Synthesis of highly stable silver colloids stabilized with water soluble sulfonated polyaniline


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A simple technique was developed for the synthesis of silver nanoparticles (NPs) in an aqueous medium using water soluble sulfonated polyaniline as a new non-covalent effective stabilizer. The narrow size distribution of the NPs was achieved through the synthesis. In neutral and basic solutions the as-prepared silver NPs demonstrated resistance toward aggregation over several months and at least a few days at pH 1. The versatility of the procedure was demonstrated also for the preparation of gold nanoparticles. Transmission electron microscopy with electron microdiffraction, UV–vis spectroscopy, XRD, XPS and FTIR analyses were used to characterize the structure and chemical composition of as obtained silver NPs.

1. Introduction

Advances over the past two decades have been revealing that silver nanoparticles (NPs) possess unique optical, electrical and catalytic properties [1,2]. They have many actual and potential applications in surface-enhanced Raman spectroscopy, metal-enhanced fluorescence, electrochemistry, microelectronics and can serve as building blocks of nanodevices [3–6]. During the past few years the field of silver NPs preparation has witnessed tremendous growth in synthetic sophistication and depth of characterization. Many techniques of silver NPs synthesis have been reported, such as the chemical reduction of silver ions in reverse micelles [7], in two-phase water–oil systems (Brust–Schiffrin technique) [8,9], in water solutions [10], in the presence of shape-controlling capping agents [11] and others [12–14].

Despite the common opinion that silver NPs are better absorbers and scatterers of light than gold NPs and have the unique ability to amplify Raman scattering and fluorescence [15,16], gold NPs are used in almost all analytical and biological applications of metallic NPs because of their resistance to oxidation and aggregation. At the same time hydrophilic silver NPs remain on the sidelines because of their propensity to oxidatively corrode and aggregate in electrolytic solutions [17,18]. As a result there is an urgent interest aimed at the improvement of current synthetic techniques and looking for new effective stabilizers that could allow stable NP solutions to exist at high ionic strength values and over a wide range of pH [10,19].

Nowadays there are plenty of works which are devoted to the formation of metal/polymer nanocomposites [20–23]. Embedding of noble metal NPs into polymer structures usually causes an increase in their electric conductivity due to the excellent conducting properties of metal NPs. Among a number of conducting polymers, polyaniline has been always attracting considerable attention because of its reasonably high conductivity and quite good environmental stability. It is widely used in the field of electroanalytical chemistry, e.g. as a coating for the electrode surface in sensor applications.

Unfortunately, polyaniline shows its redox activity only at pH not exceeding 3 or 4 [24]. On the other hand it is well known that self-doped polyaniiline derivatives present an important class of conducting polymers [25]. In contrast to polyaniline self-doped derivatives are active in a broad range of pH [26]. However, self-doped polyanilines have an important drawback, namely significantly lower electric conductivity versus polyaniline. Therefore embedding of silver NPs is especially actual for self-doped sulfonated and carboxylated polyaniline films. From this point of view it is obviously important for NPs capping agent to conduct electrically and in an ideal to have a structure similar to that of a conducting polymer film.

In this study, we applied water soluble sulfonated polyaniline as a protecting agent to prepare silver and gold NPs in an aqueous medium by the in situ chemical reduction of silver nitrate and tetrachloroauric acid with sodium borohydride in the presence of fully reduced sulfonated polyaniline. To the best of our knowledge this is the first reported procedure aimed at the preparation of highly stable (even at extremely low pH values) hydrophilic silver NPs capped with water soluble sulfonated polyaniline.

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2. Experimental

2.1. Materials

Aniline (Acros, 99%) was doubly distilled in vacuum under argon and stored in a refrigerator at −18 °C in inert atmosphere. Silver nitrate (99.9+%, Sigma–Aldrich), tetrachloroauric acid (99+%, Aldrich), sodium borohydride (Lancaster, 98+%), ammonium persulfate (99+, Acros), chlorosulfonic acid (99%, Aldrich) were of analytical grade and used without further purification. All aqueous solutions were prepared with doubly distilled water.

2.2. Measurements

The UV–vis absorbance spectra were recorded using a Shimadzu UV-1800 spectrophotometer (Japan), and 1 mm path length quartz cuvettes were used for the measurement of visible spectra.

The electronic images and diffractograms were made on Leo 912 AB Omega (Leo Ltd., Germany) transmission electron microscope (TEM) operating at 100 kV. The samples for TEM characterization were prepared by placing a drop of a colloidal solution on a formvar-coated copper grid which was dried at room temperature. All size distributions were calculated using Femtoscan Online v.2.2.91 software (Advanced Technologies Center, Russia).

The elemental analysis of sulfonated polyaniline was conducted on Elemental Analysis System (VarioEL). X-ray photoelectron spectra were taken in LAS-3000 spectrometer (Riber, France) with ESCA hemispherical electron analyzer OPX-150. The apparatus was equipped with a non-monochromatic Al Kα source of X-ray radiation (1486.6 eV). The base pressure of the spectrometer was in the 10−10−12 Torr range. The binding energies were corrected for a specimen charging by referencing the C1s peak to 284.6 eV. The XPS analyses were performed by assuming core-level spectra with Gaussian line shapes after standard Shirley background subtraction. Samples were prepared by dispersion on an aluminum sample holder prior to each experiment.

Fourier transform infrared (FTIR) spectroscopy was performed using a Nicolet IR-200 instrument (Thermo Scientific, USA). Infrared spectra of sulfonated polyaniline (SPANI) capped silver NPs in the range of 400–4000 cm−1 were recorded at 100 scans per spectrum and a 4 cm−1 resolution. Samples were dispersed in spectroscopically grade potassium bromide and compressed into pellets.

X-ray diffraction was carried out on a Dron-3 machine using Cu Kα radiation at a step of 0.02° (2θ) at room temperature. The background was subtracted with the linear interpolation method.

Cyclic voltammetry measurements were performed using an Elin PS-8 (Russia) potentiostat, interfaced to a PC computer. A one-compartment cell with a glassy-carbon working electrode, a Pt mesh counter electrode, a Ag/AgCl reference electrode. SPANI or SPANI capped silver NPs solutions in 0.5 mol L−1 aqueous H2SO4 were used as electrolyte. The scan speed was 100 mV s−1 and the potential range was from −500 to 1000 mV.

2.3. Polyaniline preparation

In this work we performed a common technique for the synthesis of emeraldine hydrochloride powder according to Refs. [24,26–28]. Aniline (4.66 g) solution in 250 mL 1 M HCl was oxidized by slowly adding (drop by drop) of 250 mL ammonium persulfate (11.41 g) water solution with vigorous stirring. Both solutions and the reaction mixture were being cooled to 0–3 °C during the synthesis. The molar ratio S2O82−/aniline was kept at 1.15. The duration of the reaction was varied between 1 and 2 h. The formed dark-green precipitate is removed by filtration and washed repeatedly with excess 1 M HCl and dried under dynamic vacuum for 48 h at 60 °C.

2.4. Synthesis of sulfonated leucoemeraldine

Sulfonated emeraldine was synthesized according to Ref. [29]. Briefly, emeraldine hydrochloride powder (4.5 g) was dispersed in 140 mL of boiling 1,2-dichloroethane. The chlorosulfonic acid (11 g) diluted with 10 mL 1,2-dichloroethane was added dropwise during 20 min to the dispersion liquid, and then the reaction mixture was held for 5 h. Produced chlorosulfonated polyanilines were separated by filtration, immersed in 250 mL of water, and heated for 4 h at 100 °C. After concentrating of the resulting greenish solution by evaporation until almost dried, sulfonated emeraldine was precipitated and washed with acetone, then collected by filtration and dried at 60 °C under vacuum. Elemental analysis shown: C, 39.7; H, 3.17; N, 8.03; O, 28.6; S, 14.8; Cl, 5.7 that corresponds approximately to 80% of sulfonated aromatic rings. These data are in a good accordance with Ref. [29].

To the solution of sulfonated polyaniline (0.5 g) in 50 mL of water aqueous NaBH4 (0.4 g) solution (20 mL) was added with stirring in argon atmosphere. The mixture was stirred for 1 h. The color of the solution has changed from dark green to light-brown.

2.5. Synthesis of silver and gold NPs

A technique consists in slow dropwise addition with vigorous stirring of 30 mL aqueous silver nitrate (0.034 g, 2.00 × 10−5 mol) solution to the previously obtained mixture of sulfonated leucoemeraldine (70 mL) and an excess of NaBH4 in argon atmosphere. The quantity of silver nitrate added was adjusted to reach the 10−3 M total concentration of silver in the reaction mixture. After complete addition of silver nitrate the mixture was stirred for 4 h.

A synthesis of gold NPs was similar to that of silver colloid with one exception, namely tetrachloroauric acid (2.00 × 10−4 mol) was used as a precursor of gold NPs.

3. Results and discussion

3.1. Synthesis of sulfonated leucoemeraldine

The reaction of sulfonated polyaniline with sodium borohydride follows two well-defined stages as can be observed visually. These are conversion of acidic emeraldine form into a basic form and consequent reduction up to leucoemeraldine (Scheme 1). In general, an excess of borohydride required for the full reduction of the acidic form depends on a degree of sulfonation of emeraldine. In the present work we performed a technique using threefold molar excess of NaBH4. It is especially important to note that fully reduced leucoemeraldine form is highly sensitive to oxygen and quickly turns into basic emeraldine form on exposing to the air. Therefore all synthetic manipulations should be conducted in inert atmosphere when preparing silver NPs via borohydride reduction.

Scheme 1. Schematic representation of the reaction of sulfonated polyaniline with sodium borohydride.
Absorption spectra of silver colloid before (a) and after (b) exposition to air.

Above-mentioned leucoemeraldine oxidation process can be easily monitored as it is characterized by color changing of the reaction mixture from light-brown to dark-blue.

However, spontaneous oxidation is a very favorable moment since it is well known that fully reduced polyaniline derivatives do not reveal any electric conductivity. Thus our primary purpose – to synthesize stable silver NPs capped with conductive polyaniline film – can be achieved without using special oxidizers for leucoemeraldine form. Fortunately, to finally obtain NPs with a conductive surface layer the reaction mixture simply should be held in air for a couple of hours.

Ideally, leucoemeraldine solution is colorless, but in fact there are always some impurities which cause light-brown color to it. However, Fig. 1 shows that the adsorption spectrum of leucoemeraldine does not contain any characteristic emeraldine bands.

3.2. Silver NPs formation

A dropwise addition of silver nitrate to leucoemeraldine solution containing an excess of sodium borohydride in inert atmosphere resulted in the immediate change in color from light-brown to dark-red. The latter corresponded to the silver colloid. Also a remarkable absorption band has appeared at about 400 nm, but no emeraldine bands were observed (Fig. 2a). Being exposed to air sulfonated leucoemeraldine oxidizes and forms emeraldine, so the solution color changed quickly to dark-blue. In a UV–vis spectrum of this solution the silver NPs absorption band at 400 nm remained and emeraldine absorption appeared at about 575 nm (Fig. 2b).

3.3. TEM investigation

The TEM micrograph of the as-prepared colloids is shown in Fig. 3a. Most of the NPs in the micrograph are 2–4 nm in size. A small number of large nanoparticles also can be seen due to possible agglomeration of the small particles. According to electron diffraction data (shown in Fig. 3) the NPs obtained are well-crystallized silver NPs. Only the diffraction rings of crystal silver are found in each ED patterns.

3.4. XPS and XRD measurement

The crystal structure of silver NPs was further verified by powder X-ray diffraction taken with a bigger quantity of the dried sample. Fig. 4 shows the XRD patterns of preliminarily centrifuged at 15,000 rpm (20 min), thoroughly washed with alcohol and dried sample of silver NPs stabilized with water soluble sulfonated polyaniline. The pattern contains peaks corresponding to diffraction from the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) crystal planes of bulk fcc silver. X-ray photoelectron spectra provide information about binding energies of inner shell electrons of Ag and stabilizer's molecules on the surface of NPs. The main peaks observed in the survey scan (not shown) of the sample are C1s1/2, N1s1/2, O1s1/2, Ag3s, Ag3p, Ag4p, and Ag4d peaks. The binding energies (BE) of Ag3d5/2 and Ag3d3/2 for silver NPs are shown in Fig. 5. Ag3d spectrum exhibits the peaks at 368.3 eV (3d5/2) and 374.6 eV (3d3/2), which correspond to that of bulk silver in the zerovalent state [30]. S2p XPS spectra obtained after analysis of the sample of silver NPs are reported (Fig. 6). Unfortunately, the corresponding energies of S2p3/2 and S2p1/2 have not been resolved. However, the peak maxima in S2p XPS spectra of sulfonated polyaniline and capped silver NPs showed an excellent correspondence between binding energies (168.4 eV for polyaniline and 168.3 eV for silver NPs) of sulfur atoms in their highest oxidation state (in –SO3− groups), so these data confirmed the presence of sulfonated polyaniline on the surface of silver NPs. The N1s1/2 region in Fig. 7 is overlapping with the signal of a silver (4p level) satellite peak, thus hindering a well correlation for the signals in the region. Although we can guess on the presence of signals corresponded to tertiary and secondary nitrogen of polyaniline in the region 399–403 eV. So, an unavoidable superposition of Ag4p (satellite) and N1s peaks does not allow to discriminate correctly the contribution of peaks corresponding tertiary and secondary nitrogen to the total signal.

3.5. FTIR study of SPANI capped silver NPs

FTIR spectra of the pure sulfonated polyaniline (SPANI) and the SPANI capped silver NPs are shown in Fig. 8. The spectrum of the pure SPANI, Fig. 8a, displays all characteristic bands attributed to the emeraldine salt at 2800–3600, 1579, 1508, 1307, 1169, 1078, and 852 cm−1 [31,32]. These bands are assigned to different vibrational modes, as shown in Table 1. The bands at 1024, 704 (SPANI) and 1026, and 706 cm−1 (SPANI capped Ag NPs), are ascribed to the absorption of the –SO3H group, confirm that polyaniline is doped with –SO3H directly [33,34].

A comparison of various bands of pure SPANI and SPANI capped silver NPs is also given in Table 1. We note that there is a significant shift in the peaks associated with C=–C, C–N and C≡N stretching indicating the presence of strong interactions between polyaniline and silver surface and confirming the crucial role of SPANI as capping agent for Ag NPs. Those interactions do not break even at low pH values, thus, providing the observed long-term stability of SPANI capped particles in strong-acid medium.
3.6. Electrochemical properties of SPANI capped silver NPs

The cyclic voltammograms of all samples (Fig. 9) show three well-defined reversible redox processes characteristic of polyaniline [35], confirming that the polymer presents electroactivity.

There are no signals attributed to the neat silver nanoparticles (silver oxidation), confirming that the nanoparticles are fully protected by the polymer. An intermediary redox process at 500–600 mV usually observed for chemically polymerized polyaniline and attributed to ortho-coupling or cross-linking of the polymer [35] was also observed on the voltammograms of SPANI capped silver NPs, which can be indicative that the process of leucoemeraldine oxidation by silver ions does not involved cross-linking of the polymer chains (483 vs. 668, 480, 670).

<table>
<thead>
<tr>
<th>Type of vibration</th>
<th>SPANI (wavenumber, cm(^{-1}))</th>
<th>Ag/SPANI (wavenumber, cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>N–H stretching</td>
<td>2800–3600</td>
<td>3000–3600</td>
</tr>
<tr>
<td>C=C stretching of quinoid ring</td>
<td>1579</td>
<td>1639</td>
</tr>
<tr>
<td>C=C stretching of benzoid ring</td>
<td>1508</td>
<td>1440</td>
</tr>
<tr>
<td>C–N stretching</td>
<td>1307</td>
<td>1344</td>
</tr>
<tr>
<td>C=N stretching</td>
<td>1169</td>
<td>1146</td>
</tr>
<tr>
<td>C–H in-plane bending</td>
<td>1078</td>
<td>1113</td>
</tr>
<tr>
<td>SO(_2) stretching</td>
<td>1024</td>
<td>1026</td>
</tr>
<tr>
<td>C–H out-of-plane bending</td>
<td>852</td>
<td>879</td>
</tr>
<tr>
<td>C–S stretching</td>
<td>704</td>
<td>706</td>
</tr>
</tbody>
</table>

Fig. 3. TEM micrographs of silver NPs stabilized by sulfonated polyaniline immediately after the synthesis (a) and 2 months later (b). Corresponding size distribution histograms and electron diffraction patterns of each sample are shown below the images.

Fig. 4. XRD patterns of centrifuged and dried sample of silver NPs stabilized with sulfonated polyaniline.

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3.7. Synthesis and properties of SPANI capped gold NPs

The gold NPs were synthesized using the same technique as of silver colloid preparation. Their size distribution is as wide as that of the silver NPs and the electron diffraction pattern indicates their crystallinity. The size of NPs in the TEM micrograph of gold colloid sample is about 2–5 nm (Fig. 10). To monitor stability of the final prepared silver colloid, we measured absorption spectra of the colloid on different days (not shown here). There was no obvious change in the shape, position, and symmetry of the absorption peak during 60 days. According to TEM micrographs of the colloid a small enlargement of NPs was observed during their aggregation. As shown in Fig. 3b most of the NPs have a diameter in range 2–6 nm.

These results demonstrate that the silver nanoparticles are well-stabilized and their colloidal solution can remain stable for about 2 months. It is well known that in the absence of a stabilizing agent silver particles aggregate directly during the reduction of Ag⁺ ions by sodium borohydride. The same phenomenon occurs when there is no sulfonated polyaniline in the NaBH₄ solution. The long-term stability of the silver NPs solution obtained indicates evidently that NPs are stabilized by sulfonated polyaniline.

The pH of the final colloid solution was near 9.5. To study the stability of silver NPs in acid medium we added to it 0.5 M H₂SO₄ until pH 1. No coagulation was observed and there was no significant change in shape and size distribution of silver NPs in TEM micrographs of the silver acidic colloid.

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4. Conclusions

In summary, very stable, sulfonated polyaniline protected hydrophilic silver NPs dispersed in water medium can be easily prepared by the in situ borohydride reduction of silver nitrate in the presence of fully reduced sulfonated polyaniline. The formation of silver and gold NPs coated with sulfonated polyaniline was clearly shown and it has been proven that polyaniline could serve as an effective protective reagent to obtain highly stable silver and gold NPs. In neutral and basic solutions the as-prepared silver NPs have demonstrated resistance toward aggregation over several months and at least a few days at pH 1.

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