Preparation of Polymer-Coated Functionalized Silver Nanoparticles

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In recent years, the study and preparation of inorganic crystalline particles on the nanometer scale has attracted considerable attention from both fundamental and applied research.[1] Metal nanoparticles, particularly silver, gold, and copper, have been the focus of great interest because of their unique optical properties, determined by the collective oscillations of electron density termed plasmons.[2] The efficiency for the absorption and scattering of light by metal nanoparticles can surpass that of any molecular chromophores.[3] Such a high efficiency for interaction with light, together with an extreme resistance to photodegradation, is stimulating the development of new applications of nanoparticles in photochemistry, analytical procedures, and as components of electronic and photonic devices. Chemical resistance and the ability to modify the metal surface are important prerequisites for many potential applications. For example, oxygen-driven etching of silver in the presence of strong ligands for Ag⁺, such as chloride ions, constrains the use of the particles in chloride-rich biological environments. Silver nanoparticles can also be etched in the presence of thiols, particularly when exposed to visible light. At the same time, the adsorption of functionalized thiols is an efficient method for the tailoring of metal surfaces, as was recently demonstrated for gold nanoparticles.[4] Aqueous suspensions of unprotected silver and gold particles are also susceptible to irreversible aggregation.[5] This aggregation is traditionally overcome through the spontaneous adsorption on the particle surface of polymeric stabilizers.[6] However, this method requires the presence in the suspension of a large concentration of stabilizers which can interfere with surface functionalization; at lower concentrations, the stability of the suspension is limited by desorption of the stabilizers from the surface.

Emulsion polymerization has been previously applied to the coating of organic and inorganic particles[7] on the micrometer and submicrometer scale. The method has the potential for producing a stable and compact polymer layer, completely enclosing the
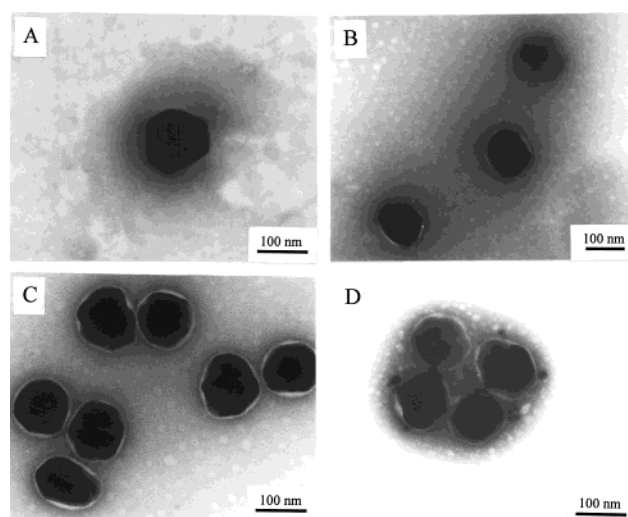
Figure 1. TEM images of silver particles: (A) uncoated particle, (B) polystyrene/methacrylate coated particles, (C) polystyrene/methacrylate coated particles with a covalently bound BSA layer, and (D) the same as panel C after exposure to gold colloids. Negative staining by phosphotungstic acid used for all images.

particle and improving its chemical resistance. Herein, we report the encapsulation of silver nanoparticles into a polymer shell via emulsion polymerization to produce a chemically stable system. The coating was produced by the polymerization of styrene and/or methacrylic acid in emulsions of oleic acid. In this system, silver particles are coated with a uniform, well-defined layer and are in a nonaggregated suspension, contrary to previously reported systems in which silver particles appeared to be imbedded into a polymer matrix. The thickness of the layer can be readily controlled by changing the concentration of monomers. The coated particles were tested in concentrated chloride solutions and exhibited a strong resistance toward etching. These can also be efficiently purified by filtration and/or precipitation, and redispersed in different media for further chemical modification. As an example of chemical tailoring of particle surface, we attached bovine serum albumin (BSA) to the carboxylate functionalities derived from methacrylic acid monomers.

TEM pictures of 100 nm silver particles uncoated and coated with the polymer are shown in Figure 1. The polymer layer has insufficient electron density to be directly observed by TEM and visualization of the coating was achieved through negative staining with phosphotungstic acid. The polymer appears as a white layer between the dark silver core and the gray halo of the stain surrounding the particles. Layers of varying thickness, ranging from 2 nm to about 10 nm, were produced and examined by TEM (Table 1). Whereas thin coatings follow the shape of the metal core, thicker ones (>10 nm) tend to assume a globular shape. The presence of oleic acid is required to obtain particle encapsulation; when the polymerization was carried out in the absence of oleic acid, only polymer particles without metal core were produced and no polymer shell was observed around the silver particles. Because carboxylic acids have high affinity for the oxide layer that is present on the surface of silver,[8] oleic acid is readily adsorbed on the particles. Since the amount of oleic acid used largely exceeds the amount required for monolayer coverage of the particles, a double layer is presumably formed, producing a vesicle structure that surrounds the silver core. This structure is

(1) Elghanian, R.; Storhoff, J. J.; Mucic, R. C.; Letsinger, R. L.; Mirkin, C. A. *Science* **1997**, *277*, 1078−1081. Alivisatos, A. P. *NATO Sci. Ser., Ser. C* **1999**, *519*, 405−416. Bruchez M., Jr.; Moronne, M.; Gin, P.; Weiss, S.; Alivisatos, P. A. *Science* **1998**, *281* (5385), 2013−2916. Schmid, G.; Hornyak, G. L. *Solid State Mater. Sci.* **1997**, *2*, 204−212. Schmid, G. *Prog. Colloid Polym. Sci.* **1833**, *111*, 52−57. Schmid, G. *Adv. Mater.* **1998**, *10* (7), 515−526. Volokitin, Y.; Sinzing, J.; de Jongh, L. J.; Schmid, G.; Moiseev, I. I. *Nature* **1996**, *384*, 621−623. Kreibig, U.; Vollmer, M. *Optical Properties of Metal Clusters*; Springer Series in Material Science, No. 25; Springer-Verlag: Berlin, 1995.

(2) Kreibig, U.; Vollmer, M. *Optical Properties of Metal Clusters*; Springer Series in Material Science, No. 25; Springer-Verlag: Berlin, 1995; pp 187−201.

(3) Bohren, C. F.; Hoffman, D. R. *Absorption and Scattering of Light by Small Particles*; John Wiley & Sons: New York 1998; pp 339−342.

(4) Mirkin, C. A.; Letsinger, R. L.; Mucic, R. C.; Storhoff, J. J. *Nature* **1996**, *382* (6592), 607−609. Watson, K. J.; Zhu, J.; Nguyen, S. B. T.; Mirkin, C. A. *J. Am. Chem. Soc.* **1999**, *121*, 462−463. Fitzmaurice, D.; Rao, S. N.; Preece, J. A.; Stoddart, J. F.; Werger, S.; Zaccheroni, N. *Angew. Chem.* **1999**, *111*, 8, 1220−1224.

(5) Kreibig, U.; Vollmer, M. *Optical Properties of Metal Clusters*; Springer Series in Material Science, No. 25; Springer-Verlag: Berlin 1995; pp 184−185.

(6) Sato, T.; Ruch, R. *Stabilization of Colloidal Dispersions by Polymer Adsorption*; Surfactant Science Series, No. 9; Marcel Dekker: New York 1980; pp 65−119.

(7) Hergeth, W. D.; Steinau, U. J.; Bittrich, H. J.; Schmutzler, K.; Wartewig, S. *Prog. Colloid Polym. Sci.* **1991**, *85*, 82−90. Van Herk, A. M. *NATO ASI Ser., Ser. E* **1997**, *335*, 435−450.

(8) Ulman, A. *Chem. Rev.* **1996**, *96*, 1533−1554. Wang, W.; Efrima, S.; Regev, O. *Langmuir* **1998**, *14*, 602−610.

Table 1. Effect of Monomer Concentration on Coating Thickness

concn of monomer	styrene/methacrylate ratio	coating thickness, nm
5×10^{-2} M styrene		2 to 10
1×10^{-3} M styrene		~2
2×10^{-3} M styrene	10/1	~2
2×10^{-4} M methacrylic acid		
4×10^{-3} M styrene	40/1	~4
1×10^{-4} M methacrylic acid		
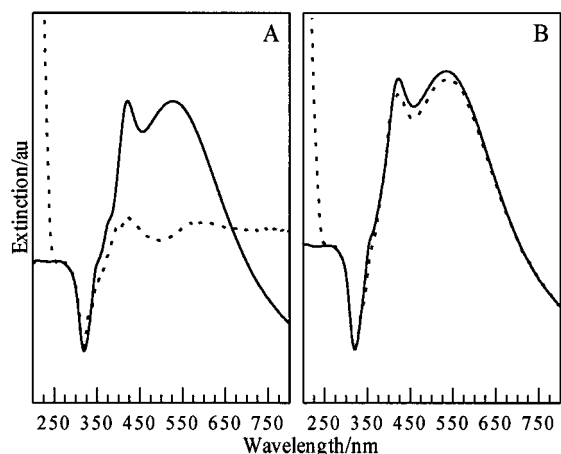
Figure 2. Extinction spectra of silver particles: (A) uncoated particles and (B) polystyrene coated particles. Solid line: suspension in water. Dotted line: suspension in water, after 1 h in 1.8 M NaCl.

an important prerequisite for emulsion polymerization.[9] The polymerization takes place in the double layer, in which monomers are readily soluble. For a low amount of monomer, the thickness of the coating was measured to be in the range expected for the double layer of oleic acid. In the presence of a larger amount of monomer, the outer surfactant layer is spaced further from the silver surface and the coating assumes a more spherical shape.

The extinction spectra of aqueous suspensions of coated and uncoated particles are shown in Figure 2. The presence of the polymer layer caused only minor changes in spectral properties. The bands corresponding to the quadrupolar and dipolar components of the plasmon resonance underwent small shifts from 422 and 528 nm to 423 and 533 nm, respectively. According to Mie theory, a red shift of the plasmon resonance frequency is expected as the dielectric constant of particle environment increases.[10] No spectral changes were noted that could be associated with interaction between particles, indicating that the suspension is mostly in a nonaggregated state. In the case of the methacrylate/styrene copolymer shell, a shift from 533 to 568 nm, a decrease and broadening of the plasmon resonance band, and a pronounced shoulder on its red side were observed at pH lower than 5. These changes were unambiguously attributed to aggregation of the particles. At the early stages of aggregation, an increase in pH could reverse the process, resulting in spectra indistinguishable from those of the unaggregated suspension. Aggregation appeared to be triggered by the protonation/deprotonation of carboxylate

(9) Furusawa, K.; Nagashima, K.; Anzai, C. *Colloid Polym. Sci.* **1994**, *272*, 1104−1110.

(10) Kreibig, U.; Vollmer, M. *Optical Properties of Metal Clusters*; Springer Series in Material Science, No. 25, Springer-Verlag: Berlin 1995; pp 26−76.

groups with a pK_a close to 4−5, as expected for a methacrylate coating. A more accurate value for the pK_a could not be determined from these experiments, because the onset of aggregation depends not only on the protonation/deprotonation of carboxylate groups, but also on particle concentration and the ionic strength of the suspension.

Polymer-coated silver particles can be precipitated by centrifugation and resuspended in deionized water, various buffers, and short-chain alcohols. This procedure can be repeated an unlimited number of times without loss of stability. However, for alcohol suspensions some irreversible adsorption of particles on glass walls was observed. Notably, the stability of uncoated metal particles is easily compromised by washing cycles, resulting in irreversible aggregation. This fact permits the separation of the coated from the uncoated particles: the latter are irreversibly aggregated whereas the former can be resuspended into a solution. The possibility to implement this simple and reliable procedure for the purification of the polymer-coated silver particles is a crucial step for the development of surface modification chemistry.

The resistance of coated particles toward hydrophilic etching agents was tested by exposing a suspension to 1.8 M sodium chloride, conditions under which uncoated particles rapidly collapse. The effect of sodium chloride on the extinction spectra of both uncoated particles and particles coated with 5 nm of polystyrene is shown in Figure 2. Minimal changes were observed in the spectrum of the coated colloid 1 h after the addition of chloride (Figure 2B). Uncoated particles, on the other hand, exhibited strong spectral changes characteristic for both aggregation and etching (Figure 2A).

The methacrylate/polystyrene copolymer coating is rich in carboxylate groups, providing the tether for coupling different molecules to the particle surface. Coupling of protein molecules is of particular interest, in that it opens the way for the application of silver particles in various bioanalytical procedures, for example in immunostaining. As a model system, we covalently attached BSA to the surface in a two-step process. Carboxylate groups were first condensed with *N*-hydroxysuccinimide, and the resulting activated esters were then allowed to react with the lysine residues of the protein. The two-step protocol ensures protein coupling without protein−protein cross-linking producing a uniform layer about 4 nm thick (Figure 1C). The presence of the protein was confirmed by adsorption of colloidal gold particles, as observed in TEM images (Figure 1D). No adsorption of the latter was observed on polymer-coated particles in the absence of protein. The protein coating was also positively stained by addition of silver nitrate for TEM measurements. The protein coating survived at least three cycles of centrifugation and washing, as expected for covalently bound protein.

In conclusion, emulsion polymerization is an efficient method for the encapsulation of silver nanoparticles into a protective layer. Encapsulated particles retain their optical properties, display a remarkable chemical stability, and are easily purified and modified. Bovine serum albumin was covalently attached to the polymer surface with a procedure that can be extended to the coupling of other proteins, oligosaccharides, and amine-containing molecules.