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Wenbin Li^a; Meifang Zhu^a; Xiaqin Wang^a; Xingping Zhou^b; Kensuke Naka^c; Yoshiki Chujo^c

^a State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Material Science and Engineering, Donghua University, Shanghai, P. R. China ^b Institute of Biological Sciences and Biotechnology, Donghua University, Shanghai, P. R. China ^c Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto, Japan

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Self-assembly of Functionalized Gold Nanoparticles with Rigid and Flexible Multifunctional Linkers

WENBIN LI,¹ MEIFANG ZHU,¹ XIAQIN WANG,¹
XINGPING ZHOU,² KENSUKE NAKA,³
AND YOSHIKI CHUJO³

¹State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Material Science and Engineering, Donghua University, Shanghai, P. R. China

²Institute of Biological Sciences and Biotechnology, Donghua University, Shanghai, P. R. China

³Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto, Japan

The interparticle spacing of carboxyl functionalized gold nanoparticles (Au-COOH) were mediated by rigid crosslinkers, octa(3-aminopropyl)octasilsesquioxane (POSS-NH₃⁺) and poly(amidoamine) dendrimer terminated with hydroxyl groups (PAMAM-OH), and a flexible polymeric linker, poly(hexanul viologen) (6-VP). Regular interparticle spacing was achieved by utilizing POSS-NH₃⁺ and PAMAM-OH dendrimer as cross linkers, whereas size growth of Au-COOH was observed featuring no interparticle spacing by utilizing 6-VP as the crosslinker.

Keywords self-assembly, gold nanoparticles, interparticle spacing, rigid linker, flexible linker

Introduction

Functionalized metal nanoparticles are currently the subject of intense investigation as building blocks of advanced materials with novel characteristics for nanoscience and nanotechnology (1). Development of simple methodology for fabrication of controlled nanostructures is indispensable for preparing new nanodevices. Several approaches have been used to obtain self-organized nanostructures of metal nanoparticles (2, 3). One of the efficient methods involves utilization of bifunctional or multifunctional chemical crosslinkers.

New classes of nanocomposite materials with organized structures obtained by manipulation of nanocrystals often lead to interesting chemical and physical properties distinctly different from those of their component parts (4, 5). Self-assembled monolayers coated on nanoparticles both stabilizes the nanoparticles and affords a method for

Address correspondence to Xiaqin Wang, State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Material Science and Engineering, Donghua University, Shanghai 200051, P. R. China. E-mail: xqwang@dhu.edu.cn

introducing diverse functionality to the nanoparticle surface, providing a link between molecules and materials (6–8). Molecular-level recognition via physical or chemical interaction between monolayer protected nanoparticles and functionalized crosslinkers is a powerful tool for the creation of multi-scale ordered materials as it provides a molecular-level control over the macroscopic properties (6, 8, 9).

We have recently reported the initial studies on the preparation of self-organized nanocomposites of carboxyl functionalized gold nanoparticles (Au-COOH) with octa(3-aminopropyl)octasilsesquioxane (POSS-NH₃⁺) via electrostatic interaction between carboxylate anions and ammonium cations under mild basic conditions (10). The results motivated us to conduct further research on self-assembly of Au-COOH with POSS-NH₃⁺ via hydrogen bonding and spatial arrangement of Au-COOH. In addition, another rigid crosslinker, poly(amidoamine) dendrimer terminated with hydroxyl groups (PAMAM-OH) was used to organize Au-COOH as well to determine the influence of rigidity of the cross linkers on multi-scale ordering of the resultant nanocomposites. The rigidity of the crosslinkers was manifested by a flexible polymeric crosslinker, poly(hexanyl viologen) (6-VP), which allowed Au-COOH to self-assemble into particles of different size and morphology.

Experimental

Materials

PAMAM-OH dendrimer (G = 4) with 64 -OH end groups was obtained from Dendritech Inc. Other solvents and reagents except Au-COOH, POSS-NH₃⁺ and 6-VP were commercially supplied and used without further purification.

Synthesis of Au-COOH

Au nanoparticles stabilized by dodecanethiol (DT) and 11-Mercaptoundecanoic acid (MUA) were prepared by reducing HAuCl₄ · 4H₂O with NaBH₄ in a two-phase (CHCl₃-H₂O) system according to the Brust reaction (11). On the basis of the ¹H-NMR and TGA results, it was determined that 1.0 mg of Au-COOH had 6.69 × 10⁻⁴ mmol of -COOH groups. The average size of Au-COOH was 2.7 ± 0.3 nm measured from transmission electron microscopy (TEM).

Synthesis of POSS-NH₃⁺

POSS-NH₃⁺ was prepared from aminopropyltriethoxysilane following the detailed experimental procedures described in previous literature (12, 13).

Synthesis of 6-VP

6-VP (Mn = 2400 by ¹H-NMR) was synthesized from 1,6-dibromohexane and 4,4'-bipyridyl as reported (14). Its counterions were transformed to hexafluorophosphate (PF₆⁻).

Results and Discussion

POSS-NH₃⁺ as a Rigid Linker of Au-COOH

In order to provide control of the nanocomposite formation process, Au-COOH and the crosslinkers were mixed in dilute solutions with the formation process proceeding over a long period. As shown in Chart 1, eight ammonium groups are located at the eight vortexes of POSS-NH₃⁺ via spacer linkage. All eight ammonium groups of POSS-NH₃⁺ are unable to attach to a single Au-COOH due to steric hindrance of the cubic structure. Thus, POSS-NH₃⁺ should act as a more efficient linker of various Au-COOH than bifunctional linking molecules. Furthermore, POSS-NH₃⁺ has an inner cubic rigid inorganic core with the size of ~ 0.5 nm containing silicon and oxygen, which offers uniform interpartical spacing, good thermal and mechanical properties, and solvent-resistance.

Time-dependent evolution of the surface plasmon resonance of Au-COOH at ~ 500 nm demonstrated that interaction between Au-COOH and POSS-NH₃⁺ is rather weak in the dilute solution without addition of NaOH. Based on our previous research (9), electrostatic interaction between Au-COOH and POSS-NH₃⁺ under mild basic conditions with the addition of NaOH is strong enough to cause immediate precipitation of the nanocomposite and fading of the deep red color of the solution of Au-COOH and POSS-NH₃⁺. Fourier transform infrared (FTIR) spectrum of the formed nanocomposite suggested that the majority of the -COOH groups were changed into -COO⁻. Accordingly, relatively weak hydrogen bonding is probably the primary interaction in this research.

The nanocomposite was visualized by TEM, as shown in Figure 1(a). It could be discerned that Au-COOH were not fused into large aggregates from the peripheral portions of the aggregates. Individual Au-COOH were separated from each other by POSS-NH₃⁺. There was a narrow distribution of the interpartical spacing, as shown in Figure 1(b), obtained by counting 300 interpartical spacings. The mean interpartical spacing is 1.12 ± 0.12 nm, in good agreement with the size of POSS-NH₃⁺. Au-COOH and POSS-NH₃⁺ were arranged alternatively in each direction, which avoided fusion of Au-COOH and offered regular interpartical spacing.

PAMAM-OH Dendrimer as a Rigid Linker of Au-COOH

PAMAM-OH dendrimer is an effective linker of Au-COOH since no free Au-COOH stayed in the solution from TEM images (Figure 2(a)). Only floccules of Au-COOH were observed by TEM. Focusing on one floccule offers the fine structure of the floccular nanocomposite. Au-COOH was separated by PAMAM-OH dendrimer, which affords uniform interpartical spacing and a narrow distribution of the interpartical spacing. In comparison with the nanostructures mediated by POSS-NH₃⁺, a much

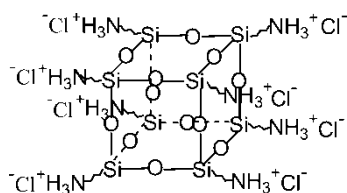


Chart 1. Molecular structure of POSS-NH₃⁺.

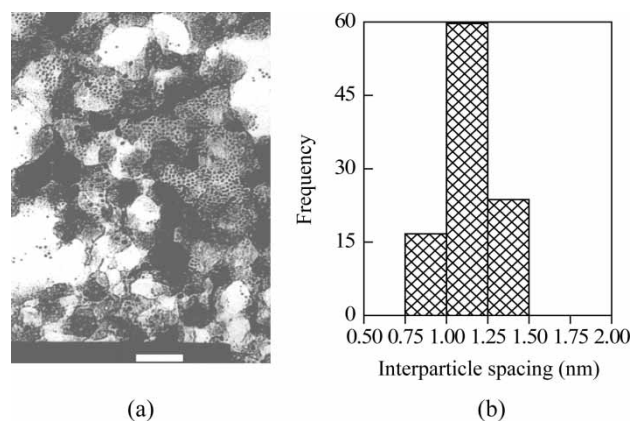


Figure 1. (a) TEM image (bar: 50 nm), and (b) distribution of interparticle spacing of Au nanoclusters self-organized by POSS-NH₃⁺.

narrower distribution of the interparticle spacing was achieved from the PAMAM-OH dendrimer, probably due to its larger rigidity. The average interparticle spacing was 1.42 ± 0.04 nm, as shown in Figure 2b, obtained by averaging 300 interparticle spaces. Rotello et al. reported controlled interparticle spacing through self-assembly of Au nanoparticles and PAMAM dendrimers terminated with amino groups (8). However, superstructures and interparticle spacing of their products are different from ours in that their approach caused rapid precipitation of spherical or irregular shapes from Au nanoparticles and PAMAM dendrimers in concentrated solutions, whereas formation of our mass fractal objects requires a time span in the dilute solution, which can be explained by a diffusion-limited monomer-cluster aggregation model. Au nanoparticles are released from the mixed solution arbitrarily far from a central cluster, sticking irreversibly at first contact with the growing cluster. Because of their Brownian trajectories, which simulate diffusion, the Au nanoparticles can not penetrate deeply into a cluster without intercepting

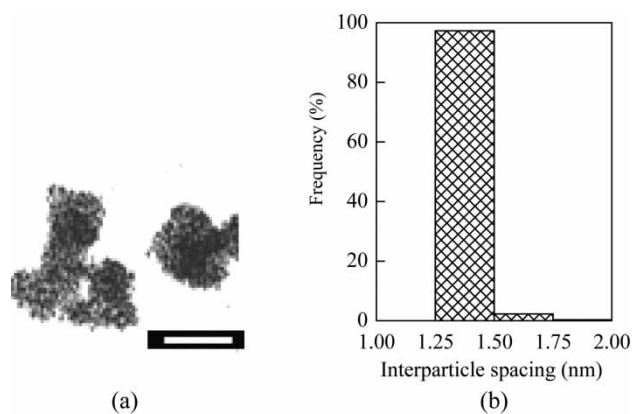


Figure 2. (a) TEM image (bar: 100 nm), and (b) distribution of interparticle spacing of Au nanoclusters self-organized by PAMAM-OH dendrimer.

a cluster arm. The arms effectively screen the interior from the flux of incoming particles. Therefore, growth occurs preferentially at exterior sites.

6-VP as a Flexible Linker of Au-COOH

One macromolecular chain of 6-VP as a polycation can theoretically link many Au-COOH at its various positively charged sites. The self-assembly manner of Au-COOH with 6-VP should thus be different from those by POSS-NH₃⁺ and PAMAM-OH dendrimer due to the flexibility and length of 6-VP molecular chains. Variation of the surface plasmon resonance band of Au nanoparticles after mixing 6-VP and Au-COOH was followed by UV-Vis spectra, as shown in Figure 3. No obvious absorption peak was discerned after mixing for 4 days except decreased absorption at the wavelength of ~500 nm. An absorption peak appeared at 518 nm after 5 days, and it shifted to 524 nm after 8 days. A decrease of the surface plasmon resonance band with the incubation time was always observed, although substantial decrease occurred only within the initial 2 days. However, the surface plasmon resonance band increased significantly during the eighth and ninth days of mixing. A sharp absorption peak for Au nanoparticles dominates over the other absorption bands and changed little since then. The color of the admixture changed from deep red to deep purple, correspondingly. TEM image of the admixture in Figure 4 illustrates that Au nanoclusters with larger size than Au-COOH are dispersed in the solution. Unlike rigid POSS-NH₃⁺ or PAMAM-OH dendrimer, 6-VP is not able to provide definite spacings distinguishable by TEM to separate the Au-COOH. Spherical self-assembly of Au-COOH is inevitably generated to reduce surface energy because molecular chains of 6-VP are sufficiently flexible. Size growth of the Au nanoclusters was not evident within the later 7 days after mixing for 12 days totally. But the total amount of the Au nanoclusters increased with the incubation time. The average size is 10.82 ± 1.30 nm by averaging 170 Au nanoclusters. It is estimated that the nanoclusters consist of several tens to several hundreds of individual Au-COOH per nanosphere. Multivalent electrostatic interaction of 6-VP with Au-COOH induces the unfolding of the compact structure of 6-VP, exposing further charged recognition units. This allows 6-VP to interact further with Au-COOH, propagating the assembly process.

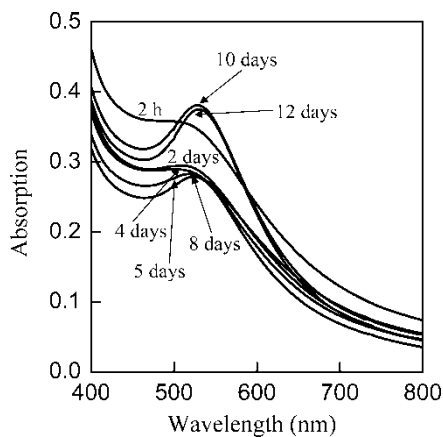


Figure 3. Time-dependent evolution of UV-vis absorption during self-organization between Au-COOH and 6-VP.

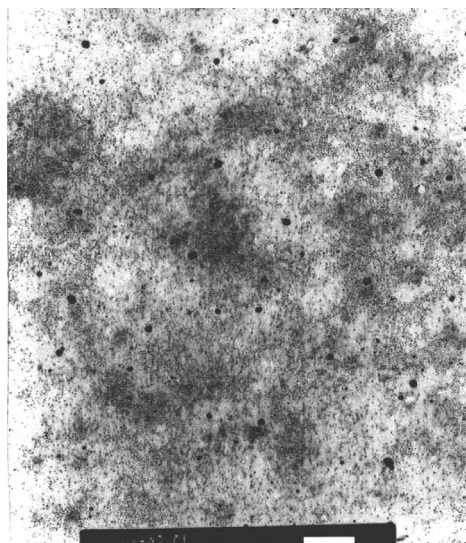


Figure 4. TEM image of Au nanoclusters self-organized by 6-VP (bar: 100 nm).

Conclusions

Rigidity of the linker molecules plays a key role to build and pattern self-assembled nanostructures from Au-COOH. It was found that rigid molecules, POSS-NH₃⁺ and PAMAM-OH dendrimer, could be utilized to create meso- and macroscopic nanostructures featuring regular interparticle spacings. In contrast, flexible molecular chains of 6-VP could be employed to enlarge the size of Au-COOH without distinguishable spatial control. Therefore, systematic control of interparticle spacing can be achieved by deliberately tuning molecular sizes and rigidity of crosslinkers. Our current research results show how the molecular recognition properties of the crosslinkers can be used to direct the placement of Au-COOH within extended self-assemblies, although more delicate control of interparticle spacing is desired to customize magnetic, optical, and electronic properties of nanocomposite materials. Our approaches are also applicable to other nanoparticles (e.g., Ag, Pt, Pd, CdS, and CdSe nanoparticles).

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