LETTER

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Size-dependent aggregates of gold nanoparticles induced by a "molecular fork"†

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A fork-like molecule can induce citrate-capped gold nanoparticles of 2.6 nm diameters to form sintered peanut-like nanoarrays and aggregates. The formation of such aggregates is size-dependent because of steric hindrance between the fork-like molecule and the 5 nm or bigger Au nanoparticles.

Recently, there has been growing interest in organizing metal nanoparticles to form complex nanostructures [1–8] for their collective electronic and optical properties being distinct from those of individual nanoparticles or the extended solid. For instance, Chen[9] and Hassenkam *et al.*[10] have reported that surfactant systems at the air–water interface can act as templates for the self-assembly of individual nanoparticles into sintered nanowires. Pei *et al.*[11] have prepared 2D networked gold nanowires by citrate reduction of $AuCl_4^-$. Cheng *et al.*[12] have reported on gold nanoparticle aggregation induced by iodine. Besides, numerous approaches based on molecular bridged nanoparticles have been developed. Mirkin *et al.*[3] and Alivisatos *et al.*[4] employed DNA as nanoparticle linkers to fabricate nanoparticle arrays. In addition, molecular wires have been used to form a two-dimensional superlattice by Andres *et al.*[2] and nanoparticle arrays such as dimers, trimers and tetramers by Feldheim and co-workers.[7] Herein, we report that a fork-like molecule can size-dependently link fine gold nanoparticles (Au NPs) into nanoarrays and aggregates. The fork-like molecule, *N*-hexadecyl-3,6-di(*p*-thioacetylphenylethynyl) carbazole, has been used to fabricate loosely packed monolayers on gold electrodes.[13] It has two rigid thiol-functionalized alligator clips[14] with angled at an estimated 84° and a flexible alkyl chain tail; the straight-line distance between the two clips is about 17 Å.[15] We named it a "molecular fork" because of its fork-like shape.

In the experiments, four Au NPs with different diameters are employed: those 2.6 nm in size are synthesized by $NaBH_4$ reduction and the 18 nm citrate-stabilized Au NPs are synthesized by citrate sodium reduction according to the literature;[16] 5 nm and 10 nm tannic protected Au NPs are obtained from a commercial supplier.[17] The molecular fork, which is dissolved in alcohol and hydrolyzed by ammonia, is added gradually according to Feldheim's procedure.[7] The UV-Vis absorbance spectra are recorded to follow the mixing process on a CARY 500 UV-Vis-NIR VARIAN spectrophotometer. Fig. 1 and Fig. 2 show the UV-Vis absorbance spectra of different cases. The 2.6 nm Au NPs have a single extinction at 521 nm and the wavelength of the surface plasma (SP) resonance is red-shifted by about 7, 14 and 27 nm after 1/2, 1 and 2 stoichiometric amounts of molecular fork is added, respectively (Fig. 2A). Besides the red-shift in the gold SP band upon molecular fork addition, a remarkable SP damping is also observed in Fig. 2A and there is no appearance of an additional longer wavelength SP band. This result is similar to those experimentally observed for much smaller NP groupings,[3,4,7] such as DNA-based NP dimers, trimers, or slightly larger aggregates. In many earlier theoretical and experimental works,[18] it has been found that extensive Au NP aggregation into NP chains leads to the appearance of an additional longer wavelength SP band (similar to the longitudinal SP in Au nanorods or nanowires) due to SP coupling among neighbouring NPs. This result indicates that the interaction of molecular forks link the Au NPs into nanoarrays and slightly larger aggregates and there are no extensive aggregates formed, which is further confirmed below. Fig. 2B, C, D, show the absorbance UV-Vis spectra of the other cases. After the addition of excess molecular forks into 5, 10 and 18 nm Au nanoparticle solutions, the wavelength of the plasma resonance remains unchanged, unlike the pronounced changes in the case of the 2.6 nm particles. These results indicate that no aggregation occurrs when excessive molecular fork is added to 5, 10 and 18 nm Au NP solutions.

For further details, the sample in Fig. 2A was dispersed onto a transmission electron microscopy (TEM) grid.[19] TEM results correlate with the UV-Vis spectra observations above. Fig. 3

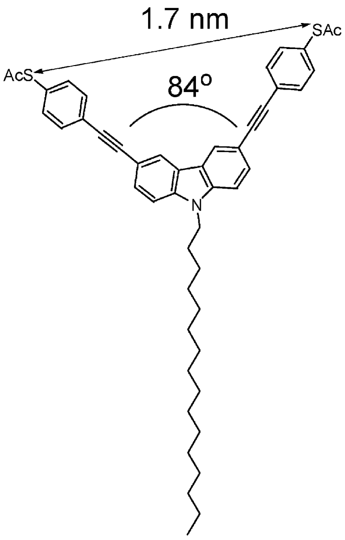

Fig. 1 Structural formula of the "molecular fork".

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† Electronic supplementary information (ESI) available: TEM images of 5 nm Au nanoparticles after addition of excess molecular fork. See http://dx.doi.org/10.1039/b500721f

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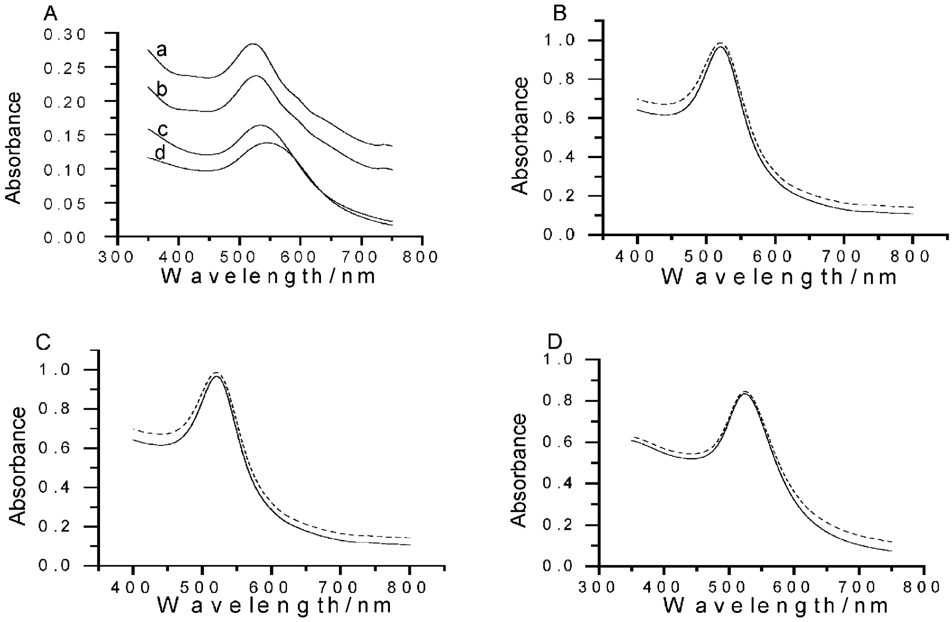

Fig. 2 (A) UV-Vis absorbance spectra of four steps after 0 (a), 1/2 (b), 1 (c), and 2 (d) stoichiometric amounts of molecular fork are added to 2.6 nm Au NP solutions, respectively. (B), (C) and (D) show the UV-Vis absorbance spectra of ~5, 10, 18 nm Au NPs before (the solid line) and after excess amounts of molecular forks are added (the dashed line), respectively.

shows the typical TEM images of 2.6 nm Au NP arrays and aggregates upon mixing Au NPs and the molecular fork under different conditions. In the control experiments, the citrate-protected 2.6 nm Au NPs are well dispersed (Fig. 3A) before the molecular forks were added to the solution. After only a half of a stoichiometric (Au NPs : molecular fork = 4 : 1) amount of molecular fork is added, the peanut-like Au NP arrays, which have two or three sintered Au NPs, are observed (Fig. 3B). When a stoichiometric amount of molecular fork is added, more nanoparticles are linked together and sintered to form nanoarrays, as shown in Fig. 3C. We believe that the molecular fork links the Au NPs and induces sintering. Besides the sintered nanoparticles, necklace shaped Au NP arrays are also observed. Upon increasing the amount of molecular fork added, the aggregation becomes slightly larger and sintered Au NP aggregates are formed, as Fig. 3D shows. In the TEM sample prepared from this solution, no extensive aggregates are found. This can be attributed to the tendency of the molecular fork to attach onto single nanoarrays or the small groupings of Au NPs formed in the solution. However, it is found there are very extensive 2D Au NP aggregates at the air–water interface, as Fig. 4 shows, the Au NPs are almost sintered together. Under this condition, the molecular fork, which has a flexible alkyl chain tail, acts as a 2D template similar to the literature[9,10] that employed a surfactant system to fabricate 2D nanostructures. In our experiments, no sintered particles or aggregates are observed by TEM when 5, 10 and 18 nm Au NPs are engaged (see the supporting information†), which corresponds to the UV-Vis records.

Taken together, the molecular fork can only link the 2.6 nm Au NPs among the four sizes of Au NPs employed, indicating that the size of the Au NPs plays an important role in the

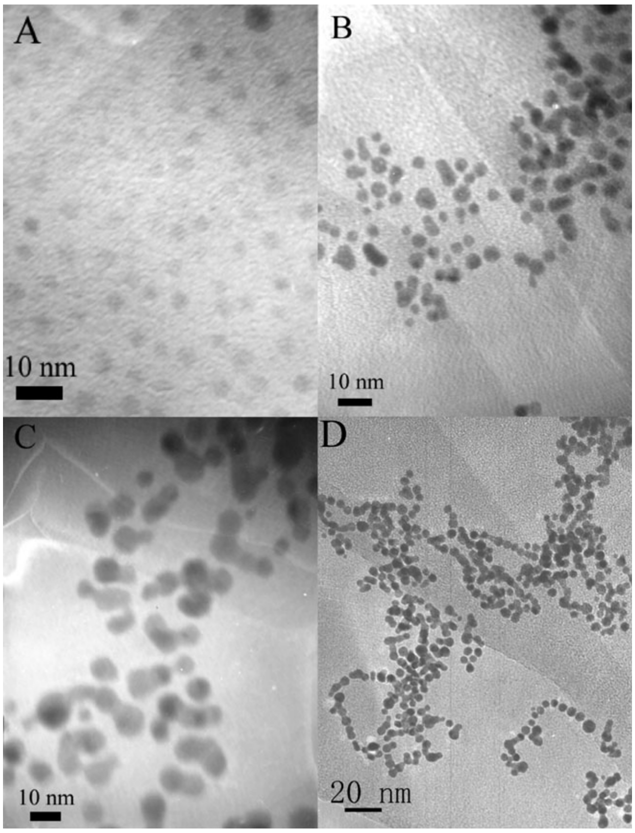

Fig. 3 TEM images of when different amounts of molecular fork are added to 2.6 nm Au NP solutions, in 0 (A), 1/2 (B), 1 (C), 2 (D) stoichiometric amounts, respectively.

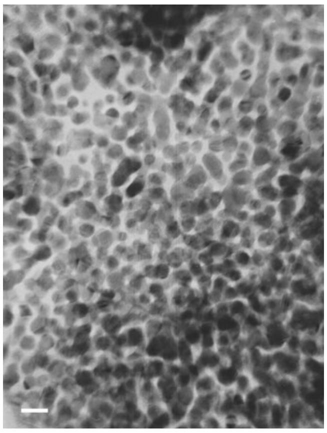

Fig. 4 TEM image of the 2D Au NP aggregates at the air–water interface after 10 stoichiometric amounts of molecular fork are added to a 2.6 nm Au NP solution (the scale bar is 10 nm).

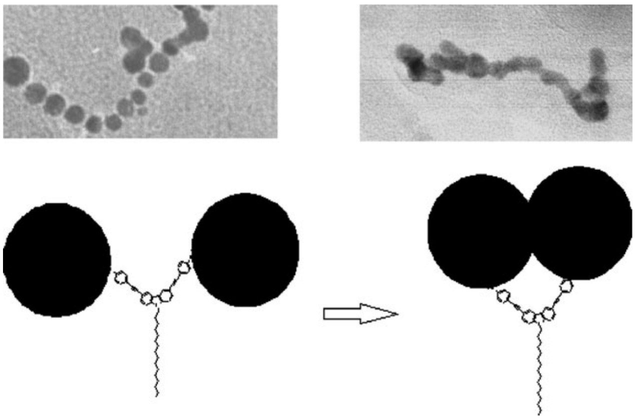

Fig. 5 A schematic model of molecular fork induced coalescence and sintering of two gold nanoparticles. The TEM results have confirmed these two possibilities, as shown above the models.

aggregation process. The Au NPs used in this study are electrostatically stabilized by tannic or citrate anions, which can be easily replaced by the molecular fork for the strong Au–S linkage. It can be explained that the molecular fork tends to attach to only one particle when 5 nm Au NPs or bigger sized parent nanoparticles are used. The experiments show that the molecular fork is obviously size-selective to link the Au NPs into aggregates. Considering the interaction between the molecular fork and Au NPs, there are two situations when such a molecule plunges into a Au NP solution: under the condition of 5 nm particles or bigger, the molecular fork attaches to only one particle; in the case of 2.6 nm Au NPs, the molecular fork can capture two particles. We believe that the size dependent property is based on the geometric structure of the molecular fork, for a 1.7 nm molecular fork with an angle 84° can hardly link two 5 nm or bigger particles and thus the two thiol-functionalized alligator clips both nip the same particle.

It is interesting that the molecular fork can link 2.6 nm Au NPs size-dependently, and the Au NPs become coalesced and sintered under the direction of such fork-like molecules, which is quite different from the molecular wires reported before.[2,7] There are two possibilities when molecular forks link Au NPs, one is the two particles remain separate like in a necklace, and the other is that the two particles sinter together induced by the molecular fork. Our model, as schematically shown in Fig. 5, illustrates the different cases of the two captured nanoparticles. When the molecular fork links two particles and the thermodynamic driving force allows them to approach to within 5 Å, strong metallic bonding could help in driving nanocrystal coalescence and subsequent sintering.[20] If the molecular fork contacts the terminus of a nanoarray, the unemployed clip is capable of linking to another nanoparticle or nanoarray, and therefore longer nanoarrays form. As the sintering process is irreversible, the aggregates become more extensive and most of Au NPs are sintered together.

In summary, we have demonstrated that the molecular fork can size-dependently link the citrate-capped Au NPs of 2.6 nm diameters and result in the formation of Au NP nanoarrays and sintered Au NP aggregates. This method can be used to prepare sintered Au nanoarrays by simply mixing 2.6 nm Au NPs with the molecular fork in aqueous solution. The aggregation is size-dependent because of steric hindrance between the fork-like molecules and Au nanoparticles.

Experimental

The general linking procedure is as follows. Two solutions are prepared and then mixed together. The first is the Au NP solution that is diluted. 5.00 ml of 2.6 nm Au NP solution (about 200 nM) is diluted with 5.00 ml of a 3 mM citrate solution. The citrate is used to buffer the stability of the particles. The 5, 10 and 18 nm Au NP solutions are not diluted. A second solution is the 10 μM molecular fork dissolved in alcohol and hydrolyzed by adding a 10 μl amount of concentrated NH_4OH in 10 ml stock solution. While stirring, the linker solution is added to the Au NP solution at an interval of 1/2 a stoichiometric amount of molecular fork (Au NPs : molecular fork = 4 : 1). The solutions are left to stir for 2 h to complete the linking procedure.

Acknowledgements

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