Directed Assembly of Cationic Gold Nanoparticles by RNA Scaffolding
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Introduction: Precise positioning of molecular components for the generation of composite, self-organizing functional devices can be accomplished with nucleic acids (1). Recently, we built a versatile programmable molecular RNA system, composed of tetramers resembling a square called tectosquares (TS), able to assemble into a wide variety of 2D supra-molecular architectures (2). In this study, we describe by atomic force microscopy (AFM) (3) the linear arrangement of cationic gold nanoparticles (NPs) directed by TS ladders.

Results: With their negatively charged central opening, TS could potentially bind cationic NPs dependent on electrostatic, size and shape recognitions. A self-assembling TS was used as a unit to create linear ladder-like assemblies (Figure 1). 3.5 nm gold nanoparticles functionalized with cationic thiocholine were electrostatically assembled along these anionic RNA scaffolds in solution. Using AFM, assemblies decorated with gold were observed to have a height of 3-5 nm while undecorated assemblies were observed to have a height of 2 nm, in agreement with the thickness of double stranded RNA. Furthermore, NPs were observed to arrange into linear aggregations 50-400 nm long with defined spacings of 11.8 ± 1.6 nm (n=222), 22.9 ± 2.1 nm (n=127) and 33.6 ± 2.0 nm (n=31) corresponding to the distance between two, three and four TS openings respectively. The observed spacing of gold NPs along TS ladders is in remarkable agreement with our 3D model, predicting an interparticle distance of 11.3 nm (Figures 1, 2 and 3). By contrast, NPs aligned along duplex DNA with the same procedure used for making TS ladder-gold NPs, were shown to have much less defined spacing, the distance of separation between 2 NPs ranging from 12 to 40 nm over 330 distance measurements averaging 22 nm (4) (Fig. 3). These data strongly suggest that the NPs formed linear arrangements by self-positioning within the center of the tetramer opening created by the phosphate backbones of RNA.

Conclusions: These results demonstrate that precise arrangement of gold nanoparticles can be achieved by controlling the precise architecture of the ribonucleic acid (RNA) scaffolding. Nano-devices with sem-conducting or magnetic properties that take advantage of RNA scaffoldings to achieve precise control over the positioning of metallic NPs could potentially find applications in nano-electronics or medicine.

Figure 1. Hierarchical supramolecular assembly of TS ladder decorated with cationic gold NPs. TS1 (blue) and TS2 (red), each made of four different RNA subunits (left), self assemble through complementary 3' tail-tail connectors (green) into a ladder (center). Once the ladder is formed, cationic, thiocholine-modified gold NPs are electrostatically assembled in solution to the RNA (right). Thiocholines on the gold NP are not to scale.

Figure 2. AFM images of TS RNA ladders decorated with gold NPs. (A) TS1 alone. (B) Cationic gold NPs alone (C) TS1-TS2 ladder (D) TS1-TS2 RNA ladder decorated with cationic gold NPs. Vertical scale bar is 10 nm for all images. Same [RNA] were deposited on the mica surface. Variation in the observed numbers of TS (2A) and ladders (2C) most likely derives from the relative ability of each TS to be retained on the mica surface compared to the ladder. (E) Section analysis of ladders decorated with gold.

Figure 3. Distributions of distance separating adjacent gold NPs along TS RNA ladder (blue, n=380) and duplex DNA (4) (red, n=330).

References
     (d) Seeman, N. C. Nature 2003, 421, 427.  