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Assembly of Phenylacetylene-Bridged Silver and Gold Nanoparticle Arrays

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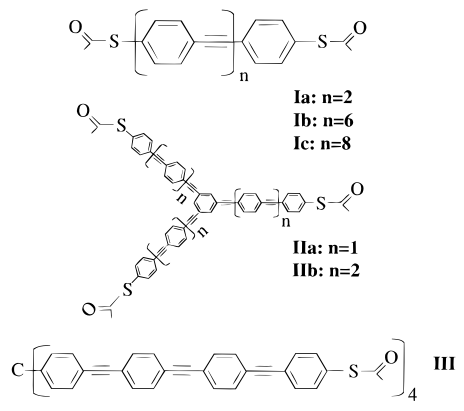
The optical properties of metal nanostructures have received a great deal of attention in the past decade because of their application in surface-enhanced spectroscopies, photocatalysis, and nonlinear optics.[1] In an attempt to understand particle size and shape−optical property relationships, a number of methods have been developed for fabricating nonspherical metal nanostructures.[2] Perhaps the simplest of these methods involves the aggregation of spherical gold or silver nanoparticles in solution or onto an optically transparent solid support.[1,3] Electromagnetically coupled particles increase electric-field enhancement factors, while the serendipitous formation of noncentrosymmetric aggregates can create large nonlinear optical responses.[3a]

Optical characterization of aggregated samples of particles have thus led to a deeper understanding of interparticle electromagnetic coupling. However, studies on randomly aggregated samples of spherical particles often suffer from uncertainties in aggregate size and symmetry. Despite these concerns, surprisingly few experimental methods have been described for arranging particles into discrete collections of spatially and symmetrically well-defined aggregates. Alivisatos reported linear arrays of DNA-linked gold particle dimers and trimers.[4] Electromagnetic interactions between particles were not observed, however. Foss used porous Al_2O_3 membranes to synthesize centrosymmetric and noncentrosymmetric particle pair structures.[5] Electromagnetic coupling and SHG were observed over large particle separation distances.

Our strategy for assembling coupled gold particle structures has been to synthesize rigid thiol-functionalized phenylacetylenes for use as molecular templates.[6] Herein we report the extension of this strategy to the assembly of coupled silver and gold particle arrays with pseudo-$D_{\infty h}$, D_{3h}, and T_d symmetries. In addition, we show that the linear optical properties of 30 nm diameter silver particle dimers agree qualitatively with recent calculations on similar systems.[7]

Gold and silver particles bridged by the thioacetyl-terminated phenylacetylene bridges shown in Scheme 1 were assembled according to published protocols.[6] Transmission electron micrographs (TEM) support the hypothesis that these molecular linkers can dictate particle array symmetry (Figure 1). The structures shown in Figure 1 are typical of those found over the entire grid.

Scheme 1



Counting ∼100 *structures* for each sample revealed estimated yields of ∼50, 30, and 10% for the dimers, trimers, and tetramers, respectively. The remainder of the sample in each case consisted predominantly of uncoupled particles.[8]

The symmetry observed by TEM for gold particle dimers and trimers was confirmed with hyper-Rayleigh scattering spectroscopy.[9] Here we focus on the linear optical properties versus separation distance for silver nanoparticle dimers. The 30 nm diameter silver particles contain a single extinction at 420 nm, corresponding to the well-known silver plasmon resonance.[1] Addition of a 9-unit phenylacetylene bridge caused a slight red-shift and absorbance increase of the silver plasmon band (Figure 2A). At separation distances corresponding to 7 phenylacetylene units, an extinction at 450 nm was observed with a more well-defined shoulder at 420 nm (Figure 2B). Both bands were more intense than the single-particle plasmon band. Further reduction in separation to 3 phenylacetylenes caused no further shift in the low-energy extinction; however, the high-energy shoulder blue-shifted to 370 nm, and both bands grew in intensity (Figure 2C).

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[1] (a) Chumanov, G.; Sokolov, K.; Gregory, B.; Cotton, T. M. *J. Phys. Chem.* **1995**, *99*, 9466. (b) Feilchenfeld, H.; Chumanov, G.; Cotton, T. M. *J. Phys. Chem.* **1996**, *100*, 4937. (c) Moskovits, M. *Rev. Mod. Phys.* **1985**, *57*, 783. (d) Shiang, J. J.; Heath, J. R.; Collier, C. P.; Saykally, R. J. *J. Phys. Chem B* **1998**, *102*, 3425.

[2] (a) Foss, C. A. Jr.; Tierney, M. J.; Martin, C. R. *J. Phys. Chem.* **1992**, *96*, 9001. (b) Sandrock, M. L.; Pibel, C. D.; Geiger, F. M.; Foss, C. A., Jr. *J. Phys. Chem. B* **1999**, *103*, 2668. (c) Yu, Y.-Y.; Chang, S.-S.; Lee, C.-L.; Wang, C. R. C. *J. Phys. Chem. B* **1997**, *101*, 6661.

[3] (a) Vance, F. W.; Lemon, B. I.; Hupp, J. T. *J. Phys. Chem. B* **1998**, *192*, 10091. (b) Collier, C. P.; Saykally, R. J.; Shiang, J. J.; Henrichs, S. E.; Heath, J. R. *Science* **1997**, *277*, 1978. (c) Freeman, R. G.; Grabar, K. C.; Allison, K. J.; Bright, R. M.; Davis, J. A.; Guthrie, A. P.; Hommer, M. B.; Jackson, M. A.; Smith, P. C.; Walter, D. G.; Natan, M. J. *Science* **1995**, *267*, 1629.

[4] (a) Peng, X.; Wilson, T. E.; Alivisatos, A. P.; Schultz, P. G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36(1/2)*, 145. (b) Alivisatos, A. P.; Johnsson, K. P.; Peng, X.; Wilson, T. E.; Loweth, C. J.; Bruchez, M. P., Jr.; Schultz, P. G. *Nature* **1996**, *382*, 609.

[5] Sandrock, M. L.; Foss, C. A., Jr. *J. Phys. Chem.* **1999**, *103*, 11398.

[6] (a) Brousseau, L. C., III; Novak, J. P.; Marinakos, S. M.; Feldheim, D. L. *Adv. Mater.* **1999**, *11*, 447. (b) Metal nanoparticle sols (∼2 nM) were prepared using methods published previously.[1−3] Phenylacetylene linkers were synthesized according to refs 6c and 6d. Gold nanoparticle arrays were assembled using the following procedure. Linker solutions were prepared by adding a stoichiometric amount of linker to 0.5 mL of a 3:2 THF/EtOH solution and 0.5 mL of 3 mM aqueous citrate buffer. In a separate flask, 3 mL of gold sol was diluted to 10 mL in the citrate solution. The linker solution was then added to the gold sol in 100 μL aliquots at 10 min intervals with rapid stirring. Silver dimers were assembled by diluting 100 μL of a 1 μM linker solution with 5 mL of 3:2 THF/EtOH, and 10 mL of H_2O. 2 mL of 1 nM Ag sol was added quickly to the linker solution. The flask was stirred for 1 h. Finally, 10 μL of 30% NH_4OH was added to deprotect the thiol endgroup. TEM grids were prepared by first diluting the solution of linked gold or silver particles by 20-fold. One drop of the solution was then placed on a Formvar-coated Cu grid in contact with filter paper. The solvent was quickly wicked away by the filter paper, preventing particle agglomeration. (c) Zhung, J.; Moore, J. S.; Xu, Z.; Aguirre, R. A. *J. Am. Chem. Soc.* **1992**, *114*, 2273. (d) Su, D.; Menger, F. M, *Tetrahedron Lett.* **1997**, *38*, 1485.

[7] (a) Jensen, T.; Kelly, L.; Lazarides, A.; Schatz, G. C. *J. Cluster Sci.* **1999**, *10*, 295. (b) Yang, W.-H.; Schatz, G. C.; Van Duyne, R. P. *J. Chem. Phys.* **1995**, *103*, 869. (c) In discrete dipole calculations, each particle is divided into a large number of dipoles. An average particle polarization is then calculated which includes electric field contributions from the incident light and dipoles on the neighboring particle. Importantly, these calculations assume that the incident electric field is polarized along the long axis of the particle pair structure. Thus, only longitudinal plasmon modes are apparent in calculated extinction spectra.

[8] For example, when dimers were the intended structure, only dimers and monomers were found. Trimers or larger aggregates were not observed. When the D_{3h} phenylacetylene bridge was used, D_{3h} particle trimers, a small number of dimers, and monomers were observed exclusively.[6a] Again, structures with other symmetries or large aggregates were absent. Control experiments, in which gold and silver particles were added to a solution of $CH_3(CH_2)_5SH$ under conditions identical to those reported in ref 6, showed relatively few dimers and no D_{3h} or T_d structures.

[9] A depolarization ratio of 1.57 ± 0.007 was determined for gold trimers using polarized hyper-Rayleigh scattering. This is close to the theoretical value of 1.5 expected for chromophores with D_{3h} symmetry. (Vance, F. W.; Novak, J. P.; Johnson, R. C.; Hupp, J. T.; Feldheim, D. L., unpublished results).

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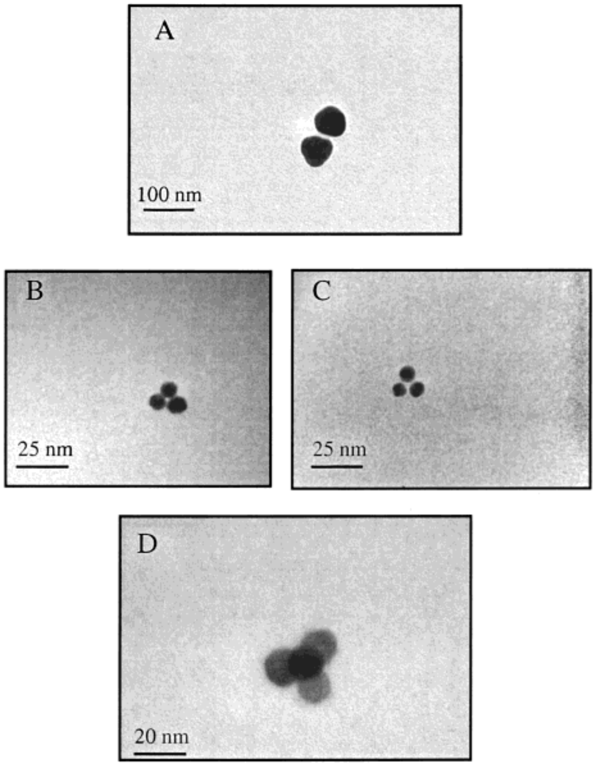

Figure 1. Representative transmission electron microscope images of (A): Silver particle dimers linked by structure **Ia**. (B) and (C): Gold particle trimers linked by structures **IIa** and **IIb**, repectively. (D) A gold particle tetramer linked by structure III.

In addition, a relatively weak extinction was observed at ∼600 nm.[10]

To rationalize the spectra of silver particle dimers, comparisons were made to recent calculations using the discrete dipole approximation. Figure 3 presents spectra calculated for 60 nm diameter particle dimers as a function of particle separation distance.[7] Note that despite the size difference, the behaviors are qualitatively in aggreement; that is, both data sets reveal a red-shift of the single-particle plasmon band, an increase in overall extinction efficiency, growth of a high-energy shoulder (∼370 nm), followed by the appearance of a band at 600 nm as interparticle distance decreases. Moreover, the ratio of extinctions at ∼450 nm to ∼370 nm approaches 1 in both data sets as separation distance decreases.

A closer look at the spectra, however, reveals a few distinct differences between theory and experiment. First, the bands observed experimentally for the 3-unit linker at 450 and 370 nm appear at ∼500 and 420 nm, respectively, in the calculated spectra. Second, the absolute extinction ratios are much higher in the calculated spectra. These subtle differences are likely due to particle size and size dispersity differences between particles in the calculated versus experimental spectra. Additional disparities could arise from the following observations. First, the appearance of an intense, high-energy band which blue-shifts with decreasing interparticle separation could be attributed to a strong quadrupole resonance which is superimposed on the transverse plasmon resonance.[11] Second, the band observed experimentally at 450 nm represents a weighted sum of extinctions for all particle orientations (plus residual monomer) and would therefore be expected to appear toward the blue of the true longitudinal mode.[2b]

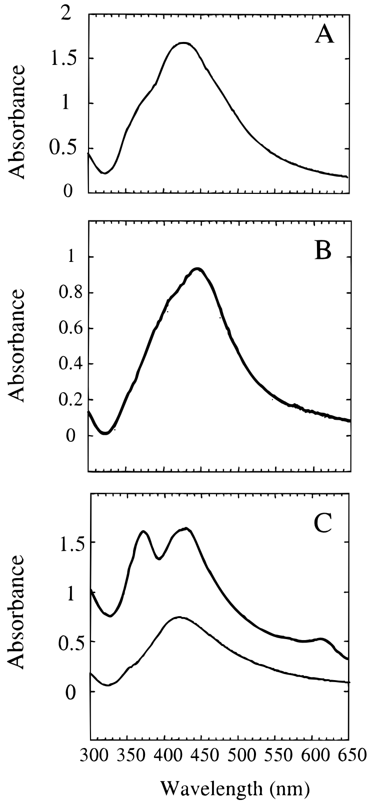

Figure 2. UV−visible spectra for: (A) 30 nm diameter silver particle dimers linked by structure **Ic**; (B) dimers linked by structure **Ib**; and (C) dimers linked by structure **Ia** (upper trace) and silver particle "monomers" (lower trace). The monomer spectrum was acquired under solvent conditions identical to those of the dimers but in the absence of a linker.

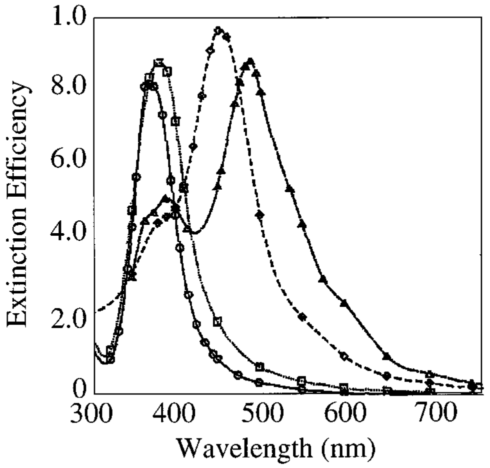

Figure 3. Silver particle dimer spectra calculated by Schatz et al. (adapted from ref 7a). Particle diameter was 60 nm. Key: ○ monomers; □ 30 nm separation; ◇ 4 nm separation; △ 2 nm separation.

We have presented new methods for coupling metal particles into symmetrically and sptially well-defined arrays of dimers, trimers, and tetramers. These structures are useful for testing theories of electromagnetic interactions between metallic spheres and could find application in chemical sensing,[12] nanoscale electronics,[13] and photonics.[3a]

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[10] All spectra shown were recorded after a period of 12 h. After this time the spectra remained relatively unchanged for periods of ∼48 h. At longer times the spectra began to show a large increase in the quadrapole extinction and a decrease in the dipole extinction. This result is most likely due to particle aggregation at long times.[11] Control experiments in which $CH_3(CH_2)_5SH$ was added to silver monomers showed no change in the visible spectrum. Further controls in which particles were slowly aggregated with $NaCl_{(aq)}$ revealed a gradual disappearance in absorbance at 420 nm with a concommitent increase at 800 nm characteristic of extended particle aggregates.

[11] Chumanov, G.; Sokolov, K.; Cotton, T. M. *J. Phys. Chem.* **1996**, *100*, 5166.

[12] Mirkin, C. A.; Letsinger, R. L.; Mucic, R. C.; Storhoff, J. J. *Nature* **1996**, *382*, 607.

[13] Keating, C. D.; Feldheim, D. L. *Chem. Soc. Rev.* **1998**, *26*, 1.