

Colloidal Metal Deposition onto Functionalized Polystyrene Microspheres

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Received January 19, 1999. Revised Manuscript Received May 27, 1999

Three different methods are described for uniformly anchoring metal colloids (Pt, Pd, and Au) onto the surface of polystyrene microspheres (PSMS). The first method we have employed is electrostatic deposition of preformed anionic colloidal particles onto a polycationic surface. In this method the functional groups on the surfaces of the microspheres (amine or carboxylic acid) are used to give the surface a net charge. These ionic spheres were then treated with polyelectrolytes of the opposite charge, which uniformly cover the surface. When the spheres have a net positive charge at the surface they show excellent adhesion of Au colloids. These metal-derivatized spheres can be prepared with electroactive viologen groups as well. In the second method investigated here, metal colloids are adsorbed to the surface of neutral functionalized PSMS. We report the synthesis and characterization of catalytically important noble monometallic colloids using various chemical and sonochemical methods. These metal colloids are then adsorbed onto suitably functionalized PSMS. The metal-immobilized microspheres are reacted with a linker such as 4-mercaptobutyl phosphonic acid and subsequently used for growing multilayers of ZrPV(Cl) (zirconium and *N,N'*-dialkyl-4,4'-bipyridinium dichloride) by alternating Zr^{4+} and PV(Cl). The third method described here for supporting metal particles on PSMS involves depositing a precursor metal oxide or hydroxide onto the PSMS, followed by reduction to give fine metal particles on the surface of the PSMS. Metal particle sizes formed by this method are 2–4 nm. The colloids, microspheres, and resulting catalysts prepared by all three methods have been characterized by electron microscopy (TEM and SEM) and by energy-dispersive X-ray (EDX) microanalysis, and those prepared by method 2 have been characterized by diffuse reflectance UV–vis spectroscopy as well.

Introduction

We have demonstrated that photoactive and electroactive self-assembled zirconium bisphosphonate multilayer films^{1,2} can be prepared on metal or oxide substrates and are efficient photocatalysts for the reduction of water.³ These films were grown by treating the substrate alternately with Zr^{4+} and $H_2O_3PCH_2CH_2$ -viologen- $CH_2CH_2PO_3H_2$ solutions (viologen = *N,N'*-dialkyl-4,4'-bipyridinium), building up the metal bisphosphonate film in an incrementally increasing fashion. In the photocatalytic process, a reduced viologen moiety in the thin film is formed photochemically, which transfers its free electron to a colloidal Pt particle. The water reduction step in these materials occurs at the Pt particle, which is incorporated into the material during growth. To maximize the contact area between

the metal particles and the metal–organic materials a microporous or zeolitic version of the metal–bisphosphonate was prepared, i.e., $Zr_2(PO_4)(O_3PCH_2CH_2$ -viologen- $CH_2CH_2PO_3)X_3 \cdot 3H_2O$ ($X = \text{halide}$),⁴ which contains intercalated Pd/Pt particles in the micropores. This porous material catalyzes the photoreduction of water⁵ and is a good catalyst for the direct production of hydrogen peroxide from dissolved H_2 and O_2 . It has also been shown that growing multilayers of zirconium and a viologen containing species onto the metal particles enhances the catalytic activity and lifetime of these catalysts.⁶

The particle sizes of these porous materials vary between ~ 0.1 and $\sim 3 \mu\text{m}$, depending on the synthesis conditions,⁷ with the intercalated metal found both at the surface and distributed throughout the micropores

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of the particle. Unfortunately, only the material near the surface of the particle is accessible to solution, making the bulk of the each particle catalytically inactive. Moreover, the fact that the metal particles are found within the pores and at the surface makes it very difficult to differentiate direct reactions occurring at the metal versus those which involve the metal organic materials (e.g., viologen groups). For example, consider the formation of H_2O_2 from dissolved H_2 and O_2 , catalyzed by our porous viologen-containing materials. In this process, the metal particles (Pd or mixed particles Pd/Pt) catalyze the reduction of viologen by H_2 , and the reduced viologen reacts rapidly with O_2 to give H_2O_2 (rate = $10^8 M^{-1} s^{-1}$).⁸ The supported Pd and Pd/Pt particles alone will also catalyze the formation of H_2O_2 from dissolved H_2 and O_2 , albeit at a lower rate than the viologen-mediated pathway.^{6,9} It would be a great benefit to be able to both eliminate the problem of having bare metal particles exposed to solution and to increase the amount of accessible material. One approach to this would be to grow a thin film directly onto the metal particle itself, in the same way films are grown on planar substrates. Our attempts to grow films directly onto metal particles failed, due to poor matching of the metal particle sizes (20–30 Å diameter) and the self-assembled monolayer (SAM) thickness (~20 Å).¹⁰ The approach described herein gets around this mismatch problem by first anchoring the metal particles onto a high surface area support (polymer microbeads), followed by growth of films onto these supported metal particles. The goal is to prepare micrometer- to submicrometer-sized particles as efficient heterogeneous catalysts using self-assembly techniques.

In the construction of heterogeneous metal-containing catalytic species via methods of self-assembly, it is important for practical purposes to maximize the surface area-to-volume ratio of the metal. Colloidal metal particles are of continuing interest because of their fascinating catalytic, electronic, and optical properties.¹¹ Owing to their extremely large surface area, monometallic and bimetallic noble metal colloids have been used as active catalysts in the hydrogenation of alkenes in biphasic or organic media,¹² hydrosilylation of olefins in organic solutions,¹³ and the oxidation of carbon monoxide in aqueous solution.¹⁴ Methods for the preparation of such colloids include controlled chemical reductions,¹⁵ photochemical¹⁶ or radiation-chemical reduction, photocatalytic reduction,¹⁷ metal vaporization

techniques,¹⁸ and sonochemical synthesis.¹⁹ It must be noted here that each of these methods yields colloidal particles of a characteristic size which is crucial since the catalytic activity of metal colloids is highly dependent on particle size as well as the synthetic route to colloid formation. We have used several different methods for the preparation of metal particles, as will be discussed below.

Our approach to using the colloidal metal particles involves anchoring them to an inert support. In this paper we discuss the use of polymer microspheres (also called latexes or latex beads) as inert supports for colloidal metal particles. The use of latex beads is well-developed in the immunological field. A typical polymer bead may consist of a polystyrene or methyl methacrylate backbone substituted with functionality such as carboxylic acid, amine, hydroxy, and sulfate groups. These beads are of particular interest as immunological sensors and drug delivery agents due to the ease with which their surface groups can be further derivatized to incorporate proteins and other biologically important molecules.²⁰ Surprisingly, the chemistry of such functionalized spheres as support for heterogeneous catalysts has not been extensively explored.²¹ It has recently been demonstrated that Ag nanoparticles can be grown onto the surface of PSMS in situ during the process of polymerization,²² but there has been little published results on the coating of such PSMS after they are formed.²³ Such systems are of immense interest because of the use of such metal nanoparticles (Ag, Au, Pt, etc.) as the active substrates for surface enhanced Raman scattering, chemical, electronic, and optical sensors,^{24,25} and photocatalysts for solar energy conversion.²⁶

Our focus has been to identify several methods for the deposition of colloidal metal particles onto the surface of functionalized PSMS. Herein, we report three such methods which will be discussed individually: controlled hydrolysis, electrostatic deposition, and simple adsorption of preformed colloids. We also report our initial studies aimed at growing SAMs onto these supported metal particles.

Experimental Section

Non-cross-linked carboxylic acid- and amino-functionalized polystyrene microspheres were obtained as a slurry from Polysciences, Inc., ranging in size from 0.25 to 3.0 μm . Slurries of cross-linked spheres (0.2–3.2 μm) were obtained from

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Polysciences, Inc., and Bangs Labs. All solutions were made with purified/deionized water using a Milli-RX20 and were filtered through a 0.45 μm filter prior to use. Characterization was performed using SEM, TEM, and EDX.

All TEM samples were prepared by placing a drop of sample on top of a copper sample grid and drying it in air. All TEM analyses were performed using a Philips EM 420 electron microscope at 120 kV accelerating voltage equipped with KEVEX energy-dispersive X-ray (EDX) analyzer. All diffuse reflectance UV-vis spectroscopy was performed on a HP8453 spectrometer fitted with a Labsphere diffuse reflectance attachment. The average size of colloids was calculated by averaging the size of over 50 particles from the TEM picture.

Synthesis of Colloids. 1. *Gold Colloids. Citrate Reduction.*²⁷ A solution of 1% (w/v) $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (0.5 mL, 0.25 M) was diluted to 50 mL (2.5×10^{-4} M) and heated to reflux in air. A 1% aqueous trisodium citrate solution (1.25 mL) was added to the refluxing gold solution (metal:citrate = 1:100). After continued refluxing for about 20 min, the solution (initially pale yellow) turned first purple and finally cherry red. The red solution was refluxed for an additional 10 min and cooled and stored for later use.

*Sonochemical Method.*²⁸ A 1% aqueous solution of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (25 μL) was added to 25 mL of distilled water and 0.8 mL of ethanol (or 1.5 mL of *i*-PrOH). The pH was either left unaltered or was adjusted to 7.0 by adding a few drops of 0.2 M K_2CO_3 solution. The two solutions (pH 7.0 or lower) were then sonicated at 90 W, 47 kHz for different times ranging from 30 min to 2.5 h and were studied using UV-vis spectroscopy, TEM, and EDX.

2. *Palladium Colloids. Citrate Reduction:* 50 mL of an aqueous 0.393 mM solution of potassium hexachloropalladate(IV) was heated to reflux (110 $^\circ\text{C}$). A 1% solution of sodium citrate (6 mL) was added. Continued refluxing for 4 h gave a dark brown colored solution, which was characterized as palladium colloids.

Ethanol Reduction: Palladium(II) chloride (12 mg, 0.066 mmol) was dissolved in 25 mL of ethanol and 25 mL of water. To the solution was added poly(vinylpyrrolidone) (PVP-K30, 290 mg, 2.64 mmol as monomer units), and the solution was allowed to reflux (100 $^\circ\text{C}$) overnight in an inert atmosphere. The resulting dark brown solution was characterized to be monodisperse palladium colloids.

Immobilization of Metal Particles on Functionalized PSMS. *Method 1. Electrostatic Deposition of Metal Colloids.*

a. Au Colloids onto Carboxylic Acid-Functionalized Spheres. Eight drops of a 2.5% aqueous suspension of 2 μm non-cross-linked carboxylic acid-derivatized PSMS (Polysciences) was treated with 0.1–1 M NaOH for 10–60 min after which the beads were centrifuged and washed with water. The spheres were resuspended in ~ 0.2 mL water by sonication and 3 mL of 0.01 g/mL aqueous poly(allylamine hydrochloride) PAH was added. The suspension was agitated for 20 min. Upon centrifugation, the excess polymer solution was decanted and the spheres were washed with 2–3 portions of water. After resuspension in 0.2 mL of water, 3 mL of gold colloid suspension (prepared by citrate reduction method) was added, and the suspension was agitated overnight after which the spheres had changed from white to purple (or red depending on the size of the sphere and the Au particles). The total absence of gold colloid from the resulting supernatant was demonstrated by UV-vis spectroscopy. SEM, TEM, and EDX revealed the presence of evenly distributed Au on the surface of the microspheres.

b. Au Colloids onto Amino-Functionalized Spheres. By using the same general procedure as above for layering, Au was coated onto the surface of aminated microspheres by protonation of the amine (treatment with aqueous HCl), then coating with the polyanionic poly(sodium 4-styrene sulfonate) (PSS), followed by a layer of polycationic PAH and subsequent exposure to Au colloids (citrate reduced).

c. Deposition of viol_4 [$\text{CH}_3\text{-(}^-\text{NC}_5\text{H}_4\text{-C}_5\text{H}_4\text{N}^+\text{-CH}_2\text{C}_6\text{H}_4\text{-CH}_2\text{)}_3\text{-}^+\text{NC}_5\text{H}_4\text{-C}_5\text{H}_4\text{N}^+\text{-CH}_3\text{)]}_8$ and Pd Colloids onto Carboxylic Acid-Derivatized Spheres. One drop of a 10% aqueous

slurry of 3 μm cross-linked carboxylic acid-derivatized microspheres (Bangs Labs) was treated with 2 drops of 2 M NaOH for 10 min after which the beads were centrifuged and the supernatant discarded. The spheres were resuspended in ~ 0.2 mL water and 3 mL of ~ 0.01 g/mL viol_4 in 1:1 water/acetone was added. The suspension was agitated for 3 h. Upon centrifugation, the supernatant was discarded and the spheres were resuspended in 0.2 mL water. An additional 3 mL of 0.01 g/mL viol_4 was added and mixed for 3 h. The slurry was centrifuged and the supernatant discarded. Without washing, the spheres were suspended in 5 mL of citrate-reduced Pd colloids. After mixing for 3 h, the Pd solution was removed and replaced with an additional 5 mL of colloidal Pd. This was repeated until a total of 30 mL of Pd had been added, resulting in black beads. Without washing, 3 mL of 0.01 g/mL PAH was added and agitated between 20 min and 3 h. The solution was removed and replaced by 3 mL of 0.01 g/mL PSS and agitated between 20 min and 3 h. This was repeated until a total of five layers each of PAH and PSS had been deposited. The spheres were washed 3 times with water and then sonicated and washed with water 3 times (30 min each) to remove excess electrolyte.

Method 2. Reaction of Preformed Colloids with Uncharged Spheres. Various kinds of commercially available surface-functionalized polystyrene microsphere PS-X (PS: polystyrene microsphere, X= COOH, NH_2 , OH) with a mean diameter of 0.2–2.0 μm were used for the purpose. The metal colloids used for the surface derivatization were either Au or Pd or with a size range of 8–15 nm. In all the cases, immobilization was done by adsorption from aqueous metal colloidal solution onto suitably functionalized PSMS microsphere. For this purpose 0.5 mL (12.5% solid) of PSMS microspheres were suspended in 5 mL of water or ethanol in a 30 mL centrifuge tube followed by addition of 5 mL of prefabricated colloidal particles. The resulting mixture was centrifuged and the supernatant decanted followed by at least two washings with water or ethanol. The sequence was repeated until the colloids were exhaustively deposited as observed by the persistence of the color of the colloids in the supernatant (confirmed by UV-vis spectrum of supernatant).

Method 3. Colloid Formation by Controlled Hydrolysis Technique. A PSMS suspension (0.1 mL) (2.65% by mass, average diameter 0.913 μm Polybead amino microspheres or 2.63% by mass, average diameter 1.941 μm Polybead carboxylic acid-derivatized microspheres, Polysciences, Inc.) was added to a previously prepared solution of sodium tetrachloropalladate (10 mL). The concentration of the sodium tetrachloropalladate solution was varied from 0.008 to 0.2 M. The pH of the tetrachloropalladate solution was adjusted by the addition of aqueous KOH.

The suspension was stirred overnight. After separation from the tetrachloropalladate solution via centrifugation, the microspheres were resuspended in 5 mL of deionized water and reduction was performed by 0.02 M aqueous hydrazine (5 mL). After 1 h of stirring at ambient temperature, the microspheres were washed several times to remove excess reducing agent.

Growth of Multilayers of ZrPV(Cl) onto Metal-Derivatized PSMS. For this purpose the metals were derivatized on the surface of PSMS by either method 2 or 3. The metal-immobilized microspheres were then dried under vacuum and multilayers were grown according to the following steps.

Step I. Metal-derivatized microspheres (50 mg) and a 1 mM 4-mercaptobutylphosphonic acid solution in ethanol (5 mL) were stirred under argon overnight. The solid was centrifuged and washed three times with ethanol and finally with water.

Step II. The microspheres from step I, with a 20 mM aqueous solution of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (5 mL) were stirred under argon for 3 h. The zirconium solution was removed by decanting the supernatant after centrifugation followed by sonication and centrifugation twice with water to remove residual Zr^{4+} from solution.

Step III. To the dispersed solution from step II in 2 mL of water was added a 1 mM aqueous *N,N*-bis(2-phosphonoethyl)-

4,4'-bipyridine dichloride (PVCl: phosphonate viologen chloride) solution (5 mL) in water, and the mixture was heated under argon at 60 °C for 6 h. The suspension was then centrifuged and washed four times with water.

Step IV. Steps II and III were repeated twice more to have three layers each of Zr^{4+} and PVCl.

Result and Discussion

We have investigated several different methods for depositing metal particles onto latex beads. The beads were purchased with either carboxylic acid or amine groups on the surface of the beads. The functional groups are very important in controlling the association of the metal particles onto the beads. The first two methods involve the association of preformed colloids onto the beads, while the third involves reduction of the metal on the surface of the latex particle.

Method 1. Electrostatic Deposition of Metal Colloids. The first method we have employed is electrostatic deposition of preformed anionic colloidal particles onto a polycationic surface. This method has been previously demonstrated on planar surfaces for use in surface-enhanced Raman scattering (SERS).²⁹ The substrate in these studies was derivatized with amine or thiol groups, for example, before treatment with the anionic metal colloid suspension to give the surfaces a net charge. Repeated treatment of the surface with the metal colloid suspension and polyelectrolyte solutions leads to controlled growth of the metal particles on the planar surface.

The surface of carboxylic acid-derivatized PSMS is made anionic by treatment of the spheres with basic solution. The anionic PSMS sample is washed with deionized water and treated with a solution of poly(allylamine hydrochloride) (PAH), followed by another extensive wash to remove any unbound PAH. The PAH coats the surface of the latex spheres, producing a cationic surface onto which the anionic Au colloids are easily deposited. When the red Au colloidal suspension is exposed to a slurry of the white PSMS coated with PAH, the red color of the solution immediately disappears and the PSMS become purple. A second treatment of the sample with a fresh Au colloid suspension leads to complete discoloration of the red suspension. Au can be exhaustively deposited onto the PAH/PSMS surface via exposure to the Au suspension until the red color of the colloidal suspension persists (typically three to four treatments). Exhaustive metalation can be followed by deposition of another layer of PAH. No appreciable amount of Au is seen to dissociate from the surface by UV-vis spectroscopy of the remaining PAH solution. The observation that more Au can be successfully deposited onto the sphere after treatment with PAH is evidence for successful PAH deposition. The deposition of Au onto aminated PSMS is similarly attained via treatment of the amine surface with HCl, followed by deposition of a polyanion [poly(sodium-4-styrene sulfonate), (PSS)], a polycation (PAH), and Au colloids. It

is important to note that no Au deposition takes place under these conditions when the surface of the PSMS is not functionalized (i.e., beads are pure polystyrene), nor is Au deposited if the beads are anionic or even if the beads are cationic but in the absence of cationic polymer (i.e., a protonated amine PSMS surface does not bind Au colloids).

These studies have been carried out using 1–3 μm diameter spheres such that the overall diameter of the sphere is not increased appreciably upon coating even 15–20 layers of polymer/oligomer/metal since the deposited layers presumably have a one monolayer thickness. The spheres have been examined by EDX to confirm the presence of Au and by SEM (10–60K magnification) to show the overall uniformity of metal particles on the surface (Figure 1). Cross-sectional TEM has also been performed to indicate the uniformity in the shape and distribution of the colloids (Figure 2).

Whereas this method of Au deposition onto a pre-treated PAH surface is successful for both cross-linked and non-cross-linked spheres, the deposition of Pd colloids is not observed under these conditions. Upon exposure of PAH-treated spheres to anionic Pd colloids, no Pd deposition is evident via SEM/EDX.

Having shown that metals and polyelectrolytes are easily coated onto the PSMS, we have begun to examine other electronically interesting polymers with properties that might assist in catalysis. One such polyelectrolyte that has been synthesized is the octacationic tetrameric viologen, viol_4 [$\text{CH}_3-(^+\text{NC}_5\text{H}_4-\text{C}_5\text{H}_4\text{N}^+-\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2)_3-^+\text{NC}_5\text{H}_4-\text{C}_5\text{H}_4\text{N}^+-\text{CH}_3$] Cl^-_8 . For solubility reasons, we have limited ourselves to the tetrameric species, although our hope is that this oligomer might be used interchangeably with much larger polycations such as PAH. However, the colloids appear to have a larger affinity for associating with viol_4 than for PAH. As a result, deposition of colloidal particles onto the PAH-functionalized PSMS directly followed by exposure to the viologen results in removal of Au particles from the surface and formation of a metal-viologen complex in solution. To circumvent this problem, it has been necessary to first deposit viol_4 followed by the metal species. At this point, the surface is not mechanically stable (i.e., stable toward sonication) and must be carefully protected by adding multiple layers of high MW polycation/polyanion atop the metal. Once the colloids are embedded securely in the polymer layers, the spheres can safely be sonicated to remove excess polyelectrolyte (i.e., leftover citrate from the colloidal preparation). This method can be used to deposit both Au and Pd. Figure 3 shows SEM and TEM micrographs of Pd-derivatized PSMS prepared in this manner. The polymer layer, used here to anchor the Pd particles onto the PSMS, may ultimately prevent the use of the metal particles for catalysis. If the polymer layer is dense it may prevent substrate from reaching the metal particles. Growth of active film on the top of PSMS-supported metal particles will alleviate this problem and will be discussed below.

Method 2. Reaction of Preformed Colloids with Uncharged Spheres. Metal colloidal synthesis for this study was accomplished by two different methods: citrate reduction and sonochemical reduction using

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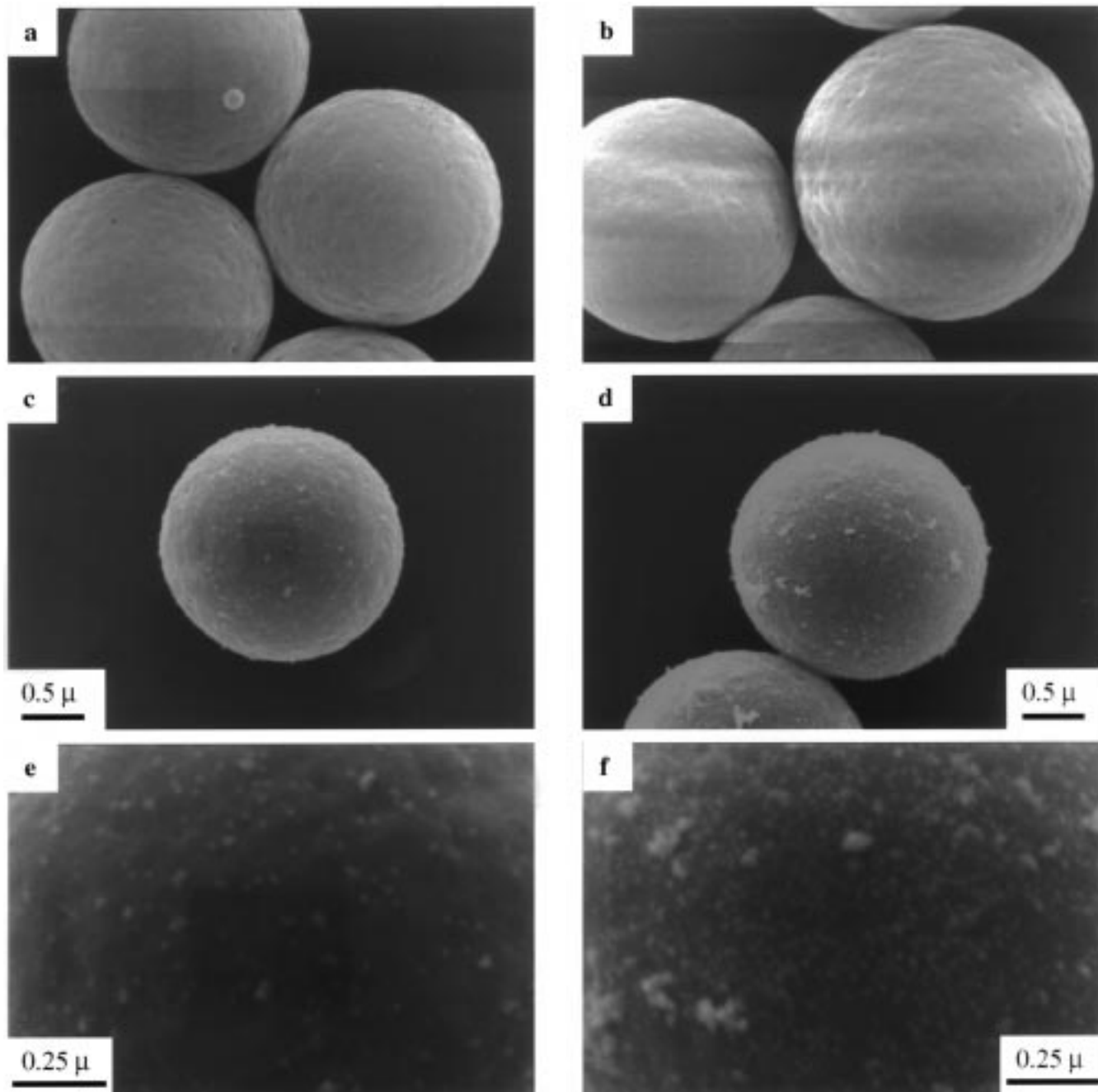


Figure 1. SEM images of (a) underivatized carboxylic acid-derivatized PSMS, (b) carboxylic acid-derivatized PSMS with deposited PAH, (c) carboxylic acid-derivatized PSMS with PAH and one treatment of Au colloid (magnification 20 000), (d) carboxylic acid-derivatized PSMS with PAH and exhaustive treatment with Au colloid (magnification 20 000), (e) carboxylic acid-derivatized PSMS with PAH and one treatment of Au colloid (magnification 60 000), and (f) carboxylic acid-derivatized PSMS with PAH and exhaustive treatment with Au colloid (magnification 60 000).

alcohols as reducing agent. The citrate reduction method allows for better control of particle size since citrate ions ($C_6H_9O_8^{3-}$) play the role of both reducing agent and protecting group. However, as previously reported, due to presence of citrate on the colloid surface, the reactivity of such colloids is diminished.³⁰ To compare the reactivity of citrate stabilized colloids with that of colloids lacking protective groups, a sonochemical method of synthesis is employed in which ethanol is used as the reducing agent.^{19,28} In sonochemical syntheses, reactive radicals are formed which reduce the metal ions to zerovalent metal species, which then grow by agglomeration to form metal colloids of a particular size.

These colloids are stable for months even in the absence of a protecting agent (e.g., citrate, polypyrrolidone, etc.). The particle size is generally larger than those formed via the citrate reduction method; citrate reduction typically gives particle sizes of 12.5 nm, while the sonochemical method gives particles ranging from 15 to 30 nm depending on reduction conditions. The size of sonochemically generated colloids is highly dependent on reaction conditions such as pH and the polarity of the medium. For instance, the particle size of colloidal gold can be easily varied by changing the pH of the presonicated solution from slightly acidic to neutral. The UV-vis spectra of colloidal suspensions produced at

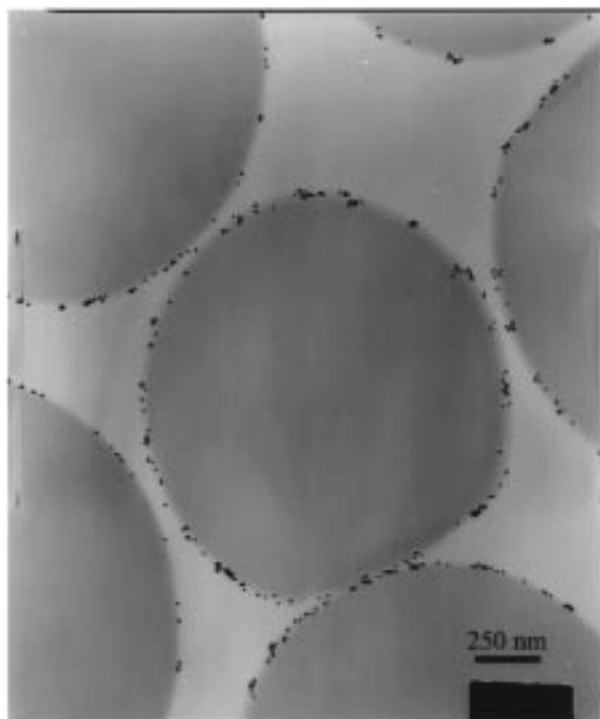


Figure 2. TEM of carboxylic acid-derivatized PSMS after treatment with PAH/Au colloids.

both acidic and neutral pH as a function of sonication time show that as the pH of the presonicated solution is increased, a shift of the surface plasmon band to higher wavelength (529 nm \rightarrow 535 nm) is observed which corresponds to an increase in the mean particle size of the colloids. Increasing the pH of the presonicated solution above 7.0 has no further effect on the particle size. However agglomeration and precipitation of the colloids occur in basic media.

The sonication method is not useful for the preparation of Pd colloids since the particles become quite large and precipitate immediately upon formation. If, however, PdCl₄²⁻ is sonicated in the presence of amine-functionalized PSMS, uniform metal deposition does occur (Figure 4c). The colloidal Pd formed on the surface in this case is \sim 8 nm. The citrate reduction method in the presence of functionalized PSMS yields palladium colloids on the PSMS surface (8.5 nm mean diameter) with a uniform size distribution. The citrate reduction method in the absence of PSMS yields palladium colloids (8.5 nm mean diameter) with a uniform size distribution (Figure 4a and 4b—for preformed colloids).

The pendant amine groups of PS-NH₂ show a large affinity for both Au and Pd nanoparticles as evidenced by their respective TEM micrographs (Figures 4 and 5). In all cases, the adsorption of colloids is instantaneous upon exposure of the surface-functionalized PSMS to the aqueous colloidal suspension. The metal particles are strongly bound as proven by a sequence of successful sonications and subsequent layer growth. The gold colloids with or without an organic protecting group (citrate vs sonochemical synthesis, respectively) show different adsorption affinity toward the amine-functionalized microspheres. The coverage in the case of sonochemically synthesized Au colloids is much greater than for the citrate-reduced analogue. Perhaps the

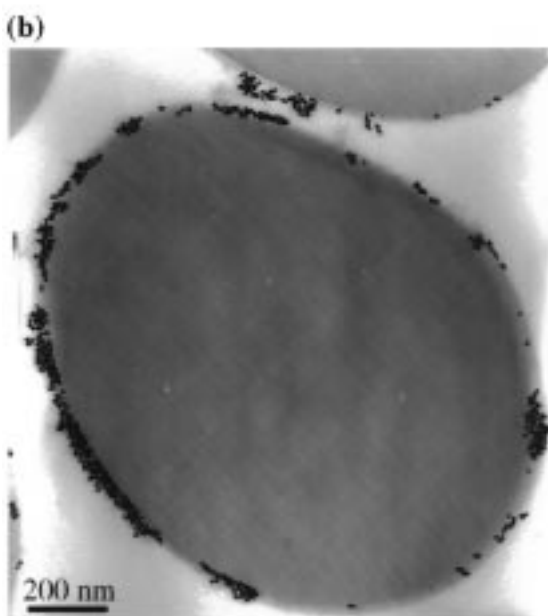
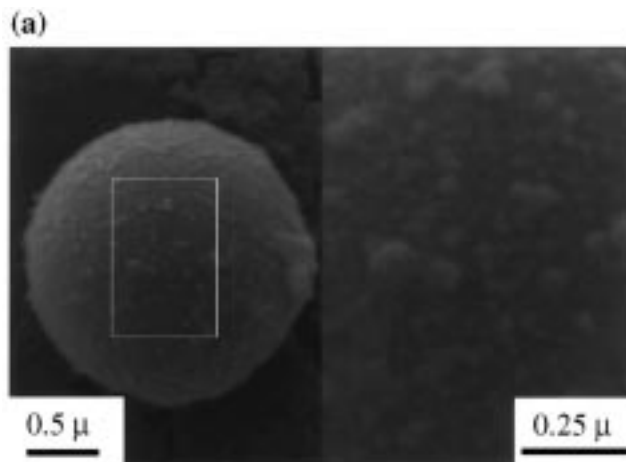


Figure 3. (a) SEM (magnifications: left, 20K; right, 60K) and (b) TEM of carboxylic acid-derivatized PSMS after treatment with viol₄/Pd colloid/PAH + PSS (five layers each).

presence of citrate ion on the surface of the colloids makes the metal inaccessible to the amine surface. This is observed as a general phenomenon since Pd surface coverage of aminated PSMS increases dramatically for sonochemically generated colloids where no organic protecting group is used (compare Figure 4b and 4c).

UV-Vis and Diffuse Reflectance Measurements. In the elastic scattering of light from small particles, the extinction coefficient³¹ is dependent on (1) the size of particle relative to the wavelength of light being used; that is, the ratio of $2\pi a/\lambda$, where a is the particle size and λ is the wavelength; and (2) the refractive index of the irradiated material. The extinction spectrum of small particles has two components, absorption and scattering. Since the light scattering properties of

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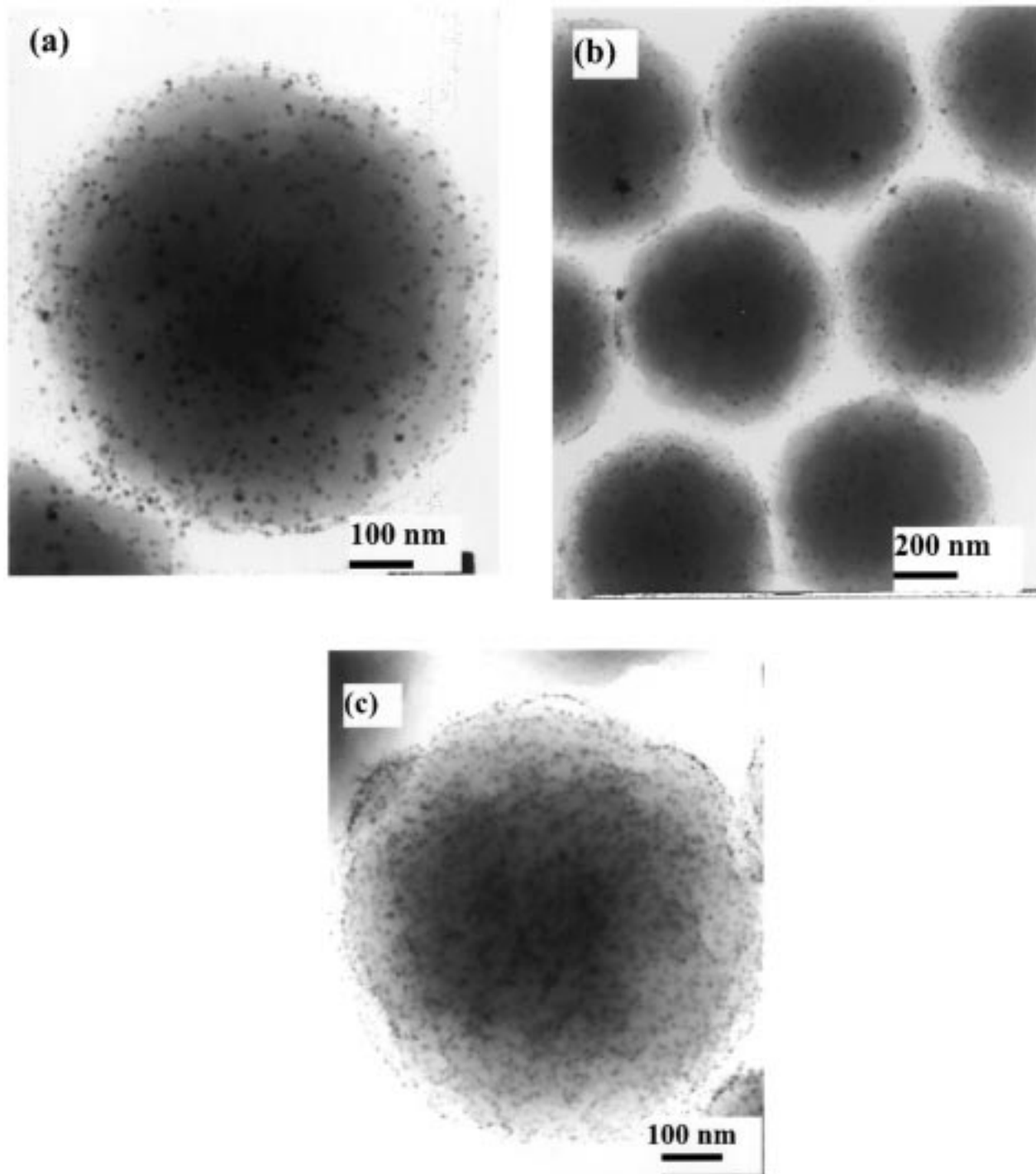


Figure 4. TEM micrographs of amino-functionalized PSMS covered with Pd nanoparticles: (a and b) prefabricated using citrate reduction ($\text{Pd} = 8.5 \text{ nm}$) and (c) in situ formation of colloids by reduction of PdCl_4^{2-} in the presence of aminated PSMS using sonochemical method.

colloidal particles depend on the chemical composition and structure of the outermost layer of the particles, gold or any other metal-coated polystyrene particles, will have the same light-scattering properties as finely dispersed pure gold or metal particles of the same size. Figure 6 compares the visible diffuse reflectance spectrum of colloidal gold solution along with suspension of gold-immobilized polystyrene microsphere. It can be observed from Figure 5 that even for a small coverage of colloidal gold on amine-functionalized polystyrene microsphere, a prominent plasmon band is seen in the spectrum as a shoulder at $\sim 680 \text{ nm}$. The shift in the

plasmon band is most likely due to a colloidal aggregation on the surface of microsphere, which is supported by the TEM images.

Growing Layers of Zirconium and Viologen Bisphosphonate Chloride (PVCL) on $\text{PSNH}_2\text{-Pd}$. To demonstrate the use of the above-mentioned metal-immobilized microspheres as a support for the subsequent growth of layers of donors and/or acceptors, multilayers of Zr^{4+} and viologen are grown onto palladium which has been adsorbed onto the surface of PS-NH_2 . The methodology for this growth is given in the Experimental Section, and is closely related to the one developed for growth

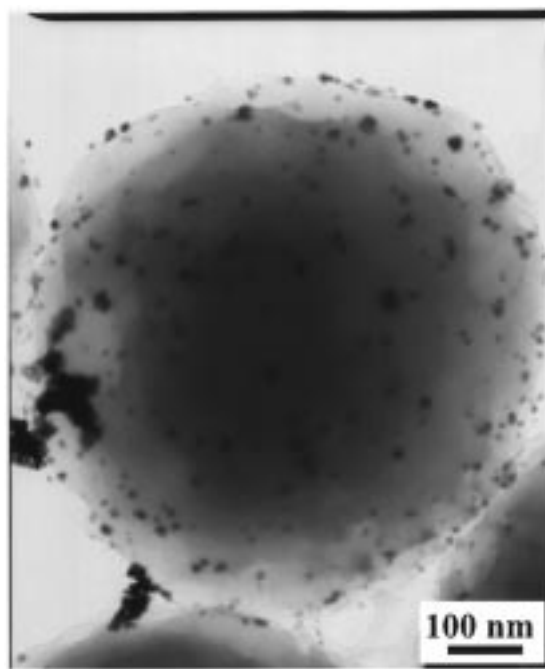


Figure 5. Surface coverage of amine-functionalized PSMS with Au colloids prepared via sonochemical method. The coverage is much greater than for citrate reduced colloids.

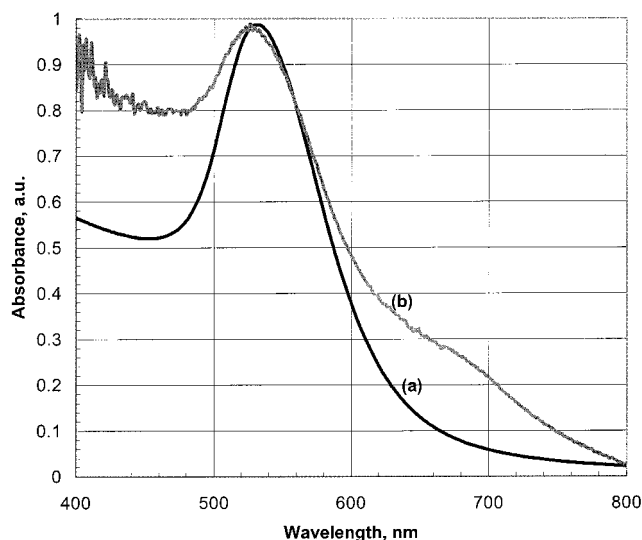


Figure 6. Visible diffuse reflectance spectra of (a) Au colloids and (b) aminated PSMS with Au-immobilized on surface.

of metal bisphosphonate SAMs on planar substrates.^{2,32} Figure 7 shows a TEM micrograph of a sample before and after layer growth. Almost no difference is observed in the surface coverage of palladium nanoparticles which confirms that the adsorption forces between surface amines and palladium particles are strong, and the subsequent layer growth does not detach the palladium from the microsphere surface. This was later confirmed by ICP-MS which gave almost same palladium loading (0.10 vs 0.12 mmol/g, respectively) in both the cases. In the case of above layered systems, ICP-MS also gave a phosphorus loading of 0.07 mmol/

g. Spot EDX analysis confirms the presence of zirconium, phosphorus, chlorine, and palladium on spheres where layers of ZrPV(Cl) have been grown atop the adsorbed Pd particles whereas only palladium is found on metalated spheres without any subsequent layer growth. Presence of viologen is also confirmed by the characteristic blue color of reduced viologen³³ when H₂ is bubbled through a suspension of the multilayered microspheres under anaerobic conditions. The blue color is extinguished instantaneously on exposure of the blue suspension to air.

Method 3. Controlled Hydrolysis. A third method for preparation of supported metal catalysts begins with the deposition of a precursor such as a metal oxide or hydroxide onto the desired surface. Reduction of these precursors leads to formation of metal aggregates. One advantage of this technique is the absence of organic protecting groups on the surface of the metal particles. In preformed colloids, this organic shell is the inevitable consequence of the presence of stabilizing agents during colloid formation. These organics can be removed from silica-supported colloids via high-temperature treatment, but this does not work for PSMS-supported colloids since PSMS are not stable at high temperature. This problem is alleviated when the metal salt itself is first associated with the support and then reduced directly on the surface thereby eliminating the need for any protective organic species.

For precursor deposition, the technique of controlled hydrolysis³⁴ was chosen. This method consists of the preparation of a concentrated solution of metal ions (e.g., PdCl₄²⁻) followed by adjustment of the pH such that the rate of the metal hydrolysis reaction³⁵ in bulk solution is extremely slow. Introduction of a support with polar surface groups (e.g., PSMS with surface-functionalized -NH₂ groups) leads to acceleration of the hydrolysis reaction near the functionalized surface. Formed nanoparticles of hydrated metal oxides are immediately adsorbed onto the surface of the microspheres.

Figure 8 shows a typical amino-functionalized PSMS covered with Pd nanoaggregates according to method 3. The average Pd particle size in this case is ~3 nm. Pd coverage is uniform both in particle size and distribution. Comparable coverage is also observed for metal similarly deposited onto carboxylic acid (-COOH)-, hydroxy (-OH)-, and thiol (-SH)-functionalized PSMS.

Electron microscopy of nonreduced microspheres (after stirring overnight in a solution of PdCl₄²⁻ and OH⁻ ions) was performed in an attempt to identify the oxidized metal species attached to the surface. The resulting micrograph is shown in Figure 9. EDX analysis of PS-NH₂ treated with the palladium salt shows that particles adsorbed onto the surface are composed of palladium and oxygen (oxygen content is at least 50 atomic %). EDX analysis of reduced samples does not show the presence of a significant amount of oxygen. These observations support the proposed mechanism³⁵

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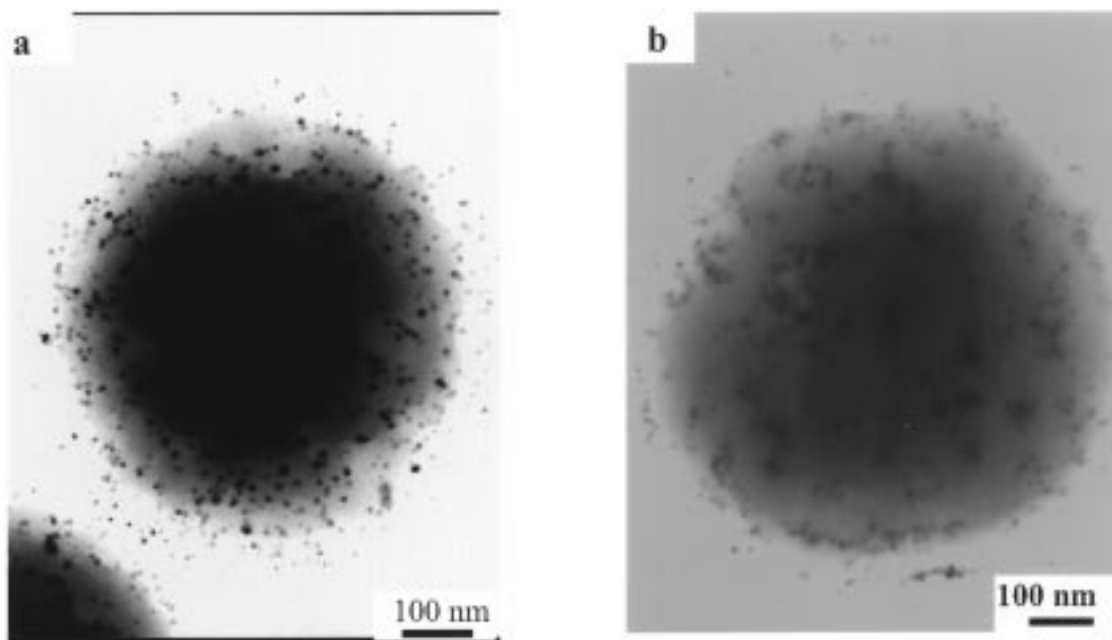


Figure 7. TEM micrographs of Pd on aminated PSMS: (a) before layer growth and (b) after growing three layers each of Zr and PV(Cl).

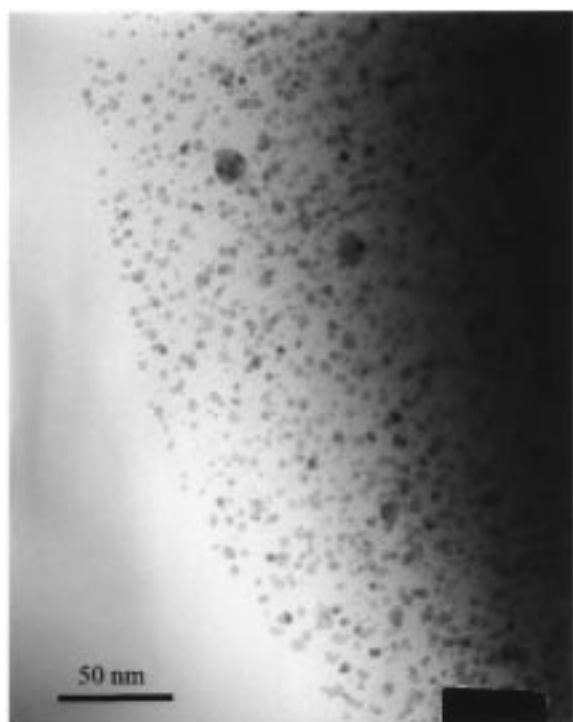


Figure 8. Typical Pd coverage of amine-functionalized PSMS obtained by controlled hydrolysis ($[\text{PdCl}_4^{2-}] = 0.02 \text{ M}$, $[\text{OH}^-] = 0.002 \text{ M}$) after reduction by aqueous hydrazine. Magnification: 300 000.

for formation of the metal particles through adsorption of oxide nanoparticles to the surface. The color change of microspheres from white (before any treatment) to brown (after stirring in the metal salt solution) and finally to black (after reduction) also supports these conclusions.

It was also found that by varying the pH of the metal solution (as well as the time of exposure and concentration of PdCl_4^{2-}) it is possible to control the degree of

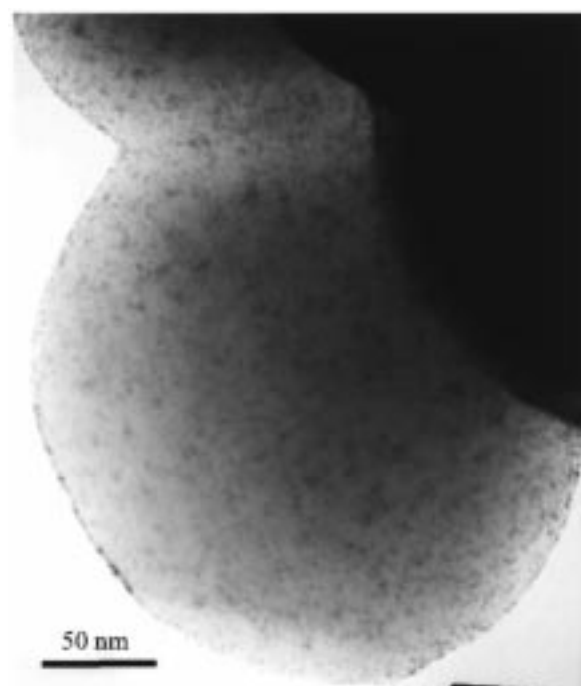


Figure 9. Surface carboxylic acid-derivatized PSMS covered with palladium oxide nanoparticles prior to reduction. Magnification: 300 000.

coverage of the microspheres and the size of nanoaggregates. As shown in Figure 10, the average size of aggregates increases from 3 nm for $[\text{OH}^-] = 2 \text{ mM}$ (Figure 10a) to 5 nm for $[\text{OH}^-] = 10 \text{ mM}$ (Figure 10b). For more basic solutions (Figure 10c), metal coverage and particle size become irregular due to increased rate of hydrolysis of PdCl_4^{2-} , resulting in the presence of more metal oxide in solution.

Microspheres coated with palladium nanoaggregates obtained by the controlled hydrolysis method are stable toward magnetic stirring or ultrasonication. It should also be noted that microspheres covered with metal

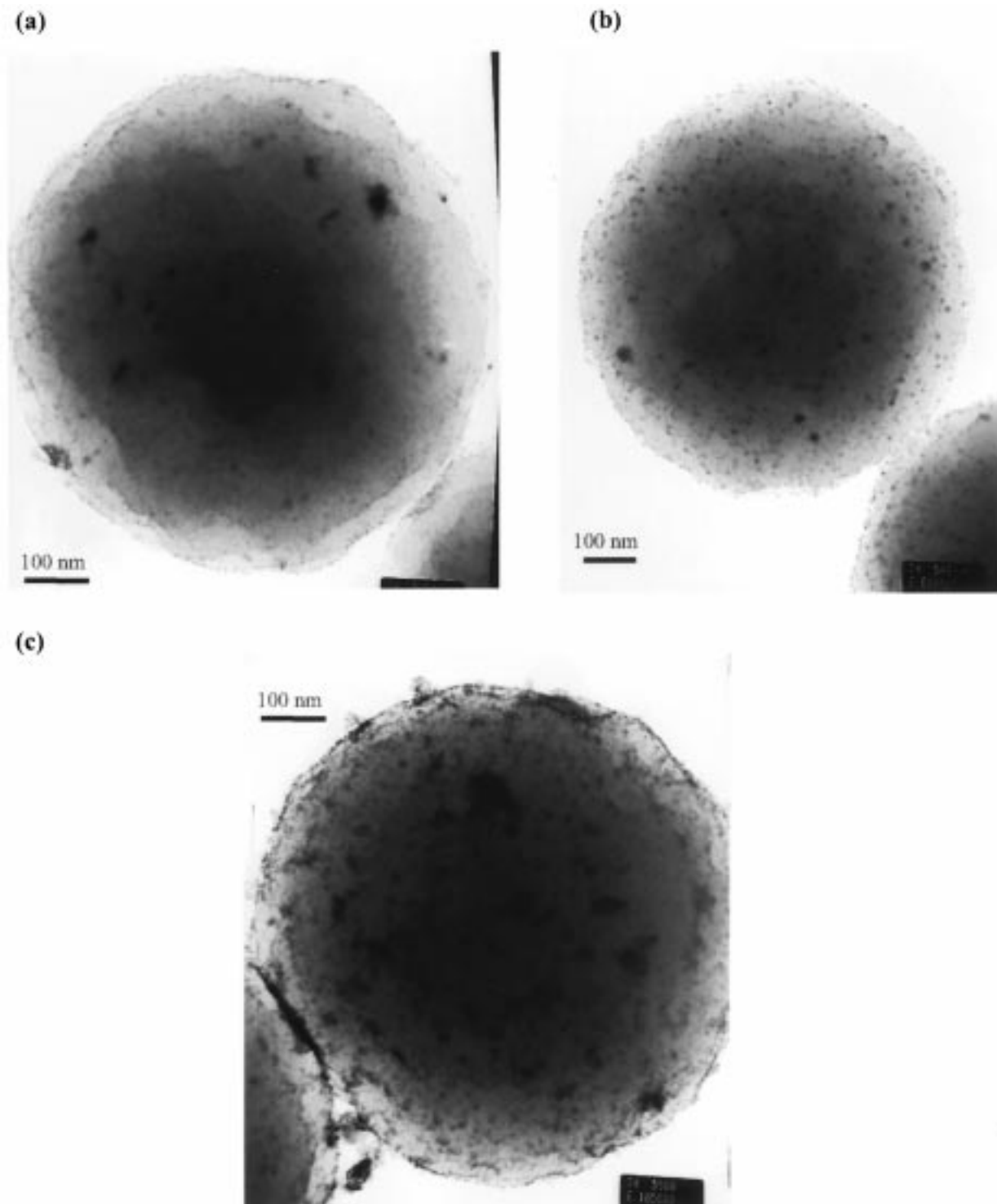


Figure 10. TEM micrographs of Pd-covered PSMS from solutions of different $[\text{OH}^-]$, $[\text{PdCl}_4^{2-}] = 20 \text{ mM}$: (a) $[\text{OH}^-] = 2 \text{ mM}$, (b) $[\text{OH}^-] = 10 \text{ mM}$, (c) $[\text{OH}^-] = 50 \text{ mM}$. (Magnifications: (a and c) 105 000 and (b) 85 000).

aggregates by this method can be used as supports for growth of SAMs, as described above for materials made by method 2.

Conclusions

We have demonstrated three different methods for anchoring fine metal particles (2–9 nm) onto the surface of polystyrene microspheres. One method involves primarily electrostatic interactions between the microsphere and the metal particles, while the other two involve stronger interactions. In all three cases, the

metal particles are bound very strongly to the surface of the microsphere and are not removed by either extensive stirring or sonication. The electrostatically bound system is an excellent way to make high surface area structures by electrostatic depositions. We have demonstrated that the particles remain bound when added polyelectrolytes are built up on top of the metal particles, making it possible to use these materials to build complicated heterostructures by electrostatic deposition methods. If the added groups have too strong an interaction with the metal particles, such as the viologen

tetramer with gold or palladium, the metal particles are stripped from the microsphere. The latter two methods, which involve binding to uncharged microspheres, led to systems that can tolerate much more harsh chemical treatment without loss of the metal particle from the PSMS surface. We have demonstrated that they can be used as substrates to grow metal bisphosphonate thin films by a sequential growth method. We are currently examining materials built on these metal-coated PSMS

as heterogeneous catalysts and photoelectrochemical catalysts.

Acknowledgment. The authors thank The Global Photonic Energy Corporation and the Air Force Office of Scientific Research MURI (Program Manager Dr. Charles Lee) for financial support of this work.

CM9900352