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Template Synthesis of One-Dimensional Au, Au−Poly(pyrrole), and Poly(pyrrole) Nanoparticle Arrays

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Research involving metal and semiconductor nanoparticles is expanding rapidly into the assembly and characterization of well-ordered 2- and 3-dimensional (2D and 3D) superstructures. Recent advances in nanoparticle organization include the 3D CdSe supercrystals synthesized by Bawendi's group,[1] Mirkin and co-workers' 2D and 3D DNA-linked Au colloid arrays,[2] and the closest-packed surface-confined monolayers of Ag, Au, and CdS colloids studied by Natan,[3] Murray,[4] Cotton,[5] Kubiak,[6] Whetten,[7] and others.[8] These novel structures have revealed electronic and optical properties distinctly different from those of individual nanoparticles (that is, ensemble average measurements on well-spaced particles) or their macroscopic equivalents; practical applications are foreseeable in optical and electronic based chemical sensing,[2,8] nanoscale electronics,[8,9] and catalysis.[5]

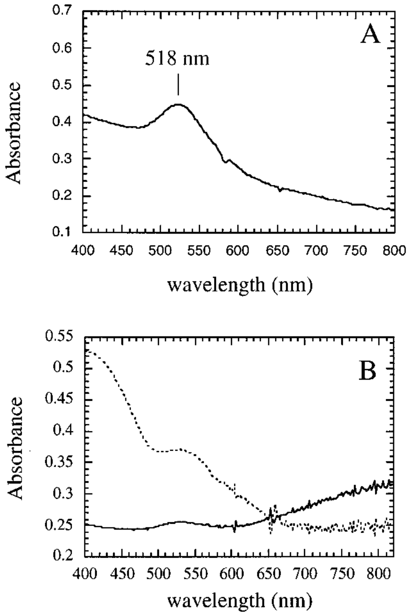

Figure 1. (A) UV−visible spectrum of an Anopore membrane following vacuum filtration of 12 nm diameter citrate-stabilized Au colloids. (B) Spectra acquired following Ppy polymerization in the pores. The dashed line is the oxidized Ppy/Au colloid composite membrane; the solid line is after chemical reduction of the Ppy with a saturated solution of NaBH$_4$ in CH$_3$CN. (Note: different membranes were used in A and B.)

Despite their potential for fundamental studies on electron and energy transfer in nanoscopic solid-state materials and for applications involving single-electron devices,[8,9] few reports have appeared regarding the synthesis of coupled 1D nanoparticle systems. Notable exceptions are the 1D strands of iron oxide particles used for navigation by magnetotactic bacteria,[10] the self-organized 1D CdS chains observed by Chemseddine *et al.*,[8h] and the dithiol-linked CdSe dimers and DNA-linked Au trimers synthesized by Alivisatos *et al.*[11] In this work, we describe two methods for assembling coupled 1D arrays of Au nanoparticles. Both methods involve aligning nanoparticles in the pores of Al$_2$O$_3$ or polycarbonate filtration membranes. The first strategy is to entrap and align particles in the pores by vacuum filtration. Similar methods have been reported by Hornyak and co-workers recently.[12] Following alignment, particles are linked by polymerizing a conductive polymer[13] inside the pores, effectively "shrink wrapping" them together. A second method employs a sequential deposition process whereby alternating layers of particles and alkyldithiols are adsorbed onto a Ag support at the base of the pores. Dissolving the membranes

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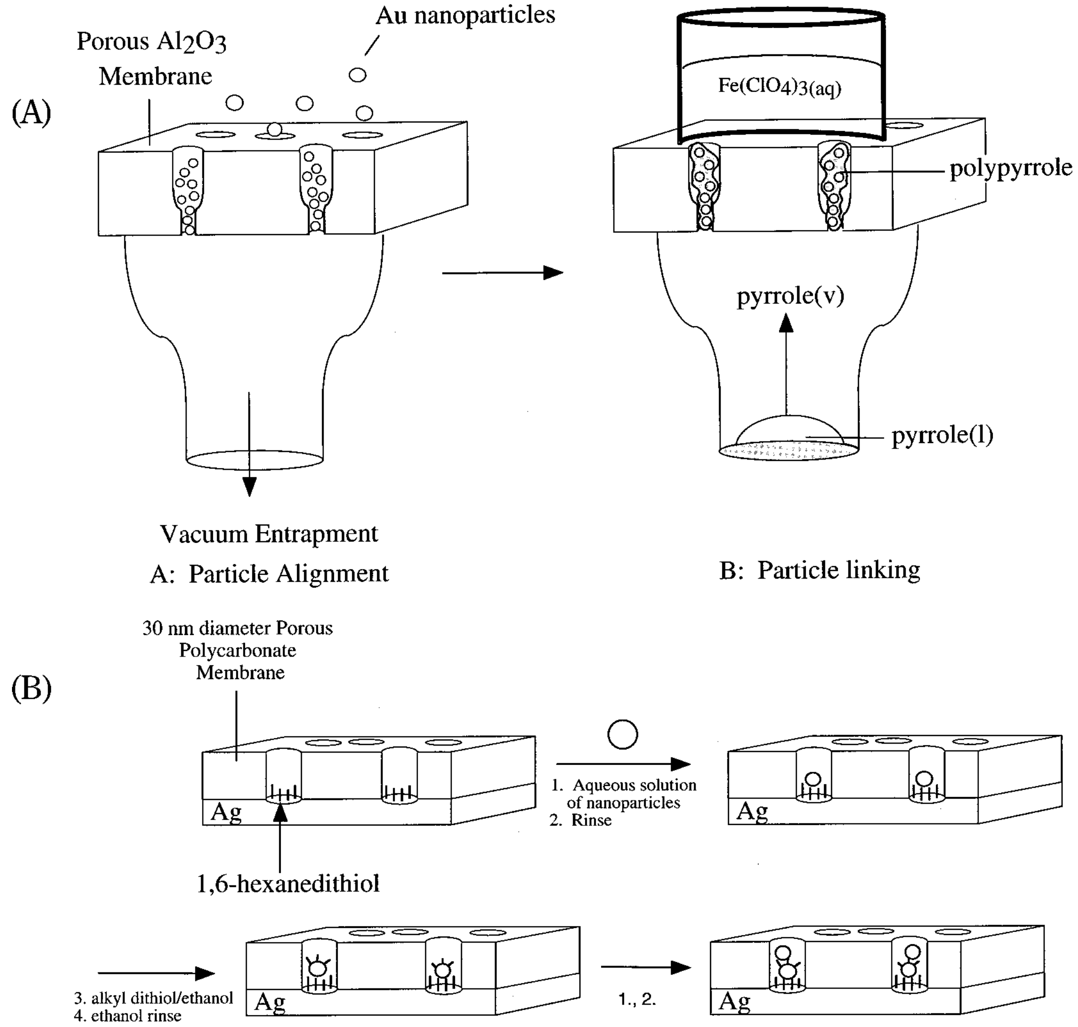
Scheme 1. Synthetic Protocols for the Synthesis of Coupled 1D Nanoparticle Arrays: Procedures for (A) Ppy-linked Au Colloids and (B) Alkyldithiolate-Linked Au Colloids



yields suspensions of discrete nanocluster "molecules" (e.g., [Au nanoparticle]$_n$, $n = 2-5$, for the latter method) or longer 1D strings of closely spaced Au nanoparticles embedded in a polymer matrix (for the former method). These methods present new opportunities for studies involving the electronic and optical properties of spatially well-organized nanoparticle superstructures.

Assembly protocols for 1D Au nanoparticle arrays are illustrated in Scheme 1. In one method (Scheme 1A), an aqueous solution of 12 nm diameter citrate-stabilized Au colloids (prepared as described in ref 3) was vacuum filtered dropwise through the pores of an Al_2O_3 filtration membrane (20 nm diameter pores; Anotech Separations, Ltd.). Nanoparticles are trapped in the pores and align along the direction of the pore axis. Polypyrrole (Ppy) was polymerized inside the pores to link the particles together by clamping the membrane in a glass U-tube apparatus, placing a 0.1 M aqueous solution of $Fe(ClO_4)_3$ above the membrane, and exposing the opposite side of the membrane to pyrrole vapor.[14] Iron(III) salts are known to oxidatively polymerize pyrrole to form polymers doped with the corresponding anion.[13,14] Finally, the membrane was dissolved with aqueous 0.5 M KOH (Fisher) to collect a suspension of 1D colloid/polypyrrole composite structures. The advantages of this method are that long 1D colloidal particle superstructures may be prepared quickly and easily.

An alternate route to 1D nanoparticle superstructures is shown in Scheme 1B. Porous polycarbonate membranes (30 nm diameter pores; Poretics) were sputter-coated on one side with a thick coating (100 nm) of Ag. Additional Ag was then electroplated inside the pores at the base of the membrane using a Ag plating solution consisting of 1.43 g of $AgNO_3$, 3.0 g of $K_4[Fe(CN)_6]$, 2.0 g of Na_2CO_3, and 15 g of KSCN in 200 mL of H_2O.[14b] The pore side of the Ag film was derivatized with 1,6-hexanedithiol (Aldrich Chemical) and rinsed with copious amounts of CH_3CH_2OH (Fisher) to remove any unbound thiol. The membrane was subsequently immersed in a solution containing Au colloids for 1 h. Colloids diffuse down the pores and bind to the free end of the dithiol at the base of the pore. Any unbound colloid was removed from the pores by rinsing the membrane in pure H_2O for several hours. Multilayers of Au colloids are assembled by alternately soaking the membrane in solutions of the dithiol and Au. To collect the superstructures, the Ag was dissolved in aqueous 10% HNO_3 and the polycarbonate membrane was dissolved with CH_2Cl_2. The advantages of this method

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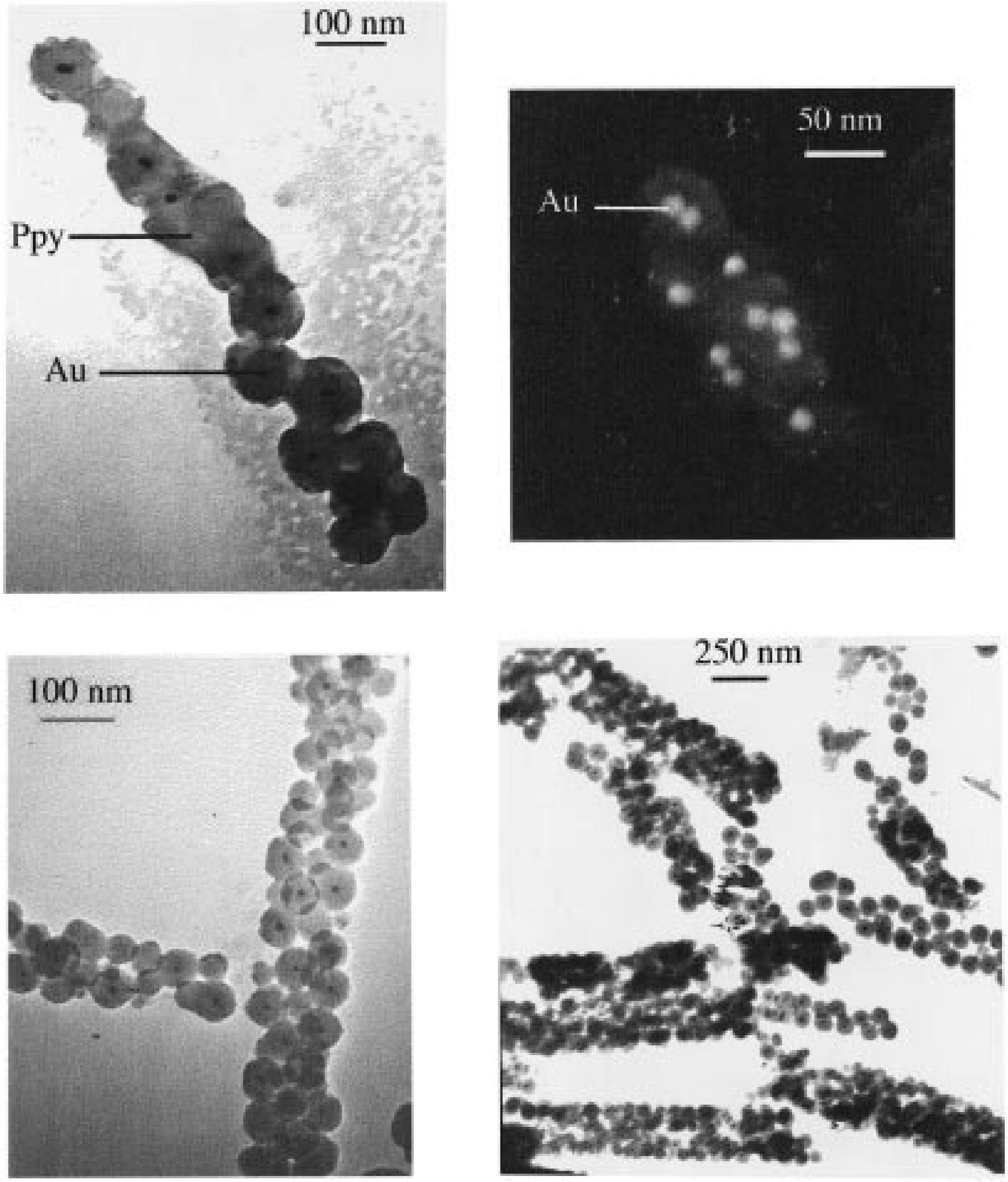

Figure 2. Transmission electron microscope images of 1D and near-1D arrays of Au colloids linked by Ppy.

over that described above are that the number of colloids in the resulting structure is controlled by the number of immersion cycles, and chemically distinct colloids could potentially be alternated in any desired sequence.

1D Arrays Synthesized by Vacuum Filtration in Anopore. UV–visible spectra of an Anopore membrane (20 nm diameter pores)[15] containing ca. 12 nm diameter Au colloids in the pores are shown in Figure 1. Prior to encapsulation with Ppy, an extinction at 518 nm was observed due to the well-known Au plasmon resonance (Figure 1A).[16] This λ_{max} represents an 8-nm blue shift compared to that for these colloids[17a] in aqueous solution. Maxwell–Garnett (M–G) theory indicates that a

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[15] (a) For Anopore membranes, 20 nm represents the minimum diameter of the pores on one side of the membrane. The diameter is larger in the interior of the membrane (Scheme 1). On the basis of TEM images of Ppy colloids, we estimate the maximum pore diameter to be between 50 and 100 nm (see Figure 3). The mechanism by which 12 nm diameter particles are trapped in nominally 20 nm diameter Al_2O_3 channels is currently not clear. Possibilities include chemical interactions between Au and the membrane, physical entrapment in the tortuous channel system which exists on the barrier side of the membrane (the 20 nm diameter side), or simply that the solution containing particles remains in the pores after filtration due to capillary forces. TEM images show that a high density of particles were trapped in the large-diameter regions of the membrane, suggesting that the entire pore was filled with particles. This supports the latter mechanism. (b) Visible spectra were acquired with a Hewlett-Packard photodiode array on membranes dipped in H_2O using a bare Al_2O_3 membrane for background subtraction.

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[17] (a) Reported λ_{max} values range from 520 to 526 nm for aqueous suspensions of Au colloids with diameters from ca. 12 to 20 nm.[2,3,12] This variation is likely a result of subtle differences in size and shape between colloids prepared in different laboratories *and* differing states of particle agglomeration. Colloidal Au particles synthesized in our laboratory absorb at 526 nm in aqueous solution. Thus we cannot discount the possibility that Au particle dimers and trimers are present in solution which are then oriented along the pore axis due to shear forces or interactions with pore walls during vacuum entrapment. However, TEM images of an aqueous solution of colloids showed mostly individual particles. (b) Al-Rawashdeh, N. A. F.; Sandrock, M. L.; Seugling, C. J.; Foss, C. A., Jr. *J. Phys. Chem.* **1998**, *102*, 361. (c) Foss, C. A., Jr.; Hornyak, G. L.; Stockert, J. A.; Martin, C. R. *J. Phys. Chem.* **1994**, *98*, 1963.

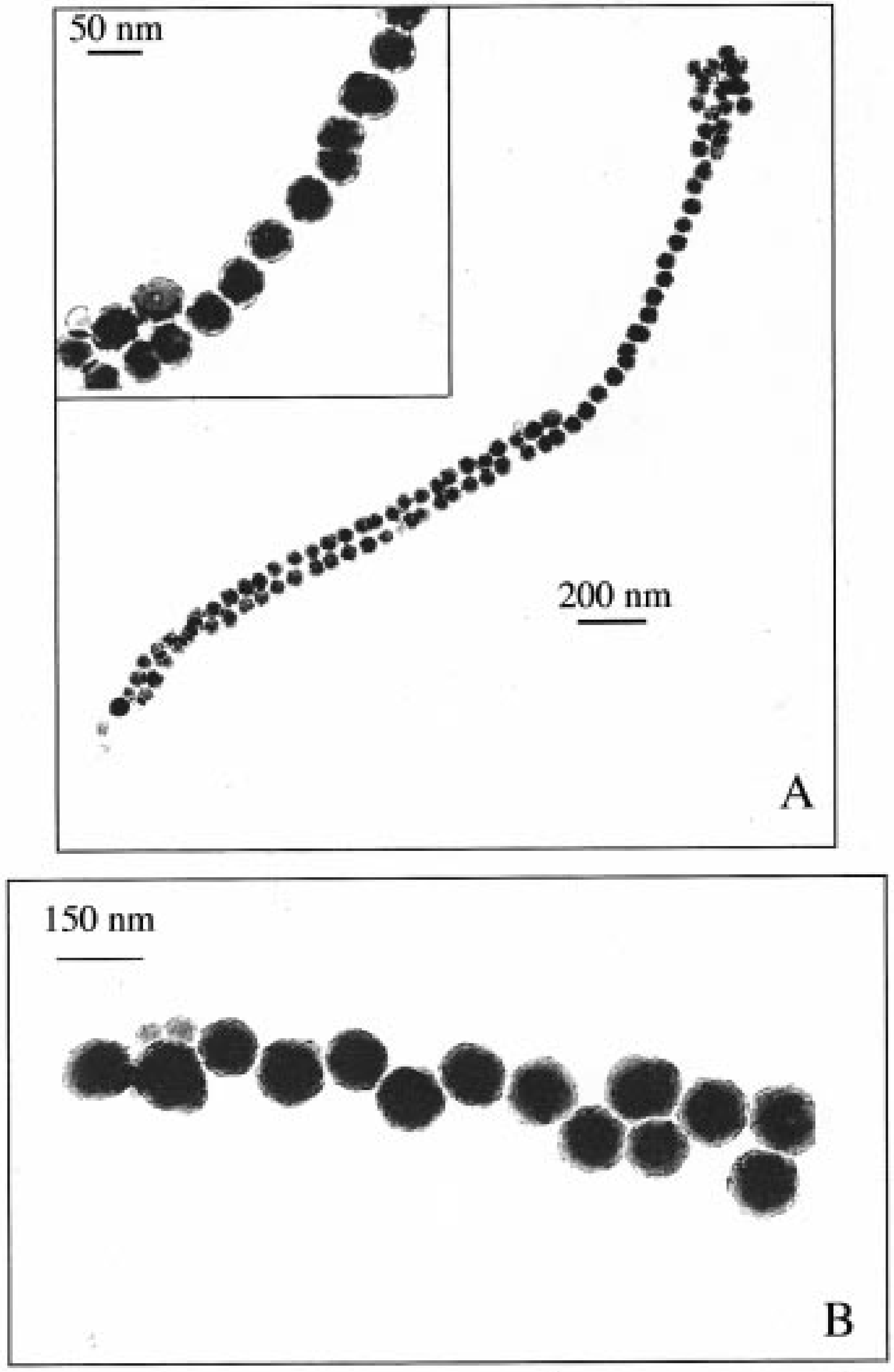

Figure 3. Transmission electron microscope images of 1D interconnected arrays of Ppy colloids. Polymerization using Al_2O_3 membranes with (A) 20 and (B) 200 nm pore diameter.

blue shift in the plasmon resonance is expected when (i) metal particles stack parallel to the propagation direction of the incident light, effectively increasing particle aspect ratio (i.e., along the long axis of the pore and not along the surface normal) or (ii) the dielectric constant of the host medium increases.[17b,c] Assuming mechanism i is operating, calculations based on an aspect ratio change suggest the shift to 518 nm indicates a predominance of closely interacting dimers and trimers in the pores. However, we note that angle-dependent polarization spectra are necessary to determine unambiguously alignment of metal nanoparticles using UV−visible spectroscopy. Preliminary studies with p-polarized light have revealed an absorbance band centered at ca. 650 nm which increases in magnitude as the angle between the propagation direction of the light and the long axis of the particle is increased. These data are qualitatively in accord with M−G theory and support a model in which nanoparticles are aligned along the long axis of the pores.[17b] Studies detailing the polarization-dependent optical properties of 1D Au nanoparticle arrays will be described in a forthcoming publication.

Following Ppy polymerization, broad absorptions in the visible spectrum were observed at 800 and 400 nm due to oxidized Ppy[13] in addition to the Au plasmon resonance band (Figure 1B, solid line). One might expect, on the basis of effective medium theories, shifts

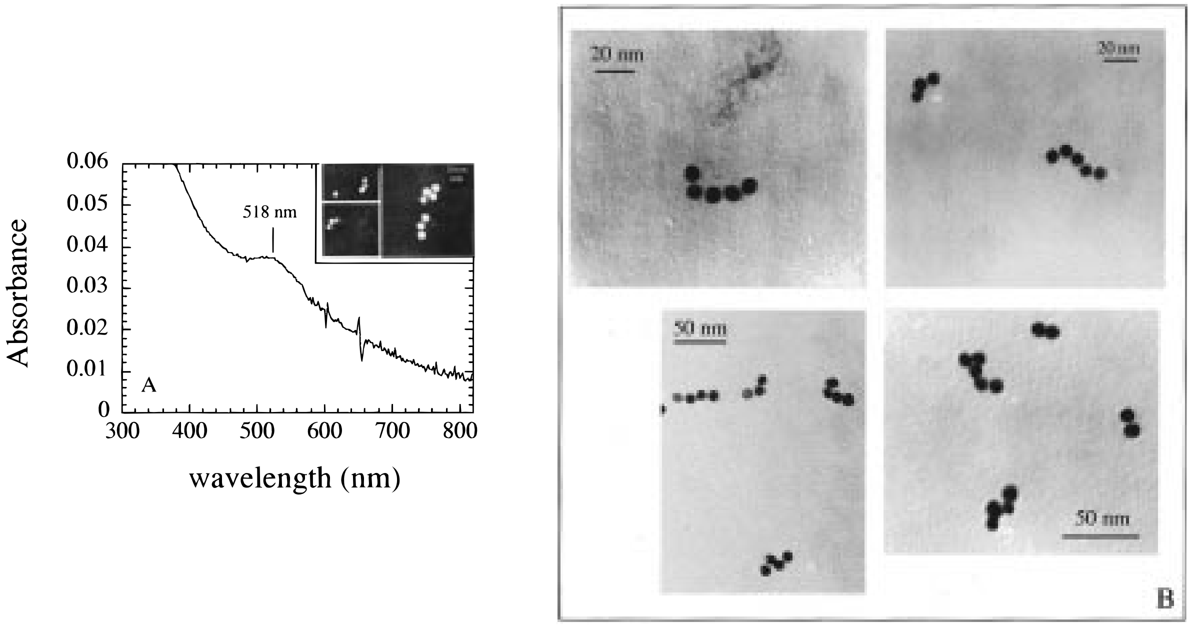

Figure 4. (A) UV−visible spectrum of a polycarbonate membrane following three sequential Au colloid/1,6-hexanedithiol deposition cycles to form Au trimers. The inset shows representative TEM images of various locations on the grid. (B) TEM images of Au colloid arrays following five sequential Au colloid/1,6-hexanedithiol deposition steps.

in the plasmon band following polymerization. Evidently, "wiring" the Au particles together with the electronically conductive polymer has little effect on the optical properties of the Au plasmon band. Treating the membrane with CH_3CN saturated in $NaBH_4$ reduced the Ppy as evidenced by the diminution in the absorbance at 800 nm and the increased absorbance at ca. 550 nm[13] (Figure 1B, dashed line). The Au plasmon band is likely masked by the Ppy absorption band ranging from 600 to 500 nm.

Transmission electron microscope (TEM) images taken after removing the Au colloid/Ppy composites from the Anopore membrane reveal a number of interesting features (Figure 2). First, micron-long, 1D and near-1D arrays of Au colloids wrapped in a polymer matrix are observed. Second, the colloids are located in the center of the Ppy matrix, suggesting that they act as nucleation sites for polymer growth. Finally, an abundance of Au dimers and trimers are found in close contact aligned along the long axis of the arrays, supporting the hypothesis that the spectral blue shifts and polarization dependence are due to particle alignment parallel to the incident radiation.

To investigate further the mechanism of Ppy deposition in the pores of the membrane, polymerization was conducted in a 20 nm pore diameter membrane in the absence of Au colloids. On the basis of previous work by Martin using polycarbonate membranes,[14] we anticipated growth of Ppy fibrils or tubules. Instead, we observed long 1D strands of spherical Ppy colloids (50 nm diameter) that appear to be fused by thin interconnects (Figure 3A). The colloids have an estimated dispersity of <4%, and the diameter can be tuned by changing the diameter of the pores in the membrane. For example, Figure 3B presents an image of Ppy colloids ca. 150 nm in diameter synthesized in a larger pore diameter Al_2O_3 membrane.

The formation of Ppy colloids rather than fibrils is likely attributed to chemical differences in Al_2O_3 and polycarbonate membranes. Martin and co-workers found that Ppy preferentially nucleates and grows on the polycarbonate pore walls because of favorable chemical and electrostatic interactions with anionic groups on the pore surface. Apparently these interactions are not present with Al_2O_3, causing the Ppy to nucleate and grow on itself rather than the pore wall. This new method for preparing conductive polymer nanospheres is not limited to Ppy. We have also prepared colloids of poly(*N*-methylpyrrole) and poly(3-methylthiophene).[18]

1D Arrays Linked by Alkyldithiolates. A UV−visible spectrum of a polycarbonate membrane[19] following three sequential depositions of 12 nm diameter Au colloids and 1,6-hexanedithiol (Scheme 1B) is presented in Figure 4A. As suggested by M−G theory,[17b] the Au plasmon resonance band is shifted to ca. 518 nm due to Au particle trimer formation along the long axis of the pore. The shift, and the absence of an absorbance at ca. 650 nm from a collective plasmon resonance,[3] is evidence for formation of chains in the pores and not on the surface of the membrane. Furthermore, on the basis of the absorbance in Figure 4A, the extinction coefficient previously measured for surface-bound Au colloids ($\epsilon = 9.3 \times 10^8$ M^{-1} cm^{-1}),[3b] and the pore density (ca. 10^9 pores/cm^2), we calculate approximately 5 Au colloids/pore, comparable to the number expected. The corresponding TEM images also indicate the presence of Au nanoparticle trimers (Figure 4A, inset). Preliminary attempts to synthesize longer 1D Au particle arrays were only modestly successful. A total of five sequential deposition cycles led to 1D pentamers, although in low yields (Figure 4B). (Several well-spaced 1D pentamers were observed on the grid in addition to linear Au tetramers, trimers and dimers.) In contrast,

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(18) Marinakos, S.; Brousseau, L. C., III; Novak, J. P.; Feldheim, D. L. (submitted for publication).

(19) Polycarbonate membranes were treated with glacial acetic acid for 12 h prior to use to remove the polyvinylpyrolidone wetting agent.

TEM images of samples prepared from a solution of Au nanoparticle starting material showed well-spaced single particles and no linear chains. We are currently attempting to increase the yields of longer 1D superstructures by attracting the particles into the pores electrophoretically[12] and separating the products with size-exclusion chromatography.

New methods for the preparation of 1D nanoparticle arrays linked by organic conductive polymers and alkyldithiolates have been described. These methods may enable (i) tuning of the electron tunnel barrier between nanoparticles via chemically or electrochemically induced changes in Ppy doping level and (ii) precise placement of chemically distinct nanoparticles in a 1D array (e.g., Au−CdS metal−insulator−semiconductor heterostructures). These structures may be useful in optimizing electromagnetic enhancements in surface-enhanced Raman spectroscopy (SERS),[20] where particle aspect ratio and agglomeration are important but not well-understood, and in developing functional nanoscale electronic circuit elements.[8,9]

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