

Poly(Vinyl Pyridine) as a Universal Surface Modifier for Immobilization of Nanoparticles

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Metal, metal oxide, and plastic surfaces were modified with poly(vinylpyridine) using adsorption, spin-coating, and dip-coating techniques and various metal, semiconductor, and dielectric nanoparticles were subsequently attached. Prior to the modification, the substrates were treated with glow discharge plasma for cleaning purposes and to introduce surface functional groups that are capable of interaction with the polymer. UV-vis absorption spectroscopy, atomic force, and electron scanning microscopies were used to characterize polymer layers and layers of immobilized nanoparticles. The surface modification with poly(vinylpyridine) via adsorption technique is suggested as a simple, effective, and highly versatile method for the preparation of single, mixed, and multilayered assemblies of various nanoparticles on different substrates.

Introduction

Nanoparticles exhibit a range of physical and chemical properties that are promising for potential applications in a new generation of optical, electronic, and chemical devices. Many of these devices will require immobilization of nanoparticles in a single layer or in multilayers on conducting or dielectric surfaces. The immobilization is often accomplished through the surface modification with functional groups that provide attractive interaction to nanoparticles. Functional groups such as thiol, pyridyl, amino, and carboxy can be used to immobilize metal nanoparticles on various oxide surfaces. The modification of glass surfaces with thiol containing siloxides was first used to improve the adhesion of vacuum-deposited gold films.¹ Later, this approach was extended to the immobilization of silver, gold, and other metal nanoparticles on glass, quartz, silicon, ITO glass, and so forth surfaces.^{2–5} The thiol group forms a covalent bond with metal nanoparticles resulting in self-assembled structures that exhibit unique electrical and optical properties.⁶ Bifunctional organic layers in which one functionality is used for anchoring to substrates and the other one for binding of particles was suggested as a generic method for the immobilization of metals nanoparticles on surfaces.⁷ The electrostatic attraction between oppositely charged entities can also be exploited for the immobilization of nanoparticles. Pioneered by Detcher,⁸ linear polycations and polyanions were used to form alternating multilayers of metal, semiconductor, and dielectric nanoparticles.^{9–14} Polymers can be very efficient adhesives for immobilization of nanoparticles because each molecule provides many binding sites for simultaneous interaction with particles and a substrate. This cooperative interaction results in overall strong binding even though each individual group may exhibit only weak affinity. The interactions need not be electrostatic; hydrogen bonding, charge-transfer, and other interactions can be used to form various nanostructured assemblies.^{15,16}

Poly(vinylpyridine) (PVP) is an attractive polymer for immobilization of nanoparticles because of the strong affinity of pyridyl group to metals and because of its ability to undergo hydrogen bonding with polar species. In addition, PVP can

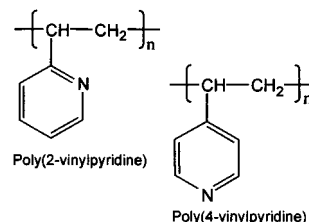


Figure 1. Structural formulas for poly(2-vinylpyridine) and poly(4-vinylpyridine).

interact electrostatically in quaternized or protonated forms with charged surfaces.^{17,18} PVP was used to prepare composite materials in which colloidal gold was dispersed in the polymer matrix. These materials were studied as models for the diffusion of metal particles in polymers.^{19,20} In the present paper, we investigate the immobilization of metal, semiconductor, and dielectric nanoparticles on a variety of substrates modified with the neutral form of poly(vinylpyridine). These substrates include metal films, glass, quartz, alumina, and indium-tin oxide (ITO) coated glass as well as plastic surfaces such as polystyrene, polycarbonate, poly(dimethylsiloxane), polyethylene, and so forth. Following mild oxidation in plasma glow discharge, we were able to modify the surface of practically any organic material with PVP and subsequently attach nanoparticles. Poly(tetrafluoroethylene) was the only type of surface to which the immobilization of nanoparticles via this procedure was unsuccessful. On the basis of this study, we suggest PVP as an efficient surface modifier for the immobilization of metal and nonmetal nanoparticles to produce different single- and multilayered assemblies.

Materials and Methods

Poly(2-vinylpyridine) ($M_w = 159,000$ and $37,500$) and poly(4-vinylpyridine) ($M_w = 160,000$) (Aldrich) were used as received (Figure 1). The polymers were dissolved in reagent alcohol (HPLC, Fisher) and the solution was used for the preparation of polymer films on various substrates by adsorption, spin-coating, and dip-coating methods. Silver nanoparticles were prepared in ultrapure, $18\text{ M}\Omega$ water from Milli-Q water system (Millipore). P25 (Degussa Corp.) titanium oxide was used in

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the study. Indium–tin oxide coated glass (100 Ω/cm) was purchased from Delta Technologies, Limited. Prior to the deposition of polymer films, silicon, glass, and quartz substrates were cleaned for 15 min in freshly prepared 1:3 mixture of 30% H_2O_2 and H_2SO_4 (piranha solution) followed by drying in the stream of the nitrogen gas. *Caution! Piranha solution is a very strong oxidizing agent and reacts violently with organic compounds. It should be handled with extreme care.* Plasma cleaner and sterilizer PDC 32G (Harrick) was employed for cleaning of alumina filters and for the oxidation of polymer substrates prior to the deposition of PVP layers.

Silver nanoparticles were coated with silica using the following procedure.²¹ Metal particles were transferred to propanol by precipitation via centrifugation. 20 mL of Ag particles in propanol (optical density 6 at 520 nm) was mixed with 500 μL of ammonium hydroxide (Fisher) and 10 μL of tetraethoxysilane (Gelest). The mixture was incubated overnight in a closed container at room temperature under vigorous stirring. Coated particles were washed several times with propanol and transferred to water.

Spin-coating was performed on Headway Research Inc. instrument at 3000 rpm. D-3400 (Mayers, Feintechik) dipper operated at 4.5 mm/s linear velocity was employed for dip-coating.

UV–vis absorption spectra were measured on spectrophotometer UV-2501PC (Shimadzu). Two instruments were used for atomic force microscopy (AFM). The first one Dimension 3100 (Digital Instruments, Veeco Metrology Group) microscope was employed in tapping mode to record topographic images in ambient air and underwater of silver nanoparticles adsorbed on PVP modified silicon wafers. Silicon tips (spring constants ca. 50 N/m) and silicon nitride tips (spring constant ca. 0.25 N/m) were used for scanning in air and water, respectively. Cantilever holder for scanning in fluids from Digital Instruments (Veeco Metrology Group) was used for imaging in water. Silver nanoparticles adsorbed on PVP modified alumina filters (Anodized 0.2 μm pore size, Whatman) were imaged on AutoProbe CP Research (ThermoMicroscopes) AFM. Noncontact mode and silicon tips with spring constant of ca. 3.0 N/m were employed. All reported images were acquired at scan rates in the range 1–2 Hz. Scanning electron microscopy images were obtained using field emission Hitachi S-4700 microscope.

Results and Discussion

Pyridine in the neutral form binds strongly to metals via the formation of the covalent bond through the donation of the lone pair of electrons of the nitrogen atom. This σ -bonding requires the aromatic ring to adopt perpendicular orientation to metal surfaces. When the plane of the aromatic ring is parallel to the surface, π -stacking type interaction can take place. Both orientations of pyridyl groups were confirmed by surface-enhanced Raman spectroscopy studies of PVP on silver.^{22–24} Adsorption of PVP from dilute solutions results in the flat orientation of the aromatic ring, whereas high concentrations of the polymer yield predominantly σ -bonding and normal orientation with the nitrogen atom down to the metal surface. At intermediate concentrations of the polymer, both types of interaction can produce tilted orientation of aromatic rings relative to the surface. Pyridyl groups of PVP can also interact with various nonmetallic polar surfaces especially those terminated with amines, carboxyl, hydroxyl, and other groups capable of undergoing hydrogen bonding. The precise nature of this interaction depends on the presence of water in the solvent. For example, when the polymer is deposited on glass and silica from

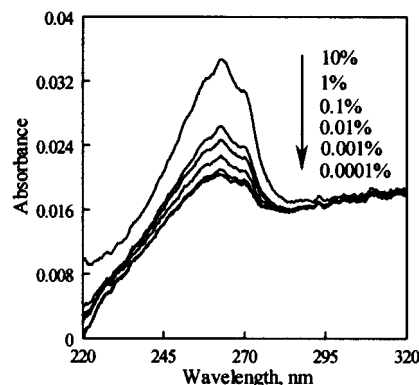


Figure 2. UV absorption spectra of PVP films on quartz substrates adsorbed from alcohol solutions of different polymer concentrations. The spectra correspond to the absorption from two sides of substrates.

an absolute alcohol solution, the surface is terminated with protonated silanol groups that form a hydrogen bond with the nitrogen atom on the pyridyl. The addition of water will cause deprotonation of silanol groups ($\text{p}K = 3\text{--}3.4$)²⁵ and, depending on the pH, the protonation of pyridyls ($\text{p}K = 5\text{--}5.2$) resulting in electrostatic or charge-dipole type interaction between the polymer and the surface. The same consideration can be applied to other oxide and polar surfaces. It is important to emphasize that the interaction on an individual pyridyl group with the surface does not have to be strong to provide overall strong adsorption of PVP. The fact that one polymer molecule simultaneously interacts with the surface through many pyridyl groups provides an entropic advantage for the quasi-irreversible adsorption of this molecule to the surface even in the presence of strong solvents. After the adsorption, PVP molecules still have numerous unbound pyridyl groups that do not participate in the interaction with the surface and that are capable of binding of nanoparticles. Essentially, only one type of functionality (pyridyl group) is required for the adhesion to surfaces and the binding of nanoparticles. Because of the strong adhesion of PVP to many metal and nonmetal surfaces, this compound is suggested as a universal monofunctional surface modifier for the immobilization and assembling of different nanoparticles.

In a typical modification procedure via adsorption, glass, silica, silicon, and alumina substrates were cleaned in a freshly prepared piranha solution for ca. 15 min. Adequate results were also obtained after cleaning the substrates in oxygen (air) plasma for several minutes or until the surface appeared uniformly hydrophilic. Because of its simplicity, rapidness, and the absence of generated toxic waste, this method is highly preferred over the piranha solution. Plasma treatment was also used to clean ITO glass and to oxidize the surface of the plastics used in this work. Mild oxidation in oxygen plasma of polymers containing hydrocarbons results in the formation of surface polar groups including carboxyl, hydroxyl, and carbonyl.²⁶ Hydroxyl groups can be incorporated into the surface of plastics via highly reactive hydroxyl radicals that are formed during the glow discharge in residual water vapor. All these groups are believed to participate in the strong adhesion of PVP to the surface of plastics via hydrogen bonding with pyridyls. After cleaning or oxidation, substrates were immersed into the alcohol solution of PVP for various times. Even though the most reproducible results in terms of uniformity of monolayers of adsorbed nanoparticles were achieved after the overnight exposure of substrates to PVP solution, good quality films were already obtained after the first hour. The concentration of the polymer solution did not have a profound effect on the morphology of nanoparticle monolayers as long as it was selected in the range

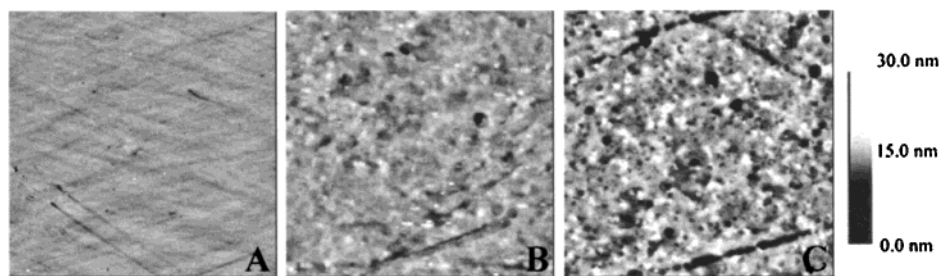


Figure 3. AFM topography images ($10 \times 10 \mu\text{m}$) of silica surface modified with PVP via adsorption method from solutions of different polymer concentrations: (A) 0.0001%, (B) 0.01%, (C) 3%.

from 0.01% to 3%. At the same time, UV–vis absorption measurements clearly indicated different amounts of PVP adsorbed on the substrate from solutions with different polymer concentrations (Figure 2). The fact that substrates with different amounts of PVP on the surface always adsorbed only a monolayer of silver nanoparticles can be explained by differences in conformations that polymer molecules adopt on the surface when adsorbed from solutions with different concentrations. It is well known that polymer molecules, when adsorbed from very dilute solutions, acquire flat conformation to maximize their interaction with the surface. In PVP, more pyridyl groups interact with the surface and fewer ones are available for the attachment of nanoparticles.²⁷ (For this reason, adsorption of PVP from less than 0.01% solutions resulted in the sharp decrease of attached nanoparticles.) As the concentration increases, the polymer accepts more globular conformation and the total number of exposed pyridyl groups that are available for the attachment of nanoparticles quickly reaches saturation providing that the entire surface is saturated with the polymer molecules. Further increase of the solution concentration results in even more globular conformation of PVP molecules and in the increase of only pyridyl groups hidden in the interior of the polymer without changing the amount of exposed groups that are accessible for interaction. Indeed, AFM images in Figure 3 clearly demonstrate progressive change of surface morphology for films deposited from solutions of different concentrations. The increase of the UV absorption in Figure 2 reflects the increase in the number of pyridyl groups hidden in the interior of the polymer and not the exposed groups that are capable of attaching nanoparticles.

After the modification with PVP, substrates were thoroughly rinsed in alcohol to remove all weakly bound polymer molecules leaving only a monolayer directly adhered to the surface. It was found that even a small amount of weakly bound polymer molecules caused the formation of aggregates of nanoparticles on surfaces, as discussed below. To improve reproducibility, PVP modified substrates were annealed at 120°C at ambient atmosphere for a few hours. After annealing, the substrates were exposed to suspensions of nanoparticles which self-assembled on the surface.

AFM images of ca. 100 nm silver particles self-assembled on PVP modified silicon wafer are presented in Figure 4. Silver nanoparticles were selected for these studies because they exhibit unique optical properties due to the excitation of the collective oscillation of electron density termed plasmons.²⁸ These properties are not only of prime interest for potential optoelectronic applications but also for allowing straightforward monitoring of the formation of nanoparticle assemblies with UV–vis spectroscopy. As can be seen from Figure 4A, silver nanoparticles formed a tightly packed (saturated) monolayer with the interparticle distance that is determined by repulsive interaction between particles in water. Exposure time and the concentration

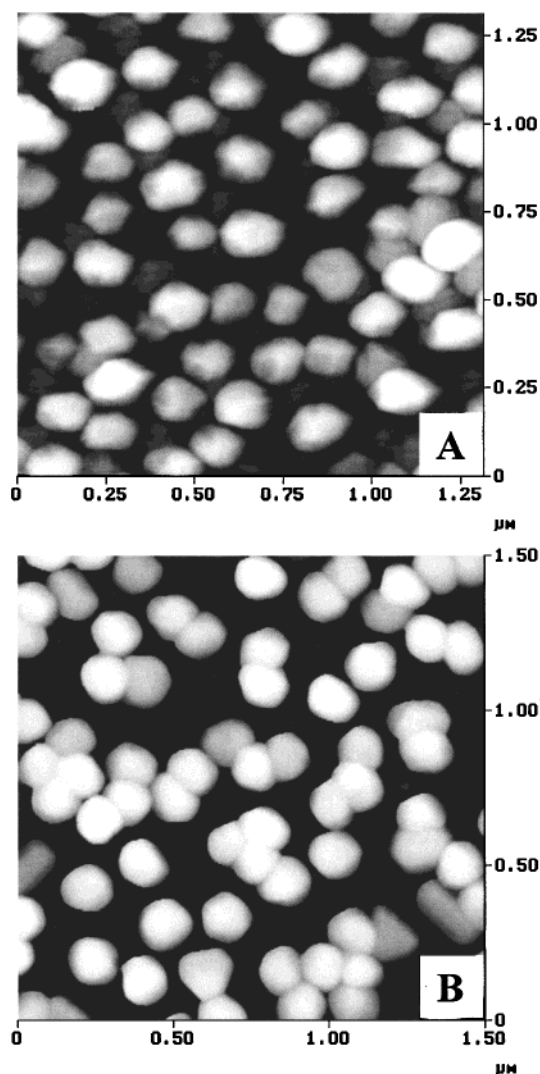


Figure 4. AFM topography images of silver nanoparticles immobilized on PVP modified silicon wafer: (A) in water, (B) in the dry state.

of the particles in the suspension controlled the density of the particles on the surface. However, the density did not exceed that depicted in Figure 4A unless another layer of PVP was deposited on top of the monolayer of silver nanoparticles and the substrate was immersed a second time into a colloidal suspension. Typically, the exposure of PVP modified substrates to a colloidal suspension of silver nanoparticles of optical density 5 under continuous mixing saturated the surface in approximately 1 h. Upon drying, silver nanoparticles underwent surface aggregation and the monolayer lost its uniformity (Figure 4B). Two factors contribute to this aggregation. First, the surface in the space between particles is covered with pyridyl groups that

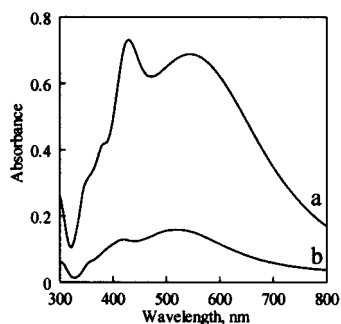


Figure 5. UV-vis absorption spectra of silver colloidal suspension in water (a) and a monolayer of silver nanoparticles assembled on PVP modified quartz surface from this suspension (b).

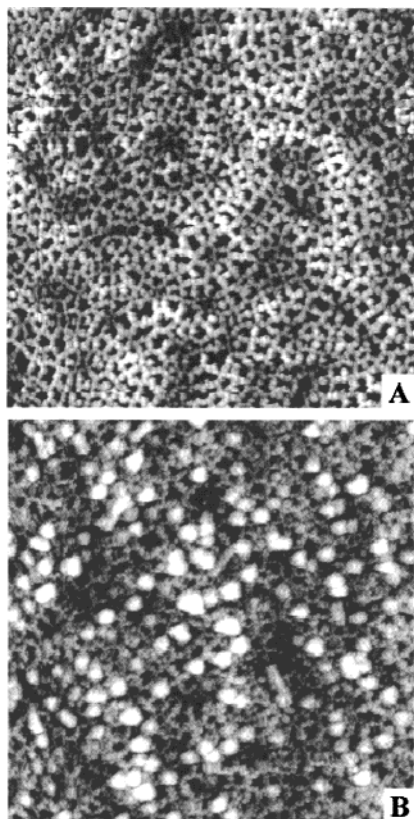


Figure 6. AFM topography images of porous alumina filters (A) and silver nanoparticles immobilized on these filters via PVP surface modifier (B).

are not directly involved in the attachment of nanoparticles but can potentially interact with these. In the absence of electrostatic repulsion between particles, the interaction with these groups will result in the diffusion of nanoparticles on the surface. Second, drying reduces electrostatic repulsion and the surface tension of evaporating water layer forces nanoparticles to clump together. Consequently, drying of substrates from solvent with smaller surface tension (e.g., alcohol) as well as blocking unoccupied pyridyl groups with metal ions reduced, but not totally eliminated, surface aggregation of silver nanoparticles. UV-vis extinction spectra of a silver colloidal suspension and the corresponding film of silver nanoparticles on PVP modified quartz slide adsorbed from this suspension are presented in Figure 5. Extinction spectra of the films that were first dried and then put back in water exhibited less pronounced plasmon maximum together with an increase on the extinction in the red spectral range—changes that typically accompany the aggregation of silver nanoparticles (spectrum is not shown).

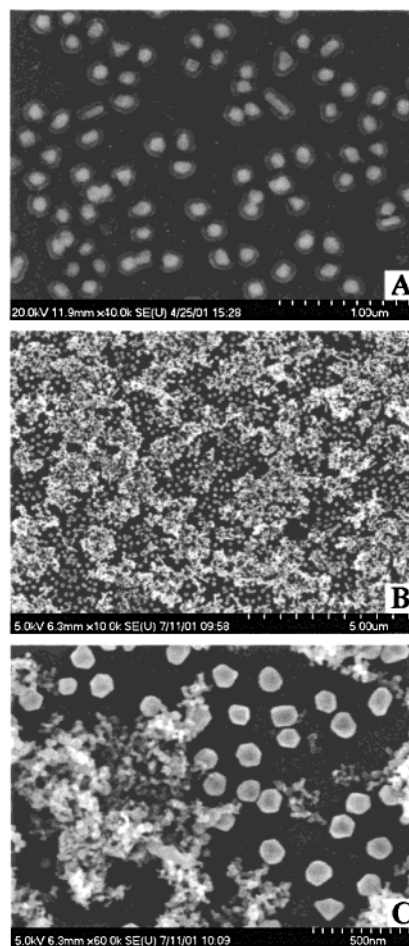


Figure 7. SEM images of a layer of silica-coated silver nanoparticles (A) and a layer of mixed titania and silver nanoparticles (B) and (C) immobilized on PVP modified, ITO coated glass.

Other oxide and plastic surfaces were modified with PVP, and various nanoparticles were immobilized. Alumina in the form of oxidized aluminum surface and in the form of porous substrate after treatment in plasma was immersed for several hours into 1% PVP solution. Followed exposure to silver colloids resulted in the surface of intense yellow color from adsorbed nanoparticles (Figure 6). In addition to silver, other nanoparticles such as gold, silica, latex, and others were attached in this way on different surfaces (Figure 7A). For many spectroelectrochemical and photochemical studies, immobilization of nanoparticles on conducting transparent substrates is required. ITO coated glass that is commonly used for such applications was modified with PVP using the above procedure, and both metal and semiconductor (TiO_2) nanoparticles were immobilized (Figure 7B and Figure 7C). It is important that neither titania nor silver nanoparticles adhere to clean ITO glass without PVP modification. Surfaces with attached nanoparticles can be exposed a second time to PVP solution followed by immersion into colloidal suspensions resulting in the formation of a second layer of nanoparticles. By repeating this procedure many times, multilayers of the same or different nanoparticles can be formed. Finally, nanoparticles can also be immobilized on the surface of many plastics modified with PVP. We attached silver, silica, and titania nanoparticles on surfaces of polystyrene, polycarbonate, polyethylene, and poly(dimethylsiloxane). Before modification with PVP, plastics were treated in plasma glow discharge to form polar groups that are capable of hydrogen bonding with pyridyl. The time of plasma treatment varied from

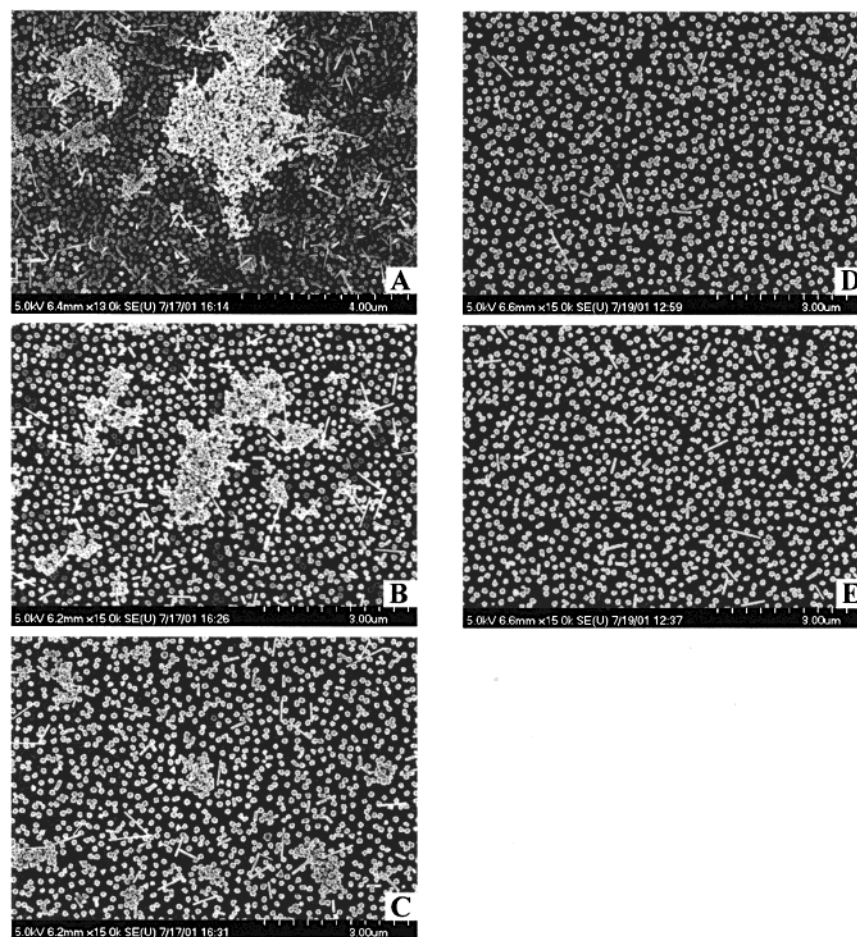


Figure 8. SEM images of silver nanoparticles immobilized on PVP modified, ITO coated glass. The modification was performed by dip-coating from 1% (A), 0.1% (B), 0.01% (C) polymer solutions and by the adsorption method from 0.01% (D) and 1% (E) polymer.

a few minutes for most of the plastics studied to 20 min for polyethylene. A simple visual test based on wettability of treated surfaces with water was used to determine whether plastics are ready for PVP modification. It is believed that by using this approach, any metal and nonmetal surface can be modified with PVP and subsequently with monolayer and multilayers of various metal and nonmetal nanoparticles.

In addition to simple adsorption of PVP on various surfaces from solutions as described above, dip-coating and spin-coating were also explored as potential methods for substrate modification. Spin-coating always resulted in nonuniform coatings with silver nanoparticles across several centimeters substrate, whereas with dip-coating it was possible to obtain uniform color throughout any large substrate except the edges. However, layers of silver nanoparticles immobilized on dip-coated and spin-coated substrates always showed signs of different degree aggregation even when very dilute solutions were used. To gain more inside in the structure of PVP films prepared with these methods, several ITO substrates were dip-coated with PVP from alcohol solutions of different concentrations followed by annealing and by exposing to the same suspension of silver nanoparticles for the same duration of time. Imaging with SEM revealed an unexpected result in that all films consisted of uniform monolayers of silver nanoparticles on top of which small and large three-dimensional aggregates of nanoparticles were attached (Figure 8A, Figure 8B, and Figure 8C). Differences between different preparations appeared only in the surface density and predominant size of these aggregates. It is clear from the SEM images that the aggregates appear on top

of the monolayer of silver particles. This fact suggests that the aggregates were first formed in the suspension and then attached to the substrates. When the same suspension of silver nanoparticles was used with substrates modified with PVP by the adsorption method, no three-dimensional aggregates were observed indicating that these did not come from the colloid itself (Figure 8D and Figure 8E). We concluded that dip-coated substrates, when immersed in the suspension of silver nanoparticles, caused the formation of three-dimensional aggregates in the following way. The PVP layer on dip-coated substrates consisted of the monolayer directly adhered to the substrate and the layer(s) of polymer molecules weakly bound to the first monolayer. These weakly bound molecules can diffuse into the suspension because of very small, though finite, solubility in water where they capture silver particles forming three-dimensional aggregates. Some of these aggregates precipitated back on the substrates forming the structures as shown in Figure 8A–8C. It is also possible that not only spontaneous diffusion of weakly bound polymer molecules into suspension takes place but also silver nanoparticles help to “strip off” these molecules from the surface. In fact, this may be a dominant mechanism by which PVP molecules leave the surface because the substrates in the described experiment were thoroughly rinsed with water after dip-coating presumably removing most of the weakly bound polymer molecules. The higher the concentration of the PVP solution used for dip-coating, the larger and more numerous are aggregates on the surface (Figure 8A–8C).

The comparison of spin-coating, dip-coating, and adsorption methods for PVP modification of various substrates clearly

demonstrated the advantages of the latter one because the adsorption yields uniform polymer and nanoparticle layers, is highly reliable, is reproducible, and is a simple method. The concentration of the polymer solution from which the adsorption takes place can be varied at least 2 orders of magnitude without noticeable changes in the morphology of nanoparticle layers (Figure 8D and Figure 8E). Finally, no differences in morphology and properties of silver nanoparticle films were noted depending upon whether solutions of poly(2-vinylpyridine) with $M_w = 159,000$ or $M_w = 37,500$, or poly(4-vinylpyridine) with $M_w = 160,000$ were used for the adsorption of the polymer on different substrates. All these polymers performed equally well as long as the concentration of the solution was within the range 0.01–1% and enough exposure time was given to saturate the surfaces.

Conclusions

Poly(vinylpyridine) is proven to be a universal monofunctional surface modifier for the immobilization of various nanoparticles on different substrates. A preferred method of modification is the adsorption of the polymer from an alcohol solution as compared to spin-coating and dip-coating followed by thorough rinsing to remove weakly bound molecules and by high temperature annealing for the further stabilization of the polymer film. It is believed that this method can be successfully applied for the modification of just about any surface including metals, oxides, plastics, and so forth. The treatment of substrates in plasma glow discharge prior to PVP adsorption provides a simple, highly efficient, and environmentally friendly method for surface cleaning as well as for the introduction to the surface of chemical groups capable of binding the polymer. Using PVP as a surface modifier, monolayers, mixed layers, and multilayers of metal, semiconductor, and dielectric nanoparticles can be formed on various substrates.

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