

## ARTICLES

## Controlled Organization of Au Colloids into Linear Assemblies

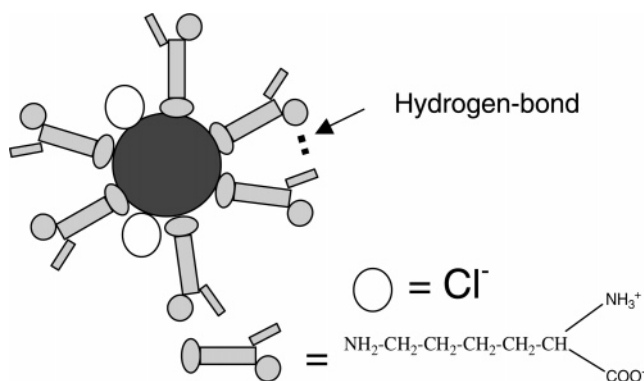
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A simple and convenient method is described to produce gold nanowires. A controlled organization of Au colloids into linear assemblies was achieved without using any templates.  $\text{HAuCl}_4$  was reduced by  $\text{NaBH}_4$  in the presence of lysine to act as capping and bridging agent. At a molar ratio of  $\text{Au/Lys} = 1:0.5$  and pH in the range 8.4–9.5, linear aggregates of Au can be prepared with a diameter of ca. 5 nm and variable lengths in the range of 80–200 nm. At lower or higher pH values, there is no control on the unidirectional growth of linear aggregates. Application of ultrasound during the preparation also impairs linear growth or disrupts the chain structure, yielding discrete colloidal particles of Au as sole product. The key factor for formation of Au linear assemblies is believed to be a subtle balance between the attractive (cross-linking) force, provided by lysine molecules, working against the electrostatic repulsion among Au colloid surfaces bearing like (negative) charges.

## Introduction

Over the last three decades, metal nanoparticle research has focused mainly on the synthesis of nanoclusters in different sizes and evaluation of their size-dependent properties.<sup>1,2</sup> Most recently, emphasis has been placed on organizing or assembling metal nanoparticles into defined architectures, mainly for two reasons. First, such metal nanoparticle aggregates can display rich optical and electrical characteristics that are distinctly different from a simple collection of individual particles or the extended solid.<sup>3</sup> Second, in relation to emerging electronic technologies, more sophisticated nanostructures are in demand (e.g., nanowires, nanotubes, and their two-dimensional (2-D) and three-dimensional (3-D) nanoparticle assemblages). Various approaches or driving forces to forming complicated nanostructures make use of such physicochemical effects as hydrogen bonding,<sup>4</sup> ion pairing,<sup>5</sup> host–guest inclusion chemistry,<sup>6</sup> van der Waals/packing interactions,<sup>7</sup> laser soldering,<sup>8</sup> DNA-directed synthesis,<sup>9</sup> metal coordination processes or using the bridging molecules that have defined symmetry,<sup>10</sup> templating methods,<sup>11</sup> or dipole–dipole interactions.<sup>12</sup> However, very few studies have achieved unidirectional assembly of Au colloids into nanowires in the absence of either solid or soft templates.<sup>13</sup>

Here, we present a template-free approach to forming Au colloids into long narrow chains via the use of the amino acid molecule lysine. It possesses two chemically distinct terminal amino groups,  $\text{NH}_2$ –I (or the protonated form) neighboring the

CHART 1: Capped Au Colloids with Adsorbed Anions and Capping Molecules<sup>a</sup>

<sup>a</sup> Their surfaces will become more negatively charged with an increase of pH value.

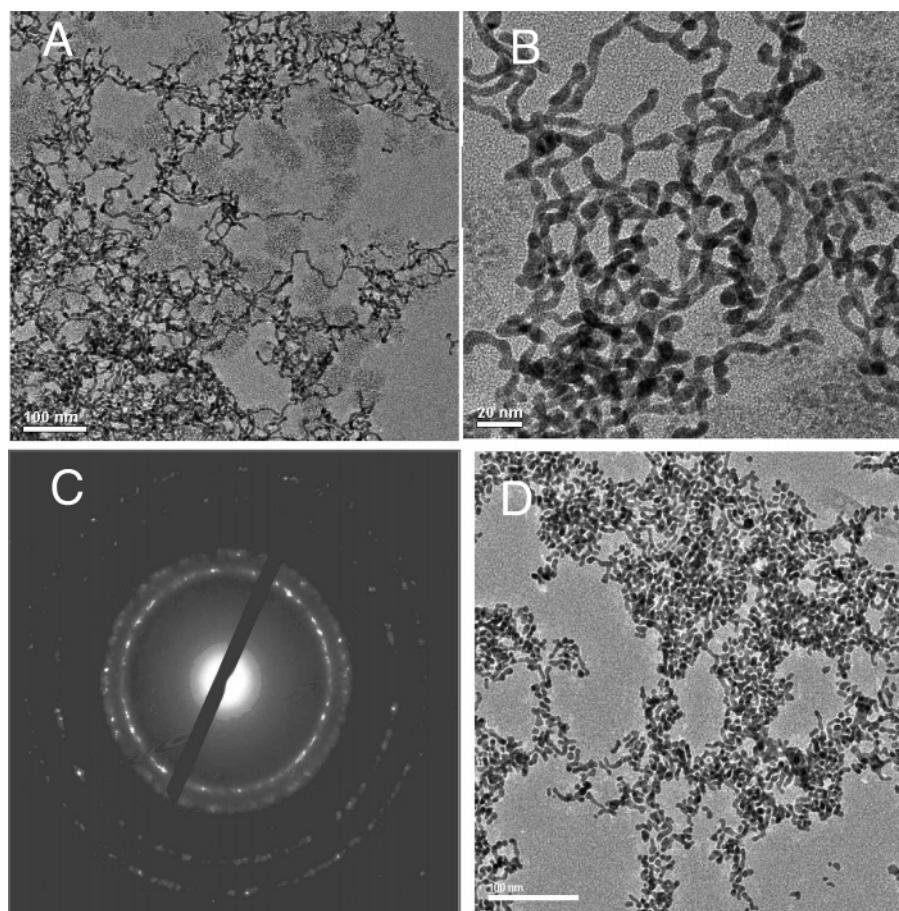
$\text{COOH}$  group and  $\text{NH}_2$ –II, remote from the  $\text{NH}_2$ –I and  $\text{COOH}$  groups. This dual functionality serves to both cap<sup>14</sup> and bridge Au colloids.<sup>15</sup> Work in this laboratory has proven that the  $\text{NH}_2$ –II moiety readily binds with the Au surface, whereas the behavior of the  $\text{NH}_2$ –I group is pH-dependent because of deprotonation of the adjacent carboxylic acid group.<sup>15</sup> With an increase in pH values, lysine first passes through the zwitterionic form. Finally, at a pH value around the  $\text{p}K_2$  value of lysine (8.5), the  $\text{NH}_3^+$ (I) species is deprotonated,<sup>16</sup> leading to capped Au nanoparticles with negative charges projecting from their surfaces (Chart 1). The configuration that best minimizes the electrostatic repulsive forces on any assembly of similarly charged colloidal particles will obviously be *linear*, in which the nearest neighbor coordination number is only 2. Thus, an

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**Figure 1.** TEM images of Au samples. (A) Au nanowires prepared by reduction of  $\text{HAuCl}_4$  with  $\text{NaBH}_4$  in the presence of lysine. The molar ratio lysine/Au is 0.5 and the end pH = 9.1. (B) Magnified detail of (A). (C) Electronic diffraction pattern from (A), confirming fcc structure. (D) Au samples prepared under the same conditions except the end pH = 11.1.

almost linear chain or “wire” is formed preferentially at slightly basic pH values. In contrast, at lower pH values where the carboxylic acid groups are only partially dissociated there is less repulsion, and aggregation of the capped Au colloids will proceed in a more nearly random or isotropic manner. At very high pH values, the high density of surface charges gives rise to increased repulsive forces among Au colloids, deterring aggregation altogether and stabilizing instead the original colloidal dispersion despite the presence of lysine. An expected trend might then be a progressive shortening of the linear chains and a growing preponderance of discrete Au particles. According to this simple view, the key factor in selectively producing the nanowire form is to control the balance between the binding ability provided by the  $\text{NH}_2$ -I group in lysine and the electrostatic repulsion exerted by the outer surface of the capped Au colloids.

## Experimental Section

All of the chemicals were purchased from Aldrich. In a typical synthesis, 10 mL of 1 mM aqueous  $\text{HAuCl}_4$  was mixed with 0.5 mL of 10 mM lysine aqueous solution, and sufficient 0.2 M aqueous NaOH was added to adjust the pH value. While the mixture was stirred vigorously, 176  $\mu\text{L}$  of 0.1 M  $\text{NaBH}_4$  was then added. At acidic pH values ( $<5$ ), the solution initially turned black and was followed by the occurrence of rapid and extensive precipitation. At intermediate pH values (6.5–10), a red color was observed in the first few seconds, but the solution gradually turned dark brown or black, suggestive of a continuous

cross-linking or aggregation process. At very high pH values ( $>11$ ), a black solution was formed, accompanied by partial precipitation. Example illustrations can be found in the Supporting Information.

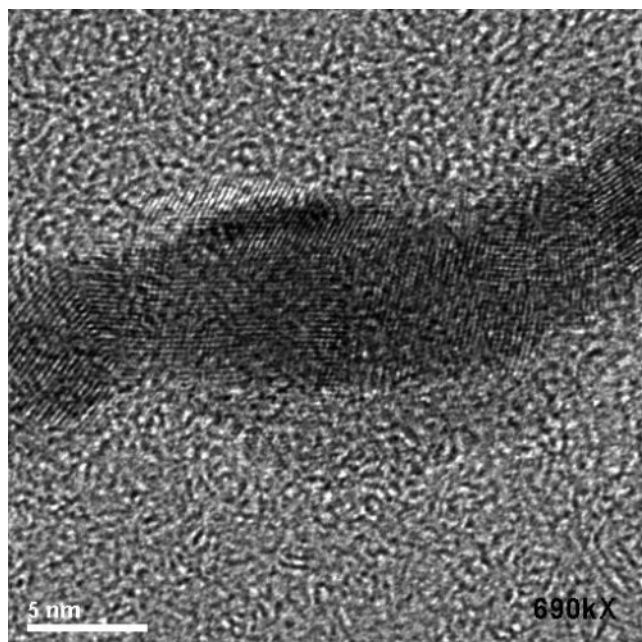
UV–vis spectra were recorded on a UV-2550 spectrophotometer (Shimadzu) and transmission electron microscopy (TEM) measurements were conducted on a TECAI TF20 SuperTwin (200 kV) microscope.

## Results and Discussion

### (1) Au Linear Chains “Wired” by Lysine Molecules.

Presented in Figure 1A and 1B are typical TEM images of Au linear aggregates prepared at pH = 9.1. These show a cross-sectional wire diameter of ca. 5 nm, which is comparable to the Au colloid size. The linear extension of the chains ranges from 80 to 200 nm, and individual interconnected Au particles are clearly visible along their length(s). In other words, the chains are indeed wired serially (one by one), a process not explicable in terms of a point-initiated mechanism. The optical images for these samples are shown in Figure 1, in Supporting Information. At high resolution, TEM (Figure 2) reveals a more elongated shape for many of the Au particles, which can be discerned clearly by their different lattice orientations, with extension parallel to the chain axis. This is quite different from the normal spherical shape of Au nanoparticles (e.g., as when capped with agents such as dithiol) in 2-D and 3-D structures. The elongation of the Au particles in the linear assemblies possibly arises because of lysine cross-linking forces acting



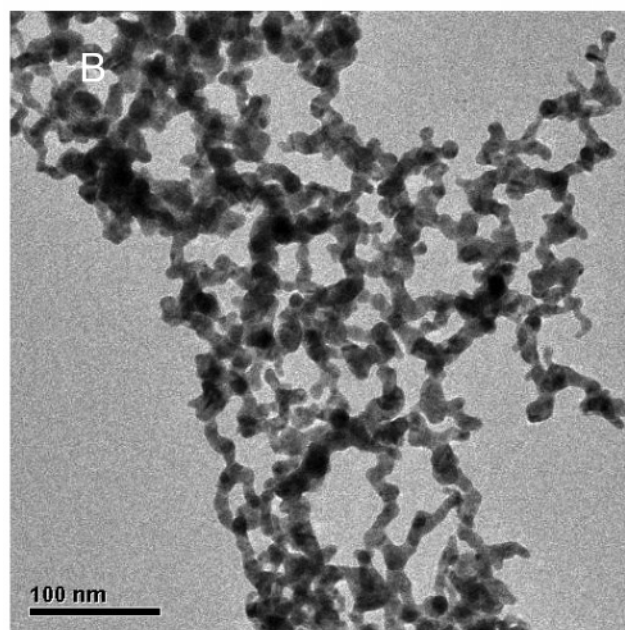
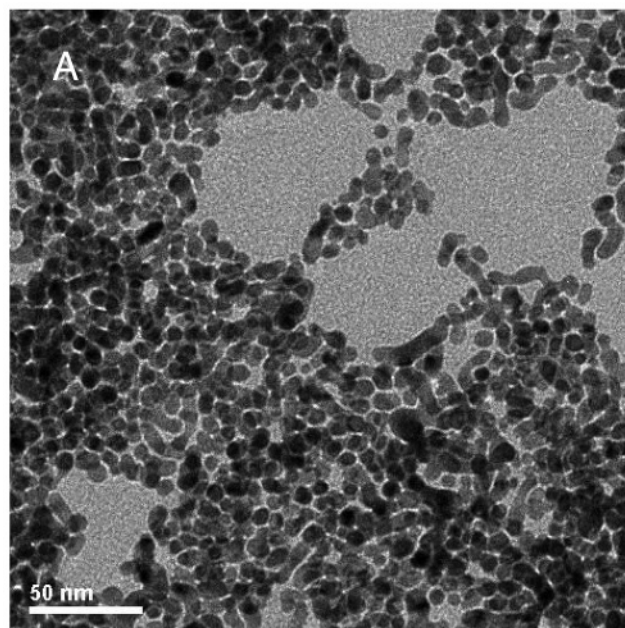


**Figure 2.** HRTEM image of Au nanowires for sample shown in Figure 1B.

along the long axis of the wires. The existence of some Y junctions in the Au nanowires reveals that the unidirectional growth is not perfect. However, the slight degree of branching may still be of relevance in nanodevice fabrication because the proper linkage of two preformed nanoassemblies with complementary functions remains a big challenge. At the adjoining point of two neighboring Au particles (Figure 2), it seems that the two Au particles are fused, indicating a strong cross-linking interaction rather than weak van der Waals or hydrogen-bonding forces at work. Another feature of the formed Au linear aggregates is their “single Au nanoparticle thickness” in cross section.

At a more basic pH value (11.1), the product consists of shorter but more thickly bound nanowires (Figure 1D). At low pH values, some linear aggregates are evident, but the major fraction consists of simple 3-D aggregates (Figure 2 in Supporting Information). Some “pearl necklace” agglomerates are also observed. Most of the Au particles are loosely bonded, and the aggregates show indefinite shape or nondirectional control in aggregation. For comparison, 5-aminovaleric acid and 1,4-diaminobutane, having one and two terminal amino groups, respectively, were examined as capping agents in the same way. For 5-aminovaleric acid, the Au product is mainly composed of spherical nanoparticles, confirming that the “wiring action” indeed requires the bifunctionality of a molecule like lysine. Although hydrogen bonding may occur between  $\text{NH}_3^+$  and  $\text{COO}^-$ ,  $\text{NH}_2$  and  $\text{COOH}$ , or between neighboring  $\text{COOH}$  groups, it is hard to conceive how such interactions can lead to selective unidirectional growth of stable Au linear aggregates, being more likely intramolecular rather than intermolecular in scope. Contrary to 5-aminovaleric acid, the use of 1,4-diaminobutane, in a wide range of pH values, invariably led to precipitation after reduction of the Au salt. The precipitate forms a 3-D network (Figure 3B), predominantly multiply stranded in nature. No unidirectional growth is observed in this case.

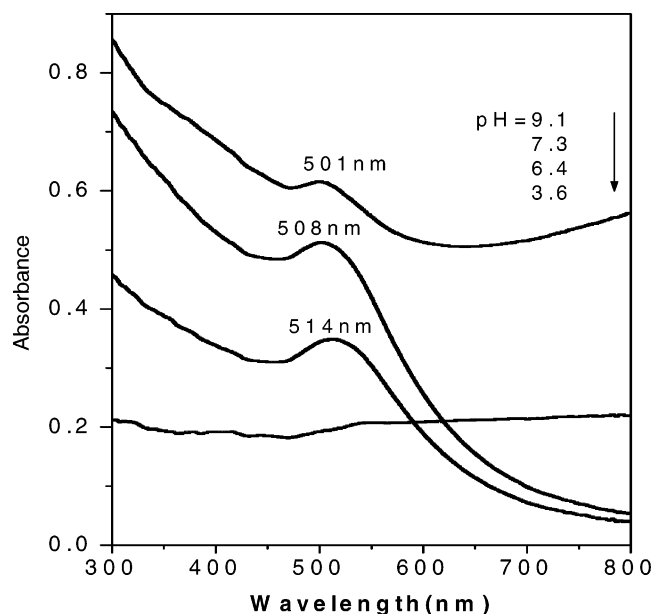
There are evidently two primary factors influencing the formation of Au nanowires, the pH value and the molar ratio of lysine/Au. According to the simplest interpretation, the change in the pH value mainly influences the bound lysine-specific



**Figure 3.** TEM images of Au particles prepared by employing (A) 5-aminovaleric acid and (B) 1,4-diamine as capping agents.

charge by tuning the deprotonation of the  $\text{COOH}$  and  $\text{NH}_3^+$  groups, whereas the lysine/Au ratio influences the density of lysine molecules on the Au surface and thus the charge-to-particle ratio. Optimum conditions for Au linear aggregates production were found to be at a molar ratio of lysine/Au = 0.5, and pH value in the range 8.4–9.5. It seems highly significant that the optimum pH range corresponds with the  $\text{pK}_2$  value of lysine (i.e., when the zwitterionic  $\text{NH}_3^+$  form is substantially deprotonated).

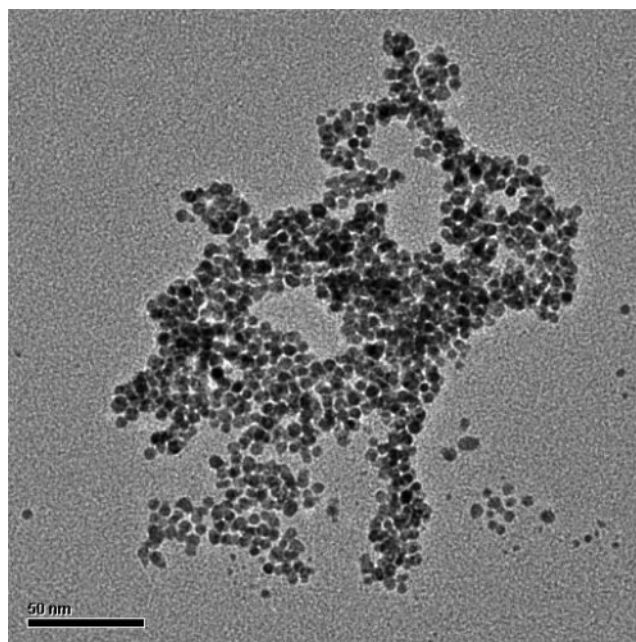
The dissociation of the proton from  $\text{NH}_3^+$  leads to a dramatic increase of negative charges on the Au colloid surface. At the same time, the amine group ( $\text{NH}_2$ –I) starts to be released from the hydrogen bond with their neighboring Lys molecules located on the same Au colloid surface and become available to bind Au colloids (Chart 1). As a result, Au colloids are more easily built up in a linear form. Another factor is the density of lysine molecules on the Au surface. A relatively low lysine coverage



**Figure 4.** UV-vis spectra of Au particles prepared at various pH values.

of the Au particle may be beneficial to the wiring process because the moderated repulsive force may, at some point, be just sufficient to allow “end on” approach of neighboring Au particles and keep appropriate space for the cross-linking. In previous studies,<sup>15,17</sup> where Au colloids were not prepared in situ, cross-linking by lysine was not observed under alkaline conditions ( $\text{pH} > 7$ ), possibly because a more fully covered surface was obtained in this case, leaving the repulsive force as the dominant factor. Another reason is that there was very limited space on Au colloid surface for the cross-linking. At present for in situ synthesis, it is reasonable to assume that a finely balanced condition obtains, Au clusters tending to link up in the desired fashion at only modest lysine coverage where the associated electrostatic repulsive forces are weaker. This may be because, during the early stage of Au cluster formation, coverage by lysine molecules is only partial. In support of this view, a poorer result was observed for selective Au nanowire assembly at a high lysine/Au ratio ( $>3$ ). Furthermore, a high concentration of lysine restricted control by pH adjustment (with NaOH addition) due to an earlier onset of precipitation of Au colloids.

One-dimensional metal nanostructures usually are prepared in solution by template methods, self-assembly, or anisotropic growth of nanoparticles.<sup>13a</sup> In polymer poly(vinylpyrrolidone) (PVP)-mediated polyol<sup>18</sup> and *N,N*-dimethylformamide<sup>19</sup> processes for Ag nanowire synthesis, different growth mechanisms are proposed. Xia et al.<sup>18</sup> suppose that the PVP molecules cover the Ag {100} facets while leaving the {111} facets largely uncovered and thus highly active. The anisotropic growth of Ag nanowires follows the Ostwald ripening process at the expense of the small Ag nanoparticles. However, Giersig et al.<sup>19</sup> propose another mechanism via high resolution transmission electron microscopy (HRTEM) observation. They verified in the solution the formation of icosahedral and cuboctahedral Ag nanoparticles as precursors. These subsequently self-assemble through preferred orientations {100} and {111} to form aligned strips and eventually fuse each other to yield single crystalline nanowires. In our synthesis, because any template or PVP-like macromolecules are absent, the driving force for self-assembly should come uniquely from cross-linking by lysine molecules. In our experiments with other capping agents containing only



**Figure 5.** Au colloids prepared employing lysine as capping agent at  $\text{pH} = 9$  (Au/lysine = 1:0.5) under ultrasonic irradiation. No Au linear aggregates appear under sonication.

one amino or mercapto functional group (e.g.,  $\text{NH}_2(\text{CH}_2)_n\text{COOH}$  and  $\text{SH}(\text{CH}_2)_m\text{COOH}$ ,  $n = 1, 2, 4, 7$  and  $m = 2, 5, 7, 9, 15$  (Figure 3 in Supporting Information)), Au nanowires were never observed. When lysine is used, single Au nanoparticles and pearl-necklace structures at high pH and low values were observed, respectively. These observations strongly suggest that Au nanoparticles are built up sequentially by lysine molecules, growth likely proceeding at both ends of the chain simultaneously. Thus, the linking action comes from two amino functional groups, and the electrostatic repulsion favors low-dimensionality growth.

Figure 4 shows the UV-vis absorbance spectra of colloidal Au suspensions prepared at various end-point pH values. For  $\text{pH} = 9.1$ , the absorbance curve exhibits features typical of the unidimensional Au nanostructure.<sup>15,20</sup> The maximum centered around 500 nm suggests the persistence of a very small dimension (i.e., the wire in cross section), whereas the rising tail of the spectrum at longer wavelengths (above 700 nm) can be attributed to the linking of the Au particles into chains of somewhat greater dimension. With a decrease in pH value, the maximum absorbance peak shifts slightly to longer wavelength, indicative of a modest increase in mean diameter. However, the longer wavelength feature characteristic of the wire formation is now weaker or absent. At a very low pH value (3.6), the spectrum is almost featureless and extends well beyond 500 nm. This would be expected if severe 3-D aggregation has occurred. Thus, optical spectroscopy data are quite consistent with the microscopic observations.

Suspensions of these Au nanowires are quite stable and can be stored at room temperature for more than one month without obvious deterioration.

**(2) Impact of Ultrasonic Irradiation on Aggregation of Au Colloids.** As a comparison, we prepared one sample under the same procedures except that when  $\text{NaBH}_4$  was added to the Au precursor solution the solution was subjected to ultrasonic irradiation. A purple solution was obtained, and TEM confirmed that only discrete spherical Au colloids were formed, with particle diameters in the range 3–5 nm (Figure 5). Clearly, the ultrasonic irradiation has a strong (dispersing) impact on the



aggregation state of Au colloids. Probably, the localized high pressure and high temperature produced during cavitation is not beneficial to the cross linking of Au colloids and the formation of Au linear aggregates, because these are less stable thermodynamically. However, this experiment does illustrate that spherical Au colloids are formed initially and probably act as relatively stable building blocks for linkup into linear aggregates. However, Au colloids with good dispersion can be prepared under strong sonication though bifunctional capping agent exists.

## Conclusions

We have demonstrated a very simple approach for preparing Au linear aggregates by end on linking of individual Au colloidal particles. A key aspect in their assembly is to restrict the coverage of the particle by the capping/linking agent via a subtle balancing of the repulsive surface charge and the attractive (ligating) power of the amine group in lysine. In practice, this is easily accomplished with a combination of pH end-point control and lysine/Au ratio. Such Au linear assemblies, of ~5 nm cross-sectional diameter, are also conveniently stored. Moreover under strong sonication, Au colloids with good dispersion can be obtained.

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**Supporting Information Available:** Example photographs of the Au samples at various pH values; TEM images of the prepared Au samples using lysine as capping agents at low pH value and other capping agents with only one functional group that can bind with Au nanoparticles. This material is available free of charge on the Internet at <http://pubs.acs.org>.

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