Communication

A "Nanonecklace" Synthesized from Monofunctionalized Gold Nanoparticles

Qiu Dai, James G. Worden, Jonathan Trullinger, and Qun Huo

J. Am. Chem. Soc., **2005**, 127 (22), 8008-8009• DOI: 10.1021/ja042610v • Publication Date (Web): 13 May 2005

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 15 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

J|A|C|S
COMMUNICATIONS

Published on Web 05/13/2005

A "Nanonecklace" Synthesized from Monofunctionalized Gold Nanoparticles

Qiu Dai, James G. Worden, Jonathan Trullinger, and Qun Huo*

Department of Coatings and Polymeric Materials, North Dakota State University, 1735 NDSU Research Park Drive, Fargo, North Dakota 58105

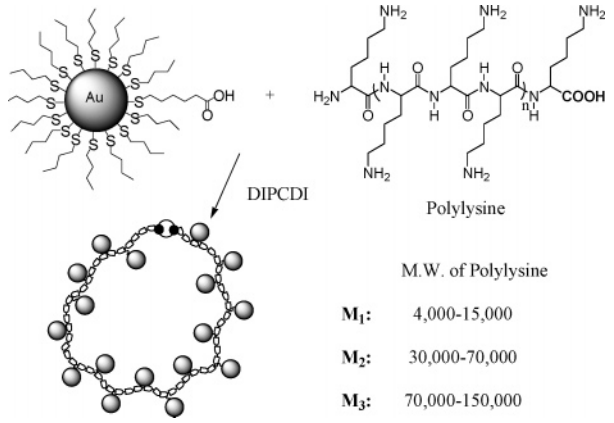
Received December 8, 2004; E-mail: Qun.Huo@ndsu.nodak.edu

Current nanomaterial research rests heavily on the "bottom-up" approach[1] compared to the "top-down" approach. The bottom-up approach offers better flexibility and versatility in terms of material design. However, a significant challenge of this approach is how to assemble the nanobuilding blocks into predefined and sophisticated nanomaterial structures. A major effort in this area has focused on the use of self- or templated-assembling techniques based on supramolecular interactions to control the nanomaterial network structures.[2−5] Despite the tremendous progress achieved in this field, there still remain significant limitations of self-assembled nanomaterials, which prevent their further development for applications. For example, self-assembled nanomaterials are often not sufficiently stable due to the weak noncovalent interactions that can be disrupted by dissolution, pH change, or heating. Many self-assembled systems are substrate-dependent, which means such materials lack the stand-alone capability and cannot be easily manipulated, transferred, or mixed into other systems to fine-tune the materials' properties.

In contrast to the extensively studied self- or templated-assembling approach, we raised the question in our research that possibly nanobuilding blocks can be assembled together into precisely defined nanomaterial structures using covalent bonding. Recently, our group and subsequently another group reported a solid-phase technique for the synthesis of monofunctionalized gold nanoparticles.[6,7] With a single functional group attached to the surface, such nanoparticles can be treated and used as molecular nanobuilding blocks to react with other chemicals, for example, a polymer, to form a nanomaterial with all the nanoparticle building blocks linked together by covalent bonding.

To demonstrate the potential of such an approach, we prepared the monocarboxylic group-modified gold nanoparticles with an average core diameter around 2 nm according to the procedure reported previously (also refer to ESI).[6] We then used these nanoparticles as a typical chemical agent to react with polylysine in the presence of an amide coupling agent, diisopropylcarbodiimide (DIPCDI, Scheme 1). Polylysine is a linear polypeptide with side amino groups from lysine residues available for coupling with the monocarboxylic nanoparticles. It was, therefore, expected that nanoparticles would attach to polylysine like beads dangling around a string to form nanoparticle chains. While the use of polymers including DNA as a template for the assembly of nanoparticles into nanoparticle wires by noncovalent interactions has been studied extensively,[8−11] examples of using covalent bonding for such a purpose are limited. Willner et al. reported the synthesis of a nanoparticle−polymer conjugate by attaching a commercially available 1.4 nm Au_{55} nanoclusters to DNA or polylysine through covalent bonds.[12] However, the triphenylphosphine-protected Au_{55} nanoclusters are well-known for their poor stability in many conditions, such as high ionic strength and elevated temperatures.[13] For this reason, the utility of this material is limited compared to that of the more stable alkanethiolate-protected gold nanoparticles used in the current study.

Scheme 1



Polylysine with three different ranges of molecular weight of, namely, 4000−15 000 ($\mathbf{M}_1$), 30 000−70 000 ($\mathbf{M}_2$), and 70 000−150 000 ($\mathbf{M}_3$) Da was used in the coupling reaction with the monofunctional nanoparticles. During the reaction, it was noticed that after the addition of activation agent DIPCDI to the solution, nanoparticle precipitates were formed within about 30 min. The reaction mixture was sonicated occasionally to obtain more complete coupling. After 2 h of reaction time, the precipitates were separated from the solution and further purified by centrifugation. The precipitates were found to be soluble in mixed dichloromethane and methanol solution with the addition of a trace amount of trifluoroacetic acid (TFA ∼ 1%).

Both the solution and precipitate portions of samples $\mathbf{M}_1$ to $\mathbf{M}_3$ were subjected to TEM analysis. TEM micrographs of the solution portion of all three samples showed mostly individual nanoparticles along with a small percentage of nanoparticle aggregates (shown in Figure 1a is the image from sample $\mathbf{M}_3$). This suggests that the solution mainly contains unreacted nanoparticles or nanoparticle−polymer conjugates with very few particles attached. For the precipitated portion of the samples, different results were observed. For $\mathbf{M}_1$ prepared from polylysine with the lowest molecular weight, TEM images showed mostly small aggregates made of a few nanoparticles with no clearly defined shape (Figure 1b). Occasionally, a small ring or half-ring structure was observed from the image (inset in Figure 1b). In contrast, some very interesting "nanonecklace" structures were observed from samples $\mathbf{M}_2$ and $\mathbf{M}_3$, aside from random aggregate and linear chain structures (Figure 1c and d). There is a distribution of the length of the nanonecklaces (estimated from the circumference of the ring structures in the images) in both samples. The average length of the necklace of $\mathbf{M}_3$ is clearly longer than that of $\mathbf{M}_2$. There is a good correlation between the length of the nanonecklace and the length of the polymer chain. For example, the calculated length of polylysine with molecular weight $\mathbf{M}_2$ and $\mathbf{M}_3$ is 47−110 and 110−235 nm,

10.1021/ja042610v CCC: $30.25

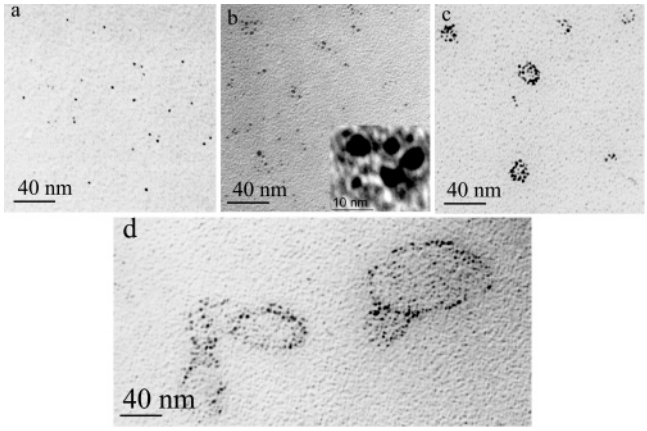


Figure 1. TEM images of the solution portion of sample $\mathbf{M}_3$ (a), and the precipitate product of $\mathbf{M}_1$ (b), $\mathbf{M}_2$ (c), and $\mathbf{M}_3$ (d) dissolved in dichloromethane/methanol (1/1, v/v, with 1% TFA).

respectively. The observed average lengths of the nanonecklaces in samples $\mathbf{M}_2$ and $\mathbf{M}_3$ are around 60 and 150 nm, respectively.

We believe that the nanonecklace structures were formed by covalent attachment of nanoparticles to the polylysine backbone followed by ring closure of the polylysine chain. The covalent bond linkage between the nanoparticles and polylysine was supported by the following key facts. First, the UV−vis absorption spectrum of the coupled NP−polylysine product showed a clear red shift of the surface plasmon resonance band, while the physically mixed nanoparticle−polylysine solution without coupling did not exhibit any SPR band shift (ESI). The spectra were taken at very dilute concentrations with the presence of trifluoroacetic acid in the solvent. This result showed that the SPR band shift of the conjugated NP−polylysine product was not due to the random aggregation or self-assembling of nanoparticles in solution. Second, TEM analysis of the physically mixed NP−polylysine solution without coupling indicates only the presence of randomly scattered individual nanoparticles (ESI), supporting that the nanoparticle chains observed from the coupled product were not due to self-assembling or solvent-drying process.

The closed loop structure of the nanonecklace is attributed to the ring closure of the polylysine chain. Each polylysine chain has a carboxylic acid end group. With the presence of amide coupling agent, DIPCDI, the carboxylic end group could have reacted with the end or one of the side amino groups from the same polylysine to form a cyclic polypeptide. To further confirm this result, we conducted the following two control experiments. In the first control experiment, the monocarboxylic nanoparticles were coupled with an ethylenediamine linker to obtain single amino group-modified nanoparticles. Such nanoparticles were then allowed to couple with a poly(acrylic acid) (PAA, $M_W \sim 90\,000$ Da) in the presence of DIPCDI. PAA cannot be cyclized under the mentioned coupling conditions. Indeed, TEM analysis of this coupled product dissolved in the same solvent as that used for the NP−polylysine product only showed some linear nanoparticle chains and random aggregates (ESI). In the second control experiment, we used a Boc-protected ethylenediamine molecule to block the carboxyl group of the polylysine by reacting a large excess of Boc−ethylenediamine with polylysine in the presence of DIPCDI. The blocked polylysine was then coupled with monocarboxylic nanoparticles. TEM analysis of this coupled product did not show any evidence of nanoring structures (ESI), but instead, some random aggregates and linear chains of nanoparticles. These two control experimental results demonstrate reliably that the loop structures observed from the NP−polylysine coupling product were due to the ring closure of the polylysine chain by covalent bonding, rather than by any self-assembling process.

Although there are some examples of nanoring and nanoloop structures reported previously,[14] almost all of these structures were formed due to self-assembling or a solvent-dependent drying process. In contrast, in our NP−polymer hybrid materials, all of the nanoparticle building blocks are covalently bonded together, and the material can be easily manipulated, transferred, and mixed with other solvents or materials without destroying the assembled nanomaterial structures. During the sample preparation for various studies, the NP−polylysine conjugated samples were repeatedly dried and redispersed in various solvents, and under all solvent conditions, the nanonecklace and linear chain structures remained intact.

It also should be pointed out that the monofunctional nanoparticles are critical for the successful synthesis of the NP−polymer conjugate materials described here. If a nanoparticle contains multiple functional groups, even if it is only a limited few, the multiple functional groups will cause cross-linking of the polymers, leading to unpredictable and insoluble network materials. As a comparison, we prepared nanoparticles containing approximately 5−10% functional groups in the monolayer by solution phase place exchange reaction.[6b] The coupling reaction of these multifunctionalized nanoparticles with polylysine resulted in a product that is insoluble in any solvents tested, a clear sign of a cross-linking reaction.

In summary, our work demonstrated the potential of covalent bond chemistry in the bottom-up approach toward the nanomaterial development. Not limited to nanochains, nanorings, and nanoloops, this approach can be readily extended to the fabrication of other types of more sophisticated nanomaterials with well-controlled structures and properties.

Acknowledgment. This work was financially supported by a National Science Foundation CAREER Award DMR 0239424.

Supporting Information Available: Experimental details of the synthesis of monocarboxylic group-modified gold nanoparticles and NP−polymer conjugates; UV−vis spectra of the products, and TEM analysis of NP−PAA conjugates. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Schmid, G. *Clusters and Colloids: From Theory to Applications*; VCH: New York, 2004.
(2) Daniel, M.-C.; Astruc, D. *Chem. Rev.* **2004**, *104*, 293−346.
(3) Shenhar, R.; Rotello, V. M. *Acc. Chem. Res.* **2003**, *36*, 549−561.
(4) Hamley, I. W. *Angew. Chem., Int. Ed.* **2003**, *42*, 1692−1712.
(5) Feldheim, D. L.; Keating, C. D. *Chem. Soc. Rev.* **1998**, *27*, 1−12.
(6) (a) Worden, J. G.; Shaffer, A. W.; Huo, Q. *Chem. Commun.* **2004**, 518−519. (b) Shaffer, A. W.; Worden, J. G.; Huo, Q. *Langmuir* **2004**, *20*, 8343−8351. (c) Worden, J. G.; Dai, Q.; Shaffer, A. W.; Huo, Q. *Chem. Mater.* **2004**, *16*, 3746−3755.
(7) Sung, K.-M.; Mosley, D. W.; Peelle, B. R.; Zhang, S.; Jacobson, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 5064−5065.
(8) Nakao, H.; Shiigi, H.; Yamamoto, Y.; Tokonami, S.; Nagaoka, T.; Sugiyama, S.; Ohtani, T. *Nano Lett.* **2003**, *3*, 1391−1394.
(9) Harnack, O.; Ford, W. E.; Yasuda, A.; Wessels, J. M. *Nano Lett.* **2002**, *2*, 919−923.
(10) Xin, H.; Woolley, A. T. *J. Am. Chem. Soc.* **2003**, *125*, 8710−8711.
(11) Warner, M. G.; Hutchison, J. E. *Nat. Mater.* **2003**, *2*, 272−277.
(12) Patolsky, F.; Weizmann, Y.; Lioubashevshi, O.; Willner, I. *Angew. Chem., Int. Ed.* **2002**, *41*, 2323−2327.
(13) Schmid, G. *Chem. Rev.* **1992**, *92*, 1709−1727.
(14) (a) Tripp, S. L.; Pusztay, S. V.; Ribbe, A. E.; Wei, A. *J. Am. Chem. Soc.* **2002**, *124*, 7914−7915. (b) Deegan, R. D.; Bakajin, O.; Dupont, T. F.; Huber, G.; Nagel, S. R.; Witten, T. A. *Nature* **1997**, *389*, 827−829.

JA042610V