure of the linking-molecules. This feature is responsible for the specific recognition capacity observed for biological systems, and has been efficiently used to design synthetic routes to obtain NP's dimers.

For all these experimental approaches, several challenges need to be overcome in order to increase the purity and the yields of the tailored structures. The highest yields without purification can be obtained by biomimetic self-assembly. The “non-bio” methods can be competitive in terms of purity of the tailored structures only by using appropriated separation methods. Therefore, the development of new separation techniques will be a relevant issue in the future of this field.

The better understanding of the “sweet spots” leading to controlled self-assembly of nanoparticles and the development of new strategies to select and tune colloidal interactions could have a positive impact in the development of this emerging field. In this sense, the contribution of theoretical modelling and simulations will be essential. Additionally, interdisciplinary cross-linking with advanced organic synthesis and separation methods, as well as confinement within nano-fabricated templates will lead to a considerable improvement of the synthetic routes to obtain nanoparticle dimers.

Recent reports have also addressed the relevance of nanoparticle hetero-dimers to answer fundamental questions in material science and nanotechnology, and therefore we foresee that considerable efforts will be devoted to this topic in the next few years.<sup>113</sup> In parallel, the development of advanced characterization tools able to probe local properties of nanoparticles can also contribute to the understanding of the interactions in nanostructured systems and open new applications of these systems.<sup>19,157</sup>

A breakthrough in this field will be achieved when the selectivity of biomolecules interactions are combined with the electronic transport properties of conjugated organic molecules, leading to nanostructures able to perform complex tasks, like logic operations or reversible information storage. The increasing interest of the scientific community on the synthesis and the application of self-assembled NP dimers suggests that despite the impressive achievements, the potential of this field is far from being depleted. In this respect, the visionary words from Richard Feynman back in 1959 can inspire the future, because *there is still plenty of room at the bottom*<sup>158,159</sup> and even more *in the middle*.<sup>160</sup>

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