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Preparation of nanochain and nanosphere by self-assembly of gold nanoparticles

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A self-assembly method is demonstrated to link nanoparticles into nanostructure of nanochain or nanosphere. Gold nanoparticles were covered with capping molecules by forming Au–S bonds with thiol group at one terminate. Another terminating group, carboxylic acid, showed strong complex interaction with inorganic linker Zr^{4+} to form covalent complex bond. The different nanostructures were obtained by moving a balance between two opposite interactions, the linking interaction of Zr^{4+} and the electrostatic repulsive interaction of net surface charge. When the capping molecule with different chain length was used, the linked nanochain feature exhibited a tunable interdistance between the neighboring nanoparticles. © 2008 American Institute of Physics. [DOI: 10.1063/1.2955504]

Gold nanoparticles, nanorods, nanoprism, etc., are basic moieties used to construct various kinds of nanostructures due to their stability and easy synthesis process.¹ For example, an isotropic ring of gold nanorods was recently produced by drying a drop of water on a substrate.² The aggregated nanostructure of nanoparticle can also be dispersed to get individual ones once again, suggesting a reversible constructing process. Laromaine *et al.* employed protease to trigger the disassembly process of a nanoparticles' nanonetwork. The protease was used to produce positively charged amino groups onto the individual gold nanoparticles' surface, which led to the disassembly of the formed nanonetwork.³ Gold nanoparticles were not only used as the building blocks to fabricate nanostructures but also were etched to get fluorescent and water-soluble gold nanoclusters.⁴ All those fabricated nanostructures, however, are isotropic. The anisotropic nanostructure is also interesting and several fabricating methods have been reported.^{5–7} DeVries *et al.* produced a nanochain of nanoparticle by placing linker molecules at two polar defects on the individual nanoparticle surface.⁸ The gold nanoparticle was seemingly charged with divalent electrostatic interaction. Beyond nanochain, Aldaye and Sleiman selected DNA as the template to assemble discrete gold nanoparticles into triangle- and square-shaped arrangement.⁹ More recently, Maheshwari *et al.* fabricated a micrometer-long one-dimensional network of cemented gold nanoparticles.¹⁰ Although all those anisotropic nanostructures have been obtained, the approaches were complicated and more study was desirable. For example, Zhong *et al.* reported that gold nanoparticles were capped with cysteine or lysine during the nanoparticle's synthesis process to produce aggregated nanostructure, such as nanochain. They found that the resulting aggregation morphology was modifiable by adjusting the proportion of cysteine and lysine.⁵ Recently, they replaced the capping reagents with 3-mercaptopropionic acid (MPA)

and investigated the aggregation's dependency on the ratio of MPA to gold, the pH value of solution, and the nanoparticle concentration.⁶

The challenge to fabricate all kinds of nanostructure from the individual nanoparticles is the irreversible and uncontrollable aggregation of the small nanoparticles due to the stable energetic state of the large particles. Therefore, the surface of nanoparticle is usually capped with alkanethiolate to increase the stability. Even solid nanoparticle powder can be obtained using this method.^{11,12} Alternative to the surface capping protection, surface charge is another item that protects them from aggregating due to the electrostatic repulsive interaction. In order to fabricate a robust nanostructure from the individual nanoparticles, covalent bond is preferable to enhance the connection interaction by introducing a linker.¹⁰ After producing the isotropic or anisotropic nanostructure from the nanoparticles, another difficulty is how to control the interdistance between the neighboring nanoparticles on nanoscale, for example, 3 nm or less.⁸ In this report, we demonstrate a simple method to fabricate an assembled nanostructure from gold nanoparticles. First, the individual gold nanoparticles were covered with capping molecules not only to increase the stability but also to functionalize the particles' surface with carboxylic acid groups. The carboxylic acid was further derivated with a linker of Zr^{4+} by immersing into an incubation solution. Then the Zr^{4+} -derivated nanoparticles were dispersed into a buffer solution with different pH value to self-assemble the individual nanoparticles into nanostructure.

The approach used here is schematically shown in Fig. 1. The nanoparticles were covered with $HS-C_2H_4-COOH$ (C3) or $HS-(CH_2)_{10}-COOH$ (C11) to functionalize the chargeable carboxylic acid group ($-COOH$) onto the gold nanoparticle's surface. Zirconate salt was used as linker.¹³ The net surface charge density on an individual nanoparticle is adjusted by changing the pH value of dispersing buffer solution, as shown in the following (also in Supporting Information).¹⁴

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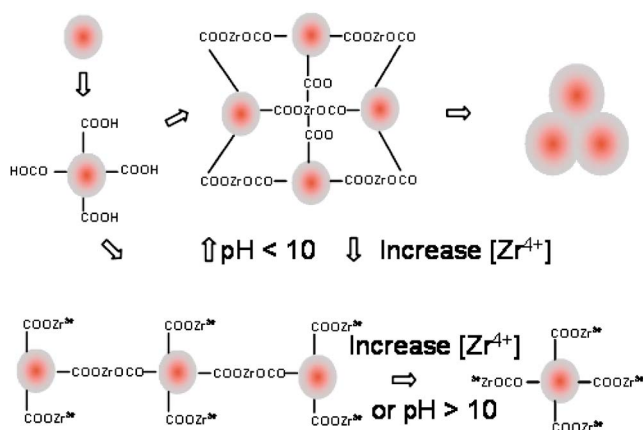
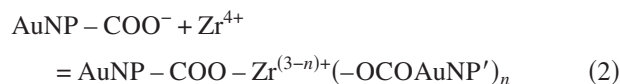


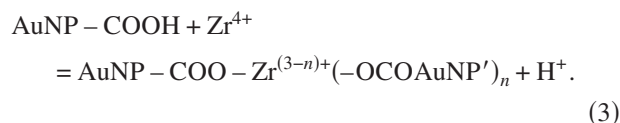
FIG. 1. (Color online) Schematic drawing of the different nanostructures prepared from gold nanoparticles.



or by controlling the concentration of Zr^{4+} in the incubation solution,



putting together,



Here AuNP is the individual gold nanoparticle. A linker of Zr^{4+} can complex with one or two $-\text{COOH}$ groups simultaneously, which maybe come from one or two nanoparticles.¹⁵ If they are from two different nanoparticles, those two nanoparticles are linked together. Therefore, there are two kinds of opposite interactions among the individual nanoparticles: the linking interaction of Zr^{4+} since Zr^{4+} can react with at least two carboxylic acid groups and the electrostatic repulsive interaction from the net surface charges since carboxylic acid can be deprotonated. The former links them together whereas the latter keeps them far away from each other. By carefully adjusting the two opposite interactions, a controllable nanostructure is fabricated when those interactions reach a balance, as shown in Fig. 1. In other words, by controlling the concentration of Zr^{4+} and H^+ carefully, the two opposite interactions lead to the appearance of different nanoparticle arrangements, from nanochain to nanosphere, as shown in Fig. 2.

From Fig. 1, it can be seen that a nanosphere, an aggregate of nanoparticles with a sphere shape, is formed when the concentration of Zr^{4+} is low in comparison with that of the individual nanoparticles. That is, an ion of Zr^{4+} has the possibility to complex with at least two $-\text{COOH}$ groups from two nanoparticles and links them together. The other linkers derivated onto those two nanoparticles' surface can link more nanoparticles and so on. Consequently, several nanoparticles, perhaps decades or hundreds of nanoparticles, are linked together, which leads to the appearance of an isotropic nanosphere.

As pointed out by others,^{5,6} the formed nanosphere [Fig. 2(b)] can be fused or melted together to get a dense structure, as shown in Fig. 2(c). The low pH value of the dispersing

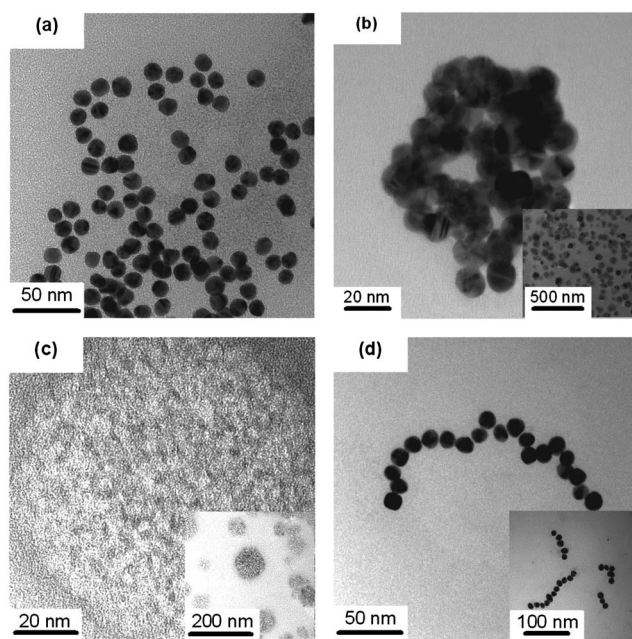


FIG. 2. TEM pictures of (a) individual gold nanoparticles, (b) nanospheres, (c) melted nanosphere, and (d) nanochains. The concentration of Zr^{4+} in the incubation solution, and the pH values of the dispersing buffer solution are (a) 25 mM, pH 10.4; (b) 1 mM, pH 10; (c) 1 mM, pH 7.5; and (d) 5 mM, pH 10.4, respectively. In all cases, the surface of nanoparticle was covered with C3.

buffer solution leads to a low surface charge density and a less repulsive interaction in turn. Therefore, it is easy for the nanoparticles in the nanosphere to be arranged closely and melted. Another factor is the high accelerate voltage of transmission electron microscopy (TEM), which can also lead to the fusion of the nanosphere. Sometime the morphology of as-prepared nanosphere was found to be changeable during the TEM scanning process.^{5,6}

When the electrostatic repulsive interaction was increased by increasing the pH value or the concentration of Zr^{4+} , the nanosphere structure was destroyed. As a consequence, an anisotropic line arrangement of individual nanoparticles, nanochain, was produced, as shown in Fig. 2(d). If the concentration of Zr^{4+} was further increased, the individual nanoparticles were obtained [Fig. 2(a)]. Therefore, the pH value of the dispersing buffer solution must be selected carefully. The high pH value, for example, $\text{pH} > 11$, leads to the serious hydrolysis of Zr^{4+} , which is unhelpful for the self-assembly of nanoparticles.

Another evidence for the connection of the individual nanoparticles is shown in Fig. 3. When the capping molecules with different chain length were used, C3 or C11, the different interdistance between the neighboring nanoparticles was observed. The estimated distance (from at least ten pieces of different TEM pictures) is 1.1 ± 0.2 nm for C3 and is 2.3 ± 0.5 nm for C11. Those estimated values differ slightly from the real value (Chemdraw), 1.2 and 3.3 nm, respectively. The possible reason is due to the folding of the linking chain, as suggested by others.⁸ Especially when the chain of capping molecule gets longer, a weaker electrostatic repulsive interaction exists between the neighboring nanoparticles, and the higher possibility occurs for the linking chain to be folded. It should be pointed out that the measurement of interdistance was conducted from the largest interdistance in the TEM nanochain pictures since the different

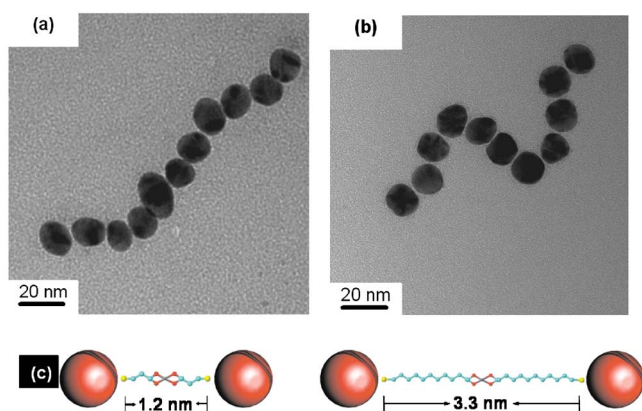


FIG. 3. (Color online) Dependence of the interdistance on the chain length of the capping molecules. From TEM pictures, the interdistance is estimated to be (a) 1.1 ± 0.2 nm for C3 and is (b) 2.3 ± 0.5 nm for C11, respectively. The value is a little different from the drawing in (c).

view angle led to a serious error due to the irregular ball-shaped nanoparticles.

In general, the different nanostructures were produced by linking the individual gold nanoparticles together. By carefully adjusting the concentration of Zr^{4+} during the incubation process and the pH value of the dispersing buffer solution, the two opposite interactions reach a balance between the linking and repulsive interactions to obtain different nanostructures. Compared with the method of Zhong *et al.*, this method is simple (beginning from nanoparticle, not from the synthesis process), controllable, and robust (using Zr^{4+} as linker to form covalent bond, not just H bond). Although the dispersing solution is not stable and gets precipitated after approximately 1 day, the precipitation process is reversible to some degree. Sonication can refresh the dispersing solution if any precipitation is observed. Furthermore, the interdistance between the neighboring nanoparticles in the linked nanochain feature is adjustable by

selecting different chain length of capping molecules. The further investigation on the possible application of this nanostructure is in progress, such as used as surface-enhanced Raman scattering substrate, as conductive tag for nanogap biosensor¹⁶ and so on.

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