A facile synthesis of Ag nanoparticles for mercury ion detection with high sensitivity and selectivity

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A facile one-step synthesis of Ag nanoparticles (NPs) with particle sizes less than 5 nm is presented. The average size, size distribution and morphology of the NPs were determined using a number of techniques, including UV-visible absorption spectroscopy, transmission electron microscopy, energy-dispersive X-ray spectroscopy (EDX) and a particle size analyzer (PSA). Furthermore, the resulting Ag NPs, without extra treatment, could be used as a probe to detect Hg(II) ions in aqueous media. The response in absorbance was linearly proportional to the concentration of mercury ions in the range 0.2–3 nM. Unlike some recent reports, this absorbance-based detection scheme does not require surface modification of the NPs or oligonucleotides as targeting elements, or complicated detection systems. The method is very simple yet highly sensitive, with an observed detection limit down to 0.2 nM. Most other common ions, at 100-fold higher concentrations, have little interfering effect on the mercury ion detection.

Introduction

Mercury is a pollutant with a well-known toxicological profile.[1,2] The soluble inorganic Hg(II) ion, which provides a pathway for contaminating large amounts of water, is a caustic and carcinogenic material with a high cellular toxicity.[3] Methyl mercury is usually generated through microbial methylation in aquatic sediments from Hg(II) ions, and the subsequent accumulation of methyl mercury by humans through the food chain may lead to serious and permanent damage to the brain. Therefore, it is very important for the routine detection of Hg(II) ion in the environmental monitoring of rivers and larger bodies of water, and in the evaluation of the safety of aquatically-derived food supplies.

There have been many methods developed for the detection of Hg(II) ions, such as atomic absorption/emission spectroscopy, inductively-coupled plasma atomic mass spectrometry and electrochemical sensors.[4–6] While these approaches can achieve very low detection limits, the procedures involved in the analysis tend to be time-consuming and/or laborious. Alternative methods using colorimetric sensors and fluorescence sensors have drawn a lot of attention in recent years, with varying degree of success with respect to sensitivity, selectivity and stability.[7–13] With the maximum allowable level of Hg(II) ions set by the US Environmental Protection Agency (EPA) in drinkable water as 10 nM,[14] there is ongoing demand for the development of detection methods that are sensitive, specific and easy to use.

It is well known that Ag nanoparticles (NPs) exhibit strong absorption bands in the UV-vis region, due to collective excitations of the surface plasmon band.[15] As the Hg(II) ion has a high enough electrochemical potential to oxidize Ag to Ag^+, it would alter the absorption band of Ag NPs. It is therefore possible that Ag NPs could be used for the detection of mercury ions. The most common synthesis of Ag NPs is the chemical reduction of a silver salt solution by a reducing agent such as citrate, $NaBH_4$ or ascorbate.[16–22] The normal use of citrate, a relatively weak reductant, resulted in a slow reduction rate, and the size distribution was far from narrow. With the use of a strong reductant, such as borohydride, although small particles resulted that were somewhat monodisperse, controlling the generation of the larger particles was difficult. Moreover, these syntheses very often required materials that are not environmentally benign. Much more attractive processes do not require additives such as surfactants or reducing agents at all.

It is known that polymeric materials contain size-confined, nanosized cells of inter- and intramolecular origin that can be used in the preparation of NPs. Dendritic and linear polymers have been successfully applied to NP synthesis.[23,24] In the approach reported here, only an $AgNO_3$ aqueous solution and polyethylene glycol (PEG) were utilized to prepare Ag NPs. PEG serves as both an environmentally benign solvent and a reductant, since it has an extensive number of hydroxyl groups that can facilitate the complexation of Ag^+ to the molecular matrix and reduce Ag^+ to form Ag NPs. It is worthwhile mentioning that the polymer can act as a stabilizing agent to prevent the formed Ag NPs from agglomerating. Thus, PEG also serves as a protecting agent for the produced Ag NPs. To the best of our knowledge, PEG has never been reported to serve as a reducing reagent and a stabilizer of the formation of Ag NPs at room temperature. Here, we demonstrate an absorption-based method to detect Hg(II) ions using polymer-protected Ag NPs that is very simple yet highly sensitive and specific.

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Experimental

Chemicals and materials

Polyethylene glycol 200 (PEG200) was purchased from Fisher Scientific. Silver nitrate (99.9%) was obtained from Sigma-Aldrich. A Hg(II) ion stock solution was prepared by dissolving $Hg(ClO_4)_2 \cdot xH_2O$ (Sigma-Aldrich) in water. The selectivity for Hg(II) ions was confirmed by adding other metal ion stock solutions (as their perchlorate salts) instead of Hg(II) ion in a similar way. All reagents were used as received without further purification. De-ionized water, with a resistivity greater than 18.0 MΩ cm (Millipore Milli-Q system), was used to prepare the aqueous solutions. All the glassware used in the following procedures was cleaned with freshly prepared aqua regia and rinsed thoroughly in water prior to use.

Preparation of colloidal Ag NPs

The Ag NPs were synthesized by slowly adding $AgNO_3$ to PEG200 under rigorous stirring. With its abundance of hydroxyl groups (–OH), PEG200 serves both as a mild reducing agent, to form the Ag NPs, and a protecting agent, to stabilize the resulting Ag NPs and prevent them from aggregating. The schematic of formation of the Ag NPs in PEG200 (Ag/PEG-NPs) is illustrated in Fig. 1. For the preparation of 1.0 mM Ag/PEG NPs, 50 mM $AgNO_3$ (0.2 ml) was dropped slowly into a 9.8 ml PEG200 solution under vigorous stirring. To begin with, the mixture was a clear solution without any color. After 6 h of stirring at room temperature, the mixture solution had changed to yellow. Next, the yellow solution was kept in a refrigerator at 4 °C for 3 weeks.

Extinction spectra measurements

Extinction spectra were recorded by a Shimadzu 2550 spectrophotometer (Shimadzu Corporation Japan) using a 1 cm path length quartz cell at room temperature.

TEM and EDX measurements

A drop of suspension containing Ag or Ag/Hg NPs was deposited on a Formvar-covered carbon-coated copper grid (Electron Microscopy Sciences, PA). The samples were allowed to dry at room temperature overnight. A Jeol 2010 high-resolution transmission electron microscope (HRTEM) was used to obtain the TEM images and EDX spectra with a 200 kV accelerating voltage.

PSA measurements

The synthesized Ag NPs before and after reaction with Hg(II) ions were characterized by a particle size analyzer (PSA, Microtrac) based on dynamic light scattering. The average values of the NP size and polydispersity, defined as a relative width of the size distribution, were determined from the PSA measurements.

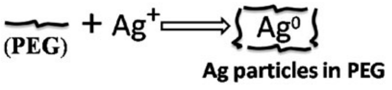

Fig. 1 Schematic of Ag NP synthesis.

Results and discussion

Absorbance of Ag/PEG-NPs and their stability

As shown in Fig. 2, the Ag/PEG-NPs display an intense yellow color due to the surface plasmon absorption.[13] It is known that the surface plasmon absorption band is very sensitive to the Ag NP size, solvent and chemisorbed solute molecules.[25] With PEG200 as the protecting agent, the Ag/PEG-NPs demonstrate a superior spectral stability, which was studied by the measurement of the absorbance over a long period of time. Also shown in Fig. 2, there was little difference in the absorbance spectra over a period of 8 h. The reaction between $AgNO_3$ and PEG was reasonably fast, reaching a steady-state in approximately 6 h under vigorous stirring. All the Ag/PEG-NPs in this study were aged for three weeks before use. Note that the results would not be affected if the measurements had been performed with different ageing times, as long as the reaction had reached a steady-state.

Detection of Hg(II) ions using Ag/PEG-NPs

The detection of Hg(II) ions using Ag/PEG-NPs is based on the simple electrochemical reaction between Ag and Hg(II) ions, resulting in the fading of the yellow color of the Ag/PEG-NPs. To evaluate the sensitivity of the Ag/PEG-NPs, different amounts of Hg(II) ion from a stock solution were added into a cuvette containing a fixed quantity of Ag/PEG-NPs. The absorbance was monitored by a UV-vis absorption spectrometer after approximately 10 min of incubation. As shown in Fig. 3, the absorbance of the Ag/PEG-NPs was highly sensitive to the concentration of Hg(II) ions, and the intensity of the 418 nm band decreased nearly linearly with increasing Hg(II) concentration. There was also another band appearing at around 510 nm that may have been due to the adsorption of Hg on the Ag/PEG-NPs. The data points in Fig. 3 lead to a directly observed detection limit of 0.2 nM for Hg(II) ions.

The selectivity of this Ag/PEG-NP-based detection scheme for Hg(II) ions was also investigated. A number of common

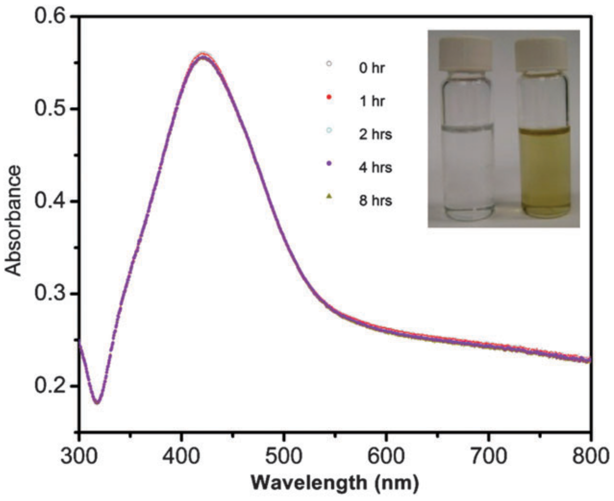

Fig. 2 Absorbance spectra of the Ag/PEG-NPs at different times after ageing for three weeks at 4 °C. Insert picture: the color/appearance of PEG (left) and the Ag/PEG-NPs (right).

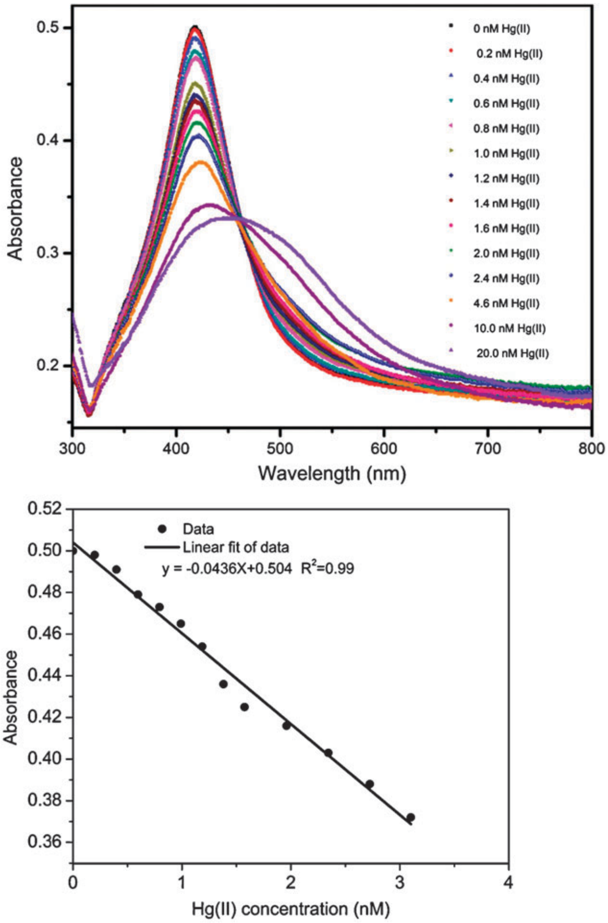

Fig. 3 Top: UV-vis absorption spectra of the Ag/PEG-NPs in the absence and presence of different amounts of Hg(II). Bottom: A plot of the absorbance intensity *vs.* [Hg(II)]. A linear correlation exists over the range 0.2–3.2 nM, with $R^2 = 0.99$.

metal ions, at a final concentration of 200 nM, were individually added to the Ag/PEG-NPs while being monitored in a similar manner. The results in Fig. 4 show the relative absorbance change at 418 nm of the Ag/PEG-NPs, respectively, in the presence of 2 nM Hg(II) and other metal ions with a concentration 100 times higher than that of the Hg(II) ions. It was observed that the Ag/PEG-NPs exhibit an excellent selectivity toward Hg(II) ions over a variety of other metal ions. We noted that, unlike some previous reports,[12,13] no chelating agent was needed to improve the selectivity.

The remarkable selectivity of Ag/PEG-NPs toward Hg(II) ions is in direct contrast to previous observations of Ag NPs prepared in different ways, where Cd(II), Ni(II) and Hg(II) were all shown to cause a shift in the absorption band of the Ag NPs.[25,26] In our case, the PEG200 molecules appear to have shielded the Ag NPs well, preventing ions such as Cd(II) and Ni(II) from attaching to the Ag NPs through chemisorption. Thus, these potential interfering ions have no obvious effect on the absorption band of the Ag/PEG-NPs. In addition, most commonly encountered metal ions, as listed in Fig. 4, do not have a high enough electrochemical potential to oxidize Ag to Ag^+. Only Hg(II) ions in this list can react with the Ag/PEG-NPs and substantially alter the absorption band.

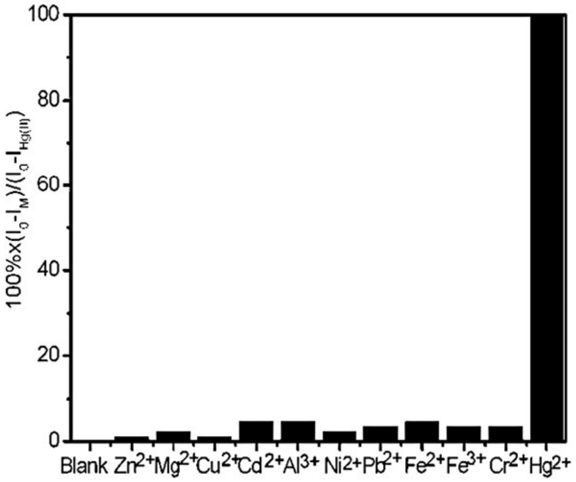

Fig. 4 The relative absorbance change [100% × (I_M − I_0)/($I_{Hg(II)}$ − I_0)] of Ag/PEG-NPs at 418 nm in the presence of 2.0 nM Hg(II) and 200 nM of some other common metal ions, respectively.

TEM, PSA and EDX of the Ag/PEG-NPs before and after reacting with Hg(II) ions

TEM and PSA measurements were carried out to investigate the NP size change of the Ag/PEG-NPs before and after their reaction with Hg(II) ions. Fig. 5 shows the TEM images and PSA results of the Ag/PEG-NPs before and after this reaction. It can be seen from the TEM images that the size of the Ag/PEG-NPs increases from less than 5 nm to more than 5 nm after their reaction with Hg(II) ions. The PSA results further show that the average NP size of the Ag/PEG-NPs increased from 3.6 to 5.8 nm after the reaction with Hg(II) ions. These results support the notion that the change of absorbance of Ag/PEG-NPs is due to a redox reaction between the Hg(II) ions and the Ag NPs.

EDX measurements were further carried out to support the notion that the interaction between Hg(II) ions and Ag/PEG-NPs is indeed due to a redox reaction between Hg(II) ions and Ag NPs. The EDX spectra of the Ag/PEG-NPs (a) before and (b) after their reaction with Hg(II) ions are shown in Fig. 6. They clearly show the presence of Hg element in the Ag/PEG-NPs after reacting with Hg(II) ions, indicating the formation of Hg on the surface of the Ag NPs.

We would like to point out that this UV-vis absorption-based detection method is very simple, cost-effective and could be completed within a few minutes, using mostly commercially-available materials. The Ag NPs can be used after their synthesis without any further treatment. Unlike some recent reports, this detection scheme does not require surface modification of the NPs or oligonucleotides as targeting elements, or complicated detection systems.[27–29] The low detection limit (0.2 nM) of this method is below the EPA limit for Hg(II) ions in drinking water, making it well-suited to many routine water monitoring applications.

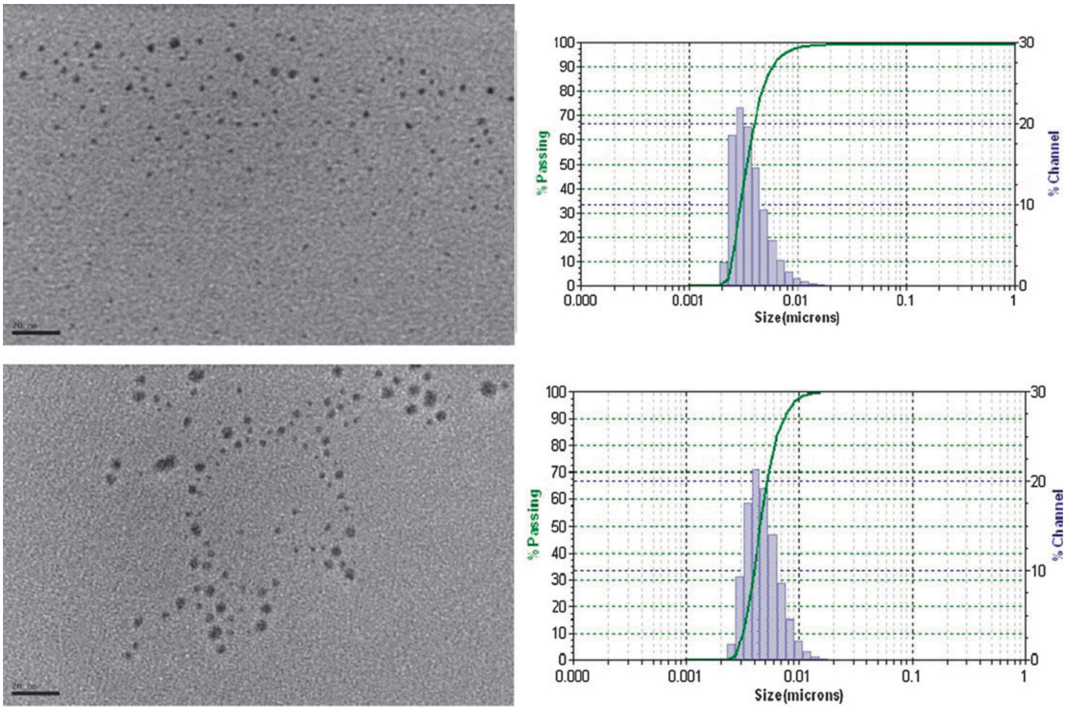

Fig. 5 TEM images and PSA of Ag/PEG-NPs before (top) and after (bottom) their reaction with Hg(II) ions. Scale bars: 20 nm.

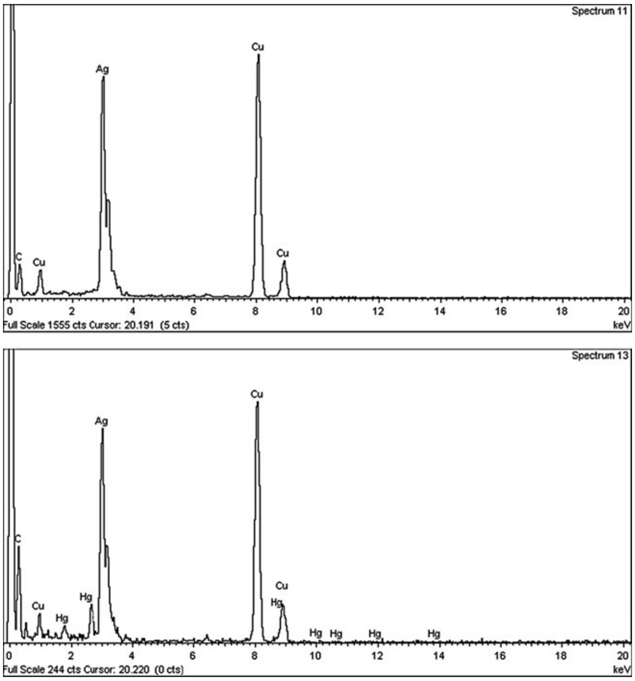

Fig. 6 EDX spectra of the Ag/PEG-NPs before (top) and after (bottom) their reaction with Hg(II) ions. Cu and C peaks appear due to scattering caused by the carbon film and copper of the TEM grid.

Conclusions

In summary, we have developed a facile, green method to prepare Ag NPs with a particle size of less than 5 nm. The Ag/PEG system could detect Hg(II) ions with high sensitivity, selectivity and good stability. By using UV-vis absorption spectroscopy investigations of the surface plasmon absorption band of Ag/PEG, due to the reduction of Hg(II) ions by the Ag NPs, this detection method is simple, cost-effective and could be completed within a few minutes. It requires no covalent modification of the Ag NPs, uses only commercially-available materials, exhibits a higher sensitivity and is more convenient than similar approaches for Hg(II) ion detection. The method also has a very good detection limit of 0.2 nM for Hg(II) ions.

Acknowledgements

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