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Hierarchical Pattern Formation in the Diffusion-Controlled Reduction of $HAuCl_4$ in Poly(vinyl alcohol) Hydrogels

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Gold nanoparticles (AuNPs) were incorporated in poly(vinyl alcohol) (PVOH) hydrogel cylinders via diffusion-controlled reductions of tetrachloroauric acid dissolved in the gels using sodium borohydride or ascorbic acid. At certain reagent concentrations, the two reducing agents formed very different hierarchical structured patterns due to their different chemical nature. Sodium borohydride reduction, which likely follows the classical "supersaturation" mechanism, results in the formation of spherical and monodisperse AuNPs of ~4 nm in diameter located in micrometer-scale stripes in the outer region of the gels. The mobility of the small colloids in the gels allows the formation of alternating particle-rich and particle-depleted stripes. The reaction of sodium borohydride with water and the −OH groups of the gel matrix diminishes its reducing ability over time and limits the AuNP formation to the outer region of the gels. AuNPs of >20 nm in diameter are formed throughout the gel matrices by ascorbic acid reduction, which is consistent with an "organizer" mechanism. Concentric bands of different colors from the outer to the inner regions of the gels—along the direction of ascorbic acid diffusion—are formed as the result of increased particle size and percentage of nonspherical shapes. The lack of stripes on the micrometer scale in the ascorbic acid system is likely due to the impeded mobility of the larger AuNPs. The structural features observed in this study are attributed primarily to the nature of the reaction matrix: reduction is controlled by the diffusion of reducing agents in the hydrogel matrix and the PVOH matrix polymer facilitates the dispersion and stabilization of the AuNPs formed.

Introduction

There are many examples of materials in nature exhibiting remarkable motifs, often hierarchically arranged from the nanometer to the macroscopic length scales.[1−3] Material composition as well as integration of structural design at each length scale can contribute to the stability and function of the resulting objects or assembly of objects. The basic building blocks in bone, for example, are carbonated hydroxyapatite nanoplates, collagen fibrils, and water, that form highly complex structures with seven levels of organization.[3] From the viewpoint of materials science, the underlying construction principles of nature can help us to design and prepare better composite materials.

Materials of nanoscopic dimensions are abundant in nature and have also been prepared synthetically since the 17th century, when the brilliant color of metallic nanoparticles (NPs) was taken advantage of in the preparation of stained glass.[4] Interesting material properties arise at nanoscopic length scales due to quantum confinement effects and large surface area to volume ratios. For example, in noble metals, the decrease in size below the electron mean free path results in the localization of electronic motions, increase in separation between the valence and the conduction bands, and intense surface plasmon absorption in the near UV−vis regions. Experimental correlations between size, polydispersity, and shape of NPs and their absorption spectra (maximum wavelength, spectral width, and extinction coefficient) have been reported.[5] Given their intrinsic difference due to size, it is not surprising that nanomaterials have had impact on applications in catalysis,[6] sensing,[7] imaging,[8] and optical,[9] electronic,[9] and magnetic[7] devices.

In addition to inorganic NPs, natural materials generally contain two other major components: polymer and water. Very often, these two components are present in the form of hydrogels. Synthetic biocompatible hydrogels, such as poly(vinyl alcohol) (PVOH), are evaluated as articular cartilages and soft contact lens materials, and for their applications in drug release and enzyme immobilization.[10] PVOH hydrogels can be prepared by

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(1) Aizenberg, J. A.; Weaver, J. C.; Thanawala, M. S.; Sundar, V. C.; Morse, D. E.; Fratzl, P. *Science* **2005**, *309*, 275.
(2) Mayer, G.; Sarikaya, M. *Exp. Mech.* **2002**, *42*, 395.
(3) Weiner, S.; Wagner, H. D. *Annu. Rev. Mater. Sci.* **1998**, *28*, 271.
(4) Kerker, M. *J. Colloid Interface Sci.* **1985**, *105*, 297.
(5) Link, S.; El-Sayed, M. A. *J. Phys. Chem. B* **1999**, *103*, 8410.
(6) Hirai, H.; Wakabayashi, H.; Komiyama, M. *Chem. Lett.* **1983**, 1047.
(7) Thomas, J. M. *Pure Appl. Chem.* **1988**, *60*, 1517.
(8) Michalet, X.; Pinaud, F. F.; Bentolila, L. A.; Tsay, J. M.; Doose, S.; Li, J. J.; Sundaresan, G.; Wu, A. M.; Gambhir, S. S.; Weiss, S. *Science* **2005**, *307*, 538.
(9) Schön, G.; Simon, U. *Colloid Polym. Sci.* **1995**, *273*, 202.
(10) Hassan, C. M.; Peppas, N. A. Adv. Polym. Sci. **2000**, *153*, 37 and references therein.

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physical cross-linking due to the formation of crystallites via repetitive freeze−thaw cycles.[10] Physically cross-linked gels have the advantage of being free of toxic cross-linking agents and can be as mechanically stable as gels cross-linked by chemical or irradiative techniques. Diffusion characteristics and mechanical properties of PVOH hydrogels are affected by the degree of crystallinity and gel mesh size, which are dependent on the molecular weight of the polymer, the concentration of the solution, the temperature and time of freezing and thawing, and the number of freezing and thawing cycles.[10−12] Many of the studies involving physically cross-linked PVOH gels have been related to diffusion and were carried out in order to evaluate and control drug release characteristics. Very few reactions in PVOH gel matrices have been studied. To the best of our knowledge, only precipitation reactions that involve the diffusion of an inorganic reagent from an aqueous solution into a PVOH hydrogel and reaction with a different inorganic reagent dissolved in the gel matrix have been investigated.[13,14] Such diffusion-controlled reactions in hydrogels can lead to patterns on submillimeter scale, such as cardioids, spirals, and stripes, which are produced by the Liesegang phenomenon where colloidal precipitate forms behind a moving reaction front.[13,14] In general, the specific patterns formed are the result of nucleation and growth and depend on reagent concentrations, which affect relative rates of diffusion and reaction and the extent of reaction.[14] A detailed explanation of these patterns has not been provided; the presence of smaller structural features on the nanoscopic level has neither been probed nor discussed in these systems.

There are advantages of embedding NPs in hydrogel systems, for example, the matrix polymer can stabilize NPs[15] and hydrogels can be prepared in any shape or size. Composites of NPs in hydrogel matrices have been commonly prepared by diffusion of NPs into hydrogel matrices or dispersion of NPs in polymer, prepolymer, or monomer solutions and subsequent gelation.[16,17] In-situ reduction of metal precursors in poly(*N*-isopropylacrylamide) (PNIPAM) microgels,[18] dendrimers,[19] and hydrophilic polymer brushes[20,21] has also been reported. Nanocomposites prepared using these methods are isotropic in nature and hierarchical structural control cannot be achieved. A diffusion-controlled reduction approach has been reported for the synthesis of AuNPs inside PNIPAM hydrogel discs. In this approach, $KAuCl_4$ was allowed to diffuse and distribute uniformly in the hydrogel before exposure of the disk to $NaBH_4$ (external solution), which diffused into the gel matrix and reduced the precursor salt to AuNPs.[17] The uniformity of particle distribution in the gels and patterns/features on macroscopic scales were not reported.

In this report, two reducing agents—sodium borohydride and ascorbic acid, with different reducing strength and NP capping capability—were evaluated for the reduction of hydrogen tetrachloroaurate (III) in PVOH hydrogel cylinders. Different hierarchical structured features from nanoscopic to macroscopic scales—as the result of size, shape, and distribution of AuNPs formed in PVOH gel matrices—were observed. The pattern formations depend on the chemical nature of the reducing agents and the stabilizing effect of PVOH and are direct consequences of diffusion-controlled reductions.

Experimental Section

Materials. Colloidal gold solutions and a low viscosity Spurr kit were purchased from Ted Pella, Inc. Poly(vinyl alcohol) (PVOH) (M_w = 89 000−98 000, 99+% hydrolyzed), hydrogen tetrachloroaurate (III) trihydrate, sodium borohydride, ascorbic acid, and rhodamine B, were obtained from Aldrich and used as received. House reverse-osmosis-treated water was further purified using a Millipore Milli-Q system that involves reverse osmosis, ion exchange, and filtration steps (18.2 MΩ/cm).

Freeze−Thaw Preparation of Poly(vinyl alcohol) Hydrogels. A 10 wt % PVOH aqueous solution was prepared by dissolving PVOH powder in Milli-Q water at 95 °C for 3 h. After cooling to room temperature, the solution was transferred to 10 mL Norm-Ject plastic syringe barrels that were sealed with Parafilm. These samples were exposed to four freeze−thaw cycles: freezing at −20 °C for 20 h and thawing at room temperature for 4 h. They were removed from the syringe barrels and soaked in fresh Milli-Q water (changed twice daily) for at least four days to remove un-cross-linked polymer and impurities. The samples were stored in Milli-Q water at room temperature and were used within 1 month of preparation. The gel samples used for diffusion and reduction studies were cylindrical in shape with a diameter of 1.5 cm and a length of 2.5 cm. PVOH gel samples were fractured at 77 K, freeze-dried, and sputter-coated with a ∼100 Å thick gold film (Polaron 5100 sputter coater) before being characterized using a FEI Quanta 200 scanning electron microscope (SEM) operating at 10 kV.

Diffusion Studies. A PVOH gel cylinder was immersed in a 5.66×10^{-6} M rhodamine B solution in a test tube. The mass of rhodamine B that diffuses across a unit area of interface was monitored using a Cary 50 UV−vis spectrophotometer by transferring a small amount of solution to a clean UV−vis cuvette and measuring its absorbance at 555 nm as a function of time. The solution was immediately returned to the test tube after each measurement. PVOH gels were also immersed in 5, 10, and 20 nm colloidal gold solutions. Absorbance of the solutions at 520 nm was monitored over time in a similar fashion.

Formation and Characterization of AuNPs in PVOH Hydrogels. A 25 mM $HAuCl_4$ stock solution was prepared by weighing solid $HAuCl_4 \cdot 3H_2O$ in a glovebox and subsequently dissolving in Milli-Q water. A PVOH gel cylinder was submerged in 5 mL of $HAuCl_4$ solution of desired concentration for 24 h in a test

(11) Yonese, M.; Kondo, M.; Miyata, I.; Kugimiya, S.; Sato, S.; Inukai, M. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 883.
(12) Chu, K. C.; Jordan, K. J.; Battista, J. J.; Van Dyk, J.; Rutt, B. K. *Phys. Med. Biol.* **2000**, *45*, 955.
(13) Hantz, P. *J. Phys. Chem. B* **2000**, *104*, 4266.
(14) Hantz, P. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1262.
(15) Khanna, P. K.; Gokhale, R.; Subbarao, V. V. V. S.; Vishwanath, A. K.; Das, B. K.; Satyanarayana, C. V. V. *Mater. Chem. Phys.* **2005**, *92*, 229.
(16) Caseri, W. *Macromol. Rapid Commun.* **2000**, *21*, 705.
(17) Wang, C.; Flynn, N. T.; Langer, R. *Adv. Mater.* **2004**, *16*, 1074.
(18) Kim, J.-H.; Lee, T. R. *Langmuir* **2007**, *23*, 6504.
(19) Knecht, M. R.; Garcia-Martinez, J. C.; Crooks, R. M. *Langmuir* **2005**, *21*, 11981.
(20) Lu, Y.; Mei, Y.; Drechsler, M.; Ballauff, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 813.
(21) Mei, Y.; Lu, Y.; Polzer, F.; Ballauff, M.; Drechsler, M. *Chem. Mater.* **2007**, *19*, 1062.

tube at room temperature in the dark. The gel sample was then rinsed briefly with Milli-Q water to remove excess $HAuCl_4$ solution from the gel surface and placed in 5 mL of aqueous $NaBH_4$ or ascorbic acid of desired concentration for a desired amount of time. Cross sections embedded with AuNPs were cut from the middle of the gel cylinders and imaged using an HP scanjet 4850, an Olympus BX51 optical microscope, and a Philips CM100 transmission electron microscope (TEM) with an accelerating voltage of 80 kV. A 0.14 g portion of a gel specimen containing AuNPs was also dissolved in 10 mL of Milli-Q water at 90 °C for 30 min before being characterized by UV−vis and TEM. Samples for TEM analyses were prepared by either gel-sectioning or solution-casting methods (see the Supporting Information for details). TEM images were analyzed using ImageJ software (http://rsb.info.nih.gov/nih-image/).

Titration of Sodium Borohydride during Reaction with PVOH Gels (a Control Reaction). PVOH gel cylinders were submerged in 20 mL of 0.025 M sodium borohydride solution. A 10 μL portion of sodium borohydride solution was drawn out after a desired amount of time and was added to 1 mL of 0.5 mM $HAuCl_4$ solution. The amount of AuNPs formed, as measured by UV−vis at 545 nm (absorption maximum), was quantified as a function of reaction time.

AuNP Formation in Solution. A 1 mL portion of either 2.5 mM $NaBH_4$ or 5 mM ascorbic acid was added to 1 mL of 0.25 mM $HAuCl_4$ in a UV−vis cuvette. The formation of AuNPs was monitored over time using dynamic light scattering (DLS, Malvern Zetasizer Nano Series). The AuNPs were also analyzed using TEM.

Results and Discussion

Characterization of the PVOH Hydrogel Matrix. Structural analysis and diffusion studies of the gel matrix were first carried out. Scanning electron micrographs of 10 wt % PVOH hydrogels (Figure 1) indicate that pores are aligned with the main axis of the gel cylinder. Pores are formed due to spinodal decomposition of the polymer solution into polymer-rich and water-rich domains upon freezing; ice crystals apparently grow preferentially in the direction of the cylinder axis, which is consistent with what has been reported in the literature.[22] Pores up to 6 μm are formed; the pore size distribution appears to be broad, which could be caused by secondary spinodal decomposition of the polymer-rich domains during the later freeze−thaw cycles. Due to the resolution limit of SEM, the lower limit of the pore size distribution was determined using nitrogen adsorption, which was carried out using freeze-dried hydrogels at 77 K. Adsorption and desorption isotherms (not shown) indicate the absence of micropores (<2 nm) and mesopores (between 2 and 50 nm). Thus, the smallest pores in the prepared PVOH gels are at least 50 nm in size.

Diffusive characteristics of reagents and NPs were studied because they affect reaction rates and distribution/redistribution of NPs in gel matrices, respectively. Rhodamine B was chosen as a model compound for the diffusion studies because it has a large extinction

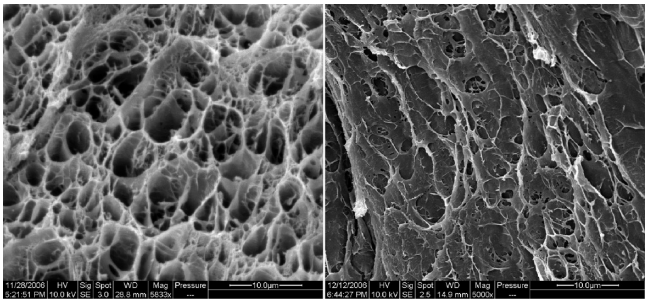


Figure 1. SEM micrographs of gel sections perpendicular (left) and parallel (right) to the cylinder axis (scale bar is 10 μm).

coefficient in the visible region that allows the monitoring of its diffusion using UV−vis spectrophotometry. The diffusion coefficient of rhodamine B in PVOH hydrogels was determined using Fick's law of diffusion (eq 1),

$$M(t) = 2(Kc_1 - c_0)\sqrt{\frac{Dt}{\pi}} \quad (1)$$

where the mass of rhodamine B that diffuses across a unit area of interface, M, depends on the diffusion coefficient, D, the partition coefficient, K, and time, t, and c_1 and c_0 are initial concentrations of the solute in solution and gel, respectively. D was determined to be 1×10^{-7} cm^2/s, which is in agreement with the reported value of Fe^{3+} in PVOH gels.[12] The diffusion coefficient in 10 wt % PVOH gels is 2 orders of magnitude smaller than values in aqueous solution (typically on the order of 10^{-5} cm^2/s) indicating that most reactions involving diffusion of reagents into PVOH gels are diffusion-controlled.

Diffusion studies of gold colloids of different sizes—after verification of particle size and monodispersity by DLS—were also carried out to understand the distribution and redistribution characteristics of NPs in gels. During the diffusion experiments, surface plasmon resonance peaks of the different AuNPs studied remained at ~520 nm indicating the absence of nanoparticle aggregation and thus allowing the diffusion to be studied in a similar fashion. Although adsorption of gold colloids at the gel/solution interface was visible by eye, diffusion does not occur for NPs $\geq$ 10 nm in diameter as shown in Figure 2, where M (eq 1) is plotted a function of square root of time for all particle sizes. Nitrogen adsorption studies discussed earlier, however, indicate that pores in 10 wt % PVOH gels are bigger than 50 nm. The impeded movement of AuNPs greater than 10 nm in the PVOH gels is thus attributed to the strong interaction/complexation between the PVOH and gold colloids. This conclusion is consistent with the reports that PVOH adsorbs from solution to flat gold substrates spontaneously[23] and PVOH can stabilize gold colloids in the reduction of $HAuCl_4$.[15]

Diffusion-Controlled Reduction of $HAuCl_4$ and Pattern Formation in PVOH Gels. Numerous reduction methods have been reported for the synthesis of

(22) Trieu, H. H.; Qutubuddin, S. *Colloid Polym. Sci.* **1994**, *272*, 301.

(23) Serizawa, T.; Hashiguchi, S.; Akashi, M. *Langmuir* **1999**, *15*, 5363.

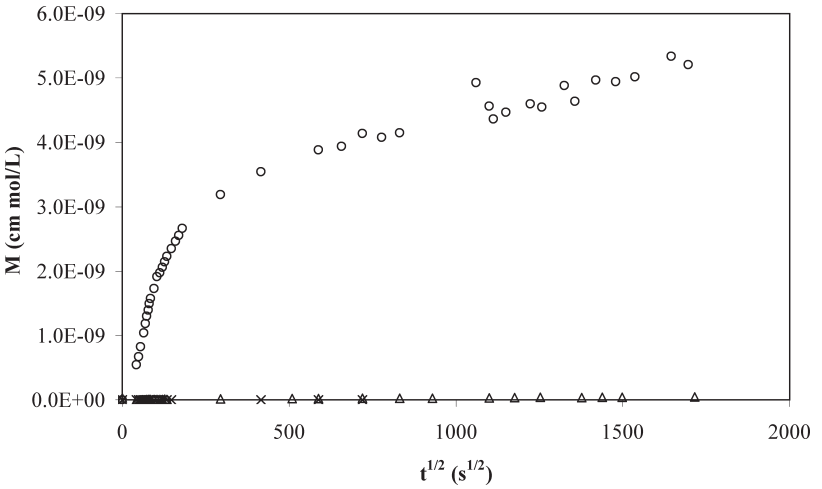
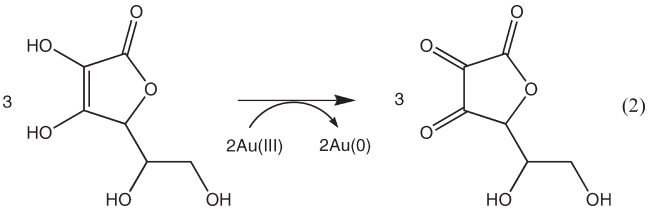


Figure 2. Diffusion of AuNPs, 5 (○), 10 (△), and 20 nm (×), into 10 wt % PVOH gel cylinders by monitoring absorbance of the AuNP solutions at 520 nm over time.

AuNPs.[15,24−28,31,32] Ascorbic acid (eq 2) and $NaBH_4$ were chosen to reduce $HAuCl_4$ in PVOH hydrogels due to the differences in size and shape of AuNPs produced from reduction of gold precursors using the two reagents in solution at room temperature.[24−27] The control of size, shape, and monodispersity is the key issue in the preparation of colloids in solution. Particle size is an important parameter not only in electronic and optical applications but also in biomedical applications; for example, 3−6 nm AuNPs are required for labeling in immuno-cytochemistry to avoid steric hindrance.[24] Sodium borohydride is reported to produce spherical particles in this size range.[24,25] Considerably larger AuNPs (10−50 nm) are produced by ascorbic acid reduction;[26,27] shape-control—from spherical, to cubic, to dendritic—was accomplished by the addition of increasing amounts of a stabilizer, poly(vinyl pyrrolidone).[27] The higher surface area-to-volume ratio and unique optical properties of nonspherical NPs can be taken advantage of in chemical and biological sensing applications.

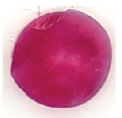
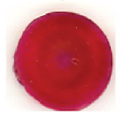
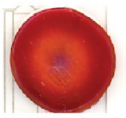
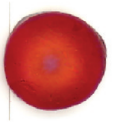
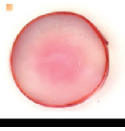
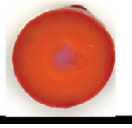
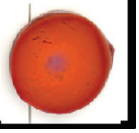


(2)

Reduction using ascorbic acid was first examined as a function of concentration. To ensure that the entire gel contains uniform Au(III) ion concentration and that reduction reaches completion, gels were immersed for 24 h each in $HAuCl_4$ and reducing agent solutions. Diffusion occurs from the gel/solution interface to the gel interior. Since the patterns generated from the diffusion-controlled reduction are identical in the longitudinal and the radial directions despite of the anisotropy of the gel structure, only cross sections along the radial plane are examined here. Table 1 shows scanned images of cross sections of PVOH hydrogels containing AuNPs. The concentration ranges were chosen such that the macroscopic color patterns due to the presence of AuNPs are not too faint to observe nor too intense to resolve. It was also found necessary to have the concentration of the reducing agent be higher than that of $HAuCl_4$ so that the formation of AuNPs takes place in the gel matrices rather than in solution—AuNPs formed primarily in solution rather than in gel matrix when comparable concentrations of reagents were used in the preparation of sample 4A. At first glance, the color of the gel cross sections due to surface plasmon resonance of AuNPs is independent of ascorbic acid concentration but varies as a function of the gold precursor concentration, from pink (row 1) to multicolored concentric bands (rows 2 and 3) to brown (row 4) in Table 1. To obtain quantitative information on size and distribution of AuNPs, six gels prepared using varying concentrations of $HAuCl_4$ and ascorbic acid were dissolved in hot water and analyzed by TEM. The NP sizes in these samples (Figure 3) confirm the observations based on the color variations of the gel cross sections. The dependence of AuNP size on reagent concentration can be explained by the "organizer" mechanism suggested for citrate and amino acids.[28−30] It has been shown that reducing agent molecules (or their oxidized intermediates) and Au(III) ions initially form polymeric complexes and that subsequent growth of the polymeric species leads to the reduction and formation of stable nuclei. The nucleation step is rate-limiting since the formed nuclei can catalyze particle growth by diffusional deposition at later stages. It has also been suggested that

(24) Liu, Y.; Male, K. B.; Bouvrette, P.; Luong, J. H. *Chem. Mater.* **2003**, *15*, 4172.
(25) Chen, S.; Kimura, K. *Langmuir* **1999**, *15*, 1075.
(26) Wagner, J.; Köhler, J. M. *Nano Lett.* **2005**, *5*, 685.
(27) Zhou, Q. F.; Bao, J. C.; Xu, Z. *J. Mater. Chem.* **2002**, *12*, 384.
(28) Bhargava, S. K.; Booth, J. M.; Agrawal, S.; Coloe, P.; Kar, G. *Langmuir* **2005**, *21*, 5949.
(29) Turkevitch, J.; Stevenson, P.; Hilier, J. *Discuss. Faraday. Soc.* **1951**, *11*, 55.
(30) Kumar, S.; Gandhi, K. S.; Kumar, R. *Ind. Eng. Chem. Res.* **2007**, *46*, 3128.
(31) Tang, X.-L.; Jiang, P.; Ge, G.-L.; Tsuji, M.; Xie, S.-S.; Guo, Y.-J. *Langmuir* **2008**, *24*, 1763.
(32) Lim, B.; Camargo, P. H. C.; Xia, Y. *Langmuir* **2008**, *24*, 10437.

Table 1. Cross Sections of PVOH Hydrogel Cylinders (Diameter is 1.5 cm) Containing AuNPs Prepared at Different Concentrations of $HAuCl_4$ and Ascorbic Acid

$[HAuCl_4]$ (mM)	[Ascorbic acid] (mM)				
	10 (A)	25 (B)	50 (C)	100 (D)	200 (E)
1 (1)					
2.5 (2)					
5 (3)					
10 (4)					

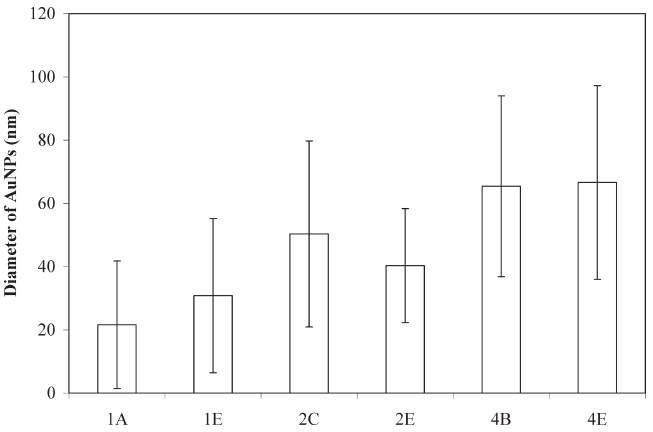


Figure 3. Size of AuNPs prepared using different concentrations of $HAuCl_4$ and ascorbic acid: 1A, 1E, 2C, 2E, 4B, and 4E as shown in Table 1.

reducing agents containing electron-donating groups and π electrons abide by the "organizer" mechanism: the electron-donating groups can effectively coordinate to Au(III) ions and the π electrons can stabilize the oxidized forms of the reducing agents.[29] Ascorbic acid seems to fit the criteria with two alcohol groups, one ene diol, and one lactone moiety to coordinate with and reduce Au(III) ions. That the size of AuNPs formed is independent of ascorbic acid concentration is likely because the excess amounts of ascorbic acid used (to ensure the reduction occurs in the gel matrices) do not restrict the extent of nucleation. At low ascorbic acid concentrations (the left side of the table), however, the reducing agent does not diffuse to the center of the gel, which results in a AuNP-depleted region. On the other hand, the size of AuNPs prepared in the gel increases to some extent as gold precursor concentration increases. This trend can be explained by the fact that an increase in Au(III) concentration results in more extensive nucleation as well as depositional growth to form larger particles.

An interesting feature observed in the gel cross sections is the multicolored concentric bands that are formed at intermediate gold precursor concentrations. TEM images of the sectioned samples from the three regions (red, brown, and purple) in sample 2C were obtained and are shown in Figure 4. The magnification is chosen such that particle shapes are well resolved. Very few particles are shown in Figure 4 because particles are large and particle distribution is sparse. Particle size calculation takes into account at least 100 particles in each region; the average size of the particles in the outer region (26 ± 7 nm, red) is less than those in the middle (44 ± 21 nm, brown) and inner (43 ± 23 nm, purple) regions. The particles in each region are individually more monodisperse than those described in Figure 3. Another striking difference among the three regions is that the percentage of nonspherically shaped particles (mostly polygons) differs, ~24% (outer), ~68% (middle), and ~55% (inner): the AuNPs formed in the middle and inner regions of the gels have similar size and shape. The size and shape variation from the outer region to the interior can be rationalized by the reduced amount of ascorbic acid in the interior of the gel due to the diffusion-controlled process: the formation of fewer nuclei results in the growth of larger particles while the more selective adsorption/capping by the reducing agent to certain crystalline faces of the developing AuNPs attributes to the formation of more nonspherically shaped particles.[31,32] The favorable formation of polygons at low ascorbic acid concentrations is confirmed by close examination of TEM images of samples 1A, 1E, 2C, 2E, 4B, and 4E (not shown).

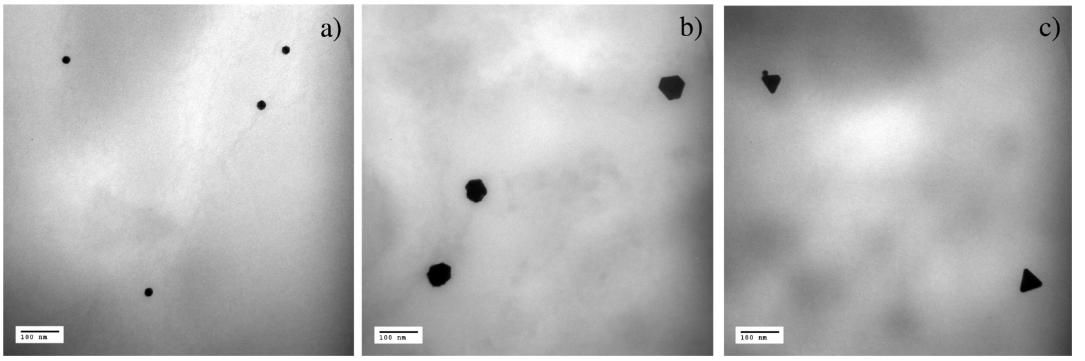


Figure 4. TEM micrographs of (a) outer, (b) middle, and (c) inner sections of a gel cylinder embedded with AuNPs (sample 2C in Table 1, scale bar is 100 nm).

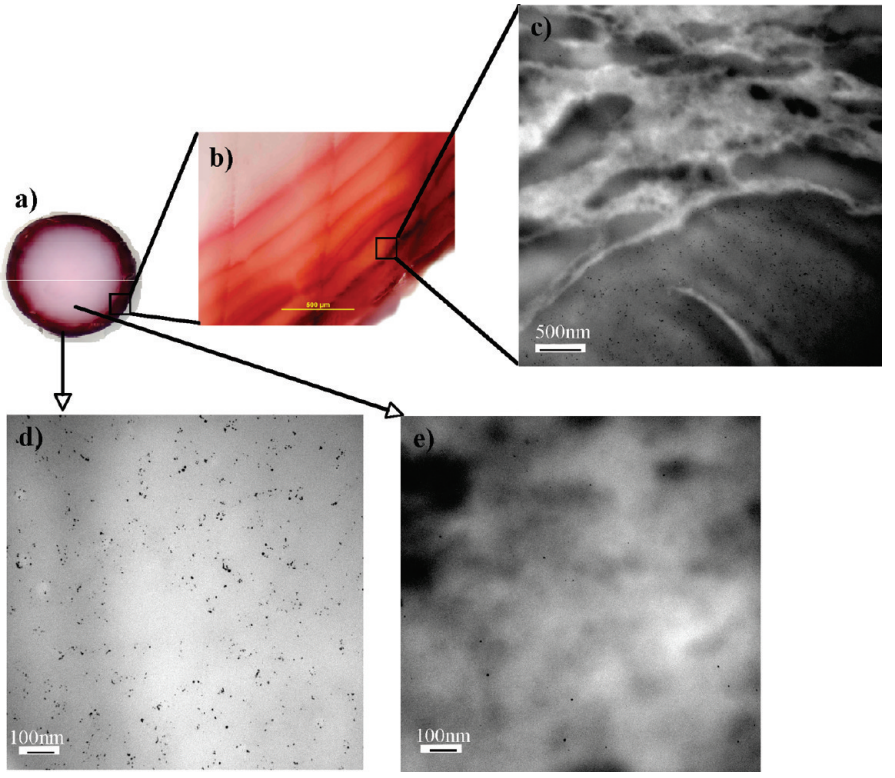
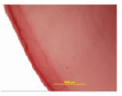
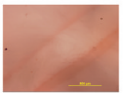
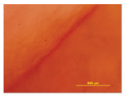
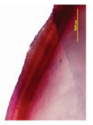
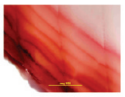
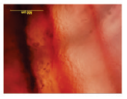
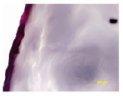
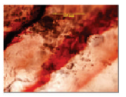
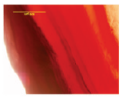


Figure 5. Hierarchical structured features formed as the result of diffusion-controlled reduction of $HAuCl_4$ (2.5 mM) by $NaBH_4$ (25 mM) in a PVOH hydrogel cylinder: (a) a cross sectional image of the gel (diameter is 1.5 cm), (b) an optical micrograph of the outer region (scale bar is 500 μm), (c) a TEM micrograph showing a dark stripe with particles (bottom) and a light stripe with no particles (top), (d) a TEM micrograph of the gel outer region, and (e) a TEM micrograph of the gel interior.

Reduction kinetics using the same reagent concentrations as for sample 2C show that the colored bands appeared within 10 min (not shown). As the reaction progressed further, the color intensities of all three regions increased with no noticeable change in the color shades, and the width of the outer band increased at the expense of the decrease in width of the inner region. Reduction appears to be complete within 2 h, which is indicated by no further change in the color patterns. The increase in color intensity over time indicates that nucleation occurs continuously for an extended period of time, which explains the polydispersity of the AuNPs obtained. Particle growth seems to be limited by the adsorbed reducing agent (and matrix polymer molecules) since there is no indication of increase in particle size (red shift in color) in the three regions as a function of time. TEM images of the three regions after a reaction time of 11 min show average sizes of 25 ± 16 (outer red), 71 ± 28 (middle brown), and 50 ± 15 nm (inner purple). That the sizes of AuNPs formed after 11 min are not statistically different from those obtained after 24 h of reaction time confirms the growth mechanism proposed based on the scanned images of gel cross sections from the kinetics studies. The slightly larger AuNPs produced in the interior of the gels at the shorter reaction time is likely due to the continued particle growth from the remaining Au(III) ions in the gel interior after the removal of the reducing agent.

Reduction of $HAuCl_4$ using sodium borohydride was similarly studied. Interesting structural features on different length scales for a representative sample are shown in Figure 5.

Table 2. Optical Micrographs of PVOH Hydrogels Containing AuNPs Prepared at Different Concentrations of $HAuCl_4$ and Sodium Borohydride[a]

$[HAuCl_4]$ (mM)	$[NaBH_4]$ (mM) 500 μm				
	5 (A)	10 (B)	25 (C)	50 (D)	100 (E)
1 (1)					
2.5 (2)					
5 (3)	No Pattern				
10 (4)	No Pattern	No Pattern			

[a] The edges of the gels are to the left of the images.

The outer region of the gel appears deep red (a) due to densely populated AuNPs of ~4 nm in diameter (d) while the inner region resembles the native gel with very few particles present (e). Optical microscopy revealed that the outer region consists of stripes with periodicity of ~100 μm (b) along the direction of diffusion. TEM microscopy (c) indicates that NPs are only present in the dark stripes. The same concentration ranges (in terms of molar equivalence of electrons transferred) were surveyed in the $NaBH_4$ reduction (shown in Table 2) as in the ascorbic acid system while keeping the soaking and reduction time at 24 h for ease of comparison. When sodium borohydride is not in significant excess (the entries in the lower left corner of Table 2), AuNPs are formed mostly in solution and no stripe formation was observed. Stripes are thin and faint when Au(III) concentrations are low and appear to be thick and intense at high Au(III) concentrations. TEM studies indicate that the characteristics of AuNPs formed by sodium borohydride reduction are independent of reagent concentrations: they are small (3−5 nm), spherical, and monodisperse. Sodium borohydride does not have obvious capability to coordinate with Au(III) ions, thus it is reasonable to assume that the reduction follows the classical "burst nucleation theory," i.e. nucleation is the result of supersaturation.[33] The small and monodisperse AuNPs formed imply that only a limited amount of Au(III) ions is available for depositional growth after a fast and extensive nucleation step. The size of the AuNPs is independent of the $HAuCl_4$ concentration indicating that the number of nucleation sites formed is proportional to the gold precursor concentration in the "supersaturation" mechanism.

Most of the differences between the two reduction systems are due to the different reduction mechanisms in operation. Small, spherical, and monodisperse particles are formed by sodium borohydride reduction, and large, nonspherical, and polydisperse particles are prepared by ascorbic acid reduction. It was puzzling, however, why micrometer-scale stripes form only in the sodium borohydride system and why reduction by sodium borohydride is limited to the outer region of the gels. The stripe patterns are similar to the Liesegang stripes observed in the precipitation reactions in PVOH hydrogels. A competitive growth model is a well-accepted theory to explain Liesegang patterns resulting from precipitation reactions.[34−36] It states that nuclei initially distribute evenly throughout the gel matrix and that the less stable small particles dissolve into precursor ions, which diffuse throughout the gel and are adsorbed and reduced on larger particles; mobility of the particles and phase segregation can result in formation of stripes and other patterns. These patterns are thermodynamically more stable than the uniform pattern resulting from the homogeneously distributed colloids. Optical micrographs of samples from kinetics studies of $NaBH_4$ reduction show the advancement of the reaction front and the evolution of stripes from a uniform red hue as a function of time, which is consistent with the theory. Our diffusion studies indicate that particles smaller than 10 nm have

(33) LaMer, V. K.; Dinegar, R. H. *J. Am. Chem. Soc.* **1950**, *72*, 4847.
(34) Flicker, M.; Ross, J. *J. Chem. Phys.* **1974**, *60*, 3458.
(35) Venzl, G. *J. Chem. Phys.* **1986**, *85*, 2006.
(36) Feeney, R.; Schmidt, S. L.; Strickholm, P.; Chadam, J.; Ortoleva, P. *J. Chem. Phys.* **1983**, *78*, 1293.

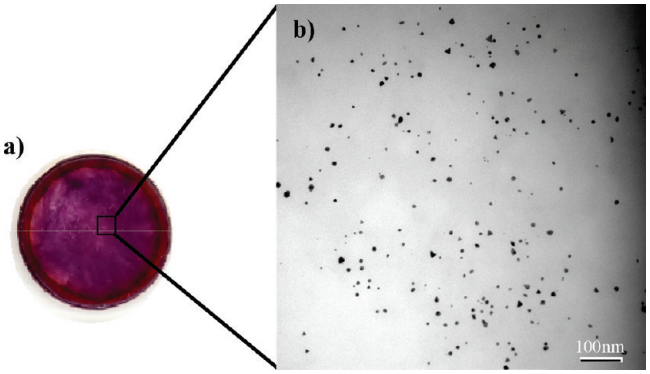


Figure 6. (a) Cross-sectional image and (b) TEM micrograph of a gel cylinder after sequential reduction of $HAuCl_4$ by sodium borohydride and ascorbic acid.

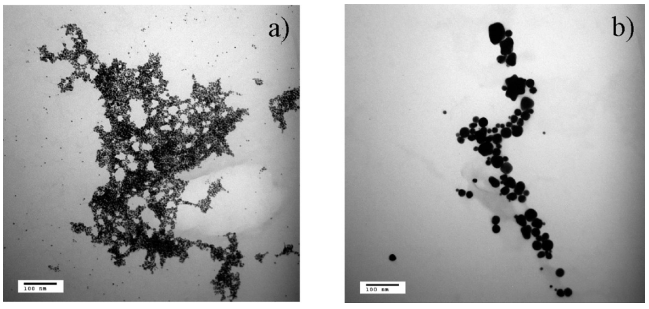


Figure 7. TEM micrographs of AuNPs prepared in solution without PVOH: reduction of $HAuCl_4$ by (a) $NaBH_4$ and (b) ascorbic acid (scale bar is 100 nm).

significant mobility in the PVOH gel matrices. Stripe formation as the result of alternating particle-rich and particle-poor regions requires particle mobility in the matrix according to the competitive growth model, which is possible given the small particle size in the $NaBH_4$ reduction and, on the other hand, is unlikely in the ascorbic acid system where the particles are too large to be mobile.

The reduction of $HAuCl_4$ presoaked in PVOH hydrogels via diffusion of reducing agents is controlled by the rate of diffusion. Ascorbic acid successfully diffuses and reduces $HAuCl_4$ to AuNPs from the outer to the inner regions of the gels; however, the reduction of Au(III) by sodium borohydride is limited to the outer region of the gels. The absence of AuNPs in the gel interior has to be due to the lack of either $HAuCl_4$ or $NaBH_4$. In a control experiment, PVOH gel cylinders were submerged in a sodium borohydride solution and small aliquots of sodium borohydride solution were drawn out at different soaking time and "titrated" with a $HAuCl_4$ solution. The amount of AuNPs formed, as monitored by UV−vis spectrophotometry, decreased drastically over time and the formation of NPs was negligible after 2 h. The loss of reducing ability as sodium borohydride diffuses to the interior of the gels is attributed to its reaction with water and −OH groups of PVOH hydrogels. The cross section of a gel cylinder after undergoing sequential reduction using 0.025 M sodium borohydride (condition 2C in Table 2) for 24 h and 0.05 M ascorbic acid for 24 h is shown in Figure 6a. The stripe pattern in the gel outer region as the result of $NaBH_4$ reduction is retained as shown in Figure 5b. The formation of AuNPs in the interior of the gel by ascorbic acid reduction indicates the presence of Au(III) ions in the gel interior. TEM (Figure 6b) indicates that the purple interior contains relatively monodisperse AuNPs of ~10 nm in diameter with a portion being polygons. The significantly smaller, but much denser, AuNPs prepared by the sequential reduction compared to those by the one-step ascorbic acid reduction is most likely caused by nucleation in the gel interior during the initial $NaBH_4$ reduction, which is evident by the light pink color of the region (Figure 5a). The ultimate particle size would then depend on the density of the pre-existing nuclei and the amount of Au(III) ions available for growth. The presence of polygons is due to the capping ability of ascorbic acid during the particle growth stage. The sequential reduction experiment not only confirms the restricted location/limited extent of sodium borohydride reduction but also presents an alternative method to prepare AuNPs of controlled size and shape as a function of the location in the gel.

Reduction of $HAuCl_4$ in Solution. Reduction in solution was carried out to elucidate the role of the PVOH gel matrix and to address whether the reduction mechanism is affected by the reaction medium. All reagents were one-tenth the concentrations used for the two fully characterized gel samples (samples 2C in the ascorbic acid and $NaBH_4$ systems) to allow accurate characterization by dynamic light scattering (DLS) and TEM of the AuNPs formed in solution.

In the reduction of $HAuCl_4$ by $NaBH_4$, AuNPs form clusters/aggregates up to hundreds of nanometers in size based on DLS and TEM (Figure 7a). This is not surprising since sodium borohydride (and its oxidized intermediates) does not provide significant stabilization of the AuNPs formed. The individual spherical AuNPs are 5 ± 2 nm, which is comparable in size to those formed in the PVOH gels.

Aggregates of AuNPs are also formed in the reduction of $HAuCl_4$ using ascorbic acid in solution (Figure 7b). The "primary" AuNPs are 22 ± 12 nm in diameter and mostly spherical in shape, which are comparable to those formed in the outer region of sample 2C. This confirms that the formation of larger and nonspherically shaped particles in the interior of the gels is inherent to the diffusion-controlled process in gel matrices. Small particles (~7 nm in diameter) were detected by DLS during the first 2 h of ascorbic acid reduction and are likely growing nuclei. Figure 7b also shows the presence of very small AuNPs and the polydispersity of the particles. These observations indicate that nucleation takes place continuously over an extended period of time for ascorbic acid reduction. This also appears to be taking place in the gel system.

Aggregation in the ascorbic acid system is not as extensive as that in the $NaBH_4$ system implying the better coordination/stabilization of AuNPs by ascorbic acid. The aggregates are stringlike, and neighboring AuNPs

are not as close as those in the sodium borohydride system (Figure 7), suggesting that functional groups in ascorbic acid are capable of bridging neighboring AuNPs. The difference in the aggregation states of AuNPs produced by the two reduction systems is consistent with the difference in the chemical nature of the reducing agents. The "primary" AuNPs formed by sodium borohydride and ascorbic acid reduction in solution have similar size and shape as those formed in the outer regions of gel matrices indicating that reaction mechanisms are independent of reaction media.

Conclusions

AuNPs were prepared via the reduction of tetrachloroauric acid by ascorbic acid and sodium borohydride in PVOH hydrogel cylinders. Hierarchical structured features, from nanoscopic to macroscopic scales, were produced and were a function of the reducing agent identity and, more importantly, the diffusion-controlled process. Size and shape control of AuNPs on the nanoscopic level is accomplished by taking advantage of the different reduction mechanisms—"organizer" and "supersaturation"—of ascorbic acid and sodium borohydride, respectively. PVOH matrix polymer facilitates the dispersion and stabilization of the AuNPs formed by reduction. Furthermore, diffusion-controlled reduction in PVOH gels imparts size and shape control of AuNPs produced in different regions of the gel, which results in macroscopic color patterns developed along the direction of diffusion. Stripe features on the micrometer-scale are the consequence of the mobility of small AuNPs (< 10 nm) formed by sodium borohydride reduction.

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Supporting Information Available: TEM sample preparation. This material is available free of charge via the Internet at http://pubs.acs.org.