# One-Step "Green" Synthesis and Stabilization of Au and Ag Nanoparticles Using Ionic Polymers

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*Received November 9, 2007. Revised Manuscript Received May 29, 2008*

Generally, metal nanoparticles are prepared by a variety of chemical methods that are not environmentally friendly. We report on the use of aqueous solutions of ionic polymers containing arsonic acid groups for the green synthesis of Au and Ag nanoparticles of intriguing shapes at room temperature without using additional reducing reagent. Our results indicate that these ionic polymers are not only capable of reducing metal ions but also can protect the nanoparticles in the colloidal solutions. In general, the process of metal ions reduction using these ionic polymers is very slow, but the ability of the polymers to protect the Au and Ag nanoparticles permits us to obtain colloidal solutions that are stable for several months. This method would be very much useful for the preparation of other metal nanoparticles.

## 1. Introduction

Metal nanostructures have been of considerable interest in recent years because of their unique properties and potential applications in catalysis, biodetection, optics, photonics, electronics, and magnetism with superior performance over their bulk counterparts.[1–9] The performance of metal nanostructures in those applications depends mainly on their size, shape, composition, and structure.[10] A variety of chemical synthesis methods can be found in the literature. However, the chemical synthesis of metal nanoparticles generally involves the reduction of metal ions using reducing agents such as hydrazine, sodium borohydride, and dimethyl formamide. All of these are highly reactive chemicals and pose potential environmental and biological risks.[11]

Recently, there has been an increased emphasis on the topics of "green" chemistry and chemical processes.[12] For instance, Raveendran et al.[11] reported the green synthesis of silver nanoparticles using environmentally benign and renewable materials as the respective reducing and protecting agents. The three main steps in the preparation of nanoparticles that should be evaluated from a green chemistry perspective are the choice of the solvent medium used for the synthesis, the choice of an environmentally benign reducing agent, and the choice of a nontoxic material for the stabilization of the nanoparticles.[11] The use of environmentally benign and renewable materials in the production of metal nanoparticles is very important for pharmaceutical and biomedical applications.

In our previous work,[13] we reported the synthesis of two new metallorganic ionic polymers containing arsonic acid group ($AsO(OH)_2$) attached covalently to the phenyl ring of the monomeric unit: the poly(*o*-acryloylaminophenylarsonic acid) and poly(*p*-acryloylaminophenylarsonic acid), abbreviated as poly(*o*-AAPHA) and poly(*p*-AAPHA), respectively. In the first, the arsonic acid group is localized at the ortho position of the phenyl group, whereas in the second, the arsonic acid group is placed at the para position, as can be seen in Figure 1. In this paper, we present the "green" synthesis of Au and Ag nanoparticles at room temperature, using aqueous solutions of the ionic polymers poly(*o*-AAPHA) and poly(*p*-AAPHA) as both reducing and stabilizing agents. The obtained nanoparticles are characterized by

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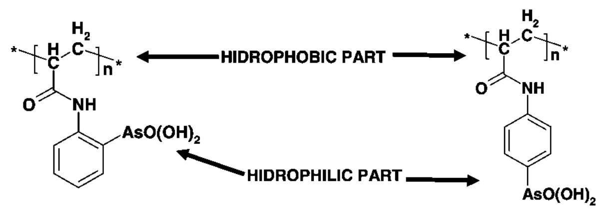

**Figure 1.** Molecular structure of the ionic polymers poly(*o*-AAPHA) and poly(*p*-AAPHA).

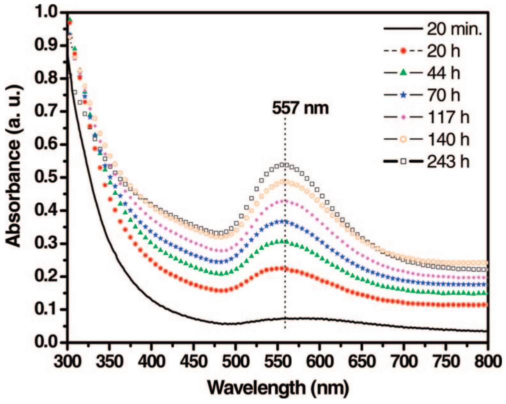

**Figure 2.** Temporal evolution of UV−visible absorption spectra after addition of $HAuCl_4$ solution into poly(*p*-AAPHA) solution.

ultraviolet−visible (UV−vis) absorption spectroscopy, transmission electron microscopy (TEM), and Fourier-transform infrared (FTIR) spectroscopy. Our results show that these ionic polymers are capable of producing metal nanoparticles of intriguing shapes which are stable for several months.

## 2. Experimental Section

The details of the synthesis of poly(*o*-AAPHA) and poly(*p*-AAPHA) ionic polymers were reported earlier.[13] In short, the ionic polymers were synthesized via free radical polymerization using 2,2′-azoisobutyronitrile (AIBN) as a free radical initiator in dimethylformamide at 70 °C. The resultant ionic polymers were isolated by precipitation in acetone and dried at 80 °C in a vacuum for 12 h. The average molecular weights (in g $mol^{-1}$) of poly(*o*-AAPHA) and poly(*p*-AAPHA) were 38 759 and 32 347, respectively, as determined by light scattering measurements. The molecular structure and composition of the ionic polymers were verified by $^1H$ NMR, $^{13}C$ NMR, and FT-IR spectroscopy. It must be mentioned that arsenic in these polymers remains in As(V) oxidation state, which is the most thermodynamically stable state of As. On the other hand, the polymers have good thermal stability even beyond 200 °C.[13]

Anhydrous $AgNO_3$ and $HAuCl_4$ were purchased from Sigma-Aldrich and used as received. Deionized water (18MΩ) was used as solvent in all the experiments. In a typical synthesis process, 25 mL of a $5 \times 10^{-4}$ M metallic salt ($HAuCl_4$ or $AgNO_3$) aqueous solution was added to 25 mL of a $5 \times 10^{-5}$ M ionic polymer aqueous solution under magnetic stirring at room temperature. No other reducing agent was added to the reaction mixture. Under these experimental conditions, the initial reaction mixtures were yellowish and colorless for gold and silver salts, respectively. The growth of the Ag and Au nanoparticles was monitored at different intervals using UV−visible absorption spectroscopy.

**Characterizations.** UV−visible spectra of the colloidal samples were recorded with a Shimadzu (model UV-3101PC) UV−vis-NIR spectrophotometer using 10 mm optical path length quartz cuvette. Transmission electron microscopy (TEM) images of the Ag and Au nanoparticles were taken with a Tecnai $G^2$ F30 S-Twin transmission electron microscope operating a 300 kV. The microscope was equipped with a Schottky-type field emission gun and an S-Twin objective lens ($Cs = 1.2$ mm; $Cc$ 1.4 mm; point-to point-resolution, 0.20 nm). For the TEM observations, the colloidal samples were dispersed on carbon-coated copper grids and dried in a vacuum. A Nicolet Magna 750 FTIR spectrometer was used to record the IR absorption spectra in the 4000−400 $cm^{-1}$ spectral range. For FTIR studies, 1 mg of solid sample was mixed with 99 mg of dry KBr homogeneously to make pellets 7 mm in diameter and 0.5 mm thick.

## 3. Results and Discussion

**Formation of Au Nanoparticles Using Poly(*p*-AAPHA).** Figure 2 shows the UV−vis absorption spectra obtained at different time intervals after mixing $HAuCl_4$ aqueous solution with poly(*p*-AAPHA) aqueous solution at room temperature. Formation of Au nanoparticles in the colloidal solution was monitored from their absorption spectra as the small noble metal particles reveal absorption band in the UV−vis spectral region due to surface plasmon resonance (SPR).[14] The process of reduction of the $AuCl_4^-$ ions using the poly(*p*-AAPHA) was slow, yielding a broad absorption band centered at about 557 nm until 20 min of reaction, which was assigned to the SPR of Au nanoparticles. The broadband indicates a relatively high polydispersity, both in size and shape of the Au particles.[15] The intensity of the SPR band increased systematically with the increase of reaction time, to reach a maximum after about 243 h. There after, the intensity of the SPR band did not change. The reduction of $AuCl_4^-$ ions with poly(*p*-AAPHA) aqueous solution at room temperature leads to the formation of Au nanoparticles that are stable in solution for several months. This indicates that the poly(*p*-AAPHA) serves as both reducing and protecting agent.

Figure 3 shows typical TEM images of Au nanoparticles stabilized by the poly(*p*-AAPHA) in aqueous solution, after 200 h of reaction. TEM images revealed the formation of Au nanoparticles with size in the range from 5 to 80 nm. This result confirms the polydispersity of the nanoparticles observed in their optical absorption spectra. TEM observations indicate that the smaller particles have a polyhedral shape, whereas the bigger particles, which are formed by the aggregation of smaller particles, have several different shapes, including some triangular structures.

**Formation of Au Nanoparticles Using Poly(*o*-AAPHA).** Figure 4 shows the UV−vis absorption spectra taken at different intervals after mixing $HAuCl_4$ aqueous solution with poly(*o*-AAPHA) aqueous solution at room temperature. As in the case of Au in poly(*p*-AAPHA) solution, the formation of Au nanoparticles in solutions with poly(*o*-AAPHA) proceeded slowly for 140 h. The optical spectra obtained after a few seconds of reaction revealed only an absorption band at round 318 nm, which has been assigned to the

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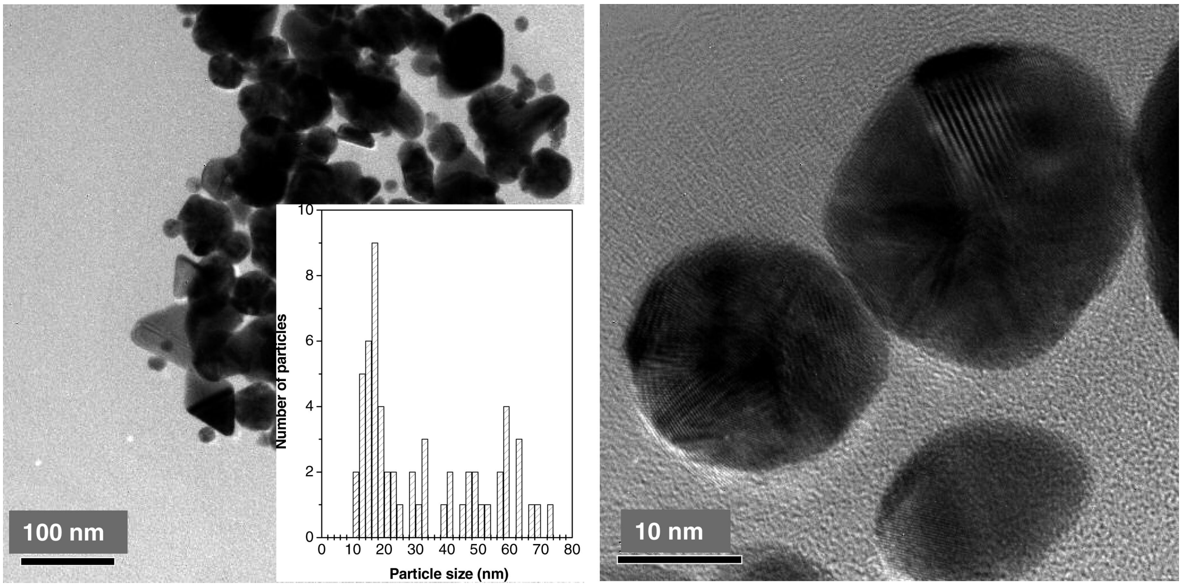

**Figure 3.** Typical TEM micrographs of Au nanoparticles formed in poly(*p*-AAPHA), after 200 h of reaction.

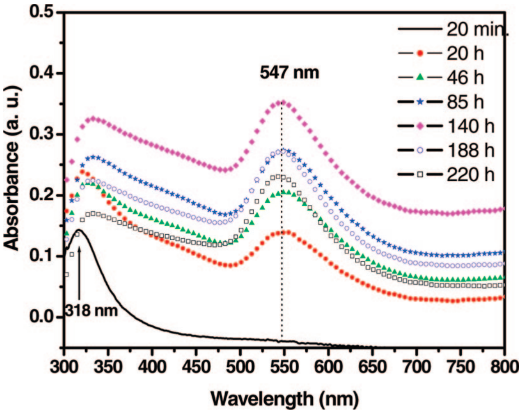

**Figure 4.** Temporal evolution of UV−visible absorption spectra after addition of $HAuCl_4$ solution onto poly(*o*-AAPHA) solution.

absorption of $AuCl_4^-$ ions.[16] The formation of Au nanoparticles was evident after only 20 min of reaction, when in addition to the band at around 318 nm, the absorption spectra revealed a broad absorption at around 547 nm, corresponding to the SPR of Au nanoparticles. The intensity of the SPR absorption band increases progressively from 20 min to 140 h, because of the increase in the density of particle in the colloidal solution. After 140 h, the intensity of the SPR band starts to decrease. Decrease of SPR band intensity on prolonged reaction time apparently indicates that the concentration of the polymer was not sufficient to stabilize the high density of Au particles formed in the reaction mixture, thus resulting in their aggregation and subsequent precipitation. In fact, we observed the precipitation of the Au nanoparticle at the bottom of the reaction vessel after 140 h of reaction.

On the other hand, with the increase in reaction time, the band located in 318 nm shifts from its starting point (318 nm) to 321 nm for a time of reaction of 2.5 h and finally to 329 nm for 140 h, whereas its intensity and width increased. This gradual higher wavelength shift of this band might be associated either with the gradual change of the oxidation state of Au or a slow charge transfer at the interface of metal ions and adsorbed organic polymer to balance their electrochemical potentials.[17,18]

To verify the ability of poly(*o*-AAPHA) to stabilize Au nanoparticles further, we repeated the synthesis process utilizing double amount of poly(*o*-AAPHA) in the reaction solution ($10 \times 10^{-5}$ M solution). However, a similar decrease in SPR band intensity in the absorption spectra of gold colloidal solution was observed. Therefore, we believe that the poly(*o*-AAPHA) is not as capable of stabilizing Au nanoparticles as poly(*p*-AAPHA). The reason behind such poor stabilizing capacity of poly(*o*-AAPHA) is presently under study.

Figure 5 shows TEM images of the Au nanoparticles stabilized with poly(*o*-AAPHA), after 200 h of reaction. TEM images revealed the formation of Au nanoparticles of sizes between 5 and 80 nm. The majority of the particles have intriguing shapes, such as tetrahedral, pentagonal, hexagonal, decahedral, and other polyhedral structures.

The results obtained from UV−vis spectroscopy and TEM, clearly demonstrate that the process of reduction of Au ions by the poly(*p*-AAPHA) is faster than the poly(*o*-AAPHA). In fact, the absence of the absorption band related to Au ions in the absorption spectra of the solution with poly(*p*-AAPHA) suggests that the reduction process in this case is almost immediate. Precipitation of the Au nanoparticle in the colloidal solutions of poly(*o*-AAPHA) after 140 h of reaction indicates that poly(*p*-AAPHA) stabilizes Au nanoparticles in a more efficient manner than poly(*o*-AAPHA). It is important to note that both the polymers produced a great number of Au nanoparticles of decahedral structure, which is rarely reported in the literature. We believe the slow reduction process of gold ions by the polymers leads to the formation of this type of structures.

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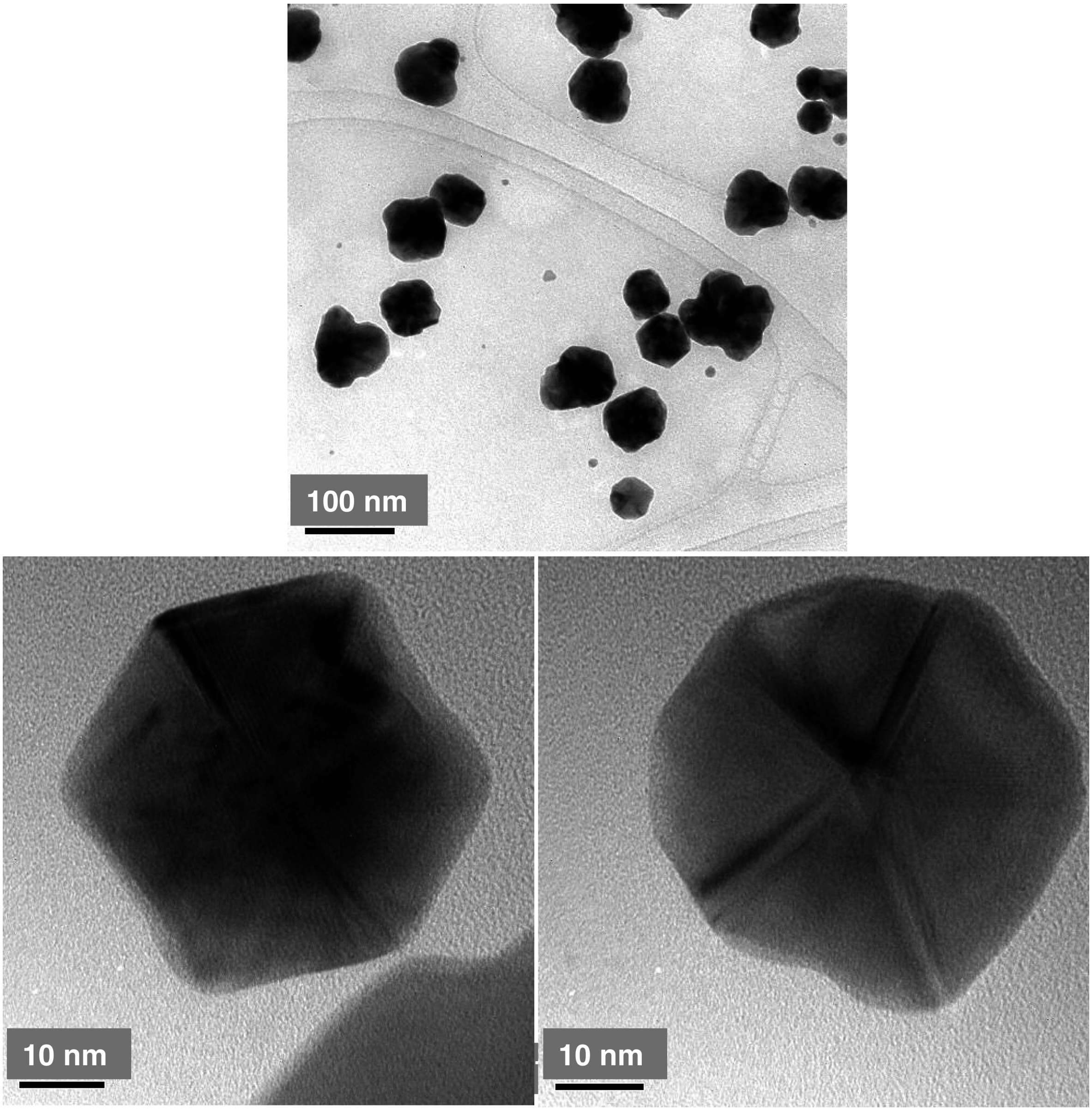

**Figure 5.** Typical TEM micrographs of Au nanoparticles in poly(*o*-AAPHA).

**Formation of Ag Nanoparticles Using Poly(*p*-AAPHA).** Formation of the Ag nanoparticles using the ionic polymers poly(*p*-AAPHA) and poly(*o*-AAPHA) in aqueous solution was monitored by UV−vis absorption spectroscopy. Figure 6 show the time evolution of UV−vis absorption spectra after addition of $AgNO_3$ $5 \times 10^{-4}$ M solution into the poly(*p*-AAPHA) solution at room temperature. The first evidence of the reduction of $Ag^+$ was the change of color observed in the solutions. The solutions that initially were colorless acquired a tenuous pink color after 4 h. Formation of Ag nanoparticles was confirmed by the presence of the characteristic SPR band in the UV−vis spectra. There appeared two absorption bands at around 387 and 540 nm, which can be assigned to the SPR absorption bands of Ag nanoparticles with two different size distributions.

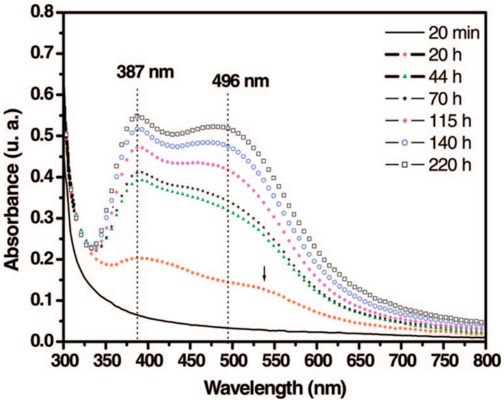

**Figure 6.** Temporal evolution of UV−visible absorption spectra after addition of $AgNO_3$ solution onto poly(*p*-AAPHA) solution.

With the increase in the reaction time, two distinct behaviors of the SPR absorption bands were observed: (i) The intensity of both the absorption bands increased progressively, and (ii) although the SPR band at around 540 nm shifted toward shorter wavelength (∼496 nm), the band at round 387 nm did not change its position.

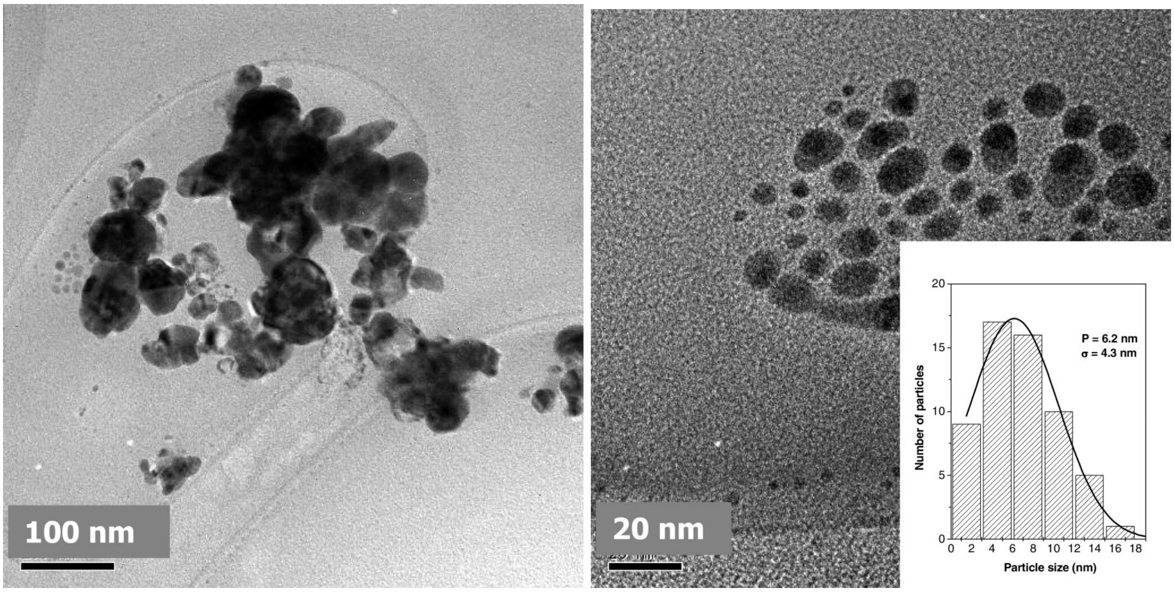

**Figure 7.** Typical TEM micrographs of Ag nanoparticles in poly(*p*-AAPHA).

The SPR band position of metal colloids can vary over a wide range depending on the metal, the dielectric, and geometry of the colloid.[19] An isolated pseudospherical silver nanoparticle in aqueous solution is characterized by a single intense near UV−vis absorption at ~400 nm, which arises because of the excitation of the dipolar surface plasmon of the silver nanoparticles.[20] The UV−vis absorption spectra of a well-diluted dispersion of colloidal particles can be calculated from the Mie theory.[21] The absorbance, $A$, for a dispersion of $N$ particles per unit volume is given by[22]

$$A = CNl/2.303$$

where $C$ and $l$ are the absorption cross-section and the optical path length, respectively. As in the present case, the optical path length $l$ is 1 cm and fixed, the increase in absorbance of the SPR bands indicates that the observation (i) in our case is due to an increase in Ag nanoparticle concentration with reaction time. As the reduction of Ag ions by poly(*p*-AAPHA) is slow, the nucleation process is slow and consequently with time, apart from the growth of already formed nucleus, some new particles are formed that contribute to the increase in particle density in the solution.

For the small metal particles in quasi-static limit, i.e., $2\pi R < \lambda$ (where $R$ is the particle radius and $\lambda$ the wavelength of light), the absorption spectrum depends strongly on the dielectric constant of the surrounding media. On the other hand, when the particles are in close packed assembly or in aggregation, the electromagnetic field of one particle influences its neighbor, leading to another plasmon absorption at longer wavelength because of a collective plasmon oscillation of the aggregated system. The frequency and intensity of the second band depend on the degree of aggregation and orientation of the individual particles within the aggregate.[8] Therefore, along with the dipole plasmon, the quadrupole resonance grows. With the growth of particle size, generally both the absorption band shift toward higher wavelengths.

The second absorption band in the UV−vis spectra of metal colloids might also have an origin of nonspherical shape the metal particles. In the case of nonspherical metal particles or 1D metal structures, the appearance of the second SPR band is the longitudinal dipole plasmon. Although the position of the transverse plasmon band does not vary with the variation of aspect ratio, the longitudinal plasmon bands shifts toward longer wavelength with the increase of aspect ratio. In our absorption spectra of Ag colloids prepared with poly(*p*-AAPHA), although the first absorption band did not change its position, the second absorption band shifted gradually toward shorter wavelengths. Though from the TEM micrographs of the samples (presented latter), we can observe some of the particles are of nonspherical shape and some of them are agglomerated, the evolution of the higher wavelength band (observation ii) does not indicate its origin as either of these two. Therefore, the second behavior (observation ii) can in principle be attributed to the change in size distribution of the bigger particles in the colloids. The evolution of the absorption bands indicates the presence of bimodal size distribution in the solution, which was maintained until the end of the reduction process. Figure 7 shows some images of TEM of the final solution, that is to say, after 190 h of reaction, when no longer considerable variations of the UV−vis spectra were registered. The TEM results corroborated the existence of bimodal size distribution of the particles, one with sizes between 2 and 15 nm and the other with sizes between 40 and 60 nm.

**Formation of Ag Nanoparticles Using Poly(*o*-AAPHA).** Figure 8 show the evolution of UV−visible absorption spectra after addition of $AgNO_3$ $5 \times 10^{-4}$ M solution onto poly(*o*-AAPHA) solution at room temperature. Formation of the Ag nanoparticles using the poly(*o*-AAPHA) showed a similar evolution to those with poly(*p*-AAPHA). The

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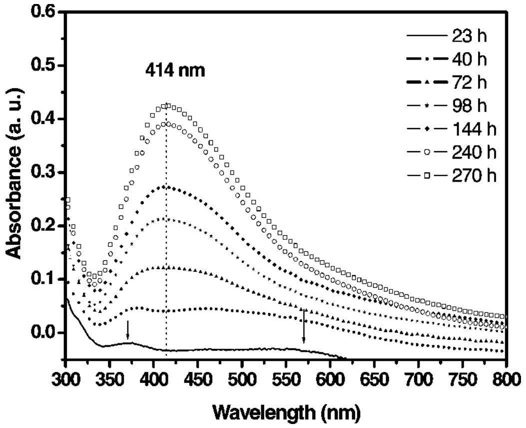

**Figure 8.** Evolution of the surface plasmon absorption band indicating the continuous formation of the Ag nanoparticles in poly(*o*-AAPHA).

absorption spectrum of the colloidal solution after 23 h of reaction shows two bands at round 375 and 575 nm, which were assigned to the SPR of Ag nanoparticles with two different size particles distributions (see previous section). With the increase in the reaction time, the 375 nm band shifted to higher wavelengths, whereas the 575 nm band shifted to shorter wavelengths. For a reaction time of about 40 h, these two bands overlapped and only a broad absorption band at around 414 nm appeared. The intensity of this band increased with reaction time, and reached its maximum value after 270 h; which suggests that the reduction process of the Ag ions was slow. After 270 h, the intensity of the absorption band did not change. Such results indicate that the growth process of the Ag nanoparticles using poly(*o*-AAPHA) is very different from that with poly(*p*-AAPHA).

The evolution of the SPR bands in the absorption spectra suggests that the Ag nanoparticles are formed through the follow process: At the beginning, the nucleation process starts through the reduction of Ag ions; which followed by the growth process. Because the reduction process of Ag ions using poly(*o*-AAPHA) is very slow, the Ag ions reduced the latter, contributing to both the formation of new nucleus and the growth of the previously formed nucleus. Thus, at a certain time, the colloidal solution would contain Ag particles of dispersed sizes. However, the time evolution of the absorption spectra indicates that the process of formation of newer nucleus and their growth dominates over the growth of the particles formed earlier. The lower wavelength shift of the 575 nm band suggests that the growth of bigger particles in the reaction mixture is less favored, and their density in the solution does not increase considerably with time. TEM images of the Ag particles in the final colloidal solution (see Figure 9) demonstrate that indeed the majority of the Ag nanoparticles have sizes between 2 and 15 nm, and one small portion of particles have sizes between 25 and 40 nm.

**Interaction of the Ionic Polymers with Au and Ag Nanoparticles.** To understand the formation process of Au and Ag nanoparticle from their corresponding metallic salts using the poly(*o*-AAPHA) and poly(*p*-AAPHA) polymers in aqueous solution, we performed IR measurements on solid samples obtained from the precipitation of the colloidal solutions. Assignments of IR bands appeared for the poly(*o*-AAPHA) and poly(*p*-AAPHA) ionic polymers with and without Au and Ag metal particles are summarized in Tables 1 and 2, respectively. IR study revealed that the intensity of the typical absorption band corresponding to the O−H stretching vibration of the $-AsO(OH)_2$ group, which was observed at around 2915 cm$^{-1}$ in the spectra of the ionic polymers without metal nanoparticles, decreased considerably for the ionic polymers with Au nanoparticles and practically disappeared in the spectra of the polymers with Ag nanoparticles. It indicates that the metallic ions in the solution are exchanged for the mobile H$^+$ ions of the $-AsO(OH)_2$ group. It is evident that the exchange of silver ions is considerably higher than that of the gold ions.

IR spectra of the ionic polymers containing Ag nanoparticles revealed two important features: (i) The intensity of the absorption bands due to the As−O stretching vibration decreased compared with the polymer without Ag. Also, the band corresponding to the As═O stretching vibration shows a similar intensity change and exhibited a shift toward higher frequencies from 1001 to 1023 cm$^{-1}$ for poly(*o*-AAPHA) and from 1008 cm$^{-1}$ to 1021 cm$^{-1}$ for poly(*p*-AAPHA), whereas the absorption bands due to the N−H deformation vibration (known as amide II band) and C−N stretching vibration (amide III band) shift toward higher frequencies, from 1534 to 1541 cm$^{-1}$ and from 1289 to 1298 cm$^{-1}$ for poly(*o*-AAPHA) and from 1526 to 1531 cm$^{-1}$ and from 1313 to 1316 cm$^{-1}$ for poly(*p*-AAPHA), respectively. (ii) The presence of two new absorption bands located around 1385 and 1105 cm$^{-1}$, which we assign tentatively to the interaction between Ag atoms with the nitrogen atom of the amide and with the oxygen atoms of the $-AsO(OH)_2$ group, respectively. These behaviors suggest that the poly(*o*-AAPHA) and poly(*p*-AAPHA) polymers maintained a strong interaction with the Ag particles through both the nitrogen atom in the amide group and oxygen atoms in the arsonic acid.

On the other hand, similar characteristics were observed in the IR spectra of the poly(*o*-AAPHA) and poly(*p*-AAPHA) polymers containing Au nanoparticles. However, the intensity of the new bands, assigned to the interaction between Au atoms with the ionic polymers was very much low (see Table 1), indicating that such interactions are very weak.

The shift of IR frequencies in several organic-surfactant-capped metal nanocrystals like oleylamin, dodecanethiol, and nonanethiol-capped Ag particles[23–25] have been reported and attributed to the constraint of capping molecular motion, which presumably resulted from the formation of a relatively closed-packed surfactant layer on the Ag nanoparticle surface.[26] To the best of our knowledge, there is no report on the interaction of ionic polymer on metal nanoparticles. The small increase in the wavenumbers for the deformation and stretching vibrations of amide bands in the polymer capped metal nanoparticles probably indicates the formation

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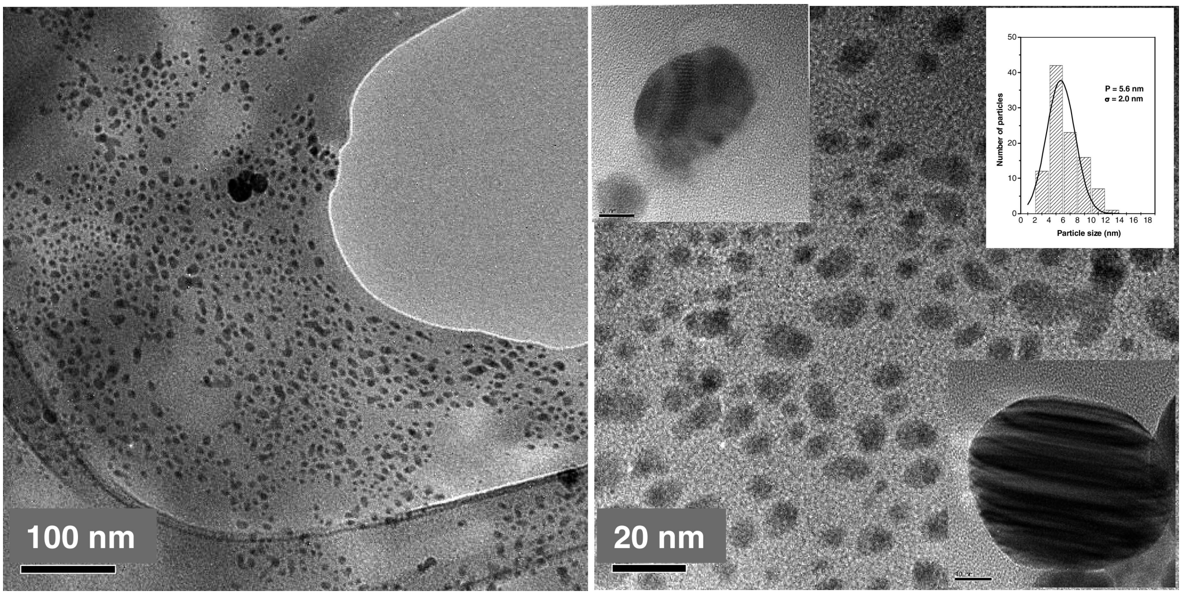

**Figure 9.** Typical TEM micrographs of Ag nanoparticles in poly(*o*-AAPHA). Typical high-magnification TEM images of the particles are shown in insets. The scale bar for the high-magnification images is 10 nm.

**Table 1. Assignment of the FTIR Absorption Bands of the Ionic Polymers with and without Au Nanoparticles**[a]

| frequency (cm$^{-1}$) | | | | |
|---|---|---|---|---|
| poly(*o*-AAPHA) | Au/poly(*o*-AAPHA) | poly(*p*-AAPHA) | Au/ poly(*p*-AAPHA) | assignment |
| 2915 (vs) | 2922 (s) | 2923 (vs) | 2923 (m) | $\nu$(O−H) |
| 1663 (m) | 1659 (vs) | 1672 (m) | 1668 (m) | $\nu$(C=O) amide I band |
| 1534 (s) | 1540 (m) | 1526 (s) | 1531 (s) | $\delta$(N−H) amide II band |
| | 1388 (w) | | 1388 (sh) | Interaction between Ag nanoparticles with amide group |
| 1289 (s) | 1292 (s) | 1313 (m) | 1315 (w) | $\nu$(C−N) amide III band |
| 1129 (w) 1068 (w) | 1129 (w) 1068 (w) | 1097 (s) | 1097 (m) | $\nu$(As−O) |
| | 1108 (sh) | | | interaction between Ag nanoparticles with arsonic acid group |
| 1001 (w) | | 1008 (s) | 1021 (vw) | $\nu$(As=O) |

[a] Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; $\nu$, stretch; and $\delta$, deformation.

**Table 2. Assignment of the FTIR Absorption Bands of the Ionic Polymers with and without Ag Nanoparticles**[a]

| frequency (cm$^{-1}$) | | | | |
|---|---|---|---|---|
| poly(*o*-AAPHA) | Ag/poly(*o*-AAPHA) | poly(*p*-AAPHA) | Ag/ poly(*p*-AAPHA) | assignment |
| 2915 (vs) | 2925 (vw) | 2923 (vs) | 2925 (vw) | $\nu$(O−H) |
| 1663 (m) | 1661 (vs) | 1672 (m) | 1661 (m) | $\nu$(C=O) amide I band |
| 1534 (s) | 1541 (m) | 1526 (s) | 1531 (s) | $\delta$(N−H) amide II band |
| | 1384 (s) | | 1385 (s) | interaction between Ag nanoparticles with amide group |
| 1289 (s) | 1298 (w) | 1313 (m) | 1316 (w) | $\nu$(C−N) amide III band |
| 1129 (w) | 1129 (sh) | 1097 (s) | 1097 (vw) | $\nu$(As−O) |
| 1068 (w) | 1066 (w) | | | |
| | 1105 (m) | | | interaction between Ag nanoparticles with arsonic acid group |
| 1001 (w) | 1023 (vw) | 1008 (s) | 1021 (vw) | $\nu$(As=O) |

[a] Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; $\nu$, stretch; and $\delta$, deformation.

of $\sigma$-bonds between the N−H and C−N groups of the polymers and the metal surfaces (end-on coordination), respectively. However, a considerably lower energy shift (13 cm$^{-1}$ for poly(p-AAPHA), and 22 cm$^{-1}$ for poly(*o*-AAPHA)) of the (As=O) stretching vibration also indicates its interaction with the metal surfaces, the nature of which is not yet clear. Appearance of additional bands at about 1108 cm$^{-1}$ (for Au) and 1105 cm$^{-1}$ (for Ag) in the present study could be attributed to the end-on coordination of the amide (C−N) groups with the surfaces of Au and Ag nanoparticles, respectively.

IR results indicate that the process of formation of Au and Ag nanoparticles in aqueous solutions of the ionic polymers involves the exchange of metal ions by H$^+$ ions of the poly(*o*-AAPHA) and poly(*p*-AAPHA) polymers, followed by the reduction of the metal ions to the zero- valent metal. The neutral metal atoms or clusters remain bonded with the polymers through end-on $\sigma$-bonding. Therefore, the ionic polymers, not only are capable of reducing Au and Ag ions, but also protect the formed Au and Ag nanoparticles through the interactions with the nitrogen and oxygen atoms of the amide and arsonic acid group, preventing their aggregation.

## 4. Conclusions

Stable Au and Ag nanoparticles can be synthesized in water using environment friendly ionic polymers like poly(*p*-AAPHA) and poly(*o*-AAPHA). The process of formation of the Au and Ag nanoparticles using the ionic polymers involves the exchange of metal ions with $H^+$ ions of the polymers, followed by the reduction of the metal ions to the zerovalent metal in the polymers. However, the exact mechanism for the reduction of the metallic salts using the ionic polymers poly(*p*-AAPHA) and poly(*o*-AAPHA) is still under investigation. In general, the process of metal ions reduction using these ionic polymers is very slow, but the ability of the polymers to protect the Au and Ag nanoparticles permits to obtain colloidal solutions which are stable for several months. The weak interaction of the ionic polymers with gold and silver metals permits us to grow their nanoparticles slowly, but without any drastic modification of their surface energy along different facets. Thus the stable, multifaceted Au and Ag nanoparticles could be grown. This method would be very much helpful for the preparation of other metal nanoparticles using the principles of green chemistry.

**Acknowledgment.** The work was supported partially by PROMEP, VIEP-BUAP, and CONACyT (Grant 46269), Mexico.

**Supporting Information Available:** IR spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM703201D