Novel Colorimetric Sensing of Anion with Gold Nanoparticles-Embedded Plasticized Polymer Membrane

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The design of anion sensors has long been a focus of research as it can provide on-site, real-time detection and quantification of beneficial and toxic anions. In general, specific interaction such as hydrogen bonds/electrostatic interactions[1-5] and ion-pair complexation[6] between anion and anion receptor has been utilized for sensing of anion. The combined processes of these molecular-scale recognitions and surface assembly offer a powerful route to the development of refined sensing systems and, more generally, new technological devices based on controlling and analyzing interactions on the nanometer scale. The construction of receptors which can selectively recognize and sense anionic guest species *via* a macroscopic physical response is a current area of chemical sensor technology receiving considerable attention.[7-9]

Metal nanoparticles have extraordinary size-dependent optical properties, not present in the bulk metal and have, consequently, been the subject of intense research during the past decade. Specifically, gold and silver nanoparticles have been of increasing interest in applications to biological and chemical nanosensors. In recent years, optical[10-13] and electrochemical[14,15] nanoprobes have been developed by modifying the surface of metal nanoparticles with various functional molecules. Gold nanoprobes capable of optically sensing biological macromolecules such as polynucleotides have been extensively studied.[10,11] However, there are few nanoparticle-type optical probes for specific anions. As gold nanoparticles have tremendously high molar absorptivity in the visible region (the molar absorptivity for the 8 and 13 nm-diameter particles was reported to be 7.5×10^7 M^{-1} cm^{-1} at 520 nm and 4.7×10^9 M^{-1} cm^{-1} at 524 nm, respectively),[16] they must have considerable potential for colorimetric reporters of ions and molecules as well as macromolecules.

Herein, we report the fabrication of a novel gold nanoparticles-embedded plasticized poly(vinyl chloride) (PVC) membrane useful for sensing of specific anion. The Au nanoparticles in the membrane can directly react with anions. We can confirm the existence of anion by color change of the membrane as a result of interaction between nanoparticles and anions. This nanoparticles-based sensor recognizes only iodide among various anions, *i.e.*, F^-, Cl^-, Br^-, I^-, N_3^-, NO_2^-, NO_3^-, and CH_3COO^-.

Experimental Section

$HAuCl_4$, undecanethiol, 2-nitrophenyloctyl ether (2-NPOE), and PVC were purchased from Aldrich. Other chemicals, unless specified, were reagent grade.

In the first place, the undecanethiol-coated gold nanoparticles were prepared by following the literature with difference only in the molar ratio of $HAuCl_4$ to alkanethiol.[17] Namely, to a vigorously stirred solution of 0.50 g of tetraoctylammonium bromide (6 eq) in 80 mL of toluene was added 0.06 g of $HAuCl_4$ (1 eq) in 5 mL of deionized water. The yellow $HAuCl_4$ aqueous solution quickly cleared and the toluene phase became orange-brown as the $AuCl_4^-$ was transferred into it. The organic phase was isolated, 0.057 g of undecanethiol (2 eq) was added, and the resulting solution was stirred for 10 min at room temperature. To the reaction solution was added $NaBH_4$ (0.08 g, 10 eq) in 5 mL of deionized water over periods of 5 min. The now very dark organic phase was further stirred for at least 12 h. The organic phase was then collected, and the solvent was removed on a rotary evaporator. The black product was suspended in 50 mL of ethanol, briefly sonicated to ensure complete dissolution of byproducts, collected on a glass filtration, and washed with at least 100 mL ethanol. The product was dried in vacuum. 0.10 mg of the prepared thiol-coated gold nanoparticles was dissolved in 10 mL of chloroform for preparing nanoparticle-embedded PVC membrane.

Preparation of plasticized membrane has been performed according to the procedure of Moody and Thomas.[18] 67 wt% plasticizer (2-NPOE, 119.1 mg) and 33 wt% PVC (59.3 mg) were dissolved in 1.0 mL chloroform solution of gold nanoparticles. The mixed solution was put into a glass ring of 30 mm diameter and left for 24 h to allow evaporation of the chloroform. To test the sensing ability of the membrane toward anions, sodium salts of various anions (NaX, X = F, Cl, Br, I, N_3, NO_2, NO_3, and CH_3COO) and iodine-containing salts (LiI, KI, CsI, $NaIO_3$, and $NaIO_4$) were dissolved in deionized water. The concentration of each salt solution was 1.0×10^{-2} M. The prepared PVC membranes were then put into each salt solution and check the color change of the membrane.

The extinction spectra were recorded with a UV-vis absorption spectrometer (SINCO S-3100). Transmission electron microscopy (TEM) images were obtained with a JEOL JEM-2010 transmission electron microscope operating at 200 kV.

Results and Discussion

Organic suspension of undecanethiol-coated gold nanoparticles was prepared by two-phase synthetic method as described above. Figure 1 shows the UV-vis absorption spectrum of chloroform solution of gold nanoparticles. The spectrum shows the presence of weak absorption feature around 500 nm. Optical properties of gold nanoparticles have received considerable attention, including studies of naked particles in gas, polymer, and solvent phases, as well as for monolayer-protected particles in solutions. Very small particles exhibit a strong UV absorption feature which decays approximately exponentially into the visible, with a superimposed broad band at ~500 nm (surface plasmon, SP band) that decreases in intensity and energy with decreasing gold nanoparticle size.[19] The experimentally observed weak absorption in the spectrum of our sample can thus be ascribed to small particle size. The actual particle structure and size can be determined by TEM. Figure 2 shows a typical TEM image of undecanethiol-protected gold nanoparticles on TEM grid. The image reveals that spherical-shaped gold nanoparticles with average size of 2.1 ± 0.8 nm are formed.

We have investigated the ability of the plasticized PVC membrane loaded with the gold nanoparticles to act as a colorimetric sensor for the detection of anions in aqueous solutions. We made the membrane from the prepared gold nanoparticles, plasticizer, and PVC as mentioned in Experimental section. The nanoparticles were uniformly mixed into the plasticized PVC membrane and the color of the membrane was brown. The membrane was cut into small pieces and put into vials containing aqueous sodium salt solutions of various anions. After predetermined time, the membranes were taken out from the solution and the color change of them was examined. The experimental results are shown in Figure 3a. As illustrated in the figure, distinct color change of the membrane occurs from brown to violet when it is soaked into the NaI solution. In a control experiment, we have performed same experiment with plasticized PVC membrane that was prepared without nanoparticles. However, we could not observe any color change of the membrane for all anions. These results indicate that the membrane loaded with nanoparticles selectively recognize iodide through a certain type of interaction between the gold nanoparticles and iodide anions. To validate the sensing ability of the membrane toward iodide anion, we have also carried out same experiments with other iodine containing salts, *i.e.*, LiI, KI, CsI, NaIO$_3$, and NaIO$_4$. The experimental results are shown in Figure 3b. For comparison, the result obtained with NaI is also shown in Figure 3b. We could observe obvious color changes of the membranes for all iodide salts. However, we could not observe any color change for iodate and periodate. This may be due to the fact that oxygen atoms of iodate or periodate can inhibit the interaction between iodine and gold nanoparticles. The overall experimental results thus clearly show the iodide-selective property of our system.

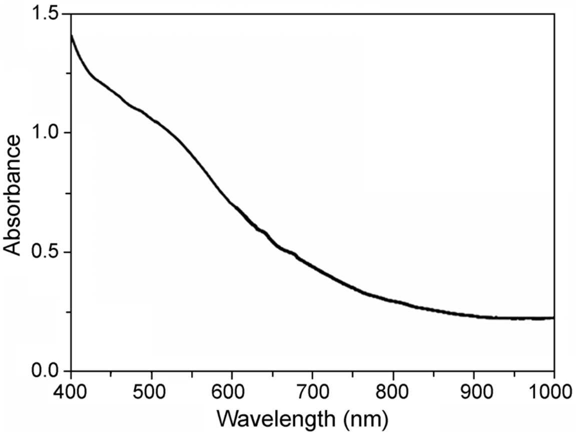

Figure 1. UV-vis spectrum of the undecanethiol-protected gold nanoparticles in chloroform.

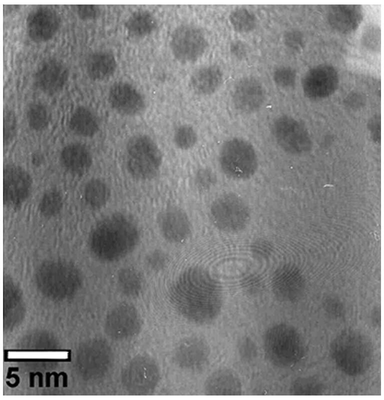

Figure 2. TEM image of the undecanethiol-coated gold nanoparticles.

The color change of nanoparticles-embedded membrane may be ascribed to nanoparticle aggregation by the adsorption of iodine on the gold nanoparticle surface. In the past, Finklea described that a monolayer of iodine atoms has been known to form spontaneously on immersing a bulk-gold surface in dilute iodide solution.[20] Recently, Wang and coworker reported the aggregation of gold nanoparticles by iodide. Iodine adsorption on gold nanoparticle lowers the surface potential, as result, increasing van der Waals attrac-

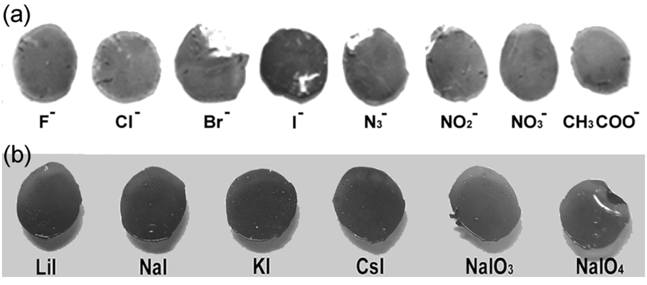

Figure 3. Photograph of the gold nanoparticles-embedded plasticized PVC membranes after addition of (a) sodium salts of various anions and (b) iodine-containing salts.

tive forces between I-coated nanopartilces drive the aggregation of particles.[21] Similar mechanism can be applied to our case. Place exchange of undecanethiols adsorbed on the high surface energy sites with iodide ions can decrease steric repulsion between nanoparticles, results in the formation of particle aggregates. (In fact, small metal nanoparticles such as the particles prepared in this work have relatively large fraction of active sites on their surface as compared with large particles. The molecules adsorbed on these sites can be easily replaced by foreign adsorbents.[22] Experimental results show that only iodide is effective for this place exchange reaction.) This particle aggregation induces the color change of the membrane. It is well-known that as gold or silver colloidal particles aggregate into stringlike structures, there is growth of a higher wavelength component in the extinction spectrum that shifts to the red and increases in intensity as the aggregation proceeds.[19] The long wavelength component (the longitudinal plasmon resonance) arises due to coupling of the plasma modes of the individual clusters. Actually, we choose gold nanoparticles as the colorimetric reporter group because previous work has shown that different aggregation states of metal nanoparticles can result in distinctive color changes.[10,11]

A still remaining question about the sensing mechanism is how gold nanoparticles can move in the membrane. In fact, small host systems that can recognize specific ions can move in plasticized PVC membrane. For example, Zhang *et al.* reported that dimer formation of porphyrin conjugate in PVC membrane can be useful for fluorescence sensing toward imidazole derivatives.[23] According to this report, the sensor was constructed and applied for fluorescence assay of histidine in aqueous solution by immobilizing the sensing material in a plasticized PVC membrane. With the presence of histidine in the sample solution, histidine was extracted into the membrane phase and bridged with the Zn(II) center of the porphyrin, causing the monomer porphyrin to be converted to its dimeric species. The formation of porphyrin dimer was accompanied by the enhancement of pyrene excimer emission, the chemical recognition process could be directly translated into a fluorescent signal. This result is important evidence that fluorophores and analytes can move in PVC membrane.

Iodine is an essential part of the thyroid hormones that play an important role in the development of brain function and cell growth, and its deficiency cause serious delays in neurological development.[24,25] Since excess of iodine or iodide can cause goiter and hypothyroidism as well as hyperthyroidism, the determination of iodide in natural waters and biological samples is important in environmental and biological terms. Most of the analytical methods for iodide sensing require expensive instrumentation, rather complicated techniques, and insufficient sensitivity, time consuming (classical titrimetry or spectrophotometry) and/or sample pretreatments especially in complicated matrix such as wastewater. On the contrary, iodide selective membrane developed in this study has unique advantages including no requirement of instruments, easy preparation, relatively low cost, possibility of using in complex and color media, nondestructive analysis and adequate selectivity. Therefore, it can be a promising alternative for iodide detection in biological, environmental and industrial fields.

In summary, we have demonstrated that the plasticized PVC membrane loaded with gold nanoparticles can selectively recognize iodide by colorimetric sensing. The color change of the membrane is believed to the result of nanoparticle aggregation by the adsorption of iodine on the nanoparticle surface. Currently, we are attempting to detect other anions by using plasticized PVC membrane with various metal nanoparticles and trying to improve the efficiency of sensing.

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