Immobilization of Silver Nanoparticles on Responsive Polymer Brushes

Smrati Gupta,*,† Petra Uhlmann,† Mukesh Agrawal,† Severine Chapuis,†,‡ Ulrich Oertel,† and Manfred Stamm*,†

Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Strasse 6, 01069 Dresden, Germany, and Ecole Européenne de Chimie Polymères et Matériaux, Louis-Pasteur University, 67087 Strasbourg, France

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ABSTRACT: We report on a facile route for the immobilization of silver nanoparticles (Ag NPs) onto the pH-responsive poly(2-vinylpyridine) (P2VP) brushes. The process involves chemical grafting of P2VP chains on the underlying substrate in brush conformation followed by the in situ synthesis of Ag NPs via chemical reduction of silver nitrate ($AgNO_3$) in the presence of P2VP brushes. The effect of various reaction parameters, such as the employed concentration of $AgNO_3$ salt and reduction time on the immobilization process, has been demonstrated. The quantitative analysis of the loaded amount and surface coverage of the Ag NPs on polymer brushes as a function of the employed $AgNO_3$ salt concentration has been discussed. Immobilization of Ag NPs onto the P2VP brushes has been confirmed by atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and ultraviolet–visible (UV–vis) spectroscopy. Finally, the system was used to fabricate the nanosensors for detecting the pH of surrounding aqueous medium. The concept is based on the variation in surface plasmon resonance of immobilized Ag NPs with changing the interparticle distances, caused by the swelling/deswelling of the responsive polymer brushes.

Introduction

Nanometer-sized inorganic particles potentially have unique properties because of quantum confinement effects and their large surface area relative to their volume. The versatility of physical and chemical properties of metal and semiconductor NPs render them as promising materials in the fields ranging from optoelectronics,[1] sensors,[2] catalysis,[3] to medicine.[4] Thus far, great research interests have been involved in fabricating nanoparticle assemblies because they represent a popular route toward the preparation of advanced functional materials as well as a central concept in nanoscience and nanotechnology.[5] Among the noble metal nanoparticles, Ag NPs have attracted special attention[6–8] for their advantage in various studies, such as photosensitive components,[9] catalysts,[10,11] and surface-enhanced Raman spectroscopy.[12]

The most prominent problem associated with metal NPs is that they are very keen to be agglomerated, owing to the high surface energy. To exploit their optical properties in all areas outlined above, they must be stabilized in solution/matrix to prevent the aggregation. To this end, polymer–nanoparticle composites are promising candidates, where NPs can render the unique optical properties to the resulting nanoassemblies and the polymer matrix can control host–guest interactions to ensure a well-defined spatial distribution of NPs. Until now, a great number of carrier systems have been developed for the immobilization of metal NPs, such as dendrimers,[13,14] latex particles,[15–17] microgels,[18,19] or other polymers.[20] Malynych et al.[21] reported the immobilization of metal/metal oxide NPs on a variety of substrates using poly(vinyl pyridine) macromolecules as the universal surface modifier for the attachment of various kinds of NPs. Recently, planar and spherical polyelectrolyte brushes have been introduced as carrier systems of metal NPs.[22,23] These brushes have been successfully used for the immobilization of CdTe NPs and as nanoreactors for the generation of Au, Pt, or Pd NPs. Polymer brushes refer to an assembly of polymer chains, which are tethered by one end to a surface or interface.[24,25] Tethering of the chains in close proximity to each other forces the chains to stretch away from the surface to avoid overlapping. However, in most cases, the polymer matrix only serves as a suitable scaffold for immobilizing the NPs and preventing them from aggregation. In some specific applications, it would be highly desirable to modulate the spatial distribution between NPs arising from the change in polymer chain conformations in response to some external chemical or biochemical species. For example, Ionov et al.[26] reported the fabrication of nanosensors based on the CdSe NPs immobilized on pH-responsive poly(2-vinyl pyridine) (P2VP) brushes. Similarly, Tokareva et al.[27] demonstrated the change in optical properties of gold NPs, attached on P2VP brushes by means of surface plasmon resonance spectroscopy.

Herein, we report on the immobilization of Ag NPs on pH-responsive P2VP brushes, grown on planar substrates, and demonstrate the change in optical properties of immobilized Ag NPs in response to the pH of surrounding media by a simple and easily available tool: UV–vis spectroscopy. We synthesized Ag NPs within the brush layers by electrostatic interaction of silver cations with the pyridyl ring. The effect of various reaction parameters on the size and concentration of adsorbed Ag NPs has been discussed. The quantitative modulation in the loaded amount and surface coverage of the Ag NPs on polymer brushes with the employed $AgNO_3$ salt concentration has been discussed. P2VP brushes, being the weak polyelectrolyte brushes, show the swelling–deswelling behavior in response to pH of surrounding aqueous media.[28] Swelling of P2VP chains in pH 2 water results in an increase in the interparticle distances of immobilized Ag NPs and hence leads to hypsochromic shift of 20 nm in UV–vis peak maxima. On the other hand, deswelling of P2VP brushes in pH 6 water leads to the decrease in interparticle distances and causes a bathochromic shift in peak maxima. It has been realized that stimuli-responsive variation in the thickness of polymer brushes leads to the change in optical

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* To whom correspondence should be addressed. E-mail: gupta@ipfdd.de (S.G.); stamm@ipfdd.de (M.S.).

† Leibniz-Institut für Polymerforschung Dresden e.V.

‡ Louis-Pasteur University.

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properties of immobilized NPs and hence opens the new avenue for fabrication of nanosensors.[26]

Experimental Section

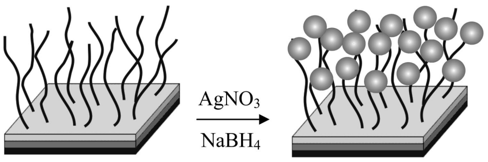
Materials. Carboxy-terminated poly(2-vinylpyridine) (P2VP, $M_n = 40\,600$ g mol^{-1}) and poly(glycidyl methacrylate) (PGMA, $M_n = 17\,500$ g mol^{-1}) were purchased from Polymer Source, Inc. and used as received. Silver nitrate ($AgNO_3$) and sodium borohydride ($NaBH_4$) were purchased from Aldrich and used as received. Highly polished single-crystal silicon wafers of {100} orientation with ca. 1.5 nm thick native silicon oxide layers were purchased from Semiconductor Processing Co. and used as substrates. Chloroform ($CHCl_3$) and dichloromethane (CH_2Cl_2) were dried using standard methods before use. Millipore water was employed throughout the experiments.

Instrumentation. Thickness and swelling of polymer layers were measured on a spectroscopic ellipsometer M-2000VI (J.A. Woollam Co., Inc.) equipped with an automatic computer-controlled goniometer and a horizontally mounted sample stage. The measurements were performed for each sample after each step of the modification to use the measurements of the previous step as a reference for the simulation of ellipsometric data. Dry thickness of the layers was measured at incidence angles varying from 65° to 75° (wavelength range of 370–1700 nm), and swelling of the brush layer with and without particles were performed in a quartz cuvette (Helma) filled with pH 2 water at an incidence angle of 68° (wavelength range of 370–1000 nm). The advancing water contact angle was measured using "DSA-10" Krüss equipment. XPS experiments were performed with an AXISULTRA spectrometer (Kratos Analytical, U.K.) equipped with a monochromized Al Kα X-ray source of 300 W at 20 mA. The survey and high-resolution spectra were obtained at analyzer's pass energy set value of 160 and 20 eV, respectively. For UV–vis measurements, samples were prepared on a glass substrate, which has been cleaned using the same procedure as employed for silicon substrates. Samples were put in a cleaned quartz cuvette and then filled with the respective pH water. In a reference cuvette, a cleaned and bare glass substrate (without brushes and NPs) was taken and filled with the same pH water. After 2 min, samples were irradiated with UV light and spectra were recorded with a Cary 50 spectrophotometer (Varian). While investigating the effect of the pH of surrounding media on the UV–vis absorption band position of immobilized Ag NPs, the sample was perfectly rinsed by a solution containing the desired pH after each measurement and then allowed to incubate for 2 min prior to taking the absorption spectrum. AFM studies were performed with a Dimension 3100 (Digital Instruments, Inc., Santa Barbara, CA) microscope. Tapping mode was used to map the film morphology at ambient conditions.

Preparation of Polymer Brushes. P2VP brushes were prepared on a underlying substrate (silicon/glass), exploiting the well-known "grafting to" approach.[29] Before grafting the polymer brushes, substrates (silicon or glass) were cleaned with dichloromethane in an ultrasonic bath for 30 min, placed in 1:1 mixture of 29% ammonium hydroxide and 30% hydrogen peroxide (Warning: This solution is extremely corrosive and should not be stored in tightly sealed containers because of the evolution of gas) for 1.5 h, and finally rinsed several times with water. A thin layer of PGMA (ca. 2 nm) was deposited by spin coating from a 0.02% solution in chloroform and annealed at 110 °C for 10 min. On top, a thin film of carboxy-terminated P2VP (2% solution in chloroform) was spin-coated and annealed for 3 h at 150 °C. Ungrafted polymer was removed using Soxhlet extraction in chloroform for 4 h.

Immobilization of Ag NPs onto P2VP Brushes. P2VP-grafted silicon or glass substrates were stirred in aqueous 0.005 M $AgNO_3$ solution for 30 min under argon flow. Thereafter, substrates were removed and quickly dipped and stirred into aqueous 0.2 M $NaBH_4$ solution. Finally, substrates were washed several times with Millipore water, dried under argon, and used for characterizations.

Scheme 1. Schematic Presentation of the Immobilization of Ag NPs onto the P2VP Brushes



$$AgNO_3 + NaBH_4 \rightarrow Ag^0 + 1/2H_2 + 1/2B_2H_6 + NaNO_3$$

Results

Well-defined and homogenously distributed P2VP brushes were chemically grafted on the silicon/glass substrates, exploiting a thin anchoring layer of PGMA. It has been investigated earlier that PGMA can serve as a universal anchor for different types of polymer brushes on a wide range of substrates, including silicon, glass, alumina, gold, and silver, by virtue of the high reactivity of its epoxy groups toward hydroxyl groups of these surfaces.[30] The chemical reaction between −COOH groups of end-functionalized P2VP chains and epoxy units located in the "loops" and "tails" sections of the attached PGMA macromolecules leads to the chemical attachment of P2VP chains on the underlying substrate. The thickness of washed and dried P2VP brushes was measured as 8.2 ± 0.5 nm by ellipsometry. It corresponds to a grafting density of about 0.14 chains nm^{-2}, estimated by $\sigma = 1/d_g^2$, where d_g is the distance between two grafting sites. It can be derived as $d_g = M_n^{1/2} (N_A d \rho)^{-1/2}$, where M_n is the number average molecular weight of polymer chains, N_A is Avogadro's number, and ρ (1.18 g cm^{-3}) is the density of P2VP. Because the d_g has been estimated as 2.63 nm, which is smaller than the radius of gyration of the P2VP polymer coils ($R_g \sim 5$ nm); therefore, the polymer layer can be considered as polymer brushes.[26] We know that P2VP brushes are weak polyelectrolyte brushes and display a change in thickness in response to the pH of surrounding media.[31] At pH 2 water, the pyridyl groups, present along the polymer chains, are highly protonated and hence render positive charges to the macromolecular chains. Because of the repulsion between the charged polymer segments, a 4 times swelling (~32.8 nm) as compared to the dry thickness has been observed by ellipsometry (as shown in Figure S1a in the Supporting Information). In contrast, when the pH of surrounding media was switched to pH 6, P2VP brushes were found to deswell to the dry thickness, because of the deprotonation of the polymer segments. We note that this change in thickness of the P2VP layer has been found to be reversible in nature.

Ag NPs have been immobilized on the P2VP brushes to achieve P2VP−Ag nanoassemblies, by carrying out the in situ reduction of $AgNO_3$ salt. The presence of pyridyl groups on the P2VP chains renders a strong affinity toward the electron-deficient metal ions.[21] First, the silver ions (Ag^+) have been absorbed on P2VP chains from the aqueous solution of $AgNO_3$ by electrostatic interaction with the electron-rich pyridyl groups and subsequently reduced into Ag NPs via chemical reduction. We believe that immobilization of Ag NPs on the lower part of the polymer brush layer would be suppressed by the steric hindrance caused by the polymer chains, and hence, most of Ag NPs are immobilized on the upper part of the polymer brush layer. Scheme 1 shows the schematic presentation of the immobilization of Ag NPs onto polymer brushes.

The obtained P2VP−Ag nanoassemblies were characterized by a number of analytical tools. It should be underlined that all of the measurements were carried out after washing of the samples with Millipore water, ensuring the removal of nonimmobilized particles from the P2VP brushes. An advancing water contact angle of Ag NPs immobilized P2VP brushes has been

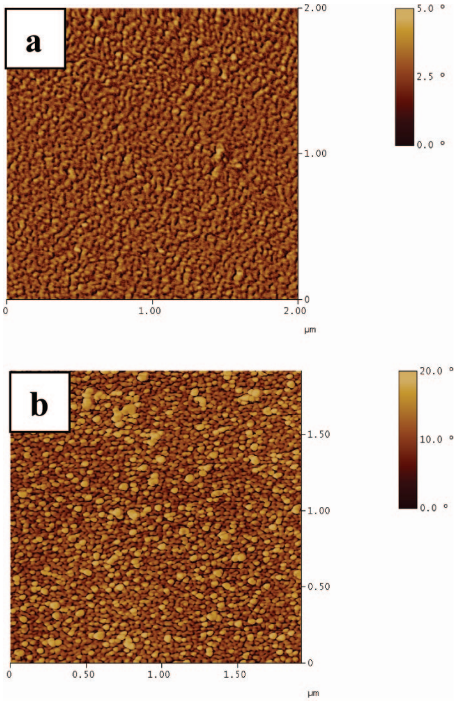


Figure 1. AFM phase images (2 × 2 μm) of P2VP brushes (a) before and (b) after immobilization of Ag NPs at 0.005 M AgNO$_3$ concentration.

found to be 78 ± 1.2°, as compared with ~58 ± 1.1° for bare P2VP brushes, which can be attributed to the presence of metallic silver.[32] Parts a and b of Figure 1 illustrate AFM images of polymer brushes in dry state before and after the immobilization of Ag NPs at 0.005 M AgNO$_3$ concentration, respectively. The root-mean-square (rms) roughness of the bare polymer brushes has been measured as ≤0.7 nm, which increased significantly to 5.7 nm after the immobilization of Ag NPs. Moreover, Figure 1b reveals that immobilized particles are present in the form of domains, probably because the AFM analysis was performed in the dry state. Upon drying, Ag NPs underwent surface aggregation and uniformity has been lost.[21] Moreover, in the dry state, all of the polymer chains remain in the collapsed state, bringing the adsorbed particles close to each other. AFM images of the P2VP brushes immobilized with Ag NPs at 0.0025 and 0.01 M AgNO$_3$ concentrations are shown in Figure S2 in the Supporting Information.

The surface coverage (φ) of immobilized Ag NPs on P2VP brushes has been estimated using the AFM images as follows:[26]

$$\varphi = \frac{100\% N\pi d^2}{4A} \tag{1}$$

where d is the diameter of the NPs and N is the number of NPs detected per area A.

These calculations reveal 3.2, 5.7, and 7.2% surface coverage of Ag NPs on P2VP brushes, immobilized at 0.0025, 0.005, and 0.01 M AgNO$_3$ concentrations, respectively. To have better insight into the quantitative analysis of immobilized Ag NPs, AgNO$_3$ solutions left after the immobilization process have been titrated against the standard NaCl solution. These results revealed immobilization efficiencies as 4.3, 6.6, and 7.9% at 0.0025, 0.005, and 0.01 M AgNO$_3$concentrations, respectively. It should be noted that here immobilization efficiency implies the ratio of the immobilized amount of "Ag" to the initially taken amount of the "Ag" in reaction media.

Figure 2a shows UV−vis absorption spectra (taken in the dry state) of P2VP brushes before and after the immobilization of Ag NPs at 0.005 M AgNO$_3$ concentration. In the case of bare P2VP brushes, no absorption band has been observed, while Ag NPs immobilized polymer brushes revealed an absorption band at 429 nm. This peak arises from the surface plasmon absorption of immobilized Ag NPs.[33,34] It can also be seen that the plasmon absorption band is rather sharp and symmetric, indicating the narrow particle size distribution of immobilized Ag NPs. In agreement with AFM results, aggregation of the immobilized Ag NPs in the dry state of the P2VP brushes caused a red shift in the peak position to the 429 nm as compared to that of 400 nm expected for the homogenously distributed particles.[35] Furthermore, the absence of the signature peak at a higher wavelength excludes the fact of the large aggregation of immobilized Ag NPs even in the dry state of P2VP brushes.[36]

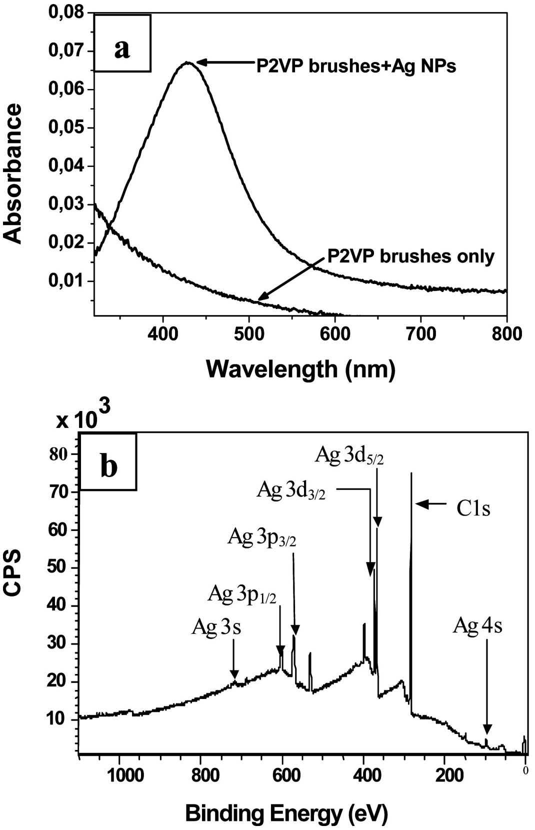


Figure 2. (a) UV−vis spectra of P2VP brushes (taken in the dry state) before and after the immobilization of Ag NPs at 0.005 M AgNO$_3$ concentration. (b) XPS wide-scan spectrum of P2VP brushes immobilized with Ag NPs at 0.005 M AgNO$_3$ concentration.

To prove the presence of Ag NPs on polymer brushes, samples were further investigated by XPS analysis. Figure 2b shows XPS data for the samples prepared at 0.005 M AgNO$_3$ concentration. The appearance of "Ag" signals at the characteristic binding energies in the wide-scan spectra strongly confirms the presence of Ag NPs on P2VP brushes. The XPS results of the remaining two samples, prepared at 0.0025 and 0.01 M AgNO$_3$ concentrations, are shown in Figure S3 in the Supporting Information. These results revealed an increase in the immobilized amount of Ag NPs with an increase in the employed concentration of AgNO$_3$ salt in reaction media. XPS results revealed the atomic concentration of "Ag" as 3.16, 4.06, and 4.73% for the samples prepared at 0.0025, 0.005, and 0.01 M AgNO$_3$ concentrations, respectively.

To investigate the effect of different reaction parameters on the immobilization process, Ag NPs have been immobilized by varying the concentration of AgNO$_3$ salt in reaction media and reduction time. Figure 3a illustrates the UV–vis spectra of P2VP brushes immobilized with a different amount of Ag NPs (in terms of Ag atomic concentrations as estimated by XPS) at

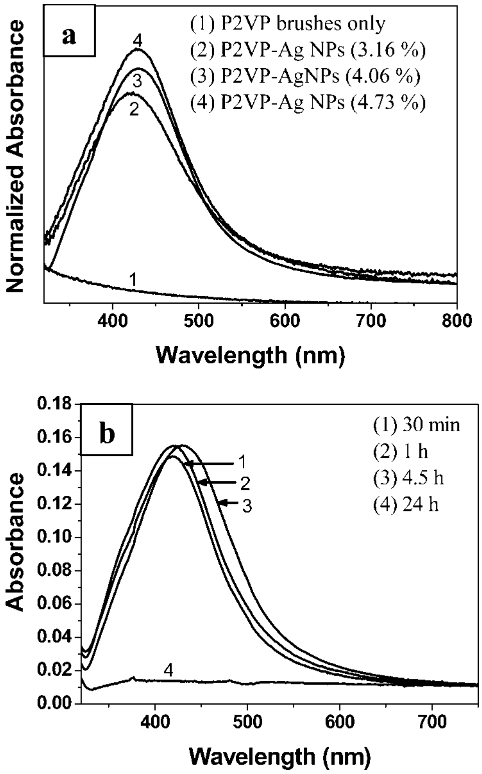


Figure 3. (a) UV–vis spectra of P2VP brushes immobilized with a different amount of Ag NPs (in terms of Ag atomic concentrations, estimated by XPS analysis). These samples have been prepared at different $AgNO_3$ concentrations: (1) 0.0 M, (2) 0.0025 M, (3) 0.005 M, and (4) 0.01 M. (b) UV–vis spectra of P2VP brushes immobilized with Ag NPs at 0.005 M $AgNO_3$ concentration at different reduction times in $NaBH_4$.

different $AgNO_3$ concentrations, namely, 0.0025, 0.005, and 0.01 M. As expected, one can observe an increase in the intensity of the absorbance band with an increase in the Ag concentration on P2VP brushes. Moreover, a closer look of these results reveals the bathochromic shift from 421 to 429 nm with an increase in the Ag atomic concentration from 3.16 to 4.06%. On the other hand, no significant shift in the band position has been observed with an increase from 4.06 to 4.73%. However, a slight but continuous broadening of the absorption bands can be seen with an increase in Ag atomic concentrations on polymer brushes. These data confirm that Ag NPs immobilized on P2VP brushes at 0.005 M $AgNO_3$ concentration are relatively more aggregated as compared to those immobilized at 0.0025 M. As a consequence of this, a bathochromic shift and broadening of the absorption band have been observed.[37] Both the intensity and position of $\lambda_{\max}$ reflect the extent of aggregation, resulting from the coupling of surface plasmons between closely spaced particles. In addition, it can also be concluded that an increase in the Ag atomic concentration from 4.06 to 4.73% does not cause a sufficient enhancement in the degree of agglomeration, which can lead to the significant shift in band position. Similar results were reported by Lu et al.[38] for Ag NPs immobilized into thermo-responsive microgels. They described the variation in interparticle distances of immobilized NPs as a function of the temperature and reported that variation in temperature from 10 to 20 °C leads to a decrease of the interparticle distance because of a slight shrinkage of the employed microgel template; however, this change in the interparticle distance of immobilized Ag NPs was not enough to further shift the plasmon absorption band position.

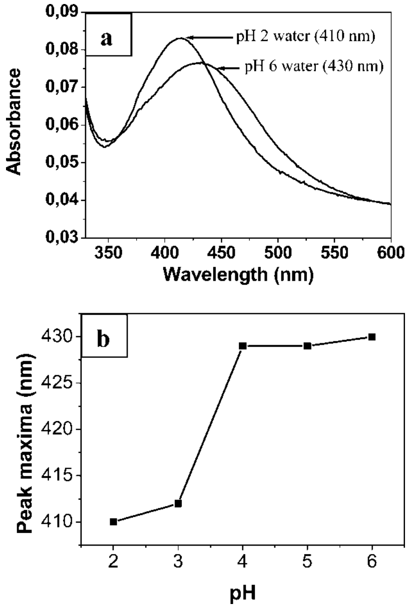


Figure 4. (a) UV–vis spectra of P2VP brushes immobilized with Ag NPs, in the fully stretched (pH 2 water) and fully collapsed (pH 6 water) state. (b) Shift in UV–vis absorption peak maxima of immobilized Ag NPs as a function of the pH of surrounding media.

When Ag NPs were immobilized at 0.005 M $AgNO_3$ concentration by varying the exposure time to the $NaBH_4$ solution (0.2 M) from 30 min to 4.5 h (reduction time), no significant change in the intensity of the UV-absorption band has been observed (as shown in Figure 3b). However, a slight bathochromic shift in the band position has been occurred with an increase in the reduction time. It can probably be attributed to the increase in the size of NPs with an increase in the reduction time.[39] A higher reaction time promotes the self-aggregation of small Ag colloids formed during the first stage of the reduction process via the diffusion process.[40] Chou et al. also reported an increase in the size of Ni NPs as a function of the reduction time, prepared by chemical reduction of $NiCl_2$ with $NaBH_4$.[41] When samples were stirred for 24 h in $NaBH_4$ solution, no absorption band appeared in UV–vis spectra. Such a long time exposure of samples with a reducing agent resulted into the removal of P2VP brushes from the substrate because of the reduction of the anchoring layer itself.

We know that optical properties of the metal NPs are a function of their shape, size, and interparticle distance. The former two can be varied by changing the reaction parameters during particle synthesis, and the latter can be modulated by the variation in dimensional parameters of polymer supports by an external trigger, where the NPs are incorporated or immobilized. We demonstrated the application of obtained P2VP–Ag nanoassemblies as the nanosensors for the detection of the pH of surrounding media. We explored the pH-induced swelling–deswelling of P2VP brushes to modulate the interparticle distances of immobilized Ag NPs. As shown in Figure 4a, the absorption maximum of the UV–vis absorption band of the immobilized Ag NPs has been found to shift by 20 nm when the pH of the surrounding media was changed from pH 6.0 and 2.0 (from 430 to 410 nm). It can be attributed to the stretching of P2VP chains and hence an increase in the thickness of Ag NPs immobilized P2VP brushes from 8 to 20 nm (as shown in Figure S1b in the Supporting Information). The swelling of the polymer brushes[27] at lower pH causes an increase in the interparticle distance of the immobilized Ag NPs, leading to a blue shift in their absorption maxima. As mentioned earlier, this swelling in P2VP brushes has been found to be reversible in nature. When surrounding media was shifted from pH 2 to 6, it resulted into a shift of absorption maxima from

410 to 430 nm. Shrinkage of the polymer brushes brings the immobilized Ag NPs closer to each other, causing the aggregation, and hence, a red shift in the band position is observed. Figure 4b illustrates the variation in the position of absorption band maximum of immobilized Ag NPs against the pH of the surrounding media.

Discussion

We demonstrated a simple and facile approach of the immobilization of Ag NPs onto the responsive polymer brushes. The Ag NPs were synthesized by $NaBH_4$ reduction of $AgNO_3$ salt in the presence of P2VP brushes, and the interaction of nanoparticle precursors with pyridyl rings of the P2VP chains has been exploited as the driving force for the immobilization process. In addition, the effect of various reaction parameters on the adsorption of Ag NPs on P2VP brushes has been discussed. Owing to the multifunctional properties of Ag NPs and responsiveness of P2VP brushes with the pH of surrounding media, the obtained P2VP−Ag nanoassemblies can be used as pH nanosensors. In comparison to the previously reported studies on the fabrication of nanosensors,[26,27] the described system possesses the following advantages: (1) It needs an extremely simple and easily available analytical setup (UV–vis spectroscopy), which gives a fast and strong signal to detect the variation in optical properties of immobilized NPs. (2) It exploits an electrostatic interaction between electron-deficient Ag NPs and the electron-rich pyridyl ring of P2VP brushes as the driving force for the immobilization of NPs. This interaction is stronger than the hydrophobic−hydrophobic interaction, used by Ionov et al.[26] for grafting the CdSe NPs on P2VP brushes. The strong bonding between NPs and the polymer brush avoid or delay the leaching of NPs, increasing the lifetime of the sensor. In addition, it makes our system more environmental friendly because leaching of loosely attached NPs may cause harmful effects in the environment. (3) It is quite stable at lower pH; unlike the P2VP−CdSe system reported by Ionov et al.[26] (4) It is not limited to the reflecting surfaces only because it detects variation in interparticle distances of immobilized NPs because of the change in thickness of P2VP brushes in response to the external trigger.

Apart from above-mentioned pH-sensing application, the described approach offers the effective way toward the stabilization of Ag NPs on the macroscopic surfaces, which can be further used as the antibacterial substrates. In addition, we believe that immobilized NPs can offer the large surface area as compared to the bulk ones; therefore, these nanoassemblies can effectively be used as the catalyst in photocatalytic reactions. In comparison to previously reported studies on the immobilization of NPs on macroscopic surfaces,[21] the presented approach offers high loading of the Ag NPs. It can be attributed to the fact that the brush conformation of the P2VP layer offers a large number of binding sites for the immobilization of NPs. In addition, the covalent bonding between the substrate and the P2VP brush layer provides enhanced stability to the system. Furthermore, particles are smaller in size and well-distributed on the surface as evident by the single and symmetric peak in UV–vis spectra even in the dry state. Moreover, unlike the previously reported studies,[21,26,27] the presented system demonstrates variation in the loaded amount of NPs on polymer brushes by varying the key reaction parameters during the immobilization process.

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Supporting Information Available: Swelling curves for P2VP brushes in pH 2 water before and after the immobilization of Ag NPs and AFM images and XPS analysis of P2VP brushes immobilized with Ag NPs at 0.0025 and 0.01 M $AgNO_3$ concentrations. This material is available free of charge via the Internet at http://pubs.acs.org.

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